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IN THE PHYSICAL SCIENCES AND INDUSTRY

VOL. III

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III

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FOREWORD

The Conference on the Use of Radioisotopes in the Physical Sciences and Industry, which took place in Copenhagen in September 1960, was the latest of a series of isotope conferences which began in 1951 at Oxford and continued with those held in 1954, again at Oxford, and in 1957 in Paris. The development of the uses of radioisotopes had been so rapid and many-sided that this Copenhagen Conference, organized by the IAEA with the co-operation of UNESCO, had to be restricted to applications in the physical sciences and industry. Applications of radioisotopes in animal biology and the medical sciences were discussed at the Conference held in Mexico City in November 1961. Even so, more than 500 scientists attended the Conference in Copenhagen and over 140 contributions were presented and discussed by this international gathering. Many more papers of great interest were submitted but could not be fitted into the programme.

The proceedings of this Conference demonstrate the advances which had taken place since the earlier meetings in Oxford and Paris. It is hoped that this publication will contribute towards the stimulation of further research in the application of radioactive techniques.

The Agency wishes to express grateful acknowledgement for the co-operation of UNESCO in organizing the Conference, to the authors of papers, to the scientists who kindly consented to act as Chairmen of Sessions, and to the external scientific secretaries who ably supported its own staff by acting as scientific secretaries of the Conference and by assisting with the scientific editing of these Proceedings.

Sincere appreciation is due to the Danish Government for their kindness in providing the facilities for this Conference.

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CONTENTS OF VOLUME III

J. PREPARATION OF LABELLED COMPOUNDS AND RELATED PROBLEMS

Labelling of organic compounds by electric discharge in tritium gas 3
K. E. Wilzbach and L. M. Dorfman (United States of America)

Синтез меченых по тритию циклических углеводородов с помощью ядер отдачи трития 13
А. Н. Несмеянов, Б. Г. Дзантиев, В. В. Поздеев, Ю. М. Румянцев (СССР)

Получение меченных по сере соединений в результате реакций горячих атомов серы-35 с циклическими углеводородами 27
Б. Г. Дзантиев и И. М. Баркалов (СССР)

Extensions of the techniques for the accelerated unspecific isotopic labelling of organic compounds 43
N. A. Ghanem (United Arab Republic) and T. Westermark (Sweden)

Production de composés marqués au ^{14}C à partir de $^{14}CO_2$ accéléré dans un champ électrique—Analyse physico-chimique de quelques composés radioactifs obtenus 69
M. Guillaume (Belgique)

Preparation of very small amounts of tritium-labelled polyphenols and the isolation of the tritiated compounds by "normal freezing" 73
H. Schildknecht and F. Schlegelmilch (Federal Republic of Germany)

The synthesis of the insecticides Aldrin and Dieldrin labelled with carbon-14 at high specific activity 83
D. J. Thomas and A. E. Kilner (United Kingdom)

Preparation of C^{14}-labelled tetrazolium salts and tracer study of the tetrazene-formazan rearrangement 91
J. Márton, J. Meisel and T. Gosztonyi (Hungary)

Synthesis of methyl 3-0-α-D-glucopyranosyl-C_6^{14}-β-D-xylopyranoside and methyl 2-0-α-D-glucopyranosyl-C_6^{14}-L-novio-pyranoside 97
S. A. Barker, M. C. Keith, M. Stacey and D. B. E. Stroud (United Kingdom)

A general method for preparing C^{14}-labelled isocyanates. Tracer study of the dimerization of isocyanates 103
L. Ötvös, J. Márton and J. Meisel (Hungary)

Изучение реакций изотопного обмена углерода между цианистым калием и карбонатами и применение их для получения цианистого калия, меченного изотопом C^{14} 111
О. И. Андреева и Г. И. Костикова (СССР)

Synthèses spéciales de certains composés organiques iodés 123
R. Henry, D. Debuchy et E. Junod (France)

A new method for the preparation of I^{131}-labelled *p*-iodo-benzenesulphonic acid anhydride (pipsan) 131
N. Hesselbjerg-Christensen (Denmark)

Nouvelle méthode de préparation par voie biologique de quelques substances soufrées marquées au soufre-35 139
F. Chapeville, H. Maier-Huser et P. Fromageot (France)

Examples of the use of preparatory gas chromatography in the manufacture of labelled molecules 145
L. Pichat, C. Baret, J. P. Guermont et M. Audinot (France)

K. RADIOISOTOPES IN ORGANIC CHEMISTRY

The self-induced exchange of tritium gas with methane 159
T. H. Pratt and R. Wolfgang (United States of America)

Some symmetrical halogen and methoxy exchange reactions in aromatic systems 179
R. W. C. Broadbank, A. H. E. Harhash and S. Kanchanalai (United Kingdom)

Preliminary experiments on the use of radioactive indicators in macromolecular chemistry 187
L. de Brouckère, R. van Leemput and R. Stein (Belgium)

Stereochemistry and radiochemistry of deamination reactions 195
C. J. Collins and B. M. Benjamin (United States of America)

Dehydrocyclization of 2,2-dimethyl-4-(methyl-C^{14})-pentane and 3-(methyl-C^{14})-heptane over chromia-alumina 205
F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes and R. S. Smith (United Kingdom)
Isotopic data to study the mechanism of the oxidation of mercaptoacetic acid 217
D. Gál and L. Guczi (Hungary)
C^{14}-isotope effects in the decarboxylation of 2-benozylpropionic acid 225
E. M. Hodnett and R. L. Rowton (United States of America)
Evaluation of deuterium isotope effects in photochemical reactions of formic-*d* acid by use of C^{14} 235
G. A. Ropp (United States of America)

L. RADIOISOTOPES IN PHYSICAL CHEMISTRY

Исследование механизма некоторых гетерогенно-каталитических процессов с применением соединений, меченных углеродом-14 245
Г. В. Исагулянц, А. А. Баландин (СССР)
Исследование изотопных эффектов при реакциях водородного обмена в жидком бромистом водороде и жидком аммиаке 255
И. Ф. Тупицын, Н. К. Семенова и Г. И. Авдулов (СССР)
Investigations on the structure of complex compounds by radioisotope exchange —The structure of cyanonitrosyl complexes 269
B. Jeżowska-Trzebiatowska and J. Ziotkowski (Poland)
Ion exchange studies of alpha-hydroxy carboxylic acid-lanthanide and actinide systems 283
G. R. Choppin, D. Moy and L. W. Holm (United States of America)
The rates and orders of electron exchange reactions in mixed solvents using tracer techniques 301
E. S. Amis (United States of America)
Contributions to the solvent effect in isotope exchange reaction 315
E. Körös, E. Schulek and L. Pataki (Hungary)
Tracer investigations of the fate of sulphur atoms in the course of high-temperature reactions 323
A. H. W. Aten, Jr. (Netherlands)
Principles and applications of heterogeneous isotope and non-isotopic ion exchange on the surface of ionic crystals 337
K. H. Lieser and W. Hild (Federal Republic of Germany)
Emploi du carbone-14 pour l'étude de l'échange élémentaire de carbone entre le méthane et les résidus de chimisorption de celui-ci sur films métalliques 351
R. Coekelbergs, J. Decot, A. Frennet et G. Liénard (Belgique)
Experimental comparison of primary and secondary isotope effects in tritium or carbon labelled compounds 361
H. Simon and D. Palm (Federal Republic of Germany)
Восстановление прометия на ртутном катоде 369
А. К. Лаврухина Г. М. Колесов, Тан Сяо-ен (СССР)
The adsorption of hydrogen on a molecular sieve at —196° C and the observation of an isotope effect 379
W. G. Duncombe (United Kingdom)
Some applications of radioisotopes in physical chemistry — two-phase equilibria and packed-column techniques 387
K. A. Kraus, H. O. Phillips and F. Nelson (United States of America)
Application of radioisotopes to the investigation of the kinetics and mechanism of reactions of some inorganic complex compounds 407
G. M. Harris (United States of America)
Some solvent extraction studies of trivalent metal halides 415
R. J. Dietz, Jr., J. Mendez and J. W. Irvine, Jr. (United States of America)
The use of radioisotopes for determination of complex equilibria 427
J. Rydberg (Sweden)
Исследование при помощи радиоактивной серы кинетики процесса $SO_3 + 0{,}5\ O_2 \rightleftarrows SO_2$, находящегося в состоянии химического равновесия, на платиновом катализаторе 435
В. А. Ройтер, Н. А. Стукановская, Г. П. Корнейчук (СССР)
Adsorption studies at ionized surface layers by means of hot atoms 449
M. Avrahami and N. H. Steiger (Israel)

The use of radioisotopes in radiation chemistry: the effect of radiation on toluene 463
K. E. Wilzbach (United States of America)
Etude de la radiolyse du pentane et du cyclopentane à l'aide d'iode radioactif 471
J. Dauphin (France)
Technique for the study of halogen atom reactions 483
G. S. Laurence and D. R. Stranks (United Kingdom)
Vapour-pressure determinations on tritium-labelled organic compounds . . . 495
A. S. Carson, R. Cooper and D. R. Stranks (United Kingdom)
The elucidation of a secondary chemical interaction in an ion-exchange resin by a radioisotope-dilution method 503
J. A. Marinsky and J. Krasner (United States of America)
Solubility of metallic mercury in organic solvents 517
E. H. Klehr and A. F. Voigt (United States of America)
The variation of solubility of strontium sulphate with particle size 531
B. V. Enüstün and J. Turkevich (United States of America)
Radioisotopes in the physical chemistry of corrosion processes and their inhibition 549
G. H. Cartledge (United States of America)
Radio-tracer techniques in the study of corrosion by molten fluorides 559
W. R. Grimes, G. M. Watson, J. H. DeVan and R. B. Evans (United States of America)
Radioisotopes as tracers for reactions in molten fluoride media 575
W. R. Grimes, J. H. Shaffer, R. A. Strehlow (United States of America)
Chairmen of Sessions 591
Secretariat of the Conference 591
List of Participants 591
Author Index 605
Transliteration Index 632

J

PREPARATION OF LABELLED COMPOUNDS AND RELATED PROBLEMS

(Sessions 13 and 14 [Part])

LABELLING OF ORGANIC COMPOUNDS BY ELECTRIC DISCHARGE IN TRITIUM GAS*

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Abstract — Résumé — Аннотация — Resumen

Labelling of organic compounds by electric discharge in tritium gas. The gas exposure technique for tritium labelling has been used successfully for many organic compounds and has received wide acceptance. The use of this technique is somewhat restricted, however, since curie amounts of tritium and exposure times of several days are needed to supply sufficient energy to introduce even a small fraction of the gas into the compound.

It has now been found that the use of an electrical discharge to promote ionization and excitation of the gas permits use of smaller quantities of tritium and shorter exposure times.

In the new technique, a small amount, about 0.5 g, of the compound to be labelled is placed in the lower cup-shaped electrode of a glass vessel, and tritium gas is admitted to a pressure of 5—15 mm. The lower electrode is grounded and the upper electrode connected to a Tesla-coil leak-tester. A discharge at approximately 100 μA and 1000 V is passed through the gas for a few minutes. As in the gas exposure technique, some decomposition occurs and the compound must be purified from tritiated by-products. Activities in the range of 3—20 mc/g, comparable to those produced by simple exposure to tritium gas, have been obtained with several organic compounds.

A particularly attractive feature of this technique is the possibility of using it in laboratories not equipped to handle the larger amounts of tritium required by the gas-exposure method.

Marquage des composés organiques par décharge électrique dans le tritium gazeux. Pour le marquage au tritium d'un grand nombre de composés organiques, on a utilisé avec succès la méthode d'exposition dans le gaz; cette méthode a été accueillie avec faveur. Toutefois, son emploi est quelque peu restreint, du fait qu'il faut des doses de l'ordre de plusieurs curies de tritium et des temps d'exposition de plusieurs jours si l'on veut avoir une énergie suffisante pour introduire dans le composé une quantité même faible de gaz.

On vient de constater qu'en ionisant et excitant le gaz par une décharge électrique on pouvait réduire la quantité de tritium et le temps d'exposition nécessaires.

Selon cette nouvelle méthode, on place une petite quantité du composé à marquer (0,5 g environ) dans l'électrode inférieure, concave, d'un récipient en verre et l'on y admet le tritium gazeux sous une pression de 5 à 15 mm. L'électrode inférieure est mise à la terre, tandis que l'électrode supérieure est reliée à une bobine Tesla détectrice de fuites. On fait passer à travers le gaz, pendant quelques minutes, une décharge d'une centaine de microampères sous 1000 V. Comme avec la méthode d'exposition dans le gaz, il se produit une certaine décomposition et il faut épurer

* Based on work performed under the auspices of the United States Atomic Energy Commission.

le composé pour en éliminer les sous-produits tritiés. On a obtenu, pour plusieurs composés organiques, des activités de l'ordre de 3 à 20 mc/g, comparables à celles qui ont été produites par simple exposition dans le tritium gazeux.

Une caractéristique particulièrement intéressante de cette technique est qu'elle peut être employée dans des laboratoires qui ne sont pas outillés pour manipuler les quantités importantes de tritium nécessaires à l'application de la méthode d'exposition dans le gaz.

Мечение органических соединений электрическими разрядами в газообразном тритии. Метод облучения газообразным тритием был успешно применен ко многим органическим соединениям и получил широкое признание. Однако использование этого метода до некоторой степени ограничено, поскольку требуется количество трития, необходимое для кюри-дозы и несколько дней облучения, чтобы получить достаточное количество энергии для введения в соединение даже небольшой доли газа.

Было установлено, что применение электрического разряда для увеличения ионизации и возбуждения газа дает возможность использования меньшего количества трития и более короткого времени облучения.

При применении этого нового метода небольшое количество соединения (около 0,5 грамма) для мечения помещается в нижний чашеобразный электрод, находящийся в стеклянном сосуде, и пропускается газообразный тритий под давлением 5—15 миллиметров ртутного столба. Нижний электрод заземляется, а верхний присоединяется к течеискателю трансформатора Тесла. Разряд приблизительно в 100 микроампер и 1000 вольт проходит через газ в течение нескольких минут.

Как и при любом методе облучения газом появляются продукты распада, и соединение должно быть очищено от побочных продуктов, насыщенных тритием. При новом методе в сравнении с активностью, получаемой при простом облучении газообразным тритием, была получена активность от 3 до 20 милликюри на грамм.

Особенно преимущество этого метода состоит в том, что он может быть применен в лабораториях, не оборудованных для использования простого метода облучения газообразным тритием, требующего наличия большего количества трития.

Marcación de compuestos orgánicos por descargas eléctricas en tritio gaseoso. El empleo de la técnica de marcación con tritio por exposición al gas, que permite marcar muchos compuestos orgánicos, se ha difundido considerablemente. Sin embargo, las aplicaciones de esta técnica son algo limitadas, porque se requieren cantidades de tritio del orden de varios curies y tiempos de exposición de algunos días, incluso para conseguir la introducción de una pequeña fracción del tritio en el compuesto a marcar.

Recientemente se ha comprobado que la ionización y la excitación producidas en el gas por descargas eléctricas permiten reducir la cantidad de tritio y trabajar con tiempos de exposición más breves.

Según esta nueva técnica, se colocan en el electrodo inferior, cóncavo, de un recipiente de vidrio unos 0,5 g de la sustancia a marcar y se introduce gas tritio a una presión de 5 a 15 mm. El electrodo inferior se conecta con la tierra y el superior con un dispositivo provisto de bobina de Tesla para comprobar escapes. Seguidamente se hace pasar durante unos minutos una descarga de, aproximadamente, 100 μA y 1000 V a través del gas. De igual modo que en el procedimiento de exposición al gas, se produce cierta descomposición, por lo que el compuesto debe purificarse a fin de eliminar otros subproductos tritiados. En el caso de varios compuestos orgánicos, se han obtenido actividades del orden de 3 a 20 mc/g que son parecidas a las que se logran por simple exposición al tritio gaseoso.

Esta técnica presenta la considerable ventaja de poder emplearse en laboratorios que no estén equipados para manipular las grandes cantidades de tritio que requiere el método de exposición al gas.

1. Introduction

In the few years since it was reported [1] that organic compounds can be labelled with tritium by exposure to the gas, the technique has been employed successfully for a wide variety of compounds, ranging in complexity from methane [2] to insulin [3]. Its use is somewhat restricted, however, by the fact that multicurie quantities of tritium are required to attain satisfactorily high levels of activity in a reasonable time. This is not a serious drawback from an economic standpoint, since the cost of tritium is low, but it does limit the use of the technique to laboratories equipped to handle large quantities of tritium in comparative safety.

The need for large quantities of tritium in the gas-exposure technique arises from the fact that tritium serves not only as the isotopic label, but also as the source of energy for the reactions leading to its incorporation in the compound. The energy expended per tritium atom introduced is, however, usually greater than 100 eV, whereas the energy available from tritium in one day is, on the average, less than 1 eV per atom. Regardless of the quantity of gas used, then, only a small fraction of it, usually less than 1%, will be incorporated per day.

It is reasonable to expect that the rate of tritium incorporation could be increased and that smaller quantities of tritium could be used, if additional energy were supplied to the system. Several sources of supplemental energy can be considered and, indeed, have already received some attention. Radiation from a cobalt-60 source has been used to promote the exchange of tritium with methane [2] and with benzene [4]. The practical value of this approach is, however, questionable, because absorption of gamma-radiation by a gas is inefficient and kilocurie amounts of Co^{60} would be needed to deliver the energy available from a curie of tritium. Further, absorption of the energy by a solid or liquid would occur predominantly in the body of the material (and cause its decomposition) where tritium might not be available for labelling. An internal source of supplemental radiation, beta-emitting krypton-85, has been used by TURTON [5] in the somewhat analogous labelling of organic compounds with $C^{14}O_2$. The technique could be applied equally well to tritium-labelling but would not eliminate the problem of handling large quantities of volatile radioisotopes.

We have recently reported [6] successful use of an electric discharge in tritium at pressures from 5 to 20 mm. The source of the discharge is a simple Tesla coil of the type commonly used as a leak-tester for vacuum systems. Labelling would be expected to occur as a result of ionization and excitation of the tritium molecules, and perhaps of the organic compound, by the discharge. Use of this technique has now been extended to the labelling of five solid organic compounds with results sufficiently promising to be of general interest. Labelling is accomplished with quantities of tritium considerably smaller than those normally used in the gas-exposure technique. In addition, the exposure time required is reduced from days to minutes. Activities in the same range as those obtainable by the gas-exposure technique have been produced, but labelled by-products are apparently formed to a greater extent.

Somewhat earlier, WOLFGANG *et al.* [7] investigated the labelling of organic compounds by a discharge in tritium in the 50-μm pressure region on the assumption that labelling occurred *via* accelerated ions. The substantially more promising results of the present experiments must be attributed, in part, to the greater amount of tritium available at the higher pressure. More recently, the labelling

of benzene [4] by a silent discharge and of *p*-aminosalicylic acid [8] by a microwave discharge in tritium have been reported, but the practical value of these techniques cannot be assessed without additional data.

2. Experimental

The discharge cell used in these experiments was a cylindrical Pyrex vessel, vol. 35 cm^3, containing Kovar electrodes 20 mm in diam. and 20 mm apart. The cell is shown in Fig. 1. The source of the discharge was simply a Tesla-coil

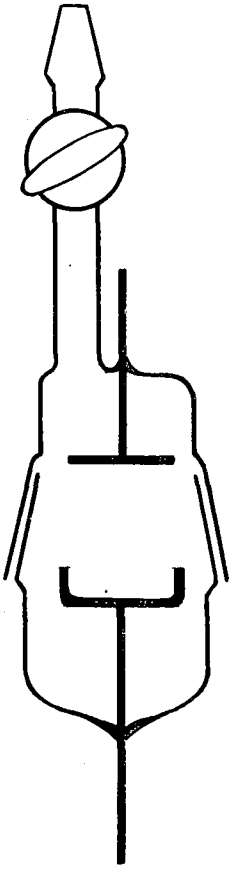

Fig. 1
Discharge cell.

leak-tester. In these experiments, the coil was connected to the upper electrode of the cell and the lower electrode was grounded. The discharge was normally operated at approx. 100 μA and in the neighbourhood of 1000 V. Arcing to the rim of the lower electrode occasionally occurred, but could be eliminated by decreasing the voltage of the discharge.

Five compounds were used: *p*-dichlorobenzene, naphthalene, palmitic acid,

benzoic acid, and cholesterol. The first two were selected for their volatility so that the products could be analysed by gas chromatography. The tritium gas used with these two compounds had an isotopic purity of 90% but contained an almost equal volume of helium-3. In the remaining experiments, the tritium gas was to all practical purposes isotopically pure and contained only a few per cent of helium-3.

A weighed quantity, about 0.5 g, of the compound was introduced into the lower cup-shaped electrode and the cell was evacuated. Tritium gas was admitted to a pressure of 5 to 20 mm, the discharge was operated for 3 to 30 min, and the gas was removed.

In the experiments with naphthalene and dichlorobenzene, the lower electrode was cooled (by keeping the tungsten lead immersed in liquid nitrogen) during the evacuations and the discharge. The tritium gas was removed through a trap cooled to —195° to condense volatile decomposition products and the bulk of the organic material was subsequently distilled into the same trap. The products were dissolved in benzene and aliquots of the solutions were injected into a vapour fractometer containing an ionization chamber connected in series with the thermal conductivity cell. The various products were identified by comparing their retention volumes with those of known compounds. Quantities of tritium in the products were determined from areas under peaks in ion current, using an appropriate calibration factor.

In the remaining experiments the dicharge cell was opened after removal of the tritium and the solids were dissolved in alcohol. Aliquots of these solutions were analysed by liquid-scintillation counting to determine the total incorporation of tritium. Labile tritium was determined by the loss in activity upon removal of the alcohol. The palmitic acid was purified by recrystallization from acetone, chromatography on Norite, and, in the second run, by conversion to the *p*-bromophenacyl ester. The benzoic acid was purified to constant activity by repeated recrystallizations from water and from hexane. Initial solutions of the benzoic acid, and of cholesterol, were treated with decolorizing carbon. The cholesterol was purified partially by several recrystallizations from aqueous alcohol and from heptane. Complete purification of the cholesterol was achieved by conversion to the dibromide and recrystallization of that product from ether-alcohol.

In addition to the experiments with tritium, two runs with naphthalene and deuterium were carried out to determine the amounts of hydrogen lost from the gas phase and formed from the organic compound during a 5-min discharge. The same discharge procedure was followed. The gas was analysed by mass spectrometry before and after the discharge.

3. Results and discussion

The conditions employed and the results obtained in labelling the five compounds by the electric discharge technique are presented in Table I. In each case, concentrations of tritium incorporated into the parent compound fall in the mc/g range. It is important to note, in addition, that these useful levels of activity are produced in significant quantities of material, in a matter of minutes, and with relatively small quantities of tritium. The results suggest that the technique may be of general use for the preparation of labelled compounds, but additional investigation is needed to assess its full practical value.

TABLE I

LABELLING BY ELECTRIC DISCHARGE IN TRITIUM

Compound	Quantity (g)	Tritium		Discharge time (min)	Activity	
		Pressure (mm)	Quantity (c)		Crude product (mc/g)	Pure product (mc/g)
p-dichlorobenzene	0.49	7	0.4	3	65	20
Naphthalene	0.58	5	0.4	5	—	4.1
	0.52	13	0.8	5	52	4.5
Palmitic acid	0.25	9	0.7	6	42	3.4
	0.35	13	1.0	5	32	3.7
Benzoic acid	0.40	19	1.9	30	540	12
Cholesterol	0.60	19	1.9	5	140	1.7
	0.57	19	1.9	30	750	0.5

With respect to possible modification of conditions, it is interesting to note, in the experiment with cholesterol, that use of a longer discharge time, under otherwise identical conditions, produces an almost proportionate increase in total tritium incorporation but actually reduces the amount appearing in the parent compound. Since recovery of cholesterol was comparably good in both experiments it would appear that labelling takes place predominantly on the surface of the particles and that molecules already labelled may be chemically altered during the longer discharge. It is possible that the optimum period of discharge for some compounds is lower than any used in these experiments, or, alternatively, that a discharge under milder conditions would be more effective. Results obtained with naphthalene and palmitic acid indicate that incorporation of tritium increases with the pressure of the gas, but, again, the increase is far from proportional.

TABLE II

LABELLING BY EXPOSURE TO TRITIUM GAS

Compound	Quantity (g)	Tritium (c)	Time (d)	Activity	
				Crude (mc/g)	Pure (mc/g)
p-dichlorobenzene	0.52	1.5	3	44	32
Naphthalene	1.0	3.4	1	28	7
Palmitic acid	20	10.4	11	41	15
Benzoic acid	1.31	6.4	5	119	14
Cholesterol	1.88	7.2	5	178	64

Results obtained in labelling these compounds by the gas-exposure technique are presented in Table II. A comparison with the data in Table I indicates that, under the conditions described, incorporation of tritium into the parent compounds by the discharge technique is somewhat lower in general and considerably lower in the case of cholesterol. The fact that this accompanies a greater incorporation of tritium into the crude products indicates that labelled by-products are formed to a greater degree in the discharge technique. This

TABLE III

LABELLED BY-PRODUCTS FORMED IN THE ELECTRIC-DISCHARGE AND GAS-EXPOSURE TECHNIQUES

By-product	Relative tritium content, parent compound = 100	
	Discharge	Gas exposure
From dichlorobenzene:		
Chlorobenzene	68	26
Benzene	87	1
Hydrocarbons, $< C_6$	39	—
Other*	—	8
From naphthalene:		
Tetrahydronaphthalene	17	23
trans-decalin	9	—
Alkylbenzenes**	57	—
Benzene	28	3
Hydrocarbons, $< C_6$	71	3

* Unidentified product less volatile than dichlorobenzene.
** *Including toluene, ethylbenzene and butylbenzene.*

is clearly demonstrated in the assay, by gas chromatography, of the labelled by-products formed from naphthalene and dichlorobenzene in the electric-discharge and gas-exposure techniques. The results, presented in Table III as relative values for tritium content of various products, indicate that labelled by-products are formed not only to a greater extent, but also in greater number by the discharge technique. The appearance of hydrogenated naphthalenes among these products (as well as the sharp drop in activity of semi-purified cholesterol upon conversion to the dibromide) indicates that hydrogenation of double bonds occurs to a significant extent in both the electric-discharge and the gas-exposure technique. Since no products other than the parent compounds could be detected by thermal conductivity, it is clear that the by-products are present as trace amounts of materials with an extremely high specific activity. Their removal is one of the major problems in labelling by these techniques. The increased formation of labelled by-products by the discharge technique did not greatly increase the difficulty of purification for these relatively simple compounds, but it could prove to be a critical factor in the labelling of more complex compounds. It should be pointed out, however, that no attempt was made in this investigation to select conditions (with regard to pressure, discharge voltage, cell design, etc.) so as to minimize decomposition.

TABLE IV

DISCHARGE IN DEUTERIUM-NAPHTHALENE

Wt. $C_{10}H_8$ (g)	Discharge time, (min)	Pressure		*Final gas composition**		
		Initial (mm)	Final (mm)	D_2	HD	H_2
0.535	5	12.2	11.0	81.7	16.6	1.6
0.501	5	14.1	13.2	83.1	12.7	1.6

* Initial composition: $D_2 = 99\,\%$, HD = 1 %.

Details and results of two experiments with the discharge technique in the deuterium-naphthalene system are shown in Table IV. From the change in pressure and composition of the gas it can be calculated that loss of deuterium from the gas phase amounted to roughly 4 μmole (16% of that initially present) and that the quantity of hydrogen formed from naphthalene was 2 μmole. Although gross chemical decomposition of the naphthalene was not observed, it is evident that isotopic dilution of the gas in a 5-min discharge was not insignificant. This effect, which might be expected to occur to a varying degree with all organic compounds, would limit the effectiveness of greatly prolonging a discharge of the intensity used in these experiments. It undoubtedly contributed to the unfavourable consequences, noted above, of prolonging the discharge time in experiments with cholesterol.

Few definitive conclusions concerning the mechanism of the process can be drawn from these experiments. The fact that labelling occurs at pressures as high as 19 mm, where the mean free path in the gas is less than 4×10^{-4} cm, renders it unlikely that accelerated tritium-ions play an exclusive role. The nature of a Tesla discharge is so complex, however, that even this conclusion cannot be reached with certainty. The discharge would be expected to produce ionization and excitation of both the organic compound and the tritium gas. Various radical and ion-molecule reactions leading to labelling could be set forth, but any attempt to assess their relative importance would be pure speculation.

4. Summary

Tritium labelling of solid organic compounds by means of an electric discharge in tritium gas in the 10-mm pressure region is described. By this procedure useful concentrations of tritium, in the mc/g range, have been incorporated into *p*-dichlorobenzene, naphthalene, palmitic acid, benzoic acid, and cholesterol. Labelling is accomplished in a few minutes with quantities of tritium considerably less than those customarily used in the gas-exposure technique.

ACKNOWLEDGEMENT

The experiments with palmitic acid were performed at the Miami Valley Laboratories of the Proctor and Gamble Company in conjunction with a consulting visit by one of us (L.M.D.). We are indebted to Messrs. Proctor and Gamble for permission to report these results.

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DISCUSSION

Replying to a question by **M. Anbar** (Israel), **K. E. Wilzbach** said that he and his colleague had not yet been able to investigate the relation between the surface/volume ratio and specific activity, but he felt certain that the latter would increase with the former.

H. Nauta (Netherlands) asked the speaker's views on the possibility of fast tritium labelling with the aid of a beta or gamma-radioactive source instead of a gas discharge.

K. E. Wilzbach said that he and his colleague had not further explored the use of beta-radioactive Kr^{85}, because it did not solve the problem of handling large quantities of gaseous radioisotopes.

They had rejected the use of a gamma-radioactive source, as they felt that it would increase the ratio of decomposition to labelling; the penetrating radiation would cause decomposition in the interior of crystals where tritium might not be available for labelling.

B. E. Gordon (United States of America) said that he and his colleagues had labelled benzene under the same conditions using the technique of Lemmon *et al.* By stirring the solution, they had obtained an eightfold increase of incorporated tritium.

K. E. Wilzbach said that Mr. Gordon's experience provided very convincing evidence that labelling was predominantly a surface reaction.

W. Schweers (Federal Republic of Germany) asked what was the chemical structure of the by-products isolated from naphthalene, labelled by the electric-discharge method.

K. E. Wilzbach replied that the by-products were largely those arising from the addition of tritium, i.e. tetralin and decalin.

J. N. Gregory (Australia) asked what was the weight yield of the pure materials after tritiation.

K. E. Wilzbach replied that for the compounds investigated, the recovery of materials after tritiation appeared to be quantitative. Gas chromatography of the products from naphthalene and dichlorobenzene showed no peaks in thermal conductivity other than that produced by the parent compound.

Replying to a question by **H. Leth Pedersen** (Denmark), **K. E. Wilzbach** said that the results so far obtained showed no marked superiority of the discharge technique over the gas-exposure technique for the purpose of labelling aromatic compounds in the nucleus — provided facilities were available for handling relatively large quantities of tritium.

Replying to a question by **H. Elias** (Federal Republic of Germany), **K. E. Wilzbach** said that the distribution of tritium within the molecule had been examined in the case of benzoic acid. The results had shown that there was some preference, but not a marked one, for the attachment of tritium at the meta positions.

R. Wolfgang (United States of America) commented that the high-T_2-pressure technique used by Mr. Wilzbach and his colleague appeared to be considerably more successful than the low-pressure technique used previously by Pratt, Rowland and himself. Incidentally, the low-pressure experiments had revealed a tendency for the discharge itself to renew the surface by agitating the particles of the material that was being labelled.

K. E. Wilzbach replied that, in his view, the more promising results obtained by the high-pressure technique were largely due to the greater quantities of tritium available for labelling at the higher pressures.

СИНТЕЗ МЕЧЕННЫХ ПО ТРИТИЮ ЦИКЛИЧЕСКИХ УГЛЕВОДОРОДОВ С ПОМОЩЬЮ ЯДЕР ОТДАЧИ ТРИТИЯ

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СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

Abstract — Résumé — Аннотация — Resumen

The synthesis of tritium-labelled cyclic hydrocarbons by using tritium recoil nuclei. The authors discuss the results of investigating the interaction of tritium recoil atoms produced by the reaction Li^6 (n, α)T with cyclohexane, cyclohexene, cyclohexadiene, methyl cyclohexane, cyclohexanol, cyclohexylammine and benzene.

Mixtures of these compounds with lithium carbonate were neutron-irradiated. From 1 g of lithium, 4 mc/h of tritium was obtained with a 4×10^{12} n/cm^2 s neutron flux. The total yield of the products depends on the amount of tritium yielded by the crystals, and, so, on the irradiation conditions. The yield from the separate components is determined by analysis.

The irradiation products were analysed by vacuum distillation, using carriers and gas-liquid chromatography. The results obtained show that 20—40% of the tritium yielded by the lithium carbonate crystals is embedded in the parent molecule of the irradiated compound. When, for instance, cyclohexene is irradiated together with 22% of the labelled parent-compound, 16% cyclohexane, 4% methyl cyclopentane and small amounts of other products are obtained.

The specific activity of cyclohexane and methyl cyclopentane separated on a chromatographic column may be high, and the only dilution is with products of radiolysis.

When other compounds are irradiated, there is a good yield only from the irradiated parent-compound, and a small yield from other products. For purposes of preparation, cyclohexane and methyl cyclopentane are best obtained by irradiating cyclohexane; other cyclic hydrocarbons can be obtained by irradiating the compounds directly with lithium salts.

The paper describes a preparation column for separating tritium-labelled cyclohexane, cyclohexene and methyl cyclopentane from irradiated cyclohexene and for separating the products yielded by the reaction of tritium recoil atoms with other cyclic hydrocarbons.

Synthèse des hydrocarbures cycliques marqués au tritium, au moyen des noyaux de recul du tritium. Les auteurs examinent les résultats d'une étude sur l'interaction des atomes de recul du tritium obtenus par la réaction Li^6 (n, α)T avec le cyclohexane, le cyclohexène, le cyclohexadiène, le méthylcyclohexane, le cyclohexanol, le cyclohexylamine et le benzène.

Des mélanges des composés susmentionnés et de carbonate de lithium ont été soumis à l'irradiation neutronique. A partir de 1 g de lithium, on a obtenu 4 mc/h de tritium avec un flux de $4 \cdot 10^{12}$ n/cm^2. Le rendement global dépend de la quantité de tritium dégagée par les cristaux et, par conséquent, des conditions d'irradiation. Le rendement des divers éléments constitutifs est déterminé par analyse.

Les produits de l'irradiation ont été analysés par distillation sous vide, à l'aide d'entraîneurs et de la chromatographie gaz-liquide. Les résultats obtenus montrent que de 20 à 40% du tritium dégagé par les cristaux du carbonate de lithium s'incorpore à la molécule mère du composé irradié. Par exemple, si l'on irradie du cyclohexène avec 22% du composé ascendant marqué, on obtient 16% de cyclo-

hexane, 4% de méthylcyclopentane et un certain nombre d'autres produits en faibles quantités.

L'activité spécifique du cyclohexane et du méthylcyclopentane lors de leur séparation dans la colonne chromatographique peut être élevée, et la dilution se produit exclusivement avec les produits de la radiolyse. Lorsqu'on irradie d'autres composés, on n'obtient un bon rendement que pour le composé ascendant irradié; le rendement est faible pour les autres produits. Pour obtenir le cyclohexane et le méthylcyclopentane, le meilleur moyen est d'irradier le cyclohexène; pour obtenir les autres hydrocarbures cycliques, il y a intérêt à irradier les composés directement avec des sels de lithium.

Le mémoire décrit une colonne permettant de séparer du cyclohexène irradié le cyclohexane, le cyclohexène et le méthylcyclopentane marqués au tritium, et d'isoler les produits de la réaction des atomes de recul du tritium avec les autres hydrocarbures cycliques.

Синтез меченных по тритию циклических углеводородов с помощью ядер отдачи трития. Рассматриваются результаты исследования взаимодействия атомов отдачи трития, получающихся по реакции Li^6 (n, α) T с циклогексаном, циклогексеном, циклогексадиеном, метилциклогексаном, циклогексанолом, циклогексиламином и бензолом.

Облучению нейтронами подвергались смеси перечисленных выше соединений с углекислым литием. Из 1 г лития в час при потоке $4 \cdot 10^{12}$ нейтронов/см^2 получается 4 мкюри/трития. Общий выход продуктов зависит от доли трития, выходящего из кристаллов, и следовательно, от условий облучения. Выход отдельных компонентов определяется анализом.

Анализ продуктов облучения проводился вакуумной разгонкой с носителями и газожидкостной хроматографией. Полученные результаты показывают, что 20+40% трития, выходящего из кристаллов углекислого лития, внедряется в исходную молекулу облучаемого соединения. В случае облучения, например циклогексена, наряду с 22% меченого материнского соединения получается 16% циклогексана и 4% метилциклопентана и ряд других продуктов в небольших количествах.

Удельная активность циклогексана и метилциклопентана при разделении на хроматографической колонке может быть велика и разбавление происходит только за счет продуктов радиолиза. При облучении других соединений получается хороший выход только исходного облучаемого соединения и малый выход других продуктов. Для препаративных целей целесообразно для получения циклогексана и метилциклопентана облучать циклогексен, а для получения других циклических углеводородов проводить их непосредственное облучение с солями лития.

Описывается препаративная колонка для выделения из облученного циклогексена меченных по тритию циклогексана, циклогексена и метилциклопентана и для разделения продуктов реакций атомов отдачи трития с другими циклическими углеводородами.

Síntesis de hidrocarburos cíclicos marcados con tritio mediante núcleos de tritio de retroceso. Los autores examinan los resultados obtenidos al estudiar la interacción de los átomos de tritio de retroceso, obtenidos por la reacción ^{6}Li (n, α)T, con ciclohexano, ciclohexeno, ciclohexadieno, metilciclohexano, ciclohexanol, ciclohexilamina y benceno.

Irradiaron con neutrones mezclas de estos compuestos con carbonato de litio. Con un flujo de 4×10^{12} n/cm^2 s se obtienen en una hora 4 mc de tritio a partir de 1 g de litio. El rendimiento total de los productos depende de la cantidad de tritio proporcionada por los cristales, así como de las condiciones en que se efectúa la irradiación. El rendimiento de cada uno de los componentes se determina por análisis.

Los autores analizan los productos de irradiación por destilación al vacío con portadores y cromatografía gas-líquido. Los resultados obtenidos indican que de 20 a 40% del tritio procedente de los cristales del carbonato de litio se fija en la molécula del compuesto irradiado. Por ejemplo, si se irradia ciclohexeno junto con

el 22% del compuesto madre marcado, se obtiene 16% de ciclohexano, 4% de metilciclopentano y pequeñas cantidades de otros productos.

La actividad específica del ciclohexano y del metilciclopentano separados en una columna cromatográfica puede ser elevada, ya que esos compuestos sólo quedan diluidos por los productos de radiólisis.

Al irradiar otros compuestos, únicamente el compuesto madre irradiado se obtiene con buen rendimiento siendo pequeño el rendimiento para los demás productos. El mejor método para obtener ciclohexano y metilciclopentano consiste en irradiar ciclohexeno; para obtener otros hidrocarburos cíclicos, conviene irradiar directamente los compuestos mezclados con sales de litio.

La memoria describe una columna para separar ciclohexano, ciclohexeno y metilciclopentano marcados con tritio obtenidos por irradiación del ciclohexeno, y para separar los productos de la reacción de átomos de tritio de retroceso con otros hidrocarburos cíclicos.

Химия атомов, образующихся в результате ядерных превращений — химия „горячих" атомов — соприкасается близко с химией при высоких температурах, радиационной химией, химией свободных радикалов и областью ионно-молекулярных реакций. Изучение реакций „горячих" атомов проливает свет на все вышеуказанные области.

Исследование продуктов взаимодействия „горячих" атомов с различного рода молекулами важно и для разработки методов синтеза меченых соединений. Можно ожидать, что „горячий" синтез, наряду с другими физико-химическими методами синтеза (синтезом изотопным обменом, синтезом в электрическом разряде, синтезом с помощью ускоренных ионов) будет конкурентоспособным по отношению к химическому синтезу меченых соединений, а в ряде случаев — особенно для сложных веществ — единственно возможным. Химический синтез сложных меченых соединений, содержащих C^{14} и H^3, начинается с углекислого газа, содержащего C^{14}, или с тритированной воды и проходит через много стадий в результате чего, во-первых, теряется большая часть радиоактивного материала, так как выход продуктов на каждой стадии реакции неполный, во-вторых, такой синтез трудоемок и, следовательно, дорог. „Горячий" синтез соединяет в себе стадии получения и выделения радиоактивного элемента и его введения в молекулу. При проведении „горячего" синтеза получается смесь продуктов, содержащих радиоактивный изотоп, из которой целесообразно выделение веществ с большим выходом. При этом продукты, отличающиеся по составу от исходной материнской молекулы, получаются с высокой удельной активностью. При проведении реакций „горячих" атомов трития в среде углеводородов с двойной связью можно ожидать появления значительных количеств продуктов присоединения водорода по двойной связи [1].

В данном исследовании была поставлена задача разработки метода „горячего" синтеза соединений, содержащих тритий. До последнего времени в литературе мало уделялось внимания реакциям „горячих" атомов с циклическими углеводородами. Однако именно циклические соединения сложны для химического синтеза и в то же время радиационно устойчивы, особенно устойчивы шестичленные соединения. Последнее обстоятельство весьма важно при подготовке препаративных методик синтеза.

Объектами работы были избраны циклогексан и его производные, циклогексен, циклогексадиены и бензол. Радиационно-химические исследования

были проведены в частности для шестичленных алифатических и ароматических углеводородов, что облегчало задачу исследования „горячих" реакций атомов трития [2—4]. „Горячие" атомы трития получали в ядерном реакторе по реакции $Li^6(n, \alpha)T$ из карбоната лития, суспензированного в соответствующем углеводороде.

Экспериментальная часть

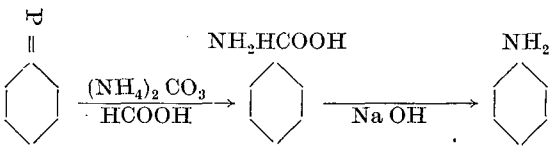
1. ИСХОДНЫЕ ВЕЩЕСТВА

Циклогексан марки „химически чистый" встряхивался сначала с концентрированной серной кислотой, затем с дымящей серной кислотой до 20 мин и, наконец, с насыщенным раствором $KMnO_4$ в 10%-ной серной кислоте. Далее он промывался водой, содой и снова водой, после чего сушился над хлористым кальцием и перегонялся над натрием. После 14-часового встряхивания с двумя порциями активированного угля перегонялся на ректификационной колонке.

Циклогексен получался путем дегидратации циклогексанола серной кислотой. Полученный продукт перегонялся над натрием в ректификационной колонке. Отбиралась фракция, кипящая в интервале 81—82° при нормальном давлении.

Циклогексанол марки „чистый" перегонялся на ректификационной колонке. Отбиралась фракция с температурой кипения 160° при 745 мм давления.

Циклогексиламин был получен по схеме:



Полученный продукт отгонялся на ректификационной колонке и отбиралась фракция с температурой кипения 131—133° при 734 мм давления.

Метилциклогексан марки „химически чистый" очищался встряхиванием с концентрированной серной кислотой с последующим промыванием содой и водой, затем сушился над хлористым кальцием и отгонялся на ректификационной колонке. Отбиралась фракция, кипящая при 100,5—101° при нормальном давлении.

Бензол марки „химически чистый" встряхивался с концентрированной серной кислотой, промывался водой и содой, сушился над хлористым кальцием и перегонялся на ректификационной колонке над натрием.

Циклогексадиен-1,4 был получен восстановлением „химически чистого" бензола натрием в жидком аммиаке.

Циклогексадиен-1,3 получался действием спиртового раствора КОН на 1,2 дибромциклогексан.

2. МЕТОДИКА ОБЛУЧЕНИЯ ИСХОДНЫХ МАТЕРИАЛОВ

Атомы отдачи трития получались при облучении медленными нейтронами активной зоны водо-водяного реактора углекислого лития. Углекислый литий негигроскопичен, а из кислорода и углерода при этом практически не образуется других радиоактивных элементов. Получающиеся атомы отдачи трития имеют энергию 2,7 Мэв, интенсивность потока нейтронов составляла

$4 \cdot 10^{12}$ нейтр/см^2 · сек. Углекислый литий суспензировался в облучаемом веществе и запаивался под вакуумом в кварцевые ампулы, которые помещались в алюминиевые или полиэтиленовые пеналы. Последние вводились в канал реактора на время 1—10 часов. После облучения пеналы с облученным материалом выдерживались перед анализом две недели.

3. АНАЛИЗ ПРОДУКТОВ «ГОРЯЧИХ» РЕАКЦИЙ

Анализ продуктов, получающихся в результате облучения, проводился с помощью газово-жидкостной, газово-адсорбционной хроматографии или методом разгонки. Ампулы с облученным материалом помещались в специальную давилку (рис. 1), присоединенную к хроматографической колонке или вакуумной системе. Из давилки пары и газы увлекались при подогревании потоком гелия.

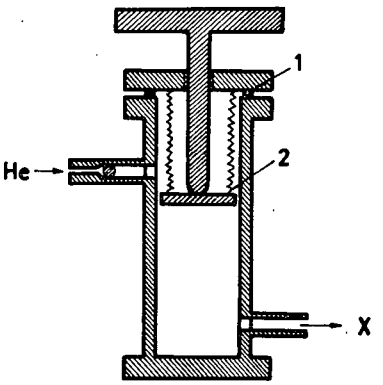


Рис. 1
Давилка. 1 — прокладка из тефлона; 2 — сильфон; He—из колонны предварительного подогрева; X—в хроматографическую колонку.

Хроматографическая колонка в виде медной спиральной трубки (диаметр спирали 25 см) длиною 6 м и с внутренним диаметром 6 мм помещалась в термостат. Колонка заполнялась фракцией 0,25—0,5 мм измельченного термоизоляционного диатомового кирпича, обработанного концентрированной соляной кислотой и промытого водой до нейтральной реакции, обработанного восьмипроцентной щелочью и водой до нейтральной реакции. Далее порошок сушился 6 часов при температуре 120° и 2 часа при 300°, после чего порошок обрабатывался эфирным раствором неподвижной жидкой фазы. В качестве неподвижной фазы применялась в большинстве случаев смесь трикрезилфосфата с дибутилфталатом (1:1). Для анализа облученного бензола использовался ββ′-оксидипропионнитрил. Разделение осуществлялось при 55°. Активность фракции измерялась на проточном счетчике Гейгера-Мюллера, работающем на смеси гелия и метана, термостатированном при 50°. Показания счетчика записывались на ленту самопишущего прибора. Идентификация продуктов производилась по удерживаемым объемам. Параллельно велась запись хроматограмм с помощью катарометра.

Для разделения больших количеств облученных веществ (5—10 г) и выделения из облученных смесей меченых соединений в препаративном мас-

штабе была сконструирована и построена установка по газово-жидкостной хроматографии (рис. 2). Установка состояла из двух медных труб, каждая длиною по 3 метра с внутренним диаметром 57 мм. Обе эти трубы соединялись медной трубкой с внутренним диаметром 6 мм. Хроматографические колонны обматывались для обогрева нихромовой проволокой и асбестовым полотном для термоизоляции. На входе хроматографической колонны находилось приспособление для раздавливания ампул с облученной смесью в токе гелия, которое также обогревалось. Гелий подогревался в колонке предварительного подогрева до температуры на 30—40° выше рабочей температуры хроматографической колонны. Скорость газа-носителя колебалась от 450 до 500 мл/мин. На выходе из хроматографической

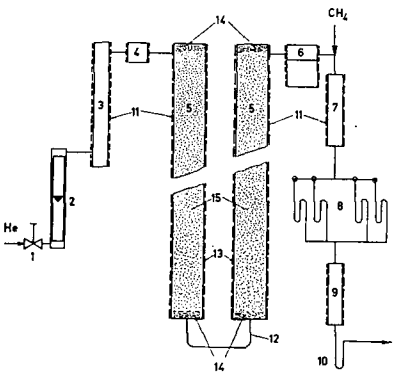


Рис. 2

Схема-блок препаративной газово-жидкостной хроматографии.

1 — редуктор; 2 — ротаметр; 3 — колонка предварительного обогрева; 4 — давилка; 5 — термоизоляционный кирпич с неподвижной фазой (30%); 6 — катарометр; 7 — счетчик; 8 — система ловушек для отбора фракций; 9 — печь с CuO для сжигания углеводородов; 10 — ловушка для улавливания тритированной воды; 11 — обогрев; 12 — медная трубка с внутренним диаметром 6 мм; 13 — медная трубка с внутренним диаметром 57 мм; 14 — пробка из стеклянной ваты.

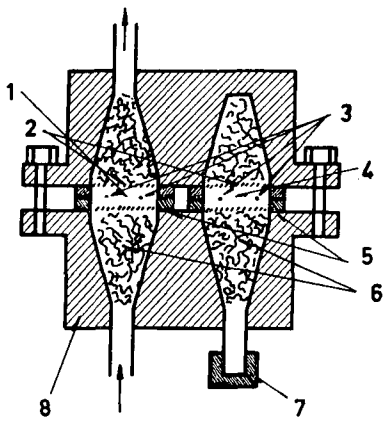


Рис. 3

Детектор для измерения теплопроводности (катарометр).

1 — измерительная ячейка; 2 — медная сетка; 3 — термисторы; 4 — сравнительная ячейка; 5 — тефлоновая прокладка; 6 — стеклянная вата; 7 — заглушка; 8 — латунный блок.

колонны помещался детектор (рис. 3). Этот тип детектора был описан Эвансом [5]. В каждую ячейку помещалось по 2 термистора типа ТШ-1, так что весь мост состоял из термисторов находящихся при одной и той же температуре и небольшие изменения в температуре не очень сильно влияли на основную линию. Детектор термостатировался таким же образом, как и колонны. В качестве измерителя температуры пользовались термобатареями из медно-константановых термопар. Последовательно с детектором помещался проточный счетчик, изготовленный из счетчика внутреннего наполнения типа СБМ-8. Счетная смесь состояла из смеси Не и CH_4 (1:1). После счетчика располагался ряд ловушек, в которых с помощью жидкого азота отбирались соответствующие фракции. Ненужные фракции сжигались над окисью меди до воды. Наполнение колонн было таким же, что и в аналитических колонках.

В ряде опытов анализ больших ампул проводился вакуумной отгонкой газовой фракции с последующим разделением жидкой фракции на ректификационной колонке около 40 теоретических тарелок и с помощью жидкостно-адсорбционной хроматографии на силикагеле. В этом случае перед разделением смеси добавлялись неактивные носители предполагаемых активных продуктов. Активность отдельных фракций измерялась в счетчике внутреннего наполнения типа СБМ-8.

4. Изучение изотопного обмена трития с циклическими углеводородами

Чтобы получить более ясное представление о процессе, происходящем при взаимодействии атомов отдачи трития со средой, необходимо было выяснить, не идет ли в условиях опытов обмен между тритием и облучаемым веществом, а также между облучаемым материнским соединением и мечеными производными соединениями. С этой целью углеводород (5 мл) и газообразный водород с активностью 1 мкюри (что соответствует примерно активности водорода, получающегося при облучении смеси углеводорода с солью лития) запаивались в ампулы и подвергались тепловому и радиационному воздействию. Одни ампулы выдерживались при температуре 60° С, что примерно соответствует температуре канала реактора, другие облучались в течение 10 часов в условиях, аналогичных тем, которые имеют место в опытах в присутствии соли лития. Выделенные из ампулы углеводороды, как показали измерения, не содержат активности. Только в случае циклогексанола наблюдался небольшой обмен (3—2%), в основном между тритием и ОН-группой (2,1%).

В системах циклогексан (Т)-циклогексанол (А = 1,3 мкюри), циклогексан (Т)-метилциклогексан (А = 1,1 мкюри) и циклогексан (Т)-циклогексен (А = 1 мкюри) также не было обнаружено обмена. Было показано, что в процессе разделения методом дистилляции также не происходит обмена.

Таким образом, в условиях проводившихся опытов и использовавшихся методик обмен не оказывает заметного влияния на распределение трития или меченых продуктов.

5. Результаты опытов

При облучении циклических углеводородов нас интересовал только выход меченых продуктов, содержащих 6—7 углеводородных атомов, поэтому и анализ проводился главным образом на эти продукты.

Таблица I

РАСПРЕДЕЛЕНИЕ ПРОДУКТОВ РЕАКЦИЙ АТОМОВ ОТДАЧИ ТРИТИЯ В ЦИКЛИЧЕСКИХ УГЛЕВОДОРОДАХ. АКТИВНОСТЬ МАТЕРИНСКОГО СОЕДИНЕНИЯ ПРИНЯТА ЗА 10. (ПОТОК НЕЙТРОНОВ $4 \cdot 10^{12}$ нейтр/см^2 сек)

Облученное соединение	Идентифицированное соединение Время облучения	Циклогексан	Циклогексен	Циклогексадиены 1,3	Циклогексадиены 1,4	Бензол	Метилциклогексан	Метилциклопентан	Гексаны и гексены
Циклогексан	5 час	100	5	—	—	2	5	6	25
Циклогексен	5 час	71	100	—	—	5	—	19	24
Бензол	5 час	1	4	2	10	100	0	0	0
Бензол	10 час	—	1,2	7,7	16,7	100	0	0	0
Циклогексадиен 1,4	10 час	39,3	91,5	31,6	100	175	—	—	—
Циклогексадиен 1,3	10 час	30	425	100	80	875	—	—	—

Распределение трития между продуктами реакций атомов отдачи трития с циклическими углеводородами показано в таблице I. Из этой таблицы видно, что циклогексен и циклогексадиены являются наиболее реакционноспособными, особенно успешно протекают реакции их гидрирования и дегидрирования. Циклогексен образует главным образом меченый циклогексан, а циклогексадиены — в больших количествах бензол и циклогексен. При облучении циклогексадиена-1,3 материнское соединение содержит на порядок меньше трития, чем при облучении циклогексадиена-1,4 или бензола.

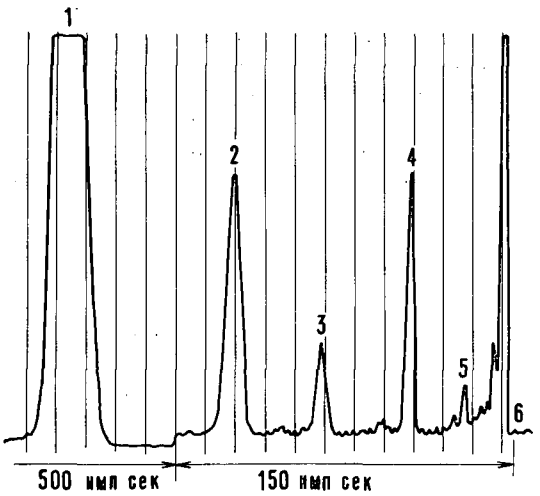


Рис. 4

Радиохроматограмма разделения облученного бензола на β′, — оксидипропионнитриле при температуре 55° С. Скорость гелия 40 мл/мин. Длина колонки 5,6 м.
1 — бензол; 2 — циклогексадиен-1,4; 3 — циклогексадиен-1,3; 4 — циклогексен; 5 — циклогексан; 6 — начало.

Значительно меньше меченых продуктов образуется при облучении бензола, *что особенно наглядно видно при сравнении хроматограммы разделения* облученных бензола, циклогексена и циклогексана (рис. 4, 5, 6). При взаимодействии атомов отдачи трития с бензолом главными мечеными продуктами, кроме самого меченого бензола, являются продукты

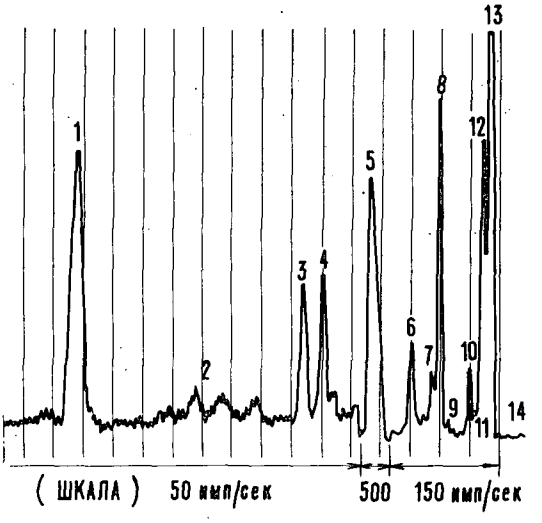


Рис. 5

Радиохроматограмма разделения облученного циклогексана на смеси дибутилфталат-трикрезилфосфат (1:1) при температуре 55° С. Скорость гелия 37 мл/мин. Длина колонки 6 метров.

1 — неидентиф. соединение (А); 2 — бензол; 3 — метилциклогексан; 4 — циклогексен; 5 — циклогексан; 6 — метилциклопентан; 7 — гексены; 8 — гексан; 9 — циклопентан; 10 — пентены; 11 — пентин; 12 — бутан; 13 — водород $\times C_1 \times C_2 \times C$; 14 — начало.

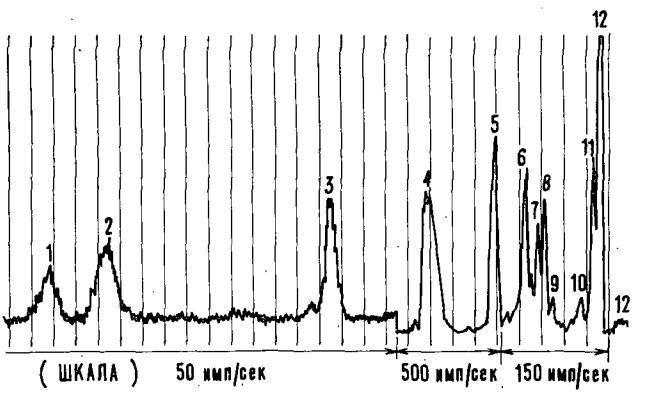


Рис. 6

Радиохроматограмма разделения облученного циклогексена на смеси дибутилфталат — трикрезилфосфат (1:1) при температуре 51° С. Скорость гелия 37 мл/мин. Длина колонки — 6 метров.

1 — неидентиф. соединение (В); 2 — неидентиф. соединение (А); 3 — бензол; 4 — метилциклогексан; 5 — циклогексан; 6 — метилциклопентан; 7 — гексены; 8 — гексан; 9 — циклопентан; 10 — пентены; 11 — бутан; 12 — водород $\times C_1 \times C_2 \times C$; 13 — начало.

гидрирования: циклогексадиен-1,4; циклогексадиен-1,3, циклогексен и в небольших количествах циклогексан. По литературным данным [3, 4], продуктов гидрирования бензола при облучении гамма-лучами и быстрыми электронами не было обнаружено. Вполне возможно, что и в наших условиях эти меченые продукты гидрирования образуются без радиолитических носителей и имеют большую удельную активность. Таким образом, система бензол-соль лития представляет практический интерес с точки зрения получения этих соединений с большой удельной активностью.

Что касается циклогексана, то он ведет себя как типичный алифатический углеводород [6—8], образуя в небольших количествах меченые продукты деструкции и изомеризации. Основная доля трития находится в виде водорода и материнского соединения.

При облучении дейтерированного на 50% циклогексана выход водородной фракции заметно увеличивается, отношение водорода к циклогексану и бензолу составляет для дейтерированного соединения 2,75:1:0,1, а для недейтерированного — 2,1:1:0,07.

Полученная удельная активность для материнских соединений возрастает от циклогексана до бензола. При времени облучения 5 часов циклогексан получался с активностью 10 мккюри/г, циклогексен — 14 мккюри/г, бензол — 15 мккюри/г. При облучении в течение 10 часов активность бензола составляла 38 мккюри/г. Удельную активность остальных меченых соединений трудно оценить, так как мы точно не знаем количество радиолитических носителей. В случае образования меченого циклогексана из циклогексена удельная активность была равна 130 мккюри/г.

Таблица II

ВЛИЯНИЕ ФУНКЦИОНАЛЬНЫХ ГРУПП В ЦИКЛЕ НА РЕАКЦИИ ЗАМЕЩЕНИЯ

(Активность материнского соединения принята за 100)

Идентифицированное соединение Облученные соединения			$H_2 + CH_4$
Метациклогексан	100	11	173
Циклогексанол	100	13	222
Циклогексиламин	100	16	189

В таблице II показано влияние заместителей на замещение тритием атомов водорода в кольце и самого заместителя. Как видно, на процессе образования меченого циклогексана из $C_6H_{11}R$ ($R = OH$, NH_2CH_3) путем замещения R на T, при примерно равных массах химическая природа заместителя не оказывает большого влияния. В случае циклогексанола было изучено распределение трития между кольцом и заместителем. Оказалось, что около 41% трития от общей активности спирта находится в гидроксильной группе, что качественно согласуется с литературными данными по облучению алифатических спиртов [9].

Здесь интересно отметить, как показали наши опыты по исследованию реакции атомов отдачи трития с этиловым спиртом, внутримолекулярное распределение трития не постоянно, а изменяется со временем. Активность гидроксильной группы падает, а активность радикала C_2H_5 растет при

постоянстве общей активности этилового спирта. Причем скорость падения активности в гидроксильной группе следует закону первого порядка.

6. Обсуждение результатов

Замещение водорода тритием в процессе ядерных превращений происходит главным образом в области энергий, соответствующих „горячим" и „надтепловым" реакциям.

В результате „горячих" реакций и других по механизму упругих соударений появляются продукты замещения водорода на тритий.

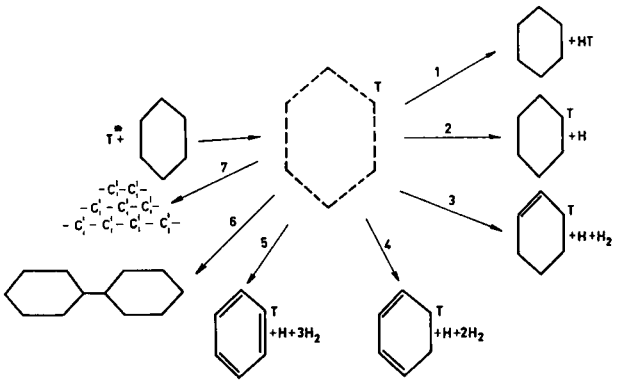


Рис. 7
Схема взаимодействия атома отдачи трития с циклическими углеводородами.

„Надтепловые реакции", протекающие путем неупругих соударений трития с молекулой в целом, идут в две стадии (рис. 7). На первой стадии образуется активный возбужденный комплекс, который стабилизуется путем ряда параллельно текущих реакций. Среди продуктов реакций должны быть молекулы материнского соединения, молекулы с образовавшимися или разорвавшимися двойными связями в кольце, разомкнутые линейные соединения с числом атомов равным или меньшим, чем в материнской молекуле, продукты конденсации и водород.

Такие продукты реакций найдены во всех исследованных циклических соединениях.

Продукты замещения атома водорода на тритий могут образоваться и в результате тепловых реакций взаимодействия трития в атомарном состоянии с материнской молекулой, как показано в работе [10] с помощью атомов дейтерия, получаемого в электроразряде.

Значительная доля трития внедряется в циклогексан и циклогексадиены. Наибольший выход циклогексена с большой удельной активностью получается при облучении циклогексана, и для препаративных целей получения циклогексана целесообразно подвергать облучению циклогексен. Одновременно с циклогексаном получаются значительные количества метилциклопентана. Для получения меченых бензола и циклогексена весьма удобно облучать циклогексадиены.

В случае дейтерированного циклогексана повышенной выход водорода может быть связан как с изменением средней энергии тритонов в дейтеросодержащей среде по сравнению с водородосодержащей средой, так и с

различным химическим поведением возбужденных молекул циклогексана различного изотопного состава.

Уменьшение вероятности внедрения трития в дейтерированную молекулу качественно согласуется с данными по пометке дейтерированного кольца изопропилбензоата [11].

В таблице II приведены данные по результатам замещения водорода и функциональных групп (CH_3, OH, NH_2) в соответствующих производных циклогексана. Во всех случаях исследовались активности молекулярного водорода (HT), исходного вещества $C_6H_{11}R$ (продукт замещения H на T) и циклогексана (продукт замещения R на T). Как видно из таблицы II для функциональных групп различной химической природы, но близких по массе, отношения близки и равны в среднем 1,92:1:0,12.

Независимость выхода реакций замещения от химической природы радикалов при практически равных массах говорит в пользу того, что реакции протекают по „горячему" механизму.

Выводы

1. Исследовано действие горячих атомов трития на циклогексан, циклогексен, метилциклогексан, циклогексанол, циклогексиламин, бензол, циклогексадиены.
2. Обсужден механизм стабилизации горячих атомов трития.
3. Показана возможность получения меченных по тритию циклических соединений с хорошим выходом „горячим" синтезом. В частности, следует рекомендовать для получения циклогексана и метилциклопентана облучение смеси циклогексана с солью лития, а для получения бензола и циклогексена 1,4-циклогексадиена — облучение в смеси с солью лития.
4. Показано отсутствие изотопного обмена в системах циклогексанол-циклогексан, циклогексан-метилциклогексан и медленный обмен в системе тритий-циклогексанол.
5. Исследовано распределение трития внутри молекулы циклогексанола и показано, что содержание трития при углероде и в гидроксильной группе различно, что требует знания распределения трития после горячих реакций и в других несимметричных соединениях.
6. Показано отличие в горячих реакциях трития в дейтерированных циклических соединениях. Дейтерированные соединения дают большое количество трития в виде водорода и следовательно менее пригодны для „горячего" синтеза тритийсодержащих молекул.

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DISCUSSION

Replying to a question by **A. Voigt** (United States of America), **A. N. Nesmeyanov** said that he and his colleagues had not made a thorough study of the gas fraction. The chromatograph of the products obtained in the liquid phase had been shown in the paper. No other products with a noticeable yield had been identified.

D. S. Urch (United Kingdom) asked the speaker whether studies had been carried out using scavengers such as iodine or oxygen in order to throw further light on the reaction mechanisms.

A. N. Nesmeyanov said that experiments of that kind were under way at present and it was possible that the results would be communicated to the Symposium on the Chemical Effects of Nuclear Transformations, to be held in Prague in October 1960.

ПОЛУЧЕНИЕ МЕЧЕННЫХ ПО СЕРЕ СОЕДИНЕНИЙ В РЕЗУЛЬТАТЕ РЕАКЦИЙ ГОРЯЧИХ АТОМОВ СЕРЫ-35 С ЦИКЛИЧЕСКИМИ УГЛЕВОДОРОДАМИ

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СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

Abstract — Résumé — Аннотация — Resumen

Method of obtaining sulphur-labelled compounds by reaction of "hot" sulphur-35 atoms with cyclic hydrocarbons. The authors discuss methods of obtaining sulphur-labelled compounds, such as aliphatic and cyclic mercaptans and sulphides, by direct synthesis employing recoil atoms from the reaction Cl^{35} (n, p) S^{35}.

Hot S^{35} atoms were obtained in the middle of the target substance by exposing mixtures of C Cl_4 and a cyclic hydrocarbon (cyclopentane, cyclohexane) to neutrons in a reactor.

A method is given for irradiating the mixtures and then separating the various sulphur-bearing compounds by specific chemical methods, rectification, and paper and gas-liquid chromatography. The purpose of the exchange is clarified. The relation of the yield of the separated sulphur-labelled products to the composition of the mixture and type of exposure was investigated, and an active-sulphur balance settled. New types of atomic sulphur reactions were established: the CH_2-group is replaced and implanted on the C-C link. The cyclic molecule is destroyed in the interaction with the hot sulphur atoms. Hot sulphur atoms can initiate the formation of polymers containing sulphur. The yields of these reactions were established. Up to 98% of the active sulphur is linked in the form of organic sulphur compounds.

It was shown that sulphur-labelled thiophene, tetrahydrothiopyrane, cyclopentylmercaptan, cyclohexylmercaptan, ethyl-propyl-butyl-mercaptans, dicyclopentylsulphide, polymeric mercaptans and sulphides could be synthesized by heat. It is possible to regulate within broad limits the yield of various labelled compounds by changing the decelerating properties of the medium.

Obtention de composés marqués au soufre par réaction d'atomes de soufre-35 excités avec des hydrocarbures cycliques. Les auteurs examinent les méthodes permettant d'obtenir des composés marqués au soufre (mercaptans et sulfures aliphatiques et cycliques) par synthèse directe à l'aide des atomes de recul obtenus par la réaction ^{35}Cl (n, p) ^{35}S.

Des atomes fortement excités de ^{35}S ont été obtenus au milieu de la substance cible par irradiation neutronique de mélanges de CCl_4 et d'un hydrocarbure cyclique (cyclopentane, cyclohexane) dans un réacteur. Les auteurs exposent la méthode d'irradiation des mélanges et les procédés chimiques permettant de séparer ensuite les divers composés contenant du soufre (rectification, chromatographie sur papier et chromatographie gaz-liquide). Ils expliquent le rôle de l'échange, examinent la mesure dans laquelle le rendement pour les divers produits marqués au soufre dépend de la composition du mélange et de la nature de l'irradiation et établissent le bilan du soufre actif. Ils déterminent de nouveaux types de réaction atomique du soufre: substitution du groupe CH_2 et incorporation dans les unions C-C. Après avoir constaté la destruction de la molécule cyclique dans l'interaction avec les atomes excités du soufre, ils font ressortir l'aptitude de ces atomes à amorcer la formation de polymères contenant du soufre. Ils ont déterminé les rendements de ces réactions et démontré que jusqu'à 98% du soufre actif se lie sous forme de composés organiques du soufre.

Les auteurs montrent la possibilité de réaliser la synthèse à chaud des produits suivants, marqués au soufre: thiophane, tétrahydrothiopyrane, cyclopentylmercaptan, cyclohexylmercaptan, éthyl-propyl-butyl-mercaptans, sulfure de dicyclopentyle, mercaptans et sulfures polymères. Ils indiquent également la possibilité de régler dans des limites assez larges le rendement des divers composés marqués, en modifiant les propriétés de ralentissement du milieu.

Получение меченных по сере соединений в результате реакции „горячих" атомов серы-35 с циклическими углеводородами. Рассматриваются методы получения меченных по сере соединений — открытых и циклических меркаптанов и сульфидов, — основанные на прямом синтезе с участием атомов отдачи, получаемых по реакции Cl^{35} (n, p) S^{35}.

Получение горячих атомов S^{35} в среде вещества мишени осуществлялось путем облучения в реакторе нейтронами смесей CCl_4 и циклического углеводорода (циклопентан, циклогексан). Излагается методика облучения смесей и последующего разделения различных серосодержащих соединений с использованием специфических химических методик, ректификации, бумажной и газо-жидкостной хроматографии. Выяснена роль обмена. Исследована зависимость выхода отдельных меченных по сере продуктов от состава смеси и характера облучения. Сведен баланс по активной сере. Установлены новые типы реакций атомарной серы: замещения CH_2-группы, внедрение по связи C—C. Обнаружена деструкция циклической молекулы при взаимодействии с горячими атомами серы. Показана способность горячих атомов серы инициировать образование серосодержащих полимеров. Установлены выходы этих реакций. Показано, что до 98% активной серы оказывается связанной в форме сероорганических соединений.

Показана возможность горячего синтеза меченных по сере тиофана, тетрагидротиопирана, циклопентилмеркаптана, циклогексилмеркаптана, этилпропилбутилмеркаптанов, дициклопентилсульфида, полимерных меркаптанов и сульфидов. Показана возможность регулирования в широких пределах выхода различных меченых соединений путем изменения замедляющих свойств среды.

Métodos para obtener compuestos marcados con azufre mediante la reacción de átomos excitados de azufre-35 con hidrocarburos. La memoria estudia métodos para obtener compuestos marcados con azufre, como sulfuros y mercaptanos alifáticos, y cíclicos, mediante síntesis directa empleando átomos de retroceso obtenidos por la reacción ^{35}Cl (n, p) ^{35}S.

Se obtuvieron átomos excitados de azufre-35 en la misma sustancia blanco, irradiando con neutrones en un reactor mezclas de CCL_4 y un hidrocarburo cíclico (ciclopentano, ciclohexano).

La memoria indica un procedimiento para irradiar las mezclas y separar después los compuestos que contengan azufre utilizando métodos químicos específicos, destilación fraccionada, cromatografía sobre papel y cromatografía gas-líquido. También explica la finalidad del intercambio. Los autores estudiaron la relación entre el rendimiento de los diversos productos marcados con azufre y la composición de la mezcla y el tipo de irradiación, y determinaron el balance de azufre activo. Establecieron nuevos tipos de reacciones de azufre atómico: la sustitución del grupo CH_2 y la inclusión en el enlace C-C. La molécula se destruye en la interacción con átomos de azufre excitados. Estos átomos pueden iniciar la formación de polímeros que contienen azufre. Se determinó el rendimiento de estas reacciones. Hasta el 98% del azufre excitado aparece en forma de compuestos orgánicos de azufre.

Se demostró que, en caliente, es posible sintetizar tiefeno, tetrahidrotiopirano, ciclopentilmercaptano, ciclohexilmercaptano, etilpropilbutilmercaptanos, sulfuro de diciclopentilo, mercaptanos polimerizados, etc., marcados con azufre. El rendimiento de varios compuestos marcados puede regularse dentro de amplios límites modificando las propiedades moderadoras del medio.

Введение

Радиоактивная сера S^{35} в свете изучения синтеза меченых соединений методом атомов отдачи и исследования горячих атомов представляет собой весьма интересный и важный объект. Сера входит в состав ряда важнейших с точки зрения химии и биологии сложных органических соединений в виде сульфо-, меркапто- и сульфидных групп. К ним относятся, например, полипептиды и аминокислоты (глутатион, цистин, цистеин, таурин), витамины (витамин B_1), лекарственные сульфамидные препараты (сульфазол), ускорители полимеризации (каптакс) и другие. Часто возникает необходимость получения подобных соединений, меченных по сере.

Применение обычных методов — химического синтеза и обмена в ряде случаев оказывается затруднительным. Химический синтез, обычно употребляемый в случае получения соединений, меченных по углероду, для биологически важных серосодержащих соединений слишком сложен и длителен. Метод обмена, который часто может быть с успехом применен для пометки по водороду, в случае серосодержащих соединений имеет лишь ограниченное значение.

В значительной части практически важных случаев сера входит в состав гетероциклов или открытых сульфидов, где обмен не приводит к цели, да и в лабильных положениях обмен серой заметен лишь в достаточно жестких условиях. В связи с этим для получения меченных по сере соединений особый интерес может представить метод пометки, основанный на использовании кинетической энергии атомов отдачи.

Для разработки методики „горячей" пометки необходимо выяснить особенности химического поведения горячих, обладающих высокой кинетической энергией атомов серы. Это тем более необходимо, что реакции атомарной серы вообще мало исследованы [1], а реакции горячих атомов серы с органическими молекулами в отличии от атомов галоидов, углерода и водорода, совершенно не изучены.

Вместе с тем радиоактивные атомы S^{35} вообще являются удобным модельным объектом для исследования процесса горячей пометки. С одной стороны, S^{35} обладает удобными физическими свойствами ($T=87{,}1$ дн., $E_m=167$ кэв), позволяющими получать значительные активности за достаточно малое время и обходиться несложными счетными устройствами. С другой стороны, сера по валентности (атом серы — бирадикал), массе и начальной энергии отличается от углерода, водорода и галоидов, и изучение реакций горячих атомов серы расширяет область физических параметров, которые могут влиять на выход горячих реакций.

Естественно, что изучение химического поведения горячих атомов серы в органических средах желательно начать с достаточно простого вещества, но вместе с тем интересного с практической точки зрения разработки методов горячей пометки. В значительной части упомянутых выше примеров биологически и химически важных соединений сера входит в состав пятичленных гетероциклов. Поэтому в качестве модельного вещества, мишени, выбран циклопентан. Вместе с тем циклопентан является достаточно простым соединением, состоящим лишь из CH_2-групп. Простота структуры молекулы циклопентана и сравнительно небольшое количество продуктов радиолиза упрощают методику исследования. В некоторых опытах использовался также циклогексан.

Целью работы является исследование химического поведения горячих атомов серы в среде циклопентана, выяснение типов протекающих при этом реакций, спектра образующихся меченных по сере соединений и установление выходов различных меченых продуктов. Исследовалась также возможность влиять на относительные выходы различных продуктов химической стабилизации горячих атомов серы путем изменения условий эксперимента.

Методика

1. ПОЛУЧЕНИЕ ГОРЯЧИХ РАДИОАКТИВНЫХ АТОМОВ S^{35}

Получение горячих атомов радиоактивной серы S^{35} производилось по реакции Cl^{35} (n, p) S^{35}. Генерирование горячих атомов серы в среде циклопентана осуществлялось путем облучения в ядерном реакторе заключенных в кварцевые ампулы смесей четыреххлористого углерода и циклопентана. Соотношение датчика горячих атомов серы (Cl) и вещества-мишени изменялось в пределах от 1:10 до 10:1.

Ядерная реакция Cl^{35}(n, p)S^{35} является экзоэнергетической ($Q = +0{,}6$ Мэв) и возбуждается тепловыми нейтронами с сечением $\sigma \simeq 170$ мбарн. При реакции на тепловых нейтронах начальная энергия атома серы $E_0 = 16{,}5$ кэв.

Несмотря на невысокое значение σ, небольшой период полураспада ($T = 87{,}1$ дн.) хлор позволяет уже при не очень длительных облучениях в реакторе получать достаточные для исследования активности. Так, при облучении в нейтронном потоке $\Phi = 10^{12}$ нейтр/см^2 сек на 1 г хлора образуется 20 мккюри/час активной серы. В условиях несколько больших потоков облучение продолжалось от 1 до 10 часов.

По сравнению с экспериментами с горячими атомами водорода H^3 (большие σ и $Q = 4{,}7$ Мэв ядерной реакции Li^6 (n, α) T), и углерода C^{14} (большой период $T = 5600$ лет, требующий длительного облучения) в опытах с серой выделяющаяся при облучении в системе энергия (за счет теплоты ядерной реакции и излучения реактора) не столь велика, что приводит к уменьшению роли радиолиза. Для уточнения роли радиолиза облучения проводились на двух ядерных реакторах (с замедлителями из обычной и тяжелой воды) с различным соотношением потоков медленных нейтронов (генерирующих активную серу) и быстрых нейтронов и гамма лучей (создающих основную часть дозы).

2. РАЗДЕЛЕНИЕ И ОЧИСТКА МЕЧЕНЫХ ПРОДУКТОВ

Разделение образующихся меченных по сере продуктов производилось с использованием техники стабильных носителей.

Выбор носителей производился на основании общих соображений о механизме остывания и стабилизации горячих атомов серы в смеси циклопентана и четыреххлористого углерода и результатов предварительных опытов. Можно было ожидать образования ряда меченных по сере соединений, являющихся результатом различных реакций горячих атомов серы на различных стадиях остывания: отрыва водорода, замещения CH_2-группы, внедрения по связям C—C и C—H, присоединения к исходной молекуле и продуктам деструкции, конденсации. В соответствии с этим предполагалось образование меченных по сере сероводорода, элементарной серы, легко гидролизующихся хлоросодержащих соединений (тиофосген $CSCl_2$, перхлорметилмеркаптан $CSCl_4$, хлористая сера S_2Cl_2), метилмер-

каптана CH_3SH, этилмеркаптана C_2H_5SH, пропилмеркаптана C_3H_7SH, бутилмеркаптана C_4H_9SH, циклопентилмеркаптана SH, тетраметиленсульфида (тиофана) , пентаметиленсульфида (тетрагидротиопирана) , дициклопентилсульфида .

Носители этих соединений, а также исходные вещества были синтезированы и подвергнуты тщательной очистке до совпадения констант с литературными данными.

Правильность выбора носителей впоследствии контролировалась сведением баланса по активной сере.

3. Схема разделения

Схема разделения жидких и газообразных меченных по сере продуктов, образующихся при реакции горячих атомов серы с циклопентаном приведена на рис. 1.

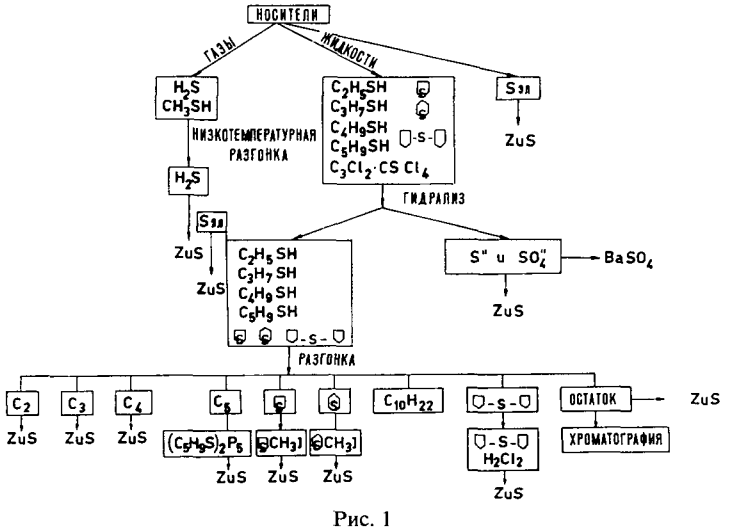


Рис. 1

Схема разделения меченых продуктов реакций горячих атомов серы с циклопентаном.

Ампула, содержащая облученную смесь циклопентана и четыреххлористого углерода, замораживалась в жидком азоте, вскрывалась и помещалась в специальную установку для разделения газофазных и жидкофазных меченых продуктов. Газообразные и жидкие продукты подвергались анализу по соответствующим методикам с применением техники носителей.

Газообразные вещества делились и очищались в специальной вакуумной установке низкотемпературной разгонкой.

Жидкие вещества разделялись ректификацией и вакуумной дестилляцией, с помощью хроматографии и путем вовлечения в цикл специфических химических реакций. В аликвотной части ампулы определялась элементарная сера и общая активность.

После отделения газообразных веществ жидкая фаза с носителями обрабатывалась 0,1-н щелочью для разрушения легко гидролизующихся соединений типа $CSCl_2$, $CSCl_4$, S_2Cl_2 до серы и сероводорода. В результате подкисления и многократной экстракции деканом смесь делилась на водную

и органическую фазы. В первой определялись продукты гидролиза в виде S″ и окисленных форм, вторая, содержащая сероорганические молекулы, общую и гидролизную серу, исходные вещества и декан, подвергалась дистилляции с помощью ректификационной колонки. После отделения исходных веществ и низших меркаптанов (34—98° С), ректификация для предотвращения термического распада высококипящих продуктов продолжалась под пониженным давлением (57 мм Hg), в результате чего тетра- и пентаметиленсульфиды и циклопентантиол t^0кип 120—140° С) разделялись при температуре не выше 70° С. Разделение контролировалось по кривым ректификации и сопоставлением результатов анализа фракций на содержание серы с теоретическим составом.

Оставшаяся смесь декана, дициклопентилсульфида и возможных высококипящих продуктов разделялась перегонкой в вакууме (10 мм Hg) при температуре не выше 100° С. Декановая фракция не содержала активности, неотгоняемый остаток экстрагировался деканом и подвергался анализу на активную серу и хроматографированию на бумаге.

В аликвотной части облученной смеси определялась активность элементарной серы до и после гидролиза.

После ректификации меченые вещества подвергались дополнительной очистке путем вовлечения в специфические химические реакции и многократной перекристаллизации продуктов реакции.

Так как циклические сульфиды в отличии от меркаптанов и открытых сульфидов дают с иодистым метилом прекрасные осадки сульфониевых солей, то тетра- и пентаметиленсульфиды осаждались из соответствующих фракций в виде йодметилатов типа $\left[\bigcirc^{S^+}-CH_3\right] J^-$. Осадки йодметилатов многократно перекристаллизовывались.

Циклопентантиол освобождался от возможных примесей в фракции вначале осаждения йодметилата специально добавленного тиофана, затем после отделения осадка йодметилата — осаждением ацетатом свинца циклопентилмеркаптида свинца. Осадок свинцового мекраптида растворялся в кислоте и несколько раз переосаждался.

Дициклопентилсульфид очищался путем осаждения ртутного комплекса $\left(\bigcirc\!-\!S\!-\!\bigcirc\right) \cdot HgCl_2$ с последующей многократной перекристаллизацией его из спирта.

Во всех случаях производился контроль удельной активности α на различных стадиях очистки. Чистота препарата определялась по достижению

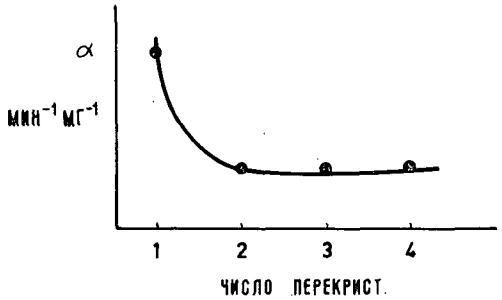


Рис. 2

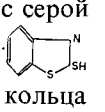
Кривая очистки. Изменение удельной активности при ряде последовательных операций очистки.

постоянства удельной активности при нескольких перекристаллизациях. Типичная кривая очистки приведена на рис. 2.

Роль обмена

При разработке методики выделения индивидуальных меченых продуктов специально исследовалось возможное влияние обмена серой между веществами в процессе облучения и разделения на перераспределение активной серы между продуктами первичных процессов.

Были поставлены опыты по исследованию обмена в системах: меркаптан-элементарная сера, элементарная сера-сульфид, меркаптан-меркаптан, меркаптан-сульфид. Опыты ставились с мечеными веществами и обмен регистрировался по изменению активности. Исследование обмена производилось при температурах от 25° до 120° С, т.е. в области, которая шире температурного интервала, имеющего место при осуществлении методики разделения и при облучении. Определялось также воздействие на обмен облучения гамма-лучами Co^{60} дозами, близкими к дозам, получаемым смесью при облучении в реакторе.

Показано, что в практически интересных системах обмен протекает медленно. Так, например, в системе меркаптан-меркаптан (циклогексил- и бутилмеркаптаны) при 80° С за 48 часов обмен достигает лишь 2%; еще более медленно протекает обмен в системе меркаптан-сульфид. Наиболее глубокий обмен достигается в системе сера-меркаптан, но лишь в достаточно жестких условиях. Например, циклогексил и бутилмеркаптаны обмениваются с серой при 120° С за 24 часа на 18—20%, но уже при 70° обмен за то же время составляет лишь 0,6—1%. В системе сера-сульфид (этилпропилсульфид) даже при 120° и при времени реакции 24 часа обмен составляет лишь 2%. Значительно меньшая подвижность сульфидной серы по сравнению с серой меркаптогруппы отмечалась также в литературе [2]. Так, в каптаксе 

удается обменять лишь серу в меркаптогруппе, сера тиазольного кольца (сульфидная) в обмен не вступает.

Из вышеизложенного следует, что в условиях температур и экспозиций, имеющих место в наших экспериментах, роль обмена серой между продуктами первичных реакций несущественна.

4. ОПРЕДЕЛЕНИЕ КОЭФФИЦИЕНТОВ ВЫХОДА МЕЧЕНЫХ СОЕДИНЕНИЙ

Коэффициент выхода данного меченого продукта определялся по отношению активности индивидуального вещества к полной активности серы в ампуле: $K = A_i/A$ 100%.

Общая активность определялась в аликвотной части смеси: а) сожжением в азотной кислоте по Кариусу и осаждением серы в виде $BaSO_4$; б) восстановительным разложением в токе водорода на платиновом катализаторе [3] и осаждением серы в виде ZnS. Второй путь предпочтителен. Он менее трудоемок и позволяет более надежно освободиться от примесей радиофосфора, возникающего при сопутствующей реакции $Cl^{35}(n, \alpha)P^{32}$, так как различие в свойствах H_2S и PH_3 гораздо больше, чем между SO_4'' и PO_4'''.

Активность индивидуальных меченых веществ определялась аналогичным образом с учетом коэффициента извлечения носителя. Измерения активности проводились в стандартных условиях с соблюдением правил, обычных при работе с мягким β-излучением.

Результаты и обсуждение

Анализами по вышеизложенной методике установлено, что в результате реакций горячих атомов серы с циклопентаном возникает значительное число меченных по сере соединений — меркаптанов и сульфидов открытого и циклического типов.

Результаты типичной серии анализов для смеси циклопентана с четыреххлористым углеродом при молярном соотношении $\nu = [C_5H_{10}]/[Cl] = 1$ приведены в таблице I.

Таблица I

РАСПРЕДЕЛЕНИЕ РАДИОАКТИВНОЙ СЕРЫ МЕЖДУ ИНДИВИДУАЛЬНЫМИ МЕЧЕНЫМИ ПРОДУКТАМИ

(полная активность $A_0 = 0{,}5$ мкюри, $\nu = [Cl]/[C_5H_{10}] = 1$)

	Вещество	Формула	Выход $K = (A_i/A_0)\,100\%$
1	Сера элементарная	$^{*}S$	1,0
2	Сероводород	H_2S	0
3	Гидролизующиеся производные CCl_4	$CSCl_4 + S_2Cl \rightarrow S$ $CSCl_2 \rightarrow S''$	0 0,01
4	Метилмеркаптан	CH_3SH	—
5	Этилмеркаптан	C_2H_5SH	0,6
6	Пропилмеркаптан	C_3H_7SH	0,6
7	Бутилмеркаптан	C_4H_9SH	0,9
8	Циклопентантиол (циклопентилмеркаптан)		7,6
9	Тиофан (тетраметиленсульфид)		0,2
10	Тетрагидротиопиран (пентаметиленсульфид)		2,2
11	Дициклопентилсульфид		2,1
12	Высокомолекулярные сульфиды и меркаптаны	$R{-}S{-}R_1$ $R{-}SH$	84,1
	Сумма:		99,3

Данные таблицы I характеризуют спектр меченых продуктов и величины их выходов $K = (A_i/A_0)\ 100\%$, выраженные в процентном отношении активности продукта A_i к независимо определенной полной активности радиосеры в образце A.

Хорошее сведение баланса по активной сере свидетельствует о правильном выборе носителей и корректности принятой методики. Практическое равенство A и ΣA_i позволяет полагать, что в спектре меченых продуктов отсутствуют сколь-нибудь значительные ($K > 0{,}5\%$) пробелы.

Достаточно большая активность в образце ($\sim 0{,}5$ мк, измеряемая активность $A = 3{,}6 \cdot 10^7$ 1/мин) позволяет достаточно надежно определять выходы продукта, в том числе и с небольшим $K \simeq 0{,}1\%$. Нулевые значения в таблице соответствуют возможным коэффициентам выхода $K \lesssim 0{,}01\%$.

При рассмотрении данных таблицы I обращает на себя внимание ряд обстоятельств, существенных с точки зрения теории и практики метода горячего синтеза:

а) образование в процессе облучения без дополнительных синтетических операций целой гаммы разнообразных меченных по сере соединений и возможность одновременного получения значительного числе меченых продуктов с применением лишь операций разделения;

б) возможность образования методом атомов отдачи „в один акт" таких достаточно сложно синтезируемых веществ как циклические сульфиды — тетраметиленсульфид (тиофан) , пентаметиленсульфид (тетрагидротиопиран , открытый сульфид с циклическими радикалами — дициклопентилсульфид;

в) образование с сравнимыми выходами целого ряда меркаптанов — от простейшего до циклопентатиола;

г) практически полное отсутствие среди меченых продуктов сероводорода и гидролизующихся серосодержащих производных четыреххлористого углерода, малый выход элементарной серы;

д) значительный выход высокомолекулярного полимерного серосодержащего продукта;

е) сведение баланса по активной сере. Индивидуальные (разделенные с соответствующими носителями) меченые соединения содержат около 15% образующейся радиосеры. Из них с наибольшими выходами образуются циклопентантиол (7,5%), шестичленный гетероцикл — пентаметиленсульфид (2%) и дициклопентилсульфид (2%). Остальная радиоактивная сера (84%) входит в состав полимерного продукта, остающегося на стенках колбы после отгонки последнего наиболее тяжелого (М-170) и высококипящего носителя.

Исследование химической природы полимерного серосодержащего продукта производилось с помощью бумажной хроматографии деканового раствора полимера (рабочая жидкость — смесь бутанола с водой) с последующим измерением активности хроматограммы. Хроматограмма, приведенная на рис. 3, показывает, что полимерный продукт не представляет собой смеси с монотонно изменяющимся свойством, а четко делится на два индивидуальных продукта, сосредоточенных в двух хорошо разделяющихся пиках.

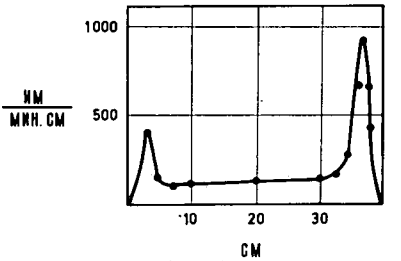


Рис. 3
Хроматограмма меченного по сере полимерного продукта.

Химическим путем установлено, что в одном из пиков вещество содержит сульфидную функциональную группу, в другом — меркаптанную. Таким образом, полимерный продукт состоит из смеси двух индивидуальных высокомолекулярных серосодержащих веществ: сульфида $R—S—R_1$ и меркаптана $R—SH$.

Исследование химического состава и молекулярного веса полимерных серосодержащих веществ продолжается. Образование полимерного продукта интересно как с теоретической, так и с препаративной точек зрения. В препаративном отношении образование и выделение полимерного продукта может оказаться перспективным в двух смыслах:

а) как быстрый метод получения сложных высокомолекулярных меченных по сере соединений;

б) как быстрый метод концентрирования основного количества образующейся при ядерной реакции радиосеры в препарате с высокой удельной активностью (весовое количество продукта ничтожно).

Сведение баланса по сере и наблюдение малых выходов элементарной серы, сероводорода и гидролизующихся производных CCl_4 позволили установить, что при горячем синтезе практически вся возникающая при ядерной реакции радиосера (до 90%) используется в процессах образования меченых сероорганических соединений.

Горячий синтез может быть дополнен химическим. Помимо того, что такие соединения, как серосодержащие гетероциклы, сульфиды и меркаптаны интересны сами по себе, они могут служить удобными продуктами для химического синтеза еще более сложных меченных по сере молекул.

Образование приведенных в таблице I меченых сероорганических соединений является результатом реакций, специфических для горячих атомов серы, не имеющих места в тепловой области [1, 4]. Схема брутто-реакций приведена на рис. 4. Здесь схематически представлены необычные реакции:

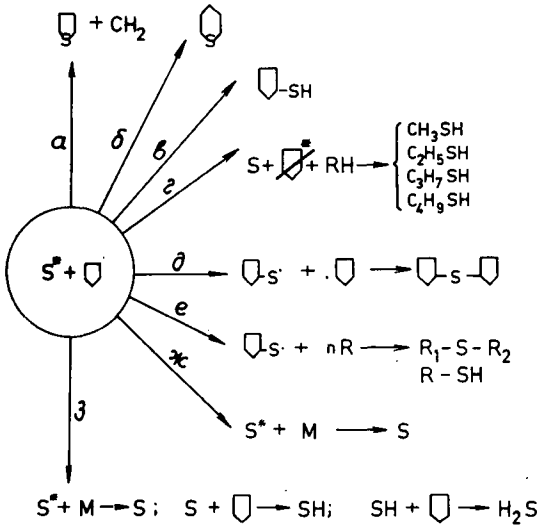


Рис. 4
Схема реакций горячих атомов серы с циклопентаном.

а) замещение горячим атомом серы CH_2-группы в циклопентане с образованием тиофана; б) внедрение атома серы по связи С—С с образованием тетрагидротиопирана; в) внедрение по СН-связи с образованием циклопентантиола; г) деструкция горячим атомом серы молекулы циклопентана с немедленным соединением замедлившейся при соударении серы с одним из осколков с образованием гомологического ряда меркаптанов CH_3SH, C_2H_5SH, C_3H_7SH, C_4H_9SH; д) конденсация атома серы с образованными им циклическими радикалами с синтезом дициклопентилсульфида; е) инициирование горячим атомом серы полимеризации с образованием высокомолекулярных сульфидов и меркаптанов в результате рекомбинации замедлившихся атомов серы с возникающими в процессе замедления радикалами.

Осуществление реакции по пути (а, в, б) возможно как по одноактному горячему процессу, так и в результате рекомбинации в жидкой клетке замедлившегося при соударении атома серы с радикалами, возникающими в результате непосредственно предшествующего неупругого процесса.

Следует отметить, что вероятность простой термализации горячих атомов серы с образованием элементарной серы (ж) весьма мала, а типичная для тепловых атомов серы в среде углеводорода [1] реакция образования сероводорода [3] через радикал SH в данной системе совершенно не проявляется.

Эти обстоятельства могут свидетельствовать о том, что в случае горячих атомов серы реакция отрыва водорода менее вероятна, чем упомянутые выше реакции (а—е), и о том, что сера в основном (на 98%) реагирует в горячем состоянии, успевая прореагировать в области достаточно высокой энергии и стабилизоваться в виде сероорганических соединений скорее, чем достичь теплового равновесия. В этом случае время реакции оказывается меньше времени замедления $\tau \simeq 10^{-12}$ сек, что характеризует высокую реакционную способность горячей серы.

Можно было бы полагать, что образовавшиеся в результате термализации элементарная сера и сероводород в дальнейшем расходуются в результате радиационно-химических процессов под действием излучения ядерного реактора. Однако результаты специальных опытов по радиационному воздействию гамма-излучения и облучению на разных реакторах в условиях различного накопления дозы делают эту точку зрения сомнительной.

Так, облучение смеси четыреххлористого углерода, циклопентана и активной серы гамма-лучами Co^{60} дозой 10^8 фэр (соответствующей дозе, достигаемой при облучении на реакторе) не привели к заметным выходам меченных по сере летучих и полимерных продуктов. С другой стороны опытами по облучению смесей циклопентана и четыреххлористого углерода на разных ядерных реакторах с существенно различным соотношением потоков медленных нейтронов $\Phi_{\text{м.н.}}$ (ответственных за выход S^{35}) и быстрых нейтронов $\Phi_{\text{б.н.}}$ и гамма-лучей ϕ_γ (в основном ответственных за создание дозы $D = D_{\text{б.н.}} + D_\gamma$ и генерацию радикалов) показано отсутствие корреляции между выходом меченых продуктов и обусловленной „внешней“ дозой концентрацией радикалов.

Установлено, что выходы серосодержащих полимерных продуктов, всего ряда открытых меркаптанов (продуктов деструкции) циклопентантиола не зависят от дозы „внешнего“ излучения, а выход сульфидов даже несколько падает с ростом дозы (что может быть связано с их радиационной неустойчивостью).

Таблица II

ВЫХОДЫ РЕАКЦИЙ ОБРАЗОВАНИЯ МЕЧЕНЫХ МЕРКАПТАНОВ ПРИ ОБЛУЧЕНИИ СИСТЕМЫ ЦИКЛОПЕНТАН-ЧЕТЫРЕХХЛОРИСТЫЙ УГЛЕРОД ($\nu = [Cl]/[C_5H_{10}] = 1$) НА РАЗЛИЧНЫХ РЕАКТОРАХ

$$K = \frac{A_i}{A_0} \cdot 100\%$$

	Вещество	Формула	I Реактор на обычной воде	II Реактор на тяжелой воде	Среднее из опытов на реакторах обоих типов
1	Этилмеркаптан	C_2H_5SH	$0{,}62 \pm 0{,}02$	$0{,}57 \pm 0{,}08$	$0{,}59 \pm 0{,}05$
2	Пропилмеркаптан	C_3H_7SH	$0{,}54 \pm 0{,}05$	$0{,}58 \pm 0{,}04$	$0{,}56 \pm 0{,}05$
3	Бутилмеркаптан	C_4H_9SH	$1{,}10 \pm 0{,}20$	$1{,}09 \pm 0{,}17$	$1{,}09 \pm 0{,}18$

Данные таблицы II иллюстрируют независимость выхода этилпропил- и бутилмеркаптанов от типа реактора и величины „внешней" дозы (I — реактор на обычной воде; II — реактор на тяжелой воде; при $\Phi^{I}_{м.н.} = \Phi^{II}_{м.н.}$, $D_I > D_{II}$).

Данные по радиационным воздействиям, балансу активных продуктов и термическому обмену серой свидетельствуют в пользу того, что реакции, приводящие к получению меченных по сере соединений, не обусловлены вторичными радиационными или тепловыми процессами, а в основном протекают по специфическим „горячим" реакциям. Последние связаны с прямыми одноактными реакциями быстрых атомов серы с молекулами среды или рекомбинацией замедлившейся при соударениях серы с радикалами, образованными самими атомами серы в процессе упругого или неупругого замедления.

Выход реакций с участием горячих атомов должен быть чувствителен к эффективной энергии атома, т.е. должен определяться замедляющими свойствами среды, её атомным составом. Изменение состава системы меняет также радикальный состав, что может сказаться на соотношении выходов конечных меченых продуктов.

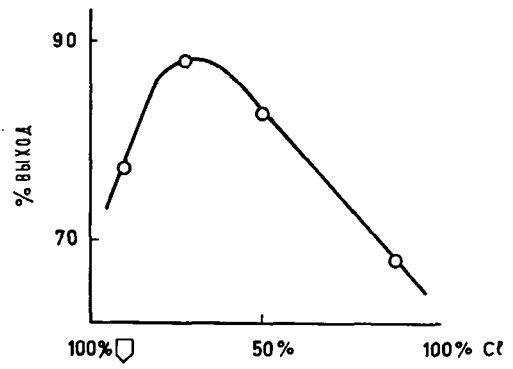


Рис. 5

Зависимость выхода меченного по сере полимерного продукта от состава смеси циклопентан-четыреххлористый углерод.

Действительно, при изменении состава облучаемой системы относительные выходы различных меченых продуктов изменяются в довольно широких пределах. В системе четыреххлористый углерод-циклопентан изменение атомного отношения $\nu = [Cl]/[C_5H_{10}]$ сказывается на выходах всех меченых продуктов, причем величина и характер этого изменения специфичны для различных индивидуальных веществ.

Выходы меченых продуктов конденсации и полимеризации в широком интервале изменения $\nu = 0{,}3-10$ уменьшаются с ростом ν. На рис. 5 приведена зависимость выхода полимерного меченого продукта от состава системы. В области малых добавок циклопентана к четыреххлористому углероду выход высокомолекулярных серосодержащих соединений K составляет приблизительно 60%, с ростом концентрации циклопентана K растет до 90% и при $\nu = 0{,}3$ проходит через максимум. В интервале $\nu = 0{,}3-10$ выход полимерного продукта уменьшается в 1,5 раза, выход дициклопентилсульфида — в 2 раза.

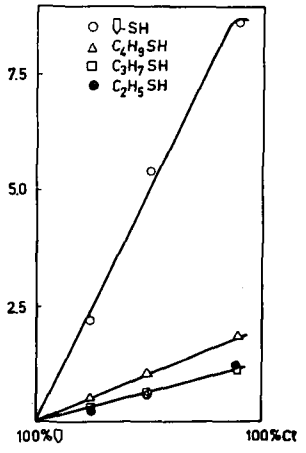


Рис. 6

Зависимость выхода этилмеркаптана C_2H_5SH(·), пропилмеркаптана C_3H_7SH (□), бутилмеркаптана C_4H_9SH (△) и циклопентантиола C_5H_9SH (○) от состава смеси циклопентан-четыреххлористый углерод.

Выход меченых соединений, являющихся продуктами реакций замещения, внедрения, деструкции в широком интервале атомных отношений ν увеличивается с ростом относительной концентрации [Cl]. Зависимость выхода циклопентантиола и этил-, пропил-, и бутилмеркаптанов от состава системы приведены на рис. 6, где значения выходов K_i для каждого состава ν усреднены по нескольким определениям. При изменении ν от 0,3 до 10 (*25—90 атомных процентов*) выходы этих продуктов увеличиваются линейно ~ в 4 раза, достигая в пределе при малых добавках циклопентана к четыреххлористому углероду значений K: для циклопентантиола 10%, для бутилмеркаптана 2%, для этил- и пропилмеркаптанов 1,3%. Одновременно с ростом [Cl] возрастает абсолютная активность.

Обращает на себя внимание равенство выходов этил- и пропилмеркаптанов, сохраняющиеся в широком интервале концентраций, что можно трактовать как результат равновероятного присоединения замедлившегося при

соударении атома серы к C_2 и C_3 осколкам, образующимися при деструкции молекулы циклопентана в результате неупругого взаимодействия с горячим атомом серы. Выход бутилмеркаптана в среднем в 1,7 раза больше. Это может быть связано с неравновероятностью распада возбужденной молекулы на осколки различной массы.

Выход серосодержащих гетероциклов резко увеличивается с ростом v.

Таким образом, изменение состава облучаемой смеси открывает пути для регулирования в достаточно широких пределах выходов индивидуальных меченых соединений.

Заключение

Разработана методика исследования реакций горячих атомов серы с углеводородами и получения меченных по сере соединений в результате взаимодействия горячих атомов серы с цикланами. Методика основана на облучении в ядерном реакторе смесей углеводорода с четыреххлористым углеродом с последующим разделением гаммы меченых продуктов с использованием техники стабильных носителей. Выяснена роль теплового обмена и радиационных воздействий.

Установлены типы реакций, характерных для горячих атомов серы, и выходы этих реакций. Сведен баланс по активной сере. Установлена высокая реакционная способность горячих атомов серы и практическое отсутствие в системе типичных продуктов реакций тепловых атомов серы. Показано, что до 98% серы расходуется на образование сероорганических соединений, образующихся в результате внедрения серы по связям С—С и С—Н, замещения CH_2-группы, деструкции циклической молекулы и соединения с ее осколками, полимеризации в треке горячего атома серы.

Показана возможность горячего синтеза серосодержащих гетероциклов (тиофана и тетрагидротиопирана), циклопентантиола, гаммы открытых меркаптанов (C_1—C_4), дициклопентилсульфида, высокомолекулярных сульфидов и меркаптанов. Установлена возможность управления выходами отдельных меченых соединений путем изменения состава облучаемой системы, даны рекомендации по достижению оптимальных выходов индивидуальных продуктов. Так как в данной системе все меченые соединения химически отличны от исходных, то могут быть достигнуты весьма высокие удельные активности. Для повышения удельных активностей целесообразно применение бумажной и газо-жидкостной хроматографии.

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DISCUSSION

R. Pitkethly (United Kingdom) asked whether disulphides had been observed among the products. If free radical reactions occurred in the presence of mercaptans, disulphides would be expected.

B. G. Dzantiev said that in these researches disulphide carriers had not been used and the formation of disulphides would in his opinion be very unlikely. It was of course possible that more than one sulphur atom would be present in the polymer products, research into the nature of which was continuing.

D. S. Urch (United Kingdom) asked whether gas-phase studies had been made in order to distinguish clearly between true hot reactions and cage reactions.

B. G. Dzantiev replied that his paper was based on the results of research into the liquid phase. Research into the gas phase was under way and the results would be published later.

EXTENSIONS OF THE TECHNIQUES FOR THE ACCELERATED UNSPECIFIC ISOTOPIC LABELLING OF ORGANIC COMPOUNDS

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Abstract — Résumé — Аннотация — Resumen

Extensions of the techniques for the accelerated unspecific isotopic labelling of organic compounds. The paper aims at reviewing new means of obtaining acceleration in the reaction of a radioactive gas with a target material to be labelled and examples of successful cases.

The techniques include the use of microwave and radiowave discharges, glow discharges affected through DC or AC sources, and simply ultraviolet radiation. Specific activities of more than 100 mc/g in purified significant quantities of products were obtained. Periods of exposure to discharge were of the order of one minute and decomposition was limited in most cases.

Calculations of utilization of the energy absorbed during the labelling process were compared with the energy from ionizing radiation used by Wilzbach and others, and G values for isotope replacement are given. In polystyrene labelling, evidence is found that the mechanisms is governed by an atom-molecule reaction.

Applications nouvelles des techniques accélérérées du marquage non spécifique de composés organiques. Les auteurs passent en revue des méthodes récentes visant à accélérer la réaction d'un gaz radioactif avec des matières à marquer; ils citent des cas de réussite.

Les techniques étudiées comportent l'emploi de décharges de micro-ondes et d'ondes hertziennes, de décharges luminescentes par des sources de courant continu ou alternatif et de simples rayons ultraviolets. On a obtenu des activités spécifiques supérieures à 100 mc/g dans des quantités importantes de produits purifiés. Les temps d'exposition à la décharge étaient de l'ordre d'une minute; dans la plupart des cas, la décomposition était limitée.

Les auteurs comparent la quantité d'énergie absorbée au cours du marquage à celle qui est nécessaire lorsqu'on emploie des rayonnements ionisants, comme l'ont fait Wilzbach et autres; ils donnent les valeurs G de remplacement des isotopes. Dans le marquage du polystyrène, il semble bien que le processus soit régi par une réaction atome-molécule.

Распространение методов ускорения мечения неспецифичными изотопами органических сложных соединений. Целью настоящего доклада является рассмотрение новых способов ускорения реакции между радиоактивным газом и материалом мишени, подлежащим мечению, а также приведение примеров успешных случаев.

Эти методы включают использование разрядов микроволн и радиоволн, тлеющих разрядов под воздействием источников постоянного или переменного токов, или просто радиации ультрафиолетовых лучей. Была достигнута удельная активность, доходящая

до 100 микрокюри на грамм, в значительных количествах очищенного продукта. Время воздействия разряда было порядка одной минуты, и во многих случаях разложение было чрезвычайно ограниченным.

Даются подсчеты эффективности использования энергии для производства мечения этими методами по сравнению с затратой для той же цели энергии ионизирующего излучения, используемой Вильцбахом и др.; кроме того, указываются значения радиационно-химического выхода G для замены изотопов. Есть указания на то, что при мечении полистирола механизм определяется реакцией атом-молекула.

Nuevas aplicaciones de las técnicas de marcación inespecífica acelerada de compuestos orgánicos. El objeto de la memoria es pasar revista a nuevos métodos para acelerar la reacción de un gas radiactivo con el material de blanco que se desea marcar, y citar ejemplos en los que este procedimiento se ha empleado con éxito.

Las diversas técnicas se basan en el uso de descargas de microondas y de ondas hertzianas, descargas luminiscentes producidas por corriente continua, o alterna, o sencillamente rayos ultravioleta. Se han obtenido cantidades considerables de productos purificados con actividades superiores a 100 mcuries/g. Los tiempos de exposición a las descargas son del orden de un minuto, y en la mayoría de los casos se observó poca descomposición.

Los autores calcularon el rendimiento energético alcanzado en estos métodos de marcación y lo comparan con el correspondiente a las radiaciones ionizantes empleadas por Wilzbach y otros investigadores; también dan los valores de G para la sustitución isotópica. Existen pruebas de que la marcación del poliestireno se produce en virtud de una reacción átomo-molécula.

1. Introduction

WILZBACH's tritium-exposure technique [1] has been much used in the preparation of tritium-labelled organic compounds. This technique increased the recoil labelling methods founded on hot-atom chemistry. Recently it has been found possible to accelerate the labelling by using various sorts of electrical discharges. In this introduction, we shall try to systematize the work up to now by dividing it into three main groups, one dealing with *accelerated ions*, the second with labelling promoted by *ionization and excitation* and the third with *excitation only*.

The group in which accelerated ions are used consists of two sections. In one of them, nuclear reactions such as Li^6 (n, α) H^3 or N^{14} (n, p) C^{14}, yielding tritons of MeV energies, and C^{14} with about 50-keV energy, are employed. The ions are stopped within certain ranges and may then become neutral atoms and finally result in labelling [2]. The other section embraces work in which ions containing isotopes of interest are accelerated electrically towards a target of an organic substance which is labelled [3]. DC electrical discharges, directing positive ions at low pressures towards a cathode coated with the organic solid to be labelled, might be included in this category, provided it is clear from the experimental conditions that the ions gain energy from the field. This can be judged from the criterion described by LOEB [13], viz. $X/p > 5$ for noble gases or > 20 for gases such as H_2 and N_2. (X is the electrical field strength in V/cm and p the pressure in mm of Hg.) According to this criterion, the tritium-labelling work by WOLFGANG, PRATT and ROWLAND [4] falls into this category ($X/p = 3000 - 6000$) as well as the C^{14}-labelling by GUILLAUME [5] ($X/p \sim 4000$).

The second group is the ionization and excitation-promoted labelling pioneered by WILZBACH [1]. This work and later papers showed that the labelling entity

need not be accelerated but only subjected to ionization and excitation, e.g. by tritium beta-radiation itself. (We shall not consider the simultaneous recoil labelling [6] here). Other researchers showed that external gamma-radiation could also promote the reaction [7]. TURTON, in an important contribution, showed that the exposure of organic compounds to $C^{14}O_2$ and Kr^{85} leads to the formation of C^{14}-labelled compounds [8], the Kr^{85} beta-radiation supplying the promoting ionizing energy. The ionization—excitation group has recently been greatly extended by means of various types of electrical discharges. These should fulfil the above criterion $X/p<5$, and are characterized by the fact that there is no acceleration of the ions, at least not in the vicinity of the substrate to be labelled. DC and 50-Hz AC glow discharges, which will be dealt with in this paper, belong to this group as well as DORFMAN and WILZBACH's Tesla discharge work [9], although the labelling might partly be due to acceleration ($X/p\sim100$). The work by WESTERMARK *et al.* [10] from this laboratory using radio waves and, in particular, microwaves also belongs here. Virtually no ion acceleration takes place with microwaves, i.e. the "ion temperature" is slightly higher than the working temperature. The work by LEMMON and TOLBERT [14] also falls into this group.

The third group includes electronic excitation (direct or sensitized) brought about by ultra-violet light [11]. The present paper will describe such work.

The work reported here, part of which has been shortly touched upon in another publication [11], describes experimental work aiming at:

(a) The preparation of labelled compounds with high specific activities,
(b) Exploring optimum conditions for obtaining high specific activities with accelerating techniques,
(c) Finding the equivalence between ionizing radiation and the discharge energy and
(d) An understanding of the mechanisms involved in the interaction of isotope gas with organic compounds.

2. Materials and techniques

MATERIALS

The polystyrene used was an easy-flowing general purpose product from the Dow Chemical Company "Styron 688". Its average mol. wt. as measured by light scattering is 170000. Its mol. wt. distribution determined by turbidimetric methods is given by the ratio $M_w/M_n=2$. It is entirely soluble in benzene. The plasticizer was removed by dissolving in benzene and precipitating in methanol.

Polymethyl methacrylate was obtained as a fine powder from AB Bofors Nobelkrut. It was stated to have been prepared by emulsion polymerization using ammonium persulphate as initiator and to be at least 99% pure. Its mol. wt. was estimated at about 1000000.

Polyethylene glycol was supplied by Mo and Domsjö Co. and had an average mol. wt. of 4000. Its small water content was removed by drying at 85°. Blood serum albumin was kindly made available by Dr. S. Ullberg. The benzene and ethylene oxide were of analytical reagent grade.

TECHNIQUES

The microwave generator and resonance cavity have been described in an earlier publication [10]. A modified cavity was constructed and tested [12].

It was silver-plated in order to give somewhat better electrical conditions and was provided with a thin window to view the plasma and with a better tuning-device. The wave frequency of the generator (a Siemens Radartherm unit) is 2425 MHz and it supplies a step-wise power output of between 40 and 250 W.

The reaction tubes for microwave discharge were made of pyrex glass with a standard side-connection to the vacuum-gauge tube. They were thoroughly cleaned, dried and fired in vacuum whenever possible. No special treatment was used to decrease the recombination of hydrogen atoms. The reaction tubes for glow discharges were similar to the discharge tubes and were provided with plate electrodes made of stainless steel and tungsten wire leads. The tubes for the UV experiments were made of transparent quartz but were otherwise quite similar. The tubes and their dimensions are shown in Fig. 1, a & b. With solid materials, the volatile constituents were removed by pumping on a vacuum line until a pressure of 10^{-5} mm was reached. With liquids, the material was degassed and distilled twice under vacuum before introducing the correct volume into the reaction tube and sealing off.

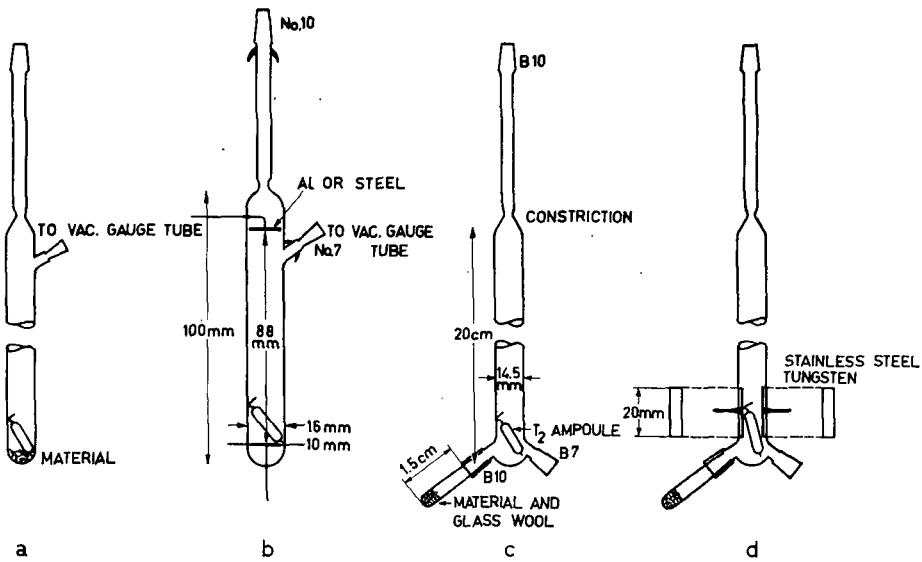

Fig. 1
The discharge tubes.
(a) A typical microwave discharge tube; (b) Tube for the AC and DC discharges; (c) Tube with a bent section; (d) Tube for study of the tritiating entities.

Tritium gas was supplied in small ampoules of about 0.4 cm^3 capacity with fragile hook-seals from the Radiochemical Centre, Amersham, United Kingdom. Using the figure of 12.26 yr as the half-life of tritium [15], it can be calculated that 1 cm^3 at NTP contains 2.602 c. The helium-3 content was stated to be less than 1%. The correct amount of tritium and the change in the tritium pressure during the reaction were measured using an L.K.B. Autovac hot-wire vacuum-gauge. The gauge reading was transferred to tritium pressure in mm of Hg by means of calibration charts. The purification of the polystyrene and polymethyl

methacrylate was performed by dissolving the polymers in small volumes of benzene followed by precipitating the filtered solute in an excess of ice-cooled methanol and then filtering and drying at 80° for 24 h. Repetition of this process did not alter the specific activities of the polymers. The blood serum albumin was purified by Dr. S. Ullberg by repeated dialysis and the benzene by isotopic dilution and preparation of *m*-dinitrobenzene followed by repeated crystallization from ethyl alcohol. The specific activity remained unchanged after the fifth recrystallization.

Measurements of the radioactivity were made using an Ekco liquid-scintillation counter, type N 612. At — 20° with toluene as solvent and diphenyl oxazole as scintillator, applying 1300 V to the photomultiplier tube with a discrimination level of 6 V, the efficiency of counting was very close to 15%. Measurements on the blood serum albumin separated by strip electrophoresis [16] were performed using the Packard Tri-carb liquid-scintillation unit.

3. Results

A. Experiments using microwave discharge

1. *Polystyrene*

The results of the experiments with polystyrene are given in Table I. The results of some of the runs were standardized to a starting tritium-content of 50 mc and a weight of polystyrene of 200 mg and are shown diagrammatically in Fig. 2. Run No. 9 is not included because it was conducted with the polymer unagitated in a bent section of the tube situated away from the discharge region as in Fig. 1c.

The tritium pressure during discharge was recorded, and typical diagrams are given in Fig. 3 for some runs with the material placed in the discharge region and in Fig. 4 for run No. 9.

The percentage of tritium fixed and the fixation yields which were calculated from the energy input and the specific activities are given in Table II.

Table I

MICROWAVE DISCHARGE IN T_2 GAS WITH POLYSTYRENE AGITATED IN THE DISCHARGE ZONE

Run No.	Wt. of polystyrene (mg)	Tritium (mc)	Energy input (Ws)	Sp. activity (of purified product) (mc/g)	Activity in the liquids (mc)
1	280	110.7	44000	36.0	—
2	200	~50	4600	47.2	2.66
3	200	~50	11900	13	3.08
4	200	~50	> 50000	9.6	1.30
5	200	~50	5400	7.9	2.06
6	200	98.5	1000	46	2.26
7	200	104	9500	65.5	2.45
8	20	148	11000	385	5.94
9*	20	54	650000	426	4.20

* Run performed with polystyrene unagitated in a bent section of the tube.

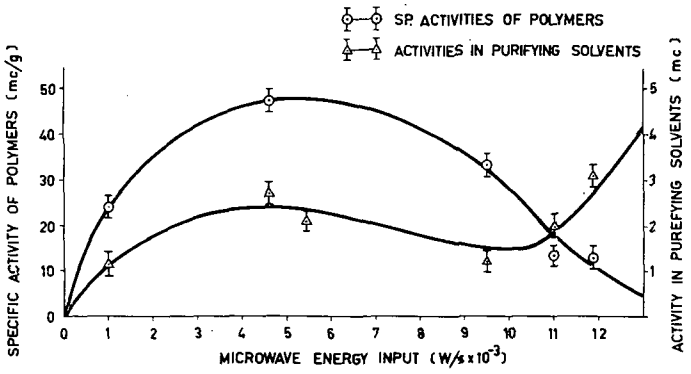

Fig. 2
Standardized specific activities and activities in purifying liquids against microwave energy in polystyrene experiments.

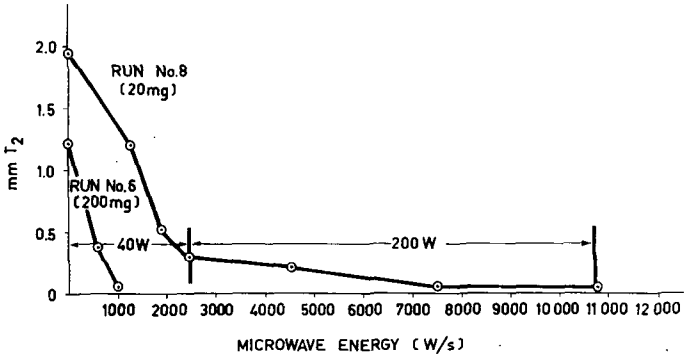

Fig. 3
The decrease of tritium pressure with microwave energy in typical runs with polystyrene.

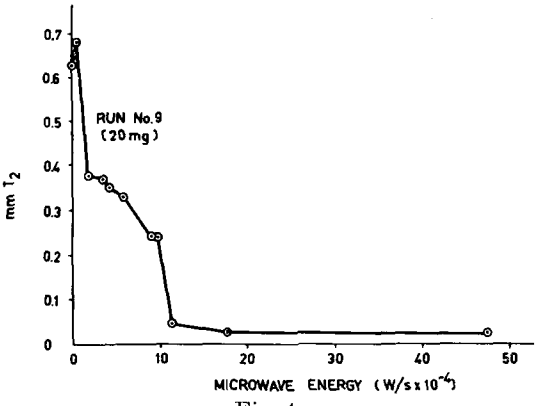

Fig. 4
The decrease of tritium pressure with microwave energy in run No. 9 polystyrene (the bent tube).

(In Figs. 2—4 above, the units in the labels of the horizontal axes should read: $\mathrm{Ws} \times 10^{-3}$, Ws *and* $\mathrm{Ws} \times 10^{-4}$ *respectively)*

TABLE II

PERCENTAGE OF TRITIUM FIXED AND FIXATION YIELD

Run No.	1	2	3	4	5	6	7	8	9
Tritium fixed (%)	9.2	18.1	5.2	3.8	3.2	9.3	12.6	5.2	15.7
Yield of fixation (mc/W s) $\times 10^3$	0.23	2.05	0.22	0.038	0.29	9.2	1.19	0.7	0.013

In order to prove the acceleration of the reaction of isotopic gas with the material and to be able to make a comparison with labelling by β-ionization under the same conditions, two runs were performed merely exposing the material to tritium gas in evacuated tubes. The results are summarized in Table III.

TABLE III

WILZBACH EXPOSURE TO POLYSTYRENE

Run No.	Wt. of material (mg)	Tritium (mc)	Time of exposure (h)	Sp. activity (mc/g)	Activity in purifying liquids (mc)
1	200	50	48	0.06	—
2	200	106.5	140	1.17	0.064

In some of the above experiments where the input energies were high, a small amount of the material (not exceeding 8%) was transformed into an insoluble mass. This was believed to be cross-linked polystyrene. The remainder, which was benzene-soluble, did not noticeably differ from the original material as shown by the identity of the UV spectra (*cf.* Fig. 5).

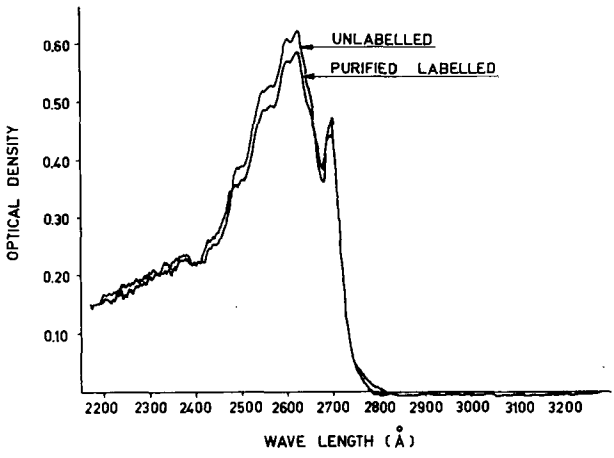

Fig. 5

UV spectra of unlabelled and purified labelled-polystyrene measured in chloroform solution in 1-cm cell. The first at 0.3 g/l, the second at somewhat lower concn.

2. *Polyethylene glycol*

300 mg of polyethylene glycol was powdered and, together with a tritium ampoule, put into a discharge tube similar to that shown in Fig. 1a. The tritium pressure in the tube was 0.90 mm which corresponds to 72 mc. The pressure was followed during discharge and, contrary to what happened in the polystyrene experiments, a steady rise in pressure was observed. The pressure of the non-condensable gases was recorded with the tube immersed in liquid air. The variation of pressure with microwave energy is shown in Fig. 6.

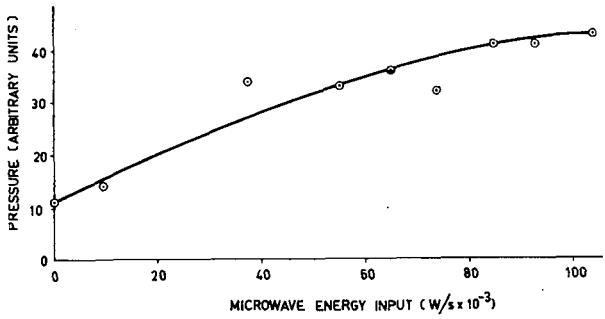

Fig. 6
The increase of pressure with microwave energy in polythylene glycol.
[The unit of the horizontal axil should read $\mathrm{Ws} \times 10^{-3}$*]*

A small portion of the product was heated at 80° C for 15 h to remove volatile matter and, thereafter a sample was dissolved in a 1:1 ethanol/toluene mixture and measured. The specific activity obtained was 87 mc/g, but this should not be considered as a final activity since the material obtained needed further purification.

3. *Blood serum albumin*

180 mg of the finely divided material, together with 51 mc of tritium, was subjected to microwave discharge. Care was taken to keep the temp. below 40° C so that the albumin would not be denaturized. A pressure-rise was noticed after each exposure. The microwave power was 110 W applied for 90.

The material, which was still completely soluble after discharge, was freeze-dried and then dialysed three times through cellophane membranes. A lowering of specific activity was noticed after each dialysis but, at the end, a steady specific activity of 5 μc/mg was obtained. This was about one tenth of the activity measured before dialysis.

TABLE IV

EXPOSURE OF BLOOD SERUM ALBUMIN TO TRITIUM GAS ACCORDING TO ULLBERG [16]

Run No.	Wt. of material (mg)	Tritium (c)	Exposure time (d)	Final sp. activity (μg/mg)
1	100	1	4	6.5
2	100	1	30	12

It is of interest to mention here the results obtained with the same material by the Wilzbach exposure method [16]. These are summarized in Table IV and show that almost the same sp. activity was obtained by our method when only 5% of the tritium and 0.026% of the time were used.

4. *Benzene*

The results obtained by subjecting benzene to microwave energy are summarized in Table V.

TABLE V

TRITIATION OF BENZENE BY MICROWAVE DISCHARGE

Run No.	Wt. of benzene (mg)	Tritium (mc)	Energy input (Ws)	Sp. activity of pure benzene (mc/g)
1	88	76	4800	225
2	88	75	2600	—
3	35.2	87	1250	70

The benzene was frozen, by means of liquid air, into a thin layer on the tube wall before discharge. A thin film of polymeric material was observed after the discharge in runs 1 and 2. The specific activities of the benzene were calculated from the measured activity of *m*-dinitrobenzene prepared by isotopic dilution with pure benzene, one step dinitration [17] and repeated recrystallizations from ethyl alcohol to constant radioactivity. The specific activities of the *m*-dinitrobenzene of runs 1 and 3 were 3.24 and 0.162 mc/g respectively.

Further confirmation of the presence of tritiated benzene was provided by a mass spectral analysis of run 3. This tube and a similar one containing pure, untreated benzene (to serve as a blank) were provided with a stop-cock and a standard joint to fit the mass spectrometer admission section. The mass spectra were obtained consecutively taking pure benzene first. The peaks obtained at mass numbers 78—85 for the treated benzene were compared with those obtained for pure benzene. At all mass numbers, the treated benzene gave a higher peak than the pure benzene but the peak at mass 80 corresponding to C_6H_5T was considerably higher than the peak at 80 in the pure benzene. The net height of the peak at 80, relative to that at 78 after allowing for C^{13} and H^2, was found to be 0.024%. Taking the sp. activity of pure tritium as 9627 c/g, this corresponds to a specific activity of 89 mc/g for the benzene in run 3.

The result agrees very well with the value found by direct radioactive measurement of the *m*-dinitrobenzene prepared from the tritiated benzene. The mass spectrometer can therefore be used as a tool for estimating labelled compounds, provided their specific activities are high enough to be distinguished among those of the natural isotopic impurities.

5. *Ethylene oxide*

Two runs were performed, using 435 mg and 64 mc tritium in one and 260 mg and 124 mc in the other. The energy input was 92300 and 18000 Ws respectively. The material was spread by means of liquid air as in the benzene experiments and was subjected to discharge as such. It was purified by fractional distillation.

The fraction corresponding to ethylene oxide contained very little activity, while that corresponding to ethyl alcohol was several million times more radioactive. It was therefore believed that tritiated alcohol had been produced from ethylene oxide and tritium by the discharge. This special case of "specific labelling" suggested by L. EHRENBERG is being examined and will be reported later on in more detail [18].

(b) EXPERIMENTS USING LOW FREQUENCY DISCHARGES

The material treated using this technique was polystyrene. Two types of LF discharges were used, viz. the DC and 50-Hz AC discharges.

1. *Results of the* DC *discharge experiments*

The results obtained by applying a positive voltage to one of the electrodes of the discharge tube (and earthing the other) are given in Table VI.

TABLE VI

DC DISCHARGES IN T_2 GAS WITH POLYSTYRENE AGITATED BETWEEN THE ELECTRODES

Run No.	Wt. of polystyrene (mg)	Tritium (mc)	Initial pressure (mm)	Average power (W)	Time (s)	Final pressure (mm)	Sp. activity of purified polystyrene (mc/g)
1	200	30	0.55	0.154	2955	0.08	24.2
2*	200	60	1.10	0.072	3500	0.045	5.2

* Discharge was enhanced by applying a Tesla coil leak-tester and a Cs^{137} gamma-source for a few seconds.

At low pressures, it was necessary to increase the voltage across the electrodes in order to maintain the discharge. The discharge had dark and glow regions similar to the well-known Faraday tube. At high voltages (near 2500 V), streamers appeared to be shot against the cathode and the polystyrene exhibited strong fluorescence. In these experiments, the average voltage applied was about 1000 V and the current produced was 100 μA. Bremsstrahlung measurements [19], using a thin-window, argon-filled Geiger tube, of the cathode plates and of a sample of polystyrene before purification revealed the presence of less than 0.05 mc in the former and about 100 mc/g in the latter. These results indicate that most of the tritium was sorbed by the polystyrene rather than on the metallic electrodes.

2. *Results of the* AC *discharge experiments*

The results obtained by using the circuit shown in Fig. 7 are summarized in Table VII.

In these experiments, the average voltage applied was about 1500 V and the current produced was 1 mA. In these runs and in the DC runs a decrease of pressure with energy input was observed and this behaviour is shown in Fig. 8. (For run No. 2, no intermediate values of pressure were recorded). The electrodes used in these runs gave negligible activities when measured by the bremsstrahlung method.

TABLE VII

AC DISCHARGE IN T_2 GAS IN PRESENCE OF POLYSTYRENE

Run No.	Wt. of polystyrene (mg)	Tritium (mc)	Initial pressure (mm)	Average power (W)	Time (s)	Final pressure (mm)	Sp. activity of P.S. (mc/g)
1	200	60	1.10	0.88	111	0.056	30.6
2*	200	49	0.90	1.97	960	0.052	20.4

* One of the two plate-electrodes was knocked off before performing the run.

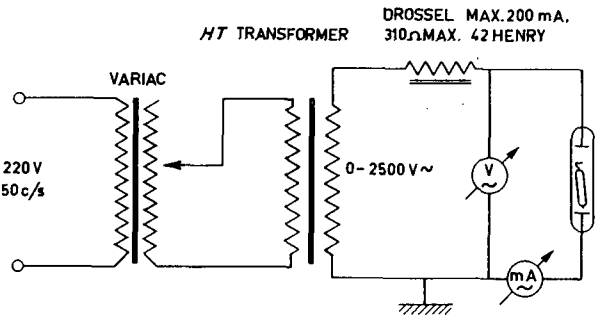

Fig. 7
The AC circuit.

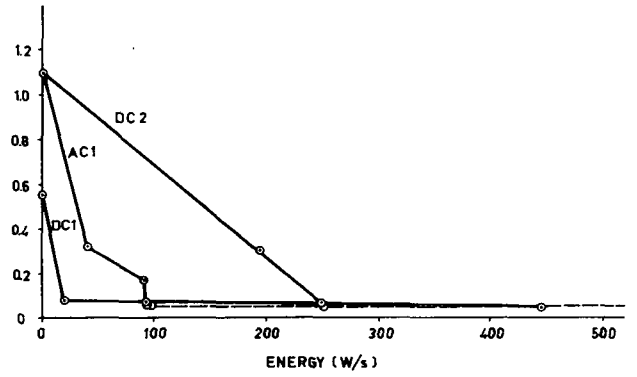

Fig. 8
The decrease of tritium pressure with energy in the DC and AC experiments.
[The unit of energy should read (Ws)*]*

(c) EXPERIMENTS USING ULTRAVIOLET RADIATION

Evacuated quartz tubes containing 300 mg of the material and a tritium ampoule were simply placed beneath a low-pressure 50-W "Mineralight" lamp at an air gap of 0.6 cm. The lamp emitted predominantly 2537 Å. Experimental conditions and results obtained are summarized in Table VIII.

The irradiated polystyrene acquired a yellowish colour but the purified material was white. Some 6% was separated as insoluble polystyrene (cross-linked).

An intense blue-greenish luminescence was observed when polymethyl metha-

TABLE VIII

UV IRRADIATION IN PRESENCE OF T_2 GAS

Material	Tritium (~ mc)	Time (h)	Sp. activity in purified material (mc/g)	Activity in purifying liquids (mc)
Polystyrene	100	24	20	1.82
Polymethyl methacrylate	100	24	31.1	12

crylate was dissolved in benzene but it disappeared completely after some minutes. Chain-end degradation was indicated by the smell of monomeric methyl methacrylate and the presence of high activity in the purifying liquids.

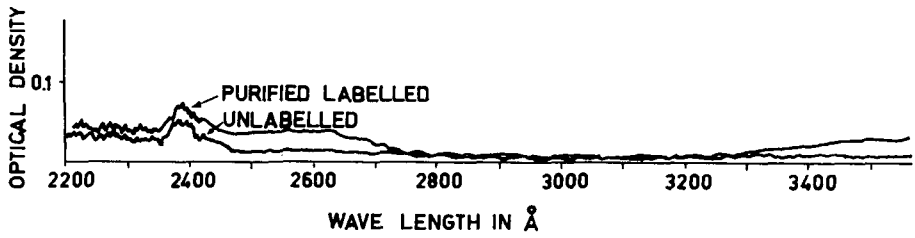

Fig. 9
UV spectra of unlabelled and purified labelled polymethyl methacrylate in chloroform solution in 1-cm cell at 0.3 g/l.

Polymethyl methacrylate hardly absorbs at all in the UV. It was thought that if any structural abnormality had occurred during exposure, it should have appeared in the UV spectrum. Fig. 9 shows the UV spectra of the unirradiated and the purified irradiated material—the latter was measured at a slightly higher concentration.

4. Discussion

FIXATION YIELD—DEFINITIONS

A labelling experiment generally gives the specific activity of the product wanted and the energy consumption required to achieve this result. A more complete experiment gives information concerning the activity of all the labelled compounds including the gases formed. Thus the total number of T atoms fixed (or generally "isotope gas" atoms) is known.

It is often difficult to estimate the energy consumption. When beta-radiation is used as "power generator", the total energy given to the gas is

$$E = P \cdot t = C \cdot \overline{E} \cdot t \cdot 5.93 \cdot 10^{-3} \text{ Ws} \qquad (1)$$

where P is the power, t time (s), $\overline{E}$ average beta-energy (MeV), C source strength (c).

This relation gives the total energy dissipation whereas, depending on the pressure, some fraction of the energy is not dissipated in the gas itself because

some of the beta-particles penetrate through the gas to the container material. Crude estimates of the useful fraction stopped in the gas can be made either by approximating the beta-absorption curve using an exponential function and considering the range or by using specific ionization data. However, scattering in the gas and on the wall will make such calculations very uncertain for beta-radiation and they will moreover depend on the shape of the vessel and also its composition. A more practical way seems to be to measure the ionization current at saturation and to use known figures for the ionization yield. For the tritium, the absorbed power (P in W) can be obtained from these two quantities:

$$P = I_{sat} \cdot J \tag{2}$$

where I_{sat} is the saturation current in amps ($J = 36$ eV/ion pair) [22]. The fraction used in the gas is of course found by comparing the power from Eqs. (2) and (1). In a few cases, we made such measurements and found that only a few tenths of 1% of the total energy was dissipated in the gas at pressures around 1 mm (tritium gas). When higher pressures are used, i.e. in the genuine Wilzbach exposures or when the substance to be labelled is in a gaseous form or when an auxiliary gas with an ionization potential higher than hydrogen is added, the fraction mentioned above is much higher but is still difficult to calculate exactly.

In the case of electrical discharges, the energy consumption is obtained from a knowledge of the power and the time of application. A correction must be introduced for the exposure due to any possible ionizing radiation from the gas (the latter correction is often negligible). For fundamental comparisons between the action of electrical discharges and ionizing radiation, the power considered should be the fraction consumed by the gas. If the power is calculated from the voltage and current, the voltage drop between the electrodes in the gas tube has to be measured (for DC and AC LF discharges). Thus any power consumption in the chokes, resistors and leads will be eliminated. Corresponding precautions have of course to be made when using wattmeters. In the case of higher-frequency discharges, the power measurements are more difficult (see for instance DORFMAN and WILZBACH [9]). These difficulties are even more pronounced for electrodeless discharges.

If the properties discussed above are known, as is the case in nearly all our experiments reported above, then the yield can be expressed simply as the total number of mc fixed per energy unit (mc/Ws). This property is directly related to the more fundamental G value of radiation chemistry. The general relation is

$$G = \frac{T_{1/2} \cdot C \cdot 3.7 \cdot 10^{10} \cdot 1.6 \cdot 10^{-12}}{\ln 2 \cdot E \cdot 10^{5}} \tag{3}$$

where $T_{1/2}$ is the half-life of the nuclide(s), C its activity (c) and E the energy consumption (Ws).

If the fixation yield S in c/Ws is known, G can be obtained from

$$G = S \cdot T_{1/2} \cdot 8.55 \cdot 10^{-7} \tag{4}$$

For tritium (if we take $T_{1/2} = 12.26$ yr):

$$G = 330 \cdot S$$

or, if the yield is given in mc/Ws (s),

$$G = 0.330 \cdot s \tag{5}$$

It should be noted that the equivalent G-values found from these equations by using the electrical energy input are *a priori* less than those obtained using ionizing radiation because of, among other things, losses due to heating. In the special case of tritium, the labelling by the $(He\text{-}H)^+$ ion resulting from beta-decay should also be considered [6].

FIXATION YIELD—EXPERIMENTAL

In Table IX, the fixation yield and equivalent G-values are given for some experiments of our own and also some of DORFMAN and WILZBACH's [9]. The material comprises a large number of energy-sources for the labelling reaction, including tritium beta-radiation, DC discharges, AC 50-Hz discharges, radiofrequency Tesla discharges and microwave discharges.

TABLE IX

SUMMARY OF SOME TRITIUM-LABELLING EXPERIMENTS TO SHOW THE DEPENDANCE OF YIELD ON POWER

Substrate	Energy source	Power (W)	Fixation yield (mc/Ws)	Equivalent G-value	η %
polystyrene**	T beta-radiation	$1.4 \cdot 10^{-8}$	22	7.5	62
p-dichlorobenzene*	T beta-radiation	$0.3 \cdot 10^{-4}$	1.3	0.43	3.6
naphthalene*	T beta-radiation	10^{-4}	3.5	1.15	9.3
palmitic acid*	T beta-radiation	$0.3 \cdot 10^{-3}$	2.4	0.81	8.7
p-dichlorobenzene*	Tesla-coil	0.1	0.5	0.16	1.3
naphthalene*	Tesla-coil	0.1	0.9	0.3	2.5
palmitic acid*	Tesla-coil	0.1	0.3	0.1	0.8
palmitic acid*	Tesla-coil	0.1	0.4	0.13	1.1
polystyrene**	DC-glow discharge	0.4	$1.2 \cdot 10^{-2}$	$4 \cdot 10^{-3}$	$3 \cdot 10^{-4}$
polystyrene**	DC-glow discharge	0.07	$6 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$
polystyrene**	AC 50-Hz glow discharge	10	$2 \cdot 10^{-3}$	$6.6 \cdot 10^{-4}$	$5 \cdot 10^{-5}$
polystyrene**	AC 50-Hz glow discharge	3	$3 \cdot 10^{-3}$	10^{-3}	$8 \cdot 10^{-5}$
polystyrene** (run 6)	Microwaves	40	$9.2 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$
polystyrene** (run 7)	Microwaves	240	$1.5 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$4 \cdot 10^{-5}$

* Wilzbach-Dorfman [9].
** This paper.

The data of LEMMON and TOLBERT [14] have not been included in the Table. They used an ozonizer type of discharge to promote the labelling of benzene. The fixation yields are apparently of the order of 10^{-5} mc/Ws. It is probable that the dielectric losses in the glass walls account for these relatively small figures, i.e. less good energy utilizations. These experiments may not therefore be directly comparable with those of Table IX.

Our result for the "Wilzbach blank", Table III (run 2), has been included in the Table. The estimation of the power is uncertain. The cylindrical form of the tube has been approximated by using a sphere of the same vol. and the average distance from any point within the gas to the wall has been taken as 3/4 of the radius according to LIND [20]. The specific ionization has been estimated to be about 0.2 ions/cm at 1 mm pressure [21] and the energy per ion pair has been taken as 36 eV [22]. From these data, it was found that only 0.4% of the power was absorbed in the gas.

It is seen from the table that the Wilzbach exposure apparently utilizes the energy most efficiently and it seems that the higher the power, the lower the equivalent G-values. We shall examine this question in the next section.

FIXATION YIELD *versus* POWER

In Fig. 10, the fixation yield and the corresponding G-values are plotted against power on a double logarithmic scale. The dotted line corresponds to an exponent of -0.5. It must be remembered that the data plotted belong to experiments

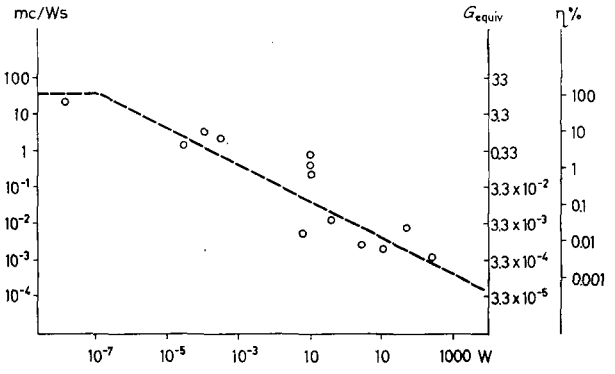

Fig. 10

Double log plot of yield of tritium fixation in mc/Ws, of equivalent G-values, and of radiomimetic efficiency as a function of power of energy source. The slope of the line corresponds to a dependence of yield on the inverse square-root of power.

with different substances and somewhat different geometries. The experiments have in common the fact that a cylindrical tube is employed, on the bottom of which is placed a solid organic substance. In the case of electronic plasmas, the active entities are formed at a distance from the solid substance, whereas in the genuine Wilzbach treatment the source of energy is to some extent mixed with the solid (depending on how far the gas can penetrate). Still, the majority of the tritium beta-particles are absorbed in the gas at some distance from the organic substance. Thus, in all cases, the active entities have to diffuse some distance in order to reach the substance investigated. To a certain approximation, therefore, the geometries can be regarded as equivalent for a preliminary discussion. We have also to neglect the differences between different substances. This seems to be justified in a discussion where only the general trend is to be studied. We shall therefore assume that the G-values for the labelling of, say, naphtalene, polystyrene and dichlorobenzene are within a factor of two of each other.

As a first approach, we shall investigate whether a simple recombination mechanism can describe the dependence on power. The entities recombining may be the positive and negative ions or free electrons (assumed to be equal in number) or they may be hydrogen atoms recombining to form molecules in pairs (probably on the walls). However, the latter process may also be monomolecular. For the recombination, we have (*cf.* LOEB, [13] Ch. VI) to a first approximation:

$$\frac{dn}{dt} = \lambda - \alpha n^2 \tag{6}$$

where $n_+ = n_- = n$

α = a bimolecular recombination coefficient,

λ = rate of production of active entities per vol. unit (the labelling reaction is not considered here).

At equilibrium, $\frac{dn}{dt} = 0$

and therefore $\lambda = \alpha n^2$

or

$$n = \sqrt{\frac{\lambda}{\alpha}}. \tag{7}$$

But λ is proportional to the power (if the vol. is constant). Thus

$$n = k \sqrt{\frac{P}{\alpha}}. \tag{7a}$$

If we assume that the number of active entities reacting is proportional to n, we then find that the fixation per unit time is proportional to the square root of the power and that the fixation yield is proportional to the square root of the energy input. The equivalent G-value is then

$$G_p = k \sqrt{\frac{1}{P \cdot \alpha}}, \tag{8}$$

i.e. G_p is inversely proportional to the power as long as recombination dominates over the labelling reactions.

This result agrees reasonably well with the experimental findings, as is seen from Fig. 10, especially when the differences in the experimental conditions are considered. At low powers, we might imagine the G-value to approach the max. corresponding to a complete utilization of the active entities. If an atomic mechanism is the correct one (see below), this G-value may be taken to be 12 or 18 according to EYRING, HIRSCHFELDER and TAYLOR ([23] p. 486).

RADIOMIMETIC EFFICIENCY

In an earlier publication [10], the radiomimetic efficiency (η) was defined as

$$\frac{dD}{dt} = \frac{\eta \cdot P}{m} \tag{9}$$

where m is mass of gas and $\frac{dD}{dt}$ the equivalent radiation chemical dose-rate. η can, in principle, be evaluated from two experiments, one utilizing ionizing radiation and the other an electrical discharge. It will be equal to the ratio of the energy consumptions for a certain, definite excitation yield produced by ionizing radiation and electrical discharge, respectively:

$$\eta = \frac{G_P}{G_0} \tag{9a}$$

where G_P is the equivalent G-value at power P.

These η-values can be read directly from Fig. 10. An extra axis showing η-values is included in this Fig. The G_0 value has, somewhat arbitrarily, been equated with 12, according to [23]. The low G-values (poor energy utilization) are of less concern for labelling experiments in the laboratory than for industrial processing. This point will be discussed further in section 5 below.

THE MECHANISM OF THE REACTION

So far we have not considered the active entities bringing about the reaction. We have a crude indication (*cf.* Fig. 10) that the active entities recombine in pairs. We shall now discuss the type of entities which are active.

A priori, a field of ionizing radiation and an electrical discharge acting on a gas both contain

Positive ions (often of free radical nature);
Negative ions (including free electrons);
Free radicals (neutral); and
Excited states.

If we restrict ourselves to the case of tritium gas being activated so that it can react with solid organic substances, then the discussion will be considerably simplified.

In the case of electrical discharges, the plasma zone and the organic solid are well separated (a few cm). This means that excited states are less probable than reactive entities. Allowed transitions often have a life-time of the order of 10^{-8} s or less and, during that time, the distance travelled due to diffusion is very short compared with the separations used in the experiments. This is of course well confirmed by experimental experience because the luminous zone is quite limited in space. In order to explain the reactions, the life-time has to be some tenths of a second or more. This renders even forbidden states, if present at all, less probable.

Gaseous ions are known to exhibit a large number of interesting reactions, e.g. so-called ion-molecule reactions [24] which have been studied in mass spectrometers. The ion density in a microwave discharge of the order of 100 W may be 10^{10} to $10^{11}/cm^3$. Recombination reduces this very quickly to 10^6 or lower and thus the majority of the ions are lost. Experiments by BONHOEFFER (quoted by GLOCKLER and LIND [25] p. 117) show this loss very clearly. It is therefore improbable that gaseous ions are the active entities in this case except perhaps at very low powers.

We have yet to discuss the free radicals, i.e. atomic tritium, in the present case. It is well-known that atomic hydrogen is produced by electrical discharges (*cf.* for instance [26]) and by ionizing radiation acting on hydrogen gas. In some important work by EYRING, HIRSCHFELDER and TAYLOR [23], the number of hydrogen atoms formed per ion pair absorbed was estimated to be 3 to 4, or even 6 when considering ionization and excitation as the generating process. Thus the G-values are about 10 to 12 or 18. There has been a more recent discussion of this calculation [27]. It is known that electrical discharges produce H atoms by rather similar mechanisms. SHAW [26] gives a yield of $6.5 \cdot 10^{-2}$

dissociations/eV or the equivalent $G_H = 13$, which is close to the figure estimated for ionizing radiation.

The H atoms are known to have life-times at low pressures of several tenths of a second ([28] p. 134). Such a value would provide a reasonable explanation of our results. If we assume the T atoms produced by the electrical discharge to be the reactive species, it is clear that they will be able to diffuse to the surface of the organic solid and even to penetrate into a side tube (the bent-tube technique, see below). The results from the bent-tube procedure thus indicate rather strongly that atoms are the reactive species.

Hence, when a solid and tritium gas are present, the labelling reaction would simply be

$$RH + T \rightarrow RT + H\,. \tag{10}$$

In addition, adsorption on the walls and on the organic solid is known to occur and this might account both for the observed pressure decrease and also for the fact that not all the tritium can be found afterwards in the organic material. A mere substitution reaction would not lead to any pressure change. The pressure increases in the early part of the discharge treatment are assumed to be in part due to atomization. In some experiments, pressure increases were found. They may have been due to the formation of volatile gases by UV-light.

Further strong support of the atomic mechanism is provided by the UV experiments. The energy supplied by the 2537 Å line is 4.88 eV. Some other lines are present but are of low intensity. One line near 1900 Å is supposed to be absorbed by the air. The energy required to split a tritium molecule into atoms is estimated to be 4.59 eV [11], which is somewhat less than the quantum energy of the 2537-Å photons.

Thus it is seen that, due to the photosensitizing action of the substrate, the formation of T-atoms is energetically possible and the suggested explanation physically plausible. It should be noted here that the 2537-Å photons have been found capable of atomizing H_2 if mercury photosensitizing is used ([28] p. 130, including footnote 1). As far as is known at present, ionization is not possible at such low energies and thus electronic excitation is the most probable explanation. Polystyrene absorbs at this wavelength but poly-methacrylate has only a minor absorption there (Fig. 9). It may absorb more during the actual experiment because of the formation of double-bonds. As pointed out in the introduction, this UV-induced tritium-labelling case has lead us to the discovery of a new general method for accelerated labelling.

If our interpretation is correct, it is not necessary to use ionizing radiation at all for the labelling of organic substances. This has been illustrated by the results of the bent-tube technique described here. This method avoids nearly all UV radiation which is supposed to extend into the very short λ-region of 1000—2000 Å (Schumann region) and even lower. This UV-radiation probably acts very destructively on virtually all covalent matter. The ideal procedure would therefore be to exclude it completely, thus resulting in a minimum of destruction. Hence, the bent-tube technique or a streaming technique, as suggested in [10], approaches the ideal. The destruction found by DORFMAN and WILZBACH [9] might be due to this UV light and to the sparking reported by them. In a microwave plasma, no such sparking tendency has been observed and it may, therefore, be preferred to the Tesla units. Some destruction has occurred in our experiments, as is seen from Tables I, III and VIII.

SEAT OF THE REACTION, CAUSE OF THE DECREASE IN SPECIFIC ACTIVITY AND STORED ENERGY

By comparing runs 8 and 9 in Table I with runs 1—7 (polystyrene), it seems quite clear that the labelling reaction takes place on the surface or down to a small depth in the solid substance. This is also indicated by the findings of other researchers, e.g. the increase obtained by shaking [29].

The decrease in the specific activity with increasing energy-input in the microwave experiments (runs 1—4, Table I) might then have the following explanation (first put forward by H. Lindroth of this laboratory): A superficial layer of the solid is initially labelled but, upon increasing the energy input, some of the labelled substance is destroyed by the action of the UV light from the plasma zone (*cf.* above). When the substance is dissolved, the labelled part is diluted by the unaffected part and the specific activity decreases because the labelled molecules destroyed are eliminated in the purification procedure. If this interpretation is correct, the bent-tube technique should not exhibit the same behaviour of a saturation specific activity and then a decrease, but instead a steady rise. This point has not yet been investigated.

The observed luminescence of the polymers treated by UV light when dissolved in benzene might be due to stored energy. The presence of stored energy has, in fact, been demonstrated previously by dissolving irradiated solids in solvents containing fluorescent solutes [30].

5. Suggestions for further developments

Experiments are already under way to substantiate the proposed mechanism of tritiation by means of tritium atoms. Discharge tubes have been constructed with plate-steel electrodes placed between the cavity and the bent section of the tube containing the target material, as shown in Fig. 1 d. Applying a potential across these electrodes will prevent any ions from reaching the material.

On the other hand, experimental conditions can be adjusted so that all the entities produced in the plasma may reach the material while the latter is still protected from the intense short-wavelength light emitted in the plasma region. A streaming system may fulfil this purpose.

The use of other "isotopic gases" is of immediate importance in this field. Research is already planned to use $C^{14}O$, $C^{14}O_2$, $S^{35}O_2$, $S^{35}O_3$ in order to produce desirable C^{14} and S^{35}-labelled compounds and to produce double-labelling directly.

Decomposition products are usually encountered in the labelling techniques already discussed. In the case of volatile material, a complete assessment of the decomposition products and their labelled "isomers" can be achieved simultaneously by means of a gas-chromatography apparatus fitted with suitable nuclear radiation detectors. Such a unit is under construction.

One consequence of the atomic mechanism is that the activation of hydrogen by a palladium thimble, by electrolysis or by metal-water reactions should also be possible for labelling purposes. Ultra-sound would also be a possibility. It is felt, however, that these techniques might prove less practicable in most cases either because of a smaller specific activity (the water reactions) or because of heating (the Pd technique).

Thus, our best suggestion at present is to use the bent-tube technique together with an electrodeless discharge or perhaps to employ the cheaper method involving an AC discharge and a choke.

Most of the above labelling experiments are supposed to yield unspecific labelling, as has been proved for the Wilzbach exposures for a lot of substances. It is interesting, however, to note that the unspecific labelling turns into a specific one in some cases. The production of ethyl alcohol from ethylene oxide resulting from the brilliant suggestion by L. Ehrenberg seems to be such a case. Cellulose seems to be another case—only one of the hydrogen positions is not exchangeable with water. Reactions of the types observed by TURTON [8] belong to this class even if they are not substitutions.

The success of labelling promoted by UV radiation (possibly also sensitized with mercury vapours for non-UV-absorbing substances) suggests that further cases of specific or group-specific reactions might be found in the future. It may be found that, in cases where a special group is responsible for the absorption of the energy-supplying light, e. g. 2537-Å line or lines of shorter λ, this group only is labelled. This would assume that the electronic energy is not transferred to another part of the molecule. For example, it is probable in the case of polystyrene that only the phenyl rings are labelled and not the methylene groups. Thus it seems that photochemically promoted labelling reactions can be more specific than radiation chemical ones, roughly speaking in the same way as photochemistry is related to radiation chemistry.

It should be pointed out that the experiments presented above do not represent optimum conditions. Further refinements and efforts to achieve optimum results may well give much higher specific activities, minimize destruction and reduce the labour involved. A specific suggestion is to try to avoid the presumed adsorption losses of T atoms by adding a rare gas at a suitable low pressure. At present, the losses amount to 60—80% of the activity. Further there are, as is known, several possibilities for treating the walls in order to decrease the atomic hydrogen recombination (*cf.* for instance [31]).

The microwave technique should be applicable to the acceleration of a diversity of commercially important chemical reactions and also to their study. Such reactions would be, for instance, the addition polymerization of monomers, and the interactions of N_2 and O_2, N_2 and H_2, and O_2 and H_2. Some studies of this kind have been published but the equivalence of this field and radiation chemistry does not seem to be generally recognized. This equivalence has been qualitatively recognized by S. C. LIND [20]. By means of the formula (9a), it is possible to make quantitative statements, although not with high precision. Some such comparisons have been made [32] and indicate that electrical discharges compete favourably, from an economic viewpoint, with ionizing radiation in the case of gases and perhaps also liquids. This subject will be dealt with in later publications.

6. Applications

Those scientific, medical and industrial institutions which are interested in the labelling of organic compounds for tracer studies will have great use of any of the above techniques. It might be stated that, whereas inorganic and metallurgical industrial processes can now be followed by tracers in a great many cases even up to full scale, the organic and biotechnical industries have, in general, lagged in this respect. The techniques now opened up might do much to alter this situation. There are, especially in industry, a lot of problems that can be solved by unspecifically labelled substances. The use of very small quantities of isotopic gas, the simplicity of the technique and the very short reaction-time are all va-

luable advantages. We have already received requests for the labelling of a diversity of chemical compounds ranging from organic polymeric substances (e.g. cellulose and carboxymethyl cellulose) to simple inorganic compounds such as lithium aluminium hydride. As soon as the technique is extended to other isotopes, it will be possible to produce doubly labelled compounds.

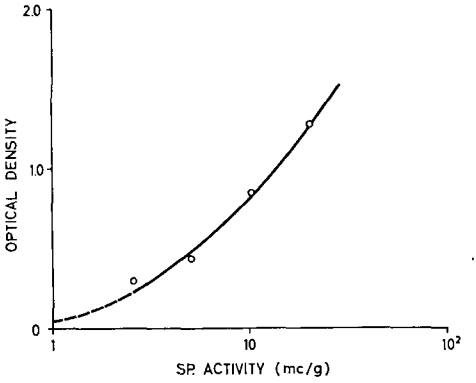

Fig. 11
Optical density against specific activities of polystyrene films (114 h on G.5, 10-μ emulsion thickness, Ilford plates).

Standard films of polystyrene were prepared ranging from 2.5 to 40 mc/g and were tested for homogeneity by exposure to G.5 Ilford plates of 10-μ emulsion thickness. The relation between their specific activities and the measured optical density for a fixed exposure-time is shown in Fig. 11. This series can be used as a staircase in autoradiographic work. Labelled polystyrene can be used in brushes for the elimination of static electricity and, hence, for the elimination of dust from insulating surfaces. It can also be used as a powerless self-luminous material. In fundamental research, labelled polystyrene is suitable for the study of radiation-induced grafting problems.

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cussions, especially on the UV work, and to Ing. H. Forsberg and Mr. A. Pettersson of the Isotope Techniques Laboratory for advice on and the performing of liquid-scintillation counting. Dr. M. Nilsson and his collaborators in the Division of Organic Chemistry of this Institute kindly obtained the UV absorption spectra. Ing. S. Forberg and Ing. H. Lindroth have given valuable assistance and contributed with many helpful discussions. Mr. R. ÖSTLING has carried out excellent glass-blowing work and Mr. P. Pederson has assisted with the electronics equipment. One of the authors (N.A.G.) is grateful to the International Atomic Energy Agency for a Fellowship. The work was financially supported by the Swedish Council of Technical Research.

APPENDIX

In the time between submitting the above paper to the Conference and August 1960, the authors made the following improvements in the techniques:

1. The bent-section technique

This technique, touched upon in the original paper, is now well explored. It consists in putting the material mixed with glass wool into a bent section of the reaction tube in order to avoid decomposition by UV radiation in the plasma zone in the main reaction tube. The materials applied, besides polystyrene, were carboxy methyl cellulose and the anaesthetic products [33]: carbocain, procaine, tetracaine, xylocaine and L 67 (an Astra product) in the base and in the hydrochloride forms. With most of these compounds, a decrease of pressure down to very low values was observed, while with the rest a gradual increase was noticed. Purified carbocaine gave a specific activity of 40 mc/g, carboxy methyl cellulose 15 mc/g. The others are not yet measured.

2. Retainment of optical activity

It is known that optically active substances racemize when subjected to ionizing radiation or gaseous discharge. By the bent-section technique preliminary measurements showed that l-cocaine, treated by this technique, has a specific activity of 20 mc/g with the specific rotation unreduced [34].

3. Simultaneous recording of pressure during treatment

The vacuum gauge was connected to a pen recorder (Speedomax) of 10-mV total range and the change of gas pressure with microwave energy was therefore simultaneously recorded. The vacuum-gauge wire was protected from the microwaves by surrounding it with two layers of metal sheet. It was found that the power of the discharge had no marked effect on the pressure change, whereas the distance between the material and the discharge zone had a much greater influence.

4. The cellulose field.

The technique was extended to labelling cellulose and its derivatives. Carboxy methyl cellulose was produced at 15 mc/g tritium-activity after removal of exchangeable tritium with water (in collaboration with Professor O. Samuelsson, Gothenburg.)

5. Measuring techniques

The liquid-scintillation-counting technique, intended for measuring small activities, is now expanded by two simple methods for high and for intermediate activities.

For high activities [35]: The principle of bremsstrahlung was applied with excellent results to measuring tritiated water and organic substances both in solution and in the solid state after calibration for self-absorption. For example, it offered a quick and easy means of following the decrease in carboxy methyl cellulose activity with the successive purification steps.

For intermediate activities [36]: The direct measurement of the current produced from a photomultiplier tube on top of which the radioactive material dissolved together with a scintillator in a common solvent was found useful and practicable for materials of intermediate activities.

6. Labelling by excitation of the substrate alone

Ideas on stored energy in irradiated solids [30] prompted us to irradiate polystyrene and polymethyl methacrylate sealed under vacuum in quartz tubes. Electronic excitation and, possibly, the rupture of some bonds should occur. Immediately after switching off the lamp, tritium in small ampoules with fragile seals placed inside the reaction tubes was brought into contact with the organic material and kept there for some hours. The purified polymers were labelled to a small extent but were definitely higher than if they were exposed to tritium at the same conditions but without previous irradiation. (The authors wish to thank Prof. M. Dole for a discussion on this point.)

Further discussion on reaction mechanism

The disappearance — in most cases — of tritium by electrical discharges and the very high activity found in the unpurified organic material suggest that tritium is firmly adsorbed on the surface of the material. The reason that with most materials a pressure fall is noticed, while with the others the pressure increases, could not be interpreted in terms of sub-microchemical structure of the material, but rather in terms of its crystalline configuration and the presence of voids in the crystal faces in which the tritium atoms can be trapped.

The activity in purified materials, even those containing no exchangeable hydrogen, usually corresponds to a content of only 1/5 of the tritium adsorbed. The rest is found partly in the purifying liquids. This should indicate that only those tritium atoms which impinge on the material surface with some kinetic energy are capable of substitution or addition (especially substitution) for normal hydrogen. The reaction can therefore be represented as:

$$RH + T \rightarrow (T\text{–}R\text{–}H) \begin{matrix} \nearrow R\text{–}H \\ \searrow R\text{–}T \end{matrix}$$

The distance between the material in the bent section and the discharge zone must be regulated so that the material is protected from the UV radiation and at the same time allowed to receive tritium atoms which have not suffered too many collisions. The activation energy can be imagined to be supplied (a) from repulsive states of T_2^+ and (b) from T^+ and T_2^+ neutralization with electrons, viz. without gaining energy from the electrical field. If the mechanism suggested is correct, our studies can be connected with those of STEACIE *et al.* [37]. It is interesting to note that many cases require 5—7 kcal/mol, which actually is very near the difference between quantum energy of the 2537-Å Hg line and the dissociation energy of T_2 (*cf.* main paper). Thus it seems that the minimum energy-requirement of T-labelling, as started from nuclear recoil labelling and ended with UV (or stored energy) excitation, is realized here.

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DISCUSSION

R. Wolfgang (United States of America) said that in the type of labelling procedure described, a number of workers had shown the existence of a tendency for most of, and sometimes all, the tritium to become incorporated in compounds other than the ones irradiated. Irradiated material purified by simple techniques such as those described in the paper was usually found to lose most of its activity on further purification by other techniques and, in order to establish purity, it was necessary to have recourse to very rigorous procedures, such as gas chromatography using several types of columns, electrophoresis and *in vivo* experiments.

Since most of the tritium was present as trace impurities, methods such as those described in the paper—i. e., the measurement of UV spectra and optical rotation—gave no indication of radiochemical purity.

N. A. Ghanem replied that the activity of benzene measured by liquid scintillation counting of a derivative had been confirmed by mass spectral analysis.

Polymers were already complex mixtures. The technique of dissolving in a non-polar solvent followed by precipitation in a polar solvent should remove all labile tritium and also labelled molecules with low molecular weight; this should be fully adequate, especially when the labelled polymer was subsequently used, for example, for making discs of uniform activity for use in autoradiographic work.

As regards blood serum albumin, repeated dialysis and electrophoresis had been used, and he could think of no better purification method.

The anaesthetic products mentioned had not been purified by simple techniques, but by repeated recrystallizations followed by paper chromatography until only one spot had been obtained, corresponding to the known R_f value of the compound in question.

The reference to optical rotation had not been intended as an indication of purity but as an illustration of the potentiality of the technique in retaining the biological activity of a compound to be used in biological tracer work.

R. Wolfgang made a further comment to the effect that a replacement reaction by thermal or low-energy tritium atoms ($T + RH \rightarrow RT + H$) was inconsistent with the known reaction of thermal hydrogen at aliphatic C-H bonds, which was a simple abstraction ($H + RH \rightarrow H_2 + R$). That was the only reaction of atomic hydrogen even at energies of up to 40 kcal. It was only with high-energy or recoil tritium that hydrogen replacement occurred in aliphatic systems.

N. A. Ghanem replied that experimental observations showed the almost complete adsorption of tritium on the target material in many cases. In work on microwave discharges in hydrogen, McCarthy had shown that hydrogen atoms were present a few centimeters outside the discharge zone, while the concentration of ionized particles decreased very quickly. Hence, the bent-section technique, together with the UV technique, provided evidence in favour of an atomic mechanism.

He agreed that in some cases, such as the aliphatic hydrocarbons, high activation energy was required for the replacement reactions, but STACIE and SCHIFF (*Canadian J. of Chem.*, **29** (1951) 1) had shown that in many cases an activation energy of only 5—7 kcal/mol was required.

Replying to questions by **G. Park** (United Kingdom), **N. A. Ghanem** said that cross-linking occurred in the case of polystyrene and degradation in the case of polymethyl methacrylate. In the first case the cross-linked product had been separated and found to form 5—8% of the original material. In the second case degradation products had been removed in the purifying liquids. No attempt had been made to compare molecular weights.

PRODUCTION DE COMPOSÉS ORGANIQUES MARQUÉS AU CARBONE-14 A PARTIR DE $^{14}CO_2$ ACCÉLÉRÈ DANS UN CHAMP ÉLECTRIQUE

ANALYSE PHYSICOCHIMIQUE DE QUELQUES COMPOSÉS RADIOACTIFS OBTENUS

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Abstract — Résumé — Аннотация — Resumen

Production of C^{14}-labelled compounds from $C^{14}O_2$ accelerated in an electric field — Physico-chemical analysis of some radioactive compounds obtained. This paper describes a method of labelling which is based on the acceleration by an electric field of $C^{14}O_2$, which can then react with an organic target in its path.

The discharge cell described operates at 500 V, 150 μA, and the organic products to be labelled are exposed to this field for about three hours with CO_2 having a specific activity of 24 mc/mmole. The maximum yield remains low (about 6%), and 60% of the $C^{14}O_2$ is destroyed. This maximum activity is obtained only for aliphatic chains (50 μc/g for glutaric acid) or for aromatic substances with an aliphatic chain (acetyl-salicylic acid).

Production de composés marqués au ^{14}C à partir de $^{14}CO_2$ accéléré dans un champ électrique — Analyse physico-chimique de quelques composés radioactifs obtenus. Le présent mémoire expose une méthode de marquage basée sur l'accélération par un champ électrique de $^{14}CO_2$, qui est alors susceptible d'entrer en réaction avec une cible organique se trouvant dans sa trajectoire.

La cellule à décharge décrite fonctionne sous 500 V, 150 μA, et les produits organiques à marquer sont soumis à ce champ pendant environ trois heures, avec du CO_2 d'activité spécifique 24 mc/mmole.

Le rendement maximum obtenu reste faible (6% environ), et 60% du $^{14}CO_2$ est détruit.

Ce rendement maximum n'est obtenu que pour les chaînes aliphatiques (50 μc/g pour l'acide glutarique) ou pour des substances aromatiques présentant une chaîne aliphatique (acide acétylsalicylique).

Производство меченных углеродом-14 соединений из $C^{14}O_2$, ускоренного в электрическом поле — Физико-химический анализ нескольких полученных радиоактивных соединений. В данной работе излагается метод мечения, основанный на ускорении электрическим полем $C^{14}O_2$, который в это время поддается вступлению в реакцию с органической мишенью, находящейся на его траектории.

Опысываемая разрядная камера действует под напряжением 500 в, 150 мка, а подлежащие мечению органические вещества вводятся в это поле и находятся там около 3 часов вместе с CO_2 удельной активности в 24 мкюри/ммоль. Максимальный выход полученных продуктов остается слабым (около 6%), а 60% $C^{14}O_2$ — разрушено.

Этот максимальный выход получается только для алифатических цепей (50 мккюри/г для глутаровой кислоты) или для ароматических веществ, представляющих алифатическую цепь (ацетилгалициловую кислоту).

Obtención de compuestos marcados con ^{14}C a partir de $^{14}CO_2$ acelerado en un campo eléctrico —Análisis fisicoquímico de algunos de los compuestos radiactivos obtenidos. La memoria describe un método de marcación que consiste en acelerar $^{14}CO_2$ en un campo eléctrico para que pueda reaccionar con blancos constituidos por sustancias orgánicas colocadas en su trayectoria.

La celda de descarga que describe la memoria funciona a 500 V y 150 μA, y los productos orgánicos que se desean marcar se exponen al campo así creado durante unas tres horas a CO_2 de una actividad específica de 24 mc/mmol. El rendimiento máximo obtenido es bajo (aproximadamente 6%) y el 60% del $^{14}CO_2$ queda destruido.

Este rendimiento máximo sólo se alcanza con cadenas alifáticas (50 μc/g para el ácido glutárico) o con moléculas cíclicas que presenten una cadena alifática (ácido acetilsalicílico).

Nous avons montré qualitativement que du $^{14}CO_2$ accéléré à une E de 500 eV était capable d'entrer en réaction avec une cible organique se trouvant dans sa trajectoire; le ^{14}C, se débarrassant de ses O, se substitue au ^{12}C de la cible et permet dès lors de se procurer, avec des moyens techniques fort réduits et peu onéreux, une substance organique marquée au ^{14}C et dont l'activité spécifique peut atteindre dans certaines conditions favorables des valeurs proches de 50 μc/g.

Nous utilisons pour ce faire une cellule à décharge en «Pyrex» munie de deux électrodes mobiles tournées en argent et distantes de 25 mm. Les deux hémisphères se joignent par rodages plats. Sur la cathode, nous avons fixé une couche mince (environ 10 à 30 mg) du produit organique à marquer. Une pression en $^{14}CO_2$ de $5 \cdot 10^{-2}$ mm de mercure est introduite dans la cellule vidée. La plus haute activité spécifique en $^{14}CO_2$ est recommandée. Nous avons utilisé dans nos expériences un CO_2 provenant de la combustion de $BaCO_3$ d'activité spécifique de 24 mc/mmole. Nous avons ainsi introduit dans la cellule une activité de 15 μc de ^{14}C. Nous soumettons ce dispositif pendant des temps variables (en moyenne 3 h) à une différence de potentiel de 500 V. Le courant enregistré est de 150 μA, tandis qu'il s'établit une ionisation homogène entre les surfaces des deux électrodes. La qualité de cette ionisation est un facteur critique pour le rendement du marquage, nous allons le voir.

Après irradiation de l'échantillon, nous procédons à la récupération du CO_2 résiduel. Nous obtenons celle-ci en condensant le CO_2 restant dans un piège à air liquide et nous réalisons ensuite dans la cellule un vide de 10^{-6} mm. Bien que le rendement maximum de l'opération pour les différents produits traités n'ait jamais dépassé 6%, nous ne récupérons après une décharge, et dans nos conditions de travail, que 40% du CO_2 mis en œuvre. Ceci provient du fait que l'ionisation par la différence de potentiel appliqué démolit une grande partie de l'anhydride et dépose le C élémentaire sur les parois de la cellule ainsi que sur la matière organique traitée. Nous devrons, lors de la purification, éliminer cette contamination labile importante due au ^{14}C élémentaire déposé, ainsi que celle due éventuellement aux produits de dégradation (en concentration minime) auxquels l'irradiation peut avoir donné lieu. Nous ne nous sommes pas occupés, jusqu'à présent, d'identifier ces composés dits de dégradation; nous nous sommes uniquement intéressés au sort de la molécule mère.

En employant cette technique récente, nous avons pu marquer quelques composés organiques de nature variable. Pour certains des essais réalisés, nous avons atteint, dans nos conditions de travail, une activité induite maximum

de 10^5 dpm/mg, soit de 50 μc/g environ. Pour 20 mg de produit déposé sur les électrodes, l'activité globale incorporée dans la molécule cible équivaut donc à 1 μc, ce qui représente un rendement de 6%. Cette valeur maximum a été obtenue avec l'acide glutarique.

Nous avons poursuivi ensuite l'étude qualitative et quantitative de cette méthode.

D'un point de vue qualitatif, on peut affirmer que:

a) La valeur de la différence de potentiel utilisée est apparue sans influence notoire sur le rendement de marquage à partir de 500 V. C'est pourquoi toutes nos expériences ont été réalisées à une valeur de 550 V, afin d'éviter au maximum la décomposition de la molécule traitée.

b) La formation dans la cellule en fonctionnement d'un plasma lumineux homogène provenant d'une ionisation elle même homogène, constitue une condition importante pour obtenir un rendement maximum. L'ionisation homogène de la cellule ne peut être obtenue pendant tout le temps de la décharge que si les électrodes sont rigoureusement parallèles et si la couche organique est déposée d'une façon uniforme sur la surface de l'électrode.

Nous avons pu obtenir un dépôt satisfaisant en utilisant une méthode adaptée au produit traité. Des dépôts d'épaisseur constante ont été réalisés tantôt par sublimation tantôt par cristallisation sur l'électrode, soit encore en immergeant celle-ci pendant quelques secondes dans le produit organique en fusion.

Sans ces dernières précautions, on voit apparaître rapidement dans la cellule un arc qui s'établit entre deux points privilégiés des électrodes, ce qui peut faire tomber le rendement, dans certains cas particuliers, d'un coefficient 20 à 30 pour des conditions de travail identiques. En effet, en utilisant l'acide succinique comme cible, nous avons montré que, dans les conditions de travail habituelles (500 V, 3 h), il était possible d'incorporer une activité atteignant 40 μc/g obtenue avec une ionisation homogène. En présence d'un arc s'établissant dès le début de l'opération, toutes autres conditions identiques, nous n'avons pu obtenir une activité maximum supérieure à 2 μc/g.

D'un point de vue quantitatif, les différentes molécules auxquelles nous nous sommes spécialement intéressés jusqu'à présent sont:

a) Dans la série aliphatique: acide malonique, acide succinique, acide glutarique;

b) Dans la série aromatique: acide benzoïque, acide salycilique et acide gallique (groupe 1), acide acétylsalycilique et acide éthylbenzoïque (groupe 2).

Dans les conditions de décharge signalées, nous avons obtenu des activités induites variables selon la nature de la molécule traitée.

Pour la série aliphatique, nous avons obtenu des activités très comparables, voisines, pour les trois acides mentionnés, de 40 μc/g après purification.

Pour le groupe 1 de la série aromatique, c'est-à-dire ne comprenant en dehors du noyau benzénique qu'un carbone situé dans la fonction carboxylique, toutes conditions de travail identiques, nous n'avons pu obtenir d'activité valable. L'activité enregistrée n'a jamais dépassé le niveau du fond continu d'une quantité mesurable reproductible.

En présence des substances du groupe 2 de la série aromatique, nous avons obtenu (toujours dans les mêmes conditions de fonctionnement) de la décharge et, après purification, une activité intéressante: 25 μc/g pour l'acide acétylsalycilique et 32 μc/g pour l'acide éthylbenzoïque.

Si, d'autre part, nous soumettons à cette technique de marquage les esters éthyliques du groupe 1, c'est-à-dire des acides benzoïque et salycilique, nous

obtenons des substances marquées d'activité comparable à celle obtenue pour les substances dites du groupe 2, c'est-à-dire voisine de 30 μc/g.

Il semble donc, d'après ces quelques résultats obtenus sur des molécules bien déterminées, que la méthode de marquage puisse s'appliquer avec succès, essentiellement aux chaînes aliphatiques. En effet, l'introduction d'un ^{14}C dans une molécule organique nécessite une rupture de liaison. Il est logique d'admettre que la probabilité de recombinaison de la molécule mère à partir de ses produits de dégradation sera beaucoup plus faible si cette dégradation affecte le noyau aromatique plutôt qu'une chaîne aliphatique.

Nous espérons que ces résultats localisés permettront d'évaluer la complexité et l'étendue des problèmes que pose cette technique récente, ainsi que des possibilités intéressantes qu'elle offre pour la préparation des composés organiques marqués.

DISCUSSION

H. Nauta (Netherlands) said that it seemed that the labelling speed did not depend to any considerable extent on the difference of potential. He would like to know what was the range of voltage within which that was true.

M. Guillaume replied that for the different compounds which had been tested, the labelling yield was independant of voltages above 450—500 V. Experiments had been performed up to a maximum of 850 V.

T. Migeal (Belgium) asked whether it was possible to use the technique just described to label directly an organic gaseous product, for example ethylene or propylene.

M. Guillaume said it was impossible to give a general reply to the question. However, there had been a successful trial labelling of a liquid ester which had vaporized, after the working discharge cell had been immersed in a medium the temperature of which had been brought to 85° C. In that particular case, an organic product had been obtained with a specific activity higher than that generally recorded for solid compounds. That showed that C^{14} labelling was possible with a gaseous substance, the yield depending on the state of dispersion of the target molecules.

B. E. Gordon (United States of America) asked whether it was possible to distinguish between the entry of C^{14} as an ion and $C^{14}O_2$ as an ion.

M. Guillaume replied that it was not possible. The ionic plasma contained ions of C, CO and CO_2, and the specific action of each had not yet been determined, although the question was being investigated by Dr. Giacomello in Rome.

PREPARATION OF VERY SMALL AMOUNTS OF TRITIUM-LABELLED POLYPHENOLS AND THE ISOLATION OF THE TRITIATED COMPOUNDS BY "NORMAL FREEZING"

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Abstract — Résumé — Аннотация — Resumen

Preparation of very small amounts of tritium-labelled polyphenols and the isolation of the tritiated compounds by "normal freezing". 0.01 mg to 0.1 mg resorcinol were labelled by an exchange reaction with tritiated water (5 c/ml) in alkaline medium and in the presence of a platinum-oxide catalyst. In addition to the desired exchange, destruction of the organic substance occured. Better results were obtained without a platinum-oxide catalyst and with a longer reaction time (10 h) and still better at an increased temperature, up to 100° C.

The separation of these small quantities of radioactive compounds from the tritiated water was made without loss by "Normal Freezing". A reaction tube with the solution which was to be concentrated, was lowered slowly into a copper-tube cooled by a freezing mixture. During this procedure the liquid above the ice was stirred vigorously. The crystallization rate was 6 cm/h and the cooling mixture had a temperature between —40 and —50°C. For isolating the labelled compounds a very small part of the frozen solution on the top of the ingot was melted and repipetted onto a paper chromatogram. This was developed with a mixture of benzene/butanol/water. The spots on the paper chromatogram were located quantitively either by a technique of "scintillation autoradiography" or by scanning with a flow counter.

The maximum specific activity of the purified samples was approx. 17 μc/mg.

Préparation de très petites quantités de polyphénols marqués au tritium et isolement des composés tritiés par «congélation normale». On a marqué de 0,01 à 0,1 mg de résorcine par une réaction d'échange avec de l'eau tritiée (5 curies/ml) en milieu alcalin et en présence d'un catalyseur constitué par de l'oxyde de platine. En plus de l'échange désiré, il s'est produit une destruction de la substance organique. Cependant, de meilleurs résultats ont été obtenus sans catalyseur d'oxyde de platine et avec un temps de réaction plus long (10 h), de préférence à une température plus élevée, allant jusqu'à 100° C.

Ces petites quantités de composés radioactifs ont été séparées de l'eau tritiée sans aucune perte, par «congélation normale». La méthode consiste à introduire lentement un tube à réaction, contenant la solution à concentrer, dans un tube en cuivre refroidi au moyen d'un mélange réfrigérant. Au cours de l'opération, on agite vigoureusement le liquide au-dessus de la glace. Le taux de cristallisation était de 6 cm/h et le mélange réfrigérant était maintenu à une température comprise entre —40 et —50° C. Pour isoler les composés marqués, on a fait fondre une très petite parcelle de la partie supérieure de la solution congelée, qu'on a ensuite aspirée au moyen d'une pipette et déposée sur un chromatogramme en papier. Celui-ci a été développé avec un mélange de benzène/butanol/eau. On a déterminé quantitativement les gouttes de composé déposées sur le chromatogramme, soit par «autoradiographie par scintillation», soit par exploration à l'aide d'un débitmètre.

L'activité spécifique maximum des échantillons ainsi purifiés était d'environ 17 μc/mg.

Получение весьма малых количеств меченных тритием полифенолов и выделение содержащих тритий составов при помощи „нормального замораживания". Резорцин в количествах от 0,01 мг до 0,1 мг был мечен посредством реакции обмена с тритированной водой (5 кюри на миллилитр) в щелочной среде и в присутствии катализатора из окиси платины. В добавление к желаемому обмену наблюдалось разрушение органического вещества. Наилучшие результаты были получены без катализатора из окиси платины при более продолжительном времени реакции (10 час.), а еще лучшие результаты были получены при повышении температуры до 100° Ц.

Выделение без потерь этих малых количеств радиоактивных составов из тритированной воды производилось посредством „нормального замораживания". Пробирка с концентрируемым раствором медленно погружалась в медную трубку, охлаждаемую замораживающей смесью. Одновременно с этим находящаяся над льдом жидкость энергично мешалась. Скорость кристаллизации составляла 6 см в час, а температура охлаждающей смеси изменялась между $-40°$ Ц и $-50°$ Ц. Для выделения меченых составов небольшая частица замороженного раствора на поверхности превращенного в льдинку образца расплавлялась и переносилась при помощи пипетки на хроматографическую бумагу. Эта бумага проявлялась смесью бензола/бутанола с водой. Количественный анализ пятен на хроматографической бумаге проводился либо при помощи „сцинтилляционной радиоавтографии", либо посредством замера поточным счетчиком.

Максимальная удельная активность очищенных образцов составила приблизительно 17 мкюри/мг.

Preparación de cantidades muy pequeñas de polifenoles marcados con tritio, y aislamiento por "congelación normal" de los compuestos tritiados. Los autores marcaron de 0,01 mg a 0,1 mg de resorcina por una reacción de intercambio con agua tritiada (5 c/cm³) en medio alcalino y en presencia de óxido de platino como catalizador. Observaron que además del intercambio deseado, se produce cierta descomposición del compuesto orgánico. Los mejores resultados se obtienen trabajando sin catalizador durante un tiempo de reaccion más largo (10 horas) y, de preferencia, a temperaturas más elevadas (hasta 100° C).

Los autores emplearon el método de la "congelación normal" para separar del agua tritiada estas pequeñas cantidades de compuestos radiactivos sin que se produzcan pérdidas. El método consiste en introducir lentamente el tubo de ensayo que contiene la solución a concentrar en un tubo de cobre refrigerado con mezcla frigorífica. El líquido que queda encima del hielo es agitado enérgicamente durante la operación. La velocidad de cristalización fue de 6 cm/hora y la temperatura de la mezcla frigorífica osciló entre —40° C y —50° C. Los autores efectuaron la separación de los compuestos marcados fundiendo una porción muy pequeña de la capa superior de la solución congelada y pasándola con una pipeta a un papel para cromatografía. Revelaron el cromatograma con una mezcla de benceno/butanol/agua. Las manchas del cromatograma fueron localizadas cuantitativamente por "autografía por centelleo" o por exploración con un contador de flujo.

La actividad específica máxima de las sustancias purificadas fue del orden de los 17 μc/mg.

1. Introduction

On the same lines as for a preparation of β-Sitosterin-H^3 (2.2 μc/mg) by the Pt-catalysed exchange method [1], we have tried to label traces of resorcinol, hydroquinone and pyrogallol in order to have a non-destructive method of identification. First it was necessary to find a simple procedure to isolate the very small amounts (1—100 μg) from the tritiated water. This seemed to be possible by

"normal freezing", a method of crystallization by which the freezing of the solvent is controlled from one direction, whereby the tritiated compounds are enriched and isolated at the surface of the volume [2].

2. "Normal freezing"

While a solution in a glass tube is slowly lowered into a cooled copper tube, the pure solvent is freezing from the bottom and the solute is collected in the last droplets at the upper end of the tube. Even in the case of very small concentrations, only one step is necessary if the liquid is vigorously stirred during the freezing process. It is also very important for the enrichment that the solute does not form mixed crystals with the solvent.

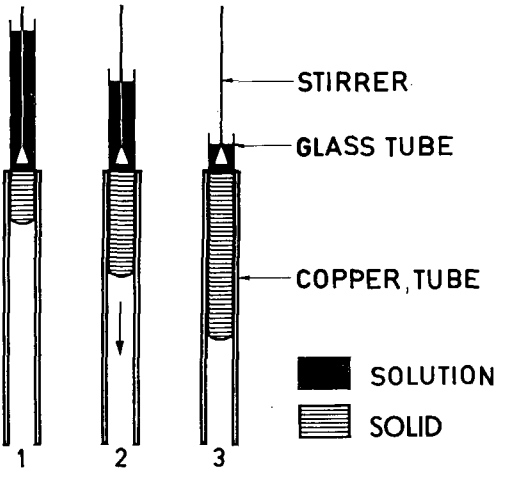

Fig. 1
Three steps of the freezing process during "normal freezing" (schematic).

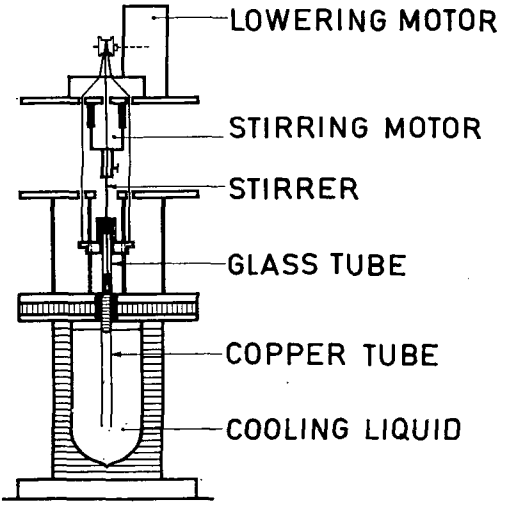

Fig. 2
Design and construction of the "normal freezing" apparatus.

In Fig. 1 the freezing process is shown schematically for three successive steps. In position 1 most of the solution is still liquid, while in 3 nearly all is frozen. During the freezing process the stirrer always remains in the same position. In Fig. 2 the whole freezing-apparatus is shown in longitudinal section and Fig. 3 is a photograph of it. The apparatus consists of three parts: the cooling system, the lowering system and the stirring installation.

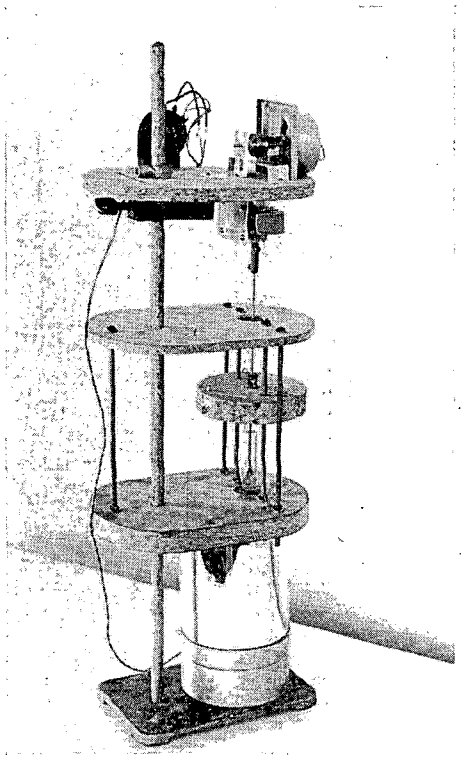

Fig. 3
Photograph of the complete "normal freezing" apparatus.

Before starting the freezing process, the glass tube is filled with the solution (from 1 to 100 cm^3) by a pipette and is fixed inside the rubber insulation of the lowering ring. During the subsequent installation of the stirrer and its traversing slide, the tube is supported by some backing material. The level of the phase boundary depends on the temp. of the cooling liquid and the rate of stirring. While the glass tube is lowered 1 to 5 mm into the copper tube, the solution is stirred slowly to facilitate the beginning of crystallization. Afterwards the rate of stirring is regulated to the desired speed (1200 to 6000 rev/min). The amount of stirring and the rate of freezing, as well as the initial concentration, have a critical bearing on just how "normal freezing" performs and what time will be needed for the whole process. Under proper conditions, the time of one freezing process could be kept to within 0.5 to 2.0 h.

As shown in Fig. 4, the tube with the frozen liquid is immersed at the end of the process in a cooling liquid and fixed by a wooden plate with rubber insulation. The tube is so positioned that the surface of the ice ingot is about 1mm above

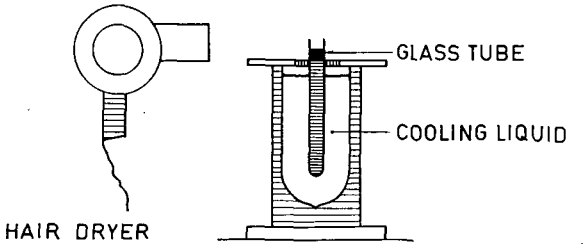

Fig. 4
Arrangement for the separation of the conc. layer from the pure ice ingot.

the wooden plate. This part is melted by a hair-dryer and withdrawn by an injection syringe. Multicompound-systems can be enriched in the same way, as was shown by experiments with aqueous solutions of resorcinol, hydroquinone and pyrogallol. These phenols were enriched at the surface gradually, so that separation became possible. This can be improved by repeated freezing procedures. The results show that it should be possible to refine radioactive materials from their decomposition products.

In non-aqueous solvents as well, good separation effects could be obtained, for example, in the case of a solution of phenol in benzene (1.0%). When freezing processes were performed on solvents with a MP between —60 and —130° C, the test conditions for aqueous systems had to be modified, especially the cooling liquid and the regulation of the stirrer.

It was found that the dissolved organic compounds could not be enriched satisfactorily in *n*-octane. In methanol, ethanol and diethyl ether the added materials could not be concentrated at all. These results could be improved neither by reducing the lowering speed and increasing the stirring rate nor by smaller concns. This behaviour is due to the fact that near the freezing zone the viscosity of the unfrozen part becomes very high, so that even extremely high stirring-rates had no effect on mixing the solution and therefore no effect on the degree of concn. The same results have been found with glycol as solvent. On the other hand, good effects could be obtained with the unpolar solvents methylenechloride and chloroform.

3. H^3-labelling of organic compounds

The best way of H^3-labelling trace amounts of organic compounds seemed to us the exchange method with tritiated water. The experiences of FUKUSHIMA *et al.* [3], BLOCH *et al.* [4], ANKER *et al.* [5] and LEROY *et al.* [6] in this technique were also useful to our problems. In these exchange experiments we used a Pt-catalyst to loosen the CH-bond and to facilitate the H^3-exchange. In addition, the experiments were carried out in alkaline medium. Also the β-irradiation itself, especially when tritiated water of high specific activity was used, was of great catalytic influence. By this threefold effect however, certain substances were damaged and the formation of radioactive by-products was favoured. Therefore in such cases it was found better to work without a Pt-catalyst.

In similar exchange experiments with D_2O or tritiated water, the solvent was separated from the labelled substances by distillation, a procedure by which large amounts of solvent are lost [7]. Using "normal freezing" as separation method, we could recover the tritiated water without losses and in high purity. The labelled compounds could be isolated from the reaction-mixture quantitatively.

3.1 Exchange experiments with tritiated water of 200 mc/cm³

All exchange experiments were carried out in the same glass tubes as are usually employed for normal freezing processes. Working at high temperatures the H^3-exchange could be greatly enhanced. In such cases we used somewhat longer tubes which were sealed. At the end of the procedure they were reduced to standard length for the "normal freezing" apparatus.

1.0 ml tritiated water was filled into a glass tube by a syringe with a 10-cm injection needle. In the case of catalytical exchange, 0.2 mg PtO_2 (81.78% Pt) was added, reduced with ordinary hydrogen, the excess hydrogen being replaced by nitrogen. Both gases were freed, before use, of oxygen and traces of water. By adding 2.8 mg KOH a $n/20$ solution was prepared and finally about 0.15 mg of the organic compound was added. The reaction tube was evacuated, sealed and shaken at various temps. At the end of this procedure the labelled material was enriched and isolated by "normal freezing" under the following conditions:

Cooling temp.	:	—40 to —50°C
Lowering speed	:	6 cm/h
Rate of stirring	:	3000 rev/min
Space of stirrer	:	1 to 3 mm

Before the activity of the H^3-labelled compounds could be determined, they had to be freed from radioactive by-products by paper chromatography. The final volumes of solution (0.018 to 0.022 cm³) were pipetted on the starting front of a chromatographic paper (2043 b S & S) and developed with benzene/butanol/water (9:1:10). Before development, traces of tritiated water were removed by an electrical hair-dryer. At the end, the paper chromatogram was analysed by autoradiography and by scanning with a windowless flow-counter.

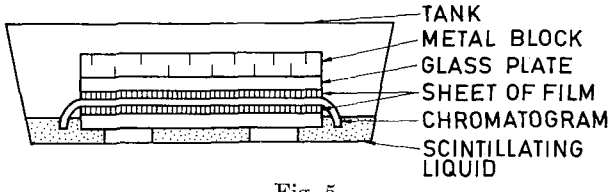

Fig. 5
Assembly for autoradiography.

As shown in Fig. 5, the radio-paper-chromatogram was placed between two sheets of film (Agfa-Röntgenfilm SSS-klar) and then between two glass plates. A metal block at the top ensures a good contact pressure between chromatogram and film. With this arrangement it was possible to perform several analyses at the same time by piling a number of chromatograms and films. The assembly is placed in the bottom of an air-tight and light-tight tank. Depending on the activity of the organic compounds, the exposure time varied from 2 to 20 d. When

radioactive spots of very low sp. activity were analysed, a technique of scintillation autoradiography was used, as described by WILSON [8]. For these tests, 3 g of *p*-diphenyl benzene were dissolved in 1 liter toluene and from this mixture a sufficient quantity was poured into the tank to cover the radio-paper-chromatogram. With long exposure times, however, it has been observed that the solvent has an aggressive influence on the film.

Counting of the radioactive spots on the paper chromatogram was carried out by scanning the paper chromatogram with a windowless flow counter in connection with a radio-paper-chromatograph, as described by FASSBENDER [9]. Besides determining the activities, it was possible to locate the radioactive spots quickly and to determine R_f-values.

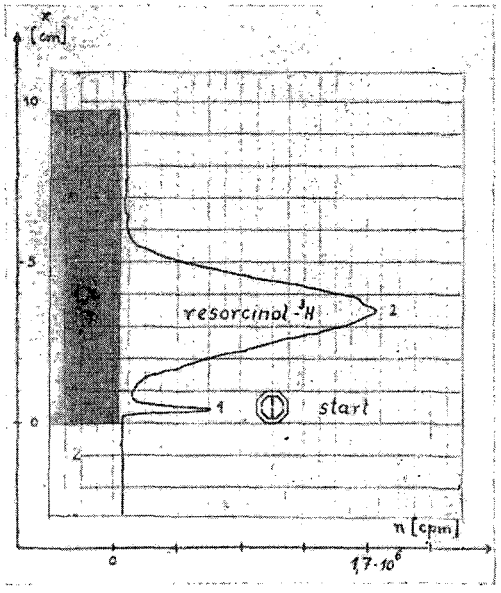

Fig. 6
Graph showing the distribution of activity in relation to the paper-chromatogram of the tritiated compounds.

Results of autoradiography and scanning procedure are shown in Fig. 6 for radioactive resorcinol. The darkened spot on the film corresponds very well with the peak of the recorder. In addition, the spots were made visible by spraying the chromatogram with a 2% aqueous solution of phosphormolybdic acid and exposing the strips to ammonia [10].

3.2 EXCHANGE EXPERIMENTS WITH TRIATED WATER OF 5 C/CM³

When tritiated water of higher specific activity is used, the activity of the labelled products should increase, but at the same time the destruction of the organic material was enhanced, as shown in Table I. In No. 1, the exposure time was not long enough to obtain a sufficient H^3-exchange. No. 2 shows that at longer exposure times H^3-exchange and radiaction damage are superimposed. And lastly in No. 3 it can be seen that at high temperatures all the organic material has been destroyed.

TABLE I

COMPARISON OF RESULTS FROM THREE EXCHANGE EXPERIMENTS WITH TRITIATED WATER OF 5 c/cm³

No.	Labelled compound	Temp. (°C)	Exposure time (h)	Colour reaction	H^3-exchange
1	Resorcinol	25	1/4	+	low
2	Resorcinol	25	40	weak	+
3	Resorcinol	180	48	—	—

3.2.1. *Exchange experiments without a Pt-catalyst*

The experiments in this test series were carried out in alkaline tritiated water of 5 c/cm³ and without a Pt-catalyst, so as to minimize the destruction of the organic material. It can be seen from Table II that it is possible to increase the H^3-exchange, firstly by longer exposure time (No. 2) and secondly by using an elevated temp. (No. 3). Thus the resulting sp. activities were 1:4.5:30. For determination of the sp. activities, the radioactive spots on the chromatogram were eluated with absolute methanol and the maximum extinction at 275 mμ determined.

TABLE II

COMPARISON OF LABELLING RESULTS OBTAINED UNDER VARIOUS CONDITIONS

No. of the assay	1	2	3
Labelled compound	Resorcinol	Resorcinol	Resorcinol
Extinction at 275 mμ	0.95	1.07	0.88
Quantity (μg)	87	98	80
Temp. (°C)	25	25	100
Exposure time (h)	0.5	10	1
Colour reaction	+	+	+
H^3-exchange	+	+	+
Sp. activity (dpm/mg)	1.238×10^6	5.618×10^6	37.575×10^6
Sp. activity (μc/mg)	0.56	2.53	16.93

The severe experimental conditions used for the H^3-exchange of resorcinol could not be extended to hydroquinone and pyrogallol, because these materials are more sensitive to highly active tritiated water. As shown in Table III, hydroquinone, for example, has been destroyed after a relatively short exposure-time (No. 3) compared with the experiment on resorcinol (No. 1). This means that hydroquinone as well as pyrogallol can be labelled more easily than resorcinol if soft reaction conditions are used (Nos. 2 and 4).

TABLE III

RESULTS FROM EXCHANGE EXPERIMENTS WITH TRITIATED WATER OF 5 c/cm³ WITHOUT A Pt-CATALYST

No.	Labelled compound	Temp. (°C)	Exposure time (h)	Colour reaction	H^3-exchange	R_f
1	Resorcinol	25	70	+	+	0.58
2	Hydroquinone	25	2	+	low	0.41
3	Hydroquinone	25	40	—	—	
4	Pyrogallol	25	1/4	+	low	0.16

3.3 RADIOACTIVE BY-PRODUCTS

As shown in Fig. 7, radioactive decomposition products could be detected by scanning the chromatogram. Their position is near the boundary of the solvent and in special cases it could be discovered by a yellow colour. Compared with resorcinol, hydroquinone and pyrogallol are more easily oxidized, therefore their sensitivity to tritiated water of high sp. activity is understandable. The radioactive by-product seems to be a quinone, because after the reduction of the spots with SO_2, they give a positive reaction when sprayed with phosphormolybdic

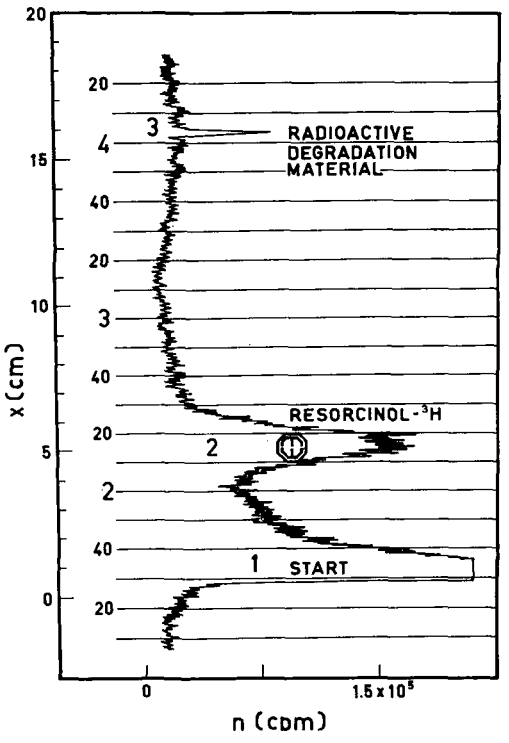

Fig. 7
Position of the active compound on the paper-chromatogram as found by the scanning method.

acid and then with ammonia. When tested by paper-chromatography techniques, the product turned out to be more hydrophile than hexaoxybenzene. These experiments indicate that it must be a system consisting of several rings and it could be a derivative of diphenyl with many OH-groups [11].

4. Summary

It is possible to isolate labelled trace amounts of organic compounds after exchange with tritiated water if the reaction mixture is worked up by normal freezing. The method is simple and often allows the labelled material to be recovered quantitatively. Practically all the tritiated water is retained in its initial purity. Quantities of 0.001 to 1 mg are purified by paper chromatography. Under certain conditions the separation from radioactive by-products should be possible in a "normal freezing" process.

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THE SYNTHESIS OF THE INSECTICIDES ALDRIN AND DIELDRIN LABELLED WITH CARBON-14 AT HIGH SPECIFIC ACTIVITY

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Abstract — Résumé — Аннотация — Resumen

The synthesis of the insecticides Aldrin and Dieldrin labelled with carbon-14 at high specific activity. Aldrin is the trade name given by Shell Chemicals to 1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-exo-1, 4-endo-5, 8-dimethanonaphthalene.

Acetylene-1, 2-C^{14} is converted successively to tetrachloroethane and trichloroethylene, and this is condensed with carbon tetrachloride by the Prins reaction in the presence of aluminium chloride to octachloro*cyclo*pentene. Dechlorination gives hexachloro*cyclo*pentadiene which undergoes a Diels-Alder addition to bi*cyclo*(2, 2, 1) hepta-2,5-diene to give aldrin-C^{14} in 12% yield from barium carbonate.

Oxidation of Aldrin gives the 6,7 epoxide, Dieldrin, in 87% yield.

The paper includes an account of the separation of octachloro*cyclo*pentene from the crude product of the Prins reaction by gas-liquid chromatography and of the separation of Aldrin and Dieldrin on a small preparative scale by reversed-phase paper chromatography.

Synthèse des insecticides aldrine et dieldrine marqués au carbone-14 de haute activité spécifique. Aldrine est la dénomination commerciale par laquelle la Shell Chemicals désigne l'hexachloro-1, 2, 3, 4, 10, 10-hexahydro-1, 4, 4a, 5, 8, 8a-exo-endo-1,4-diméthano-5, 8-naphtalène.

L'acétylène-1,2-C^{14} est successivement transformé en térachloroéthane et en trichloroéthylène, lequel se condense avec le tétrachlorure de carbone, par la réaction de Prins, en présence de chlorure d'aluminium, pour donner de l'octachloro*cyclo*pentène. La déchloruration fournit de l'hexachloro*cyclo*pentadiène, lequel, par une synthèse de Diels-Alder, se transforme en bi*cyclo*hepta(2, 2, 1)-diène-2, 5 pour donner de l'aldrine-C^{14}, avec un rendement de 12% par rapport au carbonate de baryum.

L'oxydation de l'aldrine donne l'époxyde-6 7-(dieldrine), avec un rendement de 87%.

Les auteurs décrivent, en outre, la séparation de l'octachloro*cyclo*pentène par chromatographie gaz-liquide, à partir du produit brut de la réaction de Prins, ainsi que la séparation de l'aldrine et de la dieldrine, en petite quantité, par chromatographie sur papier à phase renversée.

Синтез инсектицидного алдрина и дилдрина, меченных углеродом-14 при высокой удельной активности. Алдрин — коммерческое название, данное Шеллом Кемикалом для 1, 2, 3, 4, 10, 10-гексахлоро-1, 4, 4а, 5, 8, 8а-гексагидро эксо-1,4-эндо-5,8-диметанонафталина.

Ацетилен-1,2-C^{14} успешно превращается в тетрахлороэтилен и трихлороэтилен и конденсируется с углеродистым тетрахлоридом в реакции Принса в присутствии алюминиевого хлорида в октахлоро*цикло*пентан. Дехлоризация приводит к гексахлоро*цикло*пентадину, который добавляется в виде Дилс-Алдера к бицикло (2, 2, 1) гепта-2,5-дину для получения из бариевого карбоната 12% алдрина-C^{14}.

Окисление алдрина приводит к образованию элоксида 6,7 и дилдрина в размере 87%.

В документе содержится отчет об отделении октохлороциклопентана от сырого продукта реакции Принса путем газожидкой хроматографии и об отделении алдрина и дилдрина в небольшом количестве путем обратной фазы бумажной хроматографии.

Síntesis de los insecticidas aldrin y dieldrin de elevada actividad especifica marcados con carbono-14. Aldrin es el nombre comercial que la compañía Shell Chemicals dio al 1, 2, 3, 4, 10, 10-hexacloro-1, 4, 4a, 5, 8, 8a-hexahidro-exo-1, 4-endo-5, 8-dimetano-naftaleno.

El acetileno-1, 2-^{14}C se convierte primero en tetracloroetano y después en tricloroetileno, y éste se condensa con tetracloruro de carbono, por la reacción de Prins, en presencia de cloruro de aluminio, para dar octaclorociclopenteno. Por decloración se obtiene hexaclorociclopentadieno que, por una síntesis de Diels-Alder, da biciclo (2, 2, 1) hepta-2, 5-dieno para llegar al aldrin-^{14}C con un rendimiento del 12% referido al carbonato de bario.

La oxidación del aldrin da el 6, 7-epóxido, denominado dieldrin, con un rendimiento del 87%.

Los autores describen la separación del octaclorociclopenteno del producto bruto de la reacción de Prins por cromatografía gas-líquido, y la separación del aldrin y del dieldrin en pequeña escala, por cromatografía sobre el papel, de fase invertida.

1. Introduction

Aldrin (1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-1, 4, 5, 8 endo, exo dimethanonaphthalene) and Dieldrin (the 6,7 epoxide of Aldrin) are the registered trade names given by The Shell Chemical Company to two widely employed insecticides [1]. The skeletal formula of each of these two substances is shown in Fig. 1.

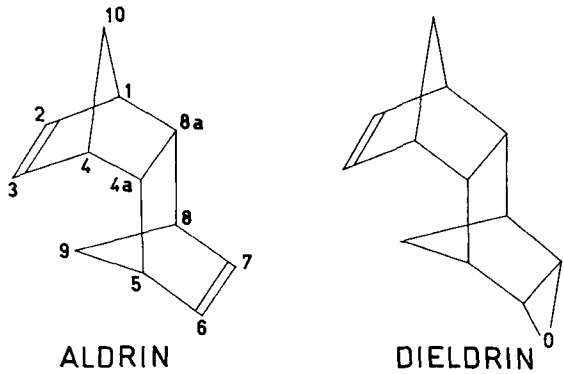

Fig. 1
Skeletal formulae for Dieldrin and Aldrin (both are endo-exo isomers).

Other isomers of both Aldrin and Dieldrin with pesticidal properties are known, but their use and applications are more limited.

Metabolism, absorption, translocation and analysis of these substances and other insecticides in insects, animals and plants are most readily and accurately determined by use of the tracer technique [2]. Such experiments demand a high sp. activity. Both Aldrin and Dieldrin have been labelled with chlorine-36 [3] but, until this work, no synthesis incorporating carbon-14 has been successful

except for the preparation of Isodrin-C^{14} (the endo, endo isomer of Aldrin) described by BROOKS [4].

We have been able to prepare both Aldrin and Dieldrin by a sequence of reactions [5] shown below in Fig. 2 at a sp. activity of 7.5 mc/mM. In order to limit

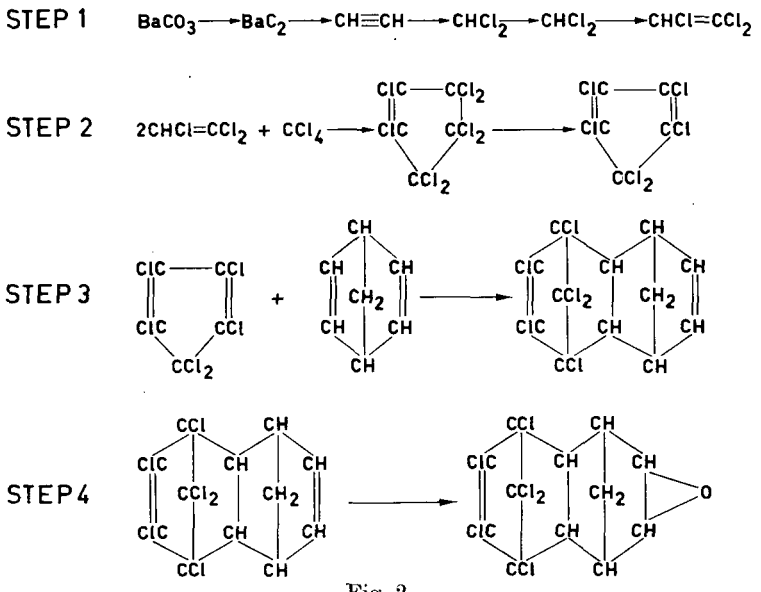

Fig. 2
Reaction scheme.

the total activity invested in the preparation, we were obliged to add carrier acetylene, octachloro*cyclo*pentene and hexachloro*cyclo*pentadiene at the appropriate intermediate stages so as to maintain the desired chemical scale. By employing barium carbonate of high sp. activity (30 mc/mM or greater) and increasing the chemical scale of the initial steps, dilution would not be necessary and a product with a sp. activity of 30—50 mc/mM should be attainable. This sequence of reactions has the particular virtue of introducing into the product molecule two or more labelled atoms and thus permitting a product of high sp. activity to be obtained. We also saw that each stage could be conveniently adapted to a semi-micro scale and the yields might be acceptable, which is an important factor in view of the high cost of carbon-14.

To discuss the experimental details of procedure it is convenient to break the eight-stage synthesis down into four steps and to consider each step in turn.

2. Experimental

STEP 1. TRICHLOROETHYLENE-1, 2-C^{14}

Acetylene-1, 2-C^{14} was prepared by the hydrolysis of barium carbide-C^{14} obtained by heating barium carbonate-C^{14} with excess barium in an atmosphere of argon. A radiochemical yield of 80% from barium carbonate was obtained. We observed, in common with others, that the chemical yield was somewhat higher than the radiochemical yield [6]. For radiochemical measurement a portion

of the active acetylene was diluted with carrier and converted to the tetrabromide.

Diluted acetylene-1, 2-C^{14} (5 mM, 75 mc) was reacted with four equivalents of chlorine in a blackened 2-liter flask containing some sand that had been digested in aqua regia and thoroughly washed. By this means the normally explosive reaction could be controlled to give almost quantitative yields of symmetrical tetrachloroethane-1, 2-C^{14} as determined by gas-phase chromatography.

De-hydrochlorination of the tetrachloroethane-1, 2-C^{14} was carried out by condensing it into a flask containing potassium hydroxide (5 g in 3 ml water) and stirring the mixture vigorously for 1.5 h at 0°C. After drying over phosphorus pentoxide the trichloroethylene-1, 2-C^{14} (4.15 mM, 68 mc) was analysed by gas-phase chromatography and the total activity as trichloroethylene was determined. To reduce radiation decomposition, it was stored at —80°C in the dark.

STEP 2. HEXACHLOROCYCLOPENTADIENE-C^{14}

Conversion of trichloroethylene-1,2-C^{14} by reaction with an excess of unlabelled carbon tetrachloride in the presence of freshly sublimed aluminium chloride to octachloro*cyclo*pentene-C^{14} by the Prins reaction was the key step in the whole synthesis (see Fig. 3). By employing inactive materials, the crude reaction pro-

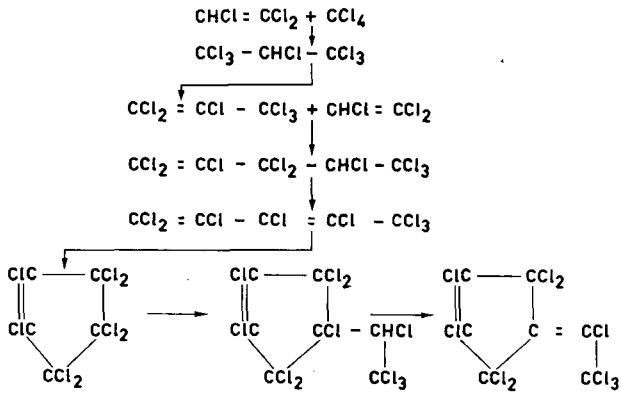

Fig. 3
Prins reaction: postulated sequence of reactions.
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duct, after removal of the excess of carbon tetrachloride by distillation, contained between 50% and 60% octachloro*cyclo*pentene (based on trichloroethylene) and best yields were obtained by using not less than a 100% excess of carbon tetrachloride. The reaction was carried out in a glass tube sealed under vacuum into which the volatile reaction components had been distilled. It contained in addition a number of small glass beads so that, when it was rotated, a thorough mixing of the reactants occurred. The tube was heated for 3 h in an oil bath at 90°C.

Trichloroethylene-1,2-C^{14} (4.15 mM, 68 mc), carbon tetrachloride (10 ml) and aluminium chloride (350 mg) were reacted under the conditions described above. The contents of the tube were washed out and extracted with ether; the ethereal extract was washed with saturated aqueous sodium bicarbonate and dried over

anhydrous calcium sulphate. The ether and excess carbon tetrachloride (which contained less than 100 μc) were removed by distillation. From the residue (1.699 g, 38 mc) octachloro*cyclo*pentene-C^{14} together with some hexachloro*cyclo*pentadiene-C^{14} (total 390 mg, 29.6 mc) was separated by gas-phase chromatography (see below). A middle fraction believed to contain a mixture of highly chlorinated C-3 hydrocarbons (total 11.5 mc) was isolated and it is probable that some other material, possibly C-9 hydrocarbons and polymers, was retained on the column.

From the weights and total activities of the starting material, trichloroethylene-C^{14}, and of the octachloro*cyclo*pentene-C^{14} obtained, it is apparent that a reduction of sp. activity of about 30% on the calculated value had occurred. This result might have been expected, as the postulated reaction scheme involves a symmetrical intermediate in a stage which is potentially reversible. It is, however, surprising that so little activity was found in the carbon tetrachloride.

For our purpose the use of gas-phase chromatography presented three problems:

(i) quantitative injection of the samples,
(ii) the design of a column of suitable characteristics to separate and to take a load of some tens of milligrams of mixture, and
(iii) quantitative separation and collection of fractions as they issue from the column.

A stainless-steel column (6 ft × 3/8 in) was packed with Celite (80—100 mesh) and coated with silicone oil 20% (Hopkin & Williams Ltd., MS 550). Dry nitro-

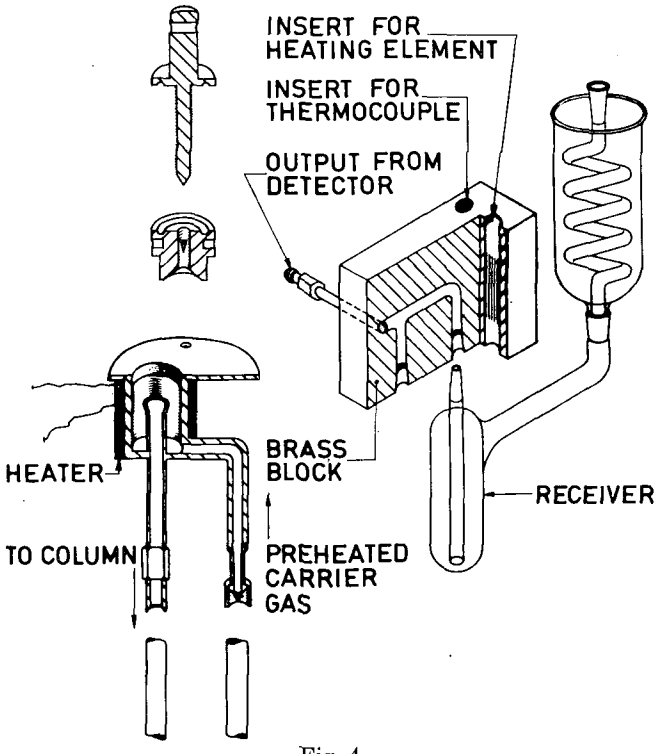

Fig. 4
Sketches of injection (on left) and collection devices.

gen preheated to oven temperature was used as carrier gas. The column operated with an input pressure of 15 lb/in^2 and an output pressure at atmospheric. Samples were introduced into the column by interrupting the gas flow and placing the sample contained in a fragile glass ampoule onto the top of the column. The nitrogen flow was started and allowed to reach a steady value, the ampoule was crushed and the contents volatilized. Emergence of components was detected with a katharometer, and fractions collected by entrainment in refluxing *n*-hexane from which they were recovered by distillation. A sketch of the injection and collection devices is shown in Fig. 4. With a flow rate of 60 ml/min of nitrogen and a column temp. of 190°C, the retention time for octachloro*cyclo*pentene was about 15 min. Some slight dechlorination of octachloro*cyclo*pentene to hexachloro*cyclo*pentadiene (retention time about 5 min over a broad band) occurred on the column at this operating temp. The recovery of octachloro*cyclo*pentene-C^{14} was 85—90% on total octachloro*cyclo*pentene-C^{14} in the crude mixture. Octachloro*cyclo*pentene-C^{14} (390 mg, estimated 1.3 mM octachloro*cyclo*pentene-C^{14} 29.6 mc) containing some hexachloro*cyclo*pentadiene-C^{14} was diluted with carrier (1 mM, total "octa" 2.3 mM) and distilled under reduced pressure over a nickel wire spiral heated at 490°C, the product hexachloro*cyclo*pentadiene-C^{14} (1.5 mM, 18 mc) was collected in a trap cooled to —80°C and then diluted with carrier (1 mM). A small amount of sublimate collected above the furnace tube; we did not isolate this material but believe it to be hexachlorobenzene [5].

Step 3. Aldrin-C^{14}

Hexachloro*cyclo*pentadiene-C^{14} (2.4 mM, 18 mc) was condensed with bi*cyclo* (2, 2, 1) hepta-2,5-diene in the mole ratio of 1:3. The reactants were sealed in a glass tube and kept at 95°C for 24 h. After removal by distillation of the excess bi*cyclo* compound, the residue, which solidified on cooling, was crystallized three times from methanol.

Aldrin-C^{14} (7 mc, 0.96 mM, mp 94—97°C, lit. 104°C) was obtained. The radiochemical purity was 95% by dilution analysis as recrystallized material and reversed-phase paper chromatography. An analysis of the mother-liquors showed them to contain a further 3 mc of Aldrin.

Step 4. Dieldrin-C^{14}

Dieldrin-C^{14} (0.47 mM, 3.5 mc, mp 147—150°C, lit. 175—176°C, radiochemical purity 95%) was obtained by the epoxidation of Aldrin-C^{14} (0.54 mM 4 mc) using perbenzoic acid (2 mM) in chloroform solution at room temp. for 30 h. After removal of perbenzoic acid and chloroform the product was crystallized from methanol.

Reversed-phase paper chromatography on a preparative scale

Dieldrin and Aldrin may be separated satisfactorily on an analytical scale by reversed-phase paper chromatography [7]. We have adapted this technique to the separation of these two substances on a semi-micro scale. The residues from the mother-liquors of both Aldrin and Dieldrin were applied as streaks (30 mg) to paper (Whatmans No. 3 MM 14 in × 32 in) coated with Apiezon Type L grease and developed with acetic acid-water 3:1 v/v. The bands of active material on the paper were located after drying, by autoradiography, cut out and the active material together with the grease extracted with ether. The ether was distilled off and the residue reapplied to paper and the Aldrin-C^{14} or Dieldrin-C^{14} eluted with

methanol-water 9:1 v/v. The material from each of these fractions was then crystallized from methanol.

Bands due to other by-products of the condensation reaction were observed but not identified. These are clearly shown on the photographs of some typical chromatograms (Figs. 5 and 6).

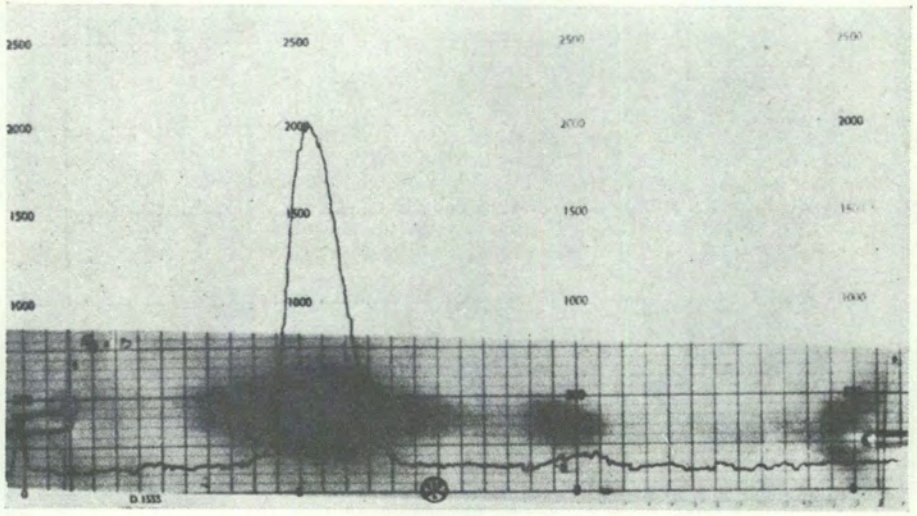

Fig. 5
Crude product of Diels-Alder condensation.
Autoradiograph and scan of analytical paper-chromatogram.

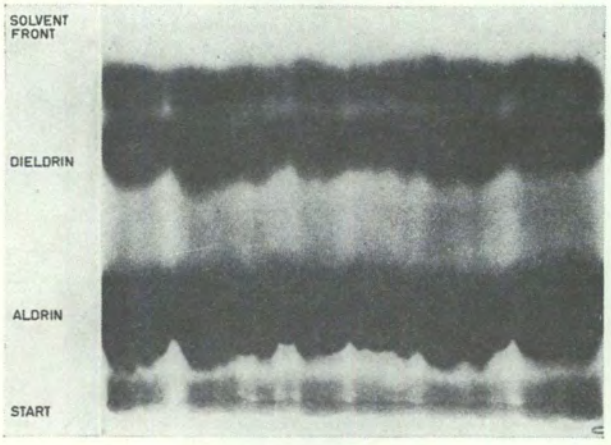

Fig. 6
Autoradiograph of preparative scale paper-chromatogram
Components present in mother-liquors from crystallization of Aldrin.

ACKNOWLEDGEMENTS

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PREPARATION OF C^{14}—LABELLED TETRAZOLIUM SALTS AND TRACER STUDY OF THE TETRAZENE—FORMAZAN REARRANGEMENT

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Abstract — Résumé — Аннотация — Resumen

Preparation of C^{14}-labelled tetrazolium salts and tracer study of the tetrazene-formazan rearrangement. The preparation of [5-C^{14}]-TTC, [5, 5′-di-C^{14}]NT (neotetrazolium) and [5, 5′-di-C^{14}]-BT (tetrazolium blue) starting from benzaldehyde-[1-C^{14}] has been accomplished. The yields for both mono- and ditetrazolium salts are high, and the products can be obtained with high sp. activity.

The purity of the samples was investigated by paper chromatography. In the case of ditetrazolium salts some impurities could be detected and conclusions drawn as to their structure and quantity. A method has been developed to prepare C^{14}-labelled ditetrazolium salts of high purity.

The formation of the formazan, the precursor of the tetrazolium salt, goes through an unstable intermediate of tetrazene-type structure which rearranges rapidly in basic medium, to yield the formazan. The tetrazene intermediate can be isolated under suitable conditions. By using C^{14}-labelled benzaldehyde phenylhydrazone this rearrangement was investigated and a verification of its intramolecular character given.

Préparation de sels de tétrazolium marqués au carbone-14 et étude de la transposition tétrazène-formazan, au moyen d'indicateurs radioactifs. On a procédé à la préparation de [5-C^{14}]—TTC, de [5,5′-di-C^{14}] NT (néotétrazolium) et de [5,5′-di-C^{14}]—BT (bleu de tétrazolium), en partant du benzaldéhyde—[1-C^{14}]. On a pu obtenir un grand rendement, tant pour les sels de monotétrazolium que pour les sels de ditétrazolium, et des produits d'une activité spécifique élevée.

La pureté des échantillons a été examinée par chromatographie sur papier. Dans le cas des sels de ditétrazolium, on a pu déceler quelques impuretés et tirer des conclusions quant à leur structure et quantité. On a mis au point une méthode permettant de préparer des sels de ditétrazolium marqués au carbone-14 et présentant une grande pureté.

Dans la synthèse du formazan, précurseur du sel de tétrazolium, on obtient un produit intermédiaire instable d'une structure analogue à celle du tétrazène; ce produit se transforme rapidement en milieu alcalin pour donner du formazan. Le tétrazène intermédiaire peut être isolé dans des conditions appropriées. On a étudié cette transformation en utilisant du benzaldéhyde-phénylhydrazone marqué au carbone-14, et l'on a pu vérifier ainsi qu'il s'agit d'une réaction intramoléculaire.

Изготовление меченных C^{14} солей тетразосоединений и исследование при помощи индикаторов перегруппировок тетразона-формазана. Исходя из бензальдегида — [1-C^{14}] удалось изготовить [5-C^{14}]-TTC, [5,5′di-C^{14}]-NT (неотеразолий) [5,5′di-C^{14}]-BT (синий

тетразолий). Выходы как для монотетразолия, так и для дитетразолия достаточно значительны и продукты могут быть получены с большой удельной активностью.

Степень чистоты образцов была исследована при помощи хроматографической бумаги. В солях дитетразолия было обнаружено некоторое количество примесей, что позволило вывести заключения относительно их структуры и количества. Был выработан метод меченных C^{14} солей дитетразолия высокой чистоты.

Образование формазана, предшественника солей тетразолия, проходит через неустойчивую промежуточную стадию структурного типа тетразона, быстро перегруппирующегося в щелочной среде, чтобы дать формазан. В подходящих условиях промежуточный тетразон может быть отделен. Использование меченного C^{14} бензальдегидфенилгидразония позволило исследовать эту перегруппировку и проверить указываемую межмолекулярную структуру.

Preparación de sales de tetrazolio marcadas con ^{14}C y estudio de la transposición tetraceno-formazan con ayuda de trazadores. Partiendo del benzaldehido-(1-^{14}C), el autor ha sintetizado el TTC-(5-^{14}C), el NT-(5, 5′-di-^{14}C) (neotetrazolio) y el BT-(5, 5′-di-^{14}C) (azul de tetrazolio). Las sales de mono- o ditetrazolio se obtienen con buen rendimiento y se logran productos de elevada actividad específica.

El autor determinó la pureza de las muestras por cromatografía sobre papel. En las sales de ditetrazolio encontró algunas impurezas, que consiguió determinar cuantitativamente; asimismo estableció algunas características de sus estructuras. Por otra parte, elaboró un método para obtener sales de ditetrazolio marcadas con ^{14}C de elevada pureza.

En la síntesis del formazan, el precursor de la sal de tetrazolio, se obtiene un producto intermedio inestable cuya estructura es similar a la del tetraceno. Este compuesto sufre una rápida transposición en medio alcalino para dar lugar al formazan. Es posible aislar el producto intermedio si se trabaja en condiciones adecuadas. El autor estudia la transposición utilizando la fenilhidrazona del benzaldehido marcado con ^{14}C, y ha podido comprobar que se trata de una reacción intramolecular.

1. Introduction

Tetrazolium salts form an important group of biochemically interesting reagents. In spite of this fact, C^{14}-labelled tetrazolium salts have never before been prepared. So far only a I^{131}-labelled tetrazolium salt had been reported [1].

This paper will report on, firstly, the preparation of C^{14} labelled mono- and ditetrazolium salts, secondly, the paper-chromatographic assay of their purity and the purification of the crude compounds, and thirdly, the tracer study of the tetrazene-formazan rearrangement. Some remarks will be made about the use of C^{14}-labelled TTC and BT for a semi-quantitative estimation of corticosteroids and that of C^{14}-labelled NT in histochemistry.

2. Preparation of C^{14}-labelled tetrazolium salts

The preparation of C^{14}-labelled mono- and ditetrazolium salts was accomplished on semi-micro scale by using well-known procedures [2—4] with benzaldehyde-1-C^{14} as starting material. Benzaldehyde was prepared according to the procedure of GEISSMANN [5] and was isolated immediately as its phenyl hydrazone. From benzaldehyde phenylhydrazone three different formazans were prepared with diazotized aniline, tetra-azotized benzidine and tetra-azotized *o*-dianisidine,

respectively. These formazans were oxidized to the proper tetrazolium salts (TTC, NT, BT) with lead tetra-acetate. The reactions are symbolized in Fig. 1.

The products can be obtained with high sp. activity. Table I summarizes the yields.

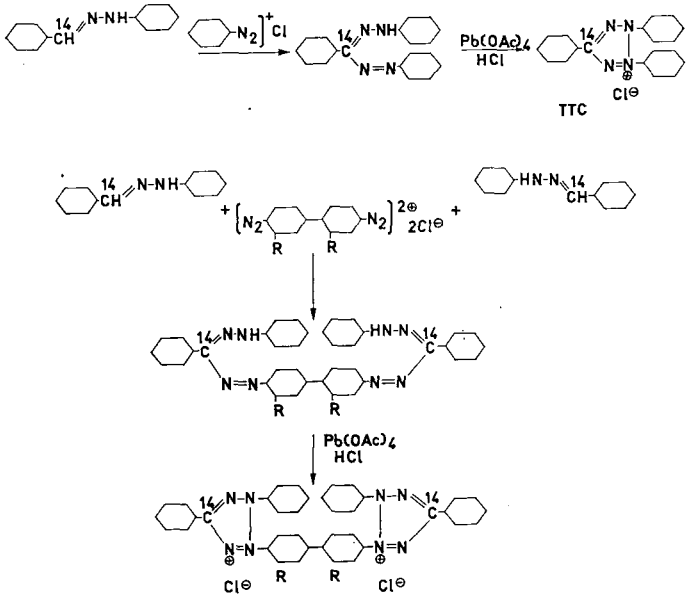

Fig. 1
R = H neo-tetrazolium
R = OCH_3 blue tetrazolium

TABLE I

YIELDS OF THE PREPARATION OF FORMAZANS from labelled benzaldehyde phenylhydrazone at —15° C in pyridine and of tetrazolium salts in chloroform solution

Symbols of the end products	Yields of	
	formazans*	tetrazolium salts**
TTC	85%	53%
NT	84%	48%
BT	87%	49%

* based on benzaldehyde phenylhydrazone.
** based on the corresponding formazan.

3. Paperchromatographic assay of the purity of the compounds

Tetrazolium salts are widely used for quantitative determination of reducing substances [6] [7]. Ditetrazolium salts, especially blue tetrazolium (BT) had been found to give higher sensitivity than TTC [6] and therefore this reagent has found greater application. Purple and red colours, which are interfering colorimetric determinations, often occur, however, during standard quantitative analysis, instead of the full deep-blue given by the BT reagent under normal conditions.

This was believed to be due to partially reduced formazans, the formation of which is caused by a difference in redox potentials of the two steps of the ditetrazolium salt reduction [8]. On the other hand, this was also attributed to some impurities which could be removed by suitable extraction or eliminated by careful preparation, because the intensity of the interfering colours was not proportional to the amount of reducing substances [9]. Another possibility may be the formation of a monoformazan, owing to an incomplete reaction during the preparation of the diformazan [10]. Although full evidence has not been given for any of these explanations, none of them can be excluded. Colour changes induced by light, colourless or abnormally coloured products, together with other complications such as the formation of colloids have also been observed by JÁMBOR [11] [12] under certain conditions.

It was believed that these complications might also be of great importance when C^{14}-labelled ditetrazolium salts and activity measurements are used for the quantitative determinations of reducing steroids or other reducing substances. Therefore a search has been made for the most simple extraction of these impurities from ditetrazolium salts.

In our experiments the highly coloured mono- and diformazans were investigated by paper chromatography. Triphenyl formazan (obtained from TTC) did not show any impurities, but the diformazans always did. When Brentamine fast blue B (Imperial Chemical Industries Ltd.) was used for tetra-azotized *o*-dianisidine, a successful chromatography could be carried out in a system of benzene : methanol : water = 2 : 1 : 1 v/v. The deep blue colour arising from the diformazan moves in front the of the developing benzene and is separated from the red spot. But the extraction of the crude product with benzene and some other solvents does not give chromatographically pure diformazans.

A complete separation can be accomplished by using freshly prepared tetra-azotized *o*-dianisidine (or benzidine) in the diformazan synthesis. In this case the red spot is moving together with the front in a system of petrolether : methanol : water = 2 : 1 : 1 v/v. The deep-blue-coloured (or violet in the second case) diformazan remains at the spot of the drop.

In this case the red impurities can be completely removed from the crude diformazans by petrolether extraction and the remaining diformazans are chromatographically pure. If any tarry or scummy impurities are present in the crude substances, they can be removed by a previous extraction with 70% ethanol.

The activity distribution on the chromatograms of purified C^{14} labelled diformazans was tested with an argon-amyl-alcohol gas-flow counter. Radioactivity peaks could only be detected at the place of the coloured spot.

The pure diformazan did not show any colour change induced by light under the conditions of analytical determinations of reducing substances. The ditetrazolium salts prepared from these purified diformazans did not give any abnormally coloured reduction products when ascorbic acid, glucose, or corticosterone were used as reducing agent in alkaline solution.

The petrolether extracts had been found very sensitive to light, decolorizing quickly, especially on paper.

The petrolether extracts could be oxidized to a pale yellow salt under similar conditions to normal formazans. They developed a red colour in alkaline solution with ascorbic acid, glucose and corticosterone. Thus, it is probable that this red compound has a real formazan structure and is formed as a monoformazan by-product originating from an incomplete azo-coupling.

4. Tracer study of the tetrazene–formazan rearrangement

By coupling the arylhydrazone of an aromatic aldehyde with an electrophilic diazonium cation in alkaline solution, the formation of a tetrazene-type intermediate, which immediately rearranges to formazan [13], or the direct formation of a formazan [14] may occur simultaneously. In neutral medium, however, intermediate can be exclusively prepared, but it quickly rearranges into formazan in alkaline solution [15]. HAUPTMANN and PÉRISSÉ [15] assumed that this rearrangement is intramolecular, because, if rearrangement was made in the presence of *p*-nitro benzaldehyde phenylhydrazone α-naphtol or R-salts formazan containing a nitro group, or azo-coupled products could not be isolated. Our tests verify their results. In the rearrangement of 1-benzal-2,4 diphenyl-tetrazene (the precursor of triphenyl formazan) in the presence of C^{14}-labelled benzaldehyde phenylhydrazone, the incorporation of radiocarbon into triphenyl formazan could not be detected. As the formazan could not be separated from benzaldehyde phenylhydrazone in radiochemically pure form after the rearrangement, the mixture was oxidized and the tetrazolium salt (TTC) formed from triphenyl formazan was separated. The activity measurement was carried out in a carbon-dioxide-methanol internal gas counter. Results are summarized in Table II.

TABLE II

ACTIVITY OF TTC SAMPLES DERIVED FROM THE REARRANGEMENT OF 1-BENZAL-2,4-DIPHENYL-TETRAZENE IN THE PRESENCE OF C^{14} LABELLED BENZALDEHYDE PHENYLHYDRAZONE

Compounds	Activity	
	nc/mM	%
Benzaldehyde phenylhydrazone	11932.7	100
TTC	94,0	0.78
TTC	92.3	0.77
TTC	96.9	0.81

5. Analytical applications of C^{14}-labelled tetrazolium salts

By using C^{14}-labelled tetrazolium salts with a sp. activity of 2 mc/g, a method has been developed for the semi-quantitative assay of corticosteroids in quantities of 0.1 μg with labelled TTC and 0.01 μg with labelled BT. Details of this work were presented at the First International Congress of Endocrinology [16]. An estimation of other reducing substances and a preliminary study for an histochemical use of C^{14}-labelled neo-tetrazolium are in the course of investigation.

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SYNTHESIS OF METHYL 3-O-α-*d*-GLUCOPYRANOSYL-C^{14}_6-β-*d*-XYLOPYRANOSIDE AND METHYL 2-O-α-*d*-GLUCOPYRANOSYL-C^{14}_6-*l*-NOVIOPYRANOSIDE

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Abstract — Résumé — Аннотация — Resumen

Synthesis of methyl 3-O-α-*d*-glucopyranosyl-C^{14}_6-β-*d*-xylopyranoside and methyl 2-O-α-*d*-Glucopyranosyl-C^{14}-*l*-noviopyranoside. Where difficulty is encountered in the chemical synthesis of a disaccharide glycoside labelled with C^{14}_6 specifically in only one of its sugar moieties it is often convenient to resort to a synthesis catalysed by microbial transglycosylases. Two examples of the application of this technique are reported; the syntheses:

Maltose-C^{14}_{12} + Methyl β-*d*-xylopyranoside $\xrightarrow[\text{transglucosylase}]{\textit{Penicillium lilacinum}}$ Methyl 3-O-α-*d*-Glucopyranosyl-C^{14}_6-β-*d*-xylopyranoside (I) + Glucose-C^{14}_6 Maltose-C^{14}_{12} + Methyl *l*-noviopyranoside $\xrightarrow[\text{transglucosylase}]{\textit{Fusarium moniliforme}}$ Methyl-2-O-α-*d*-Glucopyranosyl-C^{14}_6-*l*-noviopyranoside (II) + Glucose-C^{14}_6.

In such syntheses, it is predictable that the anomeric character of the glycosidic linkage of the donor disaccharide will be retained in the disaccharide synthezised and that the glycosyl residue transferred will be attached, through its reducing group, to the receptor monosaccharide glycoside. By using either a C^{14}-labelled donor disaccharide or a C^{14}-labelled receptor glycoside, a disaccharide can be synthesized with only one of its sugar moieties labelled. In the synthesis of II the only hydroxyl group free in the receptor methyl novioside is on C_2 and the transferred glucosyl residue can only be attached here. In the synthesis of I the methyl xyloside has free hydroxyls on C_2, C_3 and C_4 and the microbial enzyme has been found to transfer the glucosyl residue specifically to the hydroxyl on C_3, The structures of I and II have been established by the results of elemental analysis, optical rotation, infrared spectra together with an examination of the products of acid hydrolysis and periodate oxidation.

Synthèse de méthyl-3-O-alpha-*D*-glucopyranosyl-C^{14}-bêta-*D*-xylophranoside et méthyl-2-O-alpha-*D*-glucopyranosyl-C-$^{14}_6$*L*-noviopyranoside. Lorsqu'on se heurte à des difficultés dans la synthèse chimique d'un glucoside de disaccharide marqué au carbone-14 spécifiquement dans un seul des deux sucres qui le constituent, on a souvent intérêt à recourir à une synthèse catalysée par des transglucosylases microbiennes. Comme exemples de l'application de cette technique, les auteurs signalent les synthèses suivantes:

Maltose-C^{14}_{12} + Méthyl β-D-xylopyranoside $\xrightarrow[\textit{Penicillium lilacinum}]{\text{transglucosylase du}}$ Méthyl3-*O*-α-*D*-Glucopyranosyl-C^{12}_{14}-β-D-xylopyranoside (I) + Glucose-C^{14}_6 Maltose-C^{14}_{12} + Méthyl *L*-noviopyranoside $\xrightarrow[\textit{Fusarium moniliforme}]{\text{transglucosylase du}}$ Méthyl-2-O-α-*D*-Glucopyranosyl-C^{14}_6-*L*-noviopyranoside (II) + Glucose-C^{14}_6.

Dans de telles synthèses, on peut prévoir que le caractère anomérique du lien glycosidique du disaccharide donneur sera conservé dans le disaccharide synthétisé et que le reste glucosyl transféré s'unira par son groupe réducteur au glucoside de monosaccharide récepteur. En employant, soit un disaccharide donneur marqué au carbone-14, soit un glucoside récepteur également marqué au carbone-14, on peut synthétiser un disaccharide dont un seul des deux sucres est marqué. Dans la synthèse de II, le seul groupe hydroxyle libre dans le méthyl-novioside récepteur se trouve sur le C_2 et le reste glucosyl transféré ne peut être attaché qu'en ce point. Dans la synthèse de I, le méthyl-xyloside a des hydroxyles libres sur C_2, C_3 et C_4; on a constaté que l'enzyme microbienne transférait le reste glucosyl précisément à l'hydroxyle fixé sur le C_3. Les structures de I et II ont été établies par analyse élémentaire, ainsi que par l'étude de l'activité optique, des spectres infrarouges et des produits obtenus par hydrolyse en milieu acide et par oxydation au périodate.

Синтез метил-3-О-α-*D*-глюкопиранозила-C_6^{14}-β-*D*-ксилопиранозид и метил 2-О-α-*D*-глюкопиранозил-C_6^{14} — *L*-новиопиранозид. В случае затруднения проведения химического синтеза дисахарида гликозида, меченного углеродом-14, особенно только в одной из групп сахара часто целесообразно использовать катализированный синтез с помощью микробиального трансгликозилаза. В докладе сообщается о двух примерах использования данного метода:

$$\text{Мальтоза-}C_{12}^{14} + \text{метил } \beta\text{-}D\text{-ксилопиранозид} \xrightarrow[\text{трансглюкозилас}]{\text{Пенициллиум лилацинум}} \text{Метил 3-О-}\alpha\text{-}D\text{-глюкопиранозил-}C_6^{14}\text{-}\beta\text{-}D\text{-ксилопиранозид (I)} + \text{глюкоза-}C_6^{14}$$

$$\text{Мальтоза-}C_{12}^{14} + \text{метил } L\text{-новиопиранозид} \xrightarrow[\text{трансглюкозилас}]{\text{Фузариум монилиформ}} \text{Метил-2-О-}\alpha\text{-}D\text{-глюкопиранозил-}C_6^{14}\text{-}L\text{-новиопиранозид (II)} + \text{глюкоза-}C_6^{14}$$

При таком синтезе предполагается, что аномерический характер гликозидной связи донорного дисахарида будет сохранен в соединенном дисахариде и что перемещенный остаток гликозила примкнет через свою восстановительную группу к рецептору моносахарида гликозида. При использовании меченных C^{14} донорного дисахарида или рецептора гликозида возможен синтез дисахарида только с одной из меченых групп сахара. При синтезе II единственная гидроксильная свободная группа в рецепторе метилновиозида находится в C_2, и только здесь можно присоединить переносной остаток гликозида. При синтезе I метил-ксилозид имеет свободный гидроксил при C_2, C_3 и C_4, а также было обнаружено перемещение микробиального энзима в остаток гликозила особенно в гидроксил при C_3. Структуры I и II были выявлены в результате анализа элементов, оптической ротации, инфракрасного спектра совместно с проверкой продуктов кислотного гидролиза и окислением периодата.

Síntesis de la metil 3-O-α-*D*-glucopiranosil-$^{14}C_6$-β-*D*-xilopiranosido y de la metil 2-O-α-*D*-glucopiranosil-$^{14}C_6$-*L*-noviopiranosido. Cuando se encuentran dificultades en la síntesis química de un glucodisacárido marcado con ^{14}C específicamente en uno solo de los azúcares que lo componen, resulta a menudo conveniente recurrir a una síntesis catalizada por transglucosilasas microbianas. Como ejemplo de la aplicación de esta técnica, los autores describen las síntesis siguientes:

Maltosa-$^{14}C_{12}$ + metil-β-*D*-xilopiranosido $\xrightarrow[\textit{Penicillium lilacinum}]{\text{Transglucosilasa del}}$ Metil 3-O-α-*D*-glucopiranosil-$^{14}C_6$-β-*D*-xilopiranosido (I) + Glucosa-$^{14}C_6$ Maltosa-$^{14}C_{12}$ + Metil *L*-noviopiranosido $\xrightarrow[\textit{Fusarium moniliforme}]{\text{Transglucosilasa del}}$ Metil 2-O-α-*D*-glucopiranosil-$^{14}C_6$-*L*-noviopiranosido (II) + Glucosa-$^{14}C_6$.

Se puede esperar que en estas síntesis se conserve en el disacárico obtenido por síntesis el carácter anomérico del enlace glucosídico del disacárido donor y que el resto glucósido transferido se una por su grupo reductor al glucomonosacárido receptor. Si se emplea un disacárido donor o un glucósido receptor marcados con ^{14}C, se puede

sintetizar un disacárido marcado solamente en uno de los dos azúcares que lo componen. En la síntesis del compuesto II, el único grupo oxhidrilo libre en el metilnoviósido receptor se encuentra en el C_2 y el resto glucósido que se transfiere sólo puede unirse en ese punto. En la síntesis del compuesto I, el metilxilosido posee grupos oxhidrilo libres en C_2, C_3 y C_4, y se ha encontrado que la enzima microbiana transfiere el resto glucósido específicamente al grupo oxhidrilo en el C_3. Se han determinado las estructuras de los compuestos I y II por análisis elemental, así como por estudio de la actividad óptica de los espectros infrarrojos y de los productos obtenidos por hidrólisis en medio ácido y por oxidación con peryodato.

1. Introduction

The production of disaccharides labelled with C^{14} in only one of the sugar moieties is increasingly needed for studies of the mechanism of enzyme reactions and for following the course of chemical reactions. One widely applicable method is typified by the conversion [1] of 3-O-β-*d*-galactopyranosyl-*d*-arabinose to lactose-1-C^{14} (4-O-β-*d*-galactopyranosyl-*d*-glucopyranose 1-C^{14}). By using sodium cyanide-C^{14} for the preparation of the cyanohydrin intermediates, the radioactivity can be inserted specifically in the reducing group of the disaccharide. Maltose-1-C^{14} (4-O-α-*d*-glucosyl *d*-glucose-1-C^{14}) has been synthesized [2] by the same method from 3-O-α-*d*-glucopyranosyl-*d*-arabinose. The obvious limitations of this method can often be overcome by chemical synthesis of the disaccharide from the now easily obtainable C^{14}-labelled monosaccharides. However, although the synthesis of β-linked disaccharides presents few problems in this respect (cf. the chemical synthesis of 6-O-β-*d*-glucopyranosyl-C^{14}_6-*d*-glucose [3]) the analogous synthesis of α-linked disaccharides is still often beset with low yields [4] and the separation of complex mixtures of products [5]. Where such difficulties are encountered, the biosynthetic route seems to offer more flexibility and is particularly suitable for synthesis on a semi-micro-scale. We wish to report the synthesis of the methyl glucosides of two such C^{14}-labelled disaccharides catalysed by microbial transglycosylases.

(i) Maltose-C^{14}_{12} + Methyl β-*d*-xylopyranoside $\xrightarrow[\text{transglucosylase}]{\textit{Penicillium lilacinum}}$ Methyl 3-O-α-*d*-Glucopyranosyl-C^{14}_6-β-*d*-xylopyranoside (I) + Glucose-C^{14}_6

(ii) Maltose-C^{14}_{12} + Methyl *l*-noviopyranoside $\xrightarrow[\text{transglucosylase}]{\textit{Fusarium moniliforme}}$ Methyl-2-O-α-*d*-Glucopyranosyl-C^{14}_6-*l*-noviopyranoside (II) + Glucose-C^{14}

2. Synthesis of I

Prepapation of methyl β-*d*-xylopyranoside [6]

D-xylose (10 g) was refluxed for 5 h with dry methanol (100 ml) in the presence of Amberlite IR 120 (H^+) resin (10 g). On cooling, the supernatant liquid was decanted from the resin and concentrated to a syrup. Addition of ethyl acetate and ethanol induced crystallization which was allowed to proceed for two weeks. The product was twice recrystallized from ethanol and shown to be paper-chromatographically pure. It had MP 156° and $[\alpha]_d^{20}$ -65.0° (c, 0.1 in H_2O). The β-anomeric configuration was confirmed by infra-red spectra.

Preparation of Penicillium lilacinum transglucosylase

Mycelia of *Penicillium lilacinum* grown in maltose-mineral media for 5 d were shredded in an Atomix, washed and freeze-dried. Aqueous suspensions of the

cells (about 1 g) were shaken with glass beads for 20 min (with intermittent cooling) in a Mickle tissue disintegrator. After this time no intact cells remained. After centrifugation, the supernatant liquid was freeze-dried.

SYNTHESIS OF I

Maltose-C^{14}_{12} (0.05 mc; 100 mg) was incubated for 4 d at 30° with methyl β-*d*-xylopyranoside (50 mg) and enzyme extract (100 mg) dissolved in water (2 ml). After arresting enzyme action by boiling, the digest was passed down a column (length 3 in; diam. 1 in) of Amberlite IRA 400 (OH^-). The water eluate from the column, which contained only the non-reducing sugars [7], was freeze-dried. The residue was streaked across Whatman No. 3 paper and separated into component bands by irrigation in butanol, ethanol, water, ammonia (40:10:49:1) for 2 d. After exact location of the radioactive bands using an X-ray film (contact time 7 d), the band corresponding to I was cut out, eluted with water and freeze-dried (2.5 mg). Re-examination of I on a paper chromatogram showed that it was free from other radioactive and non-radioactive contaminants.

ACIDIC HYDROLYSIS OF I

The disaccharide glycoside I (1 mg) was hydrolysed with 4 *N* hydrochloric acid (0.3 ml) for 4 h at 100° C. The neutralized hydrolysate examined on a paper chromatogram contained glucose and xylose in equal amounts; only the glucose was radioactive.

PERIODATE OXIDATION OF I

I (1.5 mg) in water (2 ml) was oxidized with sodium periodate (0.08 *M*; 2.5 ml) in the dark for 12 h. After addition of lead nitrate, the filtered solution was passed down a column (length 5 cm; diam. 1 cm) of Ultrasorb charcoal. The salts eluted with water (10 ml) were discarded and the periodate oxidized I was recovered by elution with 25% aqueous ethanol (20 ml). After evaporation to a syrup, the latter was hydrolysed with 4 *N* HCl for 2 h at 100° and then neutralized with silver carbonate. Paper chromatograms revealed the presence of xylose in the hydrolysate.

3. Synthesis of II

PREPARATION OF METHYL *l*-NOVIOPYRANOSIDE

Monosodium novobiocin (40 g) in methanol (2 liters) and conc. hydrochloric acid (552 ml; sp. gr. 1.19) were heated on a steam bath for 2 h. After one hour, cyclonovobiocic acid began to precipitate. The filtrate and water washings were neutralized with sodium bicarbonate, concentrated under reduced pressure and the resulting aqueous solution was freeze-dried. Extraction of the residue obtained with acetone (10 × 500 ml) and subsequent concentration gave crystals of methyl-*l*-noviopyranoside (4.3 g). When recrystallized from acetone, this had MP 191—192° C; $[\alpha]^{20}_{d}$ —24° (methanol). Found: C, 48.30; H, 7.69; N, 5.56. Calc. for $C_{10}H_{19}NO_6$: C, 48.19; H, 7.68; N, 5.62.

SYNTHESIS OF II

Sterile digests containing maltose-C^{14}_{12} (0.05 mc; 2.08 g), methyl *l*-noviopyranoside (1.04 g) and mineral media (15.5 ml) and water (36.5 ml) were inoculated with *Fusarium moniliforme*. Paper chromatography, followed by auto-

radiography, revealed the production of a disaccharide starting on the 10th—11th day and increasing in concn. up to the 15th day. This disaccharide had $R_{\text{Novioside}}$ 0.21 in butanol, ethanol, water (40:10:50). Part (0.91 g) of the digest was sterilised by passing through a Seitz filter und fractionated on a cellulose column (length 48 cm; diam. 3 cm) eluted with butanol, ethanol, water (40:10:50) to give unchanged methyl novioside (0.402 g), radioactive II (8.6 mg) and another unidentified radioactive product with $R_{\text{Novioside}}$ 0.16 (21.0 mg).

INFRA-RED SPECTRUM OF II

3500, 3001, 2912, 1730, 1625, 1470, 1408, 1380, 1328, 1231, 1205, 1130, 1123, 1070, 1023, 989, 968, 931, 877, 852, 780, 743 cm^{-1}.

METHOXYL CONTENT OF II

II contained 14.72% OCH_3. A methy lglucosyl novioside requires 15.10% OCH_3.

ACID HYDROLYSIS OF II

A solution of the disaccharide (1.5 mg) in 2 *N* hydrochloric acid (1 ml) was heated at 100° for 3 h. The hydrolysate was neutralized and analysed on paper chromatograms. A chlorine/5% potassium-iodide reagent revealed spots having $R_{\text{Novioside}}$ values identical to methyl novioside, noviose and other products normally formed on hydrolysing methyl novioside. A silver-nitrate spray showed a similar pattern of spots as well as a spot having an $R_{\text{Novioside}}$ value identical to that of *d*-glucose.

ENZYMIC HYDROLYSIS OF II

An α-glucosidase was prepared by extraction of smashed cells of *Aspergillus niger* grown on maltose as the sole source of carbon. Incubation of the α-glucosidase (0.5 ml) with the disaccharide (2 mg) at 30° for 8 h resulted in the liberation of *d*-glucose, methyl *l*-novioside and *l*-noviose. The *d*-glucose was identified by its specific destruction with glucose oxidase. The noviose derivatives gave positive reactions with a chlorine/potassium-iodide spray.

PERIODATE OXIDATION OF II

The disaccharide glycoside II (1.5 mg) was incubated with sodium periodate (5 ml; 0.05 *M*) in the dark for 24 h. The periodate was removed with ethylene glycol. The solution was freeze-dried, taken up in a minimum of water and put on a charcoal-Celite column (length, 10 cm; diam. 1 cm). The ions present were removed by eluting with water (50 ml) and the sugar residue was recovered with 50% aqueous ethanol. Methyl novioside was detected when the solution was hydrolysed with 2 *N* hydrochloric acid and neutralied with silver carbonate.

Discussion

In syntheses represented by the equations (i) and (ii) above it can be predicted [8] that the anomeric character of the glycosidic linkage of the donor disaccharide (in the case of maltose the α-configuration) and the ring size (here pyranose) will be retained in the disaccharide synthesized (I or II) and that the glycosyl residue transferred will be attached through its reducing group (in these cases C_1) to the receptor monosaccharide glycoside (e.g. methyl *d*-xyloside or methyl *l*-novioside). By using either a C^{14}-labelled donor disaccharide or a C^{14}-labelled

receptor glycoside, a disaccharide can be synthesized with only one of its sugar moieties labelled. In II the only free hydroxyl group in the receptor methyl novioside (methyl 3-O-carbamyl 4-O-methyl-5,5-dimethyl-*l*-lyxoside) is on C_2 and the transferred glucosyl residue can only be attached here. The infra-red spectrum of II confirms that the carbamyl group is retained without substitution on the amino group and shows the absorption at 852 cm^{-1} expected from an α-glycosidic linkage. The methoxyl value of II was also in agreement with that expected from methyl 2-O-α-*d*-glucopyranosyl *l*-noviopyranoside. Acid hydrolysis confirmed the presence of the component monosaccharides, while periodate oxidation followed by acid hydrolysis revealed that, as expected, the methyl novioside moiety was resistant to attack, whereas the glucosyl moiety had been destroyed.

In the synthesis of I, the methyl xyloside has free hydroxyl groups on C_2, C_3 and C_4. Of the three possible disaccharide glycosides which could be formed, only that formed through C_3 will have a methyl xyloside moiety resistant to periodate oxidation. The demonstration that I exhibits such a property therefore establishes that I is methyl 3-O-α-*d*-glucopyranosyl-β-*d*-xylopyranoside.

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A GENERAL METHOD OF PREPARING C^{14}-LABELLED ISOCYANATES. TRACER STUDY OF THE DIMERIZATION OF ISOCYANATES

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Abstract — Résumé — Аннотация — Resumen

A general method for preparing C^{14}-labelled isocyanates. Tracer study of the dimerization of isocyanates. The tendency of isocyanates to dimerize in the presence of suitable catalysts and the thermal dissociation of the formed dimers has long been known. Recently an exchange equilibrium between isocyanates and isothiocyanates has been reported. It has been assumed that this exchange also takes place through the formation of a dimer.

The investigation of this exchange reaction with C^{14} as a tracer has been performed in order to establish the preparative usefulness of the reaction and to study its mechanism. For this purpose phenyl-isocyanate-carbonyl-C^{14} has been prepared by the Curtius reaction, on a semi-micro scale.

The compound was equilibrated with inactive aryl isothiocyanates and alkyl isocyanates, respectively, after which a C^{14}-labelled species of the originally inactive compound was isolated. The results showed that under suitable conditions this exchange reaction can be generally applied for preparing both C^{14}-labelled isocyanates and C^{14}-labelled isothiocyanates. A method for the preparation of labelled isocyanates with a good yield has been developed.

A study of the mechanism of the reaction both in the presence of and in the absence of catalysts gives evidence for the exchange of carbonyl groups between isocyanates in both cases. Therefore the intermediate dimer must possess the structure of 1,3-diaryl-1,3-diaza-cyclobutane-2,4-di-on, suggested previously on the basis of crystallographic data. It has also been shown that a series of another type of intermediates might occur during dimerization and dissociation; a general scheme is proposed for the mechanism of this reaction, involving possible intermediates, side reactions and products.

Méthode générale de préparation des isocyanates marqués au ^{14}C. Etude de la dimérisation des isocyanates, au moyen d'indicateurs radioactifs. On connaît depuis longtemps la tendance des isocyanates à se dimériser en présence de catalyseurs appropriés, de même que la dissociation thermique des dimères ainsi formés. Mention a été faite, récemment, d'un équilibre d'échange entre les isocyanates et les isothiocyanates. On a présumé que cet échange se produisait également par la formation d'un dimère.

Les auteurs ont étudié cette réaction d'échange, en se servant de ^{14}C comme indicateur, afin d'évaluer son utilité comme méthode de préparation et d'en explorer le mécanisme.

A cet effet, ils ont préparé du phényl-isocyanate marqué au ^{14}C dans le carbonyle par la réaction de Curtius, à semi-micro échelle.

Après avoir équilibré ce composé avec des isothiocyanates d'aryle et des isocyanates d'alkyle inactifs, ils ont isolé du composé primitivement inactif une espèce marquée au ^{14}C. Les résultats ont montré que, dans des conditions appropriées, cette réaction d'échange peut servir, d'une manière générale, à préparer à la fois des isocyanates

et des isothiocyanates marqués au ^{14}C. Les auteurs ont mis au point une méthode permettant de préparer des isocyanates marqués avec un rendement satisfaisant.

En étudiant le mécanisme de la réaction tant en présence qu'en l'absence de catalyseurs, les auteurs ont établi la preuve de l'existence, dans les deux cas, d'un échange des groupes carbonyle entre les isocyanates. Le dimère intermédiaire doit donc présenter la structure diaryl 1,3-diazo 1,3-cyclobutadione 2, 4 que les études cristallographiques avaient laissé prévoir. Les auteurs ont également démontré qu'une série d'intermédiaires d'un autre type pouvaient se former durant la dimérisation et la dissociation. Pour expliquer le mécanisme de cette réaction, ils proposent un schéma général indiquant les intermédiaires possibles, ainsi que les réactions secondaires et leurs produits.

Общий метод изготовления меченных C^{14} изоцианатов. Исследование при помощи индикаторов димерилизации изоцианатов. С давних пор известна тенденция изоцианатов подвергаться в присутствии подходящего катализатора димерилизации, а также термической диссоциации образуемых димеров. Недавно были опубликованы данные о равновесии обмена между изоцианитами и изотиоцианатами. Было предположено, что этот обмен также происходит посредством образования димера.

Было проведено исследование этой реакции обмена при помощи C^{14} в качестве индикатора для установления возможности использования этой реакции в качестве изготовительного процесса и для изучения его механизма.

Для этой цели был изготовлен в полумикроскопическом масштабе по методу реакции Куртиуса фенилизоционаткарбонил-C^{14}.

Это сложное соединение было уравновешено соответственно неактивным арилизотиоцианатами и алкилизоцианатами, после чего был отделен вид меченного C^{14} первоначально неактивного сложного соединения. Результаты показали, что при подходящих условиях эта реакция обмена может быть обычно использована для изготовления меченных C^{14} изоцианатов и изотиоцианатов. Был разработан метод изготовления меченых изоцианатов, дающий хороший выход.

Исследование механизма реакции как в присутствии катализатора, так и без него показало, что в обоих случаях происходит обмен карбониловых групп между изоционатами. Поэтому промежуточный димер должен иметь предположенную ранее на основании кристаллографических данных структуру, а именно: 1,3-диарил-1,3-диазациклобутан-2, 4-дион. Было доказано, что во время димерилизации и диссоциации может образовываться и другой тип промежуточных соединений; предлагается общая схема для объяснения механизма этой реакции, включая образование возможных промежуточных соединений, побочных реакций и конечных продуктов.

Método general de obtención de isocianatos marcados con ^{14}C. Estudio mediante marcadores de la dimerización de los isocianatos. La tendencia de los isocianatos a dimerizarse en presencia de catalizadores adecuados y la disociación térmica de los dímeros formados son conocidas desde hace mucho tiempo. Recientemente se ha mencionado en la bibliografía la existencia de un equilibrio de intercambio entre los isocianatos y los isotiocianatos. Se ha supuesto que este intercambio se verifica también con la formación previa de un dímero.

Los autores han empleado el ^{14}C para investigar esta reacción de intercambio con el fin de evaluar su utilidad como método de preparación y estudiar el mecanismo de la reacción.

Para ello han preparado en semimicro escala isocianato de fenilo marcado con ^{14}C en el carbonilo aplicando la reacción de Curtius.

Después de poner este compuesto en equilibrio con isotiocianatos de arilo o con isocianatos de alquilo, ambos inactivos, lograron aislar especies marcadas de los compuestos inicialmente inactivos. Los resultados demuestran que, si se trabaja en condiciones adecuadas, esta reacción de intercambio puede servir de método general para preparar tanto isocianatos como isotiocianatos marcados con ^{14}C. Los

autores han elaborado un método para preparar con buen rendimiento isocianatos marcados.

Estudiando el mecanismo de la reacción con o sin catalizadores, los autores pudieron demostrar que en ambos casos se produce un intercambio de los grupos carbonilo de los isocianatos. De ello se deduce que la estructura del dímero intermedio tiene que ser la de una 1,3-diaril-1,3-diazo-ciclobutadiona-(2,4), como se desprendía ya de estudios cristalográficos. También han podido demostrar que durante la dimerización y la disociación puede formarse toda una serie de productos intermedios de otro tipo. Los autores proponen un esquema general para explicar el mecanismo de esta reacción e indican los posibles productos intermedios, así como las reacciones secundarias y sus productos finales.

1. Introduction

Isocyanates and isothiocyanates are widely used as organic intermediates. Their derivatives, especially the isothiocyanate derivatives, form an important group of natural organic compounds. Furthermore, they are of great analytical significance. The preparation of isotopically labelled isocyanates and isothiocyanates is therefore important. This paper reports the preparation of C^{14}-labelled isocyanates by a generally applicable exchange-equilibrium. On the basis of our results some remarks will be made about the constitution of isocyanate dimers, and a mechanism for the dimerization of isocyanates and for the carbonyl exchange between isocyanates will be suggested. Some preliminary results with regard to the application of this exchange reaction for preparing C^{14}-labelled isothiocyanates will also be given.

2. The preparation of C^{14}-labelled isocyanates

From the literature, S^{35}-labelled isothiocyanates [1] [2] and C-^{14}-labelled silver isocyanate [3] are already known, but C^{14}-labelled organic isocyanates have not previously been prepared. A recently reported exchange equilibrium between α-naphtyl isocyanate and phenylisothiocyanate [4] seems to be generally applicable for preparing both C^{14}-labelled isocyanates and C^{14}-labelled isothiocyanates. This equilibrium may be formulated in general as

$$R{-}N{=}C{=}O + R'{-}N{=}C{=}S \rightleftarrows R'{-}N{=}C{=}O + R{-}N{=}C{=}S$$

For the study of the preparative usefulness and the mechanism of this exchange reaction, phenyl isocyanate-1-C^{14} has been prepared by the Curtius reaction on a semi-micro scale by SCHROETER's method [5].

$$C_6H_5{-}C^{14}OOH \rightarrow C_6H_5{-}C^{14}OOHC_3 \rightarrow C_6H_5{-}C^{14}ONHNH_2 \rightarrow C_6H_5{-}C^{14}ON_3 \rightarrow$$
$$\rightarrow C_6H_5{-}N{=}C^{14}{=}O$$

The labelled phenyl isocyanate was equilibrated with inactive alkyl isocyanates both in the presence and in the absence of catalysts. Furthermore, as a preliminary experiment, C^{14}-labelled phenyl isocyanate was equilibrated with inactive phenyl isothiocyanate in a similar way. After these equilibrium reactions a C^{14}-labelled species of the originally inactive alkyl isocyanates and C^{14}-labelled phenyl isothiocyanates could be isolated.

THERMAL REACTION

Equimolar quantities of phenyl isocyanate-1-C^{14} and inactive methyl, ethyl and isopropyl isocyanates, respectively, were placed in a tube, sealed and heated at different temperatures for 8 h. After the tubes were opened, the isocyanate mixtures were fractionated. The methyl, isopropyl and phenyl isocyanates were reacted with anilin, and the ethyl isocyanate with tert. butyl amine. The urea derivatives thus prepared were used for identification and activity-measurement. Activity results are plotted in Fig. 1. The activity of alkyl isocyanates is given as the percentage of the activity of the initial phenyl isocyanate-1-C^{14}.

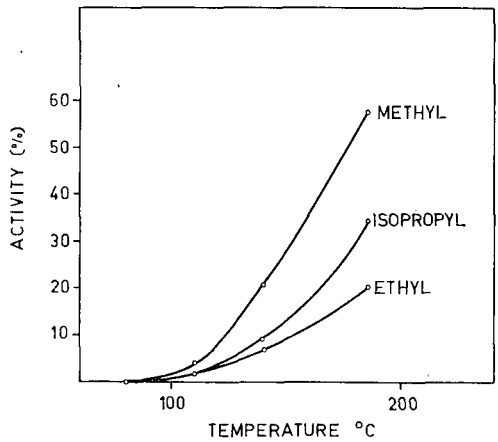


Fig. 1
The activity increase of alkyl isocyanates after heating with C^{14}-labelled phenyl isocyanate for 8 h.

Fig. 1 shows that under 100°C no activity-exchange appears. With increasing temperature the activity incorporated in the alkyl isocyanates increases gradually. This activity incorporation is accompanied by the formation of carbon dioxide and of some tarry by-products; but the quantity of these, even at 140° C, is negli-

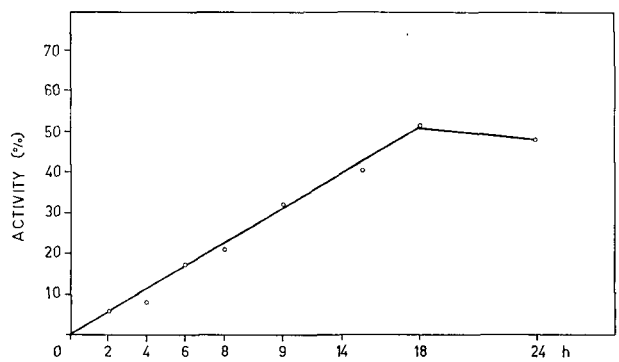


Fig. 2
Activity increase of methyl isocyanates at 140°C as a function of time.

gible. In experiments performed at 140°C or lower, the recovery of isocyanates after the equilibrium reaction was above 80% in all cases, and detectable quantities of carbon dioxide were not formed. At 180°C and higher temperatures, however, considerable decomposition, accompanied by radioactive carbon dioxide formation, always occurs, causing a significant loss of radioactivity. Therefore the optimal temperature for this exchange reaction appears to be about 140° C.

Fig. 2 shows the activity increase of methyl isocyanate at 140°C with increasing reaction time.

From Fig. 2 it may be seen that prolonged heating causes some decomposition. In experiments performed under the same conditions, but in the presence of about 5% diphenyl urea, a greater activity exchange was observable, probably due to a quite different mechanism. An investigation of this urea-catalysed activity exchange is in course.

Probably this thermal exchange equilibrium may also be applied to preparation of C^{14}-labelled alkyl and aryl isothiocyanates. Some preliminary results with regard to the formation of C^{14}-labelled phenyl isothiocyanate from phenyl isocyanate-1-C^{14} and unlabelled phenyl isothiocyanate, heated for 15 h at 180°C, are given in Table I.

TABLE I

C^{14} EXCHANGE BETWEEN PHENYL ISOCYANATE-1-C^{14} AND PHENYL ISOTHIOCYANATE AT 180°C

Before reaction		After reaction	
Compounds	Activity (nc/mM)	Compounds	Activity (nc/mM)
Phenyl isocyanate	1968	Phenyl isocyanate	1815
Phenyl isothiocyanate	—	Phenyl isothiocyanate	154

The tendency of isocyanates to dimerize in the presence of suitable catalysts and the thermal dissociation of the dimers is well known (reviewed by ARNOLD *et al.* [6]). Moreover, where different aromatic isocyanates are used, mixed dimers can even be prepared [7]. The conversion to dimers increases with decreasing temperature, and in solution dimers are dissociated even at low temperatures in the presence of phosphine catalysts. Therefore, the catalytic reaction provides us a more moderate and convenient method of preparing the labelled isocyanates than does the thermal method.

In our experiments, anisol has been employed as the solvent and phenyl dimethyl phosphine as the catalyst, because its action is moderate, thus permitting excellent control of the exothermic dimerization reaction. 20 + 20 mM of methyl, ethyl and isopropyl isocyanates, respectively, and phenyl isocyanate-1-C^{14}, 2 ml solvent and 3 to 4 drops of catalyst were placed in a small flask. After the flask stood for 12 h at room temperature, the alkyl isocyanates were distilled off, and an aliquot part was prepared for identification and activity measurement, as above. Results are summarized in Table II. The recovery of alkyl isocyanates was almost quantitative.

These results show that this exchange reaction is generally applicable for preparing C^{14}-labelled isocyanates by making initial use of a suitable single C^{14}-

TABLE II

ACTIVITY EXCHANGE OF ALKYL ISOCYANATES AND PHENYL ISOCYANATE-1-C^{14} IN THE PRESENCE OF A CATALYST

Isocyanates	Activity	
	nc/mM	%
Phenyl (starting material)	3095	100
Methyl	1268	41
Ethyl	554	14.8
Isopropyl	757	24.4

labelled isocyanate, provided that the boiling-point differences allow separation of the compounds proper. As can be seen, the catalytic reaction represents a more moderate, simple and convenient way of preparing labelled isocyanates than the thermal reaction, although the latter is also applicable under certain conditions.

It may be assumed that by this method, O^{18}-labelled isocyanates as well as C^{14}- and S^{35}-labelled isothiocyanates may be generally prepared.

Activity measurements were carried out in an internal carbon-dioxide—methanol-gas counter, unless use of another method was explicitly indicated.

3. On the mechanism of isocyanate dimer formation

A 1,3-diaryl-1,3-diazacyclobutane-2,4-dione (III) structure has been postulated for aryl isocyanate dimers [8], which was supported by recent crystallographic work [9]. The isomeric structure (II) has also been proposed recently [10] as an explanation for the reactions between phenyl isocyanate dimers and Grignard reagents or LiA_1H_4. ARNOLD *et al.* [6], however, have pointed out that the

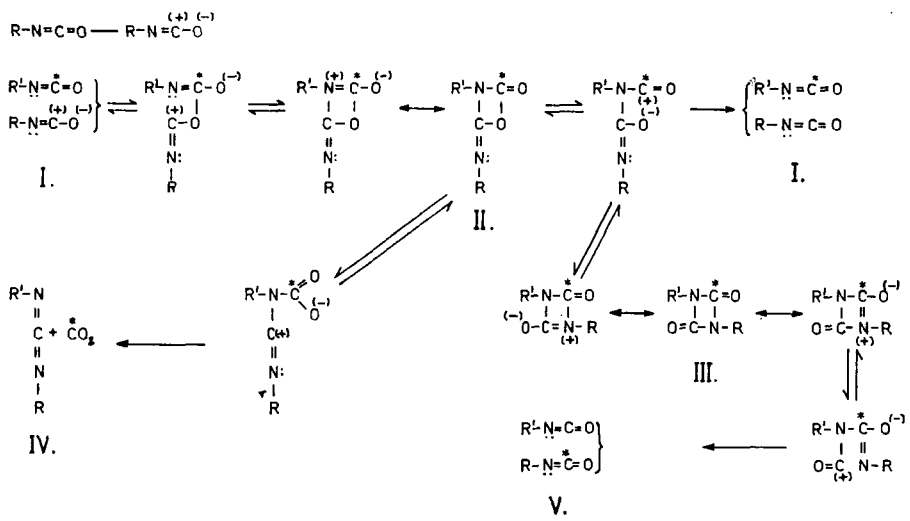
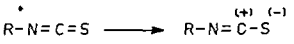


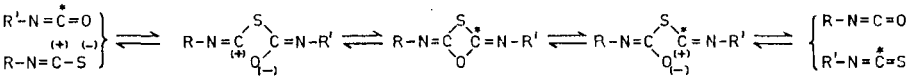
Fig. 3
Mechanism of the dimerization of isocyanates and of the carbonyl group exchange between two isocyanates.

interpretation of these reactions can equally well be given on the basis of both structures, II and III.

With regard to the structure of isocyanate dimers, these results, together with the observation of STOLLE [11] (in which he has found that, under prolonged heating and pressure, phenyl isocyanate gives carbodiphenylimide and carbon dioxide) and our own results in connection with the preparation of C^{14}-labelled isocyanates, may be treated in a unified manner, in our opinion. Therefore, a mechanism for the dimerization of isocyanates and for the exchange reaction (Fig. 3) is suggested.

Our results give direct evidence that the isocyanate dimer must have possessed the structure (III) originally postulated, because the activity exchange between alkyl isocyanates and phenyl isocyanate-1-C^{14} can be explained only through the formation of this dimer. Moreover, by this mechanism the possibility of the occurrence of isocyanate dimers with isomeric structures and the formation of carbon dioxide and carbodiimide derivatives (IV) under certain conditions can equally well be explained.





VI. VII. VIII.

Fig. 4
Mechanism of the O-S exchange between isocyanates and isothiocyanates.

In the case of the formation of C^{14}-labelled isothiocyanates, however, another mechanism may also play an important role (Fig. 4) through the formation of a dimer possessing the isomeric structure (VII). The present results do not permit a discussion of the relative importance of these dimers in an exchange equilibrium, especially not in solution and in the presence of catalysts. In such cases probably all types of dimers can exist simultaneously.

By application of C^{14} and S^{35} as simultaneous tracers more information about these problems appears to be available, but this will require further investigation.

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ИЗУЧЕНИЕ РЕАКЦИЙ ИЗОТОПНОГО ОБМЕНА УГЛЕРОДА МЕЖДУ ЦИАНИСТЫМ КАЛИЕМ И КАРБОНАТАМИ И ПРИМЕНЕНИЕ ИХ ДЛЯ ПОЛУЧЕНИЯ ЦИАНИСТОГО КАЛИЯ, МЕЧЕННОГО ИЗОТОПОМ C^{14}

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Abstract — Résumé — Аннотация — Resumen

Study of carbon-isotope exchange reactions between potassium cyanide and some carbonates, and their use for obtaining C^{14}-labelled potassium cyanide. The authors examine the results of a study on the isotope exchange of potassium cyanide with compounds differing greatly from it both in composition and structure, such as carbonates of alkaline and alkali-earth metals.

The carbon-isotope exchange reaction in the $KC^{12}N$-$BaC^{14}O_3$ system was studied at 600—800°C. The ratio between the components of this system and those given below agreed with the equimolecular ratio.

The authors show that at high temperatures complete exchange between these compounds can be secured. The exchange reaction begins when the cyanide melt is formed; later it occurs between the liquid and the solid phases, and its speed increases with temperature; at 800°C it is completed in 2 h.

With carbonates of alkali metals the exchange reaction occurs in the melt and is completed at lower temperatures.

The authors obtained cyanide-labelled potassium by the following method:

(1) The isotope exchange reaction $KC^{12}N$-$BaC^{14}O_3$ is produced at 800°C in 2 h.

(2) The mixture $KCN + BaCO_3$ is separated by extracting the KCN with liquid ammonia in a circulating extractor.

By exchanging the equimolecular quantities KCN and $BaCO_3$, potassium cyanide is obtained with a chemical yield of more than 90% and a basic-substance content of 96—97%. By using $BaCO_3$ with a high specific activity (60—70 mc/g), a KCN specific activity of over 80 mc/g may be obtained. The barium carbonate depleted of isotope C^{14} regenerates after the ammonia extraction without appreciable loss.

Etude des réactions d'échange isotopique du carbone entre le cyanure de potassium et les carbonates — leur application à l'obtention de cyanure de potassium marqué au carbone-14. Les auteurs examinent les résultats d'une étude sur l'échange isotopique entre le cyanure de potassium et des composés qui en diffèrent fortement tant par leur composition que par leur structure, comme les carbonates des métaux alcalins et alcalino-terreux.

La réaction d'échange isotopique du carbone dans le système $KC^{12}N$-$BaC^{14}O_3$ a été étudié à une température comprise entre 600 et 800° C. Le rapport entre les éléments de ce système et les éléments indiqués ci-après est équi-moléculaire.

Les auteurs ont démontré qu'à des températures élevées, il est possible d'arriver à un échange complet entre les composés mentionnés. La réaction d'échange commence dès la formation du cyanure fondu; elle se poursuit entre la phase liquide et la phase solide, sa vitesse augmentant avec température, et elle s'achève, à une température de 800°, au bout de deux heures.

Pour les carbonates des métaux alcalins, la réaction d'échange se produit dans la masse fondue et s'achève à des températures moins élevées.

Les auteurs ont mis au point une méthode pour l'obtention du cyanure de potassium marqué; cette méthode comprend les opérations de base suivantes:

1. Réaction d'échange isotopique $KC^{12}N$-$BaC^{14}O_3$ à 800°, en deux heures;
2. Séparation du mélange $KCN + BaCO_3$ par extraction de KCN au moyen d'ammoniaque liquide, dans un extracteur à flux continu.

Lors de l'échange des quantités équimoléculaires KCN et $BaCO_3$, on obtient du cyanure de potassium avec un rendement chimique de plus de 90% et contenant 96 à 97% de la substance de base. En employant du $BaCO_3$, d'activité spécifique élevée (60 à 70 mc/g), on peut obtenir du KCN d'une activité spécifique supérieure à 80 mc/g. Le carbonate de barium, appauvri en isotope C^{14}, est régénéré sans perte appréciable après extraction par l'ammoniaque.

Изучение реакций изотопного обмена углерода между цианистым калием и карбонатами и применение их для получения цианистого калия, меченного изотопом C^{14}. Рассматриваются результаты изучения изотопного обмена цианида калия с соединениями весьма отличающимися от последнего, как по составу, так и по своей структуре, а именно с карбонатами щелочных и щелочноземельных металлов.

Реакция изотопного обмена углерода в системе $KC^{12}N$—$Ba\,C^{14}O_3$ изучалась при 600—800° С. Соотношение между указанными компонентами этой системы и нижеприведенными отвечало эквимолекулярному.

Показано, что в условиях высоких температур возможно достижение полного обмена между указанными соединениями. Реакция обмена начинается с момента образования расплава цианида, следовательно реакция идет между жидкой и твердой фазами; при этом скорость реакции возрастает с повышением температуры и полное завершение реакции при 800° происходит в течение 2 часов.

С карбонатами щелочных металлов реакция обмена протекает в расплаве и завершается при более низких температурах.

Разработана методика получения меченого цианида калия, которая базируется на следующих основных операциях:

1) Проведение реакции изотопного обмена $KC^{12}N - BaC^{14}O_3$ при 800° в течение 2-х часов.
2) Разделение смеси $KCN + BaCO_3$ путем экстракции КС жидким аммиаком в циркуляционном экстракторе.

При обмене эквимолекулярных количеств KCN и $BaCO_3$ получен цианистый калий с химическим выходом выше 90% и содержанием основного вещества 96—97%. При применении $BaCO_3$ с высокой удельной активностью (60—70 мкюри/г) удельная активность КС получается выше 80 мкюри/г. Углекислый барий, обедненный изотопом C^{14}, регенерируется после экстракции аммиаком без заметных потерь.

Estudio de las reacciones de intercambio isotópico del carbono entre el cianuro de potasio y los carbonatos, y su aplicación a la obtención de cianuro de potasio marcado con ^{14}C. Los autores examinan los resultados de un estudio sobre el intercambio isotópico entre cianuro potásico y compuestos que se diferencian mucho de éste, tanto por su composición como por su estructura, tales como los carbonatos de metales alcalinos y alcalinotérreos.

Se estudió la reacción de intercambio de isótopos de carbono en el sistema $K^{12}CN$-$Ba^{14}CO_3$, a temperaturas comprendidas entre 600 y 800° C. La razón entre los componentes de este sistema y los que se indican más adelante es equimolecular.

Los autores demuestran que, a temperaturas elevadas, se puede lograr un intercambio total entre estos compuestos. La reacción de intercambio comienza al fundirse el cianuro y continúa entre las fases sólida y líquida, su velocidad aumenta con la temperatura y a 800° C queda terminada en dos horas.

Con los carbonatos de metales alcalinos, la reacción de intercambio tiene lugar en la masa fundida y se verifica cuantitativamente a temperaturas más bajas.

Los autores emplearon el método siguiente para obtener cianuro potásico marcado:

1) La reacción de intercambio de isótopos en el sistema $K^{12}CN$-$Ba^{14}CO_3$ se efectúa a 800° C en dos horas;
2) La mezcla $KCN + BaCO_3$ se separa extrayendo el KCN con amoníaco líquido en un extractor de flujo continuo.

Si la reacción se lleva a cabo con cantidades equimoleculares de KCN y $BaCO_3$, se obtiene cianuro potásico con un rendimiento químico superior al 90 por ciento y un contenido en sustancia básica del 96 al 97 por ciento. Empleando $BaCO_3$ de actividad específica elevada (60—70 milicuries/g) se obtiene KCN de actividad específica superior a 80 milicuries/g. El carbonato de bario empobrecido en ^{14}C, se regenera sin pérdida apreciable después de la extracción con amoníaco.

Настоящая работа посвящена исследованию обменной способности углерода цианидной группы с углеродом карбонатной группы при высоких температурах в гомогенной и гетерогенной средах.

Возможность обмена углерода в таких различных по составу и структуре соединениях и изучение кинетики процесса представляет значительный теоретический интерес. Кроме того, существующие химические методы получения цианистого калия, меченного изотопом C^{14}, сложны и не дают высокого выхода по изотопу, поэтому установление возможности получения его изотопным обменом облегчит условия приготовления меченого препарата.

Изотопному обмену в литературе посвящено большое количество работ, однако обмен с участием цианидов освещен недостаточно. Имеющиеся указания в зарубежной литературе относятся в основном к изучению реакции обмена цианидов, меченных изотопом C^{14}, с цианидными комплексами Mo, Fe, Co, Ni, Mn, Hg и др. в водной среде [1, 2, 3]. При этом было определено, что $Mn/CN/_6\ldots$, $Hg/CN/_4\ldots$ и $Ni/CN/_4\ldots$ очень быстро обменивают свои цианидные ионы, входящие во внутреннюю координационную сферу с цианидным ионом в KCN. Между цианидными ионами и нитрилами уксусной, янтарной и бензойной кислот изотопный обмен не обнаружен, а с нитрилом β-оксипропионовой кислоты при 100° за 1 час обмен протекает на 9% [4]. Имеется также указание на протекание обменной реакции в водной среде в системе KCN—KSeCN [5].

Исходя из того, что в литературе имеется очень мало данных о реакциях обмена между цианидами и другими углеродсодержащими веществами можно полагать, что либо цианиды трудно обмениваются с соединениями, отличающимися по своей структуре от цианидов, либо этому вопросу не уделено еще достаточного внимания.

Цианиды щелочных металлов не обладают способностью обмениваться углеродом с карбонатами в водных растворах даже в течение длительного времени контракта. Однако при высоких температурах, ввиду ослабления прочности связи, возможно ожидать большей обменной способности углерода. Нами были исследованы реакции изотопного обмена в системе KCN—$BaCO_3$ при 650—800° C и в системах KCN—Li_2CO_3, KCN—Na_2CO_3 и KCN—K_2CO_3 при 500—700° C.

Изучение реакций изотопного обмена в указанных системых проводилось в приборе, изображенном на рис. 1.

В никелевый стакан (1) загружалась смесь активного карбоната исследуемого металла и неактивного цианистого калия в соотношении 1:1 по углероду.

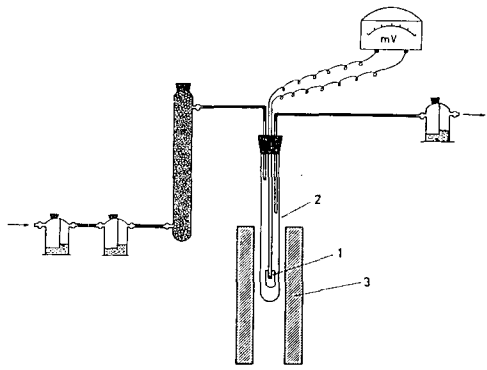

Рис. 1
Схема установки для изучения реакций изотопного обмена карбонатов с цианидом.
1 — никелевый стакан; 2 — кварцевая пробирка; 3 — печь.

Смесь указанных порошков предварительно тщательно смешивалась в ступке. Навеска смеси составляла ~2 г. Стакан помещался в кварцевую пробирку (2), через которую до начала и во время проведения опытов пропускался азот, очищенный от кислорода и влаги. В нагретую до заданной температуры печь (3) опускалась кварцевая пробирка с помещенным в нее стаканом и выдерживалась в печи определенное время при постоянной температуре, после чего пробирка извлекалась из печи и охлаждалась до комнатной температуры. Температуры печи измерялась платино-платинородиевой термопарой с точностью отсчета по шкале милливольтметра ±5°.

Исходными веществами для проведения исследований являлись: радиоактивные карбонаты лития, натрия, калия, бария и неактивный цианистый калий. Карбонат бария с удельной активностью ~1 мкюри/г готовился путем разбавления высокоактивного препарата неактивным следующим образом. Смесь радиоактивного препарата $BaCO_3$ и неактивного разлагалась хлорной кислотой. Выделяющийся CO_2 поглощался раствором баритовой воды с образованием $BaCO_3$, который затем отфильтровывался, высушивался, прокаливался при 500° и просеивался через сито с отверстиями 200 меш. Карбонаты натрия и калия готовились аналогично с тем лишь отличием, что выделяющийся CO_2 поглощался спиртовым раствором соответствующей щелочи. Карбонат лития готовился реакцией карбоната калия и хлорида лития.

Цианистый калий подвергался специальной очистке путем разложения его до HCN и последующим поглощением HCN этилатом калия. Чистота получаемого продукта составляла 98—99%.

После проведения опыта реакционная смесь системы $BaCO_3$—KCN представляла собой спек, легко отстающий от стенок никелевого стакана. Реакционная смесь в системах Li_2CO_3—KCN, Na_2CO_3—KCN, K_2CO_3—KCN при температуре опытов превращалась в расплав.

Для разделения компонентов реакционная смесь выщелачивалась водой, растворимые карбонаты осаждались азотнокислым барием и отделялись от цианистого калия фильтрованием. В фильтрате определялось содержание цианида. Анализом продуктов реакции после опытов не обнаружено потерь

карбонатов. Цианид в указанных системах под действием высоких температур разлагался на 3—6%.

Степень изотопного обмена определялась по уменьшению активности карбоната, поэтому активность последнего измерялась каждый раз до и после опыта.

Измерение активности карбонатов производилось в виде $BaCO_3$, запрессованного в таблетки на установке типа „Б“ с торцовым счетчиком. После опыта измерялась также активность цианистого калия. Для этого из раствора

Таблица I

ИЗУЧЕНИЕ РЕАКЦИИ ИЗОТОПНОГО ОБМЕНА В СИСТЕМЕ $BaCO_3$ И KCN

№№ пп	t°C	Время в часах	Активность $BaCO_3$ в имп/мин		Степень обмена	
			исходная	после обмена	в %	среднее значение в %
1.	650	3	5826	5620	7,0	7,8
2.	650	3	5826	5575	8,6	
3.	700	1	5826	5586	8,2	7,5
4.	700	1	5826	5604	7,6	
5.	700	1	5826	5631	6,7	
6.	700	3	5826	5154	23,0	23,2
7.	700	3	5826	5246	19,0	
8.	700	3	5826	5086	25,4	
9.	700	3	5826	5114	24,4	
10.	700	5	5826	4636	40,9	38,0
11.	700	5	5826	4730	37,6	
12.	700	5	5826	4794	35,4	
13.	750	1	5826	5106	24,7	23,4
14.	750	1	5826	5141	23,5	
15.	750	1	5826	5184	22,0	
16.	750	2	5826	4506	45,3	44,1
17.	750	2	5826	4578	42,8	
18.	750	3	5826	4206	55,6	58,5
19.	750	3	5826	4036	61,4	
20.	750	3	5826	4126	58,4	
21.	750	5	5826	3566	77,6	74,8
22.	750	5	5826	3726	72,1	
23.	750	5	5826	3652	74,6	
24.	800	0,5	5826	4806	35,0	32,8
25.	800	0,5	5826	4936	30,5	
26.	800	1	5826	3994	62,9	60,5
27.	800	1	5826	4058	60,7	
28.	800	1	5826	4142	57,8	
29.	800	2	5826	2896	100,6	100,6
30.	800	2	5826	2826	103,0	
31.	800	2	5826	2956	98,5	
32.	800	2	5826	2904	100,3	

ПРИМЕЧАНИЕ. Для наглядности сходимости результатов число имп/мин после обмена пересчитано на одно значение исходной активности.

KCN действием азотнокислого серебра осаждалось цианистое серебро, осадок отфильтровывался, высушивался и его активность измерялась по такой же методике, как и $BaCO_3$. Полученные результаты степени изотопного обмена совпадали с рассчитанным по $BaCO_3$. Степень изотопного обмена в % определялась по следующему уравнению:

$$x = \frac{(I_{\text{исх}} - I_{\text{опыт}}) \cdot 100}{I_{\text{исх}} - I_{\text{исх}}\,[(m_1 M_2) / (m_1 M_2 + m_2 M_1)]}, \qquad (1)$$

где x — % обмена,
$I_{\text{исх}}$ — активность исходного карбоната в импульсах,
$I_{\text{опыт}}$ — активность карбоната после опыта в импульсах,
$m_1 m_2$ — вес карбоната и цианида в г,
$M_1 M_2$ — молекулярные веса.

В тех случаях, когда компоненты взяты строго с соотношением 1:1 по углероду, расчет производился по упрощенной формуле:

$$x = \frac{I_{\text{исх}} - I_{\text{опыт}}}{(I_{\text{исх}/2})} \cdot 100. \qquad (2)$$

Реакция изотопного обмена углерода между $BaCO_3$ и KCN изучалась при температурах 650—800° и продолжительности опытов от 0,5 часа до 5 часов. Установлено, что ниже 650° никакого обмена нет, при температуре 800° за время 2 часа изотопный обмен происходит полностью. Данные опытов приведены в таблице I.

Как видно из данных таблицы, скорость реакции изотопного обмена в системе $BaCO_3$—KCN заметно возрастает с повышением температуры и при 800° обмен достигает 100%.

На рис. 2 показана зависимость % обмена от температуры при продолжительности опыта 3 часа.

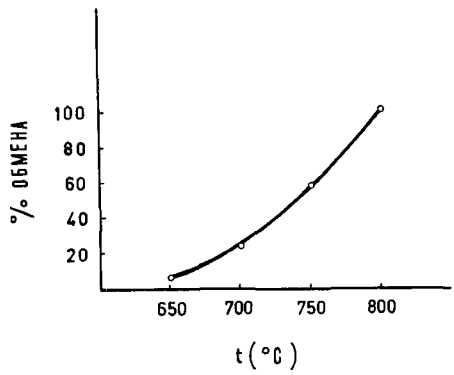

Рис. 2

Зависимость % обмена от температуры для времени 3 часа в системе $BaCO_3$—KCN.

Ввиду того, что обмен между указанными соединениями наблюдается при температуре 650°, т.е. в условиях, когда цианистый калий находится в расплавленном состояния, полагаем, что реакция обмена может осуществляться лишь между твердой и жидкой фазами. Между твердыми фазами обмен не идет. На степень обмена существенно влияет продолжительность опыта.

На рис. 3 показана зависимость % обмена от времени для различных температур.

Так, если при температуре 800° и времени опыта 0,5 часа обмен составляет ~33%, то при той же температуре за два часа времени обмен происходит полностью.

Исследование реакций изотопного обмена в системах M_2CO_3—KCN (где M—Li, Na, K) проводилось по вышеприведенной методике лишь с изменением температурных условий. Ввиду того, что в присутствии KCN температура плавления карбонатов Li, Na, K заметно понижается, изотопный обмен в системе KCN—Li_2CO_3 начинается уже при ~550°, а в системах KCN—Na_2CO_3 и KCN—K_2CO_3— при 550°.

В таблице II приведены данные степени обмена в интервале температур 500—700° С.

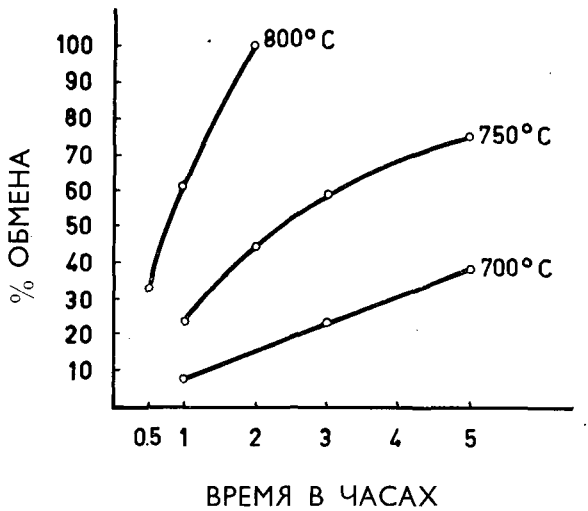

Рис. 3
Зависимость % обмена от времени при различных температурах в системе KCN—$BaCO_3$.

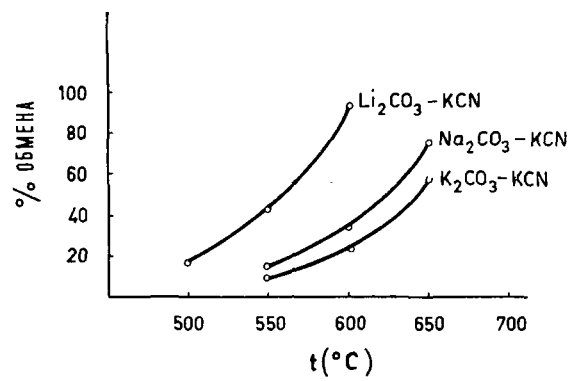

Рис. 4
Зависимость % обмена от температуры.

Таблица II

ИЗУЧЕНИЕ РЕАКЦИЙ ИЗОТОПНОГО ОБМЕНА В СИСТЕМАХ Li_2CO_3—KCN, Na_2CO_3 — KCN, K_2CO_3 — KCN (время опыта 2 часа)

t (°C)	Активность Li_2CO_3 (имп/мин)		Степень обмена		Активность Na_2CO_3 (имп/мин)		Степень обмена		Активность K_2CO_3 (имп/мин)		Степень обмена	
	исходная	после обмена	%	среднее значение (%)	исходная	после обмена	%	среднее значение (%)	исходная	после обмена	%	среднее значение (%)
300	1763	1604	18,0	—	—	—	—	—	—	—	—	—
550	1763	1382	43,2		2676	2475	15,0		2828	2686	10	
550	1763	1383	43,2	43,2	2676	2468	15,5	15,3	2828	2668	11,3	9,9
550	1763	—	43,2		2676	2470	15,4		2828	2709	8,4	
600	1772	935	94,4		2622	2185	33,3		3726	3211	27,6	
600	1772	940	93,9	92,5	2622	2207	31,6		3726	3334	21,0	
600	1772	982	89,2		2622	2152	35,8	34,5	3726	3234	26,4	25,1
600	—	—	—		2622	2126	37,8		3726	3252	25,4	
600	—	—	—		2622	2174	34,2		3726	3260	25,0	
650	1764	880	100,2		2557	1610	74,1		2784	1972	58,3	
650	1764	878	100,4	100,1	2557	1605	74,5		2784	1899	63,6	
650	1764	884	99,8		2557	1543	79,3	74,8	2784	1956	59,5	58,6
650	—	—	—		2557	1619	73,4		2784	2020	54,9	
650	—	—	—		2557	1630	72,5		2784	1992	56,9	
700	—	—	—		3394	1703	99,6		3726	1886	98,7	
700	—	—	—		3394	1686	100,6	100,4	3726	1866	99,8	99,7
700	—	—	—		3394	1682	100,9		3726	1853	100,5	

Наиболее быстро с повышением температуры обменивается углерод в системе Li_2CO_3—KCN. Так, при 650° уже наблюдается полный обмен. В системах Na_2CO_3—KCN, K_2CO_3—KCN скорость обмена ниже, но при 700° также происходит полный обмен. На рис. 4 показана зависимость % обмена от температуры для указанных систем.

На основании проведенных исследований по обмену цианида с карбонатами можно сделать вывод, что обмен между ними протекает лишь в условиях высокой температуры и при наличии расплава одного или двух компонентов.

Реакция обмена ускоряется в ряду $BaCO_3 < K_2CO_3 < Na_2CO_3 < Li_2CO_3$. Скорость реакции в системе $BaCO_3$—KCN заметно ниже остальных, что, очевидно, обусловлено протеканием реакции в гетерогенной среде.

Для изученных систем были рассчитаны константы скорости реакции обмена, приведенные в таблице III.

Таблица III

КОНСТАНТЫ СКОРОСТИ И ЭНЕРГИЯ АКТИВАЦИИ РЕАКЦИЙ ИЗОТОПНОГО ОБМЕНА МЕЖДУ КАРБОНАТАМИ И ЦИАНИДАМИ

Система	t°C	Время опыта в часах	Средний % обмена	$K_{\text{сред.}} \cdot 10^4$	$\lg K_{\text{ср.}}$	$\frac{1}{T} \cdot 10^4$	E ккал/мол
Li_2CO_3—KCN	500	2	18,0	0,275	—	—	~27
	550	2	43,2	0,787	—	—	
Na_2CO_3—KCN	550	2	15,3	0,231	4,64	12,15	31,9
	600	2	34,5	0,588	4,23	11,47	
	650	2	74,8	1,914	3,72	10,83	
K_2CO_3—KCN	550	2	9,9	0,145	4,84	12,15	32,2
	600	2	25,1	0,402	4,40	11,47	
	650	2	58,6	1,225	3,91	10,83	
$BaCO_3$—KCN	650	3	7,8	0,075	5,12	10,83	45,4
	700	1	7,5	0,217		10,27	
	700	3	23,2	0,244		10,27	
	700	5	38,0	0,266		10,27	
				ср. 0,242	4,61		
	750	1	23,4	0,741		9,78	
	750	2	44,1	0,807		9,78	
	750	3	58,5	0,815		9,78	
	750	5	74,8	0,767			
				ср. 0,783	4,11		
	800	0,5	32,8	2,22		9,32	
	800	1	60,5	2,58			
				ср. 2,40	3,62		

Константы скорости реакции рассчитывались по кинетическому уравнению первого порядка:

$$-\ln\left(1-\frac{x}{x_\infty}\right)=Kt, \tag{3}$$

где t — время обмена в секундах,
K — константа скорости реакции,
x — % обмена в опытах,
x_∞ — % обмена, достигаемый при равновесии.

Полученные значения константы скорости в зависимости от времени, представленные для системы $BaCO_3$—KCN, достаточно устойчивы. Это дает возможность полагать, что реакция обмена в системах карбонат — цианид является реакцией первого порядка.

Уравнение зависимости константы скорости реакции от температуры имеет вид:

$$K=-\frac{E}{4{,}575\cdot T}+C, \tag{4}$$

где E — энергия активации в ккал/мол,
T — абсолютная температура,
C — постоянная интегрирования.

График зависимости — $\lg K$ от обратного значения абсолютной температуры $1/T$ в соответствии с вышеприведенным уравнением (4) должен дать прямую линию.

Как показывает рис. 5, данные опытов удовлетворительно ложатся на прямую, что дает возможность графически рассчитать среднее значение кажущейся энергии активации.

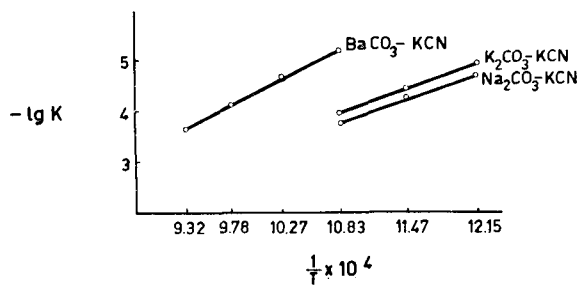

Рис. 5
Температурная зависимость изотопного обмена в координатах $-\lg K \div \frac{1}{T}$.

Для систем Na_2CO_3—KCN и K_2CO_3—KCN величина энергии активации оказалась равной ~32 ккал/мол, а для системы $BaCO_3$—KCN — ~45 ккал/мол.

Энергия активации для системы Li_2CO_3—KCN определена ориентировочно расчетным путем и составляет ~27 ккал/мол.

Достижение высокого процента изотопного обмена в системах карбонат — цианид побудило нас разработать условия разделения компонентов с целью применения метода для приготовления меченого цианистого калия взамен трудоемкого химического синтеза.

Учитывая, что наиболее распространенным сырьевым соединением, содержащим изотоп C^{14}, является углекислый барий, были изучены условия разделения $BaCO_3$ и KCN.

Из литературных данных известно, что растворимость цианистого калия в жидком аммиаке при $t = -33{,}5°$ составляет 4% [6], в то время как $BaCO_3$ в жидком аммиаке нерастворим. На основании этих данных была разработана методика разделения $BaCO_3$ и KCN путем экстракции KCN жидким аммиаком. Разделение $BaCO_3$ и KCN проводилось в приборе, изображенном на рис. 6.

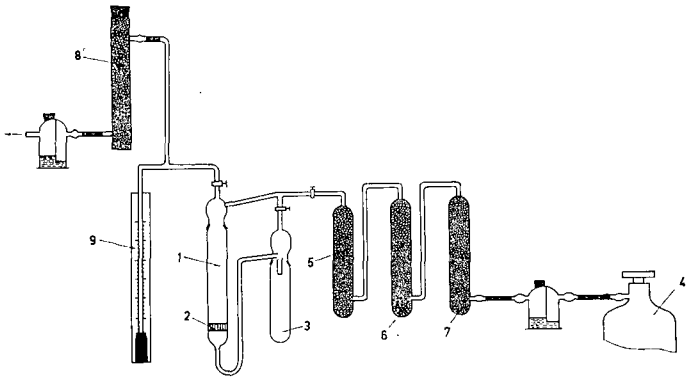

Рис. 6
Прибор для разделения $BaCO_3$ и KCN жидким аммиаком.
1 — колонка; 2 — пористая пластинка; 3 — приемник; 4 — аммиачный баллон; 5, 6, 7, 8 — склянки с CaO, KON, P_2O_5, KOH; 9 — манометр.

Смесь $BaCO_3$ и KCN, предварительного тщательно растертая в ступке, загружалась в колонку (1) на пористую пластинку (2). Колонка охлаждалась до температуры ниже $-35°$ С с твердой углекислотой в ацетоне. При этом аммиак, поступающий из баллона (4) конденсировался и растворял цианистый калий. При переносе охлаждающей бани к приемнику (3) для создания в нем вакуума раствор KCN в жидком аммиаке отфильтровывался через пористую пластинку от осадка $BaCO_3$ и поступал в приемник. Подвергая вновь охлаждению колонку, испаряющийся в приемнике аммиак поступал опять в колонку, конденсировался и повторно экстрагировал KCN. Повторяя операции 3—4 раза, KCN почти полностью извлекали из смеси одним и тем же количеством аммиака, после чего аммиак удалялся из системы, а KCN оставался в приемнике в твердом виде.

Описанная методика была проверена на активном $BaCO_3$ с целью получения меченого KCN. Смесь активного $BaCO_3$ и неактивного KCN в никелевом стакане выдерживалась в печи при 800° 2 часа; при этом происходил, согласно вышеприведенным данным, 100%-ный изотопный обмен.

Смесь активных $BaCO_3$ и KCN извлекалась из стакана, размельчалась в ступке и загружалась в колонку для проведения экстрации KCN жидким аммиаком. В каждом опыте проводилась четырехкратная экстракция ~15 мл жидкого аммиака. Результаты опытов приведены в таблице IV.

Данные показывают, что методом изотопного обмена с применением экстракции жидким аммиаком возможно получить меченый цианистый калий с чистотой 96—97% и химическим выходом выше 90%. Отделенный от цианистого калия углекислый барий, обедненный изотопом C^{14}, возвращается в неизмененном виде и может быть использован для синтезов различных продуктов с более низкой удельной активностью.

Таблица IV

ПОЛУЧЕНИЕ ЦИАНИСТОГО КАЛИЯ, МЕЧЕННОГО ИЗОТОПОМ C^{14}

Вес $BaCO_3$ (г)	Вес KCN (в пересчете на 100% г)	Активность $BaCO_3$ (имп/мин)		% обмена	Химический выход KCN (%)	Содержание KCN (%)
		исходного	после обмена			
3,3020	1,1062	3580	1783	100,4	95,5	96,5
2,7202	0,9113	3580	1843	97,0	96,1	96,9
2,8140	0,9428	3580	1809	98,9	93,7	96,7
5,4446	1,8240	3580	1746	102,4	94,5	96,2
4,5097	1,5108	3580	1801	99,4	90,3	97,1

ВЫВОДЫ

1. Изучена реакция изотопного обмена углерода между цианистым калием и карбонатами лития, натрия, калия, бария. Установлено, что обмен в системе $KCN-BaCO_3$ начинается при 650° и завершается полностью при 800° в течение 2 часов. Обмен в системах $KCN-M_2CO_3$ (где M—Li, Na, K) начинается при 500—550° и достигает 100% для Li_2CO_3 при 650°, для натрия и калия — при 700°.

2. Определены константы скорости реакции изотопного обмена и подсчитана величина кажущейся энергии активации, которая для системы $KCN-BaCO_3$ отвечает ~45 ккал/мол, для системы $KCN-Na_2CO_3$ и $KCN-K_2CO_3$ — ~32 ккал/мол, для системы $KCN-Li_2CO_3$ — ~27 ккал/мол.

3. Установлены условия получения цианистого калия, меченного изотопом C^{14}, методом изотопного обмена с последующим отделением цианистого калия от карбоната экстракцией жидким аммиаком. При этом получен меченый цианистый калий с выходом выше 90% и содержанием основного вещества выше 96%.

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DISCUSSION

H. Elias (Federal Republic of Germany) asked Mrs. Andreeva whether she had any views regarding the mechanism of the exchange reaction described.

O. Andreeva said that she and her associates had only recently begun to study the mechanism involved. Initially, they assumed that it took place through a series of intermediary reactions, the first of which might be an exchange reaction in the $KCN-C^*O_2$ system. The experiments which they had carried out had shown that the rate of exchange in the system described was considerably higher than in cyanide-carbonate systems.

SYNTHÈSES SPÉCIALES DE CERTAINS COMPOSÉS ORGANIQUES IODÉS

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Abstract* — *Résumé* — *Аннотация* — *Resumen

Special synthesis of certain iodized organic compounds. The technological difficulties of working with radioactive products call for maximum simplicity in methods of chemical synthesis.

For iodized compounds two special methods were selected: (a) Utilizing fission recoil, simple iodized compounds such as iodobenzene or methyl iodide were prepared with good yields and a good degree of purity. The method consisted in irradiating mixtures of uranium oxide and benzoic acid or ammonium acetate. The iodized product was separated by distillation after dissolution of the recoil medium in a solvent. (b) By isotopic exchange between mineral iodine with different valencies and complex molecules such as rose bengal and diodone, satisfactory labelling yields were also obtained. These reactions were arranged so as to reduce the isotopic-exchange time to the minimum. For rose bengal, a yield of 90% after several hours was obtained by exchange between NaI and the organic molecule in an aqueous medium and in the presence of oxygenated water. For diodone, the method proposed by Liebster was adapted to reduce losses during purification.

A description of the methods of analysis chosen for these different compounds is given.

Synthèses spéciales de certains composés organiques iodés. Les difficultés technologiques du travail sur les produits radioactifs font choisir les méthodes de synthèses chimiques les plus simples possible.

Pour les composés iodés, on a choisi deux méthodes spéciales. *a*) En utilisant le recul de fission, on prépare avec de bons rendements et avec une bonne pureté des composés iodés simples tels que l'iodobenzène ou l'iodure de méthyle. La méthode consiste à irradier des mélanges d'oxyde d'uranium et d'acide benzoïque ou d'acétate d'ammonium; le produit iodé est séparé par distillation, après dissolution du milieu de recul dans un solvant. *b*) Par échange isotopique entre l'iode minéral à différentes valences et des molécules complexes comme le rose bengale et la diodone, on obtient également des rendements satisfaisants de marquage; ces réactions ont été aménagées pour que le temps d'échange isotopique soit raccourci au maximum. Pour le cas du rose bengale, on a trouvé un rendement de 90% après quelques heures par échange entre INa et la molécule organique en milieu aqueux et en présence d'eau oxygénée. Pour la diodone, la méthode proposée par Liebster a été aménagée pour diminuer les pertes en cours de purification.

On décrit les méthodes analytiques choisies pour ces différents composés.

Специальные синтезы некоторых органических йодистых соединений. Технологические трудности работы над радиоактивными продуктами вынуждают прибегать к как можно более простым методам химических синтезов.

Для йодистых соединений было избрано два специальных метода: 1. Используя отдачу процесса деления, приготавливают с хорошими выходами и с хорошей чистотой простые йодистые соединения, такие как йодобензол или йодистый метил. Метод состоит в облучении смесей окиси урана и бензойной кислоты или ацетата аммония. Йодистое соединение отделяется путем перегонки после растворения среды отдачи в растворителе. 2. Путем

изотопного обмена между минеральным йодом с различной валентностью и комплексными молекулами, такими, как „роза бенгаль" и диодон, также получают с удовлетворительными выходами меченые соединения. Эти реакции проводились таким образом, что время изотопного обмена было сокращено до минимума. Для „розы бенгаль" был получен выход, достигающий 90% после несколько часов путем обмена между NaJ и органической молекулой в водной среде и с пристуствием перекиси водорода. Для диодона предложенный Лейбстером метод проводился таким образом, чтобы сократить потери во время очистки.

Описываются также аналитические методы, избранные для этих различных соединений.

Síntesis especiales de ciertos compuestos orgánicos yodados. Las dificultades tecnológicas que presenta el trabajo con productos radiactivos obligan a escoger los métodos más sencillos posibles para las síntesis químicas.

Los autores han elegido dos métodos especiales para los compuestos yodados. *a*) Aprovechando el retroceso de fisión, preparan compuestos yodados sencillos tales como el yodobenceno y el yoduro de metilo con buenos rendimientos y una pureza bastante elevada. El método consiste en irradiar mezclas de óxido de uranio y de ácido benzoico o de acetato de amonio. Separan el producto yodado por destilación después de haber disuelto el medio de retroceso en un disolvente. *b*) También se obtienen rendimientos de marcación satisfactorios por intercambio isotópico entre yodo inorgánico de diferentes valencias y moléculas complejas como el Rosa Bengala y la diodona. Los autores han modificado el modo de operar con el fin de reducir a un mínimo el tiempo de intercambio isotópico. En el caso del Rosa Bengala, han obtenido un rendimiento del 90% al cabo de algunas horas por intercambio entre el NaI y la molécula orgánica en medio acuoso y en presencia de agua oxigenada. Para la diodona, han modificado el método propuesto por Liebster a fin de disminuir las pérdidas que se producen durante la purificación.

Los autores describen los métodos analíticos que han elegido para estos diversos compuestos.

Introduction

La production routinière de molécules marquées à l'iode-131 exige l'emploi de méthodes chimiques et d'appareillages aussi simples que possible. La nécessité de manipuler à distance impose en effet de telles conditions. C'est dans cette perspective que deux méthodes portant sur l'emploi du recul de fission et sur l'échange isotopique ont été choisies. La première devait permettre l'obtention de molécules simples telles que des iodures d'alcoyle ou d'aryle. La seconde, caractérisée par son mode d'action relativement doux, a été envisagée pour le marquage de substances plus complexes. L'étude des mécanismes de réaction n'a été qu'ébauché.

Emploi du recul nucléaire

A la suite de WOLFGANG [1], l'un d'entre nous [2] a montré qu'en irradiant des grains suffisamment petits d'U_3O_8 dispersés dans une masse solide organique ou saline, on pouvait séparer avec un bon rendement les produits de fission. L'idée nous est venue de faire réagir les atomes «chauds» d'iode formés dans la chaîne de fission de masse 131 avec une substance organique, susceptible de les fixer après rupture d'une liaison C—C, employée comme dispersant de l'oxyde d'uranium.

Dans le même ordre d'idées, KENESHEA et KAHN [3] ont irradié du $TeCl_4$ en solution dans du benzène et ont recueilli 10% de l'activité I-131 sous forme d'iodobenzène formé à la suite d'une rupture d'une liaison C—H.

Nous n'avons pas étudié les probabilités théoriques de réactions de radiosynthèse; les résultats que nous donnons sont issus d'expériences encore inachevées.

Un mélange intime de 0,05—0,1 g de U_3O_8 broyé (dimension moyenne des grains: 2—5 μ) et de 1,0 g d'acétate d'ammonium est irradié 9 h à un flux de $0{,}9 \cdot 10^{11}$ n/cm^2 s. Après 8—12 jours de refroidissement, le mélange est repris à l'alcool absolu chaud et centrifugé pour séparer l'oxyde d'uranium. La solution est additionnée de 1 à 5 ml de CH_3I entraîneur, qui est redistillé, de préférence sous vide. La mesure de l'activité est effectuée en transformant l'iodure de méthyle en iodure d'argent et à l'aide d'un ensemble de comptage à scintillation, en ne tenant compte que du pic de 364 keV. D'ailleurs, le spectre gamma ne montrait plus, douze jours après irradiation, que l'activité de ^{131}I.

Le rendement de marquage est déterminé en se reportant à la quantité totale de ^{131}I formé. Celle-ci est obtenue en irradiant dans le même tube que le mélange précédent un échantillon de 0,05 à 0,1 g d'U_3O_8 dispersé dans du nitrate d'ammonium, en dissolvant le tout par HNO_3 conc. $+H_2O_2$ et en distillant l'iode. On a trouvé des valeurs variant, pour cinq essais, entre R=70 et R=94%, soit $R = 80{,}8 \pm 7{,}2\%$.

En opérant d'une manière comparable à partir de mélange U_3O_8 + acide benzoïque, nous avons obtenu des valeurs de rendements en iodobenzène variant entre 72 et 100% pour cinq essais, soit $R = 87{,}7 \pm 12{,}3\%$.

Pour tenter d'élucider le mécanisme de la réaction, nous avons effectué deux opérations accessoires. La première consistait à vérifier si l'iode de fission se trouvait bien en totalité dans le dispersant. Irradiant un mélange témoin de $U_3O_8 + NH_4NO_3$ ou NH_4CH_3COO, on reprend par l'acide nitrique dilué (0,5 N), on sépare l'oxyde d'uranium par centrifugation et on mesure l'iode dans la solution. Pour huit essais, nous avons trouvé un rendement moyen de recul de $105{,}1 \pm 8{,}1\%$. Ce rendement signifie bien que la quasi-totalité de l'iode formé recule dans le milieu dispersant.

La seconde question, plus importante, est de savoir dans quelle proportion $CH_3{}^{131}I$ s'est formé au moment de l'apparition de ^{131}I par réaction avec des radicaux CH_3 formés par le recul de fission. Il peut en effet se produire une réaction d'échange entre l'entraîneur et l'iode extrait de l'oxyde d'uranium dans la masse saline au moment de la redistillation du premier. L'échange entre CH_3I et ^{128}I ou ^{131}I est rapide et total dans l'alcool déjà à température ordinaire [4], tandis que pour l'iodobenzène il semble qu'une haute température soit nécessaire. Pour répondre à cette question, nous avons irradié un mélange témoin (oxyde d'uranium + nitrate d'ammonium), repris à l'alcool, séparé l'oxyde, ajouté de l'entraîneur (CH_3I ou C_6H_5I) et redistillé celui-ci. L'activité ^{131}I fixée sur la molécule organique s'est élevée à $43 \pm 18\%$ dans le cas de CH_3I, et de manière assez surprenante, à $67 \pm 18\%$ dans le cas de C_6H_5I. Cette dernière valeur s'explique peut-être par un état chimique de l'iode de fission favorisant la réaction d'échange ou de fixation.

Les rendements globaux de marquage s'établissant à 80 et 85% en moyenne, la réaction «chaude» de l'iode de fission serait ainsi responsable de la formation de 40% de $CH_3{}^{131}I$ et de 20% de $C_6H_5{}^{131}I$ au minimum.

TABLEAU I

FORMATION DE CH_3I^* ET $C_6H_5I^*$ PAR RECUL DE FISSION

1. Quantité d'iode sortant des particules d'U_3O_8 (dissolution du milieu dispersant, acétate ou nitrate d'ammonium dans l'acide nitrique dilué en présence de I^- entraîneur)	$105{,}1 + 8{,}1\,\%$ (8 essais)
2. Formation de CH_3I^* par recul dans le mélange NH_4—CH_3—$CO_2 + U_3O_8$ (séparation de CH_3I par distillation avec entraîneur)	$80{,}8 \pm 7{,}2\,\%$ (5 essais)
3. Formation de $C_6H_5I^*$ par recul dans le mélange $C_6H_5\,COOH + U_3O_8$ (séparation de ø I par distillation avec entraîneur)	$87{,}7 \pm 12{,}3\,\%$ (5 essais)
4. Formation de CH_3I^* par échange	$43{,}3 \pm 18{,}2\,\%$ (5 essais)
5. Formation de $C_6H_5I^*$ par échange	$67{,}5 \pm 18{,}6\,\%$ (5 essais)

De toute manière, du point de vue de la préparation de molécules marquées, la méthode décrite est simple, rapide et d'un rendement excellent. Avant de l'exploiter, nous devons néanmoins vérifier que des irradiations de longue durée nécessaires à l'obtention d'activités élevées ne modifient pas sensiblement les phénomènes en jeu et leurs résultats.

Emploi de l'échange isotopique

Le rose Bengale et le Diodrast, utilisé en diagnostic du foie et du rein, ont été préparés et marqués à l'iode-131 par des méthodes synthétiques compliquées [5, 6]. LIEBSTER [7, 8] a publié une méthode de marquage par échange pendant que nous-mêmes étions en train d'effectuer des essais sur l'échange en divers milieux: $CCl_4 + CH_3OH$, sans succès appréciable et en milieu aquo-ammoniacal à pH 8—9 où l'insuccès fut total. Nous avons soupçonné que dans ce dernier cas l'absence d'échange est dû à la forme réduite que devait présenter l'iode, car la solution de $Na^{131}I$ nous était livrée contenant un peu de thiosulfate de sodium, ajouté aux fins de la stabiliser. Or GLEASON [9] en particulier a montré que l'échange entre ^{131}I et l'iode fixé sur un cycle aromatique comme dans le cas de thyroxine n'intervient que lorsqu'il y a présence de I° libre. Ainsi avons-nous choisi d'opérer en milieu légèrement acide et d'assurer la destruction du réducteur par l'adjonction de quantités adéquates d'oxydant. Nous avons emprunté le milieu réactionnel de Liebster, soit un tampon acétique à pH 5. Mais nous y avons ajouté l'iodate de potassium puis, systématiquement, l'eau oxygénée comme agent oxydant.

Quant à l'influence de I^- entraîneur ajouté à la solution de $Na^{131}I$, nous avons fait une constatation intéressante en suivant le rendement de marquage du rose Bengale en fonction de la quantité de KI utilisée (figure 1). Le rendement est maximum pour une quantité nulle d'entraîneur et peut atteindre 91 %. Cette variation ne peut s'expliquer par la loi de masse de la réaction d'échange.

Le mode opératoire s'établit en définitive comme suit. L'appareil utilisé est représenté sur la figure 2. Dérivé du précipitateur de Stang, il est monté dans une

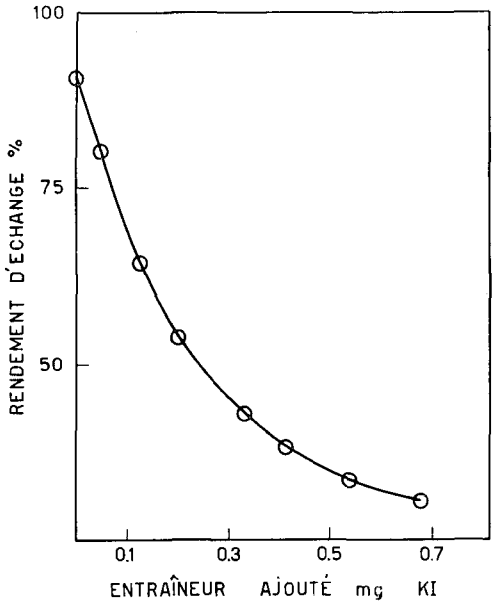

Fig. 1
Rendement d'échange.
20 mg R.B. dans 1,5—2 ml tampon acétique, pH 5, 0,005 ml H_2O_2 — 30 mn à 80° — quantité croissante d'entraîneur KI.

enceinte étanche derrière un mur de plomb. Le mouvement des liquides est contrôlé par une surpression d'azote, ce qui évite la création d'aérosols.

Rose Bengale

100 à 120 mg de rose Bengale, dissous dans 10 ml de tampon acétique (CH_3COOH, M/CH_3COONA, M, pH 5,1— la saturation est atteinte pour 20 mg/ml) sont introduits dans l'appareil avec 1—2 ml $Na^{131}I$ (10—30 mc) et 0,005—0,05 ml H_2O_2 33%. On maintient à 85° pendant 3 à 4 heures. Après refroidissement, on précipite par HCl dilué, on sépare la solution-mère, on redissout dans NH_4OH dilué et on recommence le cycle de purification une ou deux fois. En dernier lieu, le rose Bengale est dissous dans très peu de NaOH. La solution est ajustée à pH 7—7,5 et à la concentration de 10 mg/ml.

Diodrast

1 g environ de sel de diéthanolamine de l'acide diiodopyridone-acétique en solution concentrée dans l'eau est dilué à 10 ml par du tampon acétique. On ajoute l'oxydant, qui s'est trouvé être I_2 mais est plus généralement H_2O_2 et 30 mc de $Na^{131}I$. L'influence de la présence de I^- entraîneur n'a pas été trouvée égale à celle mise en évidence dans la figure 1. L'échange est plus lent que dans le cas du RB. Il nécessite 9 à 12 heures à 95—98° pour être achevé. Dans l'appareil de la figure 2, la chemise de circulation d'eau chaude est remplacée par un manchon où monte de la vapeur d'eau saturante. L'élimination des iodures solubles s'effectue comme pour le RB avec la différence suivante: l'acide diiodopyridone-acétique

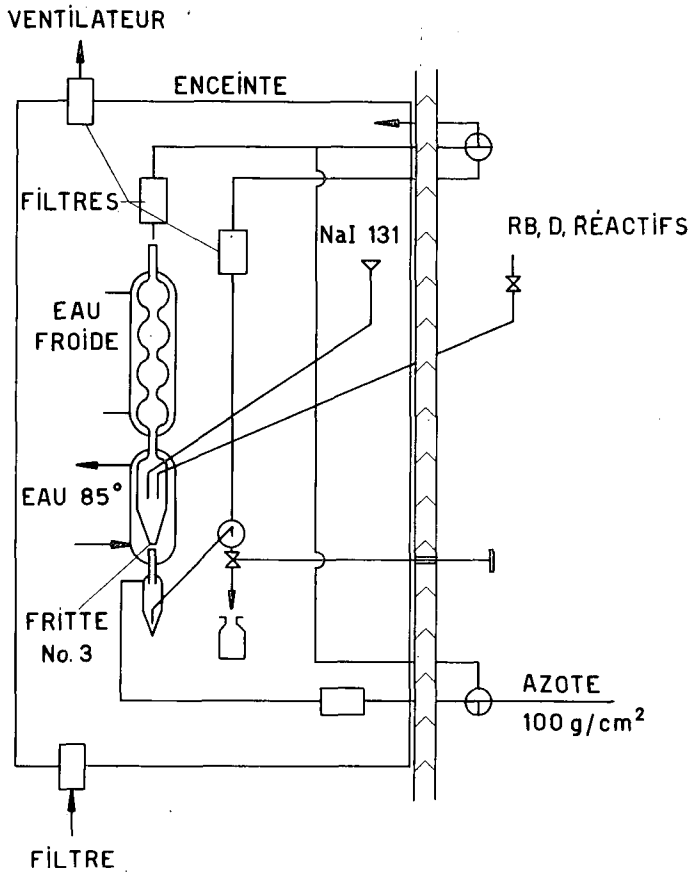

Fig. 2
Appareil pour le marquage par échange du rose Bengale.

libre est précipité par H_3PO_4 à pH < 1. Il est assez soluble, aussi faut-il attendre le refroidissement complet et la fin de la lente cristallisation en paillettes brillantes avant de séparer les eaux-mères. On compte que deux opérations de précipitation-redissolution entraînent une perte de 25% de substance. Le rendement s'établit à 70—75% de substance et 60—70% de l'activité dans le produit récupéré, qui est finalement redissous comme sel de sodium ou de diéthanolamine, à la concentration de 10 mg/ml et l'activité spécifique d'environ 40 µc/mg.

Contrôles

L'activité globale des solutions de rose Bengale et de Diodrast prêtes à l'emploi est mesurée à la chambre d'ionisation étalonnée avec une solution connue de $Na^{131}I$. La concentration en rose Bengale est déterminée par spectrophotométrie. La solution à analyser est diluée par du tampon au carbonate d'ammonium à pH 9,2, la densité optique est mesurée à 543 mµ. Quant au Diodrast, sa détermination est faite dans l'ultraviolet aux longueurs d'onde 237,5 et 280 mµ, sur la solution tamponnée à pH 5. On se rapporte à des courbes d'étalonnage.

Une caractéristique essentielle pour l'utilisateur des produits marqués est la teneur en ^{131}I sous forme d'iodure ionique. Le maximum tolérable a été fixé à 5%. Il suffit généralement de deux précipitation-redissolutions pour abaisser la proportion de I^- au-dessous de cette valeur. Le contrôle sur la solution prête à l'emploi est réalisé par électrophorèse, sur bande de papier. Le milieu est une solution 0,05 M de carbonate d'ammonium, la tension appliquée 500 V pendant 1 h. La migration de I^- est de 11 cm, celle du rose Bengale de moins de 1 cm. Si l'on prolonge l'analyse, on peut séparer le rose Bengale en quatre constituants, qui pourraient être les fluorescéines plus ou moins chlorées ou iodées. Dans le cas du Diodrast, les conditions sont les suivantes: tampon carbonate, pH 8,5, 400 V, 1 h. La détermination du pourcentage d'I^- libre se réduit à la mesure des aires des deux pics, après déduction du mouvement propre, sur l'enregistrement du chromatogramme réalisé à l'aide d'un passeur de bandes C.E.A.

Un contrôle pharmaceutique vérifie de plus la stérilité des préparations après passage à l'autoclave 30 mn à 120°; il suivra la radiolyse possible dans le cas des fortes activités.

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DISCUSSION

M. del Val Cob (Spain) asked Mr. Junod whether he had determined the radiochemical purity of the rose bengal after sterilization and whether there had been any modification in the product as a result of sterilization.

E. Junod said that he and his associates had not so far found any trace of radiolytic decomposition products.

C. Evans (United Kingdom) pointed out that Mr. Junod and his associates had found that the yield of rose bengal-I^{131} became less as the quantity of carrier iodine was increased. That might be due to the presence of an impurity which iodinated at a different rate. He therefore inquired what criteria of purity had been applied to the starting material.

E. Junod said that the rose bengal used (Kuhlman) contained a mixture of products with plus or minus chlorination—i.e. with varying numbers of chlorine atoms fixed on the molecule—and also a certain amount of foreign bodies. However, he and his associates had not attempted to establish the presence of impurities which might explain the negative effect of the carrier iodine.

A NEW METHOD FOR THE PREPARATION OF I^{131}-LABELLED *p*-IODO-BENZENESULPHONIC ACID ANHYDRIDE (PIPSAN)

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Abstract — Résumé — Аннотация — Resumen

A new method for the preparation of I^{131}-labelled *p*-iodo-benzenesulphonic acid anhydride (pipsan). I^{131}-labelled pipsan may be used, together with S^{35}-labelled pipsan, in a double-isotope-derivation technique for the analytical determination of various steroids.

The preparation of high-specific-activity I^{131}-pipsan involves serious health hazards due to the γ-radiation of I^{131}, and a shielded cell with remote-handling equipment has to be used. Earlier methods, in which I^{131} is introduced in diazo-benzenesulphonic acid, involve many steps with purification of the intermediary products and necessitate rather complicated equipment.

By the introduction of I^{131} in diazo-benzene and by sulphonation of the labelled iodobenzene with oleum, labelled pipsan is obtained directly. This method has proved feasible for remote handling in a shielded cell. The procedure is based on recent Russian papers. Chemical aspects of the procedure are briefly discussed.

Descriptions are given of some of the equipment used in the remote handling, e.g.: a micro steam-distillation apparatus for the preparation of iodobenzene, and a rotating Perspex pipetting station used for the addition of washing liquids, for air-propagation and for removal of supernatants.

Nouvelle méthode de préparation de l'anhydride p-iodo-benzènesulfonique (pipsan), marqué à l'iode-131. Le pipsan marqué à l'iode-131 peut être utilisé, conjointement avec le pipsan marqué au soufre-35, pour la détermination analytique de divers stéroïdes par la méthode du double marquage.

La préparation de pipsan-^{131}I, doté d'une activité spécifique élevée, présente des risques graves pour la santé en raison des rayons gamma émis par l'iode-131; on est obligé de la faire en cellule blindée avec des dispositifs de télémanipulation. La méthode précédemment utilisée, selon laquelle l'iode-131 était introduit dans l'acide diazo-benzènesulfonique, comportait de nombreux stades, avec épuration des produits intermédiaires, et rendait nécessaire l'usage d'un materiél assez compliqué.

En introduisant l'iode-131 dans le diazobenzène et en sulfonant avec de l'oléum l'iodobenzène produit, on obtient directement du pipsan marqué. On a constaté que cette méthode se prêtait à la télémanipulation en cellule blindée. L'auteur examine succinctement les aspects chimiques de l'opération, qui se fonde sur de récentes études de savants russes.

Il décrit ensuite certains appareils utilisés pour la manipulation à distance, tels qu'un appareil de micro-entraînement à la vapeur pour la préparation du iodobenzène et un dispositif rotatif à pipettes, en perspex, utilisé pour ajouter les liquides de lavage, injecter de l'air et éliminer les éléments surnageant.

Новый метод изготовления меченного I^{131} ангидрида пара-йодо-бензосульфокислоты (пипсана). Меченный I^{131} „пипсан" может быть использован вместе с меченным S^{35} „пипсаном" для осуществления метода двойного изотопного образования с целью аналитического определения различных стероидов.

Изготовление пипсана с высокой активностью I^{131} влечет за собой серьезную опасность для здоровья вследствие гамма-радиации I^{131}, так что следует пользоваться экранированной камерой с оборудованием для дистанционного манипулирования. Прежний метод, при котором I^{131} вводился в диазо-бензосульфокислоту, вызывает необходимость многократной очистки промежуточных продуктов и требует довольно сложного оборудования.

Путем введения I^{131} в диазо-бензол и сульфонирования меченого йодобензола олеумом, меченый пипсан получается непосредственно; этот метод оказался осуществимым при условии использования дистанционного манипулирования в экранированной камере. Кратко обсуждаются химические аспекты этого процесса, который основывается на новейших русских документах.

Дается описание некоторых предметов оборудования, использованных в дистанционном манипулировании, например: микроаппарат для перегонки пара при изготовлении йодобензола, а также вращающаяся пипеточная установка из органического стекла „перспекс", используемая для добавления промывающих жидкостей, нагнетания воздуха и удаления поверхностного слоя жидкости.

Nuevo método de obtención del anhídrido del ácido p-yodobencenosulfónico (pipsan) marcado con ^{131}I. El pipsan marcado con ^{131}I puede utilizarse, en combinación con el pipsan marcado con ^{35}S, para la determinación analítica de varios esteroides por el método de marcación doble.

La obtención de pipsan-^{131}I de elevada actividad específica entraña graves peligros para la salud debido a las radiaciones gamma del ^{131}I, por lo que es necesario trabajar con equipo de telemanipulación en una celda blindada. El método anteriormente utilizado, que consistía en introducir el ^{131}I en ácido diazobencenosulfónico, implicaba muchas etapas, con purificación de cada uno de los productos intermedios, y requiere el empleo de aparatos relativamente complicados.

En cambio, si el ^{131}I se introduce en el diazobenceno y se sulfona con óleum el yodobenceno producido, se obtiene directamente el pipsan marcado. Se ha comprobado que este método puede aplicarse en una celda blindada trabajando con un equipo de telemanipulación. El autor analiza brevemente los aspectos químicos del proceso de obtención que se basa en recientes publicaciones soviéticas.

Describe asimismo algunos de los instrumentos empleados en la telemanipulación, por ejemplo, un aparato de microarrastre con vapor para la preparación del yodobenceno y un dispositivo giratorio de "perspex" para pipetear que empleó para añadir los líquidos de lavado, inyectar aire y eliminar el líquido sobrenadante.

1. Introduction

The chloride and the anhydride of the *p*-iodo-benzenesulphonic acid, pipsyl chloride and pipsan, can be prepared with I^{131} and S^{35} labels, and such compounds have become valuable tools in a double-isotopic-derivative method for the determination of steroid hormones in microgram or nanogram quantities [1].

At the Isotope Division of The Research Establishment at Risø the preparation of milligram amounts of I^{131}-labelled pipsan was hitherto carried out with conventional "open" equipment, with the necessary radiological safety precautions. With the prospect of an increasing demand and regular preparations of this compound, it was decided to make a shielded cell with remote-handling equipment to prepare 0.1-g quantities of pipsan using 50 mc or more of the radioactive isotope I^{131} per charge.

The method of synthesis previously used [2] [3] employs four steps, each of these entailing purifications of the intermediate product:

$$p\text{—}\overline{SO}_3 \cdot C_6H_4 \cdot \overset{+}{N}_2 + KI^{131} \rightarrow KSO_3 \cdot C_6H_4 \cdot I^{131} \xrightarrow[POCl_3]{PCl_5} I^{131} \cdot C_6H_4 \cdot SO_2Cl$$

$$\xrightarrow{H_2O} I^{131} \cdot C_6H_4 \cdot SO_3H \xrightarrow{SOCl_2} (I^{131} \cdot C_6H_4 \cdot SO_2)_2\,O$$

The yield is of the order of 25% with respect to I^{131}.

To perform the above processes with remote-handling equipment was considered to be a very complicated task, and it was therefore found worth while to attempt a direct sulphonation of iodobenzene with oleum [4] [5]:

$$C_6H_5N_2Cl + KI^{131} \rightarrow C_6H_5I^{131} \xrightarrow[H_2SO_4]{SO_3} (I^{131} \cdot C_6H_4 \cdot SO_2)_2\,O$$

This method, with small modifications, proved feasible for remote handling. A suitable product is obtained in two steps with one rectification, the yield being of the order of 25%.

Although the old method has not been developed for remote handling, it may be useful to compare the number of active operations of the two procedures. The figures in the Table clearly demonstrate the superiority of the two-step method.

TABLE I

NUMBERS OF ACTIVE UNIT-OPERATIONS IN THE TWO PIPSAN SYNTHESES IN QUESTION

	Four-steps method	Two-steps method
Transfer of activity from one container to another	7	3
Addition of liquids to activity	16	11
Centrifuging	2	4
Removal of supernatants	7	8
Heating of activity (including distillations)	6	2
Cooling with ice or brine	2	3
Application of vacuum from mechanical pump	3	0
Drying with nitrogen	3	2
Shaking in separatory funnel	6—8	0
Steam distillation	0	1

A further advantage of the two-step method is the need for far fewer working hours in front of the cell-wall although the duration of the synthesis in both cases is two days.

2. Design of cell

In the design of a shielded cell, various aspects should be considered. The economical investment will depend on the availability, price and half-life of the isotope in question and on the duration and complexity of the synthesis, the frequency with which the cell has to be used, and the type of radiation and the toxicity of the isotope.

Regarding the I^{131}-pipsan, the isotope is cheap, the procedure simple and the actual work-time of relatively short duration. The protection against

γ-radiation during operations and the protection against air-borne contamination from volatile matters, I_2 and C_6H_5I, and against dusty material, pipsan, were the most important considerations. Allowances have been made for a certain degree of risk of loss of activity or even total wreck of a preparation. The problems related to cleaning after such mishap are therefore more or less similar to those of normal maintenance. Due to the relatively short half-life of I^{131}, 8 d, the decontamination of the cell after use need not be complete; thus a certain level of residual activity can be tolerated, provided the cell is left unused for a period of three to four half-lives.

While an unprotected point-source of 50 mc of I^{131} will produce a dose-rate of 130 mr/h at a distance of 30 cm, a lead wall 2-in thick will reduce this dose-rate by a factor of 10^3.

The I^{131}-pipsan cell at Risø occupies 1.5×2 m of a stainless-steel-plated fume hood. The lead walls completely surround the working area (see Fig. 1, in which

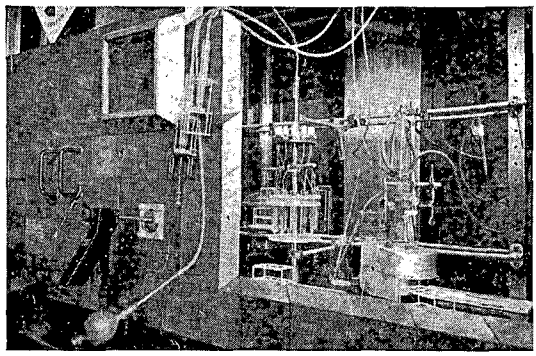

Fig. 1
Cell for preparation of I^{131}-labelled pipsan; part of the shielding has been removed to show the internal layout.

part of the wall has been removed to show the interior of the cell). To protect the lead walls and to ensure the best possible draught, Perspex sheets of 3/8-inch thickness are mounted on a framework of stainless steel on the inside of the lead wall. The workbench is coated with a removable plastic coating, which provides a smooth surface. The decontamination of this surface normally requires little effort; in serious cases the coating may be stripped from the table.

The fume cupboard is designed so that a constant air-current over the walls prevents radioactive volatile material from escaping the cell through other ducts than that of the top with the filter. The highest possible draught, 1800 m^3/h, is used when work is in progress.

The cell wall is fitted with various sphere units for shafts with tongs, a bottle-opener and a screwdriver. There are two lead-glass windows. For the insertion and extraction of equipment and activities, as well as for maintenance purposes, the two bung-ports should be used. Cables for an electrical heater and a centrifuge and tubing for cooling water, for a steam bypass, for changing of baths and for suck-blow operated pipettes are led through holes in the walls to the outside.

When the activity has been brought in, the bung-ports need not be opened before the transfer of the final product.

3. Operations in cell

In the preparation of the I^{131}-labelled pipsan the following operations are of special interest:

(a) Transport of active solution from the isotope bottle to a reaction flask with diazobenzene,
(b) Steam distillation of iodobenzene,
(c) Drying of iodobenzene and sulphonation,
(d) Washing of the pipsan and recrystallization.

The preparation of the labelled iodobenzene has been carried out in a steam micro-distillation apparatus as shown in Fig. 2.

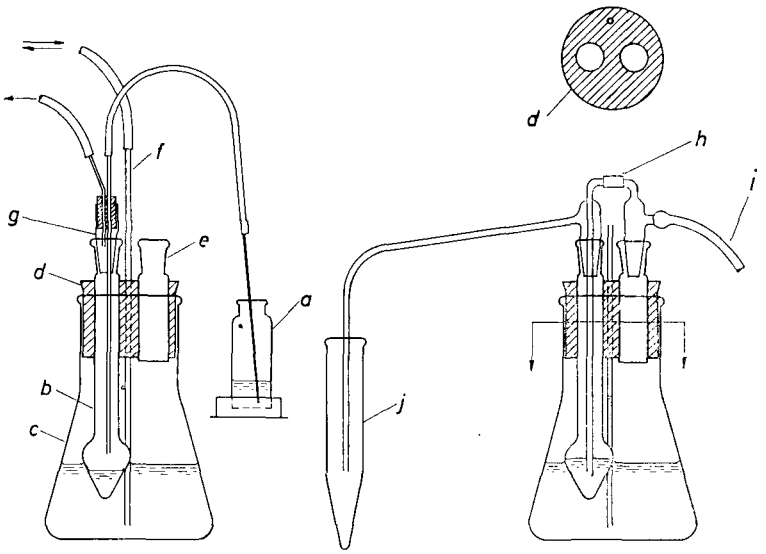

Fig. 2

Steam-microdistillation apparatus.
Left: Transfer operation. a- Isotope bottle; b- 10 ml reaction flask; c- 250-ml broad-necked flask; d- Rubber stopper; e- Tube with ground socket.
Right: Steam-distillation. f- Glass-tube (pressure-gauge); g- Glass cone (transfer-assembly); h- Polythene tubing; i- Bypass for steam-regulation; j- Receiver.

The transport of the activity from the Amersham standard isotope bottle (a) to the reaction flask, a 10-ml pear-shaped, long-necked flask (b), is shown in the left-hand figure. The transfer assembly is made of narrow polythene tubing and stainless-steel tubes, a rubber stopper and a ground glass-cone. Suction is applied with a hand-operated rubber pumpette outside the cell. The diazobenzene solution has been prepared and placed in the reaction flask, and a cold bath has been filled into the Erlenmeyer flask (c), before the assembly is fixed in a clamp in the cell.

When the activity together with carrier have been added to the diazobenzene, the ground glass-cone (g) is removed and replaced by a Liebig condenser. Re-

placing the cold bath with water of +20°C may be performed from a distance by means of the hose connected to the glass tube (f).

When the iodination has been completed, the mixture is made alkaline in preparation for steam distillation. The right-hand figure shows the apparatus with the still-head. This consists of two glass parts connected with a piece of polythene tubing (h) to ensure flexibility and thereby permitting tight connexion in both joints. The receiver (j) is a 10-ml tapered centrifuge glass cooled in a salt-ice mixture. The steam pressure may be regulated from a distance on the bypass (i).

The freshly steam-distilled iodobenzene is centrifuged, and the upper aqueous layer is removed with a pipette, e.g. one of those in the station to be described below. The iodobenzene is left for 12—16 h in the receiver in a dessicator with silica gel, which removes the last traces of water but at the same time causes a small loss of iodobenzene.

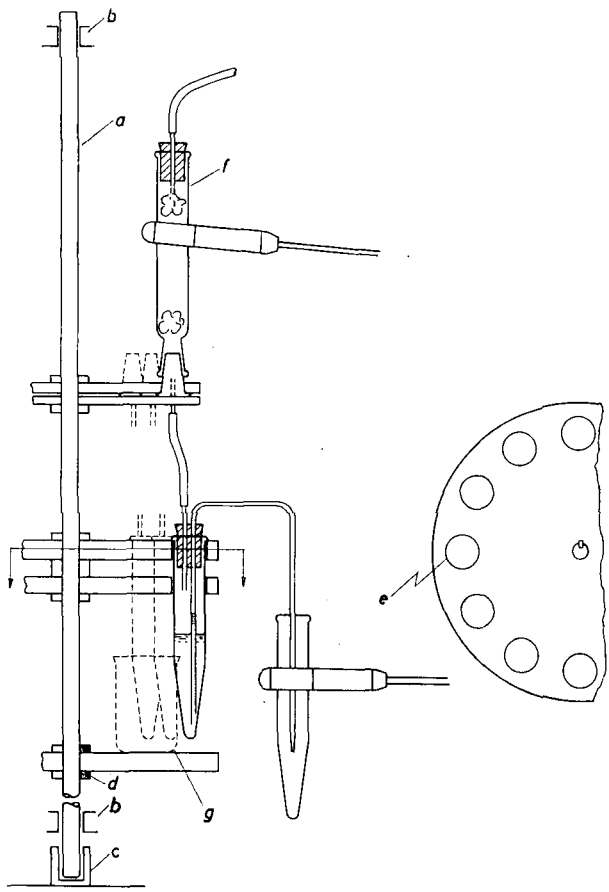

Fig. 3
Rotating pipette station.
a- Shaft with groove; b- Bearings; c- Lead jar; d- Safety disc with screw; e- Perspex disc with 12 holes; f- Tube with silica gel; g- Bath for pipette.

To one part of dry iodobenzene are added four parts of oleum containing 15% SO_3. The two phases are mixed by shaking, and the mixture takes on a colour of intense yellowish brown. White grains of pipsan appear after a few minutes. The precipitation is completed within three to four hours, and the pipsan is separated by consecutive washing of the reaction mixture with acetic acid anhydride, ether and pentane. After each washing the precipitate is centrifuged and the supernatant removed before the next washing-liquid is added. The last trace of pentane is removed by means of a stream of dry nitrogen.

The crude pipsan is dissolved in hot, purified and anhydrous chloroform and is reprecipitated by addition of ample amounts of pentane.

These operations are all performed with the rotating pipette station shown in Fig. 3. The construction is based upon a design given by Moss *et al.* [6]. It consists of Perspex and wooden discs fixed to a vertical shaft by groove and tongues and screwed safety-discs (d). Ordinary laboratory sockets (b) and a small lead jar (c) are used for bearings. Twelve tapered centrifuge glasses are placed in holes in two of the discs (e). The connection to a hand-operated pumpette is established through polythene cones on which a silica gel tube with a glass socket may be placed. Hot or cold baths for the pipettes can be placed on the lower shelf of the rack (g).

It will be noted that the pipettes are used for additions of liquids, for precise removal of supernatants and for stirring with air.

Centrifuging is carried out in a small open laboratory centrifuge at 2000 rpm.

4. Specifications of reagents

For the preparation of a batch of 80—100 mg of pipsan with a specific activity of approximately 50 mc/mM the following amounts of reagents are used.

A solution of benzenediazoniumchloride is prepared from 15 mM of anilinium and 15 mM of $NaNO_2$ in a $-5°$ cold, half-concentrated hydrochloric acid. A tenth of this solution is transferred to the pear-shaped reaction flask, and the assembly is fixed in the cell. The activity is a solution of 50-mc I^{131} in 1-ml 0.01 *N* $Na_2S_2O_3$. The carrier, consisting of 1.5 mM of KI in 2 ml of water, is added after the activity has been introduced.

Before use the oleum should be checked by titration and by reaction with inactive iodobenzene. The anhydrous chloroform should be prepared immediately before use. The rectification of the p.a. chloroform involves washing with concentrated sulphuric acid and water, drying with Na_2SO_4 and finally distillation under anhydrous conditions [1].

5. Some chemical aspects

It is emphasized that the precipitation of the pipsan may fail if the following conditions are neglected:

(a) The strength of the oleum should be 10—20% SO_3 (of $H_2SO_4+SO_3$),
(b) The amount of oleum to be added should be 3.5 to 4.5 times that of iodobenzene (by weight or volume), and
(c) The iodobenzene should be dry.

The purified I^{131}-labelled pipsan should be used for the derivation of the steroid hormones shortly after preparation. It is hygroscopic, and even a partial hydrolysis seems to spoil the derivative property completely. Storing in sealed ampoules

may be sufficient for two days, but for longer periods it is necessary to keep it at $-20°$ over P_2O_5.

The melting point of the oleum-prepared pipsan is 10° lower than that of pipsan made by the old method, 210° as compared with 220°. Investigations by infra-red spectrography have revealed with a high degree of certainty that the product made by the new method contains approximately 5% of the ortho-compound. Examinations by paper chromatography of the derivatives of the steroid hormones obtained with this pipsan did, however, show spots identical with those obtained from old-method pipsan. For this reason, and for the technical reasons mentioned above, the oleum method is preferred.

ACKNOWLEDGEMENTS

The development of this synthesis was initiated under the impression of an increasing demand for the pipsan reagents in hormone analysis. The work has been done in close collaboration with Dr. E. Bojesen, Institute of Experimental Medicine, Copenhagen; and I want to express my gratitude for Dr. Bojesen's never-failing interest throughout the work and for his final demonstration of the applicability of our product in the hormone-analysis. I also want to thank Mr. K. Heydorn, leader of the Isotope Division at Riso, for advice in the work and for help in the preparation of this paper.

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MÉTHODE NOUVELLE DE PRÉPARATION PAR VOIE BIOLOGIQUE DE QUELQUES SUBSTANCES SOUFRÉES MARQUÉES AU SOUFRE-35

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Abstract — Résumé — Аннотация — Resumen

A *new biological method for preparing certain sulphurated substances labelled with* S^{35}. Previous investigations have shown that the yolk-sac of embryonic birds' eggs can be used to produce the following reactions: (a) reduction of sulphate to sulphite; (b) fixation of the sulphite on the carbon chain produced by the desulfhydration of *l*-cysteine, with formation of *l*-cysteic acid; (c) decarboxylation of the *l*-cysteic acid into taurine. The enzymatic system which causes reaction (b) has been purified. It also acts as a catalyst in the sulphur-exchange between the cysteine and the mineral sulphide.

The authors have utilized these data in preparing sulphurated substances labelled with S^{35}: taurine S^{35}, *l*-cysteine S^{35} and *l*-cysteic acid S^{35}. For each of the three, they discuss the chemical reactions involved, the methods of preparation, the experimental conditions of extraction and purity-control, together with the yields and specific activities obtained.

Nouvelle méthode de préparation par voie biologique de quelques substances soufrées marquées au soufre-35. Des travaux antérieurs ont montré l'aptitude du sac vitellin d'œufs embryonnés d'oiseaux à réaliser les réactions suivantes: *a)* réduction du sulfate en sulfite, *b)* fixation du sulfite sur la chaîne carbonée issue de la désulfhydration de la L-cystéine avec formation de l'acide L-cystéique, *c)* décarboxylation de l'acide L-cystéique en taurine. Le système enzymatique responsable de la réaction *b* a été purifié ; il catalyse aussi l'échange du soufre de la cystéine avec celui du sulfure minéral.

Les auteurs ont utilisé ces données pour la préparation de substances soufrées marquées au ^{35}S: taurine ^{35}S, L-cystine ^{35}S et acide L-cystéique ^{35}S. Pour chacun de ces trois corps, ils décrivent les réactions chimiques mises en jeu, les modes opératoires de fabrication, les conditions expérimentales d'extraction et de contrôle de la pureté, ainsi que les résultats obtenus tant pour les rendements que pour les activités spécifiques obtenues.

Новый метод изготовления биологическим путем некоторых серосодержащих веществ, меченных серой-35. Предыдущие работы показали способность вителлинового мешка птичьих эмбриональных яиц осуществлять следующие реакции: a) восстановление сульфата в сульфит, b) фиксацию сульфита на углеродной цепи, происшедшей от сульфгидрации левовращающего цистеина с образованием левовращающей цистеиновой кислоты, c) декарбоксилирование левовращающей цистеиновой кислоты в таурин. Энзимная система, ответственная за реакцию b, была очищена; она также катализирует обмен серы цистеина с серой сернистого минерала.

Авторы использовали эти данные для изготовления серосодержащих веществ, меченных серой-35: таурина S^{35}, левовращающего цистина и левовращающей цистеиновой кислоты S^{35}. Для каждого этого вещества авторы описывают действующие химические реакции, промышленные методы изготовления, экспериментальные условия экстракции и контроля чистоты, а также результаты, полученные как для выходов, так и для полученных удельных активностей.

Nuevas biosíntesis de algunos compuestos de azufre marcados con azufre-35. Trabajos anteriores han demostrado que la membrana vitelina de los huevos fecundados de pájaro es capaz de realizar las reacciones siguientes: *a*) reducción de sulfatos a sulfitos, *b*) fijación de sulfito en la cadena de átomos de carbono resultante de la desulfhidratación de la L-cisteína con formación de ácido L-cisteico, *c*) descarboxilación del ácido L-cisteico para dar taurina. Los autores han purificado el sistema enzimático responsable de la reacción *b*). Este sistema cataliza también el intercambio de azufre entre la cisteína y el sulfuro inorgánico.

Los autores se basan en estos datos para preparar sustancias azufradas marcadas con ^{35}S: taurina-^{35}S, L-cistina-^{35}S y ácido L-cisteico-^{35}S. Describen las reacciones químicas que intervienen en cada uno de los tres casos, así como los métodos empleados en la síntesis, las condiciones experimentales de extracción y de control de la pureza, y los resultados obtenidos en cuanto a rendimiento y actividades específicas alcanzados.

Introduction

MACHLIN, PEARSON et DENTON [1], après injection de sulfate ^{35}S à un œuf embryonné de poule, en ont isolé de la taurine marquée au ^{35}S, démontrant ainsi l'aptitude de l'œuf embryonné à réaliser la synthèse de la liaison S-C à partir du soufre minéral. Nous avons montré, *in vivo* et *in vitro* [2], que cette synthèse de taurine comportait trois étapes principales: *a*) la réduction du sulfate en sulfite, *b*) la fixation du sulfite sur une chaîne tricarbonée et aminée provenant de la désulfhydration de la cystéine, et *c*) la décarboxylation de l'acide cystéique en taurine.

La première de ces réactions a lieu exclusivement dans les cellules endodermiques du sac vitellin; dans l'état actuel, elle est liée à l'intégrité de ces cellules. Elle nécessite la présence d'oxygène. Le système enzymatique catalysant la réaction *b*, qui a été mis en évidence dans ces mêmes cellules endodermiques dès les premiers stades du développement du sac vitellin [3], apparaît ensuite dans le jaune; il peut être extrait de l'ensemble sac vitellin et jaune et purifié [4]. Les préparations obtenues sont stables.

L'utilisation de telles préparations enzymatiques a permis de montrer que la fixation du sulfite sur la chaîne tricarbonée provenant de la désulfhydration de la cystéine est une réaction qui comporte deux étapes: la première, b_1, correspond à une désulfhydration réversible de la cystéine [5]:

$$b_1)\ \mathrm{COOH-CH(NH_2)-CH_2-SH} \rightleftarrows \mathrm{COOH-\underset{\displaystyle NH_2}{\underset{|}{C}}=CH_2+SH_2}$$

La seconde, b_2, correspond à la fixation irréversible du sulfite sur la chaîne carbonée et aminée, dont la structure est voisine de celle de l'acide α-aminoacrylique:

$$b_2)\ \mathrm{\underset{\displaystyle NH_2}{\underset{|}{C}}=CH_2+SO_3H_2 \rightarrow COOH-CH(NH_2)-CH_2-SO_3H}$$

On remarquera que la chaîne tricarbonée impliquée dans ces réactions reste fixée à la surface de l'enzyme; en conséquence, l'acide cystéique obtenu en présence de sulfite est de la forme L naturelle. En outre, d'autres composés soufrés

peuvent réagir avec cette chaîne carbonée. C'est le cas, par exemple, de la cystéine elle-même; on obtient alors de la lanthionine.

Enfin, la dernière réaction participant à la biosynthèse de la taurine par l'œuf embryonné de poule, la décarboxylation de l'acide cystéique, est catalysée par un enzyme dont la localisation n'est pas aussi rigoureuse que celle des enzymes précédents. La décarboxylase de l'acide cystéique est présente dans le sac vitellin comme dans divers tissus de l'embryon [6].

Le présent travail montre qu'à l'aide de ces données on peut, par synthèse biologique, obtenir la taurine ^{35}S, l'acide L-cystéique ^{35}S, et la L-cystine ^{35}S à partir, respectivement, de sulfate, de sulfite et de sulfure marqué par ^{35}S.

Préparation de la taurine ^{35}S

Principe. On met à profit la présence simultanée dans le sac vitellin d'œufs embryonnés de poule, des enzymes catalysant les réactions *a*, *b* et *c*. On introduit des ions SO_4^{--} sous forme de $^{35}SO_4H_2$ sans entraîneur. Il se forme ainsi du sulfite ^{35}S, dont la réaction avec la cystéine, normalement présente dans les tissus, conduit à la formation d'acide cystéique ^{35}S. Sa décarboxylation donne naissance à de la taurine ^{35}S, d'activité spécifique extrêmement élevée. On ajoute au mélange réactionnel de la taurine ordinaire, et après homogénéisation on extrait une taurine marquée dont l'activité spécifique dépend de la quantité d'entraîneur ajoutée.

Exemple

Matériel biologique. On prélève les sacs vitellins d'œufs embryonnés de poule âgés de 17—18 jours. On les coupe en quatre morceaux et on les lave à 37° avec une solution aqueuse de NaCl à 0,9% pour éliminer la plus grande partie du jaune. On prend soin au cours de cette opération de ne pas écraser les tissus.

Incubation. On prend 3 erlenmeyers de 200 ml; dans chacun, on introduit 10 ml d'une solution tampon de phosphates de sodium, M/15 pH 7,65, 10 mg de $MgCl_2$ 6 H_2O, 5,1 mc de $^{35}SO_4H_2$ sans entraîneur et les fragments correspondant à deux sacs vitellins (environ 7 g de tissus frais). On place ces erlenmeyers bouchés par du coton à 37°, et on les agite pendant 15 h. A la fin de l'incubation, on réunit les contenus des erlenmeyers et on ajoute comme entraîneur 100 mg de taurine pure non marquée.

Extraction. Pour éliminer les protéines, on chauffe le milieu à 70°C et on ajoute de l'alcool chaud jusqu'à une concentration d'environ 60%; après quelques minutes, on centrifuge. Le culot est suspendu dans de l'eau distillée. On chauffe à nouveau, et on ajoute dans les mêmes conditions de l'alcool jusqu'à une concentration de 70%. Après centrifugation, on réunit les deux extraits alcooliques, et on concentre sous vide à 30 ml. La solution est dégraissée par du chloroforme. La phase aqueuse est centrifugée et concentrée à 20 ml. Elle est passée sur une colonne (1,8 × 14 cm) de Dowex 50 X 8 (forme H). On lave la résine avec 80 à 100 ml d'eau, et on réunit le filtrat et les eaux de lavage, qui contiennent la taurine ^{35}S. Après concentration, on passe cette solution sur une colonne (1,8 × 10 cm) de Dowex 2 X 8 (forme OH). On lave la colonne avec 80 à 100 ml d'eau. Le pH de l'effluent est alors voisin de 7,3. On ajoute sur la colonne 50 ml d'acide acétique N, et on règle la vitesse d'écoulement à 1,5 ml/min. Le pH de l'effluent reste voisin de 7,3. Ce traitement élimine des pigments jaunes et des substances radioactives inconnues qui ne réagissent pas avec la ninhydrine.

Ces solutions sont rejetées. L'élution de la taurine est obtenue en poursuivant l'addition d'acide acétique N sur la colonne. Après que l'on a recueilli 50 ml, l'effluent ne réagit plus avec la ninhydrine. L'éluat est évaporé à sec, sous vide, et l'acide acétique est complètement éliminé par plusieurs additions d'eau suivies d'évaporations. On redissout la taurine ^{35}S dans 5 ml d'eau et on élimine par filtration un résidu insoluble. Le filtrat est évaporé à sec en présence de P_2O_5. Le résidu est extrait deux fois à 0° par 2,5 ml d'alcool absolu. L'alcool élimine les pigments. La taurine est recristallisée dans de l'alcool à 60%.

Résultat. On obtient ainsi la taurine ^{35}S. Rendement: 88 mg. Activité spécifique: 12 mc/mmole. La taurine ainsi isolée se révèle pure par chromatographie sur papier (solvant: butanol tertiaire, acide formique, eau, 75, 10, 15) et par électrophorèse sur papier (tampon: citrate phosphate 0,2 M, pH 2,7, 7 V/cm, 3 h).

Préparation de la L-cystine ^{35}S

Principe. La cystéine-désulfhydrase du sac vitellin d'œufs embryonnés catalyse l'échange du soufre du groupe thiol de la L-cystéine contre le soufre du sulfure minéral présent dans le milieu:

$$COOH—CH(NH_2)—CH_2—S^- + {}^{35}SH^- \rightleftarrows COOH—CH(NH)_2—CH_2—{}^{35}S^- + SH^-$$

Cet échange étant enzymatique, la cystéine ^{35}S obtenue est de la forme L. Elle est isolée à l'état de cystine ^{35}S.

EXEMPLE

Matériel biologique. On utilise une préparation purifiée de cystéine-désulfhydrase, isolée par les méthodes déjà décrites [4] de sacs vitellins et de jaunes d'œufs embryonnés de poule âgés de 18 jours. A partir de 1 kg du matériel biologique initial, on obtient environ 10 g de cystéine-désulfhydrase, sous forme d'une poudre légèrement jaune, stable à — 20° pendant au moins un an. 1 mg d'une telle préparation enzymatique synthétise par heure environ 5 µmole d'acide cystéique ^{35}S dans les conditions suivantes [4]: 1 mg de la préparation enzymatique en solution dans 1 ml de solution aqueuse de NaCl à 0,9%, 50 µmole de chlorhydrate de cystéine dissous dans 1 ml d'eau et neutralisé, 50 µmole de sulfite ^{35}S de sodium dissous dans 1 ml d'eau et 2 ml de tampon tris 0,5 M pH 8, *t* 37° sous azote.

Incubation. Dans un récipient muni d'un bouchon rodé on introduit 150 ml d'une solution de 0,05 M pH 9 de trihydroxyméthylaminométhane, 2 mmole de cystéine (HCl), 2 mmole de $^{35}SNa_2$ (représentant 2 mc), 500 mg de préparation enzymatique, 2 mg de phosphate de pyridoxal et 5 µmole de bromure de cétyltriméthylammonium (Cétavlon) qui empêche le développement microbien. On vérifie le pH et on le réajuste éventuellement à 9, avec HCl N/10 ou NaOH N/10. On ferme le récipient et on l'agite à 38° pendant 24 heures.

A la fin de l'incubation, on introduit dans le récipient 5 ml de HCl concentré et on chasse l'excès de SH_2 présent. La solution ainsi privée d'H_2S est passée sur une colonne (1,8 × 14 cm) de Dowex 50 X 8 forme H. La résine est lavée à l'eau; les protéines se retrouvent dans les filtrats et dans les eaux de lavage; ces solutions sont rejetées. La L-cystéine ^{35}S fixée sur la résine est éluée par HCl 4 N. On recueille une solution de L-cystine ^{35}S qui est évaporée à sec sous vide, ce qui élimine l'acide chlorhydrique libre. Après redissolution dans l'eau, on précipite la cystine à pH 4—5.

Résultats. On obtient 0,7 mmole de L-cystine ^{35}S (correspondant à 1,4 mmole de cystéine); sa radioactivité spécifique est de 0,4 mc/mmole (théorique: 0,5 mc/mmole). L'électrophorèse sur papier de cette cystine ne met en évidence qu'une tache radioactive, réagissant à la ninhydrine.

Il est clair que la radioactivité spécifique de la L-cystine ^{35}S est fonction non seulement de la radioactivité spécifique du sulfure utilisé, mais aussi du rapport de sa concentration vis-à-vis de celle de la L-cystéine introduite.

Préparation de l'acide L-cystéique ^{35}S

Principe. La désulfhydration de la cystéine en présence de sulfite ^{35}S et de la cystéine désulfhydrase isolée du sac vitellin et du jaune de l'œuf embryonné conduit à la substitution irréversible du groupe thiol de la cystéine par un groupe sulfoné. L'acide cystéique ^{35}S ainsi formé est de la forme L. C'est d'ailleurs par cette réaction que l'on mesure, dans des conditions particulières, l'activité de la désulfhydrase. La préparation de l'acide L-cystéique ^{35}S met en œuvre sensiblement les mêmes conditions expérimentales que celles utilisées pour la préparation de la L-cystine ^{35}S, modifiées cependant comme suit: tampon tris 0,05 M pH 8,5; concentration de la cystéine, 1,5 fois la concentration du sulfite employée et incubation sous azote. A la fin de l'incubation, on obtient ainsi une solution ne renfermant comme seuls acides aminés que la cystéine initiale et de l'acide cystéique ^{35}S. Celui-ci est isolé par fixation sur une colonne (1,4 × 14 cm) de Dowex 2 X 8 forme OH. Le lavage de la colonne par un excès d'acide acétique N élimine la protéine, le tampon tris et la cystéine résiduels. L'acide cystéique ^{35}S est élué par de l'acide chlorhydrique 2 N. Après élimination de l'acide chlorhydrique, l'acide cystéique ^{35}S est cristallisé dans de l'acide acétique pur. Le rendement en acide cystéique ^{35}S est de l'ordre de 70%.

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DISCUSSION

B. E. Gordon (United States of America) asked how much usable product was normally isolated.

P. Fromageot said that the quantities usually prepared were of the order of 80—120 mg.

EXEMPLES D'EMPLOI DE LA CHROMATOGRAPHIE GAZEUSE PRÉPARATIVE DANS LA FABRICATION DES MOLÉCULES MARQUÉES

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Abstract — Résumé — Аннотация — Resumen

Examples of the use of preparatory gas-chromatography in the manufacture of labelled molecules. Gas chromatography is the most commonly used in the analysis of volatile products. Certain works mention its use for preparatory purposes. Since organic labelled-molecule preparations are usually made in respect of quantities of the order of 1—10 mmole, it has been possible to use gas chromatography with very little alteration for the purification of C^{14}-labelled molecules and their separation from complex reaction mixtures.

The apparatus employed is briefly described. The chromatography columns used (diam.: 9—12 mm, length: approx. 4—6 m) made it possible to separate labelled products with boiling-points of up to 180° C and in quantities of approximately 100 mg to 1 g. The fractions detected by a conventional conductivity-cell device were condensed in traps cooled by liquid nitrogen. The radioactivity was not measured at the same time, as an ionization chamber capable of operating at up to 200°C is still only at the research stage. In all cases, the vector gas was helium and the stationary phase support was usually 80 mesh "celite 545".

Examples are given of applications to the purification of acetone 1-3-C^{14}, benzene C_6^{14} methyl or ethyl acrylate 2-3-C^{14} and butadiene D_6, and to the separation of a mixture of aromatic hydrocarbures.

Exemples d'emploi de la chromatographie gazeuse préparative dans la fabrication des molécules marquées. La chromatographie gazeuse est la plus couramment utilisée dans l'analyse des produits volatils; quelques travaux mentionnent son emploi dans un but préparatif. Les préparations des molécules organiques marquées étant effectuées habituellement sur des quantités de l'ordre de 1 à 10 mmole, la chromatographie gazeuse a pu être utilisée sans grande modification pour la purification de molécules marquées ^{14}C et leur séparation de mélanges réactionnels complexes.

Les appareils utilisés sont brièvement décrits. Les colonnes de chromatographie employées (diamètre 9 à 12 mm, longueur 4 à 6 m environ) ont permis de séparer des produits marqués ayant des points d'ébullition jusqu'à 180° C et en quantités de l'ordre de 100 mg à 1 g. Les fractions détectées par un dispositif classique à cellule de conductivité sont condensées dans des pièges refroidis par l'azote liquide. La mesure simultanée de la radioactivité n'a pas été faite, une chambre d'ionisation pouvant fonctionner jusqu'à 200° C étant seulement à l'étude. Dans tous les cas le gaz vecteur a été l'hélium; le plus souvent, le support de phase stationnaire a été la «célite 545» 80 mesh.

Les auteurs donnent des exemples d'applications à la purification de l'acétone ^{14}C-1-3, du benzène $^{14}C_6$, de l'acrylate de méthyle ou d'éthyle ^{14}C-2-3 et du butadiène D_6, et à la séparation d'un mélange d'hydrocarbures aromatiques.

Примеры использования газовой хроматографии при изготовлении меченых молекул. Газовая хроматография наиболее часто используется при анализе летучих продуктов. В нескольких работах указывается ее применение для приготовления препаратов. Изготовление меченых органических молекул обычно осуществляется на количествах порядка от 1 до 10 миллимолей. Таким образом, газовая хроматография могла использоваться без больших изменений для очищения меченых молекул углерода-14 и для их отделения от сложных реактивных смесей.

Ниже коротко описывается применяемая аппаратура. Применявшиеся хроматографические колонны (диаметром от 9 до 12 мм и длиной приблизительно от 4 до 6 м) позволили разделять меченые продукты с точкой кипения до 180° С и в количествах порядка от 100 мг до 1 г. Фракции, обнаруженные при помощи обычного устройства с парой электродов для измерения электролитической проводимости, конденсируются в ловушках, охлаждаемых жидким азотом. Одновременное измерение радиоактивности не проводилось, поскольку ионизационная камера, способная работать при температурах до 200° С, только еще изучается. Во всех случаях векторным газом является гелий; наиболее часто в качестве базы стационарной фазы употреблялся „целит-545" с 80 ячейками на квадратный дюйм.

Авторы дают примеры очистки ацетона C^{14}-1-3, бензола $C^{14}{}_6$, метилового или этилового акрилата C^{14}-2-3 и бутадиена D_6 и разделения смеси ароматических углеводородов.

Ejemplos de empleo de la cromatografía en fase gaseosa para la preparación de moléculas marcadas. La cromatografía en fase gaseosa es la que se utiliza mayormente en el análisis de productos volátiles; algunos trabajos citan su empleo como método preparativo. Suelen sintetizarse moléculas orgánicas marcadas en cantidades del orden de 1 a 10 mmole. Así pues, los autores han podido utilizar sin grandes modificaciones la cromatografía en fase gaseosa para purificar moléculas marcadas con ^{14}C y separarlas de las mezclas complejas que se obtienen en las reacciones.

Los autores describen brevemente los aparatos que han empleado. Las columnas cromatográficas utilizadas (diámetro 9 a 12 mm; largo 4 a 6 m) les han permitido separar en cantidades del orden de 100 mg a 1 g productos marcados cuyos puntos de ebullición alcanzan hasta 180° C. Recogen en trampas refrigeradas con nitrógeno líquido las fracciones detectadas por un dispositivo clásico de célula de conductividad. No han efectuado la medición simultánea de la radiactividad porque todavía está en estudio una cámara de ionización capaz de funcionar a temperaturas del orden de 200° C. En todos los casos han empleado helio como gas vector, y "célite 545", generalmente de 80 mallas como soporte de la fase estacionaria.

Los autores presentan ejemplos de aplicaciones a la purificación de la acetona ^{14}C-I-3, del benceno $^{14}C_6$, del acrilato de metilo o de etilo ^{14}C-2-3 y del butadieno D_6, y a la separación de una mezcla de hidrocarburos aromáticos.

La chromatographie en phase gazeuse est très largement employée pour l'analyse qualitative ou quantitative de produits organiques plus ou moins volatils. Cette technique, qui progresse extrêmement rapidement, a fait l'objet de revues nombreuses dont une des plus récentes est celle de [1]. Quelques travaux décrivent l'utilisation de la chromatographie en phase gazeuse dans un but préparatif pour la purification et l'isolement de quantités plus ou moins grandes de produits de très grande pureté.

Le plus souvent les préparations de molécules marquées par le carbone-14 ou le tritium sont effectuées sur des quantités de l'ordre de 1 à 10 mmole. Cette échelle de quantités est telle que l'on pouvait penser pouvoir utiliser avantageuse-

ment la chromatographie en phase vapeur pour la purification de molécules marquées et leur séparation de mélanges réactionnels complexes. Le but du présent article est de donner quelques exemples d'utilisation de cette technique. Les appareils utilisés sont certes très imparfaits, mais ils ont permis de résoudre des problèmes de purifications insolubles par d'autres techniques.

Dans la partie expérimentale, les appareils, qui ont permis la purification des produits marqués ayant des points d'ébullition jusqu'à 180° C et en quantités de l'ordre de 100 mg à 1 g, sont décrits succinctement. Les fractions sont détectées par un dispositif classique à cellule de conductivité. En toute rigueur, il conviendrait de mesurer simultanément la radioactivité du gaz effluent. Cette mesure n'a pas été faite, car au moment de ces travaux nous ne disposions pas de chambre d'ionisation pouvant fonctionner jusqu'à 200° C [2].

Acétone ^{14}C

L'acétone ^{14}C-1-3 obtenue par pyrolyse de l'acétate de baryum ^{14}C-2 à 500° C sous vide renferme des impuretés. La purification par chromatographie, dans les conditions résumées sur la figure 1, a permis une excellente séparation de ces produits. L'eau, toujours présente dans l'acétone brute, est également éliminée, car son temps de rétention sur le triéthylèneglycol est extrêmement élevé (le pic correspondant à l'eau n'est pas montré sur la figure).

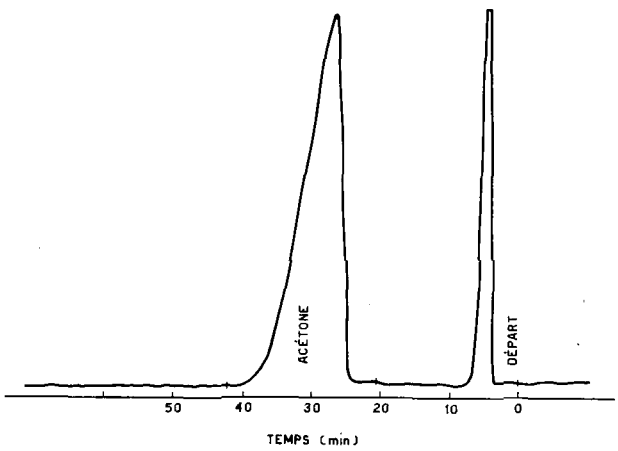

Fig. 1
Chromatographie d'acétone ^{14}C.

Appareil: Préparatif I
Echantillon: acétone ^{14}C — 0,2 cm³
Colonne: 2,5 ms triéthylèneglycol 30 % célite
Température: 65°C — *Courant pont:* 2 V
Gaz: H_2 — *Débit:* 100 cm³/min
Pression: entrée, 250 g/cm²; sortie, 1 atm
Sensibilité: 1 — *Vitesse papier:* 30 cm/h

Benzène $^{14}C_6$

La trimérisation de l'acétylène ^{14}C par le catalyseur de Reppe [3] constitue une méthode simple de synthèse du benzène $^{14}C_6$ [4]. L'isolement du benzène

du mélange réactionnel par distillation ou par formation de clathrate sur des quantités de l'ordre de 10 mmole n'ayant pas donné de bons résultats, la chromatographie en phase vapeur a permis de résoudre ce problème. Les conditions expérimentales sont celles données dans la figure 2.

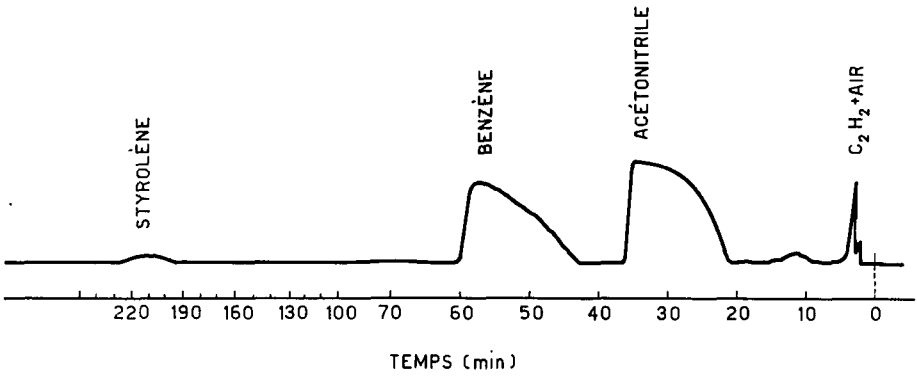

Fig. 2
Chromatographie de benzène ^{14}C.

Appareil: préparatif 1
Echantillon: benzène ^{14}C — 0.9 cm^3
Colonne: D.N.P., 20 % célite (5,5 m)
Température: 73°C — *Courant pont:* 2 V
Gaz: H_2 — *Débit:* 40 cm^3/min
Pression: entrée, 250 g/cm^2; sortie, 1 atm
Sensibilité: 1 — *Vitesse papier:* 30 cm/h et 7,5 cm/h

ACRYLATE DE MÉTHYLE OU D'ÉTHYLE ^{14}C-2-3

Nous avons déjà décrit l'adaptation de la méthode de REPPE [5] à la préparation d'acrylate de méthyle marqué au ^{14}C [6]. Lorsque ce dernier est utilisé dans la synthèse de l'acide glutamique ^{14}C-3-4, il n'est pas nécessaire de l'isoler du mélange réactionnel. Il n'en est plus de même lorsqu'on a en vue l'utilisation de l'acrylate de méthyle monomère marqué dans des études de polymérisation ou copolymérisation. L'action de l'acétylène radioactif sur le méthanol (ou l'éthanol) en présence d'eau, d'acide chlorhydrique et de nickel carbonyle selon le schéma

$$CH_3OH + C^*H \equiv C^*H + 1/4\ Ni(CO)_4 + 1/2\ HCl \rightarrow C^*H_2 =$$
$$= CH—CO_2CH_3 + 1/4\ NiCl_2 + 1/4\ H_2$$

conduit, après distillation, à un mélange qui, outre le produit cherché, renferme du méthanol, de l'eau et du nickel carbonyle. La distillation fractionnée sur des quantités de l'ordre de 10 mmole n'est pas praticable. A nouveau, la chromatographie gazeuse a permis une séparation aisée (figure 3). Deux colonnes en série ont été utilisées. La première, à remplissage de tamis moléculaire Linde type 5 A, a retenu par adsorption le méthanol et l'eau, et, grâce à ses propriétés basiques, l'acide chlorhydrique. La deuxième colonne à remplissage de dinonylphtalate a séparé le nickel carbonyle et l'acrylate de méthyle.

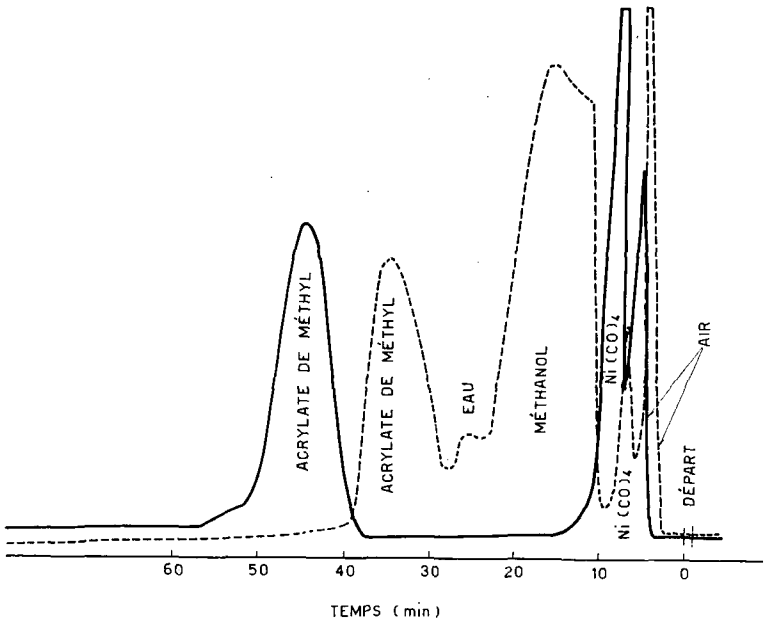

Fig. 3
Chromatographie d'acrylate de méthyle ^{14}C-2-3.

Appareil: préparatif I
Echantillon: acrylate de méthyle, 1,6 cm³
Colonne: ————: D.N.P., 20% (2 m) + tamis moléculaire 5 Å (30 cm)
---------: D.N.P., 20% (2 m)
Température: 76°C — *Courant pont:* 2 V
Gaz: H_2 — *Débit:* 40 cm³/min
Pression: entrée, 250 g/cm²; sortie, 1 atm
Sensibilité: 1 — *Vitesse papier:* 16 cm/h

Butadiène D_6 11-2-3-4-4

Ce carbure, préparé par réduction déshalogénante du perchlorobutadiène [7], renfermait encore, après un certain nombre de purifications chimiques, des impuretés de nature indéterminée. Tous autres procédés de purification ayant échoué, on a effectué une chromatographie préparative en phase vapeur. On a utilisé une colonne de ⌀ 12 mm environ, de longueur 5 m, contenant 100 g de remplissage (célite imprégnée de 40% de diméthylformamide) maintenue à 0° C par un bain de glace. Le gaz vecteur He (débit approximatif 2,7 l/m) même à 0° C entraînant à la longue la phase stationnaire, il a été nécessaire de placer à l'entrée de la colonne un barboteur à diméthylformamide. Le butadiène gazeux était introduit dans la colonne par le dispositif de la figure 4. Le chromatogramme obtenu est représenté sur la figure 5.

Séparation d'un mélange d'hydrocarbures aromatiques

Au cours d'une récente étude, nous avons eu à séparer quantitativement un mélange d'acétonitrile et des produits ^{14}C suivants: benzène, toluène, o, m, p-xylène, le volume total étant de 0,6 ml. Nous sommes parvenus à ce résultat

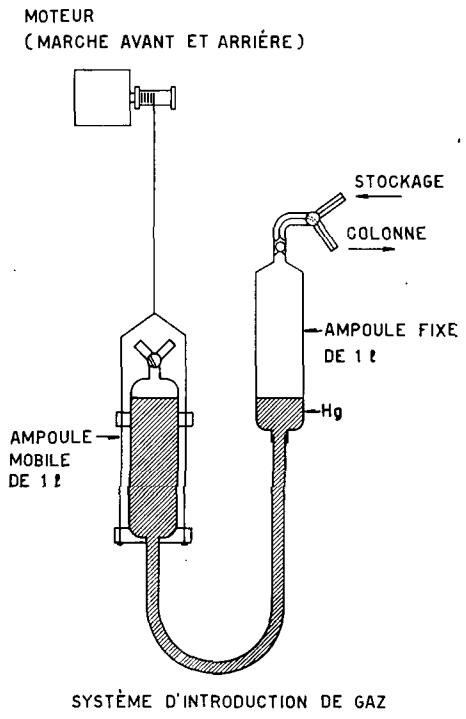

Fig. 4
Dispositif d'introduction de gaz sur colonne de chromatographie gazeuse préparative.

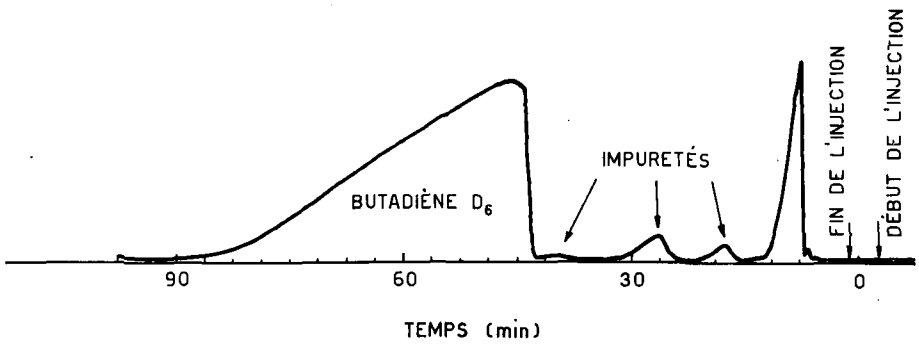

Fig. 5
Chromatographie de butadiène D_6.

sur une colonne de silicone dans l'appareil figure 6; le chromatogramme figure 7 permet de se rendre compte que la séparation est bonne, à l'exception de celle des isomères m et p-xylène.

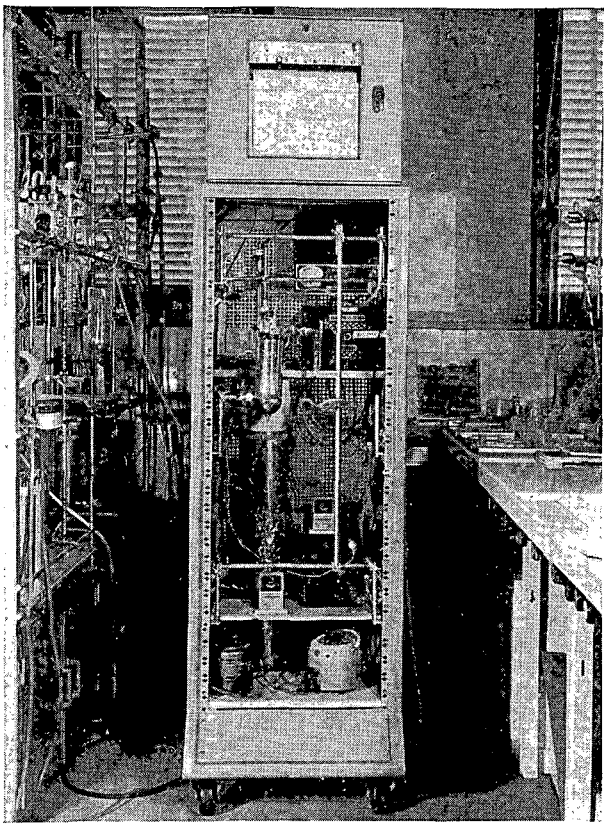

Fig. 6
Appareil de chromatographie gazeuse préparative.

Partie expérimentale

Deux types d'appareils ont été assemblés. L'un nous a permis de travailler jusqu'à 90° C environ, l'autre jusque vers 200° C. La figure 6 est une photographie du deuxième appareil.

Gaz vecteur

Le gaz vecteur utilisé a été quelquefois l'hydrogène, le plus souvent l'hélium. Le débit du gaz, mesuré au rotamètre, est stabilisé par manomètre à double détente et réglé par une valve à aiguille.

Chambre de vaporisation

Le premier appareil ne comportait pas de chambre de vaporisation à chauffage indépendant de celui de la colonne proprement dite. Néanmoins, près de l'introduction de l'échantillon (figure 8), le remplissage de la colonne est remplacé par des billes de verre. Dans le deuxième appareil, un préchauffeur indépendant, rempli également de billes de verre, a été utilisé.

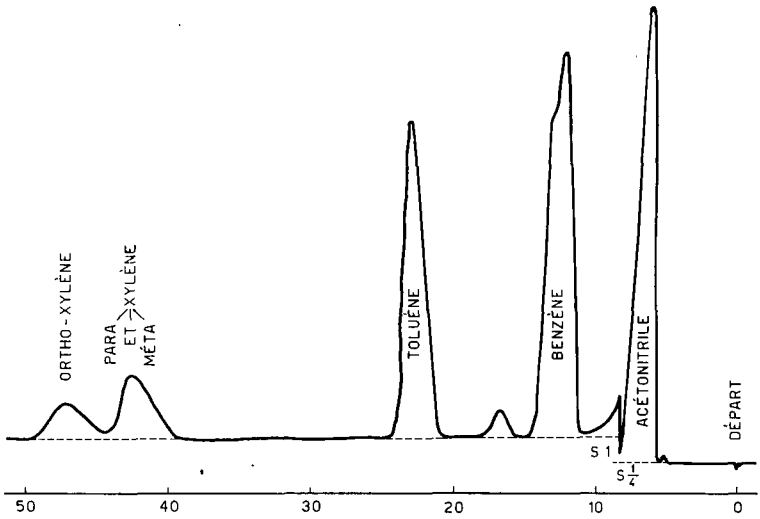

Fig. 7
Chromatographie de mélanges d'hydrocarbures benzéniques ^{14}C.

Appareil: préparatif II
Echantillon: synthèse 10 — 0,6 cm³
Colonne: silicone 10% (10 m)
Température: 80° C
Gaz: He
Pression: entrée, 500 g/cm²; sortie: atm
Sensibilité: 1/4 et 1

Courant pont: 80 mA
Débit: 250 cm³/min
Vitesse papier: 30 cm/h

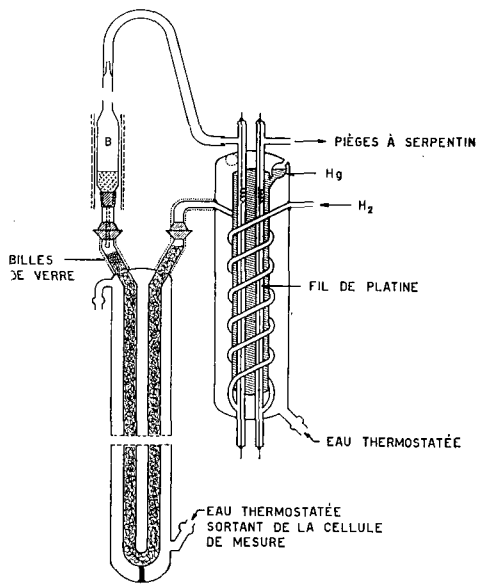

Fig. 8
Appareil de chromatographie gazeuse préparative à chauffage par circulation d'eau.

Dispositif d'introduction de l'échantillon

Echantillons liquides. Les liquides radioactifs sont condensés par distillation sous vide et refroidissement par l'azote liquide dans l'ampoule B. La figure 9 montre le dispositif utilisé. Les produits de réaction de l'autoclave A sont distillés dans le piège à serpentin C puis, après scellement de 1, sont distillés dans l'ampoule B qui est ensuite scellée (dans le cas de produits solubles dans les graisses) et se présente comme l'indique la figure 9. Cette ampoule est ensuite placée sur l'appareil à chromatographie de la figure B et est chauffé par résistance extérieure. Par rotation autour du rodage sphérique, on casse la pointe étirée. On brise la deuxième pointe étirée au travers du tube de caoutchouc d'amenée du gaz vecteur.

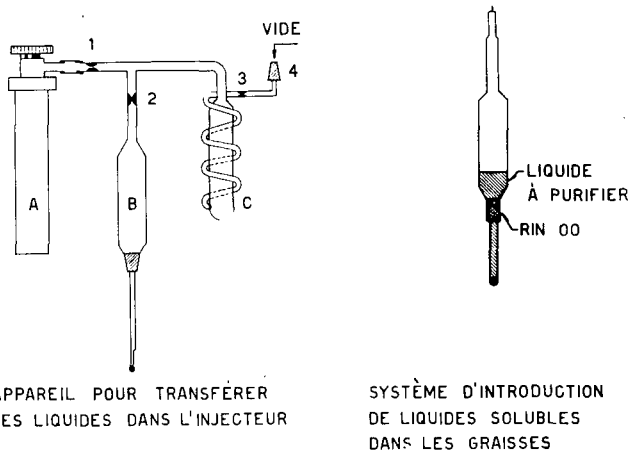

Fig. 9
Ampoule pour introduction de liquides volatils ^{14}C sur colonne de chromatographie gazeuse préparative. Appareil pour le remplissage de l'ampoule.

Echantillons gazeux. On a utilisé le dispositif de la figure 4. Durant l'introduction de l'échantillon, le débit de gaz vecteur dans la colonne de chromatographie était momentanément interrompu. La vitesse du moteur soulevant le réservoir de mercure était telle que le temps d'introduction de l'échantillon d'un litre était d'une minute.

Colonnes utilisées

Toutes les colonnes utilisées étaient en verre «Pyrex». Selon les quantités et produits à purifier, les dimensions variaient entre ⌀ 9 mm et ⌀ 12 mm, longueur 2—5, 50—10 m. Pour limiter l'encombrement, ces colonnes sont du type à double enroulement en hélice, mais leur remplissage est difficile; on a donc préféré dans le deuxième appareil des colonnes en U mises en série.

Chauffage et refroidissement des colonnes

On a utilisé dans le premier appareil un bain d'eau en circulation thermostaté dans un thermostat «Prolabo», la même circulation d'eau servant au chauffage du catharomètre (figure 8). Ce dispositif ne présente aucune innovation, mais il possède l'avantage d'utiliser du matériel courant de laboratoire. Le deuxième appareil est chauffé par un bain d'air à chauffage électrique thermostaté par

thermomètre à contact et relai. Le catharomètre, dans ce montage, est placé dans un thermostat indépendant, par conséquent la constance de la température dans la colonne est peu importante.

Matériaux de remplissage

Le support utilisé a été la «célite 545» lavée à l'acide chlorhydrique tamis: 60—80 mesh. Les liquides d'imprégnation utilisés ont été la diméthylformamide, le phtalate de nonyle, le tréthylène glycol et l'huile de silicone Rhodorsil 47 V 300.

Détecteurs

Le premier appareil construit comportait un catharomètre à filament de platine tendu dans un tube de verre «Pyrex» [8] avec des modifications mineures. Jusqu'à une température de 90° C, ce type de catharomètre a fonctionné correctement (figure 8).

Le catharomètre utilisé dans le deuxième appareil est commercial; comme il a été dit plus haut, il se trouve dans un bloc de laiton thermostaté indépendamment de la colonne.

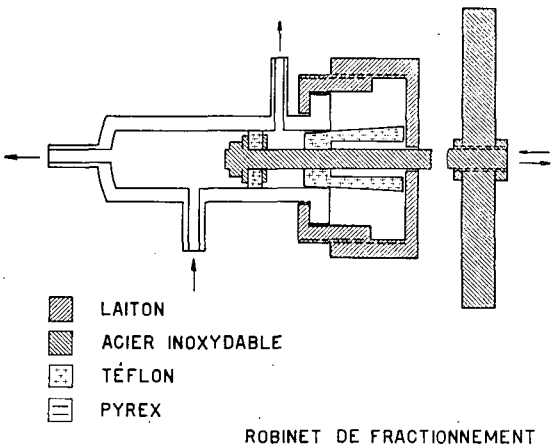

Fig. 10
Robinet chauffé pour collecte des fractions de chromatographie.

Dispositif de collecte des fractions

Il comporte un robinet chauffé permettant de diriger à volonté le courant gazeux dans deux pièges à serpentins refroidis par l'azote liquide. Ce robinet (figure 10) est constitué par un piston en téflon coulissant dans un tube de verre cylindrique rodé intérieurement. Les pièges par condensation sont du type classique à serpentin. Dans quelques cas, en particulier celui du p-cymène [9], on a observé la formation de brouillards qui mécaniquement étaient entraînés par le courant gazeux, d'où pertes de produit. L'addition d'un tampon de laine de verre à l'intérieur du piège permet dans ce cas la récupération quantitative du p-cymène [9].

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DISCUSSION

J. F. Ford (United Kingdom) said he would like to emphasize the great value of the gas-liquid chromatographic technique described in the paper just presented. He and his associates had also used that technique to purify synthesized C^{14}-labelled hydrocarbons and to separate the products of certain reactions involving those substances. Although that application was briefly described in their paper*, he wished to stress how useful in that kind of work were stationary phases which gave rise to separations dependent on the molecular structure and not simply on volatility. For example, Zlatski had used naphtylamine, and Desty and Swanton 7:8-benzoquinoline to separate *o*-, *m*- and *p*-xylenes.

Using an apparatus similar to that described in the paper by Mr. Pichat, but packed with celite impregnated with 7:8-benzoquinoline, he and his associates had been able to separate completely a mixture containing the three xylenes and ethylbenzene on a 100-mg scale, at 78°C. The high purity of the materials produced in that way had been shown by an examination of the chromatograms obtained from a glass capillary gas-chromatographic column having an efficiency of 100000 theoretical plates.

C. Burckhardt (Switzerland) asked whether Mr. Pichat thought that continuous gas-chromatography would be a great help in preparing labelled organic compounds.

L. Pichat assumed that Mr. Burckhardt was referring to the use of apparatus for "programmed" gas-chromatography, which made it possible to purify quite sizeable amounts of material (10 g to 100 g). It was only rarely necessary to purify such amounts of material labelled with C^{14} or tritium. It might, however, be necessary to purify such amounts of deuterated organic products, and in that case continuous, automatic gas-chromatography could be extremely useful.

* CANNINGS, F. R., FISHER, A., FORD, J. F., HOLMES, P. D. and SMITH, R. S., *These proceedings* **III** 205.

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RADIOISOTOPES IN ORGANIC CHEMISTRY

(Sessions 14 [Part] and 15 [Part])

THE SELF-INDUCED EXCHANGE OF TRITIUM GAS WITH METHANE

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Abstract — Résumé — Аннотация — Resumen

The self-induced exchange of tritium gas with methane. The exchange of tritium atoms between T_2 gas and methane, as induced by the radioactive decay of the tritium, has been investigated. This type of exchange forms the basis of the labelling process developed by Wilzbach.

Two distinct mechanisms appear to be involved and are quantitatively evaluated. (1) Decay of one of the atoms in T_2 yields HeT^+. This species reacts rapidly with CH_4 to give the excited ion CH_4T^+ which promptly decomposes to CH_2T^+. CH_3T is then formed by hydride ion exchange with CH_4. This postulated mechanism shows the required first-order dependence on the T_2 pressure and is unaffected by additions such as Xe, which due to their low ionization-potential-act as ion scavengers. (2) Beta-radiation from the tritium decay produces CH_4^+ which forms CH_5^+ on collision with another methane molecule. The CH_5^+ is then postulated to undergo an exchange with T_2 to form CH_4T^+ and finally CH_3T. This mechanism gives rise to an observed term in the kinetics involving a 3/2 power dependence on tritium pressure and is sensitive to ion scavengers.

Other mechanisms are considered but excluded as incompatible with observed kinetics, the action of added small amounts of Xe and NO, and known energetics. The origin of tritiated products other than methane is discussed in terms of related mechanisms. It appears that the postulated processes can be extended to Wilzbach labelling reactions in general.

Echange auto-induit entre le tritium gazeux et le méthane. Dans ce mémoire, les auteurs étudient l'échange d'atomes de tritium entre du T_2 gazeux et du méthane, échange dû à la désintégration radioactive du tritium. Ce type d'échange est à la base de la méthode de marquage mise au point par Wilzbach.

Deux mécanismes distincts semblent entrer en jeu et ont été étudiés quantitativement. 1) La désintégration de l'un des atomes de T_2 donne du HeT^+, qui réagit rapidement sur le CH_4 pour donner un ion excité de CH_4T^+, lequel se décompose rapidement aussi pour donner du CH_2T^+. Il se forme ensuite du CH_3T par échange d'ions hydrure avec le CH_4. Ce mécanisme montre qu'il doit y avoir dépendance du premier ordre par rapport à la pression du T_2, et il n'est pas influencé par l'addition de gaz tels que le Xe, qui, en raison de leur faible potentiel d'ionisation, agissent en tant que balayeurs d'ions. 2) Les rayonnements bêta résultant de la désintégration du tritium produisent du CH_4^+ qui forme du CH_5^+ par collision avec une autre molécule de méthane. On considère que le CH_5^+ subit un échange avec le T_2 pour former du CH_4T^+ et, finalement, du CH_3T. Ce mécanisme fait apparaître dans l'équation cinétique un terme dépendant de la pression du tritium élevée à la puissance 3/2, et il est sensible aux balayeurs d'ions.

Les auteurs envisagent aussi d'autres mécanismes mais ils les excluent en raison de leur incompatibilité avec la cinétique observée, avec les effets de l'addition de petites quantités de Xe et de NO, et avec ce que l'on sait au point de vue énergétique. Ils étudient l'origine des produits tritiés autres que le méthane d'après des mécanismes apparentés. Il semble que les processus considérés puissent être étendus aux réactions de marquage de Wilzbach en général.

Индуктируемый обмен между газом трития и метаном. Проводится исследование обмена атомов трития между газом T_2 и метаном при индукции радиоактивным распадом трития. Этот вид обмена образует основу процесса индукции, разработанного Вильцбахом.

В докладе дается количественная оценка двум различным способам. 1) Распад одного из атомов в T_2 дает выход HeT^+. Этот вид быстро вступает в реакцию с CH_4 с тем, чтобы дать возбужденный ион CH_4T^+, который быстро разлагается до CH_2T^+. После этого образуется CH_3T путем обмена водородистого соединения с CH_4. Этот постулированный способ показывает требуемую зависимость первого порядка от давления T_2 и не поддается слиянию аддитивов, таких, как Xe, который благодаря своему слабому ионизационному потенциалу выступает в роли ионных очистителей. 2) Бета-излучение в результате распада трития дает CH_4^+, которая образует CH_5^+ при столкновении с другой молекулой метана. CH_5^+ затем постулируется с тем, чтобы пройти обмен с T_2 для образования CH_4T^+ и в конечном счете CH_3T. Этот способ вызывает особое условие в кинетике, которое влечет за собой 3/2 энергетической зависимости от давления трития и является чувствительным к ионным очислителям.

Рассматриваются также другие способы, но они исключаются ввиду своего несоответствия рассматриваемым кинетическим условиям, действию дополнительных незначительных количеств Xe и NO и известной энергетике. Рассмотривается происхождение насыщенных тритием продуктов, помимо метана, с точки зрения приведенных способов. Из доклада видно, что процесс постуляции в общем может распространяться на индикаторные реакции Вилцбаха.

Intercambio autoinducido entre el tritio gaseoso y el metano. Los autores han estudiado el intercambio de átomos de tritio entre el T_2 gaseoso y el metano, que es inducido por la desintegración radiactiva del tritio. El método de marcación de Wilzbach se basa en un intercambio de este tipo.

Al parecer intervienen dos mecanismos distintos, que los autores evalúan cuantitativamente. 1) La desintegración de uno de los átomos de la molécula de T_2 da lugar a HeT^+. Esta especie química reacciona rápidamente con CH_4, formando el ion excitado CH_4T^+, que se descompone al cabo de un buen tiempo, produciendo CH_2T^+. Seguidamente se forma CH_3T por intercambio de ion hidruro con el CH_4. El mecanismo propuesto por los autores corresponde a una función de primer grado de la presión del T_2, tal como se requiere, y no es afectado por la adición de gases como el Xe que, debido a sus bajos potenciales de ionización, actúan como depuradores de iones. 2) Las radiaciones beta procedentes de la desintegración del tritio dan lugar a CH_4^+, que forma CH_5^+ al chocar con otra molécula de metano. Se admite que el CH_5^+ sufre luego un intercambio con el T_2, para formar CH_4T^+ y, por último, CH_3T. Según este mecanismo, debe aparecer en la ecuación cinética un término que depende de la presión del tritio elevada a la potencia 3/2 y que es sensible a los depuradores de iones.

Los autores estudian también otros mecanismos, pero los descartan porque no son compatibles con la cinética observada, con el efecto producido por la adición de pequeñas cantidades de Xe y NO, y con los conocimientos que se poseen sobre la energética. Los autores examinan el origen de otros compuestos tritiados distintos del metano basándose en mecanismos similares. Al parecer, esos procesos pueden extenderse en general a todas las reacciones de marcación de Wilzbach.

Introduction

We have attempted to determine the mechanism of a simple ion-induced reaction in the gas phase. In this reaction the exchange of T_2 gas with methane is induced by the radioactive decay of the tritium and the beta-radiation associated therewith. The system can be represented by

$$T_2 + CH_4 \rightarrow CH_3T + \text{other labelled products.}$$

Interest in this type of system stems from two main sources. One is the growing pool of information on elementary ionic reactions in mass spectrometer ion sources. This provides some hope that one may be able to understand the more complex ionic reactions occurring in gaseous chemical systems at ordinary pressures in terms of the elementary processes found in the mass-spectrometer. The system methane—T_2 was chosen for investigation because it is still sufficiently simple for an essentially unique determination of the reaction path to be possible. This system also represents a simple case of the method of labelling developed by WILZBACH [1] in which tritium gas is mixed with the compound to be labelled. Despite several investigations [1—4], the mechanism of the self-induced tritium-exchange process remains somewhat doubtful.

The experimental approach used in the present investigation involved mixing small amounts of tritium gas with methane in heat-resisting glass bulbs. From time to time small aliquots were removed from each bulb; the labelled products were separated by gas chromatography and assayed by passage through an internal-flow proportional counter [5]. The proportions of reactants were varied from run to run, and in some samples small amounts of various other substances were added. In this manner the dependence of the rate of exchange on the concentration of tritium gas and on the presence of the noble gases, iodine and nitric oxide was determined.

In developing a mechanism for the exchange from these results it became necessary to consider certain possible ion-molecule reactions which had not previously been investigated. The criterion for predicting the direction of these reactions is that they must be exothermic, remembering also that resonant or near-resonant reactions have a higher cross-section than those in which there is a large energy-difference [6]. The heats of reaction, ΔH_r, for the ion-molecule reactions used in the discussion have been evaluated from the heats of formation of the ions [7—9]. The numbers to the right of the chemical equations in the discussion are the calculated ΔH_r values in units of kilocalories per mole with a negative sign indicating that the reaction is exothermic as written.

Experimental

PROCEDURES

The samples were prepared by expansion of the gaseous constituents in the order of increasing pressure into previously evacuated (<0.1 μm) sample bulbs. These samples were immediately analysed for tritium content and then allowed to stand for several days at ambient temperature. At successive time intervals aliquots were removed for separation and analysis by gas chromatography. The masses of the eluted constituents were monitored by a thermal-conductivity detector using thermistors in a Wheatstone bridge circuit. The lower limit of this apparatus was about 1 μM, and there was never observed a mass peak of any hydrocarbon except methane. The radioactivities of the eluted constituents were monitored by a method described earlier, which consists in mixing the effluent with methane and passing it directly into an internal-flow counter [5].

The sample vessels consisted of 30 cm^3 heat-resisting-glass spheres equipped with a capillary tee stopcock; see Fig. 1. This configuration allows one to extract an aliquot which is negligible compared with the whole, but adequate for analysis, by rotating the stopcock back and forth through 90°. The vacuum system was calibrated so that a known portion of a sample could be admitted to the gas

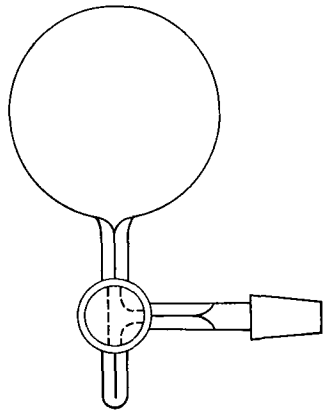

Fig. 1
Sample vessel.

chromatographic apparatus. Then from the number of observed disintegrations of tritium, the flow rates of the eluents, the volume of the counter and the fraction of the sample analysed, the concentration of the labelled reaction-products could be determined. It was found that the deviation in the reproducibility of this procedure was within 3%.

The substrates used in the gas chromatographic apparatus were (a) 40—60-mesh silica gel for the separation and analysis of hydrogen, methane, ethane, ethylene and acetylene; and (b) silicone oil (Dow Corning 703) on 40—60-mesh firebrick for the separation and analysis of the higher hydrocarbons. The aliquots were removed from the sample bulbs by expansion into a vacuum line and were injected into the gas-chromatographic apparatus by sweeping the line with helium. With this procedure, one would expect some fractionation of the higher boiling hydrocarbons; therefore, no quantitative results are taken for labelled hydrocarbons above the butanes even though hexanes and above were observed.

MATERIALS USED

Phillips Petroleum Co. "Research Grade" methane, stated to contain less than 0.04% impurities, was admitted to the vacuum line by a bulb-to-bulb distillation from liquid-nitrogen temperatures taking a centre cut from each of the three bulbs used. This procedure was used each time that a series of samples was prepared.

The tritium purchased from Oak Ridge National Laboratories was found to contain trace amounts of labelled hydrocarbons as well as its He^3 decay-product. These impurities were removed by diffusion of the tritium through the walls of a hot nickel tube [10]. Samples which contained no detectable labelled hydrocarbons at zero time could then be prepared. The manufacturers stipulated the tritium to be carrier-free; it is assumed to be in the form of T_2 when the samples are initiated.

Air Reduction Co. "Assayed Reagent Grade" noble gases were admitted to the samples without further purification. They were stipulated, by mass spectrographic analysis, to contain less than the following mole per cent impurities: Ne, 0.005%; Ar, 0.005%; Kr, 0.03%; and Xe, 0.01%. Matheson's regular-grade helium, stated to be of 99.99% purity, was admitted to the samples through a liquid-nitrogen trap.

Matheson's regular-grade nitric oxide, stated to be of 99.0% purity, was passed into a previously evacuated liquid-nitrogen trap from which a centre cut was slowly distilled into the sample vessel.

Baker and Adamson Co. "Reagent Grade" iodine was purified by vacuum sublimation into small heat-resisting-glass ampoules equipped with fragile break-off tips. These ampoules were inserted into the sample bulbs before filling; after the samples were prepared, the ampoules were broken open by vigorous shaking of the sample bulbs.

A further purification step was taken by the placing of a dry-ice trap at the entrance of the sample bulb. This prevented the mercury vapours of the vacuum system from entering the samples.

ENERGY ABSORPTION

DORFMAN [11] has shown that when the product of the radius of the spherical container and the gas density is 0.08 mg/cm², one half of the energy of the tritium-beta is absorbed. In the present investigation, the radii of the sample bulbs were 2.0 cm (30—31 cm³), in which case the methane "half-pressure" is calculated to be 41 mm Hg (at 25°C). All the samples were filled to a total pressure of 675 ± 3 mm Hg, except where noted in Table I; therefore, the absorption of energy is virtually complete. Since all the energy is absorbed, the initial step in the radiolysis of the methane, i.e. production of ions, radicals, etc., is dependent only on the concentration of tritium.

TABLE I

LIMITING RATES OF FORMATION OF LABELLED METHANE

No.	Additive	Pressure (mm Hg)	Tritium Activity, (a) (mc/cm³)	$\left(\frac{d\,CH_3T}{dt}\right)_0 \times 10^{-7}$ (mol./cm³ s)	R/R_d
1			0.15	0.47	0.84
2			0.90	6.88	2.1
3			1.8	12.7	1.8
4			2.4	29.6	3.4
5			3.1	43.8	3.8
6			5.6	107	5.2
7[b]			6.4	115	4.8
8[b]			8.7	168	5.4
9[c]			6.7	164	6.6
10[c]			5.6	121	5.8
11	He	14	4.2	74.6	4.8
12	Ne	12	1.5	27.0	4.8
13	Ar	10	1.4	20.0	3.8
14	Kr	20	1.8	28.2	4.2
15	Xe	31	1.2	1.17	0.27
16	Xe	27	3.8	4.59	0.34
17	Xe	27	7.1	10.4	0.40
18	Xe	6	6.9	9.95	0.40
19	I_2	(sat)	0.93	0.86	0.25
20	I_2	(sat)	1.2	1.22	0.27
21	I_2/Xe	(sat)/20	1.0	1.05	0.28
22	NO	20	2.8	< 0.36	< 0.036
23	NO	26	3.6	< 0.18	< 0.02
24	Xe/Ne	13/29	5.3	5.8	0.30

b Total pressure 327 mm Hg.
c Total pressure 153 mm Hg.

Results

The limiting rates of formation of labelled methane, reported in Table I, were determined by taking the slope of the concentration *vs.* time curves at zero time. These curves were of four types, and typical examples of these are

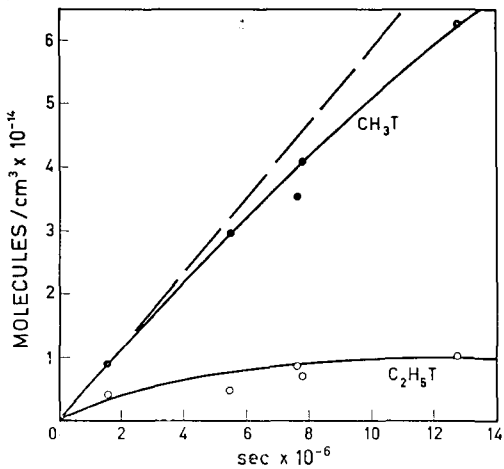

Fig. 2
Concentration of labelled methane and ethane *vs.* time in sample 2.
●: $[CH_3T]$, ○: $[C_2H_5T]$, Activity: 0.90 mc/cm³.

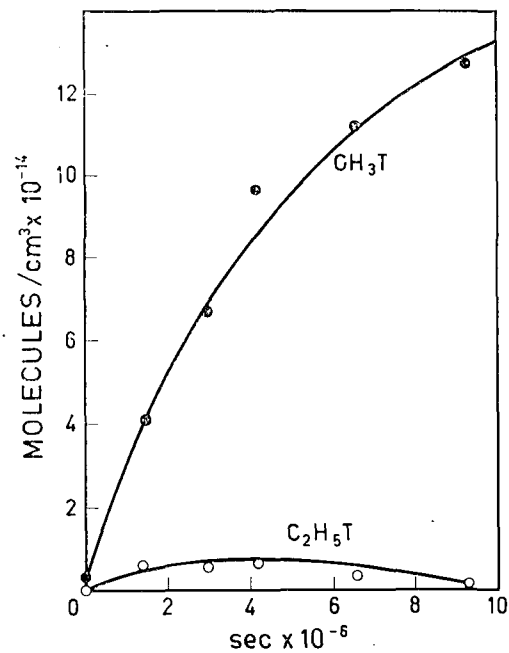

Fig. 3
Concentration of labelled methane and ethane *vs.* time in sample 12.
●: $[CH_3T]$, ○: $[C_2H_5T]$, Activity: 1.5 mc/cm³, Additive: Ne.

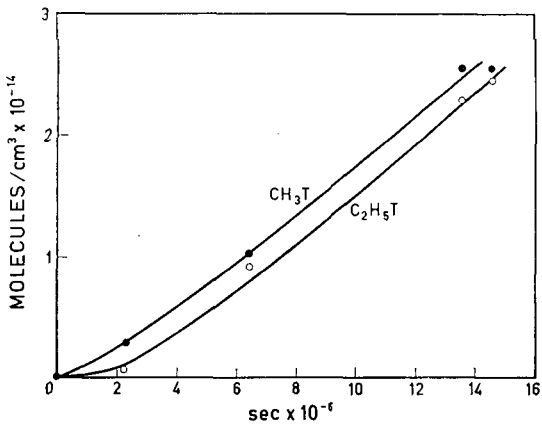

Fig. 4
Concentration of labelled methane and ethane *vs.* time in sample 15.
●: [CH_3T], ○: [C_2H_5T], Activity: 1.2 mc/cm³, Additive: Xe.

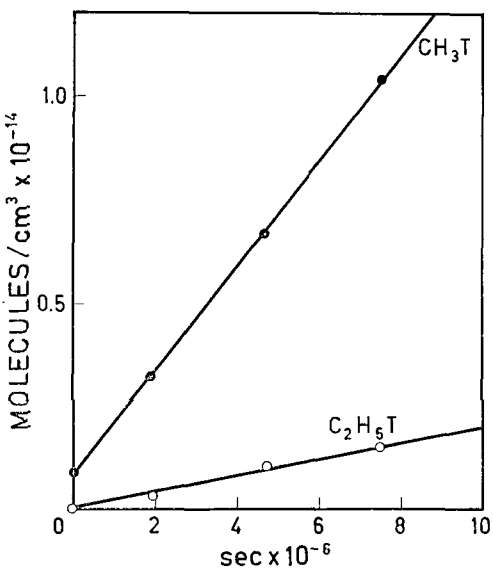

Fig. 5
Concentration of labelled methane and ethane *vs.* time in sample 20.
●: [CH_3T], ○: [C_2H_5T], Activity: 1.2 mc/cm³, Additive: I_2.

given in Figs. 2—5. Fig. 2 is representative of samples 1 to 10 inclusive where there is a slight decrease in the rate of production of labelled methane and ethane with time. Fig. 3 is representative of the samples containing noble gases with ionization potentials above that of methane, where there is a greater decrease in the rate of production of labelled methane with time, and the concentration of labelled ethane has a maximum value. Fig. 4 is representative of the xenon samples where there is an increase in the rate of production of labelled methane

and ethane with time. Fig. 5 is representative of the iodine samples where the rates of production of both labelled methane and ethane are constant with time. The iodine-plus-xenon sample is similar to the samples containing iodine only, Fig. 5; and the xenon-plus-neon sample is similar to the samples containing

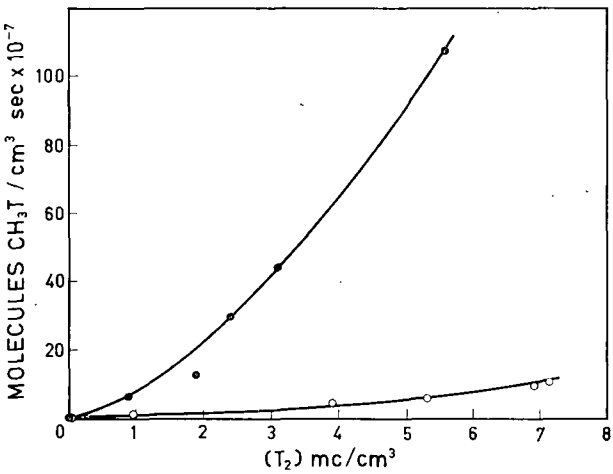

Fig. 6
Rate of formation of labelled methane *vs.* concentration of tritium.
●: unscavenged, ○: scavenged.

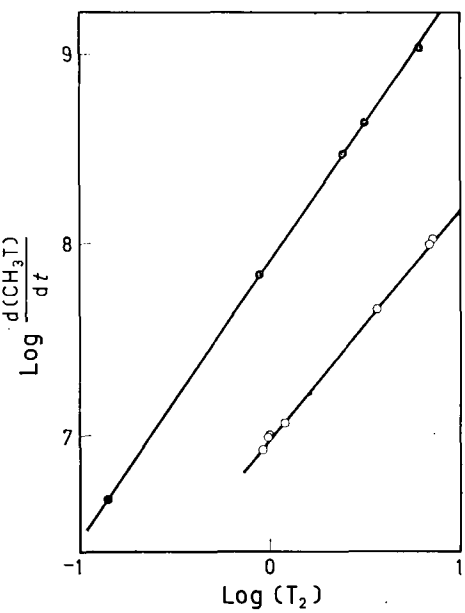

Fig. 7
Logarithm of the rate of formation of labelled methane *vs.* the logarithm of the tritium concentration.
●: unscavenged, ○: scavenged.

xenon only, Fig. 4. Since the detectable amounts of labelled methane and ethane in the nitric oxide samples were too small to monitor quantitatively, no plots were made; however, upper limits to the rates of production of labelled methane were determined and are reported in Table I.

A plot of the limiting rate of production of labelled methane *vs.* the activity of the tritium, Fig. 6, exhibits two distinct curves: one for samples 1—5 and another for samples 15—21. These samples and the resulting curves are termed unscavenged and scavenged, respectively. It is seen that xenon and/or iodine have the same quantitative effect in scavenging the reaction and that nitric oxide quenches the reaction almost completely. A plot of the logarithm of the rate of formation of unlabelled methane *vs.* the logarithm of the concentration of tritium, Fig. 7, results in a straight line for both scavenged and unscavenged samples. From the slopes and intercepts of these lines the following empirical rate equations are determined:

$$R_u = 8.0 \times 10^7 \, a^{1.50} \tag{1}$$

and

$$R_s = 9.3 \times 10^6 \, a^{1.20} \tag{2}$$

where R_u and R_s are the rates of formation of labelled methane in the unscavenged and scavenged samples respectively and a is the concentration of tritium in the sample in units of mc/cm^3. Expression (1) shows that the rate of production of labelled methane in the unscavenged samples is dependent on the 3/2 power of the tritium concentration. However, the 1.2 power of the tritium concentration in expression (2) suggests that there are two or more competing reactions which lead to labelled methane in the scavenged samples. A more convenient way to express this data is to calculate the ratios of the observed rates, R_u or R_s, to the rate of decay of tritium, R_d, in the sample. These ratios are given in Table I and plotted against the tritium concentration in Fig. 8. Here the scavenged

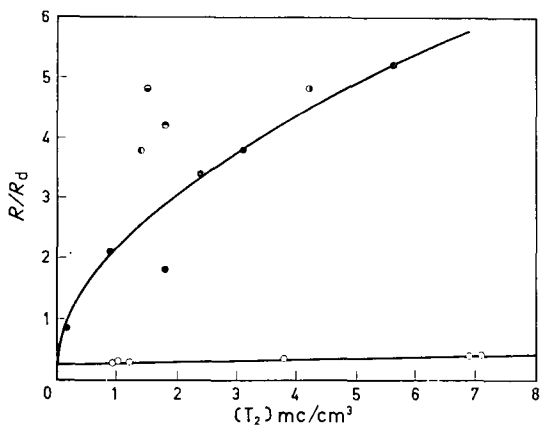

Fig. 8
R/R_d values *vs.* the tritium concentration.
●: no additive, ○: xenon and/or iodine added, ◑: He added, ◒: Ne added, ◐: Ar added, ◓: Kr added.
(R/R_d: Rate of exchange as fraction of rate of decay)

samples form a straight line with an intercept of 0.25 and a slope of 0.021, from which we obtain the expression

$$R_s/R_d = 0.25 + 0.021\ a. \tag{3}$$

Now, remembering that

$$R_d = 3.70 \times 10^7\ a \tag{4}$$

then

$$R_s = 9.2 \times 10^6\ a + 7.8 \times 10^5\ a^2 \tag{5}$$

which yields the same plots as Eq. (2) in Figs. 6 and 7, within the limits of experimental error. In other words, Eq. (2) can be reduced to the equivalent expression (5) in which the exponents of a are integers.

At this point, it is assumed that the reactions responsible for the labelling of methane in the scavenged samples also occur in the unscavenged samples as well. Therefore, the combination of Eqs. (1) and (5) forms the over-all empirical rate equation

$$R_u = 9.2 \times 10^6\ a + 7.4 \times 10^7\ a^{3/2} + 7.8 \times 10^5\ a^2 \tag{6}$$

which is an equivalent expression for (1), within the limits of experimental error.

Labelled hydrocarbons up to and including the C_6's have been observed as reaction products. All these hydrocarbons were saturated except in the samples containing iodine, in which case labelled ethylene was also detected. Table II gives the distribution of products in terms of the number of tritium disintegrations observed in a typical sample, normalized to the same initial tritium concentration, time, and 100000 counts of methane in an unscavenged sample.

TABLE II
DISTRIBUTION OF LABELLED HYDROCARBON PRODUCTS

Additive	No. in Table I	CH_4	C_2H_6	C_2H_4	C_3H_8	*iso*-C_4H_{10}	n-C_4H_{10}	CH_3I
none	2	100000	44800	0	8020	2400	3500	—
Xe	15	12400	3240	0	2190	88	960	—
I_2	19	11900	2360	2710	191	86	192	1980
$Xe + I_2$	20	13300	2280	1500	182	55	158	3500

The experimental error in the determination of the number of counts observed as a constituent passes through the flow counter is $\pm 4\%$. This is due to the accuracy with which the flow of the eluting gas was determined. An error analysis of the calibration of the analytical vacuum system showed that the determinations would be expected to have a precision with an error within $\pm 3\%$ and a standard deviation in the absolute accuracy of 30%. An error of this nature would of course be reflected in the magnitudes of the rate constants but would not change the nature of the following arguments since the relative concentrations of all radioactive constituents would be the same.

Discussion

Eq. (6) indicates that there are at least three separate mechanisms by which methane can be labelled. Two classes of reactions must be considered: (a) The initiating species is HeT^+ formed by the decay of T_2 [3] [4] [12]. This is termed the decay-induced mechanism. (b) The initiating species is produced

by the self-irradiation of the mixture with the tritium beta-rays. This is termed the irradiation-induced mechanism.

Thus we have three initiating steps:

$$T_2 \xrightarrow{-\beta^-} HeT^+$$

for the decay-induced† mechanism, and

$$CH_4 \rightsquigarrow$$
$$T_2 \rightsquigarrow$$

for the irradiation-induced mechanism. It will be shown that these initiating steps each give rise to a term in the empirical rate equation (6).

1. Decay-induced mechanism

A mechanism accounting for the first term in Eq. (6) must be consistent with the first-order concentration of tritium, scavenging by NO, but no scavenging by Xe and I_2. The rate of production of HeT^+ is first-order in tritium. Now, if the subsequent reactions of this species lead to labelled methane with the same probability at all dose rates, then the over-all kinetics will be first-order. It is therefore postulated that the formation of HeT^+ is rate-determining. This species must have a short lifetime in methane since, if not, it would be scavenged by rare-gas additives in exoergic reactions of the type:

$$HeT^+ + G \rightarrow GT^+ + He$$

HeT^+ probably reacts in the first few collisions with methane.

$$HeT^+ + CH_4 \rightarrow (CH_4T^+)^* + He \quad -89 \leqslant \Delta H_r \leqslant -67 \qquad (7)$$

This reaction is quite exothermic, and it is likely that the $(CH_4T^+)^*$ thus formed is highly excited. Its probable lifetime can be evaluated by using the Kassel model of unimolecular dissociation [14], from

$$K_E = A\,(1 - E_0/E)^{r-1} = \frac{1}{T}$$

Approximating $A \sim 10^{14}$, $(r-1) \sim 7$, $E_0 \sim 50$ and $E \sim 70$ we have that $T \sim 10^{-11}$ s, which is an order of magnitude less than that of molecular collision. Therefore the $(CH_4T^+)^*$ will dissociate — probably by the reaction

$$(CH_4T^+)^* \rightarrow CH_2T^+ + H_2 \quad 29 \leqslant \Delta H_r \leqslant 44 \qquad (8)$$

We now consider two possible mechanisms for the conversion of CH_2T^+ to CH_3T. They are denoted *IA* and *IB*.

Mechanism IA

In the mass spectrometer CH_2T^+ ions will rapidly react with methane by the reaction

$$CH_2T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2 \quad \Delta H_r = -20 \qquad (9)$$

† Gant and Yang have used the term "recoil labelling" to describe the postulated interactions of HeT^+. This term has previously been applied [13] to the chemical reactions of high-energy tritium atoms recoiling from nuclear reactions. We find it somewhat misleading to use the same term to describe the reaction of HeT^+, which has no significant recoil-energy.

There is no direct evidence from mass spectrometry on the further reaction of $C_2H_5^+$ with methane; but it is energetically possible for the $C_2H_4T^+$ ion to react further with methane to yield higher labelled-hydrocarbon ions. However, these higher hydrocarbon ions must have correspondingly longer lifetimes or else, once the chain is initiated, the reaction will continue rapidly to give polymer. The radiation chemistry of methane shows that the yield of higher hydrocarbons decreases with the number of carbon atoms [15]. In this study it was found that the longer the carbon chain, the smaller was the yield of the labelled hydrocarbon; see Table II. It is therefore to be expected that the lifetime of the $C_2H_4T^+$ ion would be sufficiently long for neutralization processes to become significant. If this is the case, then the reaction

$$C_2H_4T^+ + e^- \rightarrow CH_2T\cdot * + CH_2{:}* \quad \Delta H_r = -134 \tag{10}$$

would yield a hot $CH_2T\cdot *$ radical. By virtue of its excess energy this could then suffer an exchange reaction with methane to yield labelled methane; viz.,

$$CH_2T\cdot * + CH_4 \rightarrow CH_3T + CH_3\cdot \quad \Delta H_r \approx 0 \tag{11}$$

If the tritium remains with the CH_2* fragment, then labelled ethane could result from the reaction

$$CHT{:}* + CH_4 \rightarrow C_2H_5T \quad \Delta H_r = -61 \tag{12}$$

Although the lifetime of $C_2H_4T^+$ is postulated to be long, no effect of xenon or iodine scavenging is expected since the charge-transfer reactions (electron or proton) of this ion with xenon and/or iodine are all endothermic. This is in accord with the experimental result that reactions which give rise to the first-order term in (6) are not affected by xenon or iodine. However, scavenging of these reactions by nitric oxide is observed. This could be due to

$$C_2H_4T^+ + NO \rightarrow C_2H_4TNO^+ \quad \Delta H_r \sim 0$$

which is exothermic unless the heat of formation of $C_2H_5NO^+$ differs from that of CH_3NO^+ by some 64 kcal/mole, which is unlikely. ($\Delta H_f(CH_3NO^+) = 184$ kcal/mole [7].)

Mechanism IB.

An alternative mechanism can be postulated for the decayinduced labelling of methane, which involves hydride ion transfer [8] to CH_2T^+,produced in (8), viz.,

$$CH_2T^+ + CH_4 \rightarrow CH_3^+ + CH_3T \quad \Delta H_r \sim 0 \tag{13}$$

If (13) is to account for the labelling, it must compete successfully with (9) and the CH_2T^+ ion must have a lifetime long enough to be scavenged by nitric oxide. It is possible that the CH_3^+ ions produced from methane by electron impact are in different energy-states from the energy states of those produced by other processes. If this is the case, then the CH_2T^+ ion produced in (8) may suffer several collisions with the surrounding molecules before any reaction occurs, while CH_3^+ ions produced by the irradiation of the methane will react on first collision to yield $C_2H_5^+$, as they do in the mass spectrometer. On this hypothesis, the scavenging properties of xenon, iodine and nitric oxide can easily be accounted for. Scavenging by xenon would not be expected because the charge-transfer

reaction to xenon from CH_2T^+ is endothermic. The scavenging of nitric oxide could be due to the reactions

$$CH_2T^+ + NO \rightarrow NO^+ + CH_2T\cdot \quad \Delta H_r = -18$$
$$CH_2T\cdot + NO \rightarrow \text{scavenged products.}$$

Scavenging by iodine, through charge transfer from CH_2T^+, is energetically favourable; but this term in the rate equation is not scavenged by iodine. Even though the concentration of I_2 is 30-fold less than that of NO, the absence of such a scavenging effect casts some doubt on the mechanism *IB* and would favour mechanism *IA* instead.

The maximum rate of formation of labelled methane by the above mechanisms is the decay rate of tritium; i.e. no more than 1 CH_3T can result per HeT^+ formed. However, one would expect that CH_2T^+ would be produced by (8) in only 60% of the events, neglecting isotope effects. Since the $C_2H_4T^+$ ion would also lead to the formation of labelled higher hydrocarbons, e.g. reaction (12), the 0.25 intercept of the R_s/R_d *vs.* activity curve, Fig. 8, is not unreasonable. The decay-induced mechanisms, reactions (8) to (13), are thus compatible with experiment in view of the observations of first-order kinetics, scavenging by nitric oxide, no scavenging by xenon and/or iodine, and production of labelled higher hydrocarbons.

The above decay-induced mechanisms are not unique for the production of CH_3T from HeT^+, and several other alternatives have been considered but discarded as improbable. For example, the HeT^+ could react with methane by an electron rather than a proton transfer, i.e.

$$HeT^+ + CH_4 \rightarrow CH_4^+ + He + T\cdot * \qquad -37 \leqslant \Delta H_r \leqslant -7$$

to give a T* with about 1 eV of excess energy.

$$T\cdot * + CH_4 \rightarrow CH_3T + H\cdot$$

The latter reaction, however, is unlikely since SCHWARTZ, WILLIAMS and HAMILL have shown [16] that it does not occur with 1—2-eV hydrogen atoms.

II. RADIATION-INDUCED EXCHANGE

The second term in the kinetic expression (6) is also believed to be due to ion-molecule reactions. The data indicating this are the scavenging action of xenon, which eliminates this term, and the 3/2 power dependence of the tritium concentration. The significance of the latter becomes apparent in development of the kinetics of a general reaction mechanism involving exchange with radiation-produced ions.

The concentration of ions originating in the radiolysis of methane and eliminated primarily by neutralization is governed by the rate of production

$$CH_4 \overset{k_1}{\sim\!\sim\!\sim\!\rightarrow} \text{ions}^+ + e^-$$

and neutralization

$$\text{ions}^+ + e^- \xrightarrow{k_2} \text{uncharged products or intermediates.}$$

(A homogeneous reaction is assumed, since the lifetime of an ion does not permit migration to the walls. This can be shown by comparison of the diffusion rate as calculated by SCHAEFFER and THOMPSON [9] with the recombination lifetime

estimated by the method of STEVENSON [17].) Invoking the steady-state condition and assuming that there are no doubly charged ions,

$$\frac{\mathrm{d}(\mathrm{ion}^+)}{\mathrm{d}t} = k_1(\mathrm{T}_2) - k_2(\mathrm{ion}^+)(\mathrm{e}^-) = 0;$$

then, since

$$(\mathrm{ion}^+) = (\mathrm{e}^-),$$

$$(\mathrm{ion}^+) = \sqrt{\frac{k_1}{k_2}}(\mathrm{T}_2),$$

If exchange then occurs involving a rate-determining step of the type

$$\mathrm{ion}^+ + \mathrm{T}_2 \xrightarrow{k_3} \mathrm{CH_3T\ precursor}, \tag{14}$$

then

$$\frac{\mathrm{d}(\mathrm{CH_3T})}{\mathrm{d}t} = k_3(\mathrm{ion}^+)(\mathrm{T}_2) = k_4(\mathrm{T}_2)^{3/2}$$

where $k_4 = k_3\sqrt{k_1/k_2}$, which is the form of Eq. (1)*.

It is difficult to postulate any type of reaction, other than tritium-exchange with ions whose lifetime is electron-recombination-limited, which gives the right form of kinetic expression and could account for scavenging. Although it is thus very probable that this class of mechanism accounts for the 3/2 power-term in Eq. (6) in a unique manner, a determination of the exact ion or ions involved cannot be made with the same degree of assurance.

The ions which are formed by the action of the betas on the methane and their relative abundances may be assumed to be similar to those produced in the mass spectrometer [18]. This is justified by the fact that virtually all the ionization of the methane is caused by low-energy electrons or delta-rays. The rate of production of ions in the CH_4—T_2 system can be calculated with an average beta-ray energy of 5.69 keV and an energy-requirement per ion pair of 26.8 eV [19]. The rate of production of ions, I, comes to 7.8×10^9 ions/mc s or $7.8\times10^9 a$ ions/cm^3 s. Considering the 3/2 power-term of Eq. (6) and using $a = 5$ mc/cm^3, it is seen that the relative abundance of the ion or ions responsible for this term must exceed 2%. The most abundant ions in the mass spectrum of methane are 51% CH_4^+, 40% CH_3^+, and 4% CH_2^+.* We may therefore limit our considerations to these ions, and possible other ions formed by their reaction with methane.

The charge-exchange of CH_2^+ and CH_3^+ with xenon is energetically unfavourable. Thus, even if their lifetime is long enough to permit reaction (14) to occur, it would be difficult to account for the observed xenon-scavenging.

The CH_4^+ ion can exchange with T_2[8] by

$$\mathrm{CH_4^+ + T_2 \rightarrow CH_4T^+ + T\cdot} \qquad -14 \leqslant \Delta H_\mathrm{r} < 0 \tag{15}$$

and it can also be scavenged by xenon by

$$\mathrm{CH_4 + Xe \rightarrow Xe^+ + CH_4} \qquad \Delta H_\mathrm{r} = -23$$

However, the competing reaction with methane

$$\mathrm{CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3\cdot} \qquad -18 \leqslant \Delta H_\mathrm{r} \leqslant -3 \tag{16}$$

* This conclusion is contrary to a statement of GANT and YANG [4]. that the amount of labelling caused by the radiation *per decay* should increase linearly with T_2-concentration, i.e., that the *total* radiation-induced labelling should be second-order in the concentration of T_2.

has a rate-constant which is two orders of magnitude larger than in (15) [8]. Furthermore, the concentration of CH_4 is larger than that of T_2 by a factor of 10^4—10^5. Therefore, we may exclude reaction (15) as a significant factor in the exchange.

The lifetime of the CH_5^+-ion formed in Eq. (16) is thought [20] to be limited only by its rate of recombination with electrons. We may thus postulate the following exchange:

$$CH_5^+ + T_2 \xrightarrow{k_5} CH_4T^+ + HT \tag{17}$$

$$CH_4T^+ + CH_4 \rightarrow CH_5^+ + CH_3T \tag{18}$$

The proton-transfer reaction (18) is a familiar type of ion mechanism [8], but there is no precedent for exchange reaction (17). However, if we assume that it is the rate determining step for the 3/2 term in the kinetic expression (6), its activation energy may be estimated. This is done by comparing the rate law for this mechanism with the second term of the rate equation (6).

$$\frac{d(CH_3T)}{dt} = k_5 (CH_5^+)(T_2) = 7.4 \times 10^7 (T_2)^{3/2}$$

To approximate (CH_5^+), we take the relative abundance of the ions in the mass spectrum of methane [20] and assume that all CH_4^+ react to yield CH_5^+. Then, from the rate of production of the ions and the rate of neutralization we estimate $(CH_5^+) = 4.44 \times 10^7 \alpha_2^{\frac{1}{2}}$ ions/cm^3. From this, a value of k_5 of 1.6×10^{-6} cm^3/mol. s is obtained. Comparing this with the prediction from transition-state theory of a value of 10^{-14} to 10^{-13} for the pre-exponential factor of a reaction of a linear with a non-linear molecule, we can approximate the activation energy as being 2—4 kcal/mole. The value thus obtained on the basis of regular "non-sticky" collision kinetics is perhaps unexpectedly low, although there is very little relevant information on which such a judgment can be based. This suggests that CH_5^+ and T_2 may form an ion cluster, such as has again been postulated recently [9] [21] [22].

Charge exchange of CH_5^+ with Xe, NO, and I_2 is exoergic, and its concentration should therefore be negligible in the presence of these species. This accounts for the observed scavenging of the 3/2 power-term in Eq. [6].

Many other specific mechanisms of type (14) may be considered since other types of ions, both known and unknown, may be present in sufficient abundance. However, we have not been able to establish any more satisfactory medium for this exchange than the CH_5^+ exchange (17) and (18). Thus CH_3^+ produced by electron impact has been shown (e.g., [8]) to react rapidly with CH_4 to produce $C_2H_5^+$.

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad \Delta H_r = -20 \tag{19}$$

A sequence involving $C_2H_7^+$ (e.g., [9])

$$C_2H_5^+ + T_2 \rightarrow C_2H_5T_2^+ \quad \Delta H_r = +20 \tag{20}$$

$$C_2H_5T_2^+ + e^- \rightarrow CH_3T \quad \text{precursor} \tag{21}$$

might be possible if it were not for the fact that (20) appears exoergic. We have considered and discarded a number of such mechanisms.

III. Exchange of radiation-activated tritium

Another series of reactions which could produce labelled methane is a possible sequence initiated by the action of the betas, or secondary electrons, on tritium molecules. Such a mechanism would yield a kinetic expression dependent on the square of the tritium concentration. The square term in the empirical rate equation (6) could be ascribed to a mechanism involving initiation-reactions of this type. However, there are other mechanisms (discussed below) which may also be used to explain the square dependence.

IV. Radical and other mechanisms

Kinetic considerations show that reactions involving free radicals produced by the irradiation of the methane are not likely to be involved in the production of labelled methane. Mechanisms involving the reaction of these radicals with tritium to yield a CH_3T precursor in a rate-determining step lead to kinetic expressions of the form

$$\frac{d[CH_3T]}{dt} = k[T_2]^n$$

when a steady-state condition is invoked. If the steady-state concentration of radicals is limited by a second-order process such as radical-radical recombinations, then $n=3/2$; but if it is limited by a first-order process, such as diffusion to the walls, then $n=2$. If, however, first and second-order processes compete, then $2 \geqslant n \geqslant 3/2$, neglecting zero and/or third-order processes. With this in mind, it is difficult to imagine radical mechanisms which could lead to the first-order term in the empirical rate equation (6). It is also unlikely that the 3/2 term in (6) is due to radical reactions, since such a mechanism could not account for the scavenging by xenon.

In the case of excited states, $n=2$ if one supposes that the steady-state concentration of excited methane is limited by a first-order decay of the excitation and that there are no significant second-order mechanisms by which the excitation can be quenched. It is therefore unlikely that the linear and/or 3/2 term in (6) are due to excited states. However, the square term may be explained by reactions involving radicals or excited states or, as mentioned earlier, exchange with radiation-activated tritium.

V. Higher products

In discussing at some length the exchange to give CH_3T, we have so far largely ignored the formation of higher-labelled hydrocarbons. The production of the latter can readily be rationalized by invoking ion-condensation reactions such as (9). However, not enough is known about the elementary processes involved to make it possible to decide the relative importance of a large number of possible reaction-paths.

VI. Secondary reactions

It is obvious that as the reaction proceeds and products accumulate the system becomes too complex for meaningful analysis. The decrease in the rate of formation of methane with time (Figs. 2 and 3) could be due to (a) the dilution of the T_2 by the HT formed as a reaction product, and/or (b) the formation of reaction products of low ionization potentials (e.g. C_2H_6, C_3H_8) which act as ion scavengers. The increase in the rate of formation of labelled methane with time in the

xenon samples (Fig. 4) is probably due to a secondary reaction which is not itself scavenged by xenon.

The increases in the initial reaction rate caused by the addition of He, Ne, Ar or Kr (Fig. 8) could be due to the reaction

$$GT^+ + CH_4 \rightarrow CH_4T^+ + G \qquad \Delta H_r < 0$$

where G is one of the noble gases mentioned above. The origin of the GT^+ ion molecule is, however, unknown.

VII. Other systems

Several other tritium-hydrocarbon systems have been investigated [2—4] with the aim of studying the exchange mechanism rather than merely labelling compounds. However, the only extensive kinetic investigation is that of Gant and Yang [4] for the tritium-ethylene system. A rate expression derived from their data exhibits a first and a second-power term in the tritium concentration. The first-power term is ascribed to the exchange of HeT^+ with ethylene:

$$HeT^+ + C_2H_4 \rightarrow C_2H_3T + HeH^+$$

or to the reaction of energetic tritium atoms produced by its neutralization

$$HeT^+ + e^- \rightarrow He + T^*$$

We find it difficult to accept either of these mechanisms. The neutralization mechanism is slow and so, most probably, is the exchange. These reactions would probably not be able to compete with the rapid charge-transfer that must be expected.

$$HeT^+ + C_2H_4 \rightarrow C_2H_4T^+ + He \qquad -83 \leqslant \Delta H_r \leqslant -79 \tag{22}$$

A resonant proton-transfer reaction can then yield labelled ethylene.

$$C_2H_4T^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_3T \tag{23}$$

(The $C_2H_4T^+$ formed by (22) has sufficient excitation energy so that it may dissociate before the next collision. If so, the following reactions will intervene between (22) and (23)

$$C_2H_4T^+ * \rightarrow C_2H_2T^+ + H_2$$
$$C_2H_2T^+ + C_2H_4 \rightarrow C_2H_4T^+ + C_2H_2$$

The latter of these has been identified in the mass spectrometer [8].)

The second-power term in the tritium concentration is apparently in accord with a mechanism involving radiation-activated tritium. However, the system appears too complex to establish a unique and detailed mechanism. Nevertheless, this term appears analogous with the similar one in the tritium-methane exchange.

The tritium-ethylene reaction does not exhibit a 3/2-power term. This suggests that ethylene itself is acting as a scavenger so that there are no long-lived ions (or radicals) in the system which can react with tritium to yield labelled ethylene.

This comparison between methane and ethylene points up the differences that may be expected between systems. The mechanism types postulated are probably generally applicable, but their particular modes and relative importance will vary greatly depending on the molecules involved. In view of the scarcity of relevant information on elementary ion-molecule processes it will be difficult to ascribe detailed and unique mechanisms to more complex systems.

Conclusions

(1) Three general types of mechanisms for the exchange between T_2 and CH_4 have been identified.

(a) The decay-induced mechanism which is first-order in the concentration of T_2 and may be described by the process

$$T_2 \rightarrow HeT^+ + e^-$$
$$HeT^+ + CH_4 \rightarrow CH_3T \text{ precursor.}$$

(b) Exchange of tritium with a radiation-produced ion, the lifetime of which is recombination limited. This leads to a 3/2-order term in the concentration of T_2 and may be described by the process

$$CH_4 \sim\sim\sim\rightarrow ion^+ + e^-$$
$$ion^+ + T_2 \rightarrow CH_3T \text{ precursor.}$$

(c) Exchange of a radiation-activated tritium species which is second-order in the concentration of tritium.

(2) For the decay-induced mechanism the following sequence is likely to occur:

$$HeT^+ + CH_4 \rightarrow CH_4T^{+*} + He$$
$$CH_4T^{+*} \rightarrow CH_2T^+ + H_2$$
$$CH_2T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2$$
$$C_2H_4T^+ + e^- \rightarrow CH_2T.^* + CH_2^*$$
$$CH_2T^* + CH_4 \rightarrow CH_3T + CH_3\cdot$$

or

$$CH_2T^+ + CH_4 \rightarrow CH_3^+ + CH_3T$$

(3) For the exchange of tritium with a radiation-produced ion, the following specific sequence is postulated:

$$CH_4 \sim\sim\sim\rightarrow CH_4^+ + e^-$$
$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3\cdot$$
$$CH_5^+ + T_2 \rightarrow CH_4T^+ + HT$$
$$CH_4T^+ + CH_4 \rightarrow CH_5^+ + CH_3T$$

(4) The general types of mechanisms, as given in Conclusion (1), are applicable to the exchange of T_2 with other systems. In this sense the results of this work can be applied to T_2 exchange with other compounds to provide general mechanisms for Wilzbach labelling. However, with larger molecules the knowledge of the ions present, their state of excitation and their reactivity is so fragmentary as to make assignment of unique and detailed reaction-paths for the exchange process very difficult.

ACKNOWLEDGEMENTS

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DISCUSSION

N. A. Ghanem (United Arab Republic) suggested that in a kinetic study of electrical gaseous discharge in tritium it might be advantageous to employ a microwave discharge in which all conceivable reactive entities were produced. It would then be possible to take the target material away from the plasma zone and put it in a side section of the tube, where only free radicals could reach it in sufficient concentration, owing to their longer life. It would be even better to place electrodes between the plasma zone and the side tube and apply to them a potential of known sign, thereby eliminating the positive or negative ions as desired. That would facilitate detection of the entities responsible for the tritiation reaction. He and his associates had carried out some work in that connection and the results were reported in the paper by himself and T. WESTERMARK*.

R. Wolfgang agreed that reactions between molecules and ions and other energetic species could certainly be best studied when the source of ionization or excitation was separated from the reaction zone. If, however, the procedure involved the use of a solid as the second reactant species, two complications arose which might outweigh the simplification gained by separating the system in that way. Firstly, substances of relatively high molecular weight would have to be used, and it was far more difficult to interpret the kinetics of complex molecules than of simple gaseous molecules. Secondly, it would be necessary to study reactions at a surface, and it was notoriously difficult to keep surfaces clean and reproducible. A more desirable technique would be to produce the ions in a standard ion source,

* *These proceedings* **III** 43.

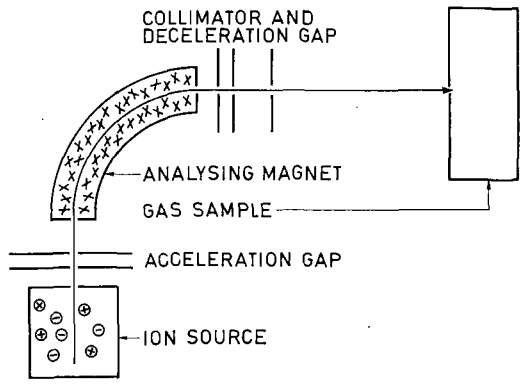

Fig. 9
Technique for studying reactions between molecules and ions

accelerate them and analyse them magnetically (*cf.* Fig. 9). Such well-controlled ionic species could then be passed through a small orifice into a chamber containing the gas with which they were to react. By using such a technique, one knew exactly what one was working with; moreover, the reaction systems one had to study were inherently simple.

SOME SYMMETRICAL HALOGEN AND METHOXY EXCHANGE REACTIONS IN AROMATIC SYSTEMS

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Abstract — Résumé — Аннотация — Resumen

Some symmetrical halogen and methoxy exchange reactions in aromatic systems. Isotopic tracers are essential in the study of the kinetics of symmetrical nucleophilic substitution reactions at an aromatic carbon atom.

The iodine exchange between iodo-nitro-aromatic compounds and iodide ions in acetone or methanol solution has been studied both qualitatively and quantitatively by labelling the iodide ions with iodine-131. The reaction mixture is sampled at convenient time intervals, the two reactants separated by toluene-water extraction, and the progress of the reaction ascertained by beta-counting with a liquid Geiger counter. Measurements have been extended to "carrier-free" concentrations of iodide ions.

The preparation of certain nitro-methoxy-aromatic compounds, labelled with carbon-14 in the methoxy group, is described. Symmetrical methoxy exchange reactions of these compounds with methoxide ions, in methanol solution, have been studied. After separation of the reactants (from samples of the reaction mixture taken at convenient time intervals) by toluene-water extraction, the aromatic compounds are recovered and their specific activities determined by beta-scintillation counting with a plastic phosphor.

In the discussion of the experimental data, special attention is paid to the effect of ionic strength on the specific rate of the reaction. Comparison is made with ionic strength effects observed in symmetrical biomolecular nucleophilic reactions at a saturated (aliphatic) carbon atom, and reference is made to certain other aromatic nucleophilic substitution reactions.

Quelques réactions symétriques d'échanges d'halogènes et de groupes méthoxyles dans les composés aromatiques. Les indicateurs radioactifs sont indispensables pour l'étude cinétique des réactions symétriques de substitution nucléophilique dans l'atome carbone de aromatique.

L'échange d'iode entre des composés iodo-nitro-aromatiques et des ions iodure dissous dans de l'acétone ou du méthanol a été étudie à la fois quantitativement et qualitativement par marquage des ions iodure à l'iode-131. Le mélange réactif a été échantillonné à des intervalles appropriés, les deux phases séparées par extraction à l'aide de toluène et d'eau, et les progrès de la réaction contrôlés par un comptage bêta fait avec un compteur Geiger pour liquides. Les mesures ont été effectuées également pour des concentrations d'ions iodure «sans entraîneur».

Les auteurs du mémoire décrivent ensuite la préparation de certains composés nitro-méthoxy-aromatiques marqués au carbone-14 dans le groupe méthoxyle, ainsi que les réactions symétriques d'échange de groupes méthoxyles entre ces composés et des ions méthoxydes dans une solution de méthanol. Après séparation des produits en réaction (échantillons du mélange réactif prélevés à des intervalles appropriés) par extraction au moyen de toluène et d'eau, les composés aromatiques sont récupérés et leur activité spécifique est déterminée par comptage bêta avec un scintillateur en matière plastique.

En analysant les données obtenues, les auteurs accordent une attention particulière aux effets de la force ionique sur la vitesse spécifique de réaction. Ils les comparent aux effets de la force ionique observés dans les réactions nucléophiliques bimoléculaires symétriques sur un atome de carbone (aliphatique) saturé et se réfèrent à certaines autres réactions de substitution nucléophilique dans les composés aromatiques.

Симметрические реакции с галоидным и метоксидным обменом в ароматических системах. Изотопные индикаторы незаменимы при изучении кинетики реакций с нуклиофильно-симметрическим замещением при ароматическом атоме углерода.

Обмен йода между йодо-нитро-ароматическими соединениями и ионами йодида в ацетоновом или метаноловом растворе изучался как с качественной, так и количественной точек зрения посредством мечения ионов йодида йодом-131. У смеси реакции при определенных интервалах времени брались образцы, два реактанта разделялись толуоловодной экстракцией, а ход реакции определялся бета-отсчетом жидкостного счетчика Гейгера-Мюллера. Измерения распространялись также на „свободные от носителя" концентрации ионов йодида.

Приводится описание приготовления некоторых нитро-метокси-ароматических соединений, меченных углеродом-14 в метоксиновой группе. Приводится исследование реакций симметрического метоксинового обмена этих соединений с метоксидными ионами в метановом растворе. После отделения реактантов (из образцов смеси реакции, взятых через удобные интервалы времени) с помощью толуоло-водной экстракции извлекаются ароматические соединения, а их удельная активность определяется бета-сцинтилляционным счетом с пластмассовым фосфором.

При рассмотрении экспериментальных данных уделялось особое внимание влиянию ионной интенсивности на удельную скорость реакции. Дается сравнение с влиянием ионной интенсивности, наблюдаемой в симметрических бимолекулярных нуклеофильных реакциях при насыщенном (алифатическом) атоме углерода; приводится ссылка на некоторые другие ароматические нуклеофильные реакции замещения.

Algunas reacciones simétricas de intercambio de halógenos y grupos metoxilo en compuestos aromáticos. Los trazadores isotópicos son indispensables para el estudio de la cinética de las reacciones simétricas de sustitución nucleofílica en los átomos de carbono aromáticos.

Con ayuda de iones yoduro marcados con yodo-131, los autores estudiaron cualitativa y cuantitativamente el intercambio de yodo entre compuestos yodo-nitro-aromáticos e iones yoduro disueltos en acetona o metanol. A intervalos de tiempo apropiados, tomaron muestras de la mezcla, separaron los reactivos por extracción con tolueno y agua y estudiaron el curso de la reacción por recuento beta en un contador Geiger para líquidos. Extendieron el intervalo de medición hasta concentraciones de iones yoduro libres de portador.

Los autores describen seguidamente la preparación de ciertos compuestos nitro-metoxi-aromáticos marcados con carbono-14 en el grupo metoxilo. Estudiaron reacciones simétricas de intercambio de grupos metoxilo entre estos compuestos e iones metoxilo disueltos en metanol. Después de separar los reactivos (en muestras de la mezcla tomada a intervalos adecuados) por extracción con tolueno y agua, recuperaron los compuestos aromáticos y determinaron sus actividades específicas por recuento mediante un fósforo de plástico.

Al analizar los resultados experimentales, dedican particular atención a la influencia ejercida por la fuerza iónica sobre la velocidad específica de reacción. Establecen comparaciones con los efectos de la fuerza iónica observados en las reacciones simétricas nucleofílicas biomoleculares en un átomo de carbono (alifático) saturado, y mencionan algunas otras reacciones de sustituciones nucleofílicas en compuestos aromáticos.

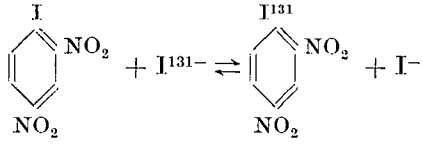
1. Introduction

In aromatic systems the delocalized π-electrons make the molecules susceptible to attack by a reagent which has orbitals available to accept electrons and which often bears a formal positive charge. It was from studies of this type of reaction that the electronic effects of substituents first became recognized, and a great deal of attention has been paid to electrophilic substitution in aromatic compounds; indeed, the term "aromatic substitution" is often used synonymously for "aromatic electrophilic substitution". Almost always the group displaced is hydrogen.

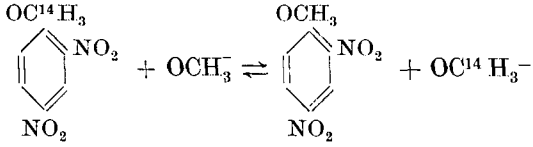
A nucleophilic attack, where the reagent wishes to share its electrons, can occur readily in aromatic molecules only when the screening π-cloud is partly removed by an electron-attracting substituent (e.g., the nitro group) suitably placed in the ring from the vicinity of the carbon atom under attack. Even then facile substitution requires that the group displaced has some potential anionic stability when, to complete the reaction, it separates with the electron pair formerly binding it to carbon. Hydrogen is, therefore, rarely displaced unless an oxidizing agent is present to produce water instead of the unstable hydride ion.

Most of the activated aromatic nucleophilic substitutions studied so far show second-order kinetics (first-order in each reactant); and, for these, two types of mechanism have been suggested. One is a simple one-step process, and the other involves two stages with the formation and decomposition of an intermediate of some stability. Although there has been much discussion on the relative merits of these mechanisms, little attention has been paid to the careful collection of compelling evidence (as was done for aliphatic nucleophilic substitution); and, as is often the case in kinetic studies, too few experimentally determined parameters to describe all the possible effects are available.

Symmetrical exchange reactions (i.e., those where the reagent and the displaced group are chemically identical) can often serve as useful systems in the study of reaction mechanism but have been rarely used in aromatic nucleophilic substitution. The systems chosen for our initial studies in this field were the iodine exchange between 2:4-dinitro-iodobenzene and labelled iodide ions:



in acetone solution, and the methoxy exchange between labelled 2:4-dinitro-anisole and methoxide ions:



in methanol solution. The seat of reaction is, of course, activated by the presence of two nitro groups, and the exchange proceeds at a speed amenable to measurement at convenient temperatures. 2:4-dinitro-anisole, labelled with carbon-14 in the methoxy group, is easily prepared, purified and stored; this compound, rather than the methoxide ion, was therefore labelled for the study of the exchange reaction.

2. Preparation of materials

Acetone

"Analar" acetone was further purified by refluxing over solid sodium hydroxide and potassium permanganate (40 g of each per two litres acetone) for three hours, distilling off with the exclusion of moisture and fractionating from fresh quantities of potassium permanganate and sodium hydroxide.

Methanol

Ethanol and acetone were removed by their reaction with iodine and sodium hydroxide to form iodoform. After filtration the filtrate was refluxed to destroy any iodoform left in solution and was then twice fractionated.

Potassium iodide

This was recrystallized from acetone and dried under vacuum at 120° C immediately before use.

Sodium methoxide

Clean sodium was roughly weighed in toluene, dried on filter paper, washed briefly in methanol and then dissolved in purified methanol in a flask provided with a reflux condenser and soda-lime guard tube. The methoxide solution was standardized by titration with sulphuric acid, with phenolphthalein as indicator, and diluted to the required concentration with methanol.

Carrier-free I^{131} solution

This was obtained, as iodide ions, in weak thiosulphate solution from The Radiochemical Centre, Amersham, United Kingdom. Approximately 0.3-mc portions were evaporated to dryness, extracted with acetone and evaporated to dryness, extracted with acetone and evaporated to dryness once more and the residue finally dissolved in pure acetone.

2:4-dinitro-iodobenzene

This was prepared by diazotizing 2:4-dinitroaniline and reacting with potassium iodide in water. It was purified by chromatography from benzene solution on an alumina column and crystallized; mp 88°C.

2:4-dinitro-anisole (methyl C^{14})

1 ml methanol was added to 0.6 g of clean metallic sodium, and the mixture was cooled in ice water until the reaction had subsided. 5 ml labelled methanol, containing approximately 0.1 mc of C^{14}, were then added and the mixture refluxed for three hours and then allowed to stand overnight at room temperature.

4 ml of this labelled methoxide solution were added to 3.5 g of recrystallized (methanol) 2:4-dinitro-chlorobenzene together with a further 3 ml methanol. The mixture was warmed for 10 min and then allowed to cool. The almost solid mass was diluted with 50 ml water and acidified with 2*N* hydrochloric acid; the crystals were filtered off. The filtrate was extracted with benzene, and the solid obtained by evaporation was combined with the crystals. This combined product was then recrystallized from a mixture of benzene and petroleum ether. Yield 3.1 g, mp 89°C.

3. General procedure for kinetic studies

The iodine exchange reaction was followed by the mixing of 20.0 ml each of standard solutions of potassium iodide and 2:4-dinitro-iodobenzene in acetone, allowing the mixture to come to temperature equilibrium in a thermostat, and injection of 1.0 ml of carrier-free I^{131-}-ions at the same temperature. After thorough mixing, the solution was sampled at suitable times by rapidly adding 2.0 ml to a mixture of 20.0 ml of distilled water and 10.0 ml of toluene. This was then shaken thoroughly and the two layers separated. The toluene layer was washed with 4.0 ml of water, and the washings were combined with the previous aqueous extract. This combined aqueous portion was then made up to 25.0 ml in a graduated flask.

The toluene and aqueous solutions were then each counted in a liquid Geiger counter of the type described by VEALL [1].

It may readily be shown, for this reaction, that:

$$2.303 \log \left[1 - \frac{x}{b} \frac{(a+c)}{a}\right] = -(a+c)\,kt,$$

where a, b and c are the initial concentrations of 2:4-dinitro-iodobenzene, I^{131} ions and I^-ions, respectively, and x is the concentration of I^{131} in the form of the aromatic iodide at time t. Thus, the specific rate, k, may be found from the slope of a plot of $\log \left[1 - \frac{x}{b} \frac{(a+c)}{a}\right]$ against t.

The ratio x/b is that of the activity of I^{131} in the toluene layer to the total activity of the sample (i.e., toluene plus aqueous solutions). However, before counting data can be used, corrections must be made for the relative volumes of the two solutions and the different efficiencies with which the beta-particles of I^{131} are counted in toluene and the denser aqueous solution. The latter correction was made by comparison of the counting rates of the two solutions with the liquid Geiger counter and with a gamma-scintillation counter (where absorption by the solution was negligible); the particular Geiger counter used was approximately 20% more efficient for counting I^{131} in toluene than in aqueous solution.

The ratio x/b was, therefore, readily expressed in terms of counting data.

The methoxy exchange was followed by a mixing of the reactants (which had previously been brought to temperature in a thermostat) and assaying samples at convenient times. The samples were quickly transferred to a mixture of toluene and water and, after separation, the toluene layer was washed and a portion of it evaporated on an aluminium planchette to give an evenly deposited source of C^{14}-labelled 2:4-dinitro-anisole less than 1 mg/cm^2 in thickness. This was normally counted with a beta-scintillation counter, using a plastic phosphor (type NE 102, Messrs. Nuclear Enterprises Ltd.) of approximately 1 mm thickness. A thin end-window Geiger counter is also suitable, although less efficient; and this was occasionally used.

In deriving the kinetic equation for this reaction, allowance must be made for the rapidly established equilibrium between the solvent (methanol) and the methoxide ion. It may readily be shown that:

$$2.303\,[\log a - \log (a - x)] = kbt,$$

where b and a are the initial concentrations of methoxide ions and labelled 2:4-dinitro-anisole, respectively, and x is the concentration of labelled methoxide

ions present at time t. The specific rate may, therefore, be found from the slope of the plot of log $(a - x)$ against t.

The observed specific activity (i.e., counts per minute per mg) of the 2:4-dinitro-anisole samples is a measure of $(a - x)$, thus enabling k to be found from counting data. It is not easy, however, to produce a completely even layer of the sources for counting, and it is desirable that as many samples as possible (certainly not less than 12) should be taken for each determination of specific rate. The precision attained is not as high as for the iodine exchange reaction, and is probably no better than with an error of $\pm 10\%$.

4. Discussion

The iodine exchange reaction (Table I) shows a marked increase in specific rate as the concentration of the source of iodide ions, potassium iodide, is reduced. A similar salt effect was reported by EVANS *et al.* [2] for certain symmetrical halogen exchange reactions between alkyl halides and halide ions. These authors ascribe the effect to the increased dissociation of the source of halide ions in the more dilute solutions.

TABLE I

IODINE EXCHANGE BETWEEN 2:4-DINITRO-IODOBENZENE AND IODIDE IONS IN ACETONE SOLUTION
(Concentration of 2:4-dinitro-iodobenzene = 0.01 M)

Temperature (°C)	Conc. KI (M)	Specific Rate (l/g mol./s)
44.0	0.0196	12.3×10^{-5}
44.0	0.0098	14.8×10^{-5}
44.0	0.0098	15.1×10^{-5}
44.0	0.00196	27.2×10^{-5}
44.0	"carrier-free"	31.6×10^{-5}
45.0	"carrier-free"	37.9×10^{-5}
37.6	0.0195	7.38×10^{-5}
37.6	0.0182	6.93×10^{-5}
37.6	0.00975	8.55×10^{-5}
37.6	0.00909	8.76×10^{-5}
37.6	0.00195	13.0×10^{-5}
37.6	0.00181	12.6×10^{-5}
30.0	0.0196	3.86×10^{-5}
30.0	0.00833	4.29×10^{-5}
30.0	0.00196	5.47×10^{-5}
20.0	0.0190	1.54×10^{-5}
20.0	0.00952	1.51×10^{-5}
20.0	0.00833	1.55×10^{-5}

This type of salt effect was examined by BROADBANK [3], who distinguished between those sources of halide ions (e.g., ammonium iodide, lithium bromide) which appear to be weak electrolytes in acetone or methanol and those (e.g., sodium, potassium or tetraethylammonium iodides) which appear to be strong. The salt effect shown by the latter group was explained on the basis that the solvation of an ion is increased when the solution in which it is situated is diluted. Solvation should be taken into account in the halogen exchange reaction, which is not simply:

$$X^- + RX \rightleftharpoons (\text{Transition State})^- \rightarrow \text{Products, but rather:}$$

$$X^- \times S_n + RX \times S_m \rightarrow (\text{Transition State})^- S_p + (n + m - p)\, S.$$

Here S represents a solvent molecule, and n, m and p are the solvation numbers of the entities concerned. Because the charge is spread in the transition state over a larger volume than in X^-, p will be smaller than n; and since RX has no net charge, m will be still smaller and, to a first approximation, negligible. Thus, the formation of the transition state involves the desolvation of approximately $(n - p)$ solvent molecules. If now the concentration of the source of halide ions is decreased, both n and p will increase; but, since X^- is smaller than the transition state, the increase in n will be greater than that in p. The factor $(n - p)$ will thus increase, which means that more solvent molecules will be "set free" during the formation of the transition state. There is thus, during the activation process, a larger increase in entropy in the solution of lower salt concentration than in that of higher salt concentration. This results in a higher value for the term A of the Arrhenius Equation:

$$k = A\, e^{-E/RT}$$

for the more dilute solution.

The activation energy of the reaction will also be affected, since the increase in solvation resulting from the decrease in salt concentration will lower the energy of X^- more than that of the transition state. The activation energy will thus be higher for the more dilute solution.

Changes in the specific rate of the reaction will, therefore, be made up of two opposing factors: an increase in A tends to increase the value of k, and an increase in E tends to decrease it. This was observed for the racemization of optically active sec-octyl iodide by iodide ions [3]; for example, in acetone solution the values of E and $\log A$ increase from 17.9 kcal/g mol. and 10.2, respectively, with 0.015 M iodide ions to 19.3 kcal/g mol. and 11.4, respectively, with 0.001 M iodide ions.

TABLE II

IODINE EXCHANGE BETWEEN 2:4-DINITRO-IODOBENZENE AND IODIDE IONS IN ACETONE SOLUTION—ARRHENIUS PARAMETERS (Concentration of 2:4-dinitro-iodobenzene: 0.01 M)

Conc. KI (M)	E (kcal/g mol.)	$\log A$
0.002	21.3	11.2
0.010	17.5	8.3
0.020	16.1	7.2

The changes in E and $\log A$ for the iodine exchange between 2:4-dinitro-iodobenzene and iodide ions, reported in Table II, are considerably greater and may possibly be associated with a larger volume over which the charge can spread in the transition state of the aromatic nucleophilic substitution. On the other hand, the specific rates for the methoxy exchange reaction in methanol, given in Table III, show little evidence that the salt effect is operating although the values for 0.0023 M methoxide lie slightly above the Arrhenius plot. BAMFORD [4] has studied the nucleophilic substitution of a nitro group by methoxide, in methanol solution, in a series of dinitrobenzenes and dinitro-

TABLE III

METHOXY EXCHANGE BETWEEN 2:4 DINITRO-ANISOLE AND METHOXIDE IONS IN METHANOL SOLUTION
(Concentration of 2:4 dinitro-anisole = 0.025 M)

Temperature (°C)	Conc. Na OCH_3 (M)	Specific Rate (l/g mol./s)
44.8	0.0023	19.5×10^{-3}
36.8	0.023	7.77×10^{-3}
36.5	0.023	6.50×10^{-3}
28.8	0.023	3.69×10^{-3}
20.0	0.023	1.43×10^{-3}
20.0	0.0023	2.00×10^{-3}

An Arrhenius plot of these figures yields a value for E of approx. 16.5 kcal/g mol. and for log A of approx. 9.7.

naphthalenes, and in no case is any salt effect of this type evident. Possibly the spreading of charge in the transition state occurs to a much smaller extent when the methoxide ion is involved, or possibly the behaviours of potassium iodide and sodium methoxide as electrolytes in acetone and methanol, respectively, are in some way different. Clearly, considerably more experimental data are required before an explanation of this type of salt effect can be given with any confidence.

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PRELIMINARY EXPERIMENTS ON THE USE OF RADIOACTIVE INDICATORS IN MACROMOLECULAR CHEMISTRY

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Abstract — Résumé — Аннотация — Resumen

Preliminary experiments on the use of radioactive indicators in macromolecular chemistry. In studies of osmotic phenomena with high polymers, two causes of error are particularly important:

(a) Diffusion of low-molecular-weight polymers across the membrane;

(b) Polymer adsorption on the membrane.

For investigations on both these phenomena radiotracer methods present decisive advantages over the classical and far less sensitive gravimetric procedures.

The polymer used in the authors' experiments was a hetero-disperse sample of (poly) chloro-butyl acrylate which was ionically chlorinated with Cl^{36} starting from a sample of (poly)butyl acrylate. This polymer was dissolved in acetone.

Diffusion chambers similar to twin-cell osmometers were set up.

Cellophane membranes with permeabilities of 6.7×10^{-5} h^{-1} to 30.6×10^{-5} h^{-1} separated the solution from the solvent. It was found that:

(a) With our apparatus, about two hundred hours were necessary to reach an equilibrium or steady state in diffusion experiments;

(b) The fraction of polymer diffusing through the membrane in a given time was independent of the concentration;

(c) The amount of polymer diffusing was related to the permeability of the membrane;

(d) A practically irreversible adsorption of polymer on the membrane was observed (30 to 40 μg/cm^2).

Expériences préliminaires sur l'utilisation des indicateurs radioactifs en chimie macromoléculaire. Dans les études sur les phénomènes osmotiques avec de hauts polymères, deux causes d'erreurs sont particulièrement importants:

a) La diffusion des polymères de faible poids moléculaire à travers la membrane;

b) L'adsorption des polymères sur la membrane.

Pour les recherches sur ces deux phénomènes, la méthode des radiotraceurs présente des avantages décisifs par rapport aux procédés gravimétriques classiques, beaucoup moins sensibles.

Le polymère utilisé dans les expériences des auteurs était un échantillon à dispersion hétérogène acrylate de (poly) chloro-butyle, obtenu par chlorruation ionique d'un échantillon d'acrylate de (poly)butyle avec du chlore-36. Ce polymère était dissous dans de l'acétone.

On a utilisé des chambres de diffusion analogues aux osmomètres à cellules jumelles. Des membranes de cellophane de perméabilité $6{,}7 \cdot 10^{-5}$ h^{-1} à $30{,}6 \cdot 10^{-5}$ h^{-1} séparaient la solution du solvant.

On a constaté:

a) Qu'avec l'appareil utilisé dans les expériences de diffusion, il fallait environ deux cents heures pour atteindre un état d'équilibre ou un état stationnaire;

b) Que la fraction de polymère se diffusant à travers la membrane dans un temps donné était indépendante de la concentration;

c) Que la quantité de polymère diffusé variait en fonction de la perméabilité de la membrane;
d) Qu'il se produisait une adsorption pratiquement irréversible du polymère sur la membrane (30 à 40 $\mu g/cm^2$).

Предварительные опыты использования радиоактивных индикаторов в макромолекулярной химии. При изучении осмотических явлений с использованием высоких полимеров особое значение представляют две причины ошибок:

a) диффузия низкомолекулярных полимеров через мембрану;
b) адсорбция полимера на мембране.

Для исследования обоих этих явлений метод радиоактивных индикаторов представляет несомненные преимущества над обычными и гораздо менее чувствительными весовыми методами.

В проведенных авторами доклада опытах был использован гетеродисперсный образец полимера (поли)-хлоробутилакрилата, который был хлорирован с помощью Cl^{36} посредством ионизации, исходя из образца (поли)-бутилакрилата. Этот полимер растворяется в ацетоне.

Были построены диффузионные камеры, аналогичные двуячеечным осмометрам.

Раствор отделялся от растворителя целофановыми мембранами, обработанными так, чтобы давать проницаемость от $6{,}7 \times 10^{-5}$ ч$^{-1}$ до $30{,}6 \times 10^{-5}$ ч$^{-1}$

Было найдено, что:

a) с нашим оборудованием понадобилось около 200 часов для того, чтобы в опытах диффузии достичь равновесия или устойчивого состояния;
b) доля полимера, диффундирующая через мембрану в определенный промежуток времени, не зависит от концентрации;
c) количество диффундирующего полимера зависит от проницаемости мембраны;
d) наблюдалась почти необратимая адсорбция полимера на мембране (30—40 $\mu g/см^2$).

Ensayos preliminares sobre el empleo de indicadores radiactivos en química macromolecular. Las dos principales fuentes de error cuando se estudian fenómenos osmóticos con polímeros de elevado peso molecular son:

a) la difusión de polímeros de bajo peso molecular a través de la membrana;
b) la adsorción de polímeros en la membrana.

Los métodos que emplean trazadores radiactivos para la investigación de estos dos fenómenos ofrecen ventajas decisivas sobre los procedimientos gravimétricos clásicos, que son mucho menos sensibles.

El polímero empleado por los autores consistió en una muestra heterodispersa de policloroacrilato de butilo obtenido por cloración iónica del poliacrilato de butilo con ^{36}Cl. Este polímero se utilizó disuelto en acetona.

Los autores emplearon cámaras de difusión semejantes a osmómetros de células gemelas.

La solución quedaba separada del disolvente por membranas de celofán de permeabilidades de $6{,}7 \times 10^{-5}$ h^{-1} a $30{,}6 \times 10^{-5}$ h^{-1}.

Han llegado a las conclusiones siguientes:

a) con el aparato empleado en los experimentos de difusión, se precisan unas 200 horas para alcanzar un estado de equilibrio o un régimen estacionario;
b) la fracción de polímero que difunde a través de la membrana en un tiempo determinado es independiente de la concentración;
c) la cantidad de polímero que se difunde depende de la permeabilidad de la membrana;
d) se observa una adsorción prácticamente irreversible del polímero en la membrana (30 a 40 $\mu g\ cm^2$).

1. Introduction

The functions of the membrane in the establishment of the osmotic equilibrium are not as yet fully understood. Moreover, it is well known that, in the case of an imperfectly semipermeable membrane, the deviation of the membrane itself from ideality is one of the principal sources of error. The source of uncertainty in the interpretation of the thermodynamic phenomena in such a non-ideal case would appear to be due to a diffusion of low-molecular-weight solute components across the membrane [1]. More refined analyses [2—4] have sought to deduce thermodynamically the contribution of each species in a heterogeneous polymer solution to the steady state attained in short-time and in long-time osmotic measurements. The distribution of the permeating solute species between the solvent and solution phases in an osmotic experiment is of primary importance in these analyses.

We have noticed in the course of our work with polymers of high molecular weight, using osmometers of large surface-to-volume ratio, an adsorption effect which, under certain circumstances, attained a value of approximately 50% of the solute present in the solution. A simple thermodynamical analysis of the process of adsorption of solute from solution on to liquid solid interfaces indicates that there is a change in the entropy of the system upon adsorption, though quantitatively the changes may be complex [5] [6]. The importance of the adsorption effect in a given solvent-membrane system appears, quite generally, to be a direct function of the molecular weight of the solute and an inverse function of the concentration of the solution.

Our experiments were designed to furnish us with preliminary indications as to methods of measurement of the diffusion effect and as to the reproducibility, and to indicate qualitatively the reversibility and, finally, the order of importance of the adsorption effect.

2. Experimental

The diffusion and adsorption experiments were carried out in simple glass, twin-cell chambers with equal volumes on both sides of the membrane. It must be stressed that these were not osmometers but only diffusion chambers, the membrane being subjected to some elastic deformation under the excess osmotic pressure (balloon effect) and the volume changes involved in attaining the osmotic steady state not being negligible.

The membranes were commercial dry cellophane sheets with permeabilities adjusted by various treatments, according to methods previously developed in this and other laboratories [7—9]. Their permeabilities were measured in modified Fuoss-Mead type osmometers with no balloon effect, as developed by us. The permeability, which we define as being an amount of liquid which passes across a unit membrane surface per unit of time and per unit of pressure difference, is expressed as follows:

$$P = \text{Permeability} = \frac{f}{F} - \frac{\ln (h_t/h_0)}{t - t_0} \ (\text{h}^{-1})$$

where f = cross-section of the measuring capillary,
F = surface area of the membrane,
t = time of measurement (in hours) and

h_0, h_t = height difference between the liquid levels on either side of the membrane at time $t=t_0$ and $t=t$ respectively.

The polymer used in these measurements was a heterodisperse sample of (poly)chloro-butyl acrylate which was ionically chlorinated with Cl^{36} starting from a sample of (poly) butyl acrylate*. The polymer was dissolved in acetone. The marked polymer is constituted as follows:

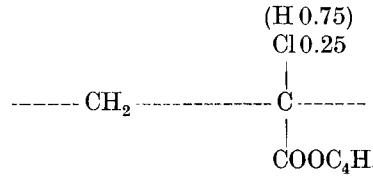
Total chlorine content = 65 mg Cl/g of polymer;

Specific activity = 0.28 μc Cl^{36}/g of polymer;

Degree of substitution (D.S.), i.e. atoms of Cl per monomer unit, = 0.25.

$$\text{Ratio of } \frac{Cl^{36}}{Cl} = 1{,}9 \cdot 10^{-4}$$

The structure to be assigned to the monomer units is, therefore:



The solvent used was acetone, distilled from acidified $KMnO_4$, redistilled over molecular sieves under an atmosphere of N_2 and finally distilled under N_2. It has a density of 0.78483 g/cm³ at 25°C, the temperature at which all measurements were carried out.

The recuperation of diffused polymer was carried out by recovering the liquid in the solvent chamber, which was scrupulously rinsed, and evaporating all the recovered liquid in a cupped aluminium planchet which revolved about its axis at a constant speed, under infra-red lamps. The final drying was carried out in a vacuum chamber.

The recovered samples were counted either with a thin end-window Geiger tube or with a scintillation counter, using plastic crystals. All counts were carried out relative to a series of standard samples (generally the same volume of solution at a concentration equal to that in the solution chamber, for each experiment).

3. Results and discussion

Adsorption

The phenomenon binding the polymer to the membrane is, in our experiments, probably composed of two parts, adsorption and absorption; under these conditions of measurement it is impossible to separate the two. Table I shows the results of a series of sorption measurements, expressed as the amount of polymer (in 10^{-6} g) associated with the membrane as a function of the treatment undergone by the membrane. The salient feature of the results cited is that the phenomenon of association of the polymer to the membrane is, in this system, only partially reversible. Membranes 4 and 5 have undergone very stringent rinsing procedures and are still found to be associated with some polymer.

No adsorption isotherms can be constructed from this type of experiment because of the difficulty of establishing a significant rinsing procedure, and isotherms of this type appear to be best obtained by analysing the residual con-

* See Acknowledgement at the end of this paper.

TABLE I

POLYMER SORPTION ON TO MEMBRANES (CELLOPHANE No. 300)

Membrane No.	1	2	3	4	5
Concentration of solution $\times 10^{-3}$ g/ml	1.92	1.92	1.92	1.92	1.92
Period of contact with solution	336 h	336 h	336 h	336 h	336 h
Number of rinses	4	4	7	10	30
Total period of rinses	1 h	1 h	2.5 h	24 h	172 h
Q = amount/cm^2 of solute remaining on the membrane $\times$ g $\times 10^{-6}$	34 ± 3	37 ± 3	40 ± 3	29 ± 2	14 ± 2

centration of a solution which has been in contact with a large membrane surface, assuming a similar solute concentration in the free solution and in the solution occluded in the interior of the membrane.

DIFFUSION

Fig. 1 shows the establishment of an equilibrium curve of the percentage of solute diffused across cellophane membranes as a function of the time of diffusion. Every point is the result of a fresh diffusion equilibrium, representing the percentage of solute recovered from the solvent chamber of the diffusion cell for the first diffusion of a fresh solution. Different concentrations of solution have been used, and it will be noted that the points lie about an equilibrium curve, the plateau of which is attained after about 200 h. The membranes in question are cellophane No. 300 A, membranes with permeabilities of $P = 9.0 \times 10^{-5}$ h^{-1}. Fig. 1 also shows the amounts diffused across other membranes, with permeabilities different from those on the line, relative to the equilibrium line established. It is easily seen that the amounts of solute diffused across the membranes are functions of the permeabilities of the membranes in question.

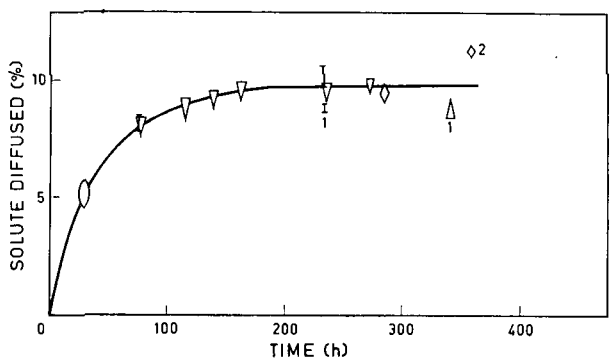


Fig. 1

% of solute diffused *vs.* time of diffusion.

Membranes 1:	cellophane 600 A	Concentrations of solutions
	$P = 6.7 \times 10^{-5}$ h^{-1}	$\triangle = 0.906 \times 10^{-3}$ g/ml
Membrane 2:	cellophane 300 B	$0 = 1.709 \times 10^{-3}$ g/ml
	$P = 30.6 \times 10^{-5}$ h^{-1}	$\triangledown = 1.915 \times 10^{-3}$ g/ml
Other membranes:	cellophane 300 A	$\mathrm{I} = 3.774 \times 10^{-3}$ g/ml
	$P = 9.0 \times 10^{-5}$ h^{-1}	$\langle\rangle = 6.290 \times 10^{-3}$ g/ml

TABLE II

DIFFUSION OF SOLUTE ACROSS MEMBRANES

Cell I Membrane: Cellophane No. 300 A
(Concentration of solution: 1.915×10^{-3} g/ml)

Solvent sample	1	2	3	4	5	6	Residue	Membrane	Total
Diffusion time (h)	115	168	193	99	66	104	746	746	—
% of solute diffused	8.7 ± 0.5	5.4 ± 0.6	3.8 ± 0.2	1.4 ± 0.2	0.9 ± 0.2	1.0 ± 0.2	74.9 ± 1.6	0.8 ± 0.4	96.9 ± 2.2

Cell II Membrane: Cellophane No. 300 A
(Concentration of solution: 1.915×10^{-3} g/ml)

Solvent sample	1	2	3	Residue	Membrane	Total
Diffusion time (h)	162	99	140	401	—	—
% of solute diffused	9.5 ± 0.5	5.0 ± 0.5	3.5 ± 0.5	78.2 ± 1.6	1.9 ± 0.9	98.1 ± 2.1

Cell III Membrane: Cellophane No. 300 A
(Concentration of solution: 3.774×10^{-3} g/ml)

Solvent sample	1	2	3
Diffusion time (h)	65	240	144
% of solute diffused	8.2 ± 0.3	6.8 ± 0.2	3.5 ± 0.1

Cell IV Membrane: Cellophane No. 600 A
(Concentration of solution: 3.774×10^{-3} g/ml)

Solvent sample	1	2
Diffusion time (h)	237	240
% of solute diffused	8.8 ± 0.2	6.0 ± 0.3

Thus, the permeation for the membrane No. 300 B ($P=30.6\times10^{-5}\,h^{-1}$) lies above the equilibrium line and those for the membranes No. 600 A ($P=6.7\times10^{-5}\,h^{-1}$) lie below the line. The errors of measurement are too large to permit the establishment of a quantitative relationship between the permeation and the permeability of the membranes, but the qualitative relationship appears to be confirmed. The close association of the points at different concentrations for equi-permeable membranes with the equilibrium line in Fig. 1 indicates that the fraction of solute diffused across a given membrane, at equilibrium, is independent of the initial concentration of solute in the solution cell. The volume changes involved in the establishment of the osmotic steady-state in these experiments do not permit any conclusions as to the effect of solute concentration in the solvent cell on the establishment of this diffusion equilibrium.

Table II shows some typical diffusion measurements obtained by replacing the solvent in the solvent chamber with fresh solvent after the intervals of time indicated in the table. The diffusion is not necessarily at equilibrium at the moment of measurement. The diffusion data reproduced in Fig. 1 are the results of the first diffusion in a number of such experiments. The equilibrium distribution of permeating solute between the two chambers is expressed by STAVERMAN [2] as follows:

If both cells have an equal volume $= V$, the total amount of polymer present is CV, where C is the concentration of polymer in the solution. Of this polymer, a part, $(1-r)\,CV$, has a high molecular weight and cannot permeate, while a fraction rCV can permeate. A fraction αrCV of this passes into the solvent cell, leaving $(1-\alpha)\,rCV$ on the solution side. The quantity measured in our experiments is given by $\alpha rCV/CV$, which appears to tend to a constant value, independent of the initial concentration of the solution. Since for a given membrane-solute system r is a constant, it appears that α is a constant, independent of the concentration. The direct verification of this, the ratio $\alpha/(1-\alpha)$ was not measured in this series of experiments on account of the sizable statistical experimental errors involved in these preliminary trials and of the character of the diffusion cells.

4. Conclusions

The experiments carried out have been used mainly as pathfinders to develop more precise methods of measurement.

They have, however, permitted the following conclusions:

(a) The diffusion equilibrium for a given membrane-solute system tends to be a constant value as a function of time, and the approach to equilibrium is independent of any concentration factor;

(b) The distribution of permeating solute about a membrane is dependent on the permeability of the membrane; and

(c) The association of polymer with the membrane appears to be practically irreversible.

These conclusions are only valid in so far as the statistical distribution of the Cl atoms along the polymer chain at a degree of substitution less than unity is independent of the degree of polymerization, an investigation which remains to be carried out.

ACKNOWLEDGEMENT

We wish to thank M. Constant of C.E.N. Mol, who very kindly evolved the method of measuring permeability and carried out the labelling for us.

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DISCUSSION

G. Park (United Kingdom) said that, as had been indicated, the diffusion of the smallest solute molecules gave rise to a very important error. The technique outlined by Mr. Stein gave a direct measure of the total mass of diffused polymer. By the use of labelled initiators or transfer agents it was possible to estimate the total number of molecules diffused; if a double labelling method were tried, it would be possible to estimate both the number and the mass of solute molecules diffused through the membrane and to calculate directly the error in the number average molecular weight determined by the osmotic method.

R. Stein thanked Mr. Park for his suggestion and added that the normal method of correcting for the diffusion was to extrapolate the osmotic pressure to zero time, after measuring the fall in the osmotic pressure difference. However, according to the theory of Staverman, an error was introduced into the number average molecular weight by the very fact that the molecules could diffuse. Thus, their thermodynamic contribution, even if they had not diffused, was abnormally low. In other words, the technique of extrapolation to zero time, after measurement of the diffusion, was in itself incorrect.

B. E. Gordon (United States of America) said he thought that the irreversible adsorption found by the authors was probably due to a M. W. effect, such as had recently been described in the literature dealing with the polyisobutylene/carbon system. In that case, the membrane was acting as a fractionating medium and it was in effect the lower M. W.-fractions that were being studied.

R. Stein said it was obvious that the membrane acted as a fractionating system. The study had been based on that assumption and the intention was, naturally, to verify, if possible, Staverman's theory and his so-called "Reflection" coefficient. The phenomena under investigation had two different components—the diffusion and the "adsorption"—and in the case in question the two were inseparable. The next step would be to study the thermodynamic contribution of the adsorbed polymers to the entropy of the system.

STEREOCHEMISTRY AND RADIOCHEMISTRY OF DEAMINATION REACTIONS

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Abstract — Résumé — Аннотация — Resumen

Stereochemistry and radiochemistry of deamination reactions. The utility of the combined radiochemical-stereochemical technique in detecting which side of the migration terminus is attacked by each of two migrating groups during reactions involving 1,2 shifts has previously been demonstrated. These same techniques have now been applied to the mechanisms of the deaminations of (1) optically active *threo-* and *erythro*-1,2-diphenyl-1-amino-2-propanol, (2) optically active *threo-* and *erythro*-1-phenyl-2-*p*-tolyl-1-amino-2-propanol, and (3) optically active 1,1-diphenyl-2-aminopropane. Both stereospecific and non-stereospecific C^{14} labels were employed. In each case the optical isomers produced were isolated, and the fate of each label was determined. Appropriate control experiments were performed with reactants which were labelled both with C^{14} and with deuterium. The absolute configurations of reactants and products for each reaction were studied through synthetic sequences which do not affect the optical integrity of the asymmetric centres. From these data it has been possible to arrive at certain definite conclusions concerning the mechanisms of the foregoing reactions. For example: (1) the fractions of each reaction proceeding through *cis-* and *trans*-transition states have been evaluated, and (2) new information has been gained concerning the importance or unimportance of "neighbouring group participation".

Finally, although classical techniques have been employed to clarify the stereochemistry of the families of compounds studied, a novel radiochemical method has also been used for the same purpose.

Stéréochimie et radiochimie des réactions de désamination. L'utilité que peut avoir la combinaison des techniques radiochimiques et stéréochimiques lorsqu'on veut déterminer quel côté du terme de migration est attaqué par l'un et l'autre groupes migrateurs dans des réactions impliquant une transposition 1, 2 a déjà été démontrée. Ces mêmes techniques ont maintenant été appliquées aux mécanismes de désamination des produits suivants: 1) *thréo*-et *érythro*-diphényl-1, 2-amino-1-propanol-2; 2) *thréo* et *érythro*-phényl-1-p-tolyl-2-amino-1-propanol-2, et 3) diphényl-1, 1-amino-2-propane, tous optiquement actifs. Deux systèmes de marquage — stéréospécifique et non stéréospécifique — au ^{14}C ont été employés. Dans chaque cas les isomères optiques produits ont été isolés, et le sort de chaque atome marqué a été déterminé. Des contrôles expérimentaux appropriés ont été effectués avec des réactants marqués au ^{14}C et au deutérium. Les configurations absolues des réactants et des produits obtenus ont été étudiées, pour chaque réaction, au moyen de synthèses qui n'ont pas d'incidence sur l'intégrité optique des centres d'asymétrie. Grâce à ces données, il a été possible de tirer certaines conclusions définitives en ce qui concerne le mécanisme de ces réactions. Par exemple: 1) on a évalué la fraction de chaque réaction passant par les états de transition cis et trans, et 2) on a recueilli des données sur l'importance ou le manque d'importance de da «participation du groupe voisin».

Enfin, bien que des techniques classiques aient été employées pour préciser la stéréochimie des séries de composés étudiées, une nouvelle méthode radiochimique a également été employée dans le même but.

Стереохимия и радиохимия реакций удаления аминогруппы NH_2 из молекулы органического соединения. Ранее уже демонстрировалось использование комбинированного радиохимического и стереохимического способа определения стороны миграционных пределов, на которую воздействует каждая из двух мигрирующих групп во время реакций, имеющих 1,2 стадии. Те же самые способы использовались в механизме удаления аминогруппы NH_2 из молекулы органического соединения 1) оптически активного *трео-* и *эритро*-1,2-дифинил-1-амино-2-пропанола, 2) оптически активного *трео-* и *эритро*-1-финил-2-р-толуол-1-амино-2-пропанола и 3) оптически активного 1,1-дифинил-2-аминопропана. Использовались как стереоспецифический, так и нестереоспецифический меченый C^{14}. В каждом случае изолировались оптически производимые изомеры и определялась судьба каждого меченого атома. Были произведены соответствующие контрольные эксперименты с реагирующими веществами, меченными как C^{14}, так и тяжелым водородом. Абсолютные конфигурации реагирующих веществ и продуктов в каждой реакции изучались через синтетический ряд, который не нарушал оптической целостности ассиметрических центров. Из этих данных стало возможным сделать некоторые определенные выводы, относящиеся к механизму происходящих реакций. Например: 1) была сделана оценка происхождения „cis" и „trans" стадий превращения для продуктов каждой реакции; 2) были получены новые сведения относительно значительности или незначительности „участия соседних групп".

Хотя использовались классические способы для выяснения стереохимии изучаемых составов соединений, для этой же самой цели также может быть использован новый радиохимический метод.

Estereoquímica y radioquímica de las reacciones de desaminación. La utilidad de una técnica que combina métodos radioquímicos y estereoquímicos para determinar qué lado del término de migración es atacado por cada uno de los dos grupos migrantes en las reacciones en que se producen desplazamientos 1,2 quedó demostrada anteriormente. Los autores aplican ahora la misma técnica a los mecanismos de desaminación del: 1) *treo-* y *eritro*-1,2-difenil-1-amino-2-propanol, 2) *treo* y *eritro*-1-fenil-2-p-toluil-1-amino-2-propanol y 3) 1,1-difenil-2-aminopropano, todos ellos ópticamente activos. Efectúan la marcación estereoespecífica y estereoinespecífica con ^{14}C. En todos los casos, aislan los estereoisómeros obtenidos, determinan el camino seguido por cada uno de los átomos trazadores y realizan experimentos testigo adecuados con reactivos marcados a la vez con ^{14}C y con deuterio. Estudian las configuraciones absolutas de los reactivos y de los productos de cada reacción por medio de series de síntesis que no afectan a la integridad óptica de los centros de asimetría. Los datos obtenidos les han permitido llegar a algunas conclusiones bien definidas acerca del mecanismo de las reacciones anteriormente citadas. Por ejemplo: 1) han determinado la fracción de cada reacción en que aparecen estados de transición *cis* y *trans*, respectivamente, y 2) han adquirido nuevos conocimientos sobre la mayor o menor importancia de la intervención de los grupos vecinos.

Por último, han aclarado la estereoquímica de las series de compuestos estudiados empleando técnicas clásicas y un método radioquímico nuevo.

1. Introduction

The deamination of stereospecifically phenyl-labelled (+)-1,1-diphenyl-2-amino-1-propanol (I) has previously been examined [1] [2]. The radiochemical results were as shown in Fig. 1, through which it was demonstrated that whereas the labelled phenyl approached the migration terminus with inversion, yielding

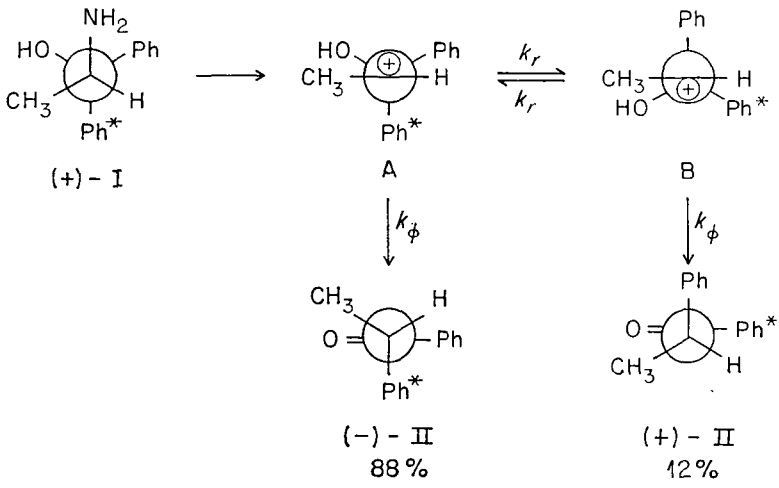

Fig. 1
Deamination of stereospecifically phenyl-labelled (+)-1,1-diphenyl-2-amino-1-propanol (I)

(—)-II in approximately 88% yield, the unlabelled phenyl approached the migration terminus with retention, yielding (+)-II in approximately 12% yield. The foregoing results foreshadowed additional experiments concerning the nature of the carbonium-ion intermediates in deamination reactions. In particular, it appeared possible to gain information about the relative importance of neighbouring-group participation [3] during these deaminations.

2. Results

We therefore undertook the stereochemical-radiochemical investigation of, (a), (+)- and (—)-*erythro*- 1, 2-diphenyl-1-amino-2-propanol (IV), labelled with C^{14} in the 1-position, and, (b), (+)-1,1-diphenyl-2-aminopropane (VII) stereoselectively labelled in one of the two phenyls. The syntheses of (—)-IV and of (+)- and (—)-VII are shown in Fig. 2.

Because there existed no *a priori* method of insuring the total stereoselectivity of the reaction sequence given in Fig. 2, we carried out the experiments illustrated in Fig. 3, in order to determine whether or not it would be possible to oximinate the model compound benzhydryl-H^2 phenyl ketone-C^{14} (XI) and then reduce the oxime (XII) to the amine hydrochloride (XIII) without loss of deuterium. It was reasoned that if the deuterium label of structure XI could survive the reaction sequence XI→ →XII→XIII, then in all probability the reaction sequence V→VI→VII could also be carried out without racemization of the labelled phenyl. The numbers under the structures of Fig. 3 refer to the C^{14}-contents of the compounds expressed as relative molar radioactivities. This series of reactions was carried out twice.

In the first run the oximination XI→XII was performed in very low yield under mild conditions. Infra-red analyses of ketones XI and XVI indicated ketone XI to be devoid of hydrogen in the benzhydryl position whereas

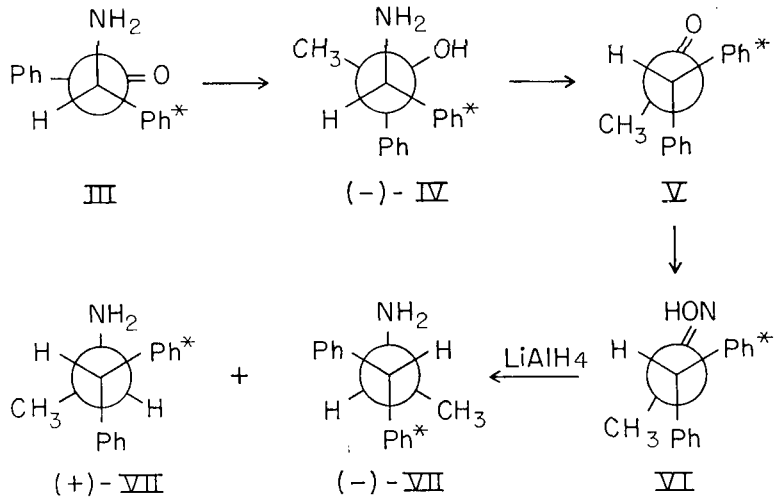

Fig. 2
Syntheses of (—)-*erythro*-1,2-diphenyl-1-amino-2-propanol (IV) and (+)- and (—)-1,1-Diphenyl-2-aminopropane (VII).

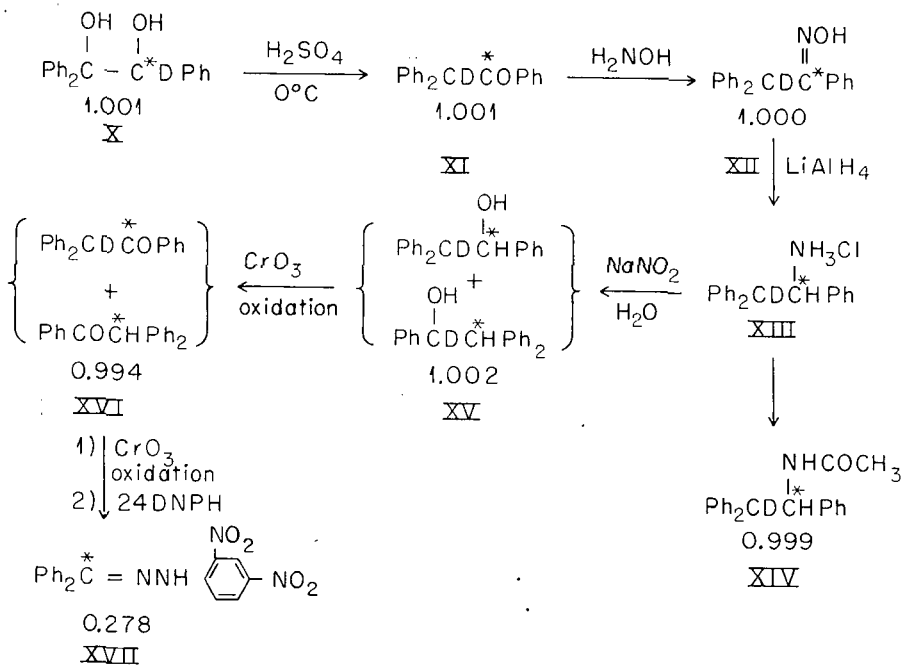

Fig. 3
Experiments performed to determine whether or not benzhydryl-H^2 phenyl ketone-C^{14} (XI) could be oximated to (XII) and then reduced to (XIII) without loss of deuterium.

ketone XVI contained approximately 26% hydrogen in the benzhydryl position. This is a very good check with the C^{14} data shown in Fig. 3, and indicates that no deuterium was lost during the sequence X→XI→XII→XIII→XIV. In the second experiment, forcing conditions were used during oximination in order to increase the yield of XII. Results of infra-red analyses indicated considerable loss of deuterium from XVI, (about 55%) in excess of the 28% to be expected on the basis of the C^{14} data. NMR spectra [4] of all the samples of Fig. 3 except XIII indicated approximately 40% loss of deuterium during oximination, but no loss of deuterium during the transformations XII→XIII→XIV. From the NMR data it could be calculated that approximately 25% rearrangement had taken place during the deamination XIII→XV, again in very good agreement with the radiochemical data of Fig. 3. We therefore concluded that under sufficiently mild conditions the oximination V→VI should take place without interchange of Ph and Ph*, and that the lithium aluminium hydride reduction VI→VII could be performed also with maintenance of the optical integrity of the benzhydryl position.

Erythro-(+)-IV, *erythro*-(—)-IV, and their corresponding hydrochlorides, were synthesized through the action of methylmagnesium iodide upon C^{14}-labelled, racemic aminodesoxybenzoin (+)-III, followed by resolution through the (+)-tartrate and (+)-10-camphorsulphonate salts. Through deamination, under conditions previously reported [2], followed by oximination and reduction (Fig. 2), the two enantiomers were converted to the isotope-position isomers of (±)-1,1-diphenyl-2-aminopropane (VII) illustrated in Fig. 4. From the two racemic mixtures of VII produced, it was possible to isolate α-(+)-VII and β-(+)-VII by resolution through their salts with (+)-camphoric and (+)-camphorsulphonic acids.

The absolute configurations of *erythro*-(+) and *erythro*-(—)-IV were demonstrated through the reactions shown in Fig. 5, *L*-(—)-2-amino-1, 1,2-triphenylethanol having previously been related to *L*-(+)-phenylglycine [5]. The configuration of *L*-(+)-glycine has been reported by INGOLD *et al.* [6], and is con-

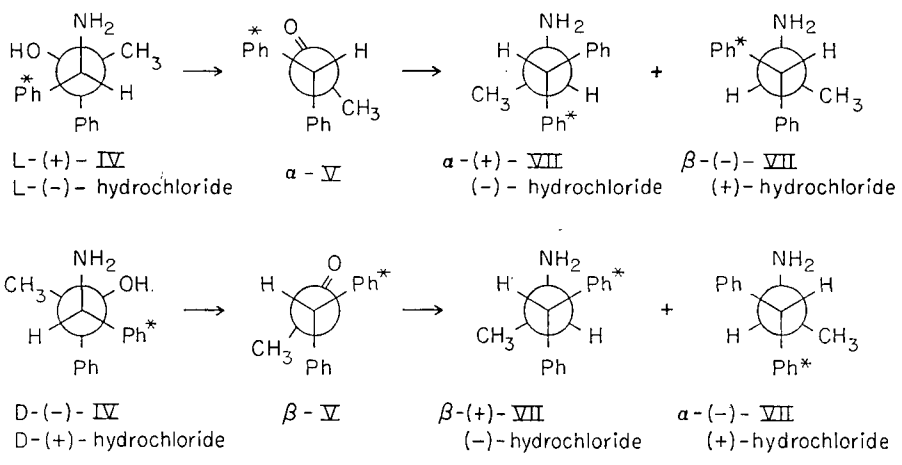

Fig. 4
Conversion of (+) and (—)-*erythro*-1,2-diphenyl-1-amino-2-propanol (IV) to the isotope position isomers of (+)-1,1-diphenyl-2-aminopropane (VII).

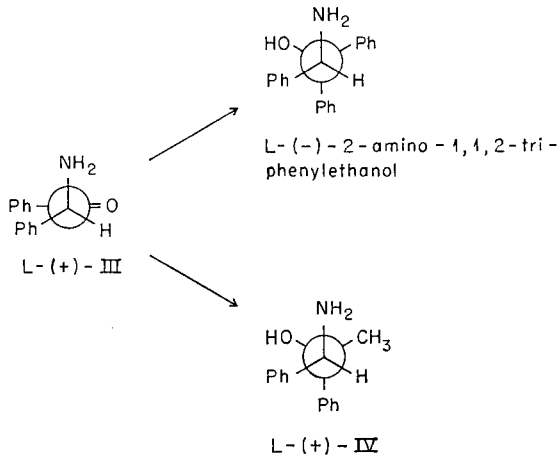

Fig. 5
Reactions demonstrating the absolute configurations of (+)-*erythro*- and (—)-*erythro*-1,2-diphenyl-1-amino-2-propanol (IV).

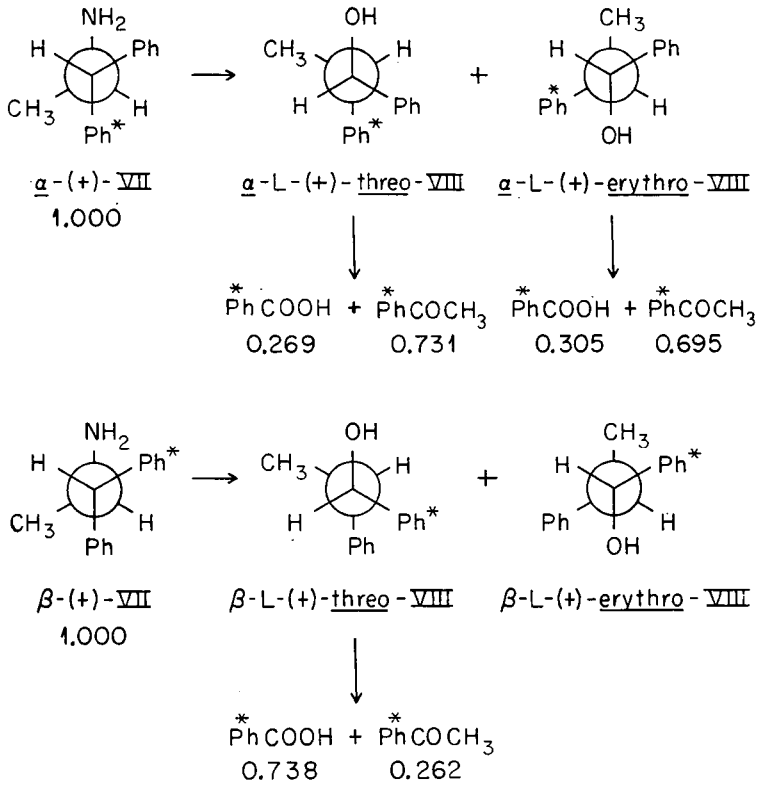

Fig. 6
Reactions performed to deduce the absolute configuration of (+)- and (—)-1,1-diphenyl-2-aminopropane (VII).

firmed by the present work when considered in conjunction with the findings of other investigators [5] [7]. The configurations of (+)- and (—)-1,1-diphenyl-2-aminopropane (VII) are deduced from the conversions of α-(+)-VII and of β-(+)-VII upon deamination, to *threo-* and *erythro*-1,2-diphenylpropanol-1 (VIII) of known configuration [8] (see Fig. 6). The conditions for deamination were those previously [2] employed.

The positions of radioactivity in the enantiomers of VII are deduced from the experimental results shown in Fig. 6, in which the molar radioactivities of reactants and degradation products are shown under the appropriate structures. The isotope-dilution method was employed to determine that (+)-VII, upon deamination yielded (+)-*threo*-VIII and (+)-*erythro*-VIII in combined yield of 65%, and in the ratio of 5.2:1. Further, not more than 1% of racemic *threo*-VIII was formed during the deamination, as shown also by the isotope-dilution method. Determination of racemic *erythro*-VIII failed because of the limited yield of the *erythro*-isomer. The degradative studies of Fig. 6 indicate, however, that the (+) forms of *threo-* and *erythro*-VIII obtained upon deamination of α-(+)-VII possess almost the same C^{14} distributions, and we deduce therefrom that in all likelihood no significant amount of racemic *erythro*-VIII was formed upon deamination of α-(+)-VII.

Finally, *threo-* and *erythro*-1-amino-1-phenyl-2-*p*-tolylpropanol-2 (IX) were synthesized through the action of *p*-tolylmagnesium bromide and methylmagnesium bromide, respectively, upon the appropriate α-aminoketones. Each racemic mixture was resolved through its salts with (+)-tartaric, (+)-10-camphorsulphonic or (+)-camphoric acids. The configurations of (+)- and (—) *erythro*-IX and (+)- and (—)-*threo*-IX were related to *D*-(—)-phenylglycine as shown in Fig. 7. The two enantiomers of *erythro*-IX were then subjected to deaminating conditions, and the isotope-dilution method was employed to determine the relative yields of (+)- and (—)-*p*-methylbenzhydryl methyl ketone (XVIII). The results are given in Table I, and were calculated from the experimental data by the method of BERSON *et al.* [9].

Finally, in one experiment, (+)-*threo*-IX was also subject to conditions of deamination. The combined yield of (+)- and (—)-XVIII was 83%. From the specific rotation of the oily material it was calculated that, after separation from approximately 20% hydroxylic material, the ketonic fraction consisted of approximately 58% (+)-XVIII and 42% (—)-XVIII.

The ketonic products of all deaminations reported in this paper were shown to be resistant to further racemization under the conditions of deamination employed.

3. Discussion

The present data allow the following conclusions:

1. The data of Fig. 3 indicate that in all probability the reaction sequence V→VI→VII should proceed without racemization, or "scrambling" of the labelled and unlabelled phenyls. Since the per cent racemization of the *p*-methylbenzhydryl methyl ketone (XVIII) produced upon deamination of optically active *erythro*-1-amino-1-phenyl-2-*p*-tolyl-propanol-2 (IX) (Table I) is experimentally identical with the C^{14} distributions shown in the degradative sequences of Fig. 6, we consider these data as excellent evidence that *erythro*-(+)-IV and *erythro*-(—)-IV suffer deamination to yield ketone V in which the C^{14} is distributed

TABLE I

DETERMINATION OF PER CENT RACEMIZATION DURING THE DEAMINATION OF (+)- OR (—)-ERYTHRO-IX

Exp. No.	Reactant	Yield of Product (%)	
		(+)-XVIII	(—)-XVIII
(1)	(+)-IX (—)-Hydrochloride*	70.4	29.6
(2)	(+)-IX (—)-Hydrochloride*	76.5	23.5
(3)	(—)-IX (+)-Hydrochloride**	25.5	74.5
(4)	(—)-IX (+)-Hydrochloride**	25.4	75.6
Average Inversion:			74.3 ± 2.0
Average Retention:			25.7 ± 2.0

* Reactants radioactive; combine yields (+)- and (—)-XVIII, 80%.
** Diluents radioactive.

between the two phenyls in the ratio 73:27 (see Figs. 4 and 6). This means that whereas during the deaminations of α-(+)-VII and β-(+)-VII, phenyl migration takes place *only* with inversion and only through *trans*-transition states, the deaminations of *L*-(+)-IV, *D*-(—)-IV and (+)-and (—)-*erythro*-IX proceed with aryl migration in which the relative importance of *trans* and *cis*-transition states are in the ratio of about 3:1.

2. The close agreement between the radiochemical distributions in α-*L*-(+)-*threo*-VIII and α--(*L*+)-*erythro*-VIII (Fig. 6) demands the presence of open carbonium ions in the deamination of VII. This statement follows, for since the *threo* and *erythro* products possess the same radiochemical distribution, they must therefore have arisen from a common ionic precursor, whose carbonium centre was capable of being attacked from either side. If bridged ions were the sole intermediates, no *erythro*-VIII should be produced.

3. The deaminations of the *erythro* isomers of IV and IX have been shown to proceed through both *trans* and *cis*-transition states, with the *trans*-transition state favoured by an approximate threefold margin. One would expect the *trans*-transition state to be of lower potential energy than the *cis*, even without participation [3]. Since the *cis*-transition state is further hindered by the requirement that its migrating aryl group proceed to the same side of the migration terminus originally bonded to nitrogen, it thus follows that during the deaminations of IV and IX neighbouring-group participation [3] in the scission of the carbon-nitrogen bond cannot be of great importance.

4. Finally, the data cited concerning the deamination of (+)-*threo*-IX seem to indicate retention of configuration through a mechanism in which the *p*-tolyl group migrates to the same side of the migration terminus which was originally bonded to nitrogen. Since the configurations of the No. 1 carbons (bonded to the amino groups) of (+)-*threo*-IX and (—)-*erythro*-IX are identical (see Fig. 7), both amino-alcohols should upon deamination yield *p*-methylbenzhydryl methyl ketone (XVIII) of the same sign of rotation, providing the *p*-tolyl group in both

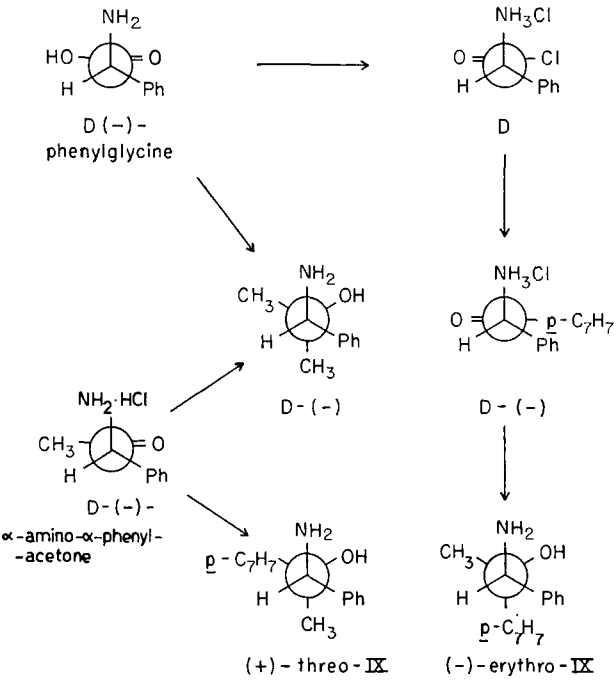

Fig. 7
Synthetic proof of the identity of No. 1 carbons of (+)-*threo*- and (—)-*erythro*-1-amino-1-phenyl-2-*p*-tolyl-propanol-2 (IX).

cases migrates with predominant inversion. Since (—)-*erythro*-IX yields (—)-ketone whereas (+)-*threo*-IX yields (+)-ketone, it is presumed that (+)-*threo*-IX yields predominantly that product whose configuration with respect to the No. 1 carbon of reactant is unchanged.

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DEHYDROCYCLIZATION OF 2,2-DIMETHYL-4-(METHYL-C^{14})-PENTANE AND 3-(METHYL-C^{14})-HEPTANE OVER CHROMIA-ALUMINA

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Abstract — Résumé — Аннотация — Resumen

Dehydrocyclization of 2,2-dimethyl-4-(methyl-C^{14})-pentane and 3-(methyl-C^{14})-heptane over chromia-alumina. The relative specific activities of the products obtained by processing the above C^{14}-labelled hydrocarbons over a potassium and cerium-promoted chromia-alumina catalyst have been measured. Products were separated by gas-chromatographic techniques, burnt to carbon dioxide and assayed as barium carbonate, using an end-window Geiger-Müller tube. The distribution of radioactivity between side chain and ring in the aromatic products was assessed by dealkylation over fluorinated alumina catalyst and the distribution between α and β carbon atoms of ethylbenzene, produced from methylheptane, by dealkylation to toluene and benzene over a nickel catalyst.

The results obtained with the first compound are consistent with an over-all mechanism in which methyl groups at both ends of the molecule become attached at adjacent sites on the catalyst surface. Rearrangement at the trisubstituted end of the molecule to give a six-membered ring, followed by dehydrogenation, gives *p*-xylene with 50% activity in the methyl groups. Toluene produced during cyclization has an activity distribution indicating that rearrangement also occurs to a lesser extent at the other end of the molecule.

The dehydrocyclization of methylheptane leads to the formation of the expected aromatics. However, the activity distribution shows that these have not arisen entirely by a simple ring-closure mechanism; a probable mechanism is the formation and subsequent rearrangement of C_5, C_6 and C_7 ring intermediates, tending to randomize the distribution of active carbon.

The labelled hydrocarbons were prepared on a one-gram scale by a Grignard reaction using a novel decomposition step.

Déshydrocyclisation du diméthyl-2, 2-(méthyle-^{14}C)-4-pentane et du (méthyle-^{14}C)-3-heptane sur l'oxyde de chrome et l'alumine. Les auteurs ont mesuré les activités spécifiques relatives des produits obtenus par traitement des hydrocarbures ci-dessus mentionnés, marqués au ^{14}C, sur un cytalyseur alumine-oxyde de chrome avec promoteur de potassium et de cérium. Les produits obtenus ont été séparés par chromatographie en phase gazeuse, transformés par combustion en anhydride carbonique, puis comptés sous forme de carbonate de baryum au moyen d'un tube Geiger-Müller à fenêtre terminale. La distribution de la radioactivité entre la chaîne latérale et le noyau dans les produits aromatiques a été déterminée par désalcoylation sur un catalyseur d'alumine fluorée, et la distribution entre les atomes de carbone α et β de l'éthylbenzène obtenu à partir du méthyl-heptane, par désalcoylation en toluène et en benzène sur un catalyseur de nickel.

Les résultats obtenus avec le premier composé correspondent à un mécanisme général dans lequel les groupes méthyle des deux extrémités de la molécule se réunissent en des points voisins de la surface du catalyseur. La transposition à l'extrémité

trisubstituée de la molécule, qui donne un cycle hexagonal, est suivie par une déshydrogénation donnant du *p*-xylène dont 50% de l'activité se trouve dans les groupes méthyle. Le toluène produit lors de la cyclisation a une distribution d'activité indiquant que la transposition se produit également, mais à un moindre degré, à l'autre extrémité de la molécule.

La déshydrocyclisation du méthylheptane conduit à la formation des produits aromatiques prévus. Néanmoins, la distribution de l'activité indique que ces produits ne se forment pas entièrement par simple clôture du cycle; les auteurs du mémoire en étudient le mécanisme probable.

Ils décrivent aussi la préparation d'hydrocarbures marqués — en quantités de l'ordre de 1 gramme — par une réaction de Grignard dans laquelle est utilisé un nouveau procédé de décomposition.

Дегидроциклизация 2:2-диметила-4-(метил-C^{14}) пентана и 3-(метил-C^{14}) гептана с помощью хром-алюминия. Проводились измерения относительной удельной активности продуктов, получаемых в результате обработки меченых углеводородов C^{14}, с помощью калия и серы при действии хром-алюминиевого катализатора. Продукты отделялись газо-хроматографическим способом, сжигались до двуокиси углерода и испытывались в качестве карбоната бария с помощью трубки счетчика Гейгера-Мюллера с окном. Распределение радиоактивности в ароматических веществах между боковой цепью и кольцом испытывалось деалкилированием (dealkylation) с помощью катализатора фторированной окиси алюминия, а распределение между альфа- и бета-атомами углерода этилбензола, получившегося из метилгептана, — деалкилированием до толуола и бензола с помощью катализатора в виде никеля.

Результаты, полученные первым соединением, находятся в соотвествии с общим устройством, в котором метиловые группы у обоих концов молекулы присоединяются к примыкающим сторонам на поверхности катализатора. Перегруппировка утрехзамещенного конца молекулы для того, чтобы дать кольцо с шестью членами с последующей дегидрогенизацией дает *p*-ксилен с 50% активностью в метиловых группах. Толуол, выработанный во время циклизации, имеет активность распределения, указывающую, что перегруппировка также происходит в меньшей степени на другом конце молекулы.

Дегидроциклизация метилгептана ведет к образованию ожидаемых ароматических веществ. Однако активность распределения показывает, что это не происходит целиком за счет простого механизма замыкания кольца. В докладе рассматриваются возможные виды таких механизмов.

Приводится также описание приготовления меченых углеводородов весом в 1 г с помощью реакции Гриньяра с использованием нового приема разложения.

Dehidrociclización del 2,2-dimetil-4-(metil-^{14}C) pentano y del 3-(metil-^{14}C) heptano mediante óxidos de cromo y aluminio. Los autores han medido las actividades específicas relativas de los productos obtenidos por tratamiento de los hidrocarburos mencionados, marcados con ^{14}C, en presencia de un catalizador de óxidos de cromo y aluminio con promotor de potasio y cerio. Los productos fueron separados por cromatografía en fase gaseosa y se transformaron en anhídrido carbónico por combustión; la actividad del carbonato de bario se midió con ayuda de un contador Geiger-Müller de ventana terminal. La distribución de la radiactividad entre las cadenas laterales y el anillo de los productos aromáticos se evaluó por dealquilación en presencia de un catalizador de alúmina fluorada, mientras que la distribución entre los átomos alfa y beta de carbono del etilbenceno obtenido a partir del metilheptano se determinó transformando el compuesto en tolueno por dealquilación en presencia de un catalizador de níquel.

Los resultados obtenidos con el primer compuesto sugieren que la reacción se produce en virtud de un mecanismo general en el que los grupos metilo de ambos extremos de la molécula se unen en puntos vecinos de la superficie del catalizador. Un reordenamiento en el extremo trisubstituido de la molécula para obtener un

anillo hexagonal, seguido de deshidrogenación, da origen al *p*-xileno, en que el 50% de la actividad se encuentra en los grupos metilo. El tolueno obtenido durante la ciclización posee una actividad cuya distribución indica que también se produce, aunque en menor grado, un reordenamiento en el otro extremo de la molécula.

El metilheptano produce por dehidrociclización los compuestos aromáticos previstos. Pero la distribución de la actividad demuestra que éstos no se forman simplemente por cierre del anillo. Los autores estudian los probables mecanismos.

Por último, describen la preparación de cantidades del orden del gramo de los hidrocarburos marcados por una reacción de Grignard en la que interviene una nueva etapa de descomposición.

1. Introduction

Previous studies of the mechanism of dehydrocyclization of hydrocarbons over metal and metal-oxide catalysts have been reviewed by HANSCH [1] and STEINER [2]. Recent Russian work [3] has contributed little to our understanding of the reaction mechanism. HERINGTON and RIDEAL [4] have proposed the most satisfactory mechanism. They showed that the aromatic products do not arise entirely by direct ring-closure and postulated an isomerization step, involving the formation and destruction of a bi-cyclic intermediate, to account for the production of *m*- and *p*-xylene from *n*-octane. The isomerization of a C_5-ring to a C_6-ring was proposed to account for the production of aromatics from substituted pentanes.

The use of *n*-heptane-1-C^{14} and *n*-octane-1-C^{14} [5] [6] to study the dehydrocyclization reaction with chromia-alumina catalysts has shown that the Herington and Rideal view of the isomerization step does not account for the distribution of radioactivity between the side chain and ring of the aromatic products obtained. PINES *et al.* [6] have shown that this distribution is greatly affected by the "isomerizing power" of the catalyst which in turn is dependent on the alumina base.

2,2-Dimethyl-4-(methyl-C^{14})-pentane and 3-(methyl-C^{14})-heptane were selected for the present study because the former cannot yield a C_6 ring directly and gives *p*-xylene as the only C_8-aromatic product, and because the latter is capable of direct ring-closure in three different ways to give three aromatics. The catalyst chosen was a chromia-alumina catalyst having a low isomerization activity.

Full use has been made of gas-liquid chromatography for the separation and estimation of the purity of small quantities of reaction products.

2. Experimental

PREPARATION OF THE LABELLED HYDROCARBONS

The preparations were carried out using conventional vacuum-manifold techniques. The high purity of the starting materials was established by examination of their infra-red spectra and gas-liquid chromatograms.

2,2-*Dimethyl*-4-(*methyl-C*^{14})-*pentane*

Methyl-C^{14} magnesium iodide in ether, prepared from methyl-C^{14} iodide (about 10 mc/mole), was allowed to react with methyl neopentyl ketone on a one-gram scale. After removal of ether the complex was decomposed in a novel manner

by heating *in vacuo* for 3 h at 200°C and the pyrolysis products were collected continuously in a cold trap. The olefinic portion of the products was isolated by gas-liquid chromatography and hydrogenated with Adam's catalyst to give hydrocarbon of purity greater than 99% in an overall yield, based on methyl-C^{14} iodide, of 55%.

3-(Methyl-C^{14})-heptane

This hydrocarbon was prepared in a similar manner from methyl-C^{14} magnesium iodide and heptanone-3 in 57% yield.

Ethyl-β-C^{14}-benzene

This was prepared by coupling methyl-C^{14} iodide with benzyl bromide by means of magnesium. (The complex obtained from methyl magnesium iodide and benzaldehyde gave only trace amounts of styrene on pyrolysis in the temperature range 70° — 250°C).

The purity of the inactive hydrocarbons obtained from trial experiments was tested by infra-red and mass-spectrographic analysis and examination of the chromatogram obtained on a capillary column (100000 theoretical plates). The last technique was also used on active materials; no significant impurity was detected.

For the cyclization experiments the active hydrocarbons were diluted about twenty-fivefold to activity levels of approximately 3.5 μc/g by addition of the respective inactive hydrocarbons of not less than 99% purity.

APPARATUS AND PROCEDURE.

Dehydrocyclization procedure

The dehydrocyclization experiments were carried out using a vertical reactor. This consisted essentially of a Pyrex-glass tube, 2 cm diameter × 30 cm long, in an electrically heated furnace. The catalyst bed occupied about 6 cm at the centre of the reactor and free space was filled with 4–8-mesh quartz. The hydrocarbon feed was introduced continuously into the reactor at about 10 ml/h by displacement from a burette with mercury which, in turn, was displaced by lubricating oil pumped by a Tecalemit micropump. The feed was vaporized in the heated reactor head and passed downwards through the catalyst bed.

Fresh cerium and potassium-promoted chromia-alumina catalyst (10 ml, 12–18 mesh) was treated before use with hydrogen (approximately 4 l/h for 16 h) at 590°C. The dehydrocyclization experiments were carried out under the following conditions: atmospheric pressure, liquid hourly space velocities in the range 0.71 to 0.44 v/v/h, 553 — 568°C (average temperatures at centre of catalyst bed) without carrier gas; 5–6-ml samples of hydrocarbon were treated in each experiment.

The reaction products were collected in an acetone solid-CO_2 cooled U-tube, packed with stainless-steel gauze Dixon rings, surmounted on the exit side by a cold-finger reflux condenser containing acetone solid-CO_2. Hydrocarbon gases were collected in a trap packed with activated alumina and immersed in liquid nitrogen.

The products condensed in the U-tube were separated into gases and liquids (C_5 — C_8 hydrocarbons) by fractionation on a vacuum manifold.

Separation of the products

Liquids

The liquid products (C_5—C_8 hydrocarbons) were further separated using a large-scale gas-chromatographic unit. The chromatographic column was of Duralumin (1 inch diameter × 47 ft) packed with Celite (44—72 mesh) impregnated with 7,8-benzoquinoline (20 wt.%) maintained at 78° C. The last 10 inches of the column were packed with anhydrous copper chloride (25 wt.%) on Celite; this considerably reduced the contamination of the detector (β-ray ionization) and traps by benzoquinoline continuously eluted under the operating conditions. Liquid samples of 1 to 4 ml were injected into the column preheater (210°C) with a syringe and eluted with nitrogen.

The eluted fractions were collected separately in U-tube traps packed with stainless-steel gauze Dixon rings and immersed in liquid nitrogen. Small fractions were collected in a tube packed with glass-wool with a surrounding glass spiral inlet. Product recoveries were about 90% (estimated in trial experiments with inactive materials).

The liquid products obtained from the dehydrocyclization of 2,2-dimethyl-4-(methyl-C^{14})-pentane were resolved into unchanged feed, benzene, toluene and *p*-xylene. All other liquid products were collected together (see Table I). In experiment No. 2, a small quantity of *m*-xylene was isolated (not greater than

TABLE I

DEHYDROCYCLIZATION OF 2,2-DIMETHYL-4-(METHYL-C^{14})-PENTANE YIELDS AND RELATIVE SPECIFIC ACTIVITIES OF PRODUCTS

	Experiment 1		Experiment 2	
Catalyst temperature(°C)	568		563	
Liquid hourly space velocity (v/v/h)	0.71		0.45	
Dehydrocyclization Products	Yield on Feed* (wt. %)	Relative Specific Activity (Iso-octane = 1.00)	Yield on Feed* (wt. %)	Relative Specific Activity (Iso-octane = 1.00)
Methane	6	1.7	8	1.8
C_2 hydrocarbons	1		1	
C_3 hydrocarbons	7	1.34	8	1.39, 1.50
Isobutane	16	0.88, 0.91, 0.95	17	0.97, 1.03, 1.00
Isobutene	24	0.88, 0.85	25	0.905, 0.895
Other hydrocarbons**	7	—	5	—
Unconverted feed	12	0.97, 0.99	6	0.97, 1.07, 0.96
Octenes	1	—	1	—
Benzene	0.3	0.85	0.5	0.86
Toluene	3.3	0.965	3.9	0.95
p-Xylene	14.4	1.00	15.6	1.03, 0.94
Other aromatics***	1	—	1	0.96, 0.995
Coke on catalyst	7	0.90, 0.91	8	—

* Estimate based on experiments with inactive iso-octane.

** Includes C_4 and C_5 aliphatics (mainly).

*** Approximately similar quantities of ethylbenzene, *m*-xylene and *o*-xylene were observed by infra-red and capillary-column gas-liquid chromatography. The specific activity determinations were carried out on isolated *m*-xylene.

TABLE II

DEHYDROCYCLIZATION OF 3-(METHYL-C^{14})-HEPTANE YIELDS AND RELATIVE SPECIFIC ACTIVITIES OF PRODUCTS

		Experiment 3	Experiment 4
Catalyst temperature	(°C)	554	553
Liquid hourly space velocity	(v/v/h)	0.44	0.44
Dehydrocyclization Products	Yield on Feed* (wt. %)	Relative Specific Activity (3-Methylheptane = 1.00)	Relative Specific Activity (3-Methylheptane = 1.00)
C_1-C_2 hydrocarbons (mainly C_1)	5	1.05	
C_1-C_2 hydrocarbons (mainly C_2)	7	0.20	
C_3 hydrocarbons	7	0.86	
C_4 hydrocarbons	9	0.77	
Other hydrocarbons**	3	—	
Unconverted feed	3.4	0.85, 0.85, 0.81, 0.82	0.81
Benzene	2.8	1.19, 1.12	
Toluene	5.7	0.92	
Ethylbenzene	8.0		0.95
Styrene	0.9		
p-Xylene	25.9	0.97	
m-Xylene	0.2		
o-Xylene	15.1	1.015	1.00
Coke on catalyst	7	0.95, 0.92	

* Estimate on experiments with inactive 3-methylheptane.
** Includes C_4-C_7 aliphatics and some C_8 olefins.

2 wt.% of total aromatics). The liquid products from 3-(methyl-C^{14})-heptane were separated into individual hydrocarbons (unconverted feed, benzene, toluene, *o*-xylene, styrene), into a bulk fraction containing other non-aromatic hydrocarbons, and a fraction consisting of ethylbenzene, *p*-xylene and a trace of *m*-xylene. Re-chromatographing a smaller sample (80 mg) of this aromatic fraction separated the ethylbenzene and *p*-xylene, which were shown to be pure by analysis on a capillary column (100 000 theoretical plates). Examination by capillary column and by infra-red analysis showed that the recovered 3-(methyl-C^{14})-heptane contained an unidentified hydrocarbon not present in the original feed. Each of the products was re-chromatographed on a small column as part of the assay procedure (see below).

Gases

These products were further separated by gas chromatography at room temperature using a 0.25-in copper column, the first 16 ft of which were packed with Celite impregnated with dimethyl sulpholane (30 wt.%) and the last 4 ft with Celite impregnated with squalane (30 wt.%). Samples (5 ml) of the gases at room temperature and pressure were injected into the column with a syringe. Four or five injections yielded sufficient barium carbonate from each gas for assay (see below). The gaseous products were resolved into the fractions shown in Tables I and II.

The product yields shown in Tables I and II were estimated from experiments with inactive materials.

Radioactivity determinations

All reaction products were burnt to carbon dioxide and their radioactivity determined as $BaC^{14}O_3$ by an end-window Geiger-Müller tube, as described by Goble and Smith [7]. The separated liquid products obtained as described above were passed through a column (0.25 in $\times$ 4 ft) packed with Celite impregnated with 7,8-benzoquinoline (30 wt.%), at 78°C before entering the combustion tube. The rate of loss of benzoquinoline from the column was insufficient to affect the assay.

The relative specific activity of a reaction product is defined as the ratio of the observed counts/min per mg of barium carbonate derived from the product to the counts/min per mg of an equal weight of barium carbonate derived from the feedstock. The latter value was read from a calibration curve of specific activity *versus* weight of precipitate.

The standard deviation of a determination of relative specific activity was 0.035 (cf. Goble and Smith [7], 0.03). This variation includes a counting error

Table III

DEHYDROCYCLIZATION OF 2,2-DIMETHYL-4-(METHYL-C^{14})-PENTANE PERCENTAGE OF RADIOACTIVITY LOCATED IN SIDE CHAIN(S) OF AROMATIC PRODUCTS

Dehydrocyclization Products	*p*-Xylene		Toluene		Toluene (from Dealkylation of *p*-Xylene)	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
Relative Specific Activity of DealkylationProducts						
Benzene	0.63	0.70	0.88	0.86	0.63	0.70
Toluene	0.86	0.88	—	—	—	—
Unreacted aromatic	1.02	0.97	0.98	0.94	0.86	0.88
Coke (on dealkylation catalyst)	1.05	1.05	0.98	0.93	1.05	1.05
Percentage Radioactivity in Side Chain(s) of Dehydrocyclization Products						
Calculated from specific activity of benzene	53	47	22	23	36	30
Calculated from specific activity of toluene	50	44	—	—	—	—
Proportion of aromatic products (wt.%)	76	74	17	19	—	—

TABLE IV

DEHYDROCYCLIZATION OF 3-(METHYL-C^{14})-HEPTANE PERCENTAGE OF RADIOACTIVITY LOCATED IN SIDE CHAIN(S) OF AROMATIC PRODUCTS

Dehydrocyclization products	Toluene	*p*-Xylene	*o*-Xylene	Ethyl-benzene*	Styrene
Relative Specific Activity of Dealkylation Products					
Benzene	0.36, 0.37	0.16	0.12	1.15	1.14
Toluene	—	0.61	0.62	1.07	—
Unreacted aromatic	0.98	0.99	—	0.93	—
Coke (on dealkylation catalyst)	1.40	1.29	1.28	—	0.72
Percentage Radioactivity in Side Chain(s) of Dehydrocyclization Products					
Calculated from specific activity of benzene	66, 65	88	91	9	14
Calculated from specific activity of toluene	—	93	93	$\alpha=7.5$ $\beta=1.5$	—
Proportion of aromatic products (wt. %)	10	44	26	14	1—2

* Dealkylated over supported nickel catalyst.

of 0.02. Results obtained from repeat dehydrocyclization experiments were not significantly different (see Tables I and II).

DETERMINATION OF THE PERCENTAGE OF RADIOACTIVITY LOCATED IN THE SIDE CHAIN(S) OF THE AROMATIC PRODUCTS

The distribution of radioactivity between side chain(s) and ring of the aromatic products was calculated from specific activities of the toluene and/or benzene obtained by the dealkylation of the aromatic products over a fluorinated alumina catalyst in nitrogen. The apparatus and procedure used has been previously described [7]. Results are shown in Tables III and IV. That this method is unambiguous for the determination of side-chain activity of these alkyl aromatics has been shown by the work of GOBLE and SMITH on the dealkylation of toluene-7-C^{14} [7] and *m*-xylene-7-C^{14} [8].

Radioactivity of α- and β-carbon atoms of ethylbenzene product

The distribution of radioactivity between the α- and β-carbon atoms of ethylbenzene obtained from the methylheptane was calculated from the specific activities of the toluene and benzene products obtained by processing the ethylbenzene in hydrogen over a nickel catalyst; the results are shown in Table IV. That a stepwise degradation of the alkyl substituent takes place over a nickel catalyst has been demonstrated by the work of HOLMES *et al.* [9] and SHUIKIN *et al.* [10]. However, proof was provided by a study of the degradation of ethyl-β-C^{14}-benzene when inactive toluene was obtained. This shows that the mechanism

of degradation does not involve a step in which the carbon atoms in the side chain become equivalent.

RADIOACTIVITY OF THE "COKE" ON THE CATALYST

This was estimated by the method of "rapid combustion" as described by GOBLE and SMITH [7].

3. Discussion

2,2-DIMETHYL-4-(METHYL-C^{14})-PENTANE

The distribution of radioactivity in the side chain(s) of the *p*-xylene and toluene products, shown in Table III, can be accounted for by a mechanism in which at some stage in the reaction sequence the methyl groups of the iso-octane are attached to the catalyst surface on adjacent sites as shown in Fig. 1.

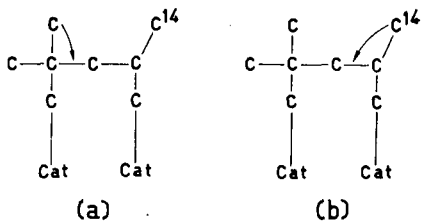

Fig. 1
Stage in catalytic dehydrocyclization of 2,2-dimethyl-4-(methyl-C^{14})-pentane, as suggested by distribution of radioactivity in reaction products.

Rearrangement can then occur at either end of the adsorbed molecule as shown in Fig. 1 (a) or (b). Rearrangement as in 1 (a) produces *p*-xylene 50% externally labelled, whilst 1 (b) produces toluene only (after loss of one of the geminal methyl groups) having no externally labelled carbon atom. From the radioactivity distribution in the toluene product (22% in side chain) and in the toluene from dealkylation of *p*-xylene (33% in side chain) it is concluded that one third (6% of yield of aromatics) of the toluene was produced by reaction 1 (b) and the ratio of the yields of reactions 1 (a) and 1 (b) is approximately 15:1.

It is not possible to obtain information from the radioactivity data concerning the process by which the iso-octane becomes attached to the catalyst as postulated, or to indicate whether isomerization occurs before, simultaneously with, or after ring closure to the naphthene. Although the formation and rearrangement of such an intermediate as proposed above is consistent with the mechanism of dehydrocyclization of alkyl-substituted pentanes first proposed by HERINGTON and RIDEAL [4], our data cannot be taken as proof of their mechanism.

It is possible to state with certainty that *p*-xylene could not have arisen by cracking of the hydrocarbon into two separate C_4-fragments which then recombine since this would yield *p*-xylene containing one-third of its radioactivity in the side chains.

The observed high yields of C_4 hydrocarbons would be expected by the ready breakage of the quaternary bond between carbon atoms 2 and 3 of the proposed intermediate. The specific activities of the isobutane and isobutene were similar

and close to that of the feed (see Table I) and show that either isobutene is derived solely from isobutane by dehydrogenation, or that if they are formed simultaneously, either half of the intermediate is equally likely to form the olefin.

The high specific activity of the C_3 hydrocarbons shows that a proportion must have arisen directly by breakage of the tertiary bond between carbon atoms 3 and 4, and not solely dealkylation of C_4 (or higher) hydrocarbons.

Although naphthenes have been postulated as intermediates they have not yet been isolated from the products of dehydrocyclization of hydrocarbons over chromia catalysts [1] [2] even where a C_5 to C_6-ring isomerization step is alleged to occur [4]. In contrast, KASANSKI and LIBERMAN [11] have obtained high yields of 1,1,3-trimethylcyclopentane from iso-octane over a platinum-on-charcoal catalyst at 310°C, 0.2 v/v/h. They suggest that the isooctane attaches to the catalyst surface so as to form a C_5 ring *via* the intermediate we postulate as occurring on a chromia catalyst. On the platinum catalyst this can desorb to give the cyclopentane. Readsorption of the cyclopentane and subsequent ring-expansion results in their observed aromatic products (*m*- and *p*-xylenes). With the chromia-alumina only a trace of cycloparaffins could have been present in the products and we observed only small amounts of *m*-xylene (not greater than 2% of the aromatics produced), whereas treatment of 1,1,3-trimethylcyclopentane under the same conditions gave mixed xylenes.

The difference in behaviour between the two catalysts possibly arises either from the greater strength of attachment, or the greater rate of removal by reaction of the adsorbed intermediate in the case of the chromia catalyst. For either reason the concentration of cyclopentane in the vapour phase is kept very low.

3-(METHYL-C^{14})-HEPTANE

The distribution of radioactivity between the side chains and the ring of the *o*- and *p*-xylene and ethylbenzene products (see Table IV) shows that approximately 90% of these aromatics were formed by direct ring-closure as expected from the mechanism proposed by HERINGTON and RIDEAL [4]. The 10% of activity in the ring of the two xylenes, the activity in the side chain of ethylbenzene (and styrene) and the small amount of *m*-xylene produced can be accounted for by the formation and subsequent rearrangement of intermediates containing C_5, C_6 and C_7-rings tending to randomize the distribution of active carbon. Such a mechanism has been suggested by PINES *et al.* [6] to account for the activity distribution in the products from the dehydrocyclization of *n*-octane-1-C^{14} over a chromia-alumina catalyst of low isomerizing power. (The present chromia-alumina catalyst similarly possessed a low isomerizing power, as shown by the low yield (less than 10%) of benzene and toluene produced respectively from methylcyclopentane and 1,2-dimethylcyclopentane at 550°C; aromatics are not isomerized). The same mechanism could also account for the radioactivity of the α-carbon atom of ethylbenzene. However, the determination of the distribution of activity between the α- and β-carbon atoms is sensitive to small errors in the determination of the specific activities of the benzene and toluene dealkylation products.

The specific activities of the benzene and toluene products and the side chain activity of the latter show that these do not entirely arise from dealkylation of the C_8-aromatic products (*cf.* toluene from iso-octane). The results obtained

can be accounted for if the toluene is also produced by dehydrocyclization of C_7 hydrocarbons formed by preferential removal of inactive methyl groups from the feed. Calculation shows that about 60% of the toluene could arise in this way. The lower contribution from C_7 hydrocarbon derived by elimination of the radioactive methyl group is reflected in the relatively low specific activity of the product methane (see Table II).

The low specific activity of the C_2 gases indicates that these were derived largely from the inactive ends of the methylheptane chain.

A specific activity of 0.83 observed for the recovered feedstock is probably partly due to the presence of an inactive hydrocarbon (possibly a cyclic hydrocarbon containing seven carbon atoms) which has the same chromatographic retention volume on the benzoquinoline column as the feed. The capillary column chromatography indicates the pressence of not less than 5% of a hydrocarbon (not identified) in the recovered feed which was not present in the original. The concentration in the recovered feed of an unreactive and non-radioactive impurity from the original feedstock can be discounted.

Coke on the catalyst

The specific activities of the carbonaceous deposits (coke) on the chromia-alumina catalyst (see Tables I and II) obtained from the two hydrocarbons were close to that of the feed. Since it has been demonstrated [12] that aromatic products contribute little to coke-formation it seems probable, therefore, that the coke is built up by interaction of whole-feed molecules as suggested by McMahon [13] for coke formation by paraffins on cracking catalysts.

It is of interest to note that the specific activities of the coke deposited on the dealkylation catalyst (see Tables III and IV) by the aromatics was greater than the feed when the side chain(s) contained the active carbon and less than the feed when it did not. These results are as expected from the mechanism of coke formation by aromatics on this dealkylation catalyst (fluorinated alumina) postulated by Goble and Smith [7].

4. Conclusion

The distribution of radioactivity between the side chain(s) and ring of the aromatic products observed on passing 2,2-dimethyl-4-(methyl-C^{14})-pentane and 3-(methyl-C^{14})-heptane over a potassium and cerium-promoted chromia-alumina catalyst (a catalyst having a low isomerizing power) is consistent with, but does not provide proof of, the mechanisms proposed by Herington and Rideal [4] for the dehydrocyclization of these hydrocarbons. Minor variations from the radioactivity distributions predicted for the aromatics obtained from the methylheptane indicate that, even where direct C_6 ring-closure is highly favoured, it seems probable that seven and five-membered rings are also formed.

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ISOTOPIC DATA TO STUDY THE MECHANISM OF THE OXIDATION OF MERCAPTOACETIC ACID

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Abstract — Résumé — Аннотация — Resumen

Isotopic data to study the mechanism of the oxidation of mercaptoacetic acid. Numerous researchers have been studying the liquid-phase autoxidation by molecular oxygen of compounds containing a mercapto group. It has been stated that, in the course of the reaction, sulphide is formed, but the exact mechanism of this process has not been determined.

The oxidation of mercaptoacetic acid, at 50°C and at a pH of 8, was investigated both in the presence of Complexon IV and in the presence of iron-ions.

Na_2S, labelled with S^{35}, was introduced into the system and it was determined that this sulphide considerably increases the rate of the oxygen uptake both in the processes catalysed by trivalent iron and free of iron-ions.

In the course of the reaction the concentration of the sulphide, its specific activity and its total activity were measured. In using these data and on the basis of the kinetic isotopic method developed by Neiman and co-workers, it was possible to calculate the rate of sulphide formation and its further oxidation.

In comparing these data with other kinetic data, it is shown that the oxidation of mercaptoacetic acid in the liquid phase is a branching chain reaction; one of its principal chains being the formation of Na_2S and its further oxidation. Moreover, it was determined that sulphate is formed in the course of the reaction only through the inorganic sulphide. Iron-ions catalyse the formation of organic disulphide and therefore also have influence on the sulphide formation.

Données isotopiques pour l'étude du mécanisme d'oxydation de l'acide mercaptoacétique. De nombreux chercheurs ont étudié l'autoxydation des composés contenant un groupe mercaptan par l'oxygène moléculaire en phase liquide. Ils ont trouvé qu'il y avait formation de sulfure au cours de la réaction, mais le mécanisme exact de ce processus n'a pas été déterminé.

L'oxydation de l'acide mercaptoacétique à 50°C et pour un pH de 8 a été étudiée en présence de complexone IV et également en présence de fer. Du Na_2S marqué au ^{35}S a été introduit dans le système et on a constaté que le Na_2S augmentait considérablement le taux d'absorption d'oxygène, tant dans le processus de catalysation par le fer qu'en l'absence de fer.

Au cours de la réaction, on a mesuré la concentration du sulfure, son activité spécifique et son activité totale. En partant de ces données, et en utilisant la méthode d'étude cinétique au moyen d'isotopes, mise au point par Neiman et ses collaborateurs, on a pu calculer le taux de formation de sulfure et le taux de son oxydation ultérieure.

La comparison de ces données avec d'autres données cinétiques révèle que l'oxydation de l'acide mercaptoacétique en phase liquide est une réaction en chaîne ramifiée, l'un des principaux éléments de cette chaîne étant la formation de Na_2S et son oxy-

dation ultérieure. On a constaté en outre qu'il se forme du sulfate, lors de la réaction, mais seulement à partir du sulfure minéral. Le fer catalyse la formation de disulfure organique et, de ce fait, influe aussi sur la formation de sulfure.

Изотопный метод исследования механизма окисления меркаптоуксусной кислоты. Многие исследователи изучали процессы самоокисления сложных веществ, содержащих меркаптоновую группу, с помощью молекулярного кислорода в жидкой фазе. Указывалось, что во время реакции образуется сульфид, но до сих пор не удавалось определить точного механизма этого процесса.

Было проведено исследование окисления меркаптоуксусной кислоты при 50° и при pH=8 как в присутствии комплексона IV, так и в присутствии железа. В систему был введен Na_2S, меченный S^{35}, и было установлено, что Na_2S значительно увеличивает скорость захвата кислорода как при процессе катализированным железом, так и в процессе, свободном от ионов железа.

Во время реакции были измерены концентрация сульфида, его удельная активность и общая активность. На основании этих данных и благодаря выработанному Нейманом и его сотрудниками кинетическому методу изотопов, представилось возможным подсчитать темп образования сульфида и его дальнейшего окисления.

Сопоставление этих данных с другими кинетическими данными показало, что окисление меркаптоуксусной кислоты в жидкой фазе является цепной реакцией одна из главных цепей в этой реакции образуется посредством образования Na_2S и его дальнейшего окисления. Кроме того, было установлено, что во время реакции образуется сульфат, но только через посредство неорганического сульфида. Железо катализировало образование органического дисульфида и поэтому оно также оказывает влияние на образование сульфида.

Estudio del mecanismo de oxidación del ácido mercaptoacético por medio de datos obtenidos con radioisótopos. Numerosos investigadores han estudiado la autooxidación en fase líquida, por oxígeno molecular, de compuestos que contienen un grupo mercaptano; si bien han llegado a la conclusión de que se forman sulfuros en el curso de la reacción, el mecanismo exacto del proceso no se conoce.

Los autores estudiaron la autooxidación del ácido mercaptoacético a 50° C y pH 8 en presencia de complexon IV y de hierro.

Añadieron al sistema Na_2S marcado con ^{35}S y comprobaron que este compuesto aumenta notablemente la velocidad de absorción de oxígeno tanto en las reacciones catalizadas por hierro como en las que transcurren en ausencia de iones de este metal.

En el curso de la reacción, los autores midieron la concentración del sulfuro, su actividad específica y su actividad total. Gracias a estos datos y empleando el método isotópico cinético establecido por Neiman y colaboradores, pudieron calcular la velocidad de formación del sulfuro y la velocidad de su oxidación subsiguiente.

Por comparación de esos resultados con otros datos cinéticos, se puede demostrar que la autooxidación del ácido mercaptoacético en fase líquida constituye una reacción en cadena ramificada, una de cuyas ramas principales es la formación de Na_2S y su oxidación subsiguiente. Los autores también comprobaron que el sulfato que aparece durante la reacción, procede exclusivamente del sulfuro inorgánico. El hierro cataliza la formación de disulfuro orgánico y, por lo tanto, ejerce también influencia sobre la formación del sulfuro.

1. Introduction

The oxidation of aminocarboxylic acids containing a mercapto group and its importance in cellular respiration processes are facts already well known for a long time. Many investigations have been carried out in order to clarify the

mechanism of the oxidation, but even at the present time the question remains unsolved.

According to data contained in the literature the oxidation starts with a dehydrogenation whereby, as a first step, organic disulphide is formed. HARRISON, SCHÖBERL and WAGNER have pointed out that this disulphide is not a stable product but that, depending on the pH, a small part of it further decomposes so that the sulphur-carbon bond may be broken to form inorganic sulphide [1].

There are a number of experimental data in the literature concerning the catalytic effect of heavy metals, mainly iron and copper, on the oxidation process. According to SCHÖBERL and PIRIE, the heavy metals promote the first step of the oxidation, i.e. the dehydrogenation process [2]. One explanation of the mechanism of the catalytic effect was that Fe^{3+} ions oxidize mercaptocarboxylic acid and that the Fe^{2+} ions thus formed are reoxidized to Fe^{3+} ions by oxygen. SCHUBERT, KOLTHOFF and LEUSSING have pointed out the fact that, for instance, in the case of mercapto-acetic acid—the compound investigated by us—an iron/mercaptoaceticacid complex is formed which may play the role of a catalyst [3].

However, the investigations made so far all refer to the first step of the oxidation, while nothing is known about the role of sulphide. The question whether iron catalyses only the starting reaction or also the further oxidation of sulphide formed, is as yet unsolved. Therefore, in the first instance we studied the role of a sulphide intermediate and the mechanism of its formation and further oxidation in the liquid phase, using mercaptoacetic acid as a model compound. Secondly, we tried to find an answer to the question whether Fe^{3+} ions catalyse only the starting reaction or also affect the oxidation of sulphide.

2. Experimental methods*

The liquid-phase oxidation of mercaptoacetic acid with molecular oxygen was investigated in a borate buffer at pH = 8, at 50°C and at a concentration of 0.1867 mole/l. The experiments were carried out in a reaction vessel kept at constant temperature, while the oxygen-uptake was measured in a burette system. The basic reaction underlying the study of the catalytic effects was done in the presence of Complexon IV at a concentration of 0.001 mole/l. When investigating the catalytic effect of sulphide and iron, Na_2S and Fe^{3+} ions were introduced into the system at different concentrations at the beginning of the reaction.

3. Experimental results

The results of investigations on the effect of sulphide on the oxygen-uptake are shown in Fig. 1.

It can be seen that sulphide already at very low concentrations, markedly increases the rate of oxygen-uptake as compared with the basic reaction. Being one of the intermediates of the reaction, it thus catalyses the further oxidation of mercaptoacetic acid. The kinetic curves are S-shaped and therefore it can

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* *The experimental data and details of the methods used will be published in the J. Phys. Chem. USSR* in the near future.

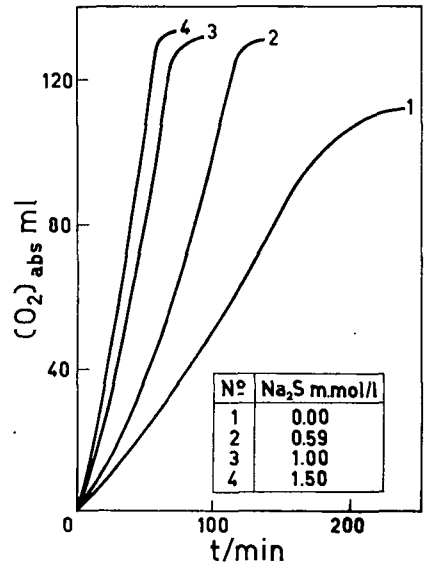

Fig. 1
The effect of sulphide on the oxygen-uptake

by assumed that the sulphide exerts an effect not on the starting reaction, but on the chain branching. Its effect must therefore be considered in the second term of Semenoff's equation as modified by SZABÓ and GÁL [4] (see Table I).

TABLE I

$$\frac{d[O_2]}{dt} = n_0 r + (\varphi + a \cdot [Na_2S])\, d[O_2]$$

$$w_{max} = w_{0,max}\,(1 + b \cdot [Na_2S])$$

$[Na_2S]$ (mmole/l)	$\varphi(S^{-1})$	b	w_{max} observed	w_{max} calculated
0.00	$1.83 \cdot 10^{-4}$	—	0.76	—
0.59	$3.38 \cdot 10^{-4}$	2.31	1.80	1.81
1.00	$4.30 \cdot 10^{-4}$	2.54	2.72	2.55
1.50	$4.90 \cdot 10^{-4}$	2.22	3.28	3.40

As can be seen, the calculated w_{max} values correspond well with the experimental ones. This seems to be a proof that sulphide really influences the chain branching and does not catalyse the initiation of the reaction.

Secondly, we were in agreement with data in the literature that Fe^{3+} ions clearly catalyse the oxidation. This effect is represented in Fig. 2.

The catalytic effect increases proportionately to the concentration of iron ions, but the reaction breaks off more rapidly than the basic reaction or the reaction catalysed by sulphide. It can be assumed that catalysis by iron ions not only contributes to the formation of dithioacetic acid, but also to the further oxidation of sulphide. The change of φ makes it probable that iron ions really affect the chain branching too.

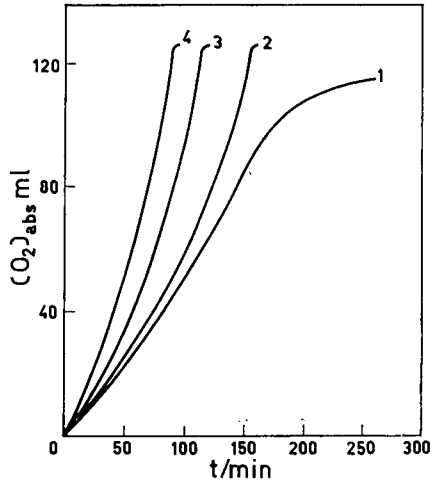

Fig. 2
Fe^{3+} ions shown to catalyse the oxidation.

No.	Fe^{3+}mmol/l	MAA*/Fe^{3+}	φ sec^{-1}
1	0.000		$1.83.10^{-4}$
2	0.175	1780	$3.08.10^{-4}$
3	0.233	1340	$3.30.10^{-4}$
4	0.335	930	$3.64.10^{-4}$

All these data represent results of formal kinetic measurements, but they are insufficient to elucidate the role played by sulphide. We were, however, able to obtain quantitative data on this by using NEIMAN's *kinetic isotope method* [5].

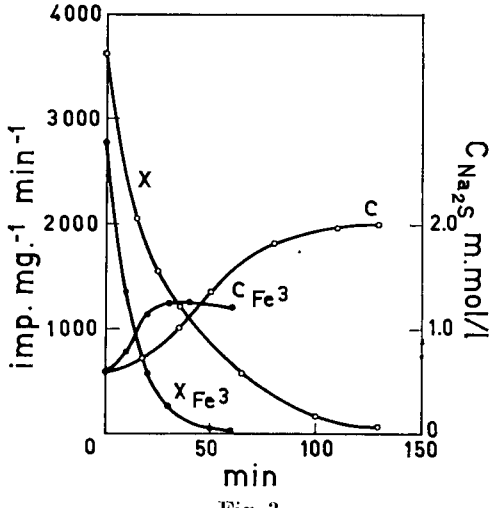

Fig. 3
The effect of iron on sulphide.

* MAA = mercaptoacetic acid.

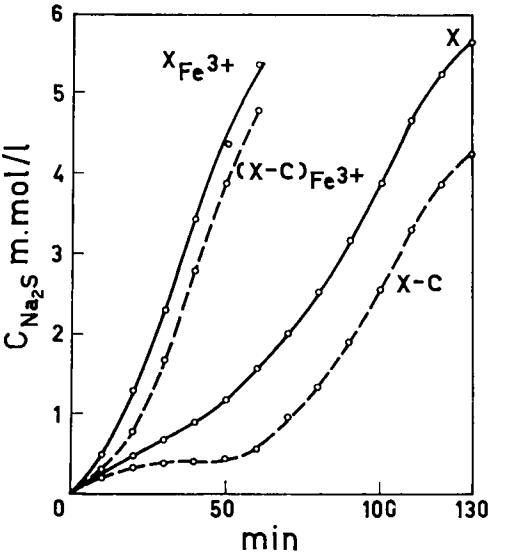

Fig. 4
The amount of sulphide formed and then further oxidized.

Na_2S of a given (0.59 mmole/l) concentration, labelled with S^{35}, was introduced into the system at the beginning of the reaction; the reaction was stopped at different times and the concentration, specific activity and the total activity of sulphide in the solution were measured. The reaction was repeated under conditions when, besides Na_2S^{35}, Fe^{3+} ions at a given concentration were also present in the solution. The latter series of experiments was undertaken to study the effect of iron on sulphide. The results of the experiments are shown in Fig. 3.

In both cases the quantities of sulphide formed and then further oxidized were calculated from experimental data (Fig. 4).

The following equations were used:

The amount formed

$$x = \int_{t_1}^{t_2} w_1 \, dt = -\int_{\alpha_1}^{\alpha_2} c \, d\ln\alpha$$

where α = specific activity; c = concentration (accumulated amount) and w_1 = rate of formation of sulphide.

The latter quantity can be calculated from the equation:

$$w_1 = -c \frac{d\ln\alpha}{dt}$$

and when

$$x \geqslant c \text{ (see Fig. 4).}$$

4. Discussion

On the basis of experimental data mentioned in this paper, the role played by sulphide and the catalytic activity of Fe^{3+} ions can be explained as follows:

1. The kinetic curve of the basic reaction of mercaptoacetic-acid oxidation in the presence of sulphide and Fe^{3+} ions is S-shaped, indicating a chain reaction with degenerated branching, the dehydrogenation of mercaptoacetic acid to dithiodiacetic acid being the first step. This elementary reaction is markedly catalysed by Fe^{3+} ions.
2. Presumably the further oxidation of sulphide is the principal reaction step determining the oxygen-uptake. This assumption is supported by the following experimental facts:
   (i) Sulphide is formed and further oxidized from the very beginning. The dithiodiacetic-acid concentration-*versus*-time curve also supports this experimental fact, namely that a small part of this product further decomposes at the beginning of the reaction. Otherwise the concentration of it might increase linearly.
   (ii) The concentration-*vs.*-time curve of the formation and further oxidation of sulphide has a similar S-shape.
   (iii) By comparing the time values belonging to the rate maxima (see Fig. 5) of sulphide formation, its further oxidation and the oxygen-uptake of the overall reaction at an initial sulphide concentration of 0.59 mmole/l, one observes a striking conformity (maxima are to be found at about 100 min) which indicates a closer relation between the oxygen-uptake of the overall reaction and the further oxidation of sulphide.

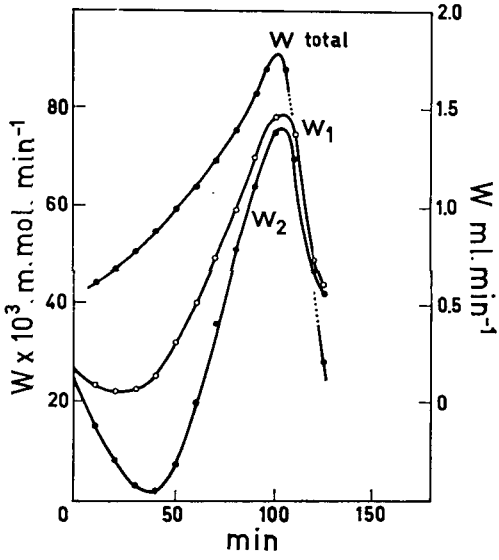

Fig. 5
The relation between the oxygen-uptake of the overall reaction and the further oxidation of sulphide.

   (iv) The presence of this relation is also witnessed by the fact that relatively small amounts of sulphide considerably catalyse the oxygen-uptake, presumably without changing the mechanism of the oxidation reaction.

3. Fe^{3+} ions have a twofold influence on the previously mentioned property of sulphide determining the oxygen-uptake. Owing to catalysis of the initiation, the concentration of dithiodiacetic acid increases, as does the rate of sulphide formation.

4. The afore-mentioned facts indicate that sulphide probably consumes a greater part of the oxygen taken up. However the oxidation of sulphide is a relatively rapid process. This is shown by the fact that the greater part (about 0.45 mmole/l) of the sulphide present at the beginning of the reaction (0.59 mmole/l) swiftly oxidizes and that the further oxidation is interrupted for a short period. However, when sufficient sulphide accumulates again, the further oxidation becomes important too. From this time on, the curves of the concentration of sulphide formed and further oxidized run parallel. The oxygen-uptake of the overall reaction begins to increase more markedly from the time when the oxidation of sulphide increases also. In the case of a catalytic effect by iron, the two curves run parallel from the very beginning of the reaction. This fact indicates, on the one hand, that the oxidation of sulphide takes place rapidly only at certain minimal concentrations (in the case of an iron catalyst, it is maintained from the beginning) and on the other hand, it permits one to assume that the formation of sulphide is the rate-determining process.

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G. Harris (United States of America) asked whether Mr. Gál had evidence that this process was a free radical reaction. The catalysis by Fe ions would seem to indicate that this might be so.

D. Gál replied that not only the catalysis, but the shape of the curves and the φ-branching factor indicated that this was a degenerated chain-branching reaction and naturally free radicals took part in the reaction.

R. C. Pitkethly (United Kingdom) asked Mr. Gál to comment on the form of the X—C curve in Fig. 4. He said there was a peculiar step in the extent of oxidation of sulphide and a number of possible explanations might be given for this behaviour. For example, an inhibition might be produced and further oxidized or there might be a radical-removing process of an order different from the normal termination reactions, giving a more complicated initiation-termination balance.

D. Gál said that in the case in question oxidation of sulphide was a fast reaction and the introduced Na_2S^{35} was rapidly further oxidized till its concentration was lower than a given level. It was therefore probable that in this reaction the initial stage was caused by the intermediate introduced at the start of the reaction.

C^{14}-ISOTOPE EFFECTS IN THE DECARBOXYLATION OF 2-BENZOYLPROPIONIC ACID

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Abstract — Résumé — Аннотация — Resumen

C^{14}-isotope effects in the decarboxylation of 2-benzoylpropionic acid. 2-Benzoylpropionic acid decomposes at temperatures near 70°C, giving carbon dioxide and propiophenone. The kinetics of this decarboxylation have been studied under a variety of conditions; the initial portion of each reaction showed first-order kinetics from which reaction-rate constants could be obtained. The results are in accord with the cyclic, concerted mechanism proposed for the decarboxylation of β-keto acids.

Three syntheses of 2-benzoylpropionic acid were made with C^{14} in the 1, 2, and carbonyl positions respectively. The isotope effect in the decarboxylation of each acid at 78° C was determined by stopping the reaction at various percentages of completion and radioassaying the products or the remaining reactant. These studies do not indicate whether the reaction is concerted.

Effets du ^{14}C dans la décarboxylation de l'acide benzoyl-2 propionique. L'acide benzoyl-2 propionique se décompose à des températures voisines de 70°C en anhydride carbonique et propiophénone. La cinétique de cette décarboxylation a été étudiée sous toute une série de conditions; la partie initiale de chaque réaction suit une cinétique de premier ordre à partir de laquelle les constantes de vitesse de réaction peuvent être obtenues.

Les résultats sont compatibles avec le mécanisme cyclique couplé qui a déjà été proposé pour la décarboxylation des β céto-acides.

Trois synthèses de l'acide benzoyl-2 propionique ont été faites avec du ^{14}C dans les positions 1-, 2-, et dans le carbonyle respectivement. L'effet isotopique au cours de la décarboxylation de chaque acide à 78°C a été déterminé par arrêt de la réaction à différents pourcentages d'achèvement et par radiodosage des produits formés ou du reste du réactant.

Действие изотопа углерода-14 при декарбоксилировании кислоты 2-бензолопропион. Бензолопропионовая кислота-2 распадается при температуре около 70° на двуокись углерода и пропиофенон. При различных условиях рассматривается кинетика декарбоксилации; начальная порция каждой реакции показала первоначальную кинетику, из которой можно составить данные о скорости констант реакции.

Результаты соответствуют цикличности и механизму, предложенному для декарбоксилирования β-кетоновой кислоты.

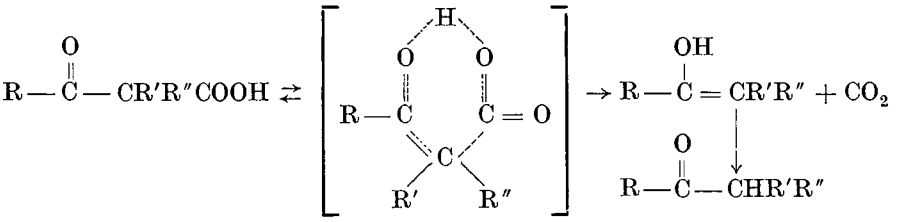
Было проведено три синтеза бензолопропионовой кислоты с применением углерода-14 соответственно в 1-, 2- и углерод-1- позициях. Изотопный эффект в декарбоксилации каждой кислоты при температуре 78° был определен путем замедления реакции при различном проценте ее завершения и путем анализа радиоактивных продуктов или остающегося реагирующего вещества.

Efectos isotópicos del ^{14}C en la descarboxilación del ácido 2-benzoilpropiónico. A una temperatura próxima a los 70° C, el ácido 2-benzoilpropiónico se descompone en anhídrido carbónico y propiofenona. Los autores han estudiado la cinética de esta descarboxilación en distintas condiciones experimentales; la fase inicial de cada reacción obedece a una cinética de primer orden y, sobre esta base, los autores han deducido las constantes de la velocidad de reacción. Los resultados obtenidos concuerdan con los que se obtendrían admitiendo el mecanismo conjugado y cíclico que ha sido propuesto para la descarboxilación de los ácidos β-cetónicos.

Los autores han sintetizado tres ácidos 2-benzoilpropiónicos marcados con ^{14}C en las posiciones 1, 2 y en el grupo carbonilo respectivamente. El efecto isotópico en la descarboxilación de cada uno de los ácidos a 78° C se determinó interrumpiendo la reacción en distintas fases de la misma y analizando por métodos radioanalíticos los productos finales o la parte que todavía no había reaccionado.

1. Introduction

Although acids generally decarboxylate by first-order reactions of their anions—that is, by the well-known carbanion mechanism [1] — β-keto acids lose carbon dioxide by a different route. On the basis of much experimental evidence, SCHENKEL *et al.* [2] proposed a concerted mechanism with a cyclic transition state for the decarboxylation of β-keto acids:



This mechanism is now generally accepted.

The object of the present investigation was to determine the C^{14} kinetic isotope effects associated with the decomposition of a β-keto acid labelled successively in the 1, 2, and carbonyl positions in the hope that significant correlations might be found between the observed effects and the cyclic, concerted reaction *mechanism*.

Simple β-keto acids have not been previously studied in this manner. Some work has been done on ketodicarboxylic acids, such as oxaloacetic acid [3], but the interest here has been in the metal-catalysed reactions.

Probably no reaction has been studied by the use of isotope effects more extensively than the decomposition of malonic acid [4]. Although this acid is not a β-keto acid, it is similar in structure; a cyclic, concerted mechanism has been suggested for its decomposition [5].

2-Benzoylpropionic acid was selected for this work because it decomposes cleanly at relatively low temperatures and is sufficiently stable at room temperature. In addition, it is a solid which can be easily recovered and purified. For this reason the isotope effects were determined by radioassay of the acid both before and after a known amount of reaction had occurred.

The decomposition of a β-keto acid should be a first-order reaction of the undissociated acid. To confirm this, the kinetics of the decomposition of 2-benzoylpropionic acid were studied under the same conditions that were used to determine the isotope effects.

2. Experimental procedures

SYNTHESIS OF COMPOUNDS

Commercial reagent-grade chemicals were used, generally without further purification. Melting points were determined with a hot-stage melting point apparatus and are uncorrected. Overall radioactivity yields were excellent in the syntheses.

Preparation of 2-benzoylpropionic acid

This compound was prepared by the method of LEVINE *et al.* [6] in which the enolate of propiophenone is carbonated with solid carbon dioxide. Use of potassium amide gave twice the yield which was obtained when sodium amide was used. The ether extract of the acid was evaporated. The crude product was dissolved in a minimum of benzene and crystallized by addition of a 2-volume excess of petroleum ether (BP 35—60°C). After the acid was recrystallized, a 61% yield was obtained, MP 77—78°C ([7] MP 82—83°C).

Preparation of 2-benzoylpropionic acid-1-C^{14}

A 50% excess of the enolate of propiophenone in dry ether was carbonated with carbon dioxide which was liberated from barium carbonate-C^{14} in an apparatus similar to that described by LAMPRECHT *et al.* [8] for the preparation of acetic acid-1-C^{14}. After the product was crystallized twice a 56% yield (based on the radioactivity of the barium carbonate) of the acid was obtained; MP 77°—78° C; radioactivity, about 8 μc/mmole.

Preparation of 2-benzoylpropionic acid-2-C^{14}

Acetic acid-1-C^{14} was prepared from 1.42 mc of barium carbonate-C^{14} by the method of LAMPRECHT *et al.* [8] and obtained as the sodium salt in 90% yield by a method described by MURRAY *et al.* [9].

A portion of the sodium acetate-1-C^{14} was converted to ethyl acetate-1-C^{14} by heating it with an excess of ethyl phosphate to 200°C. Redistillation of the product on the vacuum line gave a 95% yield of pure ethyl acetate-1-C^{14}.

The labelled ester was reduced with lithium aluminium hydride in the usual manner. After reduction was complete, the ether which had been used as the solvent was removed as completely as possible on a vacuum line. The residual solid was treated with a mixture of concentrated sulphuric acid and 48% hydrobromic acid. The 1-bromoethane-1-C^{14} thus liberated was condensed and purified by distillation on a vacuum line successively from calcium oxide and phosphorus pentoxide (92% yield).

A Grignard reagent was prepared from the 1-bromoethane-1-C^{14} in the usual manner and poured on to solid carbon dioxide. The resulting propionic acid-2-C^{14} was recovered as the sodium salt in 92% yield by the method used for preparation of acetic acid-1-C^{14}.

Propiophenone-2-C^{14} (BP 98—100°C at 14 mm, 86% yield) was prepared from sodium propionate-2-C^{14}, benzene and anhydrous aluminium chloride by the method of SPEER *et al.* [10].

The labelled ketone was converted to 2-benzoylpropionic-2-C^{14} acid in 61% yield exactly as described for the unlabelled acid; radioactivity, 8.0 μc/mmole.

Preparation of 2-benzoylpropionic acid-carbonyl-C^{14}

Benzoic acid-1-C^{14} was prepared from 2 mc of barium carbonate-C^{14} by carbonation of a 20% excess of phenylmagnesium bromide, as described for acetic acid-1-C^{14}. The acid was recovered by a method described by CHERONIS [11]; 86% yield; radioactivity, 340 μc/mmole.

A portion of the benzoic acid-1-C^{14} was converted to benzoyl chloride-1-C^{14} by refluxing with excess thionyl chloride. Upon distillation, a 91% yield of product was obtained, BP 190—193°C.

Propiophenone-1-C^{14} was prepared from benzoyl chloride-1-C^{14} and diethylcadmium in benzene by the method of CASON [12] in 72% yield, BP 100—102°C at 15.5 mm.

This compound was converted to 2-benzoylpropionic acid-carbonyl-C^{14} in 60% yield by the method used to prepare the unlabelled acid.

PROPERTIES OF THE ACIDS

All preparations of the acid had identical melting points (77—78°C). Upon decarboxylation a sample of each preparation gave a nearly quantitative yield of carbon dioxide (within 1%). Titration with a standard solution of base indicated a molecular weight of 178.0 ± 0.2 compared to a calculated value of 178.2. Absolute ethanol solutions of equal amounts of all the acids gave virtually identical ultraviolet absorption spectra over the range of 220—360 mμ. One maximum at 242 mμ was observed for each preparation.

KINETIC PROCEDURES

A 0.09—0.14-g sample of the acid was weighed into a reaction tube, and the latter was connected to a gas burette. The contents of the tube could be vigorously agitated by means of a magnetic stirrer. The apparatus was maintained at 78 or 68°C to within ±0.02°. As the acid decomposed, the volume of carbon dioxide produced was measured periodically while the pressure was maintained at atmospheric with a mercury-levelling bulb. The measured carbon dioxide volume was corrected for the solubility of carbon dioxide in the reaction mixture. The latter was determined under the various reaction conditions by means of a Van Slyke blood gas analyser. It was then possible to calculate the amount of the remaining acid at any time.

DETERMINATION OF THE ISOTOPE EFFECTS

Samples of the acid were decomposed under a variety of conditions to various extents of reaction as determined by the volume of carbon dioxide liberated. The reaction was stopped by neutralization of the acid with base. The reaction mixture was extracted with ether, and the ether extract discarded. The aqueous phase was acidified, and the remaining acid was recovered and purified as described for the preparation of 2-benzoylpropionic acid. Unreacted acid samples were subjected to this recovery procedure for purposes of control.

The recovered acids were prepared for radioassay by oxidation with chromic acid solution [13]. Determination of the radioactivity of the carbon dioxide thus produced was made on a vibrating-reed electrometer. Isotope effects were calculated from these data by means of the following equation [14]:

$$\frac{k^*}{k} = 1 + \frac{\log (A_f/A_0)}{\log (1-f)}$$

where: k^*/k = the ratio of the reaction rate constants of the labelled and the ordinary acid, A_0 = the initial specific radioactivity of the acid, and A_f = the specific radioactivity of the acid which was recovered after the reaction had proceeded to the extent of f.

3. Results and discussion

The reaction rate constants for the decarboxylation of 2-benzoylpropionic acid under various conditions are given in Table I. These were determined by plotting the logarithm of the amount of the remaining acid against time (from

TABLE I

SPECIFIC REACTION RATE CONSTANTS FOR THE DECARBOXYLATION OF 2-BENZOYLPROPIONIC ACID UNDER VARIOUS CONDITIONS

Reaction Conditions	Initial Rate Constants ($s^{-1} \times 10^3$)
78°C, pure solid	2.07 ± 0.055*
68°C, pure solid	0.83 ± 0.015
78°C, in 1,1-diphenylethane .	1.87 ± 0.068
68°C, in 1,1-diphenylethane .	0.78 ± 0.035
78°C, in propiophenone	0.92 ± 0.018

* Average deviation of the mean.

the time that thermal equilibrium and homogeneity of the mixture had been attained), determining the half-life period τ of the reaction directly from the graph and calculating the rate constant from the relation

$$k = \frac{2.3 \log 2}{\tau}$$

Fig. 1 is an example of the types of curve obtained. In the case of those runs in which no solvent was added the curvature was even more pronounced. When propiophenone was present initially, parallel straight lines were obtained over a range of 20—80% reaction.

These results can be readily explained if decomposition of the acid involves the cyclic transition state previously mentioned. The carbonyl oxygen atom of the propiophenone formed in the reaction can form hydrogen bonds with the carboxyl hydrogen atom of the acid. As the decomposition proceeds and the relative amounts of ketone increase, the acid molecules attain a cyclic configuration with more difficulty and the magnitude of the rate constant decreases. The dilution effect caused by addition of 1,1-diphenylethane, which cannot form hydrogen bonds, would be expected to straighten the curves somewhat. If sufficient propiophenone is added initially, the environment of the acid changes very little as the reaction proceeds, and a straight line is obtained in the plot of the logarithm of the remaining amount of acid *versus* time.

The rate constants given in Table I were determined from the first part of each curve because this is the most precise portion, and because the influence of the propiophenone is at a minimum.

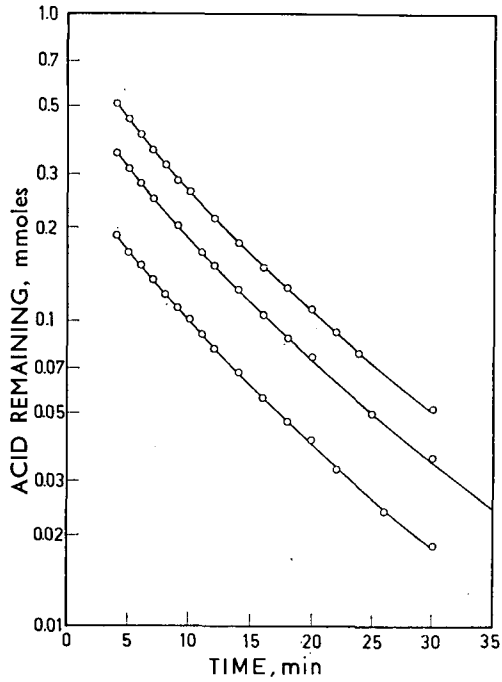


Fig. 1
Decarboxylation of 2-benzoylpropionic Acid in 1,1-diphenylethane at 78°C.

The magnitude of the activation energy calculated from the rate constants for the pure acid at 78 and 68°C is 21.8 kcal/mole. This value, along with other necessary quantities from Table I, was used to calculate the entropy of activation,

TABLE II
OBSERVED ISOTOPE EFFECTS IN THE DECARBOXYLATION OF 2-BENZOYLPROPIONIC ACID

Position of C^{14}	Temperature (°C)	Extent of Reaction (%)	Isotope Effect (k/k*)	Average k/k*	95% Confidence Limits
1	58	89.6	1.071		
		82.9	1.084	1.077	0.0139
		86.1	1.076		
1	78	83.4	1.079		
		77.4	1.072	1.074	0.0109
		60.5	1.071		
2	78	59.8	1.053		
		86.2	1.053	1.051	0.0086
		77.4	1.047		
2†)	78	87.8	1.052		
		81.3	1.054	1.053	0.0127
carbonyl	78	63.1	0.998		
		78.0	1.001	1.000	0.0043
		85.0	1.001		

†) In a solution of 1,1-diphenylethane.

ΔS^*, which was found to have a value of —11 e.u. This negative value for ΔS^* further substantiates the cyclic transition state, for internal rotations in the non-cyclic reactant become vibrations in the cyclic activated complex with a loss of entropy [15].

The observed isotope effects are given in Table II. Each isotope effect is derived from 3 to 5 radioactivity assays of each acid sample. There was no significant difference between the control samples and the original acid. The difference in the isotope effects for 2-benzoylpropionic-1-C^{14} acid at 58 and at 78°C is not significant, while the difference in isotope effects for the acids labelled in the 1 and 2 positions is statistically significant, as shown by the "t" test [16].

If the decomposition of 2-benzoylpropionic acid is a concerted reaction with a cyclic transition state, it is a six-centred reaction. Each of the six atoms in the ring has a σ or π-bond broken and a σ or π-bond formed during the reaction. Consequently, no single equation or model has been found to give theoretical values for the three isotope effects close to those experimentally determined.

However, the maximum isotope effects may be calculated by means of BIGELEISEN'S equation [17]:

$$k_1/k_2 = (m_2^*/m_1^*)^{1/2}\left(1 + \sum_i^{3n-6} G(\mu_i)\,\Delta\mu_i - \sum_i^{3n'-6} G(\mu_i^{\ddagger})\,\Delta\mu_i^{\ddagger}\right),$$

where $G(\mu_i) = 1/2 - 1/\mu_i + 1/(e^{\mu_i} - 1)$,

$\mu_i = h\omega_i/kT$,

ω_i = the vibrational frequencies of the molecule,

$\Delta\mu_i = h\,(\omega_{i(1)} - \omega_{i(2)})/kT$,

h = Planck's constant,

k = Boltzman's constant,

T = absolute temperature,

k_1 and k_2 are reaction rate constants for the normal and labelled molecules respectively, and m_1^* and m_2^* are effective masses of the complex along the coordinate of decomposition for the two molecules.

The maximum isotope effect will be found when the bond to the isotope atom is broken and no bond formed in the activated complex, that is, when

$$\sum G(\mu_i^{\ddagger})\,\Delta\mu_i^{\ddagger} = 0\ .$$

If one assumes a vibrational frequency of 900 cm^{-1} for the C^{12}—C^{12} bond which is broken in the reaction, then the frequency of the C^{12}—C^{14} bond may be calculated to be 934 cm^{-1} from the equation

$$\omega_2 = \omega_1\,(\mu_1/\mu_2)^{1/2},$$

where ω_1 and ω_2 are the vibrational frequencies of C^{12}—C^{12} and C^{12}—C^{14} respectively and μ_1 and μ_2 are the reduced masses of C^{12}—C^{12} and C^{12}—C^{14} respectively. When these values are substituted into Bigeleisen's equation and the reduced masses of C^{12}—C^{12} and C^{12}—C^{14} are used for m_1^* and m_2^*, maximum values of the isotope effects may be calculated. These are given in Table III.

If a vibrational frequency of 1600 cm^{-1} for the C=O bond in Ph—C(=O)— and a frequency of 1240 cm^{-1} for the C—O bond in Ph—C(—O)— are assumed, and if the latter is taken as the frequency of the C—O bond in the transition state, then a maximum value for the isotope effect in the decomposition of the acid labelled in the carbonyl position may be calculated. This value is given in Table III.

TABLE III

ISOTOPE EFFECTS IN THE DECARBOXYLATION OF 2-BENZOYLPROPIONIC ACID

Position of C^{14}	Calculated (Maximum)	Experimental
1	1.089	1.074
2	1.089	1.051
carbonyl	1.039	1.000

The experimental isotope effects found for decomposition of 2-benzoylpropionic acid abelled in the 1 and 2 positions are significantly less than the values calculated on the basis of fission of the C—C bond only. Consequently it appears that bond formation with other atoms occurs in the case of both carbon 1 and 2 as the bond between them breaks. This may be considered to support the proposal that the reaction is, to some degree at least, a concerted one.

The isotope effect obtained by decomposition of the compound labelled in the 2 position is significantly lower than that for the molecule labelled in the 1 position. This datum indicates that a greater degree of bond formation occurs between carbon atom 2 and the carbonyl carbon atom than between carbon 1 and the oxygen atom of the carboxyl group. In view of the greater ease of formation of C=C bonds as compared to C=O bonds, the difference seems to be justified.

The experimental value of 1.000 for the isotope effect in the decomposition of the acid labelled with C^{14} in the carbonyl position differs considerably from the calculated maximum value of 1.039. This difference may be explained in two ways.

The carbonyl carbon atom is involved in both the breaking of a C—O π-bond and the formation of a C—C π-bond either in the rate-determining step or in a subsequent step. If these changes occur in the rate-determining step an isotope effect would probably be found when the acid is labelled with C^{14} in the carbonyl position. Even if $\Sigma G(\mu^{\pm})\,\Delta\,\mu^{\pm}$ were equal to $G(\mu)\Sigma\,\Delta\,\mu$, the difference in reduced masses of the C^{12}-O and C^{14}-O atoms would still give a value of 1.0435 for the isotope effect. If the value of $\Sigma G(\mu^{\pm})\,\Delta\,^{\pm}\mu$ were sufficient larger than the value of $\Sigma G(\mu)\,\Delta\,\mu$, the magnitude of the isotope effect might be reduced to approximately one, but this seems unlikely.

If the changes in the bonds to the carbonyl carbon atom of the acid do not occur in the rate-determining step of the reaction, the value of the isotope effect in this case should be 1.000. This explanation seems more plausible than the previous one.

The question of whether this reaction is concerted is not answered by a study of the C^{14} isotope effects. The evidence, although not definite in either direction, is conflicting. Other experimental methods or more precise theoretical calculations are needed to determine whether the reaction is concerted.

5. Conclusions

Studies of the kinetics of the thermal decarboxylation of 2-benzylpropionic acid indicate that the reaction may have a cyclic transition state. Studies of the C^{14} isotope effects do not indicate whether the reaction is concerted.

ACKNOWLEDGEMENTS

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DISCUSSION

A. E. de Vries (Netherlands) said that in the calculations given for the maximum isotope effect it was assumed that the forces between the non-reacting atoms in the transition state were the same as in the original molecule. When this was not the case, the values found for isotope effects were usually smaller than calculated. It seemed probable to hin, therefore, that the authors' results might be explained by a change in bond strength and that no bond formation need be assumed. He asked wether Mr. Hodnett had made any calculations perhaps about the effect which might be induced by a change in bond strength alone?

E. M. Hodnett replied that no such calculations had been made. However, he suggested, as one possible explanation, that the results observed might be due to bond formation.

J. F. Ford (United Kingdom) asked whether Mr. Hodnett had examined the effect of added carboxylic acids of greater strength than 2-benzoylpropionic acid. This should affect the concentration of the internally bonded monomer complex suggested as a transition state, and thus the rate of decarboxylation.

E. M. Hodnett said that no other strong acids were added to the reaction mixture.

EVALUATION OF DEUTERIUM ISOTOPE EFFECTS IN PHOTOCHEMICAL REACTIONS OF FORMIC-d ACID BY USE OF C^{14}

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Abstract — Résumé — Аннотация — Resumen

Evaluation of deuterium isotope effects in photochemical reactions of formic-d acid by use of C^{14}. The usefulness of measured values of primary and secondary deuterium kinetic-isotope-effect ratios in the study of organic reactions is well known. However, measurement of such ratios by direct methods is sometimes difficult. An indirect method which can be used to circumvent difficulties in some cases is illustrated by the determination of the primary deuterium isotope effects in the vapour-phase reactions between $HCOOH + Cl_2$ and $HCOOH + Br_2$ which under the influence of visible light give CO_2 and respectively 2 HCl and 2 HBr.

For the evaluation of k_D/k_H, the ratio of specific rate constants for reaction of formic-d acid and formic acid, a 50:50 mixture of DCOOH and $HC^{14}OOH$ was added to enough chlorine (or bromine) to effect reaction of approximately 5% of the mixture of acids. The C^{14} dioxide produced was precipitated as barium carbonate-C^{14}, of which the specific activity (S_5) was then determined by radioassay of the gas released when a sample was acidified. The specific activity (S_{100}) of the barium carbonate-C^{14} representing 100% reaction of a portion of the 50:50 mixture of DCOOH and $HC^{14}OOH$ with excess chlorine was also determined. A simple equation was derived, making the reasonable assumption that the C^{14} isotope effects in the two reactions mentioned are negligibly small in comparison with the deuterium isotope effects. Using the equation, k_H/k_D values, 2.0 and 2.7, were calculated for reactions with Cl_2 and Br_2 respectively.

An earlier study (Ropp, Danby, and Dominey, 1957) showed that reaction with Cl_2 was accompanied by a much smaller C^{13} kinetic isotope effect than the reaction with Br_2. This was taken as an indication that the carbon-hydrogen bond is stretched more in the transition state for the Br_2 reaction than for the Cl_2 reaction. The difference reported here between the corresponding deuterium isotope effects is less pronounced, though in the same direction as the difference between the C^{13} effects. A reasonable conclusion is that bromine-hydrogen bonds formed in the transition state for the reaction with Br_2 largely compensate the stretching of the carbon-hydrogen bond.

Evaluation a l'aide du ^{14}C des effets isotopiques du deutérium dans les réactions photochimiques de l'acide formique-D. On sait qu'il est utile de connaître les rapports quantitatifs qui existent entre les effets isotopiques cinétiques primaires et secondaires du deutérium pour l'étude des réactions organiques. Il est quelquefois difficile cependant de mesurer ces rapports par des méthodes directes. Une méthode indirecte qui permet de tourner ces difficultés dans certains cas consiste à déterminer les effets isotopiques primaires du deutérium dans les réactions suivantes en phase vapeur:

$$HCOOH + Cl_2 \xrightarrow[\text{visible}]{\text{lumière}} 2HCl + CO_2 \qquad (1)$$

$$HCOOH + Br_2 \xrightarrow[\text{visible}]{\text{lumière}} 2HBr_2 + CO_2. \qquad (2)$$

Pour l'évaluation de k_D/k_H — rapport des constantes de vitesse de réaction de l'acide formique-D et de l'acide formique — un mélange à parts égales de DCOOH et de $H^{14}COOH$ a été ajouté à une quantité de chlore (ou de brome) suffisante pour faire réagir environ 5% du mélange d'acides. Le $^{14}CO_2$ produit a été précipité sous forme de $Ba^{14}CO_3$, dont l'activité spécifique (S_5) a été ensuite déterminée par radioexamen du gaz dégagé lorsqu'on a acidifié l'échantillon. L'activité spécifique (S_{100}) du $Ba^{14}CO_3$ obtenu après réaction totale d'une partie du mélange à parts égales de DCOOH et de $H^{14}COOH$ avec un excès de chlore, a été également déterminée. On en a tiré une équation simple en partant de l'hypothèse apparemment raisonnable que les effets isotopiques du carbone-14 dans les réactions (1) et (2) sont négligeables en comparison de ceux du deutérium. L'équation donné comme valeurs de k_H/k_D 2,0 et 2,7 pour les réactions (1) et (2) respectivement.

Une étude antérieure (Ropp, Danby et Dominey, 1957) a montré que la réaction (1) s'accompagnait d'un effet isotopique cinétique du carbone-13 bien moindre que dans la réaction (2). Les auteurs avaient interprété cela comme indiquant que la liaison carbone-hydrogène s'étend davantage, dans l'état de transition, pour la réaction (2) que pour la réaction (1). La différence signalée dans le mémoire entre les effets correspondants du deutérium est moins prononcée, encore qu'elle se manifeste dans le même sens. Il paraît raisonnable d'en conclure que les liaisons brome-hydrogène formées pendant l'état de transition dans la réaction (2) compensent largement l'extension de la liaison carbone-hydrogène.

Оценка действия изотопов дейтерия в фотохимических реакциях муравьиной-d-кислоты путем использования углерода-14. Широко известна полезность измерения объемов первого и второго порядка соотношений кинетического воздействия изотопов дейтерия при изучении органических реакций. Однако измерения таких соотношений прямыми способами в некотором роде затруднены. Применение косвенного метода, который может быть использован для того, чтобы преодолеть трудности в ряде случаев, демонстрируется на определении воздействий изотопов дейтерия первого порядка в следующих реакциях парообразной фазы:

$$H\,COO\,H + Cl_2 \xrightarrow[\text{свет}]{\text{видимый}} 2\,H\,Cl + CO_2 \qquad (1)$$

$$H\,COO\,H + Br_2 \xrightarrow[\text{свет}]{\text{видимый}} 2\,H\,Br + CO_2 \qquad (2)$$

Для того, чтобы произвести оценку κ_D/κ_H-коэффициента специфической скорости констант для реакций муравьиной-d и муравьиной кислот к достаточному количеству хлора (или брома) добавляется смесь 50:50 DCOOH и $HC^{14}OOH$ с тем, чтобы произвести реакцию с приблизительно 5% смеси кислот. Полученный диоксид углерода-14 выделяется в осадок в виде карбоната-бария-C^{14}, специфическая активность (S_5) которого затем замеряется при анализе на радиоактивность высвобожденного газа в момент окисления образца. Также определяется специфическая активность (S_{100}) карбоната бария-C^{14}, представляющего 100%-ную реакцию части смеси 50:50 DCOOH и $HC^{14}OOH$ с излишним хлором. Было выведено уравнение, что дало возможность сделать обоснованное утверждение о том, что воздействие изотопов углерода-14 в реакциях (1) и (2) очень мало в сравнении с воздействием изотопов дейтерия. Используя уравнение (3), были подсчитаны k_H/k_D объемов 2,0 и 2,7 соответственно для реакций (1) и (2).

Ранние исследования (Ропп, Денби и Доминей, 1957 год) показали, что реакция (1) проходила при значительно меньшем кинетическом воздействии изотопа углерода-13, чем реакция (2). Это было принято в качестве показателя того, что углеродно-водородная связь более усиливается в переходной стадии в реакции (2), чем в реакции (1). Отмечаемое в настоящем исследовании различие между соответствующими изотопами дейтерия менее выражено, хотя оно идет по тому же направлению, что и различие между воздействиями углерода-13. Делается обоснованный вывод о том, что бромо-водородные связи, образующиеся в переходной стадии для реакции (2), в значительной степени компенсируют увеличение углеродно-водородной связи.

Evaluación con ayuda de ^{14}C de los efectos isotópicos del deuterio en las reacciones fotoquímicas del ácido fórmico-D. Los valores medidos de las razones de los efectos isotópicos cinéticos primarios y secundarios del deuterio son de evidente utilidad para el estudio de las reacciones orgánicas. Pero algunas veces es difícil medir estas razones por métodos directos. La determinación de los efectos isotópicos primarios del deuterio en las siguientes reacciones en fase vapor constituye un ejemplo ilustrativo de un método indirecto que puede utilizarse para subsanar algunas dificultades:

$$HCOOH + Cl_2 \xrightarrow[\text{visible}]{\text{luz}} 2HCl + CO_2 \qquad (1)$$

$$HCOOH + Br_2 \xrightarrow[\text{visible}]{\text{luz}} 2HBr + CO_2 \qquad (2)$$

Para evaluar el cociente k_D/k_H, esto es, la razón de las constantes específicas de velocidad de reacción de los ácidos fórmico-D y fórmico, el autor añadió una mezcla 50:50 de DCOOH y $H^{14}COOH$ a una cantidad suficiente de cloro (o de bromo) para que reaccione aproximadamente el 5 por ciento de la mezcla de ácidos. Precipita como $Ba^{14}CO_3$ el $^{14}CO_2$ que se forma y determina su actividad específica (S_5) analizando por métodos radioanalíticos el gas que se desprende al acidificar la muestra. Determina también la actividad específica (S_{100}) del $Ba^{14}CO_3$, que representa la reacción total de una parte de la mezcla 50:50 de DCOOH y $H^{14}COOH$ con un exceso de cloro. Dedujo una ecuación simple suponiendo lícitamente que los efectos isotópicos del carbono-14 en las reacciones 1) y 2) son despreciables en comparación con los efectos isotópicos del deuterio. Partiendo de esa ecuación, calcula los valores 2,0 y 2,7 para los cocientes k_H/k_D correspondientes a las reacciones 1) y 2) respectivamente.

Un estudio anterior (Ropp, Danby y Dominey, 1957) permitió comprobar que en la reacción 1) el efecto isotópico cinético del carbono-13 es mucho menor que el correspondiente a la reacción 2). Este hecho se tomó como indicación de que, en el estado de transición, el enlace carbono-hidrógeno sufre un alargamiento mayor en la reacción 2) que en la reacción 1). La diferencia entre los correspondientes efectos isotópicos del deuterio que menciona la presente memoria es menos pronunciada, pero tiene la misma dirección que la diferencia entre los efectos del carbono-13. Conclusión lógica es que los enlaces bromo-hidrógeno creados en el estado de transición correspondiente a la reacción 2) compensan en gran medida el alargamiento del enlace carbono-hidrógeno.

1. Introduction

During the past thirty years the usefulness of measured values of deuterium kinetic-isotope-effect ratios in the study of chemical reactions has been demonstrated in many dozens of cases [1]. Investigations of deuterium kinetic isotope effects have also contributed materially to the development of the theory of reactions rates [2]. Kinetic isotope effects may be classed as *primary* isotope effects or *secondary* isotope effects. Primary isotope effects occur in reactions in which the labelled atom is critically involved in the transition state of the rate-controlling process. Secondary isotope effects occur in reactions in which the labelled atom is less directly involved in this transition state. Primary deuterium kinetic-isotope-effect ratios, k_H/k_D, usually have values between 2 and 7, while secondary deuterium-isotope-effect ratios usually have values of less than 2.

Both primary and secondary deuterium kinetic isotope effects have been evaluated by measurements of the specific reaction-rate constant for a pure deuterium-labelled compound, measurement of the specific reaction-rate constant for the corresponding unlabelled compound, and calculation of the ratio of the two separately measured rate constants. This procedure has been widely used

and frequently gives reliable results. In the study of some reactions, however, this direct approach may give questionable k_H/k_D values. In reactions which involve radical chains, for example, great care must be taken to ensure that traces of impurities present to different extents in the reactions compared do not lead to erroneous estimates of the rate-constant ratios. In many such cases it is more practical to evaluate the deuterium isotope-effect ratios by *competitive techniques* like those used in the study of carbon, nitrogen, oxygen, sulphur, and chlorine kinetic-isotope-effect ratios [3]. When these competitive techniques are employed, the deuterium compound and the corresponding hydrogen compound are mixed and undergo reaction in the same vessel. Accordingly impurities and other effects of the environment can alter the reaction rates of both isotopic species and ordinarily have no effect on the measured ratio of isotopic rate-constants. Use of a competitive technique for evaluating a kinetic-isotope-effect ratio does, of course, require that some method be available for measuring the isotopic concentration of a reactant or product during the course of the reaction [3]. A technique which employs C^{14} in the evaluation of deuterium isotope-effects is illustrated by two examples which are discussed in the following sections.

2. The photochemical reaction of formic acid with halogen atoms

The vapour-phase reactions:

$$HCOOH + Cl_2 \xrightarrow{\text{visible light}} 2\,HCl + CO_2 \tag{1}$$

and

$$HCOOH + Br_2 \xrightarrow{\text{visible light}} 2\,HBr + CO_2 \tag{2}$$

have been investigated by photochemical [4] and isotopic [5] techniques. Reaction (1) has been shown to have a quantum yield of several thousand and chloroformic acid has been suggested as an intermediate [4], although subsequent mass-spectrometric work [6] has failed to confirm the presence of chloroformic acid during the reaction. Both reactions presumably take place through a mechanism analogous to the hydrogen-chlorine reaction [4]. If the symbol X is used to represent a halogen atom the assumed mechanism is:

$$X_2 \xrightarrow{\text{visible light}} 2\,X\cdot \tag{3}$$

$$X\cdot + HCOOH \rightarrow HX + \cdot COOH \tag{4}$$

$$\cdot COOH \rightarrow CO_2 + H\cdot \tag{5}$$

$$H\cdot + X_2 \rightarrow HX + X\cdot \tag{6}$$

$$2X\cdot \rightarrow X_2 \tag{7}$$

3. Method of evaluating the deuterium isotope effects

Each of the reactions, (1) and (2), was carried out using an approximately 50:50 mixture of formic-d acid and formic-C^{14} acid (formic acid containing a very small precentage of C^{14}-labelled molecules). In each case the reaction was carried to about 5% conversion of the formic-acid mixture. The specific activity of the C^{14} dioxide produced at 5% reaction was used to calculate k_D/k_H, as indicated in section 4.

4. Derivation

For the evaluation of k_D/k_H, the ratio of isotopic specific rate-constants, it is convenient to derive a simple equation relating this ratio to S_5, the specific activity of C^{14} dioxide produced by approximately 5% reaction of a sample of the formic-d acid/formic-C^{14} acid mixture, to S_{100}, the specific activity of C^{14} dioxide produced by 100% reaction of a second sample of the formic acid mixture, and to R, the molar ratio of formic-C^{14} acid to formic-d acid in the formic-acid mixture. Although C^{14} isotope effects occur, they can be assumed to be negligible in magnitude in comparison with the deuterium isotope-effects being measured. These C^{14} isotope-effects have therefore been ignored in the following derivation.:

The specific rate-constants for reaction of the three isotopic species of formic acid with chlorine are as indicated in the equations:

$$HC^{12}OOH + Cl_2 \xrightarrow{k_H} 2\,HCl + C^{12}O_2$$

$$HC^{14}OOH + Cl_2 \xrightarrow{k_H} 2\,HCl + C^{14}O_2$$

$$DC^{12}OOH + Cl_2 \xrightarrow{k_D} HCl + DCl + C^{12}O_2.$$

For small percentages of reaction the following are reasonable approximations:

$$[C^{14}O_2] = k_H\,[HC^{14}OOH] \text{ and}$$
$$[C^{12}O_2] = k_H\,[HCOOH] + k_D\,[DCOOH],$$

where $[C^{12}O_2]$ and $[C^{14}O_2]$ = molar concentrations of isotopic species in the carbon dioxide produced; [HCOOH], $[HC^{14}OOH]$, and [DCOOH] = molar concentrations of isotopic species in the formic acid mixture used. Therefore for small reaction percentages,

$$\frac{[C^{12}O_2]}{[C^{14}O_2]} = \frac{[HCOOH]}{[HC^{14}OOH]} + \frac{k_D\,[DCOOH]}{k_H\,[HC^{14}OOH]}.$$

If $r = \dfrac{[DCOOH]}{[HCOOH]}$ = the ratio of molar concentrations of deuteroformic acid to formic acid in the acid mixture used, then $[DCOOH] = r\,[HCOOH]$ and

$$\frac{[C^{12}O_2]}{[C^{14}O_2]} = \frac{[HCOOH]}{[HC^{14}OOH]} + r\left(\frac{k_D}{k_H}\right)\frac{[HCOOH]}{[HC^{14}OOH]}.$$

Since C^{14} specific activities are proportional to concentrations of the C^{14}-labelled molecules, the preceding equation may be rewritten:

$$\frac{1}{S_5} = \frac{1}{S_F}\left[1 + r\left(\frac{k_D}{k_H}\right)\right]$$

or

$$\frac{k_D}{k_H} = \frac{1}{r}\left(\frac{S_F}{S_5} - 1\right),$$

where S_F = specific activity of formic-C^{14} acid before mixing with formic-d acid. The right-hand side of the last equation involves only experimentally measurable quantities. This equation can sometimes be used directly to evaluate k_D/k_H. In the present case, however, it is more convenient to eliminate S_F.

If a sample of the prepared formic-d acid/formic-C^{14} acid mixture is completely oxidized by excess chlorine, the resulting C^{14} dioxide will have the same specific activity as the formic-d acid/formic-C^{14} acid mixture,

$$S_{100} = \frac{[HC^{14}OOH]}{[HCOOH] + [DCOOH]} = \frac{[HC^{14}OOH]}{[HCOOH] + r[HCOOH]}$$

$$= \frac{[HC^{14}OOH]}{[HCOOH]}\left(\frac{1}{1+r}\right) = S_F\left(\frac{1}{1+r}\right)$$

and

$$S_F = (1 + r)\, S_{100}.$$

If this expression for S_F is substituted in the expression previously derived for k_D/k_H, the result is

$$\frac{k_D}{k_H} = \frac{1}{r}\left[(1+r)\frac{S_{100}}{S_5} - 1\right]$$

$$= \left(\frac{1}{r} + 1\right)\left(\frac{S_{100}}{S_5}\right) - \frac{1}{r}.$$

For convenience, substitute R for $\frac{1}{r}$ and the final result is

$$\frac{k_D}{k_H} = (R + 1)\left(\frac{S_{100}}{S_5}\right) - R$$

where R represents the ratio previously defined.

5. Experimental methods and results

The formic-d acid/formic-C^{14}-acid mixture was prepared by vacuum-distilling a 50:50 mixture of sodium formate-d and sodium formate-C^{14} (approximately 7 mc/mole) with anhydrous phosphoric acid. The distillate was dried over fused boron oxide and again vacuum-distilled. The value of R for the product was found to be 1.10 by mass-spectrometric analysis [7]. This ratio was taken to be the ratio of the peak height of the negative ion of mass 45 ($HCOO^-$) to that of the negative ion of mass 46 ($DCOO^-$).

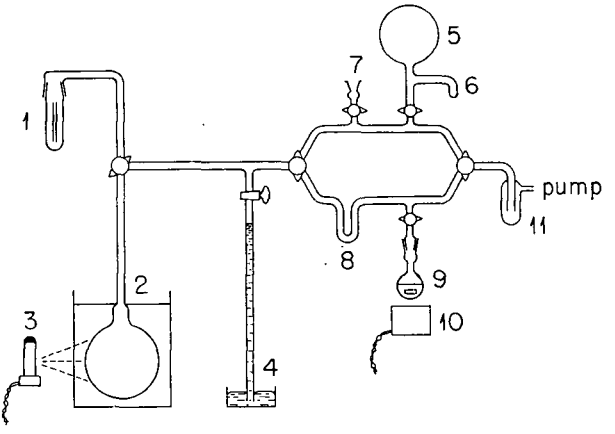

Fig. 1
Vacuum line for photochemical reactions of halogens with labelled formic acid.

The equipment used for the isotope-effect measurements is indicated in Fig. 1. The general prodecure followed will be described with reference to the numbers in Fig. 1. A 200-λ micropipette filled with the formic-d acid/formic-C^{14} acid mixture was frozen in liquid nitrogen at 1 and evacuated. The entire system was evacuated and the formic acid mixture was expanded into the reaction vessel, 2, which was a 3-l bulb immersed in water in a glass-walled constant-temperature bath. The 2-l bulb, 5, contained chlorine or bromine, which — before each run — was frozen at 6 and evacuated to remove air. The room was darkened and the desired pressure of chlorine or bromine was introduced using the manometer 4. The stopcock to the right of the manometer was closed and the light at 3 was turned on. The progress of the reaction was followed by the increase in pressure measured at the manometer. When the reaction was complete, the contents of the system were pumped into trap 8 which was cooled in liquid nitrogen. The stopcocks to the right of the manometer and to the left of the protective trap, 11, were closed. The liquid nitrogen was removed from around trap 8 and the trap contents were absorbed in excess saturated barium hydroxide solution, 9, which was stirred by a bar magnet driven by a rotating magnet, 10. Precipitated barium carbonate-C^{14} was collected on a sintered glass filter protected by a stream of carbon-dioxide-free nitrogen. The solid was washed with freshly boiled distilled water and dried at 130°C. Samples were decomposed with van Slyke solution and the C^{14} dioxide released was collected and radioassayed in a stainless-steel ion chamber [8].

TABLE I

DEUTERIUM KINETIC-ISOTOPE-EFFECTS MEASURED FOR THE PHOTOCHEMICAL REACTIONS OF CHLORINE AND BROMINE WITH FORMIC-d ACID

Halogen	Temp. (°C)	S_{100}/S_5	k_H/k_D
Chlorine	20.0	0.76	2.0
Chlorine	44.1	0.75	2.1
Chlorine	68.7	0.74	2.2
Bromine	28.3	0.69	2.8
Bromine	44.1	0.70	2.7

Table I presents the results of three runs at different temperatures for the reaction with chlorine and two runs at different temperatures for the reaction with bromine. No appreciable temperature-coefficient of the deuterium isotope-effect is indicated in either case. The apparent trend in the case of the chlorine reaction is probably not real as the method is not accurate enough to establish the presence of such small differences in the isotope effect with confidence. The ratio, k_H/k_D has a value of about 2.0 ± 0.2 at room temperature in the case of the chlorine reaction and about 2.7 ± 0.2 at 45°C in the case of the bromine reaction.

6. Conclusions

Since both the chlorine and bromine reactions exhibit C^{13} isotope effects [5] and appreciable deuterium isotope-effects (when DCOOH is used), carbon-hydrogen-bond cleavage plays a critical part in controlling the reaction rates.

The reaction mechanism previously proposed for the chlorine reaction [4], and suggested in section 2 for the bromine reaction, accounts qualitatively for the observed C^{13} and deuterium isotope-effects. However, so little is known about the details of the present formic-acid reactions that any attempt to explain the magnitudes of the observed C^{13} and deuterium isotope-effects is highly speculative. Earlier, the fact that a larger C^{13} isotope-effect was observed for the bromine reaction than for the chlorine reaction was taken as an indication that the carbon-hydrogen bond is stretched more in the transition state for the bromine reaction than for the chlorine reaction [5]. SZWARC *et al.* [9] have stated: "It is reasonable to expect that in a hydrogen-atom abstraction the extension of the C—H bond in the transition state should depend on the reactivity of the abstracting species, i.e., more reactive species would require a smaller extension of the C—H bond." However, not so much difference was observed between the magnitudes of the deuterium isotope-effects for the two reactions as was found in the case of the C^{13} isotope-effects. It may be that new bonds formed to hydrogen in the transition state of the formic acid/bromine reaction largely compensate the stretching of the carbon-hydrogen bond.

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RADIOISOTOPES IN PHYSICAL CHEMISTRY

(Sessions 15 [Part], 16, 17 and 18)

ИССЛЕДОВАНИЕ МЕХАНИЗМА НЕКОТОРЫХ ГЕТЕРОГЕННО-КАТАЛИТИЧЕСКИХ ПРОЦЕССОВ С ПРИМЕНЕНИЕМ СОЕДИНЕНИЙ, МЕЧЕННЫХ УГЛЕРОДОМ-14

Г. В. ИСАГУЛЯНЦ, А. А. БАЛАНДИН
СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

Abstract — Résumé — Аннотация — Resumen

A study of the mechanism of certain heterogeneous catalytic processes using C^{14}-labelled compounds. An investigation is made of the method of calculating individual phase velocities for parallel, consecutive and parallel-consecutive reactions from kinetic data obtained by the use of labelled atoms. The method is used for calculating individual phase velocities in the decomposition reaction of isopropyl alcohol into vanadium trioxides, dehydrogenations of butane-butylene mixtures and dehydrations of ethyl alcohol.

Compounds containing C^{14} were used in this study.

Utilisation de composés marqués au carbone-14 pour l'étude du mécanisme de certains processus catalytiques hétérogènes. Le mémoire expose une méthode par laquelle on calcule les vitesses à différents stades dans les réactions parallèles, consécutives et parallèles-consécutives en se servant de données cinétiques obtenues par l'utilisation d'atomes indicateurs. Cette méthode est utilisée pour le calcul des vitesses à différents stades de la décomposition de l'alcool isopropylique par le trioxyde de vanadium, de la déshydrogénation des mélanges butane-butylène et de la déshydratation de l'alcool éthylique.

Pour ces travaux, on a utilisé des composés contenant du carbone-14.

Исследование механизма некоторых гетерогенно-каталитических процессов с применением соединений, меченых углеродом-14. Рассмотрен метод расчета скоростей отдельных стадий для параллельных, консекутивных и параллельно-консекутивных реакций, исходя из кинетических данных, полученных с применением меченых атомов. Метод применен к расчету скоростей отдельных стадий в реакции разложения изопропилового спирта на трехокиси ванадия, дегидрогенизации бутан-бутиленовых смесей, дегидратации этилового спирта.

В работе были использованы соединения, содержащие радиоуглерод-14.

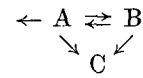
Estudio del mecanismo de algunos procesos de catálisis heterogénea con ayuda de compuestos marcados con carbono-14. Se describe un método de cálculo de las velocidades correspondientes a las distintas etapas de una serie de reacciones paralelas, consecutivas y paralelo-consecutivas, partiendo de datos cinéticos obtenidos mediante átomos marcados. El método se aplica a la determinación de las velocidades de las reacciones de descomposición del alcohol isopropílico por el trióxido de vanadio, de deshidrogenación de mezclas de butano y buteno y de deshidratación del alcohol etílico.

El trabajo se llevó a cabo con ayuda de compuestos marcados con carbono-14.

Большинство гетерогенно-каталитических процессов включает в себя ряд последовательных и параллельных реакций. Пути образования того или иного соединения в таком сложном процессе часто представляют не только теоретический, но и практический интерес.

Мы уже разбирали [1] вопрос о том, какие стадии гетерогенных процессов могут быть детермированы с помощью кинетического метода меченых атомов [2] и было показано, что метод позволяет непосредственно судить о тех стадиях процесса, для которых быстро устанавливается равновесие между газовой фазой и поверхностью катализатора, т.е. о тех стадиях, в которых скорости адсорбции и десорбции продуктов велики, по сравнению со скоростями процессов превращения на поверхности.

Многие сложные процессы могут быть изображены следующей схемой:



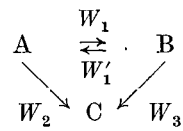
(1)

где A — исходный продукт, а B и C — продукты реакции.

Принципиально возможно составить систему уравнений (2), с помощью которых на основе определения изменения концентраций и удельных радиоактивностей A, B и C во времени вычислить отдельные скорости в схеме (1). Как, однако, показал опыт, для гетерогенных каталитических реакций не всегда возможно получить экспериментальные данные [3], точность которых была бы достаточной для использования указанной системы уравнений.

На практике приходится изыскивать упрощенные пути расчета отдельных скоростей, а также подбирать такие условия эксперимента, когда отпадает необходимость расчета всех скоростей, поскольку некоторыми из них можно пренебречь.

В таких случаях схема (1) может быть преобразована в более простую:



(2)

Для такой схемы значения отдельных скоростей могут быть определены [4] из следующих уравнений:

$$W_1 = \frac{\mathrm{d}\beta\, c_2}{\mathrm{d}\tau\,(\alpha-\beta)}; \qquad W_1' = \frac{\mathrm{d}\alpha\, c_1}{\mathrm{d}\tau\,(\alpha-\beta)};$$

$$W_2 = \frac{\frac{\mathrm{d}\gamma}{\mathrm{d}\tau} C_3 + \frac{\mathrm{d}c_3}{\mathrm{d}\tau}\,(\gamma-\beta)}{\alpha-\beta}; \qquad W_3 = \frac{\frac{\mathrm{d}\gamma}{\mathrm{d}\tau} C_3 + \frac{\mathrm{d}c_3}{\mathrm{d}\tau}\,(\gamma-\alpha)}{\beta-\alpha}, \tag{3}$$

где c_1, c_2 и c_3 — концентрации, α, β и γ — удельные радиоактивности продуктов A, B и C соответственно, а τ — время контакта. Очевидно, что при $W_3=0$ образование продуктов B и C протекает параллельно и независимо. Если B и C не связаны взаимным превращением, тогда и $W_1=0$. Это означает, что величины $\frac{\mathrm{d}\alpha}{\mathrm{d}\tau}=0$, $\frac{\mathrm{d}\gamma}{\mathrm{d}\tau}=0$ и $\gamma-\alpha=0$. Это, очевидно, некоторый предельный случай соотношения скоростей в схеме (2). Практически этот случай был обнаружен при исследовании разложения изопропилового спирта на трехокиси ванадия. При $W_2=0$ образование продукта C представляет собой чисто консекутивный процесс.

Это также предельный случай, встречающийся, видимо, не так часто. Однако дегидрогенизация бутан-бутадиеновых смесей над хромовым

катализатором [5] весьма близко подходит к нему. При проведении этого процесса с меченым бутаном было обнаружено, что удельная активность бутадиена меньше удельной активности бутилена $\gamma < \beta$ и определено, что скорость $W_2 << W_3$. Впоследствии это соотношение было уточнено и оказалось равным 1:1000 (3).

Более широко распространен случай, когда скорости W_2 и W_3 соизмеримы, что соответствует параллельно-консекутивному пути образования продукта С. Этому случаю отвечают реакция дегидрогенизации бутан-бутиленовых смесей на алюмохромовом катализаторе (3) и реакции дегидратации этилового спирта на окиси алюминия (4) и алюмокалиевых квасцах, приготовленных по способу, описанному в работе [17].

1. Параллельные реакции

РАЗЛОЖЕНИЕ ИЗОПРОПИЛОВОГО СПИРТА НА ТРЕХОКИСИ ВАНАДИЯ

Известно, что окисно-ванадиевые катализаторы обладают дегидрогенизующей и дегидратирующей активностью в отношении спиртов, причем в катализате обнаруживается высокое содержание парафиновых углеводородов. Было найдено [6], что н. бутиловый, изобутиловый, н. гексиловый, н. октиловый спирты при 380—400°, наряду с бутеном, гексеном и октеном, образуют значительные количества (до 50%) соответствующих алканов. Весьма возможно, что выделяющийся при дегидрогенизации спирта водород способен в условиях реакции гидрировать олефины. В литературе есть указание [7], что подобные катализаторы алкены способны проводить гидрирование алкенов. Вместе с тем, поскольку в ряде работ [8—10] отмечено получение алкенов, с числом углеродных атомов на I меньше, чем у исходных спиртов, весьма возможно, что алкены образуются непосредственно из спирта за счет гидрогенолиза связей С-О и С-С.

Вопрос о путях образования насыщенных углеводородов представляет не только теоретический, но и практический интерес, ибо имеет значение при определении энергии связей реагирующих атомов с ванадиевым катализатором.

А. А. Баландин и Н. П. Соколова [11] исследовали кинетику реакций разложения этилового и изопропилового спиртов и дегидрогенизации циклогексана над трехокисью ванадия. Были определены величины энергии активации дегидрогенизации углеводородов и спиртов. Для определения энергии активации реакции дегидратации необходимо было решить вопрос о том, является ли пропилен промежуточным звеном при образовании пропана и, соответственно, определять скорость реакции дегидратации по образованию пропилена или по сумме образующихся пропилена и пропана. В зависимости от этого получаются два ряда величин энергий связи атомов реагирующих с катализатором веществ. При предположении, что пропан образуется в результате вторичной реакции гидрования пропилена для величин энергий связей углерода, кислорода и водорода с катализатором получаем:

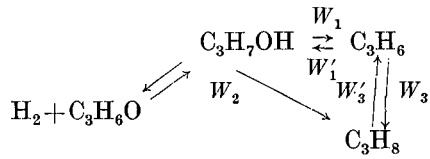
$$Q_{C-K}=20{,}6;\ Q_{O-K}=44{,}9;\ Q_{H-K}=54{,}4 \text{ ккал/моль}.$$

Если же исходить из предположения, что пропилен является конечным продуктом дегидратации, а пропан образуется за счет гидрогенолиза, получим соответственно:

$$Q_{C-K}=16{,}2;\ Q_{O-K}=40{,}1;\ Q_{K-H}=58{,}5 \text{ ккал/моль}.$$

Проверку правильности того или иного предположения можно было провести с помощью меченых атомов.

Очевидно, что различные пути разложения изопропилового спирта в рассматриваемых условиях можно изобразить следующей схемой:



(4)

Однако при низкой температуре реакция дегидрогенезации пропана мало вероятна и скорость W_3 должна быть очень мала. В таком случае правая часть этой схемы становится аналогичной схеме (2). Мы исследовали разложение изопропилового спирта с добавками пропилена, меченного углеродом-14. Исследование проводилось в проточной установке при 315° и различных временах контакта, катализатор готовился как в цитированной работе [11]. Восстановление катализатора проводилось при 415° в течение 10 часов в токе сухого электролитического водорода, очищенного от примеси кислорода. В трубку помещались порции катализатора объемом 6 мл.

Как указывалось в предыдущей работе [11] получить несколько образцов V_2O_3 со строго одинаковой исходной активностью довольно трудно.

Каждая порция катализатора использовалась только для двух опытов. Первый контрольный опыт служил для определения каталитической активности данного образца в отношении разложения изопропилового спирта при 315° и объемной скорости 0,15 мл/мин., а затем проводился опыт с добавкой меченого пропилена. Опыты с добавками пропилена проводились только на таких порциях катализатора, которые обладали приблизительно равной исходной каталитической активностью.

Пропилен, меченный углеродом-14, синтезировался дегидратацией изопропилового спирта над Al_2O_3 при 300° С. Исследование хроматографическим методом показало, что в приготовленном пропилене отсутствует пропан и другие углеводороды. Удельная активность пропилена составила 25200 имп/мин-мг $BaCO_3$. Меченый пропилен разбавлялся десятикратно водородом и подавался в каталитическую трубку из газометра в количестве 1,5 молярных процента к спирту. Скорость пропускания контролировалась реометром.

Газообразная часть катализата в опытах с добавкой меченого пропилена анализировалась и разделялась хроматографическим методом. Специальные опыты с искусственной смесью пропилена-C^{14} и пропана показали, что разделение этих газов проходит количественно. Для определения радиоактивности пропан и пропилен сжигались в токе кислорода, углекислота поглощалась баритовой водой и мишени готовились, как описано ранее [3]. Жидкая часть катализата также сжигалась, и в ней определялась радиоактивность.

В таблице I даны результаты определения удельной радиоактивности продуктов реакции в опытах, проведенных при различных временах контакта τ. (Эта величина определялась как обратная величина объемной скорости). Удельная радиоактивность дана в %% к исходной радиоактивности

Таблица I

УДЕЛЬНЫЕ АКТИВНОСТИ ЖИДКОГО КАТАЛИЗАТА (α), ПРОПАНА (β) И ПРОПИЛЕНА (γ)

Вещество	τ в сек		
	4,3	8	22,2
	Удельн. активн. в % к исходной		
Катализат	0,027	0,035	0,00 практич. неактив.
C_3H_8	0,42	0,07	0,00 практич. неактив.
C_3H_6	49,47	35,71	17,85

добавленного пропилена. Из данных таблицы видно, что радиоактивность жидкой части катализата, состоящей из спирта и ацетона, а также и величина удельной радиоактивности пропана крайне малы. Тогда величины $\frac{d\alpha}{d\tau}$, $\frac{d\gamma}{d\tau}$ и соответственно $\gamma-\alpha$ могут быть приравнены к нулю. Из уравнений (3) очевидно, что скорости W_1 и W_3 также будут равны нулю. Это означает, что в указанных условиях не происходит гидратации пропилена и источником образования пропана является скорость W_2. Пропан образуется только за счет реакции гидрогенолиза спирта, а гидрирования пропилена не происходит. Скорость реакции дегидратации изопропилового спирта в указанных условиях определяется скоростью выделения пропилена. Это дает возможность сделать правильный выбор из двух рядов значений энергий связи на трехокиси ванадия, полученных в цитированной выше работе [11].

2. Консекутивные реакции

Для случая консекутивных реакций экспериментальная часть и расчеты значительно сложнее, чем для рассмотренного случая чисто параллельной реакции. Необходимо получить подробные данные о изменении концентраций и удельных активностей веществ A, B и C в зависимости от времени контакта и необходимо производить графическое дифференцирование этих данных. Следовательно необходимы точные графики. Примером консекутивной реакции может служить дегидрогенизация бутан-бутиленовых смесей над хромовым катализатором. Описано в предыдущих работах [1, 2, 5] и доложено на Международной конференции по использованию атомной энергии в мирных целях (Париж, 1958 г.).

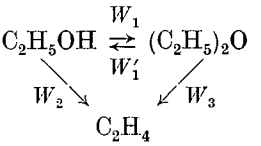
3. Параллельно-консекутивные реакции

Примером реакций этого типа является реакция образования этилена при дегидратации этилового спирта.

Вопрос о механизме каталитической дегидратации этилового спирта много лет обсуждается в литературе. Некоторые авторы считают, что образование этилена протекает лишь через стадию образования диэтилового эфира. Другие считают, что этилен и эфир образуются в результате двух независимых параллельных реакций.

В последние годы этот вопрос вновь рассматривается в работах БАЛАСЕАНУ и ЮНГЕРСА [13], ТОПЧИЕВОЙ и ЮН-ПИНА [14, 15], БОРЕСКОВА и др. [16].

Подход к решению вопроса о действительном механизме этой сложной реакции лежит в определении скоростей отдельных процессов в схеме типа схемы (2):



Нами проводилась дегидратация этилового спирта с добавкой небольших количеств диэтилового эфира, меченного радиоуглеродом C^{14}.

Пользуясь формулами (3) на основании экспериментальных данных мы определили скорости всех процессов в схеме (4).

Опыты проводились в проточной установке [12]. Исходные вещества подавались в кварцевый реактор, содержащий 5 мл (2,8 г) катализатора. Продукты реакции проходили через холодильник и собирались в приемнике, охлаждавшемся до $-50°$ С. Этилен собирался в газометр над насыщенным раствором NaCl. Катализатором служила активная окись алюминия марки А-1. Чтобы избежать проскока и диффузионного торможения употреблялись гранулы размером от 0,5 до 1 мм. После каждого опыта над катализаторами пропускался воздух при 350°. Активность катализатора была постоянной и позволяла получать хорошо воспроизводимые данные.

Эфир, меченный радиоуглеродом C^{14}, был синтезирован парофазной дегидратацией меченого этилового спирта над катализатором, изготовленным из алюмокалиевых квасцов при 220° [17]. Удельная активность эфира была 2400 имп/мин. Опыты проводились в два приема: предварительно проводилась серия опытов без меченых веществ, причем определялись изменения концентрации спирта, эфира, этилена и воды в зависимости от времени контакта. Затем проводились опыты с добавками меченого эфира. В них определялись изменения удельных активностей спирта, эфира и этилена в зависимости от времени контакта. Применялся спирт - ректификат, добавка меченого эфира составляла 3,8%, содержание воды составляло 6%.

Для определения в катализате этилового спирта и диэтилового эфира применялся метод, основанный на окислении спирта и эфира раствором $K_2Cr_2O_7$ в серной кислоте. Содержание воды в конденсате определялось по разности между общим весом конденсата и количеством спирта и эфира. Для радиохимического анализа конденсат подвергался разгонке на небольшой колонке.

Отбирались три фракции — эфирная, промежуточная и спиртовая. Специальные опыты по разделению смеси высокоактивного спирта и неактивного эфира и высокоактивного эфира и неактивного спирта показали, что в первой и третьей фракциях достигалось выделение чистых спиртов и эфира.

Результаты опытов наносились на графики зависимости изменения концентраций и удельных радиоактивностей от времени контакта. Условное время контакта τ определялось как обратная величина объемной скорости паров исходного спирта (НТД) на единицу объема раствора в секунду. По экспериментальным точкам проводились кривые; производные определялись графическим дифференцированием. По этим же кривым находились величины

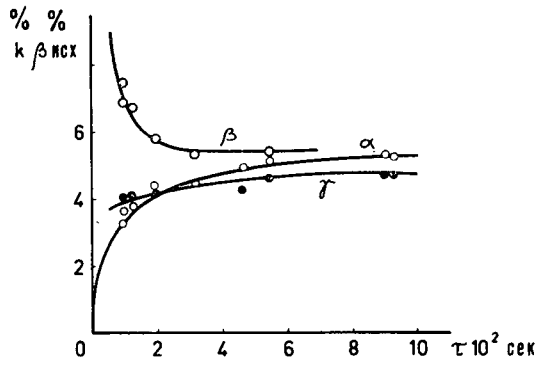


Рис. 1
Дегидратация спирта на окиси алюминия при 350°. Зависимость удельных радиоактивностей спирта (α), эфира (β) и этилена (γ) от времени контакта. Величины даны в процентах к исходной радиоактивности эфира.

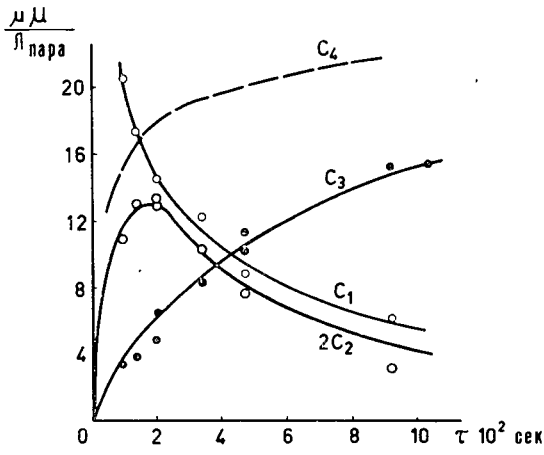


Рис. 2
Дегидратация спирта на окиси алюминия при 350°. Зависимость концентраций спирта (C_1), эфира (C_2), этилена (C_3) и воды (C_4) от времени контакта.

концентраций и удельных радиоактивностей спирта, эфира и этилена. В качестве примера на рис. 1 и 2 приводим такие кривые для 350°. Необходимые исходные данные и результаты вычисления отдельных скоростей реакции для 275, 300, 350 и 400° с помощью уравнений (3) даны в таблице II. Величины концентраций даны в миллимолях на литр пара катализата.

Из рассмотрения данных этой таблицы следует:

1. Во всех случаях превращение спирта происходит по двум параллельным направлениям в эфир и в этилен.

2. Образование этилена происходит значительно медленнее, чем взаимное превращение спирта и эфира; сравнимыми эти скорости становятся только при 400°.

Таблица II

СКОРОСТИ РЕАКЦИИ ПО СХЕМЕ 1 ПРИ ДЕГИДРАТАЦИИ ЭТИЛОВОГО СПИРТА НА ОКИСИ АЛЮМИНИЯ, ВЫЧИСЛЕННЫЕ ПО УРАВНЕНИЯМ (3)

Время контакта τ, сек. $\times 10^{-3}$	Концентрации в мМ/литр пара конденсата НТД			$\frac{dc_3}{d\tau}$	Удельные радиоакт. на мМ в %% к исходной			$\frac{d\alpha}{d\tau}$	$\frac{d\beta}{d\tau}$	$\frac{d\gamma}{d\tau}$	Скорости реакции в мМ/литр пара конденсата НТД			
	C_1	$2C_2$	C_3		α	β	γ				w_1	w_1'	w_2	w_3
						275° C								
1,3	10,8	18,7	1,02	0,95	1,3	7,6	2,8	1,0	5,0	0,8	14,8	2,8	0,60	0,35
3	11,2	23,0	2,1	0,70	3,0	6,0	3,5	0,9	0,9	0,35	6,9	3,3	0,34	0,36
4	10,1	23,3	2,8	0,63	3,5	5,5	3,7	0,8	0,45	0,23	5,2	4,04	0,25	0,38
6	8,6	22,3	3,7	0,52	4,3	5,3	3,9	0,4	0,18	0,15	4,01	3,4	0,18	0,34
8	7,9	20,9	4,1	0,47	4,6	5,1	4,05	0,2	0,08	0,10	3,3	3,1	0,17	0,30
						300° C								
0,2	19,8	15,1	1,5	6,4	1,1	12	3,3	4,2	2,5	3,3	34,6	7,6	4,7	1,75
0,4	13,7	19,3	2,6	5,6	2,0	6,4	3,4	3,1	4,5	1,1	19,7	9,7	3,2	2,4
0,6	11,3	19,7	3,7	5,0	2,9	5,4	3,6	2,2	1,6	0,8	12,6	9,9	2,4	2,6
1,2	8,9	17,1	6,4	3,5	4,1	5,2	4,0	0,8	0,46	0,35	7,0	6,5	1,8	1,7
1,8	7,85	14,3	8,55	2,5	4,35	5,1	4,1	0,52	0,31	0,2	6,2	5,5	1,0	1,5
2,2	7,1	12,7	9,5	2,1	4,6	5,1	4,2	0,32	0,19	0,15	4,8	4,6	0,9	1,2
						350° C								
0,067	20,0	10,1	2,8	32	3,0	7,8	3,8	6	55	2,2	116	25	25,4	6,6
0,2	13,8	12,2	6,4	22	4,1	5,7	4,25	3,8	5,5	1,6	42	32,8	13,7	8,3
0,3	11,5	11,35	7,9	17	4,5	5,5	4,4	2,5	2,5	1,25	28,4	28,8	8,8	8,2
0,4	10,3	9,5	9,5	14	4,8	5,45	4,5	1,5	1,4	0,9	20,5	23,8	7,4	6,6
0,6	7,9	7,5	11,9	10,8	5,1	5,45	4,6	0,7	0,6	0,6	12,9	15,8	5,9	4,9
0,8	6,5	6,0	13,7	9,0	5,25	5,40	4,7	0,3	0,3	0,4	12,0	13,0	5,0	4,0
						400° C								
0,01	23,8	6,8	3,8	357	1,4	26,4	5,8	61	600	12	168	58	292,5	64,5
0,03	15,9	6,95	8,1	145	2,6	20	6,4	61	220	9	88	55,7	109,2	35,8
0,06	11,8	5,7	11,1	83	4,3	16,2	6,6	44	70	6	33,5	43,6	61,4	21,6
0,10	8,4	4,1	13,8	51	5,5	14	6,7	29	40	4	19,3	28,7	37,3	13,7
0,20	4,85	2,5	16,7	22	6,5	11	6,9	12	15	1,5	8,3	12,9	15,2	6,8
0,30	2,6	1,3	18,3	15	6,8	9.5	7,0	6	8	0,5	3,8	5,8	10,4	4.6

3. Благодаря тому, что скорости взаимного превращения спирта и эфира (особенно при низких температурах) значительно превышают скорости превращения их в этилен, между спиртом и эфиром устанавливается некоторое равновесие, которое поддерживается, хотя и спирт и эфир превращаются в этилен и соотношение скоростей этого превращения при различных температурах весьма различно.

Именно этим объясняются наблюдавшиеся многими авторами максимумы по концентрации эфира при дегидратации спирта, а также максимум по концентрации спирта при дегидратации эфира.

4. Отсюда следует, что при низких температурах, когда в устанавливающемся равновесии концентрации эфира больше концентрации спирта, скорость образования этилена из эфира оказывается относительно большой и значительная часть этилена получается консекутивным путем (следует иметь в виду, что общая степень превращения в этилен в этом случае мала). С повышением температуры соотношение скоростей образования этилена из эфира и спирта изменяется, причем все большее и большее количество этилена образуется непосредственно из спирта. При 400° и значительных временах контакта, когда этиленообразование приближается к 100%, главная масса этилена (до 80%) получается непосредственно из спирта.

Как уже указывалось, примером параллельно-консекутивной реакции может служить также дегидрогенизация бутан-бутиленовых смесей [3], хотя в этом случае скорость W_2 относительно W_3 невелика.

В докладе рассмотрен метод расчета скоростей отдельных стадий для параллельных, консекутивных и параллельно-консекутивных реакций, из кинетических данных, полученных с применением меченых атомов. Метод применен к расчету скоростей отдельных стадий в реакции разложения изопропилового спирта на трехокиси ванадия, дегидрогенизации бутан-бутиленовых смесей, дегидратации этилового спирта.

В работе были использованы соединения, содержащие радиоуглерод-14.

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DISCUSSION

D. Gál (Hungary) asked whether it was not possible that in the case of C^{14}, as in the case of sulphur, low-energy radiation would alter the quantitative results when using the kinetic method.

B. Dzantiev, who presented the paper, replied that the specific activity of the ether was so low (2400 cpm) that it was doubtful whether the C^{14}-radiation could have any influence on the chemical process.

G. Harris (United States of America) pointed out that the kinetic scheme for the ethanol reaction had been worked out by the authors on the basis of first-order kinetics. In view of the complexity of the heterogeneous system involved, he wondered whether that might not be an over-simplification, and inquired whether the authors had direct evidence that any or all of the steps were in fact of the first order.

B. G. Dzantiev replied that unless first-order kinetics had been assumed, it would have been almost impossible to bring the calculations to a conclusion; moreover, the results as calculated were in good agreement with the experimental data. The basis and object of the method of calculation were described in various articles by Neyman and Balandin.

ИССЛЕДОВАНИЕ ИЗОТОПНЫХ ЭФФЕКТОВ ПРИ РЕАКЦИЯХ ВОДОРОДНОГО ОБМЕНА В ЖИДКОМ БРОМИСТОМ ВОДОРОДЕ И ЖИДКОМ АММИАКЕ

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Abstract — Résumé — Аннотация — Resumen

Study of the isotope effect in hydrogen exchange reactions in liquid hydrogen bromide and liquid ammonia. The subject of the investigation was the thermodynamic isotope effects in naphthalene-hydrogen bromide and benzene-ammonia systems in the presence of potassium amide acting as a catalyst. Protium, deuterium and tritium atoms were present in the system during the experiments.

In the experiments on direct and "reverse" exchange, the kinetic isotope effects of hydrogen were measured in the liquid-phase systems hydrogen bromide-diphenyl and benzene-ammonia.

The mechanisms of exchange reactions of aromatic hydrocarbons with HBr and NH_3 are considered with regard to the findings of kinetic experiments.

There is a brief description of the methods of preparation in which deuterized and tritiated compounds are used. For tritium counting a scintillation coincidence system was used; and spectroscopic and mass spectrometric methods were used for the isotopic analysis of deuterized substances.

Réactions d'échange d'hydrogène dans le bromure d'hydrogène et l'ammoniaque liquides: étude de l'effet isotopique. Les auteurs ont étudié les aspects thermodynamiques des effets isotopiques dans les systèmes naphtalino-bromure d'hydrogène et benzène-ammoniac, avec de l'amide de potassium comme catalyseur. Les essais ont été effectués en présence d'atomes de protium, de deutérium et de tritium.

Au cours d'essais sur l'échange direct et l'échange « inverse », les auteurs ont mesuré les effets cinétiques des isotopes de l'hydrogène dans les systèmes bromure d'hydrogène-diphényle et ammoniac-benzène en phase liquide.

Les auteurs examinent le mécanisme des réactions d'échange entre les hydrocarbures aromatiques et HBr ou NH_3, eu égard aux données cinétiques obtenues.

Le mémoire donne un exposé succinct des méthodes de préparation à l'aide de composés enrichis en deutérium et en tritium. Pour le comptage du tritium, on a utilisé un dispositif à scintillation par coïncidences, et l'on a eu recours à la spectroscopie et à la spectrométrie de masse pour l'analyse isotopique des substances enrichies en deutérium.

Исследование изотопных эффектов при реакциях водородного обмена в жидком бромистом водороде и жидком аммиаке. Изучались термодинамические изотопные эффекты в системах нафталин-бромистый водород и бензол-аммиак в присутствии амида калия в качестве катализатора. Опыты проводились при одновременном наличии в системе атомов протия, дейтерия и трития.

В опытах по прямому и „обратному" обмену измерялись кинетические изотопные эффекты водорода в жидкофазных системах: бромистый водород-дифенил и аммиак-бензол.

На основании данных кинетических опытов обсуждаются механизмы реакции обмена ароматических углеводородов с HB_2 и $ИН_3$.

Кратко описаны способы приготовления, используемых в работе дейтерованных и тритированных соединений. В работе использовался сцинтилляционный метод счета трития на совпадениях, применялись спектроскопические и масс-спектрометрический методы изотопного анализа дейтерированных веществ.

Reacciones de intercambio de hidrógeno en bromuro de hidrógeno y amoniaco líquidos: estudio del efecto isotópico. Se han estudiado los aspectos termodinámicos de los efectos isotópicos en los sistemas naftaleno-bromuro de hidrógeno, y benceno-amoniaco, en presencia de amida potásica como catalizador. Los experimentos se realizaron en un sistema que contenía átomos de protio, deuterio y tritio.

Se realizaron experimentos de intercambio directo e "inverso", en los cuales se midieron los efectos cinéticos ejercidos por los isótopos del hidrógeno en los sistemas difenilo-bromuro de hidrógeno, y benceno-amoniaco en fase líquida.

Se examinan los mecanismos de las reacciones de intercambio entre hidrocarburos aromáticos y HBr o NH_3, a la luz de los resultados de los experimentos cinéticos.

La memoria describe en líneas generales métodos de preparación en los que se utilizan compuestos deuterados y tritiados. Para el recuento del tritio se utilizó un contador de centelleo por coincidencias, mientras que para el análisis isotópico de las sustancias deuteradas se emplearon métodos espectroscópicos y de espectrometría de masas.

Закономерности реакций дейтерообмена ароматических углеводородов в жидком дейтероаммиаке (как представителе сильных основных растворителей) и в жидком бромистом водороде (как представителе сильных кислотных растворителей) были подробно исследованы в работах А. И. Шатенштейна и сотрудников [1].

Обмен протия с тритием в таких системах изучен гораздо хуже. Нам известна единственная работа [2], в которой кратко сообщается об измерениях кинетического изотопного эффекта при водородном обмене между флуореном и жидким аммиаком.

Какие-либо данные о распределении трития при реакциях водородного обмена органических соединений с жидким бромистым водородом в литературе отсутствуют.

В настоящем докладе представлен экспериментальный материал по кинетике и термодинамике тритийобмена в растворах ароматических углеводородов в жидких HBr и NH_3. Полученные данные используются для проверки статистико-термодинамических расчетов коэффициентов распределения. На основании изучения кинетических изотопных эффектов делается также попытка рассмотрения механизма реакции изотопного обмена водорода между ароматическими углеводородами и HBr.

Наиболее подходящим веществом для изучения изотопных эффектов водорода при обмене ароматических углеводородов является бензол, в котором все атомы водорода равноценны. Именно поэтому указанное соединение выбрано нами в качестве объекта исследований тритий - и дейтеро-обмена между ароматической CH - связью и аммиаком. Однако для сравнительного изучения обмена атомов трития и дейтерия в растворах бромистого водорода мы остановились на нафталине и дифениле. Дело в том, что закономерности дейтерообмена ароматических углеводородов в бромистом водороде изучались в работах [3], [4] только для систем $C_{10}H_8+HBr$, $C_{12}H_{10}+HBr$. Применение бензола в указанных целях неудобно потому, что в отсутствии катализатора — бромистого алюминия — скорость

водородного обмена слишком мала. Напротив, при добавлении $AlBr_3$ равновесное распределение устанавливается так быстро, что это не позволяет измерить обычными способами константу скорости обмена. Кроме того, большая скорость обмена и сильная зависимость коэффициента распределения $\alpha_{HBr-C_6H_6}$ от температуры мешают точному измерению величины α вследствие значительного смещения равновесия при испарении растворителя [3].

Методика

Для получения сухого тритированного бромистого водорода использовался метод, основанный на изотопном обмене между газообразным бромистым водородом и 48%-ной бромистоводородной кислотой, меченной тритием, в присутствии фосфорного ангидрида. Процесс обмена проводился в стальном реакторе (С), изображенном на рис. 1. На дно реактора клали

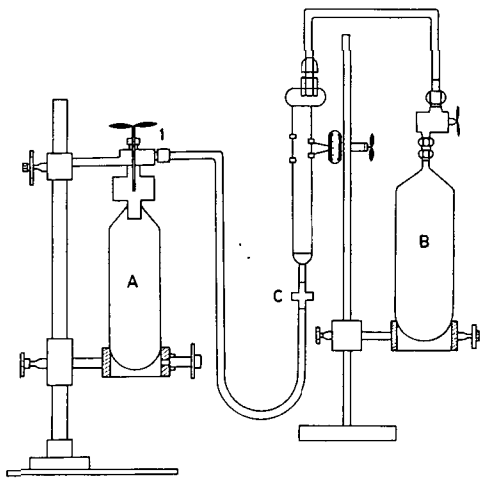

Рис. 1
Схема реактора.

тампон из стеклянной ваты и насыпали туда сухой фосфорный ангидрид. Далее на этот слой помещали небольшую, тонкостенную стеклянную ампулу, содержащую 3 мл концентрированной бромистоводородной кислоты и 0,1 мл тритиевой воды с заданной удельной активностью, и боек; сверху накладывался тонкий слой стеклянной ваты и снова насыпался фосфорный ангидрид. Реактор (А) подключался к системе, состоящей из баллончика (В) с сухим бромистым водородом и приемника, снабженных насадкой с вентилем. После проверки на герметичность система эвакуировалась, при встряхивании реактора разбивалась стеклянная ампула и из баллона (В) пропускался ток сухого HBr. Тритированный бромистый водород конденсировался в охлаждаемом приемнике (А).

Удельная активность продукта обычно составляла 2—20 мкюри/грамм. В случае необходимости она может быть легко повышена путем использования тритиевой воды с высокой удельной активностью и уменьшения

количества носителя — безводного бромистого водорода. Содержание влаги в полученном HBr(T), определяемое по увеличению веса безводного перхлората магния при пропускании заданного количества бромистого водорода, оказалось меньше 0,02%.

Тритированный аммиак готовился разложением нитрида магния тритиевой водой (с удобной для измерений концентрацией трития) в соответствии с методикой, которая описана ранее применительно к получению дейтероаммиака [5]. Полученный таким образом аммиак $NH_3(T)$ высушивали над металлическим натрием. В качестве исходных веществ для проведения обмена использовались продажные препараты химических соединений. Ниже указаны способы их дополнительной очистки и константы: бензол „х. ч. для криоскопии" кипятился с металлическим натрием и перегонялся (т. кип. 80,0—80,3° С, n_D^{20}—1,5013); нафталин „чда" дважды возгонялся (т.пл. 69,0—69,5° С).

Безводный бромистый алюминий „х.ч." и металлический калий, используемый для приготовления амида, перед употреблением перегонялись в вакууме и в расплавленном состоянии заливались в стеклянные ампулы.

Как правило, опыты по изотопному обмену проводились при одновременном присутствии в системе атомов протия, дейтерия и трития. Это делалось для большей уверенности в правильности оценки кинетических и термодинамических изотопных эффектов и возможности сопоставления наших результатов с литературными данными по дейтерообмену.

Безводный бромистый дейтерий 96—98%, который добавлялся перед опытами к тритированному бромистому водороду, получался синтезом из элементов [6], дейтероаммиак — по упомянутому выше магний-нитридному способу [5].

Для проведения реакции изотопного обмена служили стальные пробирки емкостью 120—150 мл с герметически завинчивающимися крышками, снабженными насадкой с вентилем из нержавеющей стали. Если опыты ставились в присутствии катализатора, то в стальную пробирку загружали тонкостенную стеклянную ампулу с навеской калия или бромистого алюминия, необходимой для создания заданной концентрации катализатора в растворе, и конденсировали туда 10—20 г NH_3 или HBr. Навеску ароматического углеводорода помещали в отдельную стальную пробирку, туда же помещали запаянную стеклянную ампулу с 0,1—0,3 г дистиллированной воды.

Пробирку замораживали и тщательно откачивали. Затем, охлаждая пробирку с органическим веществом до температуры —78°, вливали в нее раствор катализатора в жидком NH_3 или HBr. Пробирку выдерживали в термостате при $t=25\pm0{,}1°$ в течение определенного промежутка времени. После этого для быстрого прекращения реакции обмена при встряхивании стальной пробирки разбивали ампулу с H_2O и растворитель испаряли в охлажденный баллон-сборник.

Нафталин и дифенил, отделенные таким образом от бромистого водорода, растворяли в бензоле, раствор отфильтровывали, бензол отгоняли под вакуумом, после чего нафталин или дифенил возгоняли. Образцы тритированного бензола, полученные в результате обмена, очищались перегонкой над натрием.

Аммиак и бромистый водород, исходные и после обмена, а также бензол, нафталин и дифенил, сжигали в кварцевой трубке над окисью меди при тем-

пературе около 700°. Воду анализировали на содержание дейтерия и трития. Пробы анализируемых веществ сжигали 2—3 раза и брали средние значения.

Для количественного определения дейтерия в тяжелой воде применялся спектральный метод анализа по атомному спектру водорода, неоднократно описанный в литературе [7, 8].

В отдельных опытах помимо эмиссионного анализа дейтерия в воде применялись прямые методы: для определения концентрации дейтерия в бромистом водороде и аммиаке — эмиссионный спектральный анализ и анализ по инфракрасным спектрам поглощения; для определения дейтерия в дифениле — масс-спектрометрический метод [8].

В пределах точности измерений (при средних и высоких концентрациях дейтерия относительная ошибка составляет примерно 1% (имело место совпадение результатов изотопного анализа). Измерение активности воды, меченной тритием, производилось по методу жидких сцинтилляционных растворов с непосредственным введением активного образца в сцинтиллятор.

На установке, предназначенной для этой цели, собственный фон понижался посредством регистрации сцинтиллирующих вспышек от двух фотоумножителей, включенных в схему совпадений. Подробное описание установки приведено в статье [9].

При измерениях активности тритиевой воды применялся сцинтиллирующий раствор следующего состава: 0,9 г *n*-терфенила „о.ч.“, 0,03 г 2,5-дифенилоксазола, „о.ч.“, 300 мл толуола „сцинтилляционного“, „о.ч.“ и 39 мл абсолютного этилового спирта.

На 10 мл сцинтиллирующего раствора такого состава бралась проба анализируемой воды, равная 0,05 мл. В качестве эталона для проверки надежности работы установки каждый раз использовалась тритиевая вода с известной удельной активностью (~0,1 мк/мл).

Данные опытов по определению коэффициентов распределения изотопов водорода и их сопоставление с результатами статистических расчетов изотопных равновесий

Коэффициент распределения дейтерия α_D в системах C_6H_6-NH_3, $C_{10}H_8$-HBr рассчитывался из экспериментальных данных по обычной формуле:

$$\alpha_D = \frac{C_b^1 (100 - C_p^1)}{C_p^1 (100 - C_b^1)}, \qquad (1)$$

где: C_p^1 — концентрация дейтерия (ат. %) в аммиаке или бромистом водороде после достижения равновесия;

C_b^1 — равновесная концентрация дейтерия (ат. %) в ароматическом углеводороде.

Для вычисления величины α_T применялась упрощенная формула:

$$\alpha_T = \frac{a_b^1}{a_p^1}, \qquad (2)$$

где: α_b^1 и α_p^1 — равновесные удельные активности воды (импульсы/мин) после сожжения ароматического углеводорода и растворителя соответственно. Хотя это и не является безусловно необходимым, для большей

Таблица I

РЕЗУЛЬТАТЫ ОПЫТОВ ПО ОПРЕДЕЛЕНИЮ КОЭФФИЦИЕНТА РАСПРЕДЕЛЕНИЯ В СИСТЕМЕ $ND_3 + NT_3 + C_6H_6$ *

№№ пп	KNH_2	m_p / m_b	Температура °С	Продолжит. час.	c_p°	c_p'	c_b°	c_b'	a_p°	a_p'	a_b°	a_b'	α_D	α_T	Примечание
1	0,45	21,2	~20	24	—	—	—	—	87000	81400	—	49600	—	0,61	
2	0,24	25,5	~20	30	45,9	43,8	—	40,8	12200	12000	—	7300	0,89	0,61	
3	0,20	29,3	~20	72	55,1	50,2	—	46,6	87900	82800	—	51100	0,87	0,62	
4	0,39	25,8	~20	72	55,1	52,3	—	50,0	65000	62900	—	39400	0,91	0,63	
5	0,15	30,1	~20	30	55,1	52,1	—	48,5	23500	21600	—	14200	0,87	0,65	
6	0,40	20,1	25	36	41,8	35,7	—	33,1	124900	117400	—	75300	0,88	0,64	
7	0,38	18,5	25	9	41,8	38,9	—	35,8	124900	118000	—	76300	0,88	0,64	
8	0,12	21,8	25	24	63,4	60,5	—	56,2	—	66200	—	46200	0,91	0,69	
9	0,40	42,5	25	24	—	8,2	63,5	7,7	—	1500	38500	1000	0,92	0,67	Значения a'_p и c'_p учитывают поправку на разбавление водой при обрыве реакции
10	0,41	34,7	25	24	—	—	—	—	—	1900	46200	1200	—	0,63	
							$\alpha_{Tcp} = 0,63 \pm 0,04$								
							$\alpha_{Dcp} = 0,89 \pm 0,02$								

* В таблице приняты следующие обозначения:

m_p — число молей растворителя в реакционной смеси

m_b — число молей вещества

c°_p — концентрация дейтерия в растворителе до опыта

N — концентрация амида калия (нормальность)

a°_p — удельная активность растворителя до опыта

Таблица II

РЕЗУЛЬТАТЫ ОПЫТОВ ПО ОПРЕДЕЛЕНИЮ КОЭФФИЦИЕНТА РАСПРЕДЕЛЕНИЯ В СИСТЕМЕ $C_{10}H_8 + ДBr + TBr$ $t \sim 20^0$

№№ пп	m_p/m_b	Продолжительность, час	a_p'	a_b'	c_p'	c_b'	α_T	α_D
1	48,2	48	10400	42200	—	—	4,1	—
2	77,0	28	11700	43600	21,6	43,0	3,7	2,6
3	101,0	48	6700	28900	23,1	48,7	4,3	3,2
4	84,5	49	47400	185800	20,4	42,0	4,0	2,8
5	88,8	148	42300	151200	19,4	42,3	3,6	3,0
6	95,2	172	48200	201000	21,0	43,0	4,2	2,7
							$\alpha_{Tcp} = 4,0 \pm 0,3$	$\alpha_{Dcp} = 2,9 \pm 0,2$

уверенности в достижении равновесия обменной реакции раствор выдерживали после приготовления в течение 1—3 суток.

Как правило, бензол или нафталин нормального изотопного состава растворяли в жидком аммиаке или бромистом водороде, одновременно меченных тритием и обогащенных дейтерием, однако некоторые опыты в системе $C_6H_6+NH_3+KNH_2$ проводили в обратном порядке, т.е. достигали равновесия с двух сторон.

В таких случаях в качестве исходного вещества использовался бензол, дейтерированный и тритированный в опытах по прямому обмену. Результаты опытов сведены в таблицы I и II. Из данных таблиц были определены средние значения коэффициентов распределения.

Они оказались равными: в системе бензол-аммиак $\alpha_d = 0,89 \pm 0,02$, $\alpha_T = 0,63 \pm 0,04$, в системе нафталин-бромистый водород $\alpha_2 = 2,9 \pm 0,2$, $\alpha_T = 4,0 \pm 0,2$.

В пределах ошибок измерений численные значения величины α_d согласуются со значениями найденными в работах [3, 10].

Нами была предпринята попытка вычисления коэффициента распределения трития и дейтерия в изучаемых системах из спектральных данных с использованием для этой цели метода, изложенного в работе [11].

Применяя для выражения статистических сумм обычные в химии изотопов упрощения и не учитывая влияния промежуточных дейтеро (тритий) — замещенных форм на коэффициент распределения, авторы приходят к следующей расчетной формуле для α:

$$\alpha = \frac{\left[\prod \frac{(\nu_A)\,i}{(\nu_A)\,i} \cdot \frac{1 - e^{-\frac{hc}{KT}(\nu_A)\,i}}{1 - e^{-\frac{hc}{KT}(\nu_A')\,i}}\right]^{1/n} \cdot e^{-\frac{hc}{2KT}\frac{1}{n}[\Sigma(\nu_A')\,i + Z_{A'} - \Sigma(\nu_A)\,i - Z_A]}}{\left[\prod \frac{(\nu_B')\,i}{(\nu_B)\,i} \cdot \frac{1 - e^{-\frac{hc}{KT}(\nu_B)\,i}}{1 - e^{-\frac{hc}{KT}(\nu_B')\,i}}\right]^{1/m} \cdot e^{-\frac{hc}{2KT}\frac{1}{m}[\Sigma(\nu_B')\,i + Z_{B'} - \Sigma(\nu_B)\,i - Z_B]}} \quad (3)$$

где: ν_A' и ν_A — основные частоты колебаний полностью дейтерированных или тритированных молекул A^1 и молекул A, не содержащих дейтерия (трития).

n и m — стехиометрические коэффициенты суммарной реакции обмена $mAX_n^0 + nBX^0{}_m^* \rightleftarrows mAX^0{}_n^* + nBX^0m$

Z — поправка на ангармоничность колебаний.

Неизвестный экспериментально колебательный спектр гекса-тритийбензола был вычислен нами по методике, описанной в работе [12]. Мы воспользовались при этом данными работ [13, 14], содержащими значения кинематических коэффициентов естественных колебательных координат и силовых постоянных в координатах симметрии для всех неприводимых представлений группы D_{6h}. При вычислении тех кинематических коэффициентов, которые изменяются от замены атомов H атомами T, нами была введена „спектроскопическая" масса трития $m_T^{-1} = 3{,}156$, служащая для некоторого упрощенного учета ангармоничности [12].

Вычисление корней вековых уравнений производилось методом последовательной диагонализации. В таблице III приведены результаты решения вековых уравнений молекул C_6H_6, $C_6Д_6$ и C_6T_6, наблюденные значения частот C_6H_6 и $C_6Д_6$ (в $см^{-1}$) и дано отнесение частот по типам симметрии.

Таблица III

НАБЛЮДЕННЫЕ И ВЫЧИСЛЕННЫЕ ЧАСТОТЫ БЕНЗОЛА, ГЕКСАДЕЙТЕРОБЕНЗОЛА И ГЕКСАТРИТИЙБЕНЗОЛА (в $см^{-1}$)

№№ пп		C_6H_6		$C_6Д_6$		C_6T_6
		ν наблюд.	ν вычисл.	ν наблюд.	ν вычисл.	ν вычисл.
1	A_1g	992	990	943	947	902
2	A_1g	3062	3062	2293	2292	1973
3	E^+g I	606	600	577	571	527
4	E^+g I	1178	1170	867	854	719
5	E^+g I	1596	1589	1552	1566	1556
6	E^+g I	3047	3049	2265	2265	1935
7	B_1u	1010	1008	963	965	921
8	B_1u	3060	3059	2290	2289	1968
9	$Eū$ II	1037	1024	813	817	652
10	$E^-ū$ II	1485	1480	1333	1320	1290
11	$Eū$ II	3080	3074	2294	2306	1986
12	$Eū$ I	1037	1024	813	817	652
13	$E^-ū$ I	1485	1480	1333	1320	1290
14	$E^-ū$ I	3080	3074	2290	2306	1986
15	E^+g II	606	600	577	571	527
16	E^+g II	1178	1170	867	854	719
17	E^+g II	1596	1589	1552	1566	1556
18	E^+g II	3047	3049	2265	2265	1935
19	A_2g	1326	1319	1037	1041	929
20	B_2u	1110	1099	825	831	691
21	B_2u	1648	1655	1577	1568	1550
22	B_2g	703	705	601	599	508
23	B_2g	985	983	827	829	803
24	Eg^{-1}	849	844	662	665	592
25	Eg^{-11}	849	844	662	665	592
26	Eu^{+1}	405	405	352	354	315
27	Eu^{+11}	405	405	352	354	315
28	Eu^{+1}	970	970	793	792	731
29	Eu^{+11}	970	970	793	792	731
30	A_2u	671	669	496	497	424

Как видно из данных таблицы III, максимальная ошибка расчета частот C_6H_6 и $C_6Д_6$ составляет 30 $см^{-1}$, а средняя абсолютная ошибка—10 $см^{-1}$. Кроме того, нами выполнен по той же методике расчет частот колебаний молекулы полностью тритированного аммиака NT_3. Были использованы следующие значения силовых постоянных $L=10{,}72$, $l=0{,}05$, $t=0{,}4$, $M=0{,}79$, $m=-0{,}07$. Обозначения коэффициентов взяты из работы [12].

Таблица IV

НАБЛЮДЕННЫЕ И ВЫЧИСЛЕННЫЕ ЧАСТОТЫ NH_3, $NД_3$ И NT_3 (в $см^{-1}$)

Симметрия	NH_3		$NД_3$		NT_3
	ν наблюд.	ν вычисл.	ν наблюд.	ν вычисл.	ν вычисл.
Симметр.	3336	3329	2420	2403	1988
Симметр.	950	960	748	735	641
Вырожд.	—	3478	2556	2546	2164
Вырожд.	1630	1613	1191	1183	1005

В таблице IV приведены результаты расчета частот NH_3, $NД_3$ и NT_3 и опытные значения. Погрешность расчета весьма мала, максимальное отклонение составляет 17 $см^{-1}$.

Частота колебаний в молекуле TBr вычислялась по известной формуле, связывающей νTB с приведенными массами μ_T и μ_H и частотой колебания HBr. Она оказалась равной $\nu_{TBr}=1515$ $см^{-1}$ ($\nu_{HBr}=2559$ $см^{-1}$).

При помощи формулы (3) с использованием вычисленных частот колебаний полностью тритированных, дейтерированных и не содержащих тяжелых изотопов водорода молекул были рассчитаны значения коэффициентов распределения. Для системы бензол-аммиак при температуре 20° С эти значения суть следующие: $\alpha_D=0{,}58$, $\alpha_T=0{,}58$; для системы бензол-бромистый водород они равны $\alpha_D=2{,}60$, $\alpha_T=3{,}92$.

Таким образом, теория правильно передает характер равновесного распределения дейтерия и трития в случае обмена с участием HBr. К аналогичному результату $\alpha_D=2{,}83$ приводит расчет с использованием опытных значений частот колебаний C_6H_6, $C_6Д_6$, HBr и ДBr.

Отсутствие согласия теории с опытом при обмене в жидком аммиаке, по нашему мнению, не является следствием грубости нашего расчета основных колебательных частот в бензоле или аммиаке.

Значение коэффициента распределения дейтерия $\alpha_D=1{,}02$, найденное при расчете с наблюдаемыми частотами, также заметно отличается от экспериментального ($\alpha_D=0{,}91$). Нам представляется, что наиболее вероятной причиной указанного расхождения является пренебрежение влиянием на результаты расчетов промежуточных изотопных форм бензола и аммиака. Действительно, если какой-либо из компонентов обменной реакции содержит лишь один атом водорода (например, двухатомный гидрид), погрешности при расчетах по формуле (3) сравнительно невелики, так как отбрасыванию промежуточных изотопных форм многоатомной молекулы соответствует физически реальный случай достижения равновесия при больших избытках двухатомного дейтерида. Напротив, при реакциях обмена между двумя многоатомными молекулами приближение, лежащее в основе вывода формулы (3),

не отображает какой-либо конкретной ситуации, могущей быть реализованной на опыте. Здесь лучше использовать для количественной оценки коэффициента распределения другое приближение, в котором учитываются частоты колебаний только однозамещенных дейтерированных или тритированных молекул.

Указанное приближение отчасти соответствует случаю, когда равновесие устанавливается в системе, содержащей малое число атомов дейтерия (трития), распределенных в массе атомов протия. При рассмотрении реакции обмена бензола с аммиаком целесообразно поэтому попытаться аппроксимировать выражение для коэффициента распределения суммарной реакции, выражением для коэффициента распределения реакции:

$$C_6H_6+NH_2T=C_6H_5T+NH_3$$

Предварительные данные, полученные нами при использовании в расчетах α частот колебаний монотритийбензола и монотритийаммиака, свидетельствуют в пользу высказанного предположения.

Экспериментальные данные по кинетическим изотопным эффектам водорода и их обсуждение

Исследованиями [4] было показано, что в молекуле дифенила, растворенного в ДВr, обмениваются шесть атомов водорода, находящихся в орто- и пара-положениях. Этот вывод в основном подтверждается масс-спектрометрическим анализом наших образцов дифенила. Так например, масс-спектр препарата, который получен после суточного обмена с 95—97%-ным ДВr, взятым в избытке $m_p/m_b=40:1$, содержал следующие молекулярные массы (в скобках указан молекулярный процент данной массы): 158 (4,2), 159 (24,6), 160 (70,0), 161 (1,2).

Ввиду сказанного при проведении кинетических опытов расчет константы скорости производился в предположении, что обменоспособными являются шесть атомов молекулы дифенила. Константу скорости обмена вычисляли по уравнению первого порядка. Для прямой реакции тритийобмена это уравнение имеет вид

$$K_{T\,(пр)}=\frac{2{,}3}{t}\lg\frac{a_p^{\circ}-a_p'}{a_p-a_p^{1}}.$$

Величину a_p' — равновесную удельную активность тритированного растворителя находили расчетным путем из уравнения материального баланса для трития.

Необходимые при расчетах величины коэффициента распределения α_T считались равными $\alpha_{THBr}=4{,}0$, $\alpha_{TNH_3}=0{,}63$.

Константу скорости обратного обмена вычисляли по уравнению

$$K_{T_{ОБР}}=\frac{2{,}3}{t}\lg\frac{a_b^{\circ}-a_b'}{a_b-a_b'}.$$

Аналогичные выражения (с заменой величин a_p и a_b атомными концентрациями дейтерия c_p и c_b) применялись для расчета результатов кинетических опытов по дейтерообмену.

В таблице V приведены результаты опытов с аммиачными растворами. Результаты измерений, выполненных с жидкими HBr, представлены в таблице VI.

Таблица V

СКОРОСТЬ ИЗОТОПНОГО ОБМЕНА ВОДОРОДА В БЕНЗОЛЕ, РАСТВОРЕННОМ В ЖИДКОМ АММИАКЕ

№№ пп	KNH_2	m_p/m_b	Продолжительность опыта (мин)	C_β	C_b'	$a_p°$	a_p'	$K_Д \cdot 10^{+4}$	$K_Т \cdot 10^{+4}$	$\frac{K_Д}{K_Т}$
1	0,22	44,4	120	42,5	28,4	250000	95000	2,0	1,3	1,5
2	0,10	56,1	60	75,5	21,6	59400	10500	1,1	0,8	1,4
3	0,15	26,7	60	74,0	32,0	151000	31800	1,9	1,2	1,6
4	0,10	35,0	30	69,4	11,5	59900	5400	1,1	0,9	1,3
5	0,14	30,2	120	15,8	8,4	238000	73400	1,3	0,9	1,4
6	0,10	34,5	30	69,4	12,0	243000	25600	1,2	1,0	1,2
7	0,12	38,2	90	15,8	7,6	218000	66200	1,5	1,2	1,2
8	0,10	36,6	30	41,7	6,0	71300	4500	1,0	0,6	1,7
							$K_{Д\,ср} = 1{,}4 \cdot 10^{-4}$ $K_{Т\,ср} = 1{,}0 \cdot 10^{-4}$			

Таблица VI

СКОРОСТЬ ИЗОТОПНОГО ОБМЕНА ВОДОРОДА В ДИФЕНИЛЕ, РАСТВОРЕННОМ В ЖИДКОМ БРОМИСТОМ ВОДОРОДЕ

№№ пп	Продолжительность опыта (мин)	m_p/m_b	$c_p°$	$c_b°$	c_b	$a_p°$	$a_b°$	a_b	$K_Д \cdot 10^{+4}$	$K_Т \cdot 10^{+5}$	$\frac{K_Д}{K_Т}$
1	57	66,5	18,8	—	9,0	15000	—	7400	1,6	8,1	2,0
2	60	87,4	31,8	—	15,7	20200	—	11400	2,0	9,6	2,1
3	60	98,7	84,8	—	20,1	142700	—	48300	1,2	5,3	2,3
4	60	81,5	84,8	—	17,0	142800	—	37800	1,1	4,4	2,4
5	120	84,3	30,8	—	22,9	20900	—	20500	1,9	9,8	2,0
6	120	79,8	31,8	—	23,3	119000	—	80000	1,9	6,2	3,0
7	125	86,5	84,8	—	27,0	119600	—	43600	0,9	2,8	3,1
8	120	76,0	84,8	—	24,3	112800	—	33200	0,8	2,6	3,1
9	180	82,7	26,8	—	24,8	29800	—	24500	2,0	6,6	3,0
10	180	68,5	18,8	—	16,2	15000	—	13000	1,5	6,0	2,5
11	180	105	31,8	—	28,3	119000	—	127700	1,9	6,6	2,9
12	60	78,7	—	54,0	24,9	—	307000	208200	2,8	15,3	1,8
13	60	79,8	—	54,0	25,0	—	307000	200400	2,8	17,0	1,7
14	120	87,5	—	54,0	16,5	—	307000	158000	2,3	13,5	1,7

Судя по данным таблицы 5, константа скорости обмена водорода в бензоле, растворенном в ND_3, $K_Д = 1{,}4 \cdot 10^{-4}$ сек$^{-1}$ практически совпадает с литературным значением $K_Д(10)$, полученным при таких же концентрациях амида калия. В опытах с растворами нормального дифенила в DBr получилось значение $K_Д = 0{,}9-2 \cdot 10^{-4}$ сек$^{-1}$ — более высокое по сравнению со средним значением $K_Д = 7 \cdot 10^{-5}$ сек$^{-1}$, данным в работе [4].

В опытах по обратному обмену водорода, которые приведены в табл. VI под № 12, 13, 14, исходным веществом служили препараты дифенила, приготовление обменом с жидким бромистым водородом, содержащим изо-

топы Д и Т в необходимых концентрациях. Константа скорости реакции для этого случая оказалась равной $2-3 \cdot 10^{-4}$ сек$^{-1}$. Увеличение измеряемой скорости обмена дейтерия по сравнению с аналогичными измерениями авторов работы [4] может быть обусловлено отступлениями от кинетического уравнения первого порядка для высоких концентраций дейтерия, с которыми мы работали, или же каталитическими влиянием следов примесей — продуктов коррозии аппаратуры.

Для тритийобмена получены следующие значения констант: в системе бензол-аммиак $K_T = 1 \cdot 10^{-4}$ сек$^{-1}$, в системе дифенил-бромистый водород для прямого обмена $K_T = 3-10 \cdot 10^{-5}$ сек$^{-1}$, для обратного обмена $K_T = 1{,}5-2 \cdot 10^{-4}$ сек$^{-1}$.

Таким образом, тритийобмен в растворе аммиака протекает в 1,4 раза медленнее дейтерообмена. Скорость обмена атомов протия на атомы трития в растворе тритированного бромистого водорода в 2—3 раза меньше скорости обмена атомов дейтерия; при обратном обмене это отношение равно 1,7—1,8.

Наличие кинетического изотопного эффекта для электрофильных реакций замещения ароматических углеводородов обычно требуется так, что стадией, лимитирующей обмен, является разрыв связи между атомами углерода и водорода в переходном состоянии.

Если придерживаться указанной трактовки, то наблюдаемый в наших опытах по прямому обмену в ДBr (TBr) заметный кинетический изотопный эффект водорода свидетельствует в пользу того, что преодоление сольватационного барьера при присоединении к ароматической молекуле $Д^+$ или $Т^+$ может оказаться самой медленной стадией реакции. Тогда, казалось бы, изотопный эффект не должен наблюдаться при обмене дейтеро-тритий-дифенила с бромистым водородом. Наличие такого эффекта, по нашему мнению, можно объяснить только на основе предположения, что разрыв старой связи С—Н и образование новой связи С—Д или С—Т происходит синхронно, в единичном акте.

Выводы

Измерены коэффициенты равновесного распределения дейтерия и трития в системах бензол-жидкий аммиак и нафталин-жидкий бромистый водород. Найденные значения коэффициентов для тритийобмена оказались равными α NT_3 $C_6H_6 = 0{,}63$, $\alpha TBr - C_{10}H_8 = 3{,}8-4{,}2$. Приведен расчет коэффициентов α_D и α_T методами статистической термодинамики с использованием вычисленных нами приближенных значений частот колебаний; в случае обмена с участием бромистого водорода достигнуто удовлетворительное совпадение с экспериментом. Определены кинетические изотопные эффекты в жидкофазных системах: аммиак-бензол (в присутствии амида калия как катализатора) и бромистый водород-дифенил. Константа скорости обмена на протий атомов трития растворителя K_T меньше константы для дейтерия $K_Д$: при обмене в жидком аммиаке $\frac{K_Д}{K_T} = 1{,}4$, при обмене в жидком бромистом водороде $\frac{K_Д}{K_T} = 2-3$. На основании данных кинетических опытов обсуждается вероятный механизм реакции обмена водорода ароматических углеводородов с HBr.

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DISCUSSION

J. Turkevich (United States of America) asked the speaker whether, from his observations, the isotopes entered the aromatic molecule one after another, or whether several entered at the same time; in the case of benzene, for instance, had he observed the production of monodeutero-, then dideutero-, then trideuterobenzene, etc., or was hexadeuterobenzene obtained at once?

I. F. Tupitsyn replied that he and his colleagues had studied the composition of the various deuterobenzenes by mass spectrometry and the concentrations had proved similar to those which were theoretically probable.

INVESTIGATIONS ON THE STRUCTURE OF COMPLEX COMPOUNDS BY RADIOISOTOPE EXCHANGE. THE STRUCTURE OF CYANONITROSYL COMPLEXES

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Abstract — Résumé — Аннотация — Resumen

Investigations on the structure of complex compounds by radioisotope exchange. The structure of cyanonitrosyl complexes. The nitrosyl group as the complex ligand is of particular interest because of its structure as well as its ability to form NO^- or NO^+ groups. To study the electronic structure of $K_3Mn(CN)_6$ and $K_3Mn(CN)_5NO$, the valency of the metal and the bonding type, investigations have been carried out by applying the method of radioisotopic exchange, as well as other physico-chemical methods. It has been found that by introducing the nitrosyl group into the hexacyanate ion, the stability of the complex is largely enhanced both in the solid state and in solution. This observation was confirmed by investigation of exchange kinetics in the systems:

$$\text{(I) } K_3Mn(CN)_6 + KC^{14}N \text{ and (II) } K_3Mn(CN)_5NO + KC^{14}N$$

In both cases, the exchange reactions are of first order, taken as a function of time, but differ considerably in their velocities, as well as in their activation energies. The anion $Mn(CN)_5NO^{-3}$ is sensitive to light, so that the exchange reaction is photochemical in character. The ratio of the exchange velocity constants in the dark and at standardized illumination is 1 : 100. The first exchange reaction (I) proceeds according to the association mechanism while the second one (II) possesses a composite association-dissociation mechanism. Analysis of the partition of activity within the cyanide groups undergoing exchange in the isotopic equilibrium state, revealed the identity of at least four cyanide groups. The high stability of the nitrosyl complex, as compared with the hexacyanate, was proved in various ways. All this pointed to a NO^- structure in the complex. Previous research has shown that the nitrosyl group is coordinated as NO^+. This suggests a resonance structure of the complex by assuming the resonance of an electronic pair between the T_{2g} shell of the central atom and the p shell of the nitrogen atom.

Recherches sur la structure des complexes par échange de radioisotopes — Structure des complexes cyanonitrosyliques. Le groupe nitrosyle en tant que coordinat du complexe cyanonitrosylique est particulièrement intéressant en raison de sa structure et de son aptitude à former des groupes NO^- ou NP^+. Pour étudier la structure électronique du $K_3Mn(CN)_6$ et du $K_3Mn(CN)_5NO$, la valence du métal et le type de liaison, des recherches ont été faites au moyen de la méthode de l'échange de radioisotopes, ainsi que par d'autres méthodes physicochimiques. On a constaté qu'en introduisant le groupe nitrosyle dans l'ion d'hexacyanate, la stabilité du complexe est sensiblement renforcée, à l'état solide comme à l'état de solution. Cette observation s'est trouvée confirmée par des recherches sur la cinétique des échanges intervenant dans les systèmes suivants:

$$\text{I } K_3Mn(CN)_6 + KC^{14}N \qquad \text{II } K_3Mn(CN)_5NO + KC^{14}N.$$

Dans les deux cas, les réactions d'échange sont du premier ordre, mais leurs vitesses et leurs énergies d'activation sout extrêmement différentes. L'anion $Mn(CN)_5NO_3$ étant sensible à la lumière, la réaction d'échange est de caractère photochimique. Le rapport des constantes de vitesse d'échange dans l'obscurité et sous éclairage normalisé est de 1:100. La première réaction d'échange (I) se produit conformément au mécanisme d'association, tandis que la seconde (II) suit un mécanisme combiné association/dissociation. L'analyse de la distribution de l'activité, dans les groupes cyanure qui subissent un échange à l'état d'équilibre isotopique, a révélé l'existence d'au moins quatre groupes cyanure distincts. La grande stabilité du complexe nitrosylique, en comparaison de celle de l'hexacyanate, a été prouvée par différentes méthodes. Tout cela semble indiquer une structure NO^- dans le complexe. Des recherches antérieures ont montré que le groupe nitrosyle est coordonné sous forme de NO^+. Cela donne à penser que le complexe possède une structure de résonance, si l'on admet la résonance d'une paire d'électrons entre la couche T_{2g} de l'atome central et la couche p de l'atome d'azote.

Исследование структуры сложных соединений при помощи радиоизотопного обмена — структура сложных цианонитрозиловых соединений. В качестве сложного связующего звена нитрозиловая группа представляет особый интерес как по своей структуре, так и благодаря своему свойству образовывать группы NO^- и NO^+. Для исследования электронной структуры $K_3Mn(CN)_6$ и $K_3Mn(CN)_5NO$, валентности металла и характера соединений были произведены исследования при помощи метода радиоизотопного обмена, а также и других физико-химических методов. Было обнаружено, что добавление нитрозиловой группы к ионам гексацианата значительно увеличивает устойчивость соединения как в твердом состоянии, так и в растворе. Это наблюдение было подтверждено исследованием кинетики обмена в системах:

$$\text{I } K_3Mn(CN)_6 + KC^{14}N; \quad \text{II } K_3Mn(CN)_5NO + KC^{14}N.$$

В обоих случаях реакции обмена в функции времени являются реакциями первого порядка, но они значительно отличаются друг от друга по скорости. Энергии активации этих реакций равны $E_1 = 8{,}5$ килокалорий на молекулу и $E_{11} = 22{,}8$ килокалорий на молекулу. Анион $Mn(CN)_5NO_3$ светочувствителен, так что реакция обмена носит фотохимический характер. Соотношение постоянных скоростей обмена в темноте и при стандартизированном освещении равно 1:100. Первая реакция обмена (I) происходит по типу ассоциации, тогда как вторая реакция (II) следует сложному механизму ассоциации и диссоциации. Анализ распределения активности между цианистыми группами, подвергающимися обмену в состоянии изотопного равновесия, обнаружил идентичность по меньшей мере четырех цианистых групп. Большая устойчивость нитрозиловых соединений по сравнению с гексацианатами, а также отсутствие вторичных диссоциаций были подтверждены различными методами. Все это указывает на структуру NO^- комплекса. Предыдущие исследования показали, что нитрозиловая группа координируется в виде NO^+. Это указывает на резонансную структуру сложного соединения, исходя из гипотезы наличия резонанса электронной пары между T_{2g}-оболочкой центрального атома и p-образной оболочкой атома азота.

Estudio de la estructura de complejos por intercambio radioisotópico — Estructura de los complejos cianonitrosílicos. El grupo nitrosilo puede actuar en las dos formas NO^- y NO^+ y esta propiedad, junto con su estructura, le confiere particular importancia como grupo ligante. Los autores han estudiado la estructura electrónica del $K_3Mn(CN)_6$ y del $K_3Mn(CN)_5NO$, la valencia del metal y el tipo de enlace, empleando métodos de intercambio radioisotópico y otras técnicas fisicoquímicas. Encuentran que la introducción del grupo nitrosilo en el ion hexacianuro aumenta notablemente

la estabilidad del complejo, tanto en estado sólido como en solución. Esta observación queda corroborada por el estudio de la cinética de intercambio de los sistemas:

I) $K_3Mn(CN)_6 + K\,{}^{14}CN$ II) $K_3Mn(CN)_5NO + K\,{}^{14}CN$

En ambos casos, las reacciones de intercambio son de primer orden, pero sus velocidades y sus energías de activación respectivas son muy distintas. El anión $[Mn(CN)_5 NO]^{3-}$ es fotosensible, de modo que la reacción de intercambio tiene caracter fotoquímico. La razón entre las constantes de velocidad del intercambio en la oscuridad y bajo una iluminación tipo es 1 : 100. La primera reacción de intercambio (I) transcurre según un mecanismo de asociación, mientras que la segunda (II) obedece a un mecanismo compuesto de asociación-disociación. En el estado de equilibrio isotópico, el análisis de la distribución de la actividad entre los grupos cianuro que sufren el intercambio revela la identidad de por lo menos cuatro de los grupos cianuro. Por diferentes métodos se pudo demostrar que el complejo nitrosilado posee una estabilidad mucho mayor que el hexacianuro. Todo lo precedente indica la presencia de una estructura NO^- en el complejo. Las investigaciones anteriores habían revelado que el grupo nitrosilo está coordinado como NO^+. Ello sugiere la existencia de una estructura resonante para el complejo, admitiendo la resonancia de un par electrónico entre la capa T_{2g} del átomo central y la capa p del átomo de nitrógeno.

1. Introduction

The studies on the isotopic exchange of ligands in complex compounds, carried out by many researchers, revealed several important features concerning the structure and the type of bonding in complexes. In the case of cyanide complexes of the transition metals, extensive investigations have been carried out by ADAMSON *et al.* [1] [2] concerning exchange processes in the complexes of nickel, palladium, mercury, manganese, chromium, iron, cobalt, and molybdenum. It has been found that the exchange velocity in manganese (III) complexes [2] is exceptionally high compared to that of Cr (III), Co (III), and Fe (III).

In these complexes one CN group may be substituted by NO thus forming rather stable nitrosylcyanide complexes. The explanation of the electronic structure of the nitrosylcyanide complexes was complicated by the unsettled character of coordination of the NO group, it being different for different complexes. During the last years many investigations devoted to this subject were undertaken by WILKINSON, GRIFFITH, LEWIS and COTTON [3—9]. In spite of some interesting concepts a more general view of the character of NO bonding in these complexes has not yet been formed. It is accepted that in some complexes the group is coordinated as NO^- $K_3[Co(CN)_5 NO]$, more often as NO^+ $K_3[Mn(CN)_5 NO]$, $K_3[Cr(CN)_5 NO]$, $K_4[Mo(OH)_2(CN)_5 NO]$ and very rarely as the neutral group NO—$Na_2[Fe(CN)_5 NO]$. Recently, results based on the examination of infra-red spectra are used as the main source of information on the character of bonding of the NO group. Accordingly, the coordination of NO^- is characterized by a band lying within 1100—1200 cm^{-1} [3] and of NO^+ by a band ranging from 1595 cm^{-1} [6] (for molybdenum complexes) to 1944 cm^{-1} [9] (for iron complexes). The coordination of NO groups necessitates the assumption of lower oxidation states of metals (Mn^{+1}, Cr^{+1}, Mo^{+2}) which however, is often in contradiction to the chemical properties of the complex in question. It is expected that by simultaneously applying the isotopic exchange method and some other physicochemical methods in investigations on cyanonitrosyl complexes a more consistent explanation will be found. For the time being we have

carried out research on the pentacyanonitrosylmanganate $K_3[Mn(CN)_5NO]$ which has revealed some new information on the structure of this complex and enabled a generalization of the mode of NO-bonding in other complexes of the transition metals.

2. Exchange of radiocyanide ion in $[Mn(CN)_5NO]^{-3}$

To obtain more universal information and comparative data, radioisotopic exchange was examined in the following systems:

(I) $K_3[Mn(CN)_6] - KC^{14}N$
(II) $K_3[Mn(CN)_5NO] - KC^{14}N$.

The complex $K_3[Mn(CN)_5NO]$ was obtained from $K_3[Mn(CN)_6]$ by treatment with hydroxylamine in alkaline solution according to known methods [10—13].

After the exchange reactions, the complex compounds were separated as their low-solubility cadmium salts. The activity increase in the complexes was determined by means of a GM counter, the window-thickness of which was equal to 1.7 mg/cm². In calculations of the specific activity, correction for self-sorption was made. The exchange reactions were followed to the point where isotopic equilibrium was attained, i.e. to uniform distribution of radiocyanide between all the groups undergoing exchange. The stability of the complexes during the exchange was checked photometrically by measuring the extinction of the solution. For both the systems (I), and (II), the exchange reaction follows the simple exponential law:

$$(1 - F) = \exp\left(-\frac{a-b}{ab} R T\right)$$

where $F = x/x_\infty$,
x = activity of the complex after time t,
x_∞ = activity of the complex in isotopic equilibrium,
a, b = the concentrations of the complex and of the potassium cyanide expressed in mols of CN per liter, and
R = the rate constant of exchange.

The results of the exchange reactions are plotted as $\log(1 - F)$ *versus* time. In the calculations it was assumed that all the cyanide groups undergo exchange with practically equal velocity. This was checked in the determination of position equivalency of CN groups in the complex. The course of the experimental points in the system $\log(1 - F)$ *versus* time does not point to a complex exchange process with two different rates. Therefore the slope of the straight line expressed by $C = R\frac{a-b}{ab}$ enables one to calculate the rate-constant R responsible for the exchange. Because of the instability of the hexacyanomanganate (III) and the very high exchange-rate (independent of light), the exchange reaction (I) was examined at 0°C only. The results obtained are in agreement with those of ADAMSON [2] (Table I). The exchange reaction in system (II) does practically not take place in the dark. This is a photochemical reaction the velocity of which can be measured on exposure to light. Owing to the rather high temperature coefficient of reaction (II), all measurements were made at temperatures above 15° C. To some extent, this rendered a direct comparison of results with reaction (I) difficult. We studied in detail the velocity and the exchange mechanism of re-

TABLE I

EXCHANGE REACTION AT 0°C

$K_3[Mn(CN)_6] = 0.105$ mole CN/l KCN = 0.0515 mole CN/l pH = 10.65

C (min^{-1})	R (mole/liter min)
1.45×10^{-2}	1.15×10^{-3}

action (II), whereby the influence of light on the reaction velocity was examined, as well as the dependence on concentration, and the influence of the temperature and pH of the solution.

2.1. THE INFLUENCE OF LIGHT ON THE EXCHANGE RATE

The influence of light on the exchange reaction was examined in two series of measurements, one in the dark, and the other at standard illumination with a 40-W bulb with tungsten filament. The obtained results are shown in Table II and in Fig. 1. The ratio R_I/R_{II} is of the order of 10^{-2}.

TABLE II

EFFECT OF LIGHT ON THE EXCHANGE REACTION AT 25° C

$K_3[Mn(CN)_5NO] = 0.265$ mole CN/l KCN = 0.1901 mole CN/l pH = 10.2

	C (min^{-1})	R (mole/liter min)
A. in dark	2.5×10^{-6} *	0.068×10^{-5} *
B. standard ilumination by a 40-W bulb	112.5×10^{-6}	2.87×10^{-5}

* The isotopic equilibrium for reaction A was calculated by extrapolation of the results of reaction B.

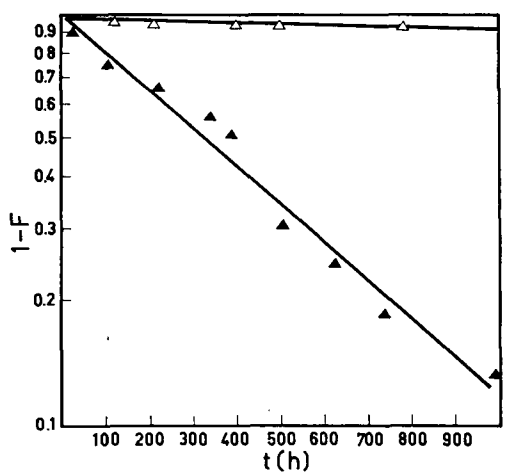

Fig. 1

Effect of light on the exchange reaction at 25°C.
$K_3[Mn(CN)_5NO] = 0.265$ mole CN/l. KCN = 0.1901 mole CN/l. pH = 10.65.
△ = exchange reaction in the dark.
▲ = exchange reaction at standard illumination.

2.2. Concentration effect on the exchange rate at 25°C

Results of four series of measurements of the exchange rate for different concentrations of the nitrosylcyanomanganate and potassium cyanide at 25°C are shown in Table III and Fig. 2. As can be seen from the data given, the ex-

Table III

EFFECT OF CONCENTRATION ON THE EXCHANGE RATE AT 25°C

Concentration		$C \times 10^5$ (min^{-1})	$R \times 10^5$ (mole/liter min)
$K_3[Mn(CN)_5NO]$ (mole CN/l)	KCN (mole CN/l)		
0.2650	0.1901	11.25	2.87
0.5045	0.1997	9.25	3.04
0.4990	0.9985	8.25	6.32
0.4990	1.9970	10.16	9.74

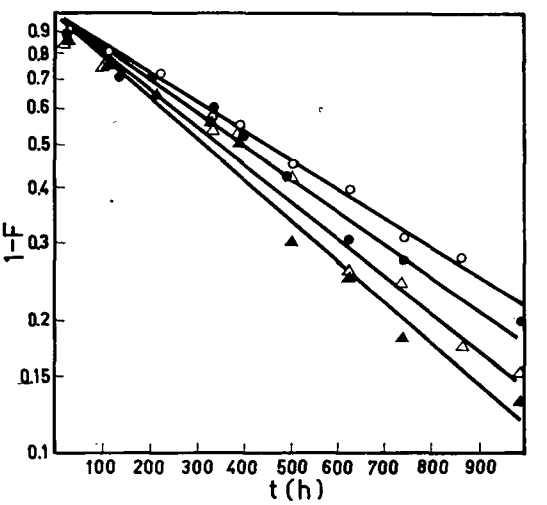

Fig. 2

Concentration effect on the exchange reaction at 25°C.
▲ = $K_3[Mn(CN)_5NO]$ = 0.2650 mole CN/l. KCN = 0.1901 mole CN/l.
● = $K_3[Mn(CN)_5NO]$ = 0.5045 mole CN/l. KCN = 0.1997 mole CN/l.
○ = $K_3[Mn(CN)_5NO]$ = 0.4990 mole CN/l. KCN = 0.9985 mole CN/l.
△ = $K_3[Mn(CN)_5NO]$ = 0.4990 mole CN/l. KCN = 1.9970 mole CN/l.

change rate depends on the cyanide concentration as well as on the concentration of the complex. This dependence points to an association-dissociation mechanism of exchange.

2.3. Effect of pH on the exchange rate

Small changes of pH of the solutions were brought about by admixing small amounts of $HClO_4$ or KOH so that the colour of the solution was not effected (Table IV) (Fig. 3). The slope of the straight lines indicates an increase in exchange

TABLE IV

EFFECT OF pH ON THE EXCHANGE RATE AT 25°C
K_3 [Mn $(CN)_5$ NO] = 0.265 mole CN/l KCN = 0.1901 mole CN/l

pH	$C \times 10^5$ (min^{-1})	$R \times 10^5$ (mole/liter min^1)
9.5	8.1	2.04
10.2	11.25	2.87
11.35	15.7	4.01

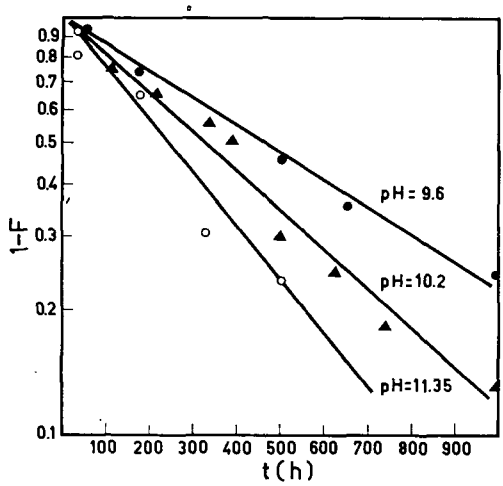

Fig. 3
Effect of pH on the exchange reaction at 25°C.
K_3 [Mn $(CN)_5$ NO] = 0.265 mole CN/l. KCN = 0.1901 mole CN/l.

rate with increasing pH. Thus, the exchange rate is inversely proportional to the concentration of hydrogen ions.

2.4. INFLUENCE OF THE TEMPERATURE ON THE EXCHANGE RATE

The influence of the temperature on the exchange kinetics was examined in three series of measurements at the temperatures 18, 25 and 38°C (Table V) (Fig. 4).

TABLE V

EFFECT OF TEMPERATURE ON THE EXCHANGE RATE
K_3 [Mn $(CN)_5$ NO] = 0.265 mole CN/l KCN = 0.1901 mole CN/l pH = 10.2

Temp. (°C)	$C \times 10^5$ (min^{-1})	$R \times 10^5$ (mole/liter min)
18	6.5	1.66
25	11.25	2.87
38	42.0	10.71

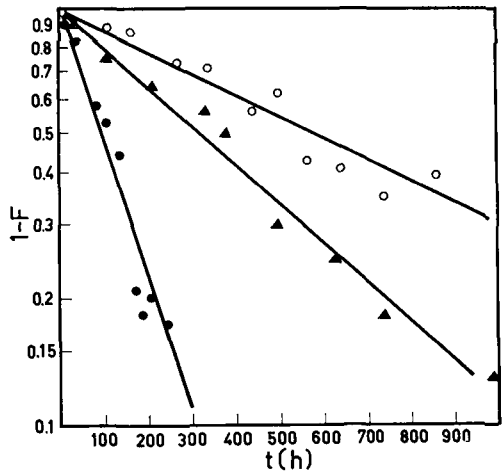

Fig. 4

Temperature dependence of the exchange reaction.
$K_3[Mn(CN)_5NO] = 0.265$ mole CN/l. KCN = 0.1901 mole CN/l. pH = 10.2.
○ = exchange reaction at 18°C.
▲ = exchange reaction at 25°C.
● = exchange reaction at 38°C.

On the basis of these results it was found that the activation energy of the exchange reaction (II) equals 22.8 kcal/mole, this value being considerably higher than the activation energy of reaction (I) which equals 8.5 kcal/mole [2].

3. Determination of position equivalency of cyanide groups

In order to determine the equivalency of cyanide groups in the nitrosylcyanomanganate $K_3[Mn(CN)_5NO]$ we carried out a quantitative analysis of the distribution grade of active $C^{14}N$ between the complex and ordinary potassium cyanide in the isotopic equilibrium. The specific activity was expressed in the number of impulses per mole of CN by assuming non-equivalency or equivalency of all the five cyanide groups. The results obtained (presented in Table VI)

TABLE VI

ANALYSIS OF DISTRIBUTION GRADE OF RADIOACTIVE $C^{14}N^-$ ION IN THE ISOTOPIC EQUILIBRIUM BETWEEN THE COMPLEX AND NON-ACTIVE KCN
$K_3[Mn(CN)_5NO] = 0.265$ mole CN/l KCN = 0.1997 mole CN/l
pH = 10.2 t = 25° C

Sample	Specific activity—A (counts/min g CN^{-1})
$K_3[Mn(CN)_5NO] + KCN$	803000
$K_3[Mn(CN)_5NO]$	510000
KCN	344000

$$\frac{\text{concentration of complex}}{\text{concentration of cyanide}} = \frac{\text{A—complex in isotopic equilibrium}}{\text{A—cyanide in isotopic equilibrium}}$$

$$1.42 \simeq 1.48$$

are close to the ones assumed for an exchange process proceeding with the same rate for all cyanide groups. Small deviations in theoretical calculations seem to indicate a certain degree of non-equivalency of the CN group in *trans* position to the NO, but they are so small that the resulting difference in exchange rate cannot be determined quantitatively with reasonable accuracy.

4. Stability and molecular state of the nitrosylcyanide complex

The complex $K_3[Mn(CN)_5NO]$ is completely stable in the dark both in the solid state and in solution. The molar extinction of a solution containing 10^{-2} mole/l does not change even after a period of two months and does not show any deviations from Beer's law.

The equivalent conductivity of the complex is 468 Ω^{-1} and does not change with time in the dark. Accordingly the complex dissociation into four ions may be assumed without secondary dissociation of the anion.

Further proof of the stability of the complex ion was supplied by polarographic examinations. The complex does not undergo any oxidation or reduction at the mercury drop electrode in a solution of 1 mole/l KCN.

The mononuclear structure of the complex was confirmed by the cryoscopical measurements of the molecular weight in fused Glauber salt ($Na_2SO_4 \cdot 10H_2O$) [14] (Table VII).

TABLE VII
CRYOSCOPIC DETERMINATION OF MOLECULAR WEIGHT IN FUSED GLAUBER'S SALT

Compound	M	G	F	D	K	
$K_3[Fe(CN)_6]$	329.26	39.99	0.4814	0.46	125.9	
$K_3[Fe(CN)_6]$	329.26	40.01	1.1001	1.06	126,9	$K_{av.} = 126.4$
$K_3[Mn(CN)_5NO]$	X	40.10	0.5657	0.52	126.4	

M = molecular weight
G = weight of $Na_2SO_4 \times 10\,H_2O$ in g
F = weight of sample in g
D = lowering of freezing point for Glauber's salt
K = cryoscopic constant

$$M_{K_3[Mn(CN)_5NO]} = 100 \times F \times K_{av.} \times \frac{1}{D \times G} = 335.2$$

$$M_{theoretical} = 332.33$$

5. Magnetic susceptibility of the nitrosylcyanide complex

The measurements of magnetic susceptibility by the GOUY method, both for the solid form and the aqueous solution of the complex $K_3[Mn(CN)_5NO]$ revealed the diamagnetic nature of this compound in both cases (Table VIII).

TABLE VIII
MAGNETIC SUSCEPTIBILITY OF THE NITROSYLCYANIDE COMPLEX

Physical state	Temp. (°K)	$\chi_g \times 10^6$	$\chi_{mol} \times 10^6$
Solid	87	—9.36	—3109.3
	137	—2.39	—797.5
	183	—1.64	—544.9
	300	—1.005	—348.9
Aqueous solution	300	—1.33	—431.9

6. Absorption spectra

The absorption spectra of both the manganese complexes $K_3[Mn(CN)_6]$ and $K_3[Mn(CN)_5NO]$ in aqueous solutions were examined in the visible range. The absorption band characteristic for the nitrosylcyanide complex lies around 540 nm. This value corresponds to the position of the absorption peaks of other Mn (III) complexes lying within the range of 475 to 550 nm. The position of the absorption band depends on the stability of the complexes. The absorption peak of more stable complexes is shifted towards longer wave lengths. Accordingly, the addition of a ligand to $[Mn(CN)_6]^{-3}$ or $[Mn(C_2O_4)_3]^{-3}$ solutions results in a bathochromic shift of the band but has no influence on the stable complex $[Mn(CN)_5NO]^{-3}$ (Table IX). The absorption bands in the ultraviolet range for both the investigated cyanide complexes of manganese lie very close to each other. The ultraviolet data presented in Table X are taken from the literature [2] [9].

TABLE IX

ABSORPTION SPECTRA OF $K_3[Mn(CN)_5NO]$, $K_3[Mn(CN)_6]$ AND $K_3Mn(C_2O_4)_3]$ IN AQUEOUS SOLUTIONS AND WITH ADDITION OF LIGANDS

Compound	Band position in aqueous solution (nm)	Band position in 2 M solution of ligand (nm)
$K_3[Mn(CN)_5NO]$	540	540
$K_3[Mn(CN)_6]$	475	500—505
$K_3[Mn(C_2O_4)_3]$	475	about 520

TABLE X

ULTRAVIOLET ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF $K_3[Mn(CN)_5]$ NO AND $K_3[Mn(CN)_6]$

Compound	Band position (nm)
$K_3[Mn(CN)_5NO]$	about 220 and 348
$K_3[Mn(CN)_6]$	about 210 and 330

7. Discussion

The investigation of the radioisotopic exchange of the CN groups in $K_3[Mn(CN)_6]$ and $K_3[Mn(CN)_5NO]$ complexes has shown that the stability of the complex is increased by substituting an NO group for one of the CN groups. The exchange reaction in hexacyanomanganate apparently proceeds through a seven-coordinative intermediate according to the association mechanism postulated by ADAMSON [2]. $K_3[Mn(CN)_6]$ is paramagnetic with a magnetic moment of 2.95—3.61 BM as found by different authors [15]. This corresponds to a d_ε^4 configuration of octahedral symmetry. Two d_ε orbitals are here occupied by two single electrons thus forming the configuration $d^2d^1d^1$ (D^2SP^3). The exchange proceeds through the association due to the coupling of the electrons, thus leaving one d_ε orbital available for the seventh ligand. This process gives rise to a very

rapid exchange. The diamagnetic nitrosylcyanide complex practically does not exchange the cyanide groups when kept in the dark, which points to the stable structure (36 electrons) $3d^2 3d^2$ (D^2SP^3). This structure leaves no possibility for an increase of the coordination number to seven, so the exchange process does not occur. Only under the influence of light is the exchange rate high enough to be examined quantitatively. This behaviour points to the possible formation of a structure with one free orbital d_ε neccessary for the exchange reaction. The dissociation mechanism causing the insignificant exchange in the dark has also some share in the exchange. The visible and ultraviolet absorption spectrum of the nitrosylcyanide complex contains the band peculiar to manganese (III) in the complexes. The purple-red colour of this complex resembles the colour of other manganese (III) complexes. It should be emphasized here that hexacyanomanganate (I) $K_5[Mn(CN)_6]$ is colourless and, in contrast to nitrosylcyanomanganate $K_3[Mn(CN)_5NO]$, unstable, (At higher temperatures it decomposed with water with evolution of hydrogen).

These facts allow the assumption that introduction of one NO group into the complex changes its electronic structure while the oxidation state of the central ion remains the same. In consequence, the $C\ddot{N}^-$ is substituted by the NO^- ion capable of forming a double bond $=N=\ddot{O}$. The direct introduction of this ion is possible by treating the cyanide complexes of metals with hydroxylamine in alkaline solution. According to PAULING [16] we assume that seven orbitals of the manganese are used for the formation of bonds in the nitrosylcyanide complex. Consequently, due to the further removal of degeneracy of d orbitals, the d_ε orbital splits into a lower doublet e_g and an upper singlet b_{2g}. The latter combines with a p_π-orbital and two electrons of nitrogen to form a π bond. Four manganese electrons are forced to occupy the doubly degenerate orbital e_g.

The doubly bonded NO group,

$$\text{(I)}\quad Mn=N=\ddot{O}$$

effects a high structural stability resulting in the lack of exchange of cyanide groups in the dark. Under the influence of light, the π bond breaks so that a single bond between manganese and nitrogen is left:

$$\text{(II)}\quad Mn-\ddot{N}=\ddot{O}$$

In structure (II) one of the d_ε orbitals of manganese is now available in the exchange reaction, thus making the association mechanism possible. The dependence of the exchange velocity on the concentration of both the complex and free cyanide being connected by an association-dissociation mechanism supplies further evidence for this structure. The investigations on the radioisotopic exchange mechanism have in general shown the position equivalency of all the cyanide groups in the excited structure. The explanation of this phenomenon is possible if it is assumed that in the equilibrium between these two structures [6], (II) is the preferred one during illumination. In the complex ion $[Mn(CN)_5NO]^{-3}$ (in the dark) two cyanide groups may be doubly bound with use of d orbitals of the manganese atom, with its pairs of electrons (Fig. 5.I), as is the case with $[Fe(CN)_6]^{-4}$ according to PAULING [16]. In the excited state, all metal-ligand bonds become single bonds. (Fig. 5.II). Weakened in this way, bonds enable to some extent the participation of an association mechanism. Because of the small difference in the electronegativity of C and N, the trans-

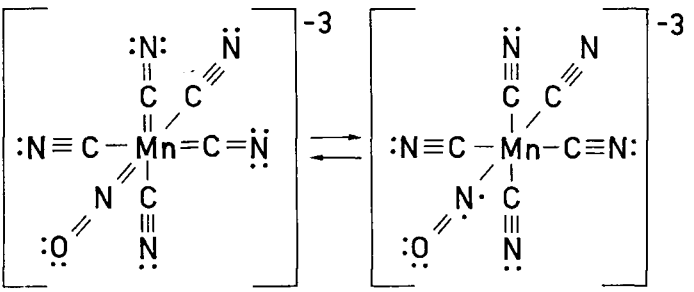

Fig. 5

I
Non-excited structure

II
Excited structure

interaction of a singly bound NO group is so very small that it was not possible to verify the non-equivalency of CN groups during the exchange process.

We have now prepared the way for discussing the structure of other nitrosyl-cyanide complexes of transition metals. In all these cases the structure may be successfully explained by assuming that the coordinated NO^- group (or in rare cases NO neutral) is in some complexes singly and in the others doubly bonded. The π bond formation involves either the electron pair of nitrogen or one nitrogen electron and one from the metal.

Finally, it should be emphasized that absorption bands in the infra-red range of different nitrosylcyanido complexes lying between 1600 and 2100 cm^{-1} correspond to doubly bound NO groups, while those between 1100 and 1200 cm^{-1} correspond to singly bound NO groups.

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DISCUSSION

G. M. Harris (United States of America) said it was not clear to him whether the rate study of the nitrose complex exchange was done thermally or photochemically.

B. Jeżowska-Trzebiatowska replied that the rate of the exchange between $C^{14}N^-$ and the complexes was studied by separation of the cadmium salts having a low solubility. The stability of the complex was checked spectro-photometrically during the exchange reaction. The exchange reaction was studied at the standard illumination all along, at three different temperatures.

ION EXCHANGE STUDIES OF ALPHA-HYDROXY CARBOXYLIC ACID-LANTHANIDE AND ACTINIDE SYSTEMS

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Abstract — Résumé — Аннотация — Resumen

Ion exchange studies of alpha-hydroxy carboxylic acid-lanthanide and actinide systems. Alpha-hydroxy carboxylic acids have been used extensively for the separation of lanthanide and actinide elements with cation exchange resins. Sorption of these elements in the same solutions occurs on strong base anion-exchange resins. A study has been made by elution and equilibrium distribution techniques of the behaviour at tracer-level concentrations of these anion-exchange systems. One objective was to measure the separation factors to assess anion exchange as a possible complement to cation exchange separation. Since very little attention has been given to characterizing the complexed species present in these separation systems, a second objective was to attempt such characterization through interpretation of both cation and anion exchange data.

Glycolic, lactic and alpha-hydroxy isobutyric acids were used together with radioactive tracers of Ce, Pm, Eu, Tb, Tm, Y, Cm and Cf. The elutions and equilibrium distributions were performed both at 25° C and 87° C.

In all three eluants, the separation factors were smaller for the anion exchange than for the analogous cation exchange. In the glycolate solutions, the separation factors were largest and the values of the distribution coefficient K_d indicated that these were the most stable complexes.

The plots of log K_d against log anion concentration pass through a maximum and then approach a slope of —1, indicating the presence of an anionic complex MX_4^-. The existence of this negative complex in the solution phase was demonstrated by electromigration studies of Tm^{170} tracer in these solutions. At the solution concentration corresponding to the maximum K_d value, it can be shown that the predominant solution species is MX_3.

Approximate successive stability constants have been calculated for these systems and with these it is possible to construct diagrams showing the relative concentration of the species M^{+3}, MX^{+2}, MX_2^+, MX_3 and MX_4^- as a function of the concentration of X^-.

Etudes, par échange d'ions, sur des systèmes de sels de lanthanides et d'actinides des acides alpha-hydroxycarboxyliques. Les acides α-hydroxycarboxyliques sont souvent utilisés pour la séparation des lanthanides et des actinides au moyen de résines échangeuses de cations. La sorption de ces éléments dans les mêmes solutions peut être réalisée avec des résines échangeuses d'anions fortement basiques. Les auteurs ont étudié les propriétés de ces systèmes d'échange d'anions, à des concentrations extrêmement faibles, en employant des techniques d'élution et des techniques fondées sur la distribution d'équilibre. L'un des buts recherchés était de mesurer les facteurs

de séparation pour voir dans quelle mesure l'échange d'anions peut compléter la séparation par échange de cations. Etant donné qu'on ne s'est guère préoccupé jusqu'à présent de caractériser les espèces chimiques qui apparaissent sous forme de complexes dans ces systèmes de séparation, les auteurs se sont efforcés de le faire — et c'était là leur deuxième objectif — en interprétant les résultats des essais d'échange de cations et d'anions.

Les auteurs ont utilisé les acides glycolique, lactique et α-hydroxy-isobutyrique avec divers indicateurs radioactifs: cérium, prométhéum, europium, terbium, thulium, yttrium, curium et californium. L'élution et la distribution d'équilibre ont été réalisées à 25°C et à 87°C.

Avec chacun des trois éluants, les facteurs de séparation sont plus faibles pour l'échange d'anions que pour l'échange analogue de cations. Ils sont à leur maximum avec les glycolates, et les valeurs du coefficient de distribution K_d montrent que les glycolates sont les complexes les plus stables.

Les courbes du log K_d en fonction du logarithme de la concentration d'anions passent par un maximum, puis ont une pente tendant vers —1, ce qui dénote la présence d'un complexe anionique du type MX_4^-. L'existence de ce complexe négatif dans la solution a été démontrée par l'étude électromigratoire de l'indicateur thulium-170. Pour une concentration de la solution correspondant à la valeur maximum de K_d, on peut démontrer que l'espèce chimique qui prédomine dans la solution du type est MX_3.

Les auteurs ont calculé approximativement les constantes successives de stabilité correspondant à ces systèmes; ces constantes permettent de tracer les courbes des concentrations relatives des espèces chimiques M^{3+}, MX^{2+}, MX_2^+, MX_3 et MX_4^- en fonction de la concentration de X^-.

Изучение ионного обмена систем альфа-гидро-оксикарболовой кислоты и лантанидов или актинидов. Альфа-гидро-оксикарболовые кислоты были широко использованы для отделения элементов группы лантанидов и актинидов при помощи смол с катионным обменом. Сорбция этих элементов в одних и тех же растворах происходит на смолах анионного обмена с сильным основанием. Методами вымывания и уравновешенного распределения были изучены процессы, происходящие в этих системах анионного обмена в ничтожных концентрациях. Одной из целей было измерение факторов отделения для оценки анионного обмена в качестве возможного дополнения к отделению катионным обменом. Так как до сих пор уделялось очень мало внимания опознаванию сложных соединений, имеющихся в этих системах отделения, второй целью было попытаться опознать эти соединения путем толкования данных как катионного, так и анионного обменов.

Были использованы гликойная, молочная и альфа-окси-изомасяная кислоты вместе с изотопами церия (Ce), прометия (Pm), европия (Eu), тербия (Tb), тулия (Tu), иттрия (Y), кюрия (Cm) и калифорния (Cf) в качестве индикаторов. Вымывание и уравновешенное распределение производились при температурах 25° C и 87° C.

Во всех этих трех элюентах факторы отделения были меньшими для анионного обмена, чем для аналогичного катионного обмена. В растворах гликолатов факторы отделения были наивысшими и значения коэффициента распределения K_d указывают, что эти сложные соединения являются наиболее устойчивыми.

Кривая log K_d в зависимости от логарифма анионной концентрации проходит через максимум, затем приближается к наклону в -1, указывая на наличие анионного комплекса MX_4^-. Наличие этого отрицательного сложного соединения в фазе раствора было доказано при помощи электромиграционного изучения поведения индикатора из тулия-170 в этих растворах. Можно доказать, что при концентрации раствора, соответствующей максимальному значению K_d, преобладающим веществом в растворе является MX_3.

Для этих систем были подсчитаны приблизительные последовательные константы устойчивости и благодаря этим константам представляется возможным построить кривые,

дающие относительную концентрацию групп M^{+3}, MX^{+2}, MX_2^{+}, MX_3 и MX_4 в функции от концентрации X^{-}.

Estudios de intercambio iónico en los sistemas de sales de lantánidos y actínidos de los ácidos alfa-hidroxicarboxílicos. Los ácidos alfa-hidroxicarboxílicos se utilizan extensamente para separar elementos lantánidos y actínidos con ayuda de resinas intercambiadoras de cationes. La sorción de estos elementos puede efectuarse con resinas intercambiadoras de aniones de carácter fuertemente básico. Los autores han estudiado las propiedades de estos sistemas de intercambio de aniones a concentraciones extremadamente bajas, empleando técnicas de elución y de estudio de los equilibrios de distribución. Una de las finalidades perseguidas era medir los factores de separación para poder evaluar en qué medida el intercambio de aniones puede utilizarse como complemento de la separación por intercambio catiónico. Puesto que se ha dedicado poca atención a la caracterización de las especies químicas que aparecen en forma de complejos en estos sistemas de separación, la segunda finalidad de los trabajos realizados por los autores fue tratar de caracterizarlos interpretando los resultados de los ensayos de intercambio aniónico y catiónico.

Los autores han empleado ácidos glicólico, láctico y α-hidroxiisobutírico con Ce, Pm, Eu, Tb, Tm, Y, Cm y Cf como trazadores radiactivos. Tanto la elución como la distribución de equilibrio se llevaron a cabo a 25° C y 87° C.

En los tres casos, los factores de separación son menores para el intercambio de aniones que para el intercambio análogo de cationes. Los mayores factores de separación se obtienen con glicolatos, y los valores del coeficiente de distribución K_d indican que dichos glicolatos constituyen los complejos más estables.

Las curvas de log K_d en función del logaritmo de la concentración aniónica pasan por un máximo y luego su pendiente tiende a —1, lo cual indica la presencia de un complejo aniónico del tipo MX_4^{-}. El estudio electromigratorio del trazador ^{170}Tm en estas soluciones confirma la existencia de este complejo negativo en la solución. Se puede demostrar que a la concentración correspondiente al valor máximo de K_d la especie química que predomina en la solución pertenece al tipo MX_3.

Los autores han calculado los valores aproximados de las sucesivas constantes de estabilidad correspondientes a estos sistemas, y dichos valores les han permitido trazar curvas de las concentraciones relativas de las especies químicas M^{3+}, MX^{2+}, MX_2^{+}, MX_3 y MX_4 en función de la concentración de X^{-}.

1. Introduction

Solutions of alpha-hydroxy carboxylic acids have been used since the Manhattan Project to separate the trivalent ions of the lanthanide and actinide elements by ion exchange techniques. The use in such separations of glycolic, lactic and alpha-hydroxy isobutyric acid with Dowex-50, a strong acid cation-exchange resin, has been studied extensively in recent years [1] [2]. However, no attention has been given to the possibility of using anion-exchange resins with these systems until recently.

If the logarithm of the elution position from a cation-exchange resin column of a trivalent lanthanide or actinide are plotted against the logarithm of the isobutyrate ion concentration, a straight line with a negative slope is obtained whose value is very close to 4 [3]. To understand the implications of this fact, one must consider the possible reactions in this system. The possible reactions in the solution phase are:

$$M^{+3} + B^- = MB^{+2} \qquad \beta_1 = \frac{(MB)}{(M)(B)} \tag{1}$$

$$MB^{+2} + B^- = MB_2^+ \qquad \beta_2 = \frac{(MB_2)}{(M)(B)^2} \tag{2}$$

$$MB_2^+ + B^- = MB_3 \qquad \beta_3 = \frac{(MB_3)}{(M)(B)^3} \tag{3}$$

$$MB_3 + B^- = MB_4^- \qquad \beta_4 = \frac{(MB_4)}{(M)(B)^4} \tag{4}$$

where M = the trivalent lanthanide or actinide ion and
B = the alpha-hydroxy isobutyrate ion.

The possible reactions in the resin (MR) phase are:

$$M^{+3} + 3\,NR = MR_3 + 3\,N^+ \qquad K_1 = \frac{(MR_3)(N)^3}{(M)(NR)^3} \tag{5}$$

$$MB^{+2} + 2\,NR = MBR_2 + 2\,N^+ \qquad K_2 = \frac{(MBR_2)(N)^2}{(MB)(NR)^2} \tag{6}$$

$$MB_2^+ + NR = MB_2R + N^+ \qquad K_3 = \frac{(MB_2R)(N)}{(MB_2)(NR)} \tag{7}$$

The resin-solution distribution coefficient K_d is defined by

$$K_d = \frac{\Sigma\,(M)\,\text{resin}}{\Sigma\,(M)\,\text{solution}} = \frac{(MR_3) + (MBR_2) + (MB_2R)}{(M) + (MB) + (MB_2) + (MB_3) + (MB_4)} \tag{8}$$

(For reasons which will be obvious later, it is assumed that the anionic complex (MB_4^-) is formed.)

When this equation is combined with those given for the resin and solution reaction equilibria, it may be derived that

$$K_d = \frac{K_1(M)(NR)^3/(N)^3 + K_2\beta_1(M)(NR)^2(B)/(N)^2 + K_3\beta_2(M)(NR)(B)^2/(N)}{(M) + \beta_1(M)(B) + \beta_2(M)(B)^2 + \beta_3(M)(B)^3 + \beta_4(M)(B)^4} \tag{9}$$

In these systems N is usually the ammonium ion and the pH is between 4.0 and 4.5. Under this latter condition and provided that M is present only in tracer concentrations, $(N) \simeq (B)$ and equation (9) can be rearranged to

$$K_d = \frac{K_1(NR)^3(B)^{-3} + K_2\beta_1(NR)^2(B)^{-1} + K_3\beta_2(NR)(B)}{1 + \sum_{n=1}^{4} \beta_n (B)^n} \tag{10}$$

Assuming that one species is predominant in each phase, then it is possible to calculate values for the slope $\frac{d \log K_d}{d \log (B)}$ for various combinations of species in the two phases.

From Table I, it is seen that the experimental slope of —4 is predicted by two combinations, MB_3—MB^{+2} and MB^{+2}—M^{+3}. However, the assumption of the predominance of a single species, particularly for the solution phase, does not seem realistic. Also, the insensitivity of a log-log plot makes it possible that a slope of —4 means that mixtures of ions are present in one or both of the two phases. This inability of cation-exchange resin data to give definitive infor-

TABLE I

VALUES OF (d log K_d/d log B) FOR COMBINATIONS OF IONIC SPECIES

Species in the solution phase	Species in the resin phase		
	M^{+3}	MB^{+2}	MB_2^{+1}
M^{+3}	—3	—1	+1
MB^{+2}	—4	—2	0
MB_2^{+}	—5	—3	—1
MB_3	—6	—4	—2
MB_4^{-}	—7	—5	—3

mation about the species in the solution and resin phases led L. W. HOLM, while at the Lawrence Radiation Laboratory, Berkeley, California in 1956, to a preliminary study of these systems with anion-exchange resin (*cf.* reference 21 in reference [2] to this paper). These studies provided evidence of the existence of anionic alpha-hydroxy isobutyrate complexes of several trivalent lanthanides and actinides. More recently, a potentiometric investigation of the stability constants of the glycolate complexes of the lanthanides has furnished evidence of the existence of an anionic complex [4]. A study of the gadolinium-glycolate system with anion resin [5] confirmed the earlier report of such complexes.

2. Experimental

CHEMICALS

Glycolic acid was purified by recrystallization from aqueous solution. Alpha-hydroxy isobutyric acid was obtained commercially as light brown crystals. The crystals were dissolved in water and the solution passed through a bed of hydrogen-form cation-exchange resin (Dowex-50) until a water-clear solution was obtained. Commercial lactic acid often exists partially as a lactone dimer [6]. To convert it completely to the free acid form, an aqueous solution of the lactic acid is neutralized with sodium hydroxide. To regenerate the acid, the solution is passed through a bed of hydrogen-form cation-exchange resin where the sodium ions are replaced by hydrogen ions.

Aqueous solutions of glycolic, lactic and alpha-hydroxy isobutyric acid were adjusted to a pH value within the range of 4.6 to 4.7 by addition of concentrated ammonium hydroxide. Mould growth in these solutions may be inhibited by adding sufficient phenol to make the solution 0.01 *M* in phenol. Without phenol, these solutions may be kept free of mould for periods of more than a month by storage in glass-stoppered bottles. The resin used was Dowex-1 (10% DVB), 200—400 mesh with a capacity of 3.2 meq/g. A fraction with a settling rate in water of 0.25 to 0.50 cm/min was selected for the column elutions. The total resin batch was washed alternately with water and 1, 3 and 9 *M* HCl, then with 3 *M* NaOH and water, and finally with ethyl alcohol and water before use. The resin was converted finally to the desired anionic form (e.g. glycolate etc.) by treatment with a solution of the proper acid. It was washed with distilled water, air-dried and stored for later use in a dessicator over sodium nitrite. Storage over $NaNO_2$

was used because it maintained the relative humidity at 63% at 25°C—approximately equal to the average humidity in our laboratory. This minimized weight changes due to gain or loss of moisture between weighings.

Tracers

The lanthanide tracers used were Ce^{144}, Pm^{147}, Eu^{152}, Eu^{154}, Tb^{160} and Tm^{170}. Na^{22} and Y^{91} were also used. All these tracers were obtained from the Oak Ridge National Laboratory and were counted either by thin-window G-M tubes or by windowless proportional counters. Cm^{244}, Cf^{250} and Cf^{252} were obtained through the generosity of Dr. S.G. Thompson of the Lawrence Radiation Laboratory, University of California. These alpha-emitting nuclides were counted in windowless proportional counters and in an alpha grid chamber connected to a 50-channel pulse-height analyser.

Equilibrium studies

The expression used to determine K_d is

$$K_d = (A_o - A_s)/A_s \times \text{ml solution/g resin} \quad \text{(II)}$$

where A_o and A_s are the activity of the solution phase before and after equilibration with the resin. To minimize the error in K_d, it is desirable to have $(A_o - A_s)/A_s$ as close to unity as possible. Proper selection of the ratio of resin weight to solution volume is necessary in approaching this situation. However, a limiting ratio of 2.0 ml solution/0.5 g resin was found to be experimentally practical for low values of K_d. A sample of resin in the proper anionic form was sealed in a tube with 2 ml of the acid solution (pH 4.6) containing approximately 10^5 counts/min of the tracer ion. The tubes were agitated for 12 hours in a constant temperature bath at 25°C or in an oven at 87°C. Duplicate aliquots of the solution before and after equilibration were prepared and counted to 0.1% probable error. The pH and concentration of the solution were checked after equilibration to allow for correction due to solvent or electrolyte uptake by the resin. Unfortunately, it was not feasible to use solutions of constant ionic strength in these runs, as addition of ClO_4^- etc., would change the chemical composition of the resin phase.

Column elutions

For elutions at 87°C, a jacketed column was used of the type described previously [7]. The resin-bed dimensions varied from 5 to 15 cm in length and 1 to 3 mm in diameter, depending on the value of the K_d for the particular eluting solution. The void volume (free column volume) of the columns was determined by passage of Na^{22} and was found to be very close to 30% of the total geometric volume of the resin bed.

The activities were dissolved in 10 to 25 μl of the eluting solution and transferred to the top of the resin bed. After this volume ran into the resin bed, an additional drop of eluting solution was used to wash all the activity into the resin bed before the bulk of the eluting solution was added to the reservoir above the resin bed. Elution was performed at a flow rate of approximately 0.25 ml/cm² min. The drops from the column were collected individually, evaporated to dryness and counted. Aluminium absorbers were used in counting, when feasible, to resolve overlapping

elution curves. From the volume (V) for the maximum in the elution curve, the free column volume (v) and weight of the resin in the column (w), the K_d could be calculated by

$$K_d = (V - v)/w. \tag{12}$$

The K_d for lactate and isobutyrate were so small that the elutions had to be performed at 87°C, since the K_d values are greater than at 25°C.

ELECTROPHORETIC STUDIES

The apparatus used for the electromigration studies consisted of two polyethylene cups for the solution into which the ends of a paper strip were dipped. A polyethylene bridge was placed midway between the two cups to allow the paper strip to be placed in an inverted V position during the experiment. The cell was covered with a glass jar to minimize evaporation of water from the solution. The paper strip (Whatman No. 1) was placed in position and, after the strip had become saturated with solution, the power supply was turned on. The same current which was to be used in the tracer experiment passed for an hour to ensure that any subsequent ionic movement would not be due to a siphoning effect. Tm^{170} or a combination of Tm^{170} and Na^{22} were placed along a thin line on the paper strip at the apex of the inverted V and the electromigration was carried out for 13 to 33 hours. At the end of the run, the paper strip was dried under a heat lamp and the profile of the band of activity ascertained by counting successive sections of the strip through a slit in a lead shield with a thin-window G-M tube.

3. Results and calculations

The results of the batch equilibrations and column elutions are shown in Figs. 1–4. A typical set of K_d data are shown in Table II to indicate the experimental quantities as well as the average deviation for a set of measurements. The concentration of the glycolate ion in the equilibration experiments was determined by a conductometric titration with a standard solution of HCl. For lactate and isobutyrate, the K_d values were too low to allow accurate measurement by batch equilibration and therefore the points in Figs. 3, 4 and 5 are calculated from column elution data. Fig. 5 shows the data for Cm, Cf, Y, Pm, and Tm obtained by column elution with isobutyrate from anion resin of a different batch. The difference in absolute K_d values is not inconsistent with that observed between different resin batches. It was found difficult to perform successful elutions at concentrations below 0.01 M. Possibly at these low concentrations of the complexing ligand, hydrolysis competes and causes tailing in the elution peaks.

The quantities which define the utility of an ion-exchange column elution in the separation of inorganic ions are the separation factors and the full width of the elution peak at the half-maximum value (i.e. the half-width). The separation factor α between two ions is defined as

$$\alpha_y^x = K_{d(x)}/K_{d(y)}\,. \tag{13}$$

The separation factors may be calculated from the peak maximum of an elution curve by the formula

$$\alpha_y^x = \frac{(\text{elution vol. to max. in curve } x) - (\text{free column vol.})}{(\text{elution vol. to max. in curve } y) - (\text{free column vol.})}.$$

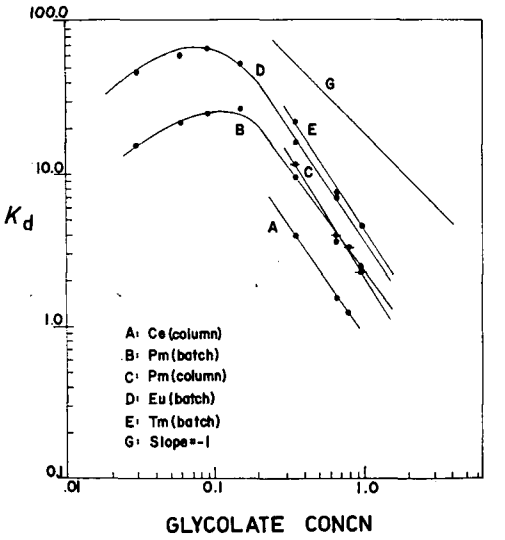

Fig. 1
Log K_d *vs* log glycolate ion concn. for several lanthanide ions at 25° C.

The separation factors determined in this investigation are listed in Table III. The separation factors are sensitive to the anion concentration and only the maximum values are given in Table III; separation factors for cation-resin elutions are listed for comparison. The separation factors are larger for the cation-resin than for the anion-resin elutions. Since the half-widths are also less for the cation-resin columns, Table III indicates that, for these acids, the most effective system

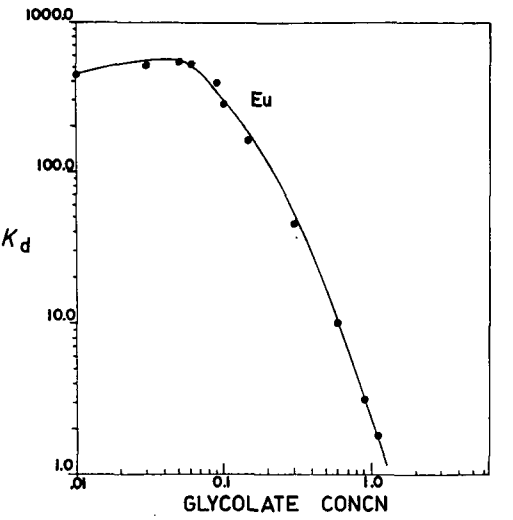

Fig. 2
Log K_d *vs* log glycolate ion concn. for europium at 87° C.

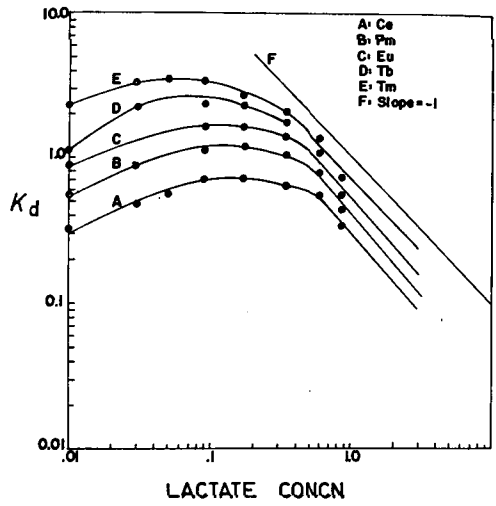

Fig. 3
Log K_d *vs.* log lactate ion concn. for several lanthanide ions at 87° C.

for separation of the lanthanide and actinide elements is that of alpha-hydroxy isobutyrate and cation-exchange resin.

Table IV summarizes the results of the electromigration studies. Na^{22} was included in two runs with lactate solution and Tm^{170} to determine whether the direction of movement of the Tm^{170} was trulg an electromigration effect. Since the Na^{22} moved to the cathode in both cases, whereas the Tm^{170} moved to the cathode in the 0.01 *M* solution and to the anode in the 0.03 *M* solution, it was

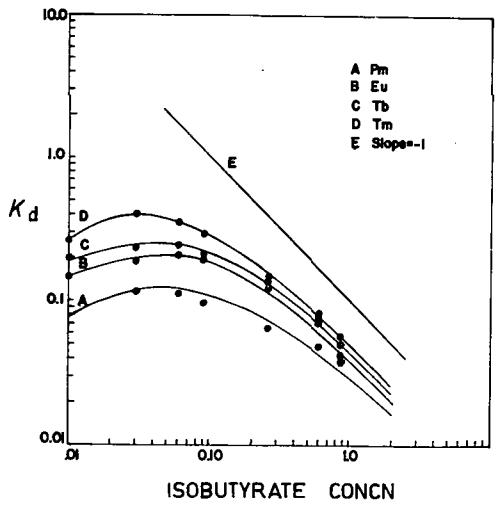

Fig. 4
Log K_d *us,* log isobutyrate ion concn. for several lanthanide ions at 87°C.

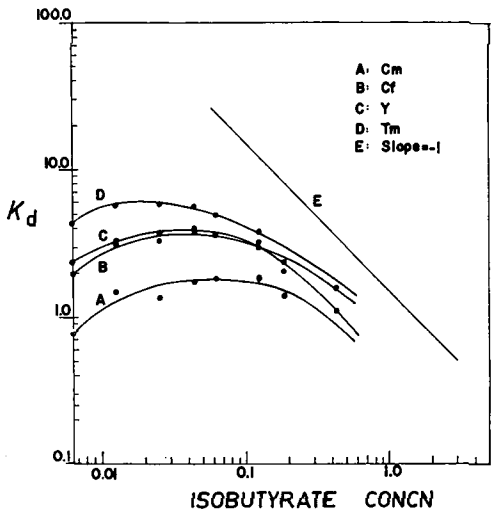

Fig. 5
Log K_d *vs.* log isobutyrate ion concn. for Cm, Cf, Y and Tm at 87°C.

concluded that the movement of thulium was due to electromigration and not to an experimental artifact. These measurements are only semi-quantitative due to the difficulties encountered in maintaining constant and reproducible operating conditions.

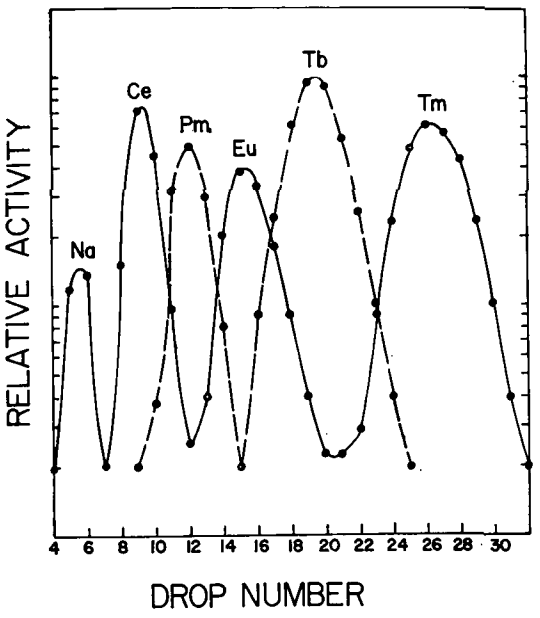

Fig. 6
Typical elution curve. Dowex-1 anion resin, 0.1 *M* ammonium lactate, pH 4.6 at 87°C.

TABLE II

K_d FOR $Eu^{152,154}$ *vs* CONCENTRATION OF GLYCOLATE ION

Concn M	A_o	A_s	Wt. resin (g)	Vol. soln. (ml)	K_d	Average K_d	% Deviation
0.97	16590	8803	0.4858	2.00	3.77	3.59	3.62
	16590	8825	0.4791	2.00	3.67		
	13420	7291	0.4858	2.00	3.46		
	13420	7348	0.4791	2.00	3.45		
0.67	16556	8002	0.3209	2.00	6.66	6.89	1.31
	14160	6680	0.3209	2.00	6.97		
	16556	8371	0.2793	2.00	6.99		
	6003	2977	0.2957	2.00	6.94		
	6003	2765	0.3433	2.00	6.89		
0.36	15674	7740	0.1361	2.00	15.44	16.21	4.75
	15874	7631	0.1271	2.00	16.98		
0.15	15802	4975	0.0883	2.00	49.30	52.45	4.23
	14044	4036	0.0883	2.00	56.18		
	15802	4840	0.0873	2.00	51.86		
	14044	4108	0.0873	2.00	55.39		
	6468	1802	0.0999	2.00	51.83		
	6468	1924	0.0949	2.00	50.14		
0.09	15842	4146	0.0828	2.00	68.17	65.74	3.70
	13984	3825	0.0828	2.00	64.16		
	15842	4570	0.0750	2.00	65.74		
	13984	4260	0.0750	2.00	60.84		
	8163	2258	0.0749	2.00	69.78		
	8163	2090	0.0907	2.00	64.08		
0.06	15191	3930	0.0958	2.00	59.81	60.38	2.21
	13385	3403	0.0958	2.00	59.68		
	15191	4123	0.0899	2.00	60.73		
	13385	3671	0.0899	2.00	58.83		
	6326	1185	0.1466	2.00	59.17		
	6326	1427	0.1072	2.00	64.05		
0.03	16131	3185	0.1684	2.00	48.27	47.18	2.50
	14100	2920	0.1684	2.00	45.76		
	16131	3760	0.1385	2.00	47.51		
	14100	3306	0.1385	2.00	47.25		
	7522	1279	0.2167	2.00	45.48		
	7522	1295	0.1957	2.00	49.13		

TABLE III

SEPARATION FACTORS RELATIVE TO Eu (III) AT 87°C

Element	Eluant	α-anion resin	α-cation resin
Ce	Glycolate	4.25	7.89
Pm	Glycolate	1.50	1.44
Pm	Lactate	1.70	2.00
Tb	Lactate	0.82	0.52
Tm	Lactate	0.77	0.42
Pm	Isobutyrate	1.95	2.93
Tb	Isobutyrate	0.90	0.35
Tm	Isobutyrate	0.91	0.07

TABLE IV

ELECTROMIGRATION DATA
Tm^{170} (III) in glycolate, lactate and α-hydroxy isobutyrate solutions

Concn	Voltage (V)	Current (mA)	Time (h)	Direction of migration	Distance moved (in)
0.50M Gl^-	100	2	23	anode	2.0
0.10M Gl^-	200	2	20	anode	1.9
0.05M Gl^-	200	1	22	anode	1.1
0.03M Gl^-	200	0.5	33	anode	0.2
0.01M Gl^-	200	0.5	12	cathode	2.1
0.10M B^-	200	1	23	anode	1.3
0.05M B^-	200	0.8	20	anode	1.3
0.03M B^-	200	0.5	28	anode	1.0
0.01M B^-	200	0.3	36	cathode	0.5
1.00M L^-	100	3	14	anode	1.1
0.10M L^-	200	2	23	anode	1.2
0.03M L^-	400	1	24	anode	0.9
0.01M L^-	*450*	*0.5*	*13*	*cathode*	*2.0*
Na^{22} in lactate solutions (run with Tm^{170})					
0.03M L^-	400	1	24	cathode	3.0
0.01M L^-	450	0.5	13	cathode	1.6

Discussion

The general anion-exchange reaction in the resin phase for the trivalent metal ions may be expressed by:

$$MB_n^{(3-n)} + (m-3)\,RB = R_{(m-3)}\,MB_m + (n-3)\,B^- \qquad (14)$$

This equation is valid for $n \geq 0$ and $m \geq 4$; i.e. for any complex in the solution phase and any negative complex in the resin phase. The exchange equilibrium constant is then

$$K_{ex.} = (R_{(m-3)}\,MB_m)\,(B)^{(n-3)}/(MB_n)\,(RB)^{(m-3)}. \qquad (15)$$

Since $(MB_n) = \beta_n (M)(B)^n$,

it follows that

$$(R_{(m-3)}MB_m) = K_{ex.}(RB)^{(m-3)}\beta_n(M)(B)^3 = \text{const}\,(B)^3$$
$$\therefore (M)_{resin} = \text{const}\,(B)^3. \tag{16}$$

Therefore:

$$K_d = \frac{\sum (M)_{resin}}{\sum (M)_{solution}} = \frac{\text{const}\,(B)^3}{1 + \sum_{n=1}^{m} \beta_n (B)^n}$$

and

$$\frac{d \log K_d}{d \log (B)} = \sum_{n=0}^{m} (3 - n), \tag{17}$$

provided that the complex with n ligands predominates in solution. The importance of this relation is seen in Table V.

TABLE V

VALUES OF (d log K_d/d log B) FOR ANION EXCHANGE*

Predomination ion in solution	M^{+3}	MB^{+2}	MB_2^+	MB_3	MB_4^-	MB_5^-	etc.
Value of [d log K_d/d log (B)]	+3	+2	+1	0	−1	−2	etc.

* This value is independent of the charge of the negative ion in the resin phase.

From the plots of log K_d against log (B) curves for glycolate, lactate and isobutyrate, it is seen that the slopes at higher concentrations approach or exceed a value of—1. This implies that at ligand concentrations above 0.2–0.5 M, at least a uninegative complex ion is the predominant species in solution. It would seem that the possibility of MB_5^{-2} can be ruled out by consideration of the steric factors hindering the formation of such a large complex. Also, the deviation of the slopes from unity are not surprising when it is recalled that in this experimental analysis, activity coefficients in both the solution and the resin phase have been neglected, very probably a serious omission for such a wide range in ionic strengths.

Let us assume, then, that the anion-exchange reaction is

$$MB_4^- + RB = RMB_4 + B^- \qquad K_4 = (RMB_4)(B)/(MB_4)(RB) \tag{18}$$

The K_d expression, assuming all possible species in the solution phase, is

$$K_d = (RMB_4)/(M^{+3}) + (MB^{+2}) + (MB_2^+) + (MB_3) + (MB_4^-). \tag{19}$$

By a derivation analogous to that used in the introduction, the expression for K_d becomes

$$K_d = \frac{K_4 \beta_4 (RB)(B)^3}{1 + \sum_{n=1}^{4} \beta_n (B)^n} \tag{20}$$

To consider the significance of the maximum in the K_d *versus* (B^-) curve, it is necessary to set the derivative $dK_d/d(B)$ equal to 0.

$$\frac{dK_d}{d(B)} = K_4\beta_4(RB)\frac{3(B)^2\left[1+\sum_{n=1}^{4}\beta_n(B)^n\right]-B^3\sum_{n=1}^{4}n\beta_n(B)^{n-1}}{\left[1+\sum_{n=1}^{4}\beta_n(B)^n\right]^2} \tag{21}$$

For $\frac{dK_d}{d(B)}=0$, two cases are possible:

(i) $(B)=0$; without interest in this system.

(ii)
$$3\left[1+\sum_{n=1}^{4}\beta_n(B)^n\right]-\sum_{n=1}^{4}n\beta_n(B)^n=0$$

$$\therefore \sum_{n=1}^{4}n\beta_n(B)^n/1+\sum_{n=1}^{4}\beta_n(B)^n=3 \tag{22}$$

FRONAEUS [8] has shown that this is the value of the average ligand number n of the complex at the concentration of B which corresponds to the maximum in K_d. Therefore, the positions of the maxima in the curves of Figs. 1—5 indicate the concentration of acid anion for which the average complex composition is MB_3. For Tm^{170} it was found that this condition is attained at 87° C at a lactate concentration of 0.05 M; below this concentration ($n<3$) there should be a net positive charge for the mixture of complexes, while above it ($n>3$) a net negative charge should exist. The electromigration results for this system confirm this, as the movement *was towards the cathode at 0.01 M lactate and towards the anode for concentrations* of 0.03 M and above. Since the electromigrations were performed at 25° C and the column elutions at 87° C, the agreement would seem to be acceptable.

From the results of the slope analysis of the anion resin and of the electromigration studies, it would seem probable that the predominant species in the solution phase for anion concentrations above 0.1 M is MB_4^-. Recently, the europium isobutyrate system has been studied with cation-exchange resin [9] and the conclusion drawn was that the predominant species was EuB^{+2} in the resin phase. This is in good agreement with our conclusions. For the promethium-isobutyrate system with the cation resin, the slope is between 4 and 5 for a log K_d against log (B) plot in the isobutyrate concentration range of 0.15 to 0.3 M. From Table I it is seen that for MB^{+2} in the resin phase, this slope implies a mixture of MB_3 and MB_4 in the solution phase.

The fact that the K_d values for the glycolate complexes are quite a bit larger than those for the lactate and isobutyrate complexes may be interpreted to mean that the larger size of the latter two anions gives rise to a steric hindrance effect. If this is correct, then it would not seem illogical to suggest that the predominant

resin-phase reaction is $MB_3 + RB = RMB_4$, rather than that in equation (18). The smaller, neutral species MB_3 would be expected to have a higher diffusion coefficient in the resin phase. This steric effect would be independent of the anion concentration, so reaction (18) would not be favoured, even at concentrations where the concentration of MB_4^- is considerably greater than that of MB_3. It must be stressed that this is conjecture since, as discussed previously, it is not possible to offer proof from this study.

It may be seen from Figs. 1—5 that the separation factors decrease as the concentration of acid anion increases beyond that for the maximum values in K_d. In high concentrations, all the ions exist as MB_4^-. At lower concentrations, where a mixture of MB_2^+, MB_3 and MB_4^- exists for each metal ion, larger separation factors will result from the difference in relative amounts of these species for each metal ion. In other words, at high concentrations, the separation factors will be functions only of the K_{ex} values (15); i.e. of the affinities of the MB_4^- species to the resin, whereas, at lower concentrations, the different complex constants will be important. Since the affinities of the large complex ions to the resin are presumably about the same for different central metal atoms, small separation factors are obtained at high concentrations.

In systems such as these in which the ionic strength changes by 2 orders of magnitude, stability constants calculated by any technique will be only approximations of meaningful values. However, since there are no data on these systems at the elevated temperatures which are commonly used in separations by column elution, constants have been calculated by the "two parameter" method [10]. This technique provides one constant and the ratio (which is assumed to be constant) between successive constants. Although the results of such a calculation are probably only valid to within a factor of 4, the technique is in line with the validity of any calculations based on systems of varying ionic strength. The results are listed in Table VI.

TABLE VI

STABILITY CONSTANTS

	Eu — 87°C		Nd — 25°C $\mu = 0.1$ M [11]	
	Glycolate	*Lactate*	*Isobutyrate*	*Glycolate*
K_1	2000	4500	3600	2500
K_2	300	800	1100	200
K_3	50	150	300	25
K_4	10	25	90	—

Finally, it would seem interesting to discuss the MB_4^- species. It is possible that these bidentate alpha-hydroxy carboxylic-acid anions could under some circumstances ionize their hydroxyl proton upon complex formation. It would be possible to have MB_2^-, and MB_3^- by this mechanism. However, the stability constants for the glycolate [4], the lactate [12] and the isobutyrate [12] complexes of the lanthanides are consistent with the assumption that tetraglycolate, etc. complexes exist and that the ligands are all functioning as chelate ligands. The consequence of this is that these complexes may represent trivalent ions with a co-ordination number of 8. Unfortunately, preliminary attempts to isolate a pure salt of this anionic complex have not been successful.

ACKNOWLEDGEMENTS

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DISCUSSION

R. Lindner (Sweden) asked Mr. Choppin if it was possible to obtain some indication concerning the rate of exchange between the species predominant in the solution and those predominant in the resin.

G. R. Choppin said he had no data on that, but, as the complexes were extremely labile, the times involved would be very short.

R. Lindner asked if it were possible that the larger half-width of the elution peak for the anion resins be due to slower diffusion in the resin.

G. R. Choppin said that was probably the explanation. Since the K_d values were lower for lactate than for glycolate and still lower for isobutyrate, this was interpreted to be indicative of a steric effect due to the larger size of the complexes as the number of methyl groups increased. If this were correct, the diffusion in the resin would also be an important factor and suggested that the exchange mechanism might be: $MB_3 + RB = RMB_4$, due to the higher diffusion coefficients of MB_3 with respect to MB_4^-.

A. H. W. Aten, Jr. (Netherlands) asked if the speaker had any information concerning the separation of samarium and europium on an anion resin. The separation of these two elements was extremely difficult when using the ordinary cation-resin method.

G. R. Choppin replied that unfortunately he had not studied the behaviour of samarium on anion resin. However, it would seem very unlikely that the separation factor would be as satisfactory as for cation resin elution.

T. Schönfeld (Austria) asked Mr. Choppin if he could estimate from the data given what percentage of the tracer was in the MB_4^- form at the highest concentration used.

G. R. Choppin replied that at those the concentrations at which the estimated stability constants were most reliable, i.e., 0.1 — 0.3 M, he estimated that the lanthanide atoms were 70 — 80% in the MB_4^- form and 30 — 20% in the MB_3 form, with a very small proportion (1 — 3%) in the MB_2^+ form.

T. Schönfeld remarked that Fig. 5 of the paper (isobutyrate system) showed an intersection of the curves for yttrium and californium. He asked whether it was in fact certain that the curves crossed each other and, if so, whether Mr. Choppin could give a physical explanation for this.

G. R. Choppin said that the data in Fig. 5 were not highly accurate and no particular significance should therefore be attached to the behaviour of the curves as indicated.

THE RATES AND ORDERS OF ELECTRON EXCHANGE REACTIONS IN MIXED SOLVENTS USING TRACER TECHNIQUES

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Abstract — Résumé — Аннотация — Resumen

The rates and orders of electron exchange reactions in mixed solvents using tracer techniques. Very interesting results on the rate and mechanism of the electron exchange reaction between U (IV) and U (VI) in hydrochloric acid solutions involving pure and mixed solvents have been obtained using uranium-233 as a tracer.

Ions, similar to the complex species postulated to explain the kinetics, were proved to exist spectrophotometrically, and similar ions were postulated to explain transference data in the case of uranyl chloride. The stability as a function of the solvent composition of the UO_2X^+ type of ion was found to be parallel, in a remarkable way, with the logarithm of the specific velocity constant of the electron exchange reaction as a function of the solvent composition in the water-ethanol solvent system. If the data on ion complex stability to the kinetic situation are extrapolated, it would appear that the effect of the solvent on the stability of the UO_2X^+ complex is a principal factor in the influence of the solvent on the rate of the electron exchange reaction between U (IV) and U (VI) ions.

Etude, au moyen d'indicateurs radioactifs, des vitesses et ordres des réactions d'échange électronique dans les solvants mixtes. En utilisant comme indicateur l'uranium-233, on a pu obtenir des renseignements très intéressants sur la vitesse et le mécanisme de la réaction d'échange électronique entre l'U (IV) et l'U (VI) dans de l'acide chlorhydrique en solution dans des solvants purs ou mixtes.

L'analyse spectrophométrique a montré l'existence d'ions semblables aux espèces complexes qui sont censées expliquer les caractéristiques cinétiques; on a admis la présence d'ions analogues pour expliquer les données relatives au transfert dans le cas du chlorure d'uranyle. On a constaté qu'il existait un parallélisme remarquable entre la stabilité de l'ion du type UO_2X^+, en fonction de la composition du solvant, et le logarithme de la constante de vitesse spécifique de la réaction d'échange électronique dans le système eau-éthanol, en fonction de la composition du solvant. En extrapolant les données obtenues sur la stabilité de l'ion complexe pour tenir compte des données cinétiques, on constate que l'effet du solvant sur la stabilité du complexe UO_2X^+ est un facteur primordial en ce qui concerne l'influence du solvant sur la vitesse de la réaction d'échange électronique entre les ions U (IV) et U (VI).

Определение скорости и порядка реакций электронного обмена в смешанных растворителях методом индикаторов. Использование в качестве индикатора урана-233 позволило получить очень интересные результаты относительно скорости и механизма реакций электронного обмена между U (IV) и U (VI) в растворах соляной кислоты с чистыми и смешанными растворителями.

При помощи спектрофотометрии было доказано наличие ионов, аналогичных тем комплексным видам, которые теоретически объясняют кинетические свойства; аналогичные ионы предположительно объясняют данные о числах переноса для хлористого уранила. Было установлено, что кривая устойчивости в функции от ионов типа UO_2X^+ в составе растворителя проходит строго параллельно кривой логарифма постоянной удельной

скорости реакции электронного обмена в функции от состава растворителя в системе растворителя вода-этанол. Экстраполяция данных устойчивости сложных ионов в зависимости от кинетического состояния указывает, что воздействие растворителя на устойчивость сложного соединения UO_2X^+ является главным фактором влияния растворителя на скорость реакции электронного обмена между ионами U (IV) и U (VI).

Determinación con ayuda de trazadores de la velocidad y del orden de las reacciones de intercambio electrónico en mezclas de solventes. Con ayuda del uranio-233 como trazador, el autor ha obtenido resultados de sumo interés para la determinación de la velocidad y del mecanismo de la reacción de intercambio electrónico entre el U(IV) y el U(VI) en solución clorhídrica en disolventes puros o mezclados.

El autor demostró por métodos espectrofotométricos la existencia de iones similares a las especies complejas que fueron propuestas para justificar la cinética, y postula la existencia de iones similares para explicar los datos de transferencia en el caso del cloruro de uranilo. Encontró que la estabilidad de los iones del tipo UO_2X^+ en función de la composición del disolvente guarda un estrecho paralelismo con el logaritmo de la constante de velocidad específica de la reacción de intercambio electrónico, en el sistema agua-metanol, como función de la composición del disolvente. Al extrapolar los valores de la estabilidad del ion complejo, se comprueba que el efecto del disolvente sobre la estabilidad del complejo UO_2X^+ es un factor primordial de la influencia que el disolvente ejerce sobre la velocidad de la reacción de intercambio electrónico entre los iones U (IV) y U (VI).

Introduction

Rona [1] has studied the electron exchange reaction between U (IV) and U (VI) chlorides in water solution as a function of U (IV), U (VI), hydrogen ion, and neutral salt concentrations. No salt effect on the reaction was found.

The Np (V)-Np (VI) reaction has been studied in water, water-glycol, and water-sucrose solvents using Np^{239} as a tracer [2]. The reaction was found to be independent of the physical properties of the mixed solvents used.

The study of the U (IV)-U (VI) reaction in mixed solvents was undertaken to acertain whether this reaction is also independent of the physical properties of the solvent.

Comments on experimental details

The tracer solution provided by the Oak Ridge National Laboratories was a citrate-nitrate mixture of U^{233} containing about 0.05 g of uranium per 15 ml of aqueous solution.

The U (IV) was separated from the U (VI) by precipitating the former with cupferron or with hydrofluoric acid.

Tank nitrogen, 99.7% pure, presaturated with solvent of the same composition as that in the run was used as an inert atmosphere above the run.

After precipitating the U (IV) from a sample taken from the run, a 50-lambda portion of the U (VI) solution was spotted on a platinum disc, diam. 1 in, evaporated to dryness under a heat lamp, heated to redness over a Fisher burner and, after cooling, was counted in a Nuclear-Chicago-type gas-flow counter to a standard deviation of 1%. The procedure was done in triplicate on each sample and averaged to obtain each point on the rate plots. The clean platinum discs were counted before spotting and this background count was subtracted from the count after spotting.

In the case of precipitation of the U (IV) with HF, the precipitate was washed with dilute HF, dissolved in a few drops of conc. nitric acid, and dried in an

oven. To the dry material, 1 ml of 6% HNO_3 was added, and 50λ of the resulting solution was spotted on platinum planchettes, dried, ignited and counted. A sample of the U (VI) solution was made as described above. Usually the half-lives calculated from U (IV) and U (VI) were in good agreement (within 10%) and the average was taken.

The Hittorf method was used in the determination of transference. An inert reference substance in a Hittorf transference measurement, as first proposed by NERNST [3], was used to determine solvation numbers of ions. A Rudolph and Sons, Model 80, high-precision polarimeter was used in conjunction with a photoelectric device developed in these laboratories for measuring angles of rotation to within ± 0.002 circular degrees.

In the case of alcohol containing solvents, each compartment was analysed for per cent ethanol by density measurements [4].

Complex ions were studied spectrophotometrically using the method of continuous variations discussed by VOSBURGH *et al.* [5]. Absorption values were measured using a Beckman DU Quartz Spectrophotometer.

Data and discussion

The reaction rates, R, were calculated using the equation

$$R = \frac{ab}{a+b}\,\frac{0.693}{t_{1/2}} \tag{1}$$

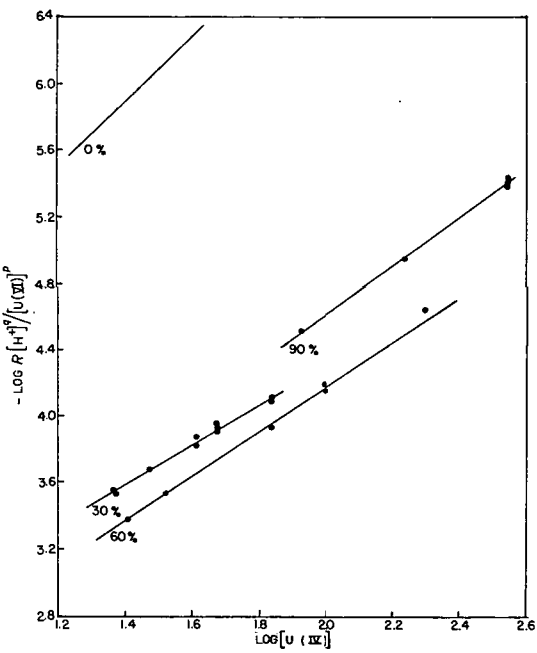

Fig. 1

Plots of—$\log \frac{R\,[H^+]^q}{[U(VI)]^p}$ *versus*—log [U (IV)] used in the determination of the order, r, of the reaction with respect to U (IV).

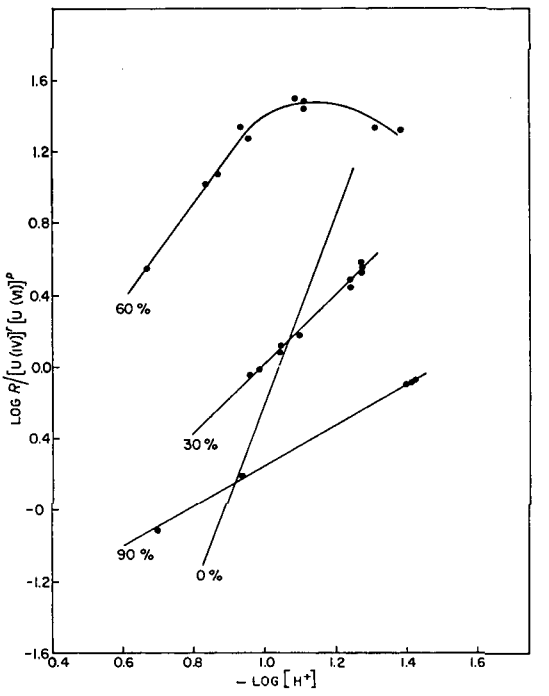

Fig. 2

Plots of $\log \frac{R}{[\mathrm{U\,(IV)}]^r[\mathrm{U\,(VI)}]^p}$ versus $-\log\,[\mathrm{H^+}]$ used in the determination of the order, q, of the reaction with respect to $[\mathrm{H^+}]$.

In this equation a and b are the concentrations of U (IV) and U (VI) in the system and $t_{1/2}$ is the half-life. Since a and b are known for a particular run, it is only necessary to determine $t_{1/2}$ in order to be able to calculate R.

Plots of log counts/min *versus* time in min were made, and from these plots the count rate at equilibrium was determined for each run. For each run the count-rate at equilibrium was subtracted from the count-rate at various times. The logarithms of these differences were plotted against time. This plot was extrapolated to zero time, and this added to the equilibrium value of the count rate to give the zero-time count-rate, whilst the half-life was determined by reading the time at which the count-rate was half that at zero time.

To find the order of a given substance in the reaction rate, the usual procedure of plotting log R *versus* log concn was used. The slope of this line is the order of the reaction with respect to the material which varied in concentration. Fig. 1 shows the plot used to obtain the order with respect to U (IV) of the U (IV)—U (VI) reaction in water and water-acetone solvents at 25° C. Such plots were made and the orders determined for each reactant in each solvent. In 60 vol.% acetone solvent, the order with respect to hydrogen ion shows an unexpected inflection in the region of dilute acid, indicating that the coefficient for the dependence of the rate on hydrogen ion concentration changes in sign from negative to positive below acid concentrations of 0.1 M (see Fig. 2). Since there was insufficient data in this region of acid concentration, the order, with respect to hydrogen ion, was not obtained

and the specific velocity constants were not therefore calculated. Lower acid concentrations in this solvent would have been investigated, except that the solutions proved unstable at lower acidities and hydrolysed complexes of uranium precipitated. The order with respect to acid in each of the other solvents was consistently constant over the whole range of acid studied [6].

The orders of the reaction with respect to U (IV), U (VI), and hydrochloric acid are presented in Table I at various solvent compositions. From Table I, the orders seem to have a marked dependence on the nature and composition of the solvent.

TABLE I

ORDERS OF THE VARIOUS REACTANTS IN THE DIFFERENT SOLVENTS

% Acetone	U (IV)	U (VI)	Hydrochloric acid
0	2.0	1.0	—3.0
30	1.25	1.0	—1.85
60	1.33	1.13	—2.85 (above 0.1M concn)
90	1.47	0.59	—1.17
% Ethanol	**U (IV)**	**U (VI)**	**Hydrochloric acid**
0	2.0	1.0	—3.0
30	0.93	1.11	—1.74
60	0.87	1.08	—0.97
90	2.89	0.10	—1.06
100	0.0	2.70	—1.26

Between zero and 90 vol. % acetone, the order of the reaction with respect to U (IV) first decreases with added acetone and reaches a minimum at approx. 40 vol. % acetone of about 1.22, then with further addition of acetone, the order with respect to U (IV) again increases and becomes about 1.50 at 90 vol. % acetone, which was as far as the data extended. The general shape of the curve is similar to that for the order with respect to U (IV) for the same reaction in ethanol-water solvents [7]. In the latter case, the minimum was lower by about 0.40 and was reached at about 50 vol. % ethanol. Also in the latter case, the decrease in the order was more rapid and the increase more abrupt with added alcohol, the value at 90 vol. % being 2.89. Since the water-acetone data extended to only 90 vol. %, it was not possible to know whether there was the abrupt decrease in order with respect to U (IV) in pure acetone compared to the 90 vol. % acetone, as was found for pure ethanol compared to 90 vol. % ethanol.

It might be mentioned that the runs in 100% acetone were not made, since pure acetone, at the acidities used in the runs, polymerized rather rapidly. It was thought that this change in the nature of the solvent might affect the electron-exchange reaction rate in a manner different from that of the other solvent factors. In water-dilute acetone, the polymerization was slower and the exchange reaction rate could be determined before extensive polymerization occurred.

In the case of the order with respect to U (VI) the shape of the curve out to 90 vol. % acetone closely resembles the curve found for the U (VI) order out to 90 vol. % alcohol. In both cases there is first a slight increase in the order

out to about 60 vol. % organic component of the solvent, and then a more precipitous decrease of the order out to 90 vol. % of the organic component. In the case of water-acetone, the order dips to 0.59 at 90 vol. % acetone, while, in the case of water-ethanol solvent, the order drops to 0.10 at 90 vol. % ethanol. In the case of acetone there is no way of knowing whether there is an abrupt rise of order beyond 90 vol. % acetone as there is beyond 90 vol. % ethanol.

It is the order of the reaction with respect to hydrochloric acid in water-acetone which contrasts sharply with that in water-ethanol, especially at the 60 vol. % component of the solvent. In the 60 vol. % acetone solvent there is the curious hook in the log R *versus* — log C curve for hydrochloric acid. Also, as the acetone component of the solvent increases there is a maximum in the order with respect to hydrochloric acid at about 30 vol. % acetone, a minimum at about 60 vol. %, and then an increase out to 90 vol. % which is as far as the data go. In the case of water-ethanol solvent, the order with respect to hydrochloric acid at first increases with increasing vol.% ethanol, reaches a maximum at about 70 vol.%, and then gradually decreases out to pure ethanol. Graphical representations of the orders as a function of solvent composition are shown in Figs. 3 and 4.

If it is assumed that the reacting species in water solutions are UOH^{+3} and UO_2OH^+, the orders in water, including a minus third order of hydrochloric acid, can be explained. The orders in some of the mixed solvents can also be

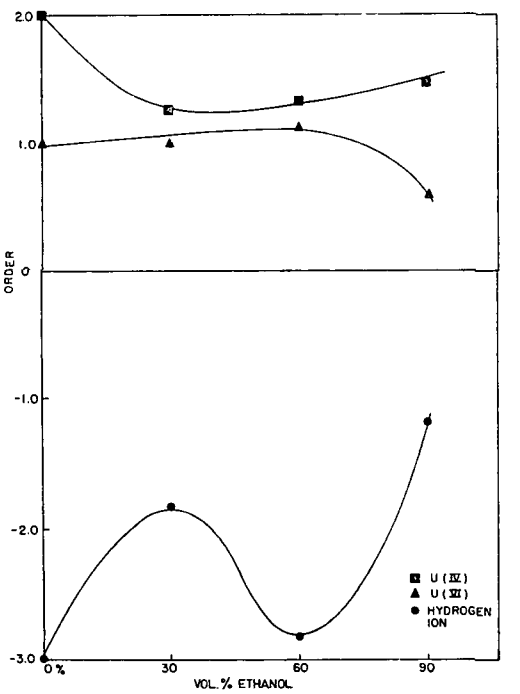

Fig. 3
Orders of the various reactants *versus* volume per cent ethanol.

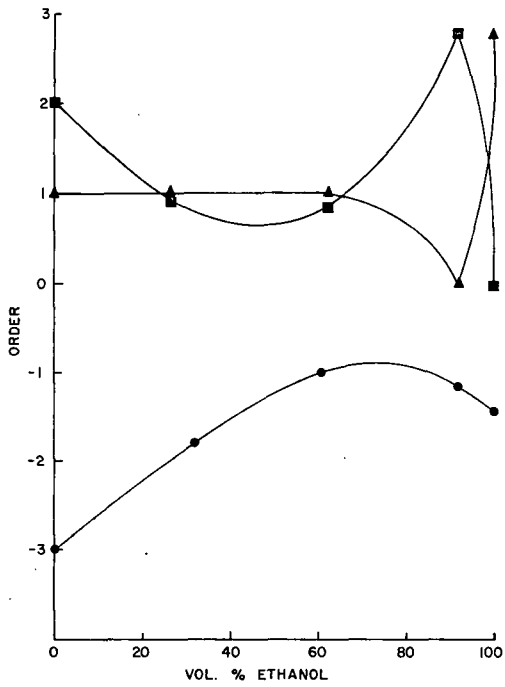

Fig. 4
Order of the various reactants *versus* the volume per cent ethanol:
● = acid; ▲ = U (VI); ■ = U (IV).

explained [7]. The equilibrium constants K_1 and K_2 for the formation of the above hydrolysed species can be written, respectively,

$$K_1 = [UOH^{+3}]\,[H^+]/[U^{+4}] \tag{2}$$

and

$$K_2 = [UO_2OH^+]\,[H^+]/[UO_2^{++}]. \tag{3}$$

The equilibrium constant K_1 is reported to be 3.4×10^{-2} [8] and the equilibrium constant K_2 to be 1.3×10^{-5} [7]. The concentracions of the hydrolysed species UOH^{+3} and UO_2OH^+ can be evaluated as follows:

$$[UOH^{+3}] = K_1\,[U^{+4}]/[H^+] = (K_1/[H^+]) \times ([U(IV)] - [UOH^{+3}]) = \\ = \frac{K_1\,[U(IV)]}{[H^+]\,(1 + K_1/[H^+])}\,. \tag{4}$$

Likewise

$$[UO_2OH^+] = \frac{K_2\,[UO_2^{++}]}{[H^+]} = \frac{K_2}{[H^+]}\,([U(VI)] - [UO_2OH^+]) = \frac{[U(VI)]}{\left[\frac{[H^+]}{K_2} + 1\right]}\,. \tag{5}$$

If the rate of reaction is expressed as

$$\frac{dx}{dt} = k'\,[UOH^{+3}]^2\,[UO_2OH^+] = k'\,\frac{[U(IV)]^2\,[U(VI)]}{\left[\frac{[H^+]}{K_1} + 1\right]^2 \left[\frac{[H^+]}{K_2} + 1\right]}\,, \tag{6}$$

the rate would have a second-order dependence on [U (IV)] and a first-order dependence on [U (VI)], as was found by RONA [1] for aqueous solutions.

For the limiting case $[H^+]/K_1 > 1$ and $[H^+]/K_2 > 1$, the reaction would be minus third order with respect to $[H^+]$, as was again observed by Rona [1]. If $[H^+]/K_1$ became less than 1 while $[H^+]/K_2$ remained greater than 1, the order of the reaction could become —1 with respect to $[H^+]$. This is approximately the case for solvents 60 vol.% or richer in ethanol.

Writing the rate expression for the electron exchange reaction as

$$\frac{dx}{dt} = k'' [UOH^{+3}] [UO_2OH^+] = k'' \frac{[U(IV)] [U(VI)]}{[([H^+]/K_1) + 1] [([H^+]/K_2) + 1]} \qquad (7)$$

the reaction would be first order with respect to both [U (IV)] and [U (VI)] and, in the case of the limiting conditions $[H^+]/K_1 > 1$ and $[H^+]/K_2 > 1$, minus second order with respect to hydrochloric acid concentracion. This was approximately the case for both 30 vol.% ethanol and 30 vol.% acetone. Under certain limiting conditions, the order of the reaction could become —1 with respect to hydrochloric acid, as in 60 vol.% ethanol.

To explain the orders found in 60 vol.% acetone, the hydrolysed species $U(OH)_2^{++}$ and UO_2OH^+ have to be postulated and the kinetic expression written as

$$\frac{dx}{dt} = k''' [U(OH)_2^{++}] [UO_2OH^+] = k''' \frac{[U(IV)] [U(VI)]}{[([H^+]^2/K_3) + 1] [([H^+]/K_2) + 1]} \qquad (8)$$

In the limit $[H^+]^2/K_3 > 1$ and $[H^+]/K_2 > 1$ the reaction would approach an inverse third order dependence on $[H^+]$ and at the same time would be first order with respect to both [U (IV)] and [U (VI)]. These approximate the orders found in 60 vol.% acetone.

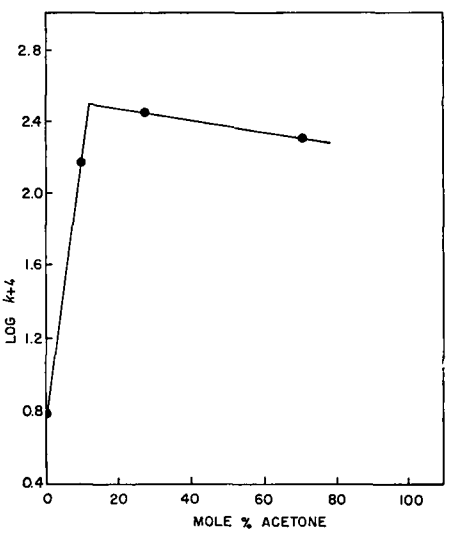

Fig. 5
Logarithm of the specific velocity constant *versus* the mole per cent acetone in the solvent.

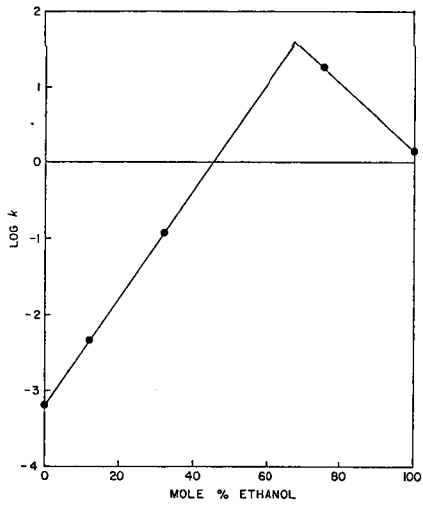

Fig. 6
Logarithm of the specific velocity constant *versus* the mole per cent ethanol in the solvent.

For 90 and 100 vol.% of organic components of the solvents, yet other complexes and kinetic rate expressions would have to be postulated.

Thus it would appear that the mechanism of the exchange reaction changes with the solvent.

While it is not justifiable to average the specific velocity constants for a given solvent when the concentrations of highly charged ions and acid vary so widely, and while it is not justifiable to compare the average of the constants in the different solvents, since the orders change so drastically, yet a rough idea of the marked effect of the solvent upon the reaction rate constants can be demonstrated by plotting the logarithms of the average of the constants in the different solvents against the mole % organic component of the solvent. Such plots, the segments of which are assumed to be straight lines, are presented in Fig. 5 and Fig. 6.

The angles between the segments of the curves in both solvent systems are approximately 90°. However, the maximum in the water-acetone solvent system occurs at 10—15 mole % acetone, while the maximum in the water-ethanol system occurs at 60—70 mole % ethanol.

The precision of the kinetic data was calculated to be between 5 and 7%. Our care in weighing, volume measurements, counting, and analytical procedures was such that we feel our accuracy to have been well within the limits of our precision.

To test whether the near-zero orders found in some instances arose from wall or light effects, runs were made with crushed glass inside the glass reaction flask and identical runs without the crushed glass in the flask. Also, runs were made in vessels with the outside wall painted black and wrapped in aluminium foil and identical runs in vessels unpainted and unwrapped. No wall or light effect was found [9].

The activation energy for the reaction was also measured [9]. The rate data fit the equation

$$\log R = A - \frac{B}{T}. \tag{9}$$

The temperature coefficient data are recorded in Table II. In general, the increase in rate with increasing alcohol concentrations can be correlated with the decrease

TABLE II

ACTIVATION ENERGY OF THE REACTION U (IV) → U (VI) AS A FUNCTION OF THE ALCOHOL CONCENTRATION

Alcohol Concn (Vol. %)	A	B	ΔE (kcal)
0	—	—	33.4
30	16.21	6032	27.6
60	15.32	5741	26.3
90	12.07	5047	23.1
100	6.41	3141	14.4

in activation energy. The dependence of activation energy on alcohol concentration is rather similar to that found for the conductivity of UO_2Cl_2 in the water-alcohol system [10].

A spectrophotometric study [11] of the complexes formed by uranyl and chloride ions in water and water-ethanol solvents reveals that in water at 25° C the UO_2Cl^+ ion exists in dilute solutions and the UO_2Cl^+, UO_2Cl_2 and $UO_2Cl_3^-$ complexes exist in solutions 0.237 to 1.58 M in uranyl ion. With 30, 60 and 90 vol. % ethanol

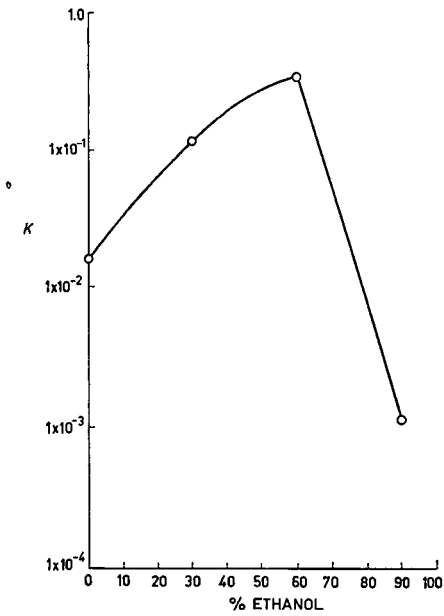

Fig. 7
Equilibrium constants of $[UO_2Cl]^+$.

in the solvent, UO_2Cl^+ ion was found. The dissociation constant, K, for the UO_2Cl^+ ion in water and in 30, 60 and 90 vol.% ethanol was found to be 2.28×10^{-2}, 1.65×10^{-1}, 5.10×10^{-1}, and 1.47×10^{-3} respectively.

A plot of log K *versus* % ethanol is shown in Fig. 7. It is observable that the dependence of log K on the amount of ethanol in the solvent resembles the dependence of the logarithm of the specific velocity constant, for the U (IV)—U (VI) electron exchange reaction, on the amount of ethanol in the solvent. The maxima in the two curves fall at almost the same vol.% in the solvent. If the data on the UO_2Cl^+ complex can be extrapolated to the UO_2OH^+ ion in the kinetic situation, it would appear that the effect of the solvent on the stability of the UO_2X^+ ion is a principal factor in the influence of the solvent on the rate of the electron exchange reaction between U (IV) and U (VI) ions.

In Table III data are recorded for the equilibrium constant and free energy of dissociation at 25°C of the UO_2Cl^+ complex in water and water-ethanol solvents.

TABLE III

EQUILIBRIUM CONST AND FREE ENERGY OF DISSOCIATION AT 25°C OF THE UO_2Cl^+ COMPLEX IN VARIOUS SOLVENTS

Vol. % ethanol	pH	Molarity* of $HClO_4$	Ionic strength	$K \times 10^{-3}$	ΔF deg (cal/mole)
0	0.50	—	1.238	22.8	2240
30	—	0.1411	1.238	165.	1070
60	—	0.1411	1.238	510.	400
90	—	0.0088	0.078	1.47	3880

* In alcohol containing solvents the molarity of the acid rather than the pH of the solution is given.

Similar ions to those found spectrophotometrically, i.e., UO_2Cl^+ and $UO_2Cl_3^-$. were postulated to explain transference data in the case of uranyl chloride [4], In Fig. 8 the transference number of chloride ion in uranyl chloride in water at 25°C is plotted against wt.% uranyl chloride. The transference number

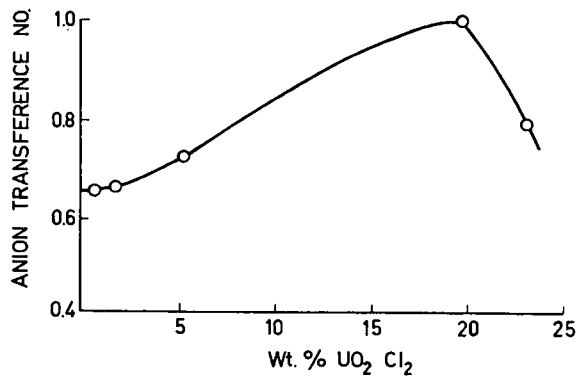

Fig. 8
Anion transference number of uranyl chloride in water solution plotted against concentration.

of the anion would extrapolate to about 0.64 at zero salt concentration This would *give a transference number for the cation of* 0.36. The *transference number* of the anion increases with wt. % UO_2Cl_2 out to 19.5 wt. % where the transference number reaches a maximum of unity. This indicates complex ion formation at high UO_2Cl_2 concentrations. Ions found spectrophotometrically, which could account for this value of unity of the anion transference number, are $[UO_2Cl_3 \times$ solvent$]^-$ and $[UO_2Cl \times$ solvent$]^+$. If these two ions had the same mobilities, but were traveling in opposite directions, the only apparent transfer would be that of the chloride ions. This would explain the observed maximum in the transference number *versus* UO_2Cl_2 curve. To explain the drop beyond the maximum, further complex formation would have to be postulated.

In Fig. 9 the anion transference number is plotted against wt. % ethanol in the solvent at a uranyl chloride concentration of 10.24 wt. %. The anion transference number is seen to decrease at first with increasing wt. % alcohol, then remain

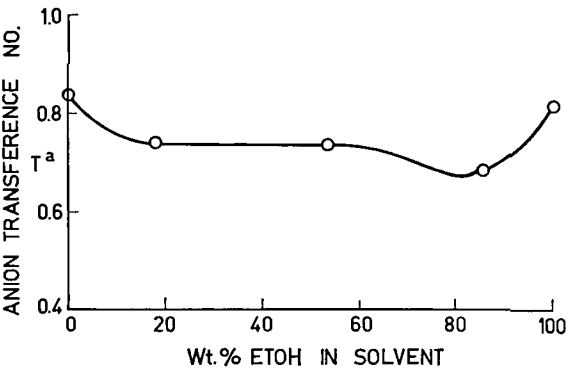

Fig. 9
Anion transference number versus per cent ethanol in solvent at 10.24 weight per cent UO_2Cl_2.

constant from about 19 to 54 wt. % alcohol, after which it decreases to a minimum at about 81 wt.% alcohol, finally showing a relatively rapid increase up to 100 wt.% ethanol. Except for the decrease of the anion transference number with the first additions of alcohol, the shape of the anion transference number *versus* composition of solvent curve is rather similar to the order of U (VI) ion *versus* solvent composition curve for the electron exchange reaction between U (IV) and U (VI) ions in water-ethanol solvents and in the presence of hydrochloric acid. The decrease from the constant portions of the curves and the minima of the two curves occurs at about the same alcohol composition of the solvent. These correllations are striking and could indicate the influence of similar ion complexes on the transference and kinetic phenomena. The striking dependence of both these phenomena on solvent composition would imply that the uranyl ion species vary with the percentage of alcohol in the solvent over certain ranges of composition.

Studies on the solvation of the ions of uranyl chloride were made simultaneously with the transference studies [4]. The moles of water transferred from anode to cathode were extrapolated graphically to 10.24 wt.% UO_2Cl_2. The moles of water transferred when plotted against ethanol content of the solvent

gave a sine-like curve. There is first an increase in moles transported with increasing ethanol concentration up to about 19 wt.% alcohol. The number of moles of water transported from anode to cathode then decreases to a minimum at 53 wt.% ethanol and then increases as the ethanol is increased up to 84 wt.%, which is as far as the solvation data extend.

This sine-like curve could result from differential dehydration or the differential alcoholation of the two ion species, depending on the amount of alcohol in the solvent. More probably, it is a combination of the two. Thus the outer layer of water of the larger volume anion ($UO_2Cl_3^-$) would seem to be more susceptible to dehydration attack than would the outer layer of the lesser volume cation (UO_2Cl^+). It would seem reasonable that the next most susceptible layer of water would be the outer layer of cation hydration. The next most susceptible point of attack would seem to be the inner solvation layer of the larger volume anion, and the least susceptible layer to dehydration attack would apparently be the inner hydration layer of the cation. Presumably, alcohol would tend to replace the removed water layers.

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DISCUSSION

M. Anbar (Israel) asked whether there was any evidence that the reaction in question was in fact an electron transfer reaction; might it not be an atom transfer reaction, in which chlorine was transferred between the two species? The point could, perhaps, be elucidated by comparing the system in chloride with that in perchlorate.

Secondly, he asked what explanation could be given for the fact that the decrease in activation energy with increasing ethanol concentration was accompanied by a decrease in the value of the frequency factor.

E. S. Amis replied that it was impossible to decide, from the data available, whether the reaction was an electron exchange or a chloride ion transfer. Taking the Np (V)—Np (VI) reaction in perchloric acid media, he had made various calculations on the hypothesis that it was an electron transfer reaction and had obtained good agreement with experimental results.

However, that afforded no proof of the hypothesis, and it would certainly be useful to compare the systems in chloride and in perchlorate, as Mr. Anbar had suggested.

In answer to Mr. Anbar's second question, he said that the change in frequency factor probably indicated a change in the comparative complexity of the activated complex and of the reactants resulting from the changed composition of the solvent. However, the frequency factor was of less importance than the activation energy in determining the rate.

J. Rydberg (Sweden) asked what was the accuracy of the equilibrium constants given by Mr. Amis for the dissociation of uranyl chloride complexes (Table III).

E. S. Amis replied that the figures were accurate to within 5—7%. They were probably correct to at least two significant figures.

CONTRIBUTIONS TO THE SOLVENT EFFECT IN ISOTOPE EXCHANGE REACTION

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Abstract — Résumé — Аннотация — Resumen

Contributions to the solvent effect in isotope exchange reaction. The effect of solvent on the exchange rate and the possible ways of accelerating the studied exchange reaction, at constant temperature and concentration, was investigated.

The exchange of iodine atoms between 1-phenyl-2,3-dimethyl-4-iodopyrazolone (4-iodo-antipyrine) and elementary iodine was chosen as a model reaction.

First the effect of the dielectric constant (ε) was examined and it appears that the rate of exchange is affected not solely by ε. The structure of the solvent, and the micro-conditions prevailing in the single spatial particles of the solvents also play an important role.

The rate of exchange was also studied in a homologous series. In addition, the effect of the water content of the solvents was examined. The results show that there is a possibility of measuring the concentration of solvents, which encourage a quick exchange, in solvents where the exchange is slow.

Exchange was also studied in aromatic solvents and the rate is markedly increased by electrophilic substituents.

Further, the exchange reaction was carried out in the presence of compounds which promote the heterolytic dissociation of iodine (such as $HgCl_2$, $AgNO_3$).

The important role of I^+ ions in the exchange reaction is clearly shown by the experiments. Also, the possibility of demonstrating the intermediate formation of I^+ -ion in certain chemical reactions is pointed out.

Contribution à l'étude de l'influence du solvant sur les réactions d'échange isotopique. Les auteurs ont étudié l'influence du solvant sur la vitesse d'échange, ainsi que les moyens d'accélérer la réaction d'échange considérée, à une température et pour une concentration constantes.

La réaction type choisie est celle de l'échange d'atomes d'iode entre la phényl-1-diméthyl-2,3-iodo-4-pyrazolone (iodo-4-antipyrine) et l'iode élémentaire.

Les auteurs ont tout d'abord étudié l'effet de la constante diélectrique (ε) et ils ont constanté que la vitesse de l'échange n'est pas influencée exclusivement par ε. La structure du solvant et les micro-conditions qui règnent dans les particules du solvant jouent aussi un rôle important.

Les auteurs ont étudié aussi la vitesse de l'échange dans une série homologue, ainsi que l'effet de la teneur en eau des solvants. Les résultats obtenus montrent qu'il est possible de mesurer la concentration des solvants qui favorise un échange rapide dans les solutions où cet échange est normalement lent.

Les auteurs ont également étudié l'échange dans les solvants aromatiques et examinent l'effet des substituants.

En outre, la réaction d'échange a été provoquée en présence de composés (tels que $HgCl_2$ et $AgNO_3$) qui favorisent la dissociation hétérolytique de l'iode.

Le mémoire traite du rôle important que les ions I^+ jouent dans la réaction d'échange. Les auteurs soulignent également qu'il est possible de prouver qu'il y a formation intermédiaire d'ions I^+ dans certaines réactions chimiques.

Исследование воздействия растворителя на реакции обмена изотопов. Было изучено воздействие растворителя, при постоянной температуре и концентрации, на скорость реакций обмена и были исследованы возможные способы ускорения этих реакций.

В качестве типовой реакции был взят обмен атомов йода между 1-фенил-2,3-диметил-4-йодопиразолоном (4-йодоантипирином) и элементарным йодом.

Прежде всего изучено воздействие диэлектрической константы (Е). По-видимому, скорость обмена зависит не только от Е. Структура растворителя и микроусловия, преобладающие в отдельных пространственных частицах растворителей, также играют важную роль.

Скорость обмена была также изучена для гомологичного ряда. Кроме того, было изучено воздействие содержания воды в растворителях. Результаты показывают, что представляется возможным определить концентрацию растворителей, способствующую ускорению обмена в растворителях, обмен в которых происходит медленно.

Были также изучены процессы обмена в ароматических растворителях, скорость значительно повышается при использовании электрофилических заменителей.

Далее были проведены реакции обмена в присутствии веществ, способствующих гетеролитической диссоциации йода (как, например, $HgCl_2$, $AgNO_3$).

Эксперименты показали важную роль ионов I^+ в реакциях обмена. Указывается также на возможность получения промежуточного образования в некоторых химических реакциях ионов I^+.

Contribuciones al estudio del efecto de los disolventes en las reacciones de intercambio isotópico. Los autores investigaron a temperatura y concentración constantes el efecto ejercido por el disolvente sobre la velocidad de determinada reacción de intercambio y los posibles medios de acelerar ésta.

Eligieron como reacción modelo el intercambio de átomos de yodo entre la 1-fenil-2, 3-dimetil-4-yodo pirazolona (4-yodo-antipirina) y el yodo elemental.

En primer lugar, examinaron la influencia de la constante dieléctrica (ε) y comprobaron que la velocidad de intercambio no depende únicamente de ε. También desempeñan un papel importante la estructura del disolvente y las microcondiciones que prevalecen en las partículas espacialmente aisladas del disolvente.

Estudiaron asimismo la velocidad de intercambio en una serie homóloga. Además, examinaron el efecto del contenido de agua de los disolventes. Los resultados demuestran que es posible medir la concentración de los disolventes que favorecen un intercambio rápido en disolventes en que el intercambio es lento.

También investigaron el intercambio en disolventes aromáticos y encontraron que los grupos sustituyentes electrofílicos aumentan apreciablemente la veloicdad de ese proceso.

Por otra parte, llevaron a cabo la reacción de intercambio en presencia de compuestos que favorecen la disociación heterolítica del yodo (tales como el $HgCl_2$ y el $AgNO_3$).

Los experimentos destacan claramente el importante papel que los iones I^+ desempeñan en la reacción de intercambio. También indican la posibilidad de demostrar la formación intermedia de iones I^+ en ciertas reacciones químicas.

1. Introduction

The scope of the present work was mainly to investigate the effect of solvent on the exchange rate and, in addition, to examine how the rate of the exchange reaction can be influenced at a constant temperature and constant concentration.

Primarily, we desired to choose a reaction where I^+ ions may play a role in the exchange process. For this purpose the exchange reaction between 1-phenyl-2,3-dimethyl-4-iodo-pyrazolone (I-antipyrine) and elementary iodine was studied. In the molecule of I-antipyrine, the iodine atom on C-4 is of a rather nucleophilic

nature. Thus, one can presume that I^+ ions will dissociate in polar solvents. Furthermore, the chosen compound is soluble in the majority of solvents to a satisfactory degree, and its preparation and purification are simple.

A survey of literature disclosed relatively few treatises on isotope exchange reactions where elementary iodine played the part of the inorganic partner. The problem of solvent effect was discussed by only a small number of authors. It must be noted here that these papers are mainly devoted to the kinetics of exchange reactions, and thus they hardly touch the problems investigated by us [1—8].

We must emphasize, however, that the present work is considered merely as the first phase of an extended research, the aim of which is to find the solution to certain problems of solvent effect. Up to the present, our work has served mainly as a compilation of experimental data, the study of the problems in detail being still in progress.

2. Experimental

Preparation of I^{131}-antipyrine

Antipyrine was reacted, in a medium of sodium acetate, with a solution of I^{131}-labelled iodine and potassium iodide. The I-antipyrine formed was extracted by shaking with chloroform, and the excess iodine reduced by sodium thiosulphate. On removing chloroform by distillation, the oily residual substance was recrystallized from hot water and dried at 80°C. The specific activity of the compound ranged from 2500 to 3000 cpm/mg.

Preparation of cyanogen iodide

A solution of mercury (II) cyanide in ether was reacted with iodine, the precipitated mercury (II) iodide was filtered, ether was then removed by distillation and the residual cyanogen iodide refined by repeated sublimation under reduced pressure. The analytical control of the product showed a 99.8% content of cyanogen iodide.

Preparation of a solution of sodium hypoiodite

Iodine was dissolved, under cooling with ice, in an approximately 2 N solution of sodium hydroxide prepared with previously boiled distilled water.

Solvents

The solvents used in the present experiments were purified and dehydrated by the conventional methods. In the case of alcohols, the content of water was determined by Karl-Fischer titration. The content of water of the anhydrous alcohols used in the present experiments never exceeded 0.3%.

Procedure

The exchange reactions were carried out in an ultrathermostat at 19.0 ± 0.02°C and 21.0 ± 0.02°C, respectively. The reactions were started by adding an iodine solution to I^{131}-antipyrine dissolved in various solvents. (In all experiments I-antipyrine was labelled). The concentration of each of the components was 7×10^{-3} M, with the exception of the experiments carried out in an aqueous medium, where these concentrations were equal to 2×10^{-3} M, due to the poorer solubility of the substances.

After the reaction period had elapsed, an aliquot was taken from the solution by a pipette and transferred into a solution of arsenious acid to quench the reaction. On precipitating the formed iodide with a mixture of 2 ml of 5% silver nitrate solution and 4 ml of 10% perchloric acid solution, the silver iodide precipitate was centrifuged, filtered and washed, first with a dilute solution of perchloric acid and then with ethanol. Subsequently, the precipitate was coated by some drops of a collodion solution, dried under an infra-red lamp, weighed and its activity measured. From these data, the specific activity was calcualted. As the weight of the precipitates ranged only from 4.0 to 4.5 mg/cm^2, no correction was made for self-absorption. The activity was measured by a 2.6 mg/cm^2 end-window GM counter.

On plotting the values of log $(1\text{-}x_t/x_\infty)$ against time, where (x_t/x_∞) is the fraction exchange, the half-time of exchange $(t_{1/2})$ was calculated. The specific activity measured at infinite time (x_∞) was established by observing the 20-min exchange values in 50% ethanol. In fact, according to our pre-experiments the half-time of the exchange in this solvent is about 10 s).

In the case of solvents which are immiscible with water, the reaction was quenched in a separatory funnel, by shaking the mixture vigorously with arsenious acid, and subsequently processing the aqueous phase.

In the exchange experiments carried out in the presence of mercury (II) chloride, the precipitated substance also contained silver chloride which latter was dissolved from the precipitate by repeated treatment with ammonia.

The exchange reaction between hypoiodite and I-antipyrine was conducted in an aqueous solution at 0°C. The reaction was stopped with arsenious acid, then the pH value of the solution was reduced to about 8, in the presence of phenolphthalein as indicator, by introducing carbon dioxide. On extraction of I-antipyrine, by shaking with 3 to 5 ml of chloroform, the aqueous phase was processed. As the solution of hypoiodite disproportionates relatively quickly even at 0°, no reaction periods over 1 h were chosen.

In investigating the exchange reaction between cyanogen iodide and I-antipyrine, in an aqueous medium, the reaction was quenched by sodium arsenite, and the mixture then processed as in the case of hypoiodite. Silver cyanide was removed from the silver iodide precipitate by treatment with ammonia.

The investigation of the exchange reaction between iodate and I-antipyrine was similarly carried out in an aqueous medium. On stopping the reaction, by

TABLE I

RESULTS FROM AN EXCHANGE REACTION USING CHLOROFORM WITH 5 VOL. % NITROBENZENE

Time (min)	AgJ (mg)	cpm*	cpm/mg (x_t)	$\log/[1-(x_t/x_\infty)]$
1	13.1	1122	86	0.972
5	12.6	4230	336	0.877
10	14.6	8515	583	0.757
20	13.8	12690	919	0.510
30	13.4	15100	1128	0.233
40	13.4	16160	1206	0.053

* Average of 3 measurements.

shaking the mixture with chloroform to remove I-antipyrine, the activity of the aqueous phase was measured in a liquid counter.

In order to illustrate how the curves of the exchange reactions were plotted from the data of measurements, the data observed in the exchange reaction carried out in chloroform containing 5 vol. % of nitrobenzene are presented in Table I.

3. Results and discussion

During the present experiments, the effect of the dielectric constant, one of the principal macroproperties of solvents, on the exchange rate was investigated first. When the value of the dielectric constant was varied within broad limits, the following values for the half-time of the exchangerate were obtained at 21.0°C:

Solvent	$\varepsilon_{20°}$	$t_{1/2}$
Dioxane	2.22	55 min
Benzene	2.28	32 min
Chloroform	4.81	40 min
Pentanol	14.3	160 min
Ethanol	25.1	40 min
Nitrobenzene	35.7	<20 s
Ethanol/water (50 vol. %)	54.8	$\sim$10 s
Formamide	109.0	$\sim$10—15 min

In water ($\varepsilon_{20°} = 80.4$), the half-time of exchange was about 1 min for a concentration of 2×10^{-3} mol/l of I-antipyrine and iodine.

It appears from the above data that the rate of exchange is not uniformly affected by the dielectric constant. Presumably the structure of the solvent, which manifests itself in the viscosity as a macroproperty, as well as the micro-conditions prevailing in certain spatial areas of the solution, may play an important role. This problem will be discussed later.

In the systematic study of solvent effect, almost insuperable difficulties are encountered in that by varying one of the parameters of the solvent, e.g., the value of ε, its other parameters are also altered.

However, monotonous changes can be expected within a series of homologues, where the macro-parameters change in a uniform sense. For this purpose, the half-time of the exchange was measured in aliphatic alcohols. The results obtained at 21.0°C are:

Solvent	$t_{1/2}$
Methanol	6.5 min
Ethanol	40 min
1-Propanol	95 min
1-Butanol	111 min
Pentanol	160 min

During the experiments with alcohols, we observed how appreciably the exchange rate is affected by the water content of the solvent. Some of our data showing this effect are as follows:

Solvent	$t_{1/2}$
Ethanol	40 min
Ethanol/water (3 vol. %)	26 min
1-Propanol	95 min
1-Propanol/water (4 vol. %)	45 min
Dioxane	55 min
Dioxane/water (2.5 vol. %)	20 min

The above results also appear to be of interest by showing that a few per cent of water cannot markedly influence the viscosity and the dielectric constant of the solvents. However, even in the presence of such small water contents, the formation of intermediate associates can be presumed where the exchange is faster. The formation of intermediate associates of this type does not manifest itself in the macro-properties of the solvent.

In the knowledge of the results presented, the idea arose to calculate the water content of the solvents from the values of $t_{1/2}$, on the basis of the calibration curve. On generalizing this principle, it seems possible to establish the concentration of a solvent which would encourage a quick exchange in a solvent where the exchange is slow.

On the basis of the above consideration, the dependence of the value of $t_{1/2}$ on the water content of ethanol, and on the content of nitrobenzene in chloroform, was examined. An empirical correlation can be established: specifically, on plotting the logarithmic value of the half-time of exchange against the vol. % of water, in the case of ethanol, and of nitrobenzene, in the case of chloroform, a straight line was obtained, as shown in Figs. 1 and 2.

In the cases where an exchange reaction takes place very rapidly in several solvents, it is impossible to distinguish these solvents in the effects they have on the exchange rates. However, it is expected that solvents may be distinguished by diluting them with solvents in which the exchange is slow.

The number of data available are for the time being insufficient for a generalization of the above consideration. In our opinion, however, it seems possible to approach the solution of certain problems of solvents by further investigations in this direction.

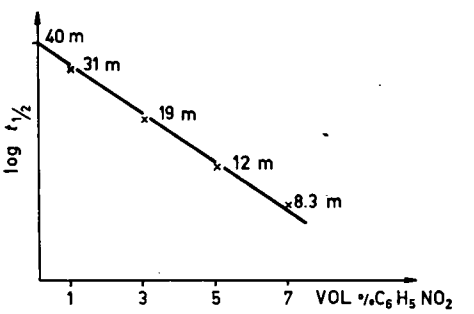


Fig. 1
The log $t_{1/2}$ of the I-antipyrine — I_2 isotope exchange reaction plotted against the nitrobenzene content of chloroform.

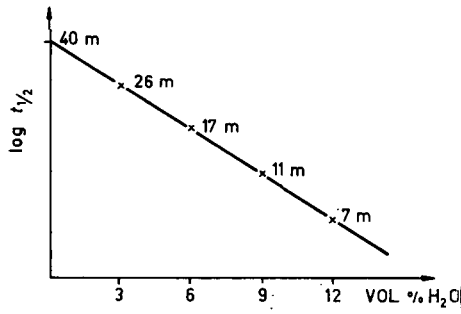
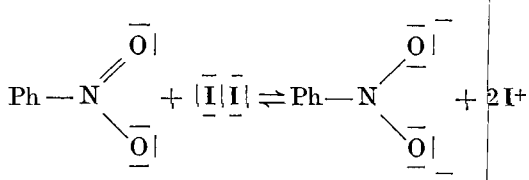


Fig. 2
The log $t_{1/2}$ of the I-antipyrine — I_2 isotope exchange reaction plotted against the water content of ethanol.

The solvent effect was also examined in the case of some aromatic compounds. Data of measurements carried out at 19.0°C are as follows:

Solvent	$t_{1/2}$
Benzene	35 min
Toluene	26 min
Chlorobenzene	9 min
Nitrobenzene	< 20 s

It can be seen from the results that the exchange rate markedly increases in the case of electrophilic substituents, (—Cl or —NO_2) particularly in the case of nitrobenzene. In nitrobenzene, iodine is probably converted into a potential electrolyte to a small extent, and yields I^+ ions which, as will be discussed in detail later, are instantaneously exchanged with I-antipyrine:



The problem arises, from the results discussed above, of knowing the mechanism according to which these exchange reactions occur. Owing to the nucleophilic nature of the iodine attached to C-4 in the molecule of I-antipyrine, the dissociation of I^+ ions may be expected in polar solvents. In order to demonstrate the role of I^+ ions in the exchange process, the reaction was carried out in the presence of compounds, such as mercury or silver salts [9], which promote the heterolytic dissociation of iodine molecules. Mercury and silver salts are capable of binding one of the components formed during heterolytic dissociation (iodide ions) as a poorly dissociated and poorly soluble compound, respectively:

$I_2 \rightleftharpoons I^+ + I^-$

$I^- + HgCl_2 \rightarrow [HgCl_2I]^-$ and $[HgCl_2I_2]^{-2}$, respectively

$I^- + Ag^+ \rightarrow AgI \downarrow$

and so the concentration of I^+ in the solution increases.

In our experiments carried out in an ethanolic medium, when the solution contained 0.01 M mercury (II) chloride and silver nitrate respectively, the following results were obtained:

Solvent	$t_{1/2}$
Ethanol	40 min
Ethanol + $HgCl_2$	< 1 min
Ethanol + $AgNO_3$	< 10 s

As the overall reaction between Ag^+ and I_2 is:

$$6\,Ag^+ + 3\,I_2 + 3\,H_2O = 5\,AgI + AgIO_3 + 6\,H^+,$$

it seemed necessary to examine whether any exchange takes place between I^+ and I-antipyrine, and IO_3^- and I-antipyrine respectively, and whether the half-time of the exchange reaction is affected by the acid.

The experimental results proved that in an aqueous solution iodide was exchanged only extremely slowly with I-antipyrine, in that the half-time of the exchange ranged from about 6 to 7 d at a pH of 6.5. This very slow, although actually existing exchange can be interpreted by the known equilibrium:

$$\begin{array}{c} = CI \\ | \end{array} + I^- + H^+ \rightleftharpoons \begin{array}{c} = CH \\ | \end{array} + I_2$$

which clearly shows the strong dependence of the exchange reaction between iodide and I-antipyrine on the pH of the solution.

No exchange was observable between iodate and I-antipyrine.

In the experiments carried out with the aim of investigating the effect of acid, enough ethanolic perchloric acid was added to the solution so as to attain a concentration of 0.01 N in respect of perchloric acid. The exchange reaction between iodine and I-antipyrine proved to be influenced by the presence of acid only to a small extent, in that the value of $t_{1/2}$ was reduced by only a few minutes.

Results above show that I^-, IO_3^- and H^+ do not influence the rate of the exchange to any appreciable extent. It seems probable, therefore, that in the first step of the Ag^+—I_2 reaction, I^+ is forming:

$$Ag^+ + I_2 = AgI^+ + I\,.$$

I^+ quickly disproportionates:

$$3\,I^+ + 3\,H_2O = 2\,I^- + IO_3^- + 6\,H^+\,.$$

The exchange with I-antipyrine, however, is faster than the above transformation.

On the basis of the afore-mentioned, it seems obvious that the exchange reaction will be slower when the heterolytic dissociation of iodine is suppressed by the addition of iodide ions. We succeeded in proving this presumption, as the half-time of the exchange process increased from 40 min to 18 h when the exchange reaction was carried out in an ethanolic medium with I_3^- ions.

Subsequently, it appeared to be of interest to examine whether an exchange reaction takes place when the experiment is carried out with compounds such as OI^- or ICN, which contain iodine of +1 oxidation number. The technique of

these reactions was described in detail in the experimental part. The experimental data indicated that in an aqueous medium no exchange takes place between OI^- and I-antipyrine, nor between ICN and I-antipyrine.

This shows that the bonds I—O and I—CN are extremely stable, and that the compounds mentioned yield no I^+ ions through dissociation. If this way, we also proved that the presence of I^+ ions is one of the indispensable prerequisites of the quick exchange.

It can be seen in the descriptions presented in the experimental part that, in the case of the exchange reactions between OI^- and I-antipyrine, a technique was used differing widely from those applied in our other experiments. This is explained as follows: In our first experiments, before precipitating iodide by a silver nitrate solution containing perchloric acid, the reaction was stopped by adding arsenious acid. In all cases a rather appreciable zero-time exchange was observed. On a more thorough consideration, it was possible to interpret this phenomenon satisfactorily: In a solution of hypoiodite, a certain amount of iodate is always present which is not reduced by arsenious acid in an alkaline medium. However, on the addition to the solution of a silver nitrate solution containing perchloric acid, I^+ ions also form as intermediate, due to the interaction of IO_3^- I^-, Ag^+ and H^+. The presence of I^+ ions accounts for the apparent exchange, and this is why it is necessary to remove I-antipyrine from the system by extraction with chloroform, before adding silver nitrate.

It is quite obvious from the above experiments that iodine cations play an essential role in the exchange reaction. As the iodine atom of I-antipyrine is instantaneously exchanged by the I^+ ion, the possibility of demonstrating the intermediate formation of I^+ ions in certain chemical reactions in this way seems real.

We must still point to the fact that the rapid exchange observed in an aqueous medium can only be interpreted by presuming that a heterolytic dissociation of iodine molecules takes place before the hydrolysis of iodine:

$$I_2 \rightleftharpoons I^+ + I^-$$
$$I^+ + H_2O \rightleftharpoons I(H_2O)^+$$
$$I(H_2O)^+ \rightleftharpoons HOI + H^+$$

During the hydrolysis of iodine, therefore, HOI forms which is not exchanged by I-antipyrine, while the rapid exchange of I^+ was actually proved by our experiments described above.

Finally, it must be noted that the formation of I^+ ions is only possible in polar solvents. As, however, an exchange reaction also takes place in apolar solvents, another mechanism must be presumed in these apolar solvents.

One of our next tasks will consist in studying in detail the kinetics of the exchange reaction.

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DISCUSSION

M. Anbar (Israel) asked whether the effect of Ag^+ on the rate of exchange, using the described technique, could not in fact be an electrophilic attack on the organic compound resulting in de-iodination.

E. Körös replied that the effect of Ag^+ on the organic compound did not result in de-iodination. It had been found earlier that, since I-antipyrine did not yield **I** -ions through dissociation, there was no reaction between Ag^+ and I-antipyrine, even in acid media.

Furthermore, he thought it worth mentioning that a fast exchange was observed if an Ag Cl suspension was used instead of $Ag\,NO_3$. Because of solubility differences, the heterolytic dissociation of I_2 was promoted by AgCl too.

He would refer those who were interested in detailed information on these problems to a paper by SCHULEK *et al.* [9] "The Formation of Interhalogens", which would be published in *Talanta* in the near future.

M. Anbar asked whether the mechanism of I^+ dissociation would not imply a fast de-iodination of the organic compound by an attack of H^+ on the R^- anion.

E. Körös replied that H^+ had no effect on I-antipyrine. A fast de-iodination of I-antipyrine took place in the presence of I^--ions in a strong acid medium. I^--ions, however, were bound immediately by Ag^+.

M. Anbar asked whether the authors could give data concerning the kinetic order experimentally found in respect to RI.

He said the authors also mentioned effects of parameters on the half-lives of exchange. How could these be expressed in terms of activation energies and frequency factors ?

E. Körös replied that unfortunately he was unable to answer those two questions at the moment as kinetic studies and calculations of activation energies had only just started.

TRACER INVESTIGATIONS OF THE FATE OF SULPHUR ATOMS IN THE COURSE OF HIGH-TEMPERATURE REACTIONS

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Abstract — Résumé — Аннотация — Resumen

Tracer investigations of the fate of sulphur atoms in the course of high-temperature reactions. The fact that sulphur occurs in many different chemical conditions suggests a number of interesting problems in connexion with the movement of the sulphur atoms in the course of reactions between different compounds of this element. Quite an amount of information is available concerning reactions between compounds of sulphur in solution and, in general, the different sulphur fractions do not mix under these conditions.

An entirely different situation is found in reactions between gases and solid compounds. For these processes much higher temperatures are, in general, required and at these higher temperatures the sulphur atoms in the different fractions tend to mix to a very large extent. This behaviour is illustrated by means of data obtained on the exchange of radiosulphur between sulphur vapour and sulphur dioxide, between sulphur dioxide and solid sulphite and between sulphur dioxide and solid sulphate. The same behaviour has been observed in the chemical decomposition of thiosulphate, labelled in one of the two sulphur fractions and in the oxidation of this compound. Finally, it has been shown that mixing is also very strong in the reaction between sulphur vapour and solid sulphate.

Etude, au moyen d'indicateurs, du comportement des atomes de soufre dans des réactions à haute température. Le fait que le soufre peut se trouver dans de nombreux états chimiques différents met l'accent sur certains problèmes intéressants relatifs au mouvement des atomes de soufre dans des réactions entre divers composés de cet élément. On a un assez grand nombre de renseignements sur les réactions entre les composés du soufre en solution, et d'une façon générale les différentes fractions de soufre ne se mélangent pas dans ces conditions.

La situation est tout à fait différente dans les réactions entre les gaz et les composés solides. Ces réactions nécessitent en général des températures beaucoup plus élevées et les atomes de soufre des différentes fractions ont alors tendance à se mélanger dans une très large mesure. Ce comportement est illustré au moyen de données obtenues sur l'échange de soufre radioactif entre la vapeur de soufre et l'anhydride sulfureux, entre l'anhydride sulfureux et le sulfite solide et entre l'anhydride sulfureux et le sulfate solide. Le même comportement a été observé dans la décomposition chimique du thiosulfate marqué dans l'une des deux fractions de soufre, et aussi dans l'oxydation de ce composé. Enfin, on a constaté qu'il y a très fort mélange aussi dans la réaction entre la vapeur de soufre et le sulfate solide.

Исследование мечеными атомами поведения атомов серы в ходе высокотемпературных реакций. Тот факт, что сера встречается во многих различных химических соединениях, предлагает ряд интересных проблем в связи с движениями атомов серы в ходе реакций между различными соединениями этого элемента. Имеется достаточно информации относительно реакций между соединениями серы в растворе, а вообще различные фракции серы не смешиваются в этих условиях.

Совершенно отличное положение обнаружено при реакциях между газами и твердыми соединениями. Для этих процессов обычно требуются значительно более высокие температуры, и при этих более высоких температурах атомы серы в различных фракциях имеют тенденцию смешиваться в весьма значительной степени. Это поведение иллюстрируется посредством данных, полученных при обмене радиоизотопов серы между серным газом и двуокисью серы, между двуокисью серы и твердым сульфитом и между двуокисью серы и твердым сульфатом. Такое же поведение наблюдалось при химическом разложении тиосульфата, меченного в одной из двух фракций серы, и при окислении этого соединения. Наконец, показано, что происходит также очень сильное смешивание при реакции между серным газом и твердым сульфатом.

Estudio mediante marcadores del comportamiento de los átomos del azufre en reacciones a elevadas temperaturas. El hecho de que el azufre se presente en muchas formas químicas diferentes plantea diversos problemas de interés por lo que respecta al movimiento de los átomos de azufre en las reacciones entre distintos compuestos de este elemento. Los abundantes datos de que se dispone acerca de las reacciones entre los compuestos del azufre en solución permiten afirmar que, en general, las diferentes fracciones de azufre no se mezclan en tales circunstancias.

No ocurre lo mismo cuando se trata de reacciones entre compuestos gaseosos y sólidos. Estos procesos sólo se verifican a temperaturas mucho más elevadas, a las cuales los átomos de azufre presentes en las distintas fracciones suelen mezclarse en grado muy considerable. Ofrecen una ilustración de este comportamiento los datos obtenidos sobre el intercambio de azufre radiactivo que se produce entre los vapores de azufre y el anhídrido sulfuroso, entre el anhídrido sulfuroso y el sulfito sólido y entre el anhídrido sulfuroso y el sulfato sólido. Se ha podido observar el mismo comportamiento en la descomposición química del tiosulfato, marcado en una de las dos fracciones de azufre, y en la oxidación de este compuesto.

Por último, se ha demostrado que la mezcla es también muy intensa en la reacción entre el vapor de azufre y el sulfato sólido.

1. Introduction

Since the days when chemists first came to accept the atomic theory one of the most attractive aims in their science has been to follow the movement of various atoms in the course of the transformation of molecules. The means to realize this ideal have been presented by the discovery of radioactive tracers and, indeed, the elucidation of the mechanism of chemical reactions has been one of the most striking successes of this principle. The main field of these studies has been organic chemistry and by far the most important tracers have been the isotopes of carbon and hydrogen. Most other elements do not often occur in a simple system in fractions which are chemically different. In general most metals are only present as ions. In inorganic chemistry, a special case is presented by sulphur which can also play many different chemical roles and is, in this respect, similar to the principal components of organic compounds. In the following report we shall present some examples of reactions in which sulphur compounds are involved which have been investigated by means of the isotope S^{35}.

A great number of publications have appeared which deal with the fate of sulphur atoms when reactions take place involving various sulphur compounds in aqueous solution [1] [2]. As a rule, in such systems the atoms of the various sulphur fractions remain well separated and mixing between the different groups has been observed in a few cases only and then, in general, only as a result of rather rare side-reactions. It should be kept in mind that reactions in solution

are essentially low-temperature processes and that the lack of mixing of atoms of different sulphur fractions under these circumstances does not permit extrapolations to the behaviour of sulphur compounds at high temperatures. For this reason we have investigated a number of reactions in systems containing more than one type of sulphur at temperatures well above the boiling point of water. It is of interest to notice that under these conditions a very strong tendency is generally observed for the radioactive sulphur atoms to spread equally over all sulphur fractions in the system. In those cases where the processes studied were essentially exchange reactions, the temperature could be determined at which these processes set in. In those cases where we dealt with processes involving a chemical change, the mixing was quite strong at the temperature where the chemical reaction became first observable.

It should be understood that all our work has been of an exploratory nature and that very much more remains to be done on each of these subjects.

We shall now discuss a few examples of redistribution of radiosulphur. It will be noticed that in these experiments sufficient information can be obtained from changes observed in a gas stream, a technique which is much simpler than experimenting in static systems. In several cases, an analysis of the gaseous products is not even necessary, as the ratio in which the two reactants have participated in the process can frequently be deduced from the radioactivity balance.

2. Exchange between sulphur vapour and sulphur dioxide *

This reaction is easily carried out by evaporating sulphur in a stream of sulphur dioxide which is passed through a furnace having controllable temperature. We used a porcelain tube to which a glass tube was sealed on either side. After the gas left the furnace it passed a plug of glass wool to condense the sulphur vapour. Although it is not possible to define accurately the part of the tube in which the exchange takes place, its volume can be estimated very roughly to be about 30 cm^3. The sulphur dioxide is absorbed in potassium hydroxide. Barium sulphate is obtained from this solution, from the original sulphur (oxidized by means of conc. nitric acid) and from the sulphur condensed on the glass wool. The

TABLE I

LOSS OF RADIOACTIVITY FROM SULPHUR VAPOUR TO SULPHUR DIOXIDE AT VARIOUS TEMPERATURES

Temp. (°C)	Duration of experiment (min)	Relative sp. activity (original sulphur = 1)		Fraction activity lost by sulphur vapour
		sulphur after exchange	SO_2 after exchange	
500	5	0.67	0.060	0.33
	5	0.78	0.026	0.22
600	5	0.24	0.20	0.76
	5	0.26	0.24	0.74
700	10	0.25	0.098	0.75
	5	0.24	0.089	0.76
800	10	0.18	0.074	0.82
	20	0.17	0.066	0.83

* This work was done with Mr. A. van Kammen.

specific activities of the three fractions make it possible to calculate the concentration of the sulphur vapour in the gas stream, assuming that this concentration has been constant throughout the experiment. The latter assumption is, of course, only an approximation and the results listed in Table I show that a complete exchange has not been observed, even at the highest temperature, which is evidently due to the variation of the sulphur concentration in the course of the experiment, (At 700°C and 800°C the exchange should, of course, be more nearly complete than at 600°C). However, at 500°C the exchange is definitely incomplete and for this temperature a rough estimate can be made of the exchange rate. If we assume that the reaction is bimolecular, the value of the rate constant turns out to be $k \approx 10$ l/mol. s at 500° and > 10 l/mol. s at higher temperatures. This rate constant is calculated on the assumption that it is the main fraction of the sulphur vapour that reacts with the sulphur dioxide. Should the exchange process be due to a rare component in equilibrium with the main component (S_8), then the value of the constant would not be correct for this rare component, as an incorrect concentration would have been used in the computation. In view of the uncertainty of the exact circumstances of the experiment, the value of k should not be considered to be much more than an indication of the order of magnitude.

3. The exchange between sulphur dioxide and alkali sulphite *

Radioactive sulphite was heated in a current of inactive sulphur dioxide at various temperatures. Samples of the sulphite as used as a starting material, and of the sulphite after treatment in the gas-current, were oxidized by means of permanganate and precipitated as barium sulphate. The results are given in Table II.

TABLE II

LOSS OF RADIOACTIVITY FROM ALKALI SULPHITE TO SULPHUR DIOXIDE

Sulphite	Temp. (°C)	Duration of experiment (min)	Wt. of sample (mg)	Fraction of the activity of the sulphite lost to the sulphur dioxide
Na_2SO_3	470	60	63	0.856
			122	0.831
			250	0.700
Na_2SO_3	470	15	250	0.661
K_2SO_3	420	40		0.072
K_2SO_3	530	60		0.16

The interpretation of a reaction between a gas and a solid is rather difficult because diffusion processes are extremely important, as they determine both the diffusion into each crystal of the reacting molecules and the penetration of the gas from the top of the layer of solid to lower layers of the sample. At any rate in the case of Na_2SO_3 the percentage activity loss in our experiments varies only slightly with the amount of material, which shows that exchange is almost equally efficient all the way through the solid. Also, in 15 min the exchange process has gone almost as far as it will go in a reasonable time, which suggests

* This work was done with Mr. P.W.F. Louwrier and Miss C.J. Rierink.

that results obtained after a period of 1 h should be quite comparable, at least for Na_2SO_3. In the case of potassium sulphite the reaction was much slower, but we cannot exclude the possibility that this difference may have been due, at least in part, to differences in crystal size or other experimental circumstances.

4. The exchange between sulphur dioxide and alkali sulphate*

This reaction we investigated by a technique similar to that mentioned in the preceeding section. Radioactive potassium sulphate was heated in a current of inactive sulphur dioxide at various temperatures and the decrease in the spe-

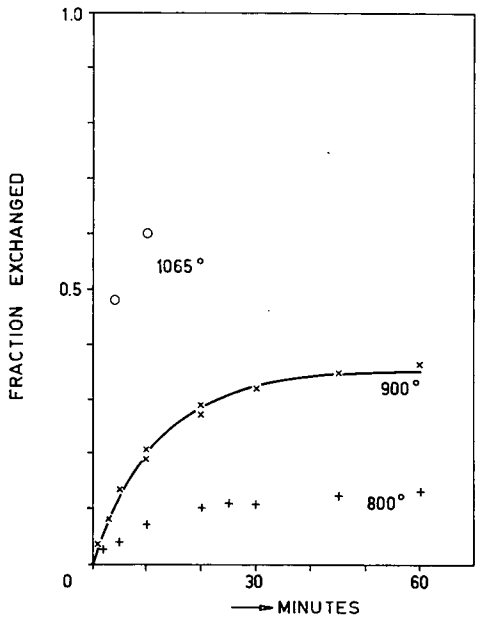

Fig. 1
The fraction of radioactivity lost by K_2SO_4 in SO_2 at different temperatures.

cific activity of the sulphate was measured as a function of the duration of the experiment. The results are shown in Fig. 1. The points in the figure were all obtained in one investigation.

In a different series of experiments, using a different sample of $K_2S^{35}O_4$, points were obtained at 800°C and at 900°C after 10 min, which could not be drawn because they coincide too closely with those obtained in the main series. The data obtained at 900°C can be represented with fair approximation as an exchange reaction involving only 35% of the solid with a half-time of 8 min, although after 1 h the exchange process does not seem to have stopped entirely. Probably a much slower process involving either a larger part or all of the potassium sulphate goes on for a much longer time. A similar curve with about the same half-time would represent the loss of activity at 800°C, but

* This work was done with Mr. J.F.Heyting and Mr. A. van Kammen.

in this case only about $12\frac{1}{2}\%$ of the material is involved. At 1065°C most of the potassium sulphate takes part in the exchange process. (At 1085°C, where potassium sulphate is present as a melt, the exchange is almost complete after 10 min). A behaviour of this type is by no means rare in reactions in the solid state, e.g., it is often observed in annealing processes of the products of Szilard-Chalmers reactions. Under these circumstances, it is, of course, meaningless to try to calculate activation energies.

One point which certainly should be noted is that much higher temperatures are needed to bring about the exchange of SO_2 with sulphate than with sulphite. This temperature difference, which is much larger than would be expected to correspond to differences in crystal size, layer thickness, etc., may possibly reflect the extra activation energy required for the change in the valency of the sulphur which takes place in the first process and not in the second.

5. Decomposition of sodium thiosulphate*

If sodium thiosulphate is heated in the absence of oxidizing materials, the main reaction is the formation of sulphur vapour and of sodium sulphate. However, for stoichiometric reasons these two materials cannot be the only products, and the course of the reaction may be represented—at least in a formal way—by the following formula [3]:

$$8\ Na_2S_2O_3 \rightarrow 6Na_2SO_4 + 2\ Na_2S + S_8 \qquad (1)$$

It has been known for some time, however, that this is not the only process to take place and that, to a minor degree, another type of decomposition occurs which may be formulated [4] as (2), whereas the possibility of (3) should also be considered:

$$8\ Na_2S_2O_3 \rightarrow 8\ Na_2SO_3 + S_8 \qquad (2)$$

$$4\ Na_2S_2O_3 \rightarrow 3\ Na_2S + Na_2SO_4 + 4\ SO_2 \qquad (3)$$

It is evident that to investigate this reaction represents quite formidable problems in analytical chemistry which we have not been able to solve to our satisfaction. Not only were we unable to recover all the sulphur from the vapour phase, but part of the sulphur dissolved in the wash-bottles with the formation of sulphide and probably sulphite. None the less, we have been able to isolate—although not in a pure condition—sulphur and sulphur dioxide fractions from the gas and sulphide, and sulphate and sulphite fractions from solid reaction products. (It should be borne in mind that, of the elementary sulphur formed, part enters the gas phase and part remains, or may remain, in the solid residue as polysulphide). If the heating is carried on for a sufficiently long period practically all the thiosulphate will disappear, which makes the chemical separation a little easier. (The analytical technique is similar to that described under section 7).

The material used for our experiments was a sodium thiosulphate containing S^{35} in the outer sulphur atom only. It was heated in a current of nitrogen. After the gas left the furnace, most of the elementary sulphur formed was con-

* This work was done with Mr. C. Pijpers and Mr. J.H.W. van Buuren.

densed on the inside of the tube. Finally, the gas was washed in two wash-bottles containing *NaOH* or *KOH* solution to collect SO_2. However, some of the elementary sulphur was also carried into these bottles by the gas stream, where it hydrolysed to sulphide and—presumably—also to sulphite.

The amount of sulphur dioxide produced turned out to be very small. Although some was found in the wash-bottles in most cases, the quantities were hardly in excess of what should have been provided by the hydrolysis of sulphur, considering the quantity of sulphide formed in this process. Thus reaction (3) certainly does not account for more than a few per cent of the thiosulphate in our experiments. In some of our experiments we obtained a sulphite fraction from the solid residue, indicating that reaction (2) did take place. As far as we can trust our analysis, we can say that 1 mol. of thiosulphate may have decomposed according to (2) as compared to about 10 decomposing by reaction (1). However, this conclusion does not take into account any reactions except (1) and (2), and we shall see later that it is not impossible that our results on the decomposition of thiosulphate have been complicated by secondary reactions between the primary decomposition products. Table III indicates the results of several experiments

TABLE III

RELATIVE SPECIFIC ACTIVITY OF DECOMPOSITION PRODUCTS OF Na_2SO_3S*, EXPRESSED AS PARTS OF THE AVERAGE SPECIFIC ACTIVITY OF THE TOTAL SULPHUR IN THE ORIGINAL THIOSULPHATE

Temp. (°C)	Duration of experiment (h)	Relative sp. activity					
		residue sulphate	residue sulphite	residue sulphide	Sulphur condensed in tube	Sulphide in wash-bottle	Sulphite in wash-bottle
470	3	0.96	—	0.92		—	—
470	3	0.90	—	0.89			0.92*
470	3				0.90		
640	0.5	0.93	0.98	0.88			0.94*
640	0.5	1.17	—	0.90		—	—
460	7	1.03	0.95	1.00	0.93	1.00	0.86
640	*1.5*	*1.06*	*0.91*	*0.96*	*1.05*		*0.87*

In samples indicated by — the amount of sulphur was negligible.
The last two experiments were performed as a separate series under slightly different circumstances.
Samples marked * may have contained some sulphide.
In many cases the sulphide contained polysulphide.
In the sulphite obtained from the wash-bottles, which was precipitated from a solution containing much alkali salt, a contaminated $BaSO_4$ may have been obtained, which would give low values for the sp. activity. Both the sulphide and the sulphite fractions in the wash-bottles may have been formed by hydrolysis of sulphur vapour. In this case the sp. activities in the two last columns are bound to be equal to that of the sulphur condensed in the tube.

in which the standard material (all samples were measured as barium sulphate) was obtained from the total sulphur in the sodium sulphate. In other words, a relative specific activity of 1.00 indicates that the material of the fraction involved contains sulphur atoms coming in equal parts from the two different sulphur atoms in the thiosulphate. Within the accuracy of the experiment, it is evident that complete mixing of the inner and the outer sulphur of the thiosulphate has taken place in all sulphur compounds produced in the decomposition process.

6. Oxidation of thiosulphate*

When thiosulphate is heated in an air current the material decomposes quite easily, the reaction becoming observable already at temperatures a little above 100° C. The products of the oxidation process are much less complicated than those obtained in the decomposition in an inert atmosphere. The main process [3] is (4),

$$2\,Na_2S_2O_3 + 3\,O_2 \rightarrow 2\,Na_2SO_4 + 2\,SO_2 \qquad (4)$$

although reactions requiring less oxygen seem to occur too, but presumably only as a side-reaction. It should be borne in mind, however, that in an oxidizing atmosphere such processes may well be masked by subsequent oxidation of its products, elementary sulphur dioxide and sulphite, to sulphate. Thus it is not possible to assert definitely that reaction (4) takes place directly, although the low temperature at which it is observed, makes it unlikely that it passes through a preliminary partial process identical with (1) or (2). On the other hand, the presence of elementary sulphur and sulphite in the solid residue of the decomposition proves that reactions different from (4) are possible under the circumstances of our experiments. The quantities of these side-products are, however, met in small quantities only.

The results of our measurements are given in Table IV. Mixing of the two sulphur fractions of the thiosulphate is complete or almost complete in all cases. It is of special importance that this complete mixing is observed even at a temperature as low as 250°C.

TABLE IV

RELATIVE SPECIFIC ACTIVITIES OF THE OXIDATION PRODUCTS OF Na_2SO_3S*

Temp. (°C)	Duration of experiment (h)	Relative specific activity			
		residue sulphate	residue sulphite	residue thiosulphate (non-decomposed)	SO_2 from gas
250	5	0.95	—		0.94
250	5	1.00	0.80	1.02	0.99
600	4	0.98	—		0.99
600	4	1.00	—		0.98

The specific activity of the total sulphur in the original thiosulphate has been taken to be 1.00.
The activity measurement of the sulphite fraction in the second experiment was made on a very small amount of material and has a low accuracy for this reason.

7. Reaction between sulphur vapour and solid potassium sulphate**

It has been known for a long time that sulphates at high temperatures are reduced by sulphur vapour [5] [6]. The reaction products are mainly sulphide and sulphur dioxide according to (5).

$$K_2SO_4 + (n+2)\,S \rightarrow K_2S_{1+n} + 2\,SO_2 \qquad (5)$$

* This work was done with Mr. J. Schut.
** This work was done with Mr. R. Visser and Mr. R. Leur.

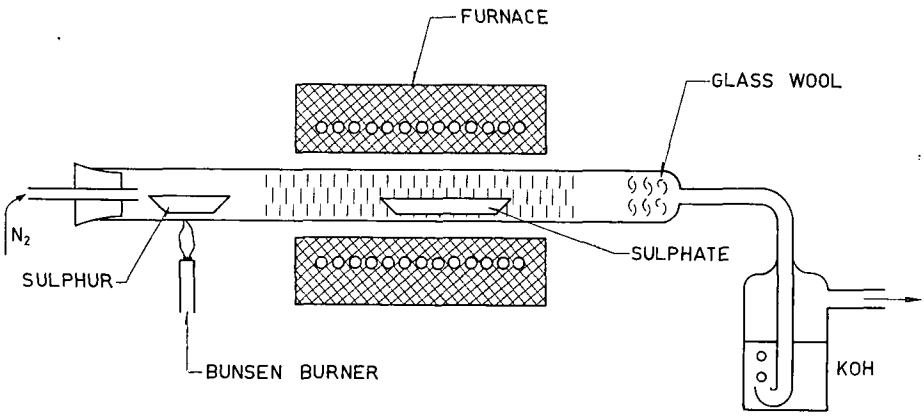

Fig. 2
Apparatus for the reduction of potassium sulphate by sulphur vapour.

(In our experiments, at about 800°C and 900°C the value of n was around 1.5.) It has, however, often been observed [7] that other products, like sulphites and thiosulphates, are also formed, though in smaller quantities. It seemed very interesting to determine the provenance of the sulphur atoms contained in the different reaction products. The reactions were performed in an apparatus of the type shown in Fig. 2. The sulphate was heated in a current of nitrogen which carried the sulphur vapour. After the reaction, the sulphur vapour was condensed in the plug of glass wool and the SO_2 was absorbed in alkali.

The residue of the reacted sulphate was dissolved in water. The solution was weakly alkaline and a very small quantity of elementary sulphur was isolated by flocculation with lanthanum nitrate. The sulphide was isolated with cadmium carbonate. The sulphate was precipitated from a solution to which formaldehyde had been added and the final solution obtained in this way was oxidized to give a "sulphite + thiosulphate" fraction.

Two sets of experiments were carried out, one with radioactive sulphur and one with radioactive potassium sulphate. The results are given in Tables V and VI. The oxygen balance is satisfactory in both tables. In Table VI, the sulphur balance

TABLE V

RELATIVE SPECIFIC ACTIVITY OF PRODUCTS OF THE REACTION BETWEEN POTASSIUM SULPHATE AND RADIOACTIVE SULPHUR VAPOUR (based on the sp. activity/mg S of the original vapour = 1.00)

Duration of experiment (min)	Relative specific activity			
	sulphate in residue	sulphide in residue	sulphur condensed	SO_2 from gas
16	0.49 (0.65)	0.72 (0.55)	0.95	0.92 (0.47)
90	0.46 (0.64)	0.87 (0.65)	0.92	0.93 (0.60)

The numbers between brackets indicate the number of moles or g atoms formed per mole of K_2SO_4. About 7 atoms of sulphur were used per mol. of sulphate (temp. 790°C).
Sulphite and thiosulphate were found in the residue in very small quantities.

TABLE VI

RELATIVE SPECIFIC ACTIVITY OF THE PRODUCTS OF THE REACTIONS BETWEEN SULPHUR VAPOUR AND RADIOACTIVE POTASSIUM SULPHATE based on the sp. activity of the sulphur in the original sulphate = 1.00

Temp. (°C)	Duration of experiment (min)	Relative sp. activity				
		sulphate in residue	sulphite + thiosulphite in residue	sulphide in residue	sulphur condensed	SO_2 from gas
790	35	0.45 (0.77)	0.20 (0.11)	0.21 (0.33)	0.06 (5.0)	0.12 (0.49)
795	35	0.54 (0.76)	0.15 (0.06)	0.17 (0.63)	0.10 (5.0)	0.11 (0.50)
790	5	0.81 (0.88)	0.09 (0.12)	0.09 (0.34)	0.08 (5.2)	0.07 (0.27)
795	4	0.66 (0.78)	(0.05)	0.22 (0.49)	0.06 (5.0)	0.06 (0.45)
795	150	0.52 (0.71)	0.08 (0.15)	0.08 (0.56)	0.09 (4.9)	0.10 (0.55)
795	120	0.38 (0.71)	0.10 (0.07)	0.10 (0.83)	0.12 (4.9)	0.11 (0.61)
910	50	0.08 (0.54)	0.05 (0.11)	0.06 (1.07)	0.18 (4.3)	0.28 (0.92)
910	60	0.16 (0.61)	(0.03)	0.09 (0.87)	0.17 (4.5)	0.23 (0.78)

The numbers between brackets indicate the number of g atoms or moles formed per mole of K_2SO_4. 5.5 atoms of sulphur were used per mol. of sulphate.

is good too. in Table V this balance could not be checked, as the amount of elementary sulphur deposited was not determined. Potassium balances could not be obtained from our sulphur determinations as the sulphide fractions contain polysulphides. Radioactivity balances could not be made with any accuracy for the experiments in Table V due to the large activity in the elementary sulphur. In Table VI the activity balances are satisfactory, the agreement being within 20%.

We have already mentioned experiments which demonstrated that sulphur is exchanged easily at temperatues of 800°C or higher between sulphur vapour and sulphur dioxide. This fact should certainly be reflected in the measurements that are under discussion and it is satisfactory to see that specific activities are equal in the SO_2 and in the sulphur vapour, as reported in Table V, where the reservoir of the large excess of radioactivity is in the sulphur vapour. In Table VI, where this reservoir is in the solid potassium sulphate, approximate equality of the specific activities of elementary sulphur and of sulphur dioxide is to be expected too, but the activity of the sulphur should be somewhat lower, as the reaction is likely to have been slower during one part of the time than during other parts. Such a difference is especially evident in the first experiment and in the two last experiments of Table VI.

For the reduction of sulphate by sulphur vapour, BRUECKNER [7] has suggested the mechanisms (6) and (7). (The question is left open as to which component of the sulphur vapour takes part in the reaction).

$$\begin{cases} 4\,K_2SO_4 + 2\,S \rightarrow 4\,K_2SO_3 + 2\,SO_2 \\ 4\,K_2SO_3 \rightarrow 3\,K_2SO_4 + K_2S \end{cases} \quad (6)$$

$$\begin{cases} 4\,K_2SO_3 + 4\,S \rightarrow 4\,K_2S_2O_3 \\ 4\,K_2S_2O_3 \rightarrow 3\,K_2SO_4 + K_2S_5 \end{cases} \quad (7)$$

The products of the two reaction sequences are not in the first instance equivalent, but absorption or splitting-off of sulphur vapour can render their final results identical, at least from a gravimetric point of view. There would be little sense in discussing the movement of the radioactive atoms between the different salts for, as we have seen above, at 800° C the exchange of sulphur between SO_2 and sulphate takes place with reasonable velocity. However, the general balance of radioactivity in the solid is of appreciable interest and can be discussed with profit. If the reaction would run according to (6) (i.e. in such a way that all the sulphur atoms which leave the solid do so as SO_2), and if we assume complete equalization of the specific activity of SO_2 with sulphate, but no exchange with sulphide, we can write formula (8) which does not depend on the exact mechanisms of the reaction:

$$\mathrm{d} \ln [K_2S^*O_4] = -3 \mathrm{d} \ln [K_2SO_4] \tag{8}$$

Even a simple reaction like (9) would lead to the same result.

$$K_2SO_4 + 2\,S \rightarrow K_2S + 2\,SO_2 \tag{9}$$

Formula (8) indicates that the relative sp. activity of the sulphate sulphur given in Table VI should not be lower than the square of the fraction of the sulphate remaining in the residue. (The relative sp. activity might, of course, be higher in case some of the original sulphate had not participated in the exchange with the SO_2.) The fact that this conclusion is in contradiction with the last two experiments of Table VI indicates that there also exists some other mechanism by which exchange occurs between the sulphur of the sulphate and of the sulphur vapour. This may be a direct exchange reaction or it may go through some intermediate, like SO_2 (for which the exchange both with sulphate and with sulphur vapour has been demonstrated above) or sulphide (for which such exchange processes have not been demonstrated but where they may well take place. The absence of formation and decomposition of polysulphide would even be quite unexpected, and these combined processes would amount to an exchange of sulphur between sulphide and sulphur vapour). The fact that the specific activity for SO_2 is higher than that for sulphate in the two last experiments of Table VI does not exclude SO_2 as an intermediate, as the SO_2 value is an average which includes contributions from the early part of the experiment when the specific activity of the sulphate sulphur was much higher than it was at the end. Formation and possibly decomposition of thiosulphate might also be responsible for part of the loss of the activity from the sulphate sulphur, if exchange takes place between sulphate and the salts involved in (7).

In this connection it should also be borne in mind that in (6) and (9) we have assumed that all sulphur atoms which, participating in the reaction, leave the solid are oxidized. Although we do not know what kind of sulphur molecule is responsible for the chemical process, it certainly will not be a single sulphur atom. Thus it is by no means impossible that sulphur atoms leave the activated complex without being oxidized and, if this is the case, these atoms may well carry away in the vapour a part of the activity from the sulphate.

One cannot help wondering, however, whether the use of such well-defined chemical compounds in the explanation of the transfer of radiosulphur is not too artificial. It might well be that, in the reaction between sulphur vapour and solid sulphate, chemical bonds are weakened and even temporarily broken, and that

the intermediate stages during which S^{35} is transferred from one compound to the other do not really correspond to any of the stoichiometric formulations normally used for ordinary chemical substances.

In any case, it is evident that all sulphur fractions exchange easily at the temperatures of our experiments, if it is kept in mind that the specific activity of some fractions represent, conditions at the end of the experiment, whereas the activity of others corresponds to an average over the duration of the experiment, as mentioned above. The process observed in this system may also have been instrumental in transferring the radiosulphur in the decomposition of sodium thiosulphate in an inert atmosphere, if, at least, these reactions can take place at temperatures as low as those which are sufficient for the last-mentioned conversion.

ACKNOWLEDGEMENT

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DISCUSSION

R. Lindner (Sweden) said that the rate of the exchange $K_2SO_4 \rightleftarrows SO_2$ might be governed by the self-diffusion of sulphur in the sulphate, and asked whether Mr. Aten had tried to evaluate the curves assuming a diffusion process. He suggested that the point could be clarified by using potassium sulphate particles of uniform grain size, applying the diffusion equation of Serin and Ellickson and seeing whether the results obtained in that way agreed with the experimental results.

A. H. W. Aten said he was sure that diffusion had an important effect on the rate of the reaction, though it was interesting to note that a higher temperature was required for the sulphate reaction than for the sulphite reaction, which seemed to point to a chemical effect as well. However, he was grateful to Mr. Lindner for his suggestion and would certainly bear it in mind.

PRINCIPLES AND APPLICATIONS OF HETEROGENEOUS ISOTOPIC AND NON-ISOTOPIC ION EXCHANGE ON THE SURFACE OF IONIC CRYSTALS

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Abstract — Résumé — Аннотация — Resumen

Principles and applications of heterogeneous isotopic and non-isotopic ion exchange on the surface of ionic crystals. Ionic crystals which are in contact with an electrolytic solution exchange isotopic and non-isotopic ions on their surfaces. These processes are treated quantitatively and measured as a function of time.

In general, two different processes are observed: exchange with the surface ions, and recrystallization of the ionic crystals in the solution. During ion exchange, recrystallization is only observed if mixed crystals are formed.

The rate of the ion exchange on the surface is determined by the surface reaction, not by diffusion in the solution.

The following systems are discussed as examples of isotopic and non-isotopic ion exchange reactions:

$$Sr^{90++}/SrSO_4,\ Sr^{90++}/CaSO_4 \cdot 2H_2O,\ Sr^{90++}/BaSO_4.$$

These investigations are important for the separation of carrier-free nuclides from aqueous solutions.

One practical application is the separation of Sr^{90} on "barium sulphate columns".

Principes et applications de l'échange hétérogène d'ions isotopiques et non isotopiques à la surface des cristaux ioniques. Les cristaux ioniques qui se trouvent en contact avec une solution électrolytique échangent à leur surface des ions de nature isotopique et non isotopique. Ces phénomènes sont étudiés du point de vue quantitatif et mesurés en fonction du temps.

En règle générale, on observe deux phénomènes: échange avec les ions de la surface et recristallisation des cristaux ioniques dans la solution. Durant l'échange d'ions, ce phénomène de recristallisation n'est observé que s'il se forme des cristaux mixtes.

La vitesse de l'échange ionique à la surface est en général déterminée par la réaction qui se produit en surface et non par la diffusion dans la solution.

Pour montrer les réactions d'échange d'ions isotopiques et non isotopiques, les auteurs du mémoire examinent, à titre d'exemple, les systèmes suivants:

$$Sr^{90++}/SrSO_4,\ Sr^{90++}/CaSO_4 \times 2H_2O,\ Sr^{90++}/BaSO_4.$$

Ces études revêtent une certaine importance pour la séparation de nuclides sans entraîneur dans des solutions aqueuses.

Une application pratique serait, par exemple, la séparation de strontium-90 sur des «colonnes de sulfate de baryum».

Основы и применение гетерогенного изотопного и неизотопного ионного обмена на поверхности ионных кристаллов. На поверхности ионных кристаллов в растворе электролита происходит обмен изотопных и неизотопных ионов. Эти процессы обмена определяются количественно и в зависимости от времени.

Как правило, наблюдают два процесса: ионный обмен на поверхности и рекристаллизацию ионных кристаллов в растворе. При ионном обмене рекристаллизация наблюдается только в том случае, если образуются смешанные кристаллы.

Скорость ионного обмена на поверхности, как правило, определяется по поверхностной реакции, а не по диффузии в растворе.

В качестве примера таких реакций изотопного и не изотопного ионного обмена рассматриваются следующие системы: $^{90}Sr^{++}/SrSO_4$, $^{90}Sr^{++}/CaSO_4 \cdot 2\,H_2O$, $^{90}Sr^{++}/BaSO_4$.

Эти исследования имеют значение для извлечения из водных растворов изотопов без носителя.

В качестве примера применения приводится отделение стронция-90 на „колонках с сульфатом бария".

Fundamentos y aplicaciones del intercambio heterogéneo de iones isotópicos y no isotópicos en la superficie de cristales iónicos. En los cristales iónicos puestos en contacto con una solución electrolítica, se produce un intercambio superficial de iones isotópicos y no isotópicos. El autor estudia los aspectos cuantitativos de estos procesos y los evalúa en función del tiempo.

En general, se observan dos procesos: intercambio con los iones de la superficie, y recristalización de los cristales iónicos de la solución. Durante el intercambio iónico sólo se produce una recristalización cuando se forman cristales mixtos.

La velocidad del intercambio iónico en la superficie es función de la reacción superficial, pero no de la difusión en la solución.

Como ejemplo de reacciones de intercambio de iones isotópicos y no isotópicos, el autor estudia los siguientes sistemas: $^{90}Sr^{++}/SrSO_4$, $^{90}Sr^{++}/CaSO_4 \cdot 2H_2O$ y $^{90}Sr^{++}/BaSO_4$.

Estas investigaciones revisten importancia para la separación de núclidos libres de portador en soluciones acuosas.

La separación de ^{90}Sr en "columnas de sulfato de bario" constituye un ejemplo de estas aplicaciones.

1. Introduction

The heterogeneous isotopic and non-isotopic ion exchange between ions in solution and ions on the surface of ionic crystals is influenced by the structure of the surface of the solid particles. Corresponding to the conditions, the precipitation of ionic crystals leads to either uncharged (equivalent), positively charged (cationic), or negatively charged (anionic) particles. The excess or potential-determining ions are part of the solid particles. The excess charge of these cationic or anionic particles is balanced by counter-ions of opposite charge in the solution. These different structures of the surface are shown schematically in Fig. 1. Uncharged (equivalent) particles must be considered to be a limiting case.

PANETH [1] has shown that the amount of heterogeneous isotopic or non-isotopic ion exchange on the surface of ionic crystals is a measure for the surface area. His method of surface determination is called the surface-exchange method. Several objections to the simple treatment of Paneth have been made [2]. More accurate methods for surface determination are now available, for instance the BET-method. Heterogeneous isotopic or non-isotopic ion exchange, however, is a good tool for studying surface reactions and the structure of a surface.

In a specially constructed simple apparatus, the heterogeneous exchange was investigated as a function of time. The investigations were carried out with the sulphates of calcium, strontium and barium; these compounds were chosen for several reasons:

(a) The solubility decreases sharply from calcium sulphate to barium sulphate; the influence of solubility on ion exchange should become evident.

(b) The sulphates of barium and strontium are isomorphous; they are not isomorphous with $CaSO_4 \cdot 2\,H_2O$. Therefore the influence of the formation of solid solutions should become noticeable too.

(c) Strontium ions and barium ions are precipitated by a saturated solution of calcium sulphate. This fact is made use of in qualitative analysis. The question was: what happens with very dilute or even carrier-free solutions of strontium or barium ions in the presence of $CaSO_4 \cdot 2\,H_2O$? Are these ions enriched or precipitated on the surface of $CaSO_4 \cdot 2\,H_2O$ or not?

(d) The exchange reactions of isotopic and non-isotopic ions on the surface of the sulphates of calcium, strontium and barium are of great interest because they offer possibilities for separating radioactive ions, especially Sr^{90}, from aqueous solutions.

2. Principles

On the surface of ionic crystals two different types of exchange reactions are possible which can be derived directly from Fig. 1.

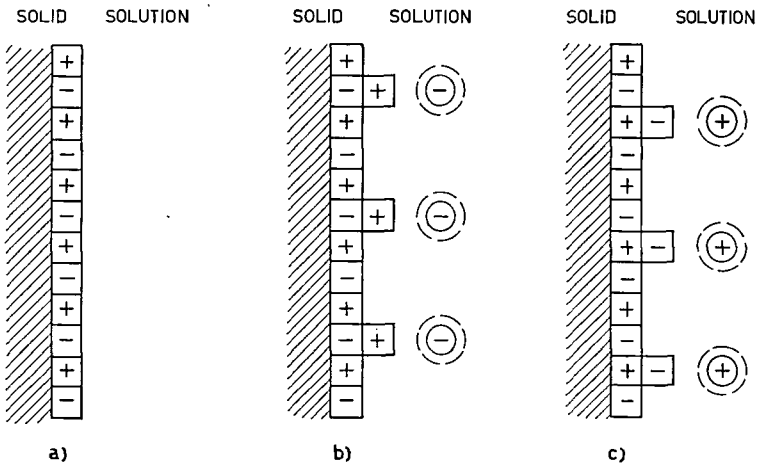

Fig. 1
Structure of the surface of ionic crystals (schematically);
a) equivalent particles: equivalent numbers of cations and anions on the surface;
b) cationic particles: excess of cations on the surface (potential-determining ions), equivalent number of counter-ions in the solution;
c) anionic particles: excess of anions on the surface (potential-determining ions), equivalent number of counter-ions in the solution.

(1) Exchange with ions on the surface (lattice ions or potential-determining ions). This type of exchange may take place on the surface of equivalent particles, cationic particles and anionic particles.

(2) Exchange with the hydrated counter-ions in the solution. This type of exchange may take place with anions on the surface of cationic particles and with cations on the surface of anionic particles.

For both types of exchange reactions some characteristics can be derived:

(1) EXCHANGE WITH IONS ON THE SURFACE

(a) The rate of exchange will generally be determined by the surface reaction at the interface between crystals and solution, for this reaction needs an energy of activation.

(b) The amount of exchange on the surface is a measure for the surface area. Introducing the area equivalent f^+ of an exchanging cation and f^- of an exchanging anion, the following relations are obtained (see Fig. 1):

exchange of cations

for equivalent particles: $f^+ = f^+_{eq.}$

for cationic particles: $\frac{1}{2} f_{eq}{}^+ < f^+ < f^+_{eq.}$

for anionic particles: $f^+ > f^+_{eq.}$

exchange of anions

for equivalent particles: $f = f^-_{eq.}$

for cationic particles: $f^- > f^-_{eq.}$

for anionic particles: $\frac{1}{2} f^-_{eq.} < f^- < f^-_{eq.}$

The area equivalents f^+ and f^- can be estimated from density or lattice parameters. But they depend on the faces of the crystals and the numbers of exchanging cations and anions (i.e. f^+ and f^-) are not necessarily equivalent. If the exact values of f^+ and f^- are not known, different values for the surface area may then be obtained by the surface-exchange method using cations or anions. Different values for the surface area of strontium sulphate have been found by STOW and SPINKS [3] who measured the exchange of strontium ions and of sulphate ions.

(c) If the non-isotopic ions are able to form solid solutions with the solid particles, this formation of solid solutions will be observed during the continuous recrystallization of the solid particles by a slow decrease of the concentration or activity of exchanging ions in the solution. This slow process will follow the recent rapid process of exchange on the surface.

(2) EXCHANGE WITH COUNTER-IONS

(a) Generally no activation energy will be necessary; the rate of exchange will therefore be determined by diffusion of the ions in the solution.

(b) Cationic particles can only exchange anionic counter-ions; anionic particles can only exchange cationic counter-ions.

(c) Recrystallization has no influence on the exchange with counter-ions.

For the case of exchange of isotopic ions, PANETH [1] used the following equilibrium relation between the number of ions on the surface ($^*N_o$, N_o) and in solution ($^*N_L$, N_L)

$$\frac{^*N_o}{^*N_L} = \frac{N_o}{N_L} \tag{1}$$

This relation leads to the following equation for calculating the surface area:

$$F = \left(\frac{i_0}{i} - 1\right) c_L \times V \times L \times f, \tag{2}$$

where i_0 = concn or counting rate of the exchanging ions in the solution at the beginning of the exchange reaction,

i = concn or counting rate of the exchanging ions in the solution in equilibrium,

c_L = total concn of the exchanging ions in the solution,
V = vol. of the solution,
L = Avogadro's number and
f = area equivalent of the exchanging ions.

In the case of exchange of non-isotopic ions of equal charge, we have the following equilibrium:

$$A_L^{n+} + B_o^{n+} \rightleftharpoons A_o^{n+} + B_L^{n+}$$

(the index L indicating ions in solution and the index o indicating ions on the surface).

The equilibrium constant

$$K = ([A^{n+}]/[B^{n+}])_o/([A^{n+}]/[B^{n+}])_L \tag{3}$$

can be calculated from the amount of exchange, if the number of exchangeable ions on the surface (F/f) is known. It follows that

$$K = \frac{[c_B{}^0/c_A{}^0] + [(i_o - i)/i_0]}{\left(\frac{i_0}{i_0 - i} \times \frac{F}{f} \times \frac{1}{c_A{}^0 \times V \times L} - 1\right)\frac{i}{i_o}} \tag{4}$$

where $c_B{}^0$ = concentration of the ions B in the solution at the beginning and
$c_A{}^0$ = concentration of the ions A in the solution at the beginning.

Before applying formulas (2) or (4) it has to be proved that the decrease in concentration or activity observed is not due to precipitation, recrystallization or adsorption. In most cases this can be done by measuring the exchange reaction as a function of time and as a function of temperature. In this way errors can be avoided.

3. Experimental

(a) Apparatus

The simple apparatus shown in Fig. 2 was used for all investigations of the heterogeneous ion exchange reactions. In this apparatus, samples of the solutions were sucked in, small volumes of 0.1 or 0.2 ml were taken with a pipette and the solution was pressed out again by applying nitrogen or air pressure. The apparatus was held at constant temperature, normally at 20°C.

(b) Solids

The solids were prepared by precipitation reactions from pa grade reagents. Equivalent particles were obtained by precipitation from equivalent amounts of solutions and thorough washing of the solid several times. Cationic particles were obtained by using an excess of cations, anionic particles by using an excess of anions; the excess of cations or anions was not removed but was present during the exchange reaction.

(c) Ion exchange

The concentrations of the exchanging ions in the added solutions were estimated by titration with EDTA. Schwarzenbach's method of titration was improved; 10^{-5} mole of calcium, strontium or barium were determined with an error of 1%. In order to avoid adsorption effects on the walls of glass vessels and pipettes, they were rinsed with solutions of the corresponding ions. The solutions added were saturated with the sulphates of calcium, strontium or barium. Then

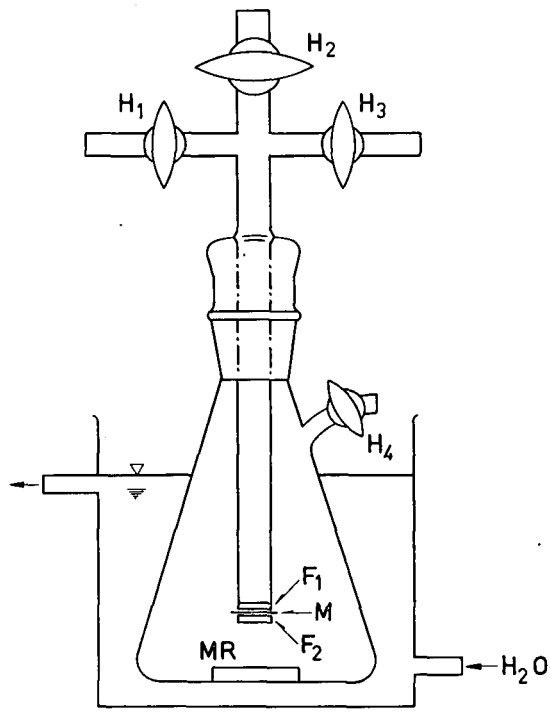

Fig. 2
Apparatus for measuring the heterogeneous ion exchange as a function of time;
H_1, H_2, H_3, H_4 = stopcocks,
F_1, F_2 = glass frits,
M = membranous filter,
MR = magnetic stirrer.

were added appropriate small amounts of Ca^{45} (high specific activity), of carrier-free Sr^{89} or carrier-free $Sr^{90} + Y^{90}$ or of carrier-free $Ba^{140} + La^{140}$. 0.1 or 0.2-ml samples of the solutions were taken at the beginning of the experiment and at short intervals afterwards. These samples were dried on dimpled source trays of aluminium and counted with a Geiger or scintillation counter.

4. Results

The most interesting results of the isotopic and non-isotopic exchange reactions studied in the systems $Me^{(1)++}$ (aq)/$Me^{(2)}$ So_4(s) ($Me^{(1)}$, $Me^{(2)}$ = Ca, Sr, Ba) are presented and discussed.

(A) Isotopic ion exchange in the system $*Sr^{++}(aq)/SrSO_4(s)$

Fig. 3 gives the result with equivalent particles. Two reactions are observed, ion exchange and recrystallization. Both reactions follow a rate-law of the first order. When anionic particles are used — excess of sulphate ions in solution — precipitation occurs, Fig. 4. It is interesting to note that the half-time for this precipitation reaction is identical with the half-time for isotopic ion-exchange

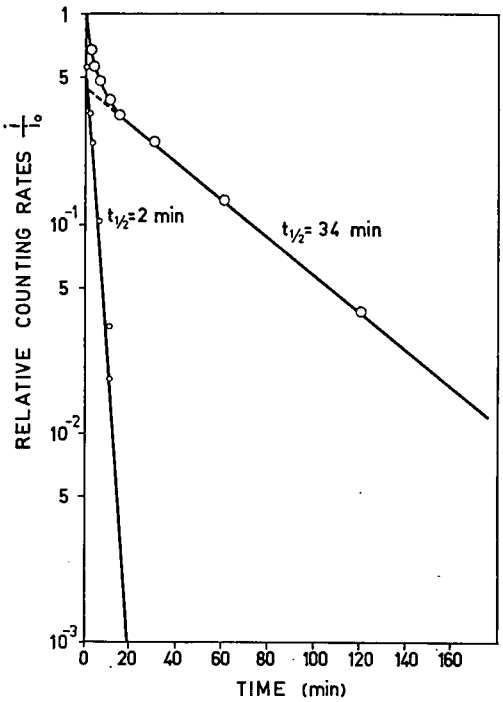

Fig. 3
System $*Sr^{++}(aq)/SrSO_4(s)$, equivalent particles; Isotopic ion exchange and recrystallization as a function of time.

(Fig. 3). In another experiment, carrier-free Sr^{90} was added in order to avoid precipitation; in this case no precipitation occurs but only isotopic exchange (Fig. 5).

The rate-law of the first order, which is observed in all experiments, indicates that the ion-exchange reaction is controlled either by diffusion in the solution or by the surface reaction. Table I lists the rate constants calculated for diffusion and the rate constants observed for some exchange reactions. These figures show that the exchange reactions are many times slower than expected for diffusion-controlled reactions. Therefore the surface reaction itself is the rate-determining step in the exchange reactions.

The exchange reaction has also been measured at different temperatures (20° and 50°C). At higher temperatures the amount of exchange is the same, but the rate of exchange is very much higher. By evaluating the different rates of exchange at different temperatures, the activation energy for the surface reaction was found to have a value of about 19 kcal/mole. This activation energy seems to be necessary for stripping off the water molecules of the hydrated ions in solution.

Using formula (2) the calculation of the specific area of the solids yields rather good values for equivalent particles. When calculating the specific area of anionic particles by inserting the same area equivalent as in the case of equivalent particles and by inserting the concentration of strontium ions in solution (as given by the

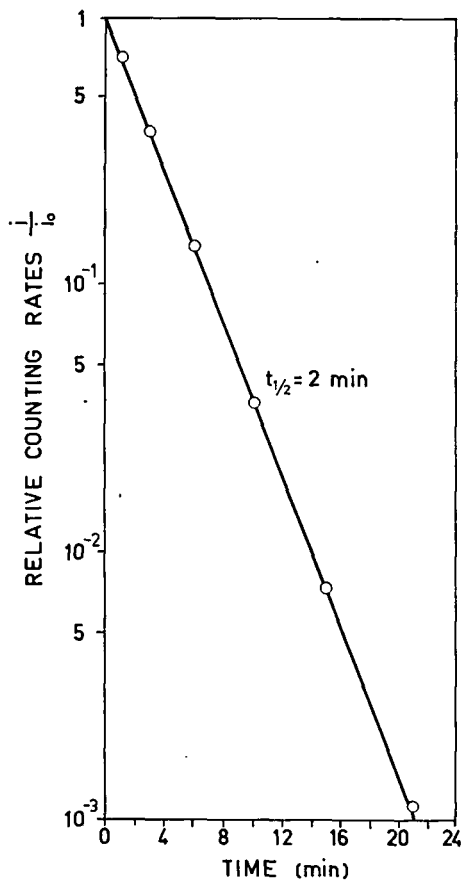

Fig. 4
System $*Sr^{++}(aq)/SrSO_4(s)$, excess of sulphate ions in solution (anionic particles); precipitation of $SrSO_4$, showing the same half-time as the isotopic ion exchange.

solubility product and the concentration of sulphate), the specific area obtain is about 40 times too small. There are two reasons for this deviation:

1. The area equivalent for anionic particles is greater than for equivalent particles, as stated in section 2: ($f^+ > f^+_{eq}$).
2. In the solution there are not only strontium ions but undissociated strontium sulphate is present too, its concentration being independent of the sulphate-ion concentration. In the presence of sulphate ions this concentration of undissociated strontium sulphate is relatively high compared with the concentration of strontium ions. This result has been proved directly by measuring the concentration of strontium sulphate in solutions of sulphuric acid.

(B) ION EXCHANGE IN THE SYSTEM $*Sr^{++}(aq)/CaSO_4 \cdot 2H_2O(s)$

The solubility of calcium sulphate is much higher than the solubility of strontium sulphate. In this system only a small decrease of activity in solution was

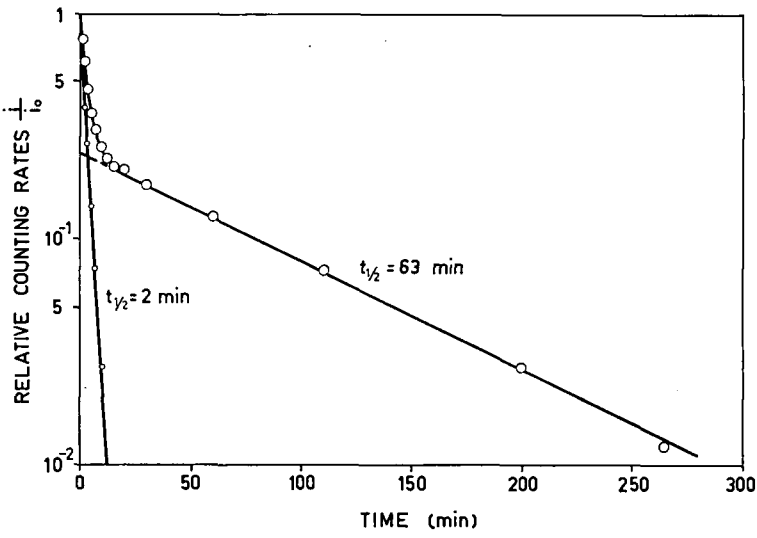

Fig. 5
System $*Sr^{++}(aq)/SrSO_4(s)$, excess of sulphate ions in solution (anionic particles); using carrier-free Sr^{90}, no precipitation but isotopic ion exchange and recrystallization are observed.

TABLE I

RATE CONST. CALCULATED FOR ION-EXCHANGE REACTIONS CONTROLLED BY DIFFUSION AND RATE CONSTANTS OBSERVED

Strontium sulphate solids	rate const. calculated for ion-exchange controlled by diffusion (sec^{-1})	rate const. observed (sec^{-1})
equivalent particles (from 1-M solutions)	> 0.2	0.006
equivalent particles (from 0.1-M solutions)	> 0.06	0.001
anionic particles (from 1-M solutions)	> 0.1	0.006
anionic particles (from 0.1-M solutions)	> 0.01	0.0009
cationic particles (from 1-M solutions)	> 0.6	0.003
cationic particles (from 0.1-M solutions)	> 0.06	0.003

observed in the presence of equivalent and anionic particles, although the solubility product of strontium sulphate was exceeded considerably. This is shown in Fig. 6. There seems to be an ion exchange on the surface, but even after a long time no further decrease of activity is observed.

As a result of these experiments it follows that strontium ions are not enriched on the surface of solid $CaSO_4 \cdot 2H_2O$. Using formula (4), a value of about 0.8 was calculated for the equilibrium constant K of the ion-exchange reaction. Further-

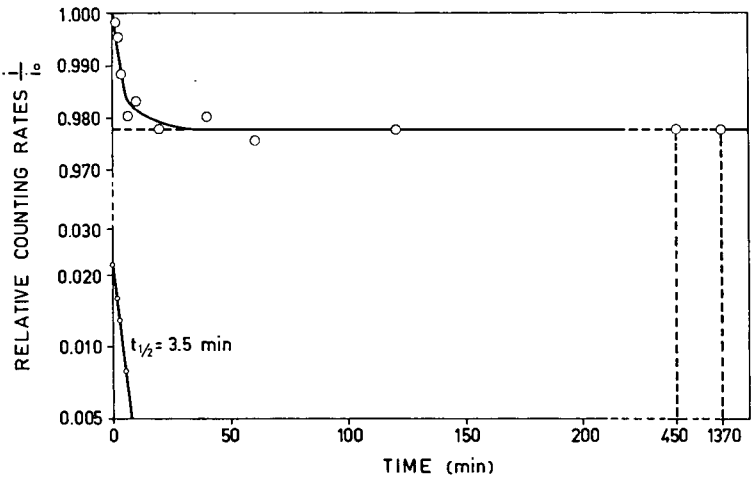

Fig. 6
System $*Sr^{++}(aq)/CaSO_4 \cdot 2H_2O(s)$; the solubility product of $SrSO_4$ is exceeded considerably; after a very low decrease at the beginning the activity remains constant.

more, in the presence of solid $CaSO_4 \cdot 2H_2O$ and an excess of sulphate ions in solution — i.e. when the solubility product of strontium sulphate is exceeded considerably — strontium ions are not precipitated. Strontium ions do not take part in the recrystallization of $CaSO_4 \cdot 2H_2O$ because the formation of solid solutions is not possible; therefore the activity in the solution remains constant after the falling-off at the beginning.

(c) Ion exchange in the system $*Sr^{++}(aq)/BaSO_4(s)$

The solubility of barium sulphate is much lower than the solubility of strontium sulphate. Solutions of strontium ions in contact with solid barium sulphate show ion exchange and recrystallization. The equilibrium constant for this exchange reaction was found to be of the order of $K = 0.1$.

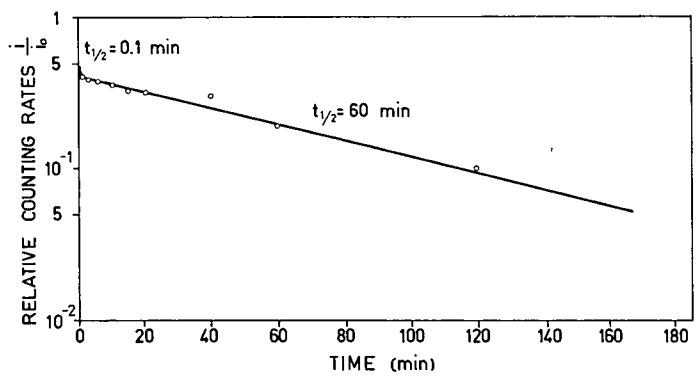

Fig. 7
System $*Sr^{++}(aq)/BaSO_4(s)$
The solubility product of $SrSO_4$ is not exceeded; a fast precipitation reaction occurs because the solubility of $SrSO_4$ is lowered considerably in the presence of solid $BaSO_4$.

In the presence of a small excess of sulphate ions in solution (anionic particles), a very rapid precipitation of strontium ions is observed, as shown in Fig. 7. Under these conditions the solubility product of strontium sulphate is not exceeded. It follows that the solubility of strontium sulphate is lower if the solution is in contact with solid barium sulphate. In agreement with this result, SUNDERMAN [4] observed that precipitation of strontium sulphate is more quantitative in the presence of solid barium sulphate. The solubility product of strontium sulphate under these conditions has been calculated from the data of the heterogeneous exchange reactions in the system $*Sr^{++}(aq)/BaSO_4(s)$. The results are listed in Table II. These results must be explained by the fact

TABLE II

SOLUBILITY PRODUCT OF STRONTIUM SULPHATE IN PRESENCE OF SOLID BARIUM SULPHATE
(solubility product of strontium sulphate in presence of solid strontium sulphate 4.1×10^{-7})

Barium sulphate solids	Concn of SO_4^{--}-ions in solution (mole/l) given	Concn of Sr^{++}-ions in solution (mole/l) found	Solubility product of $SrSO_4$
anionic particles ..... (from 25 ml 0.1 *m*-$Ba(NO_3)_2$ and 25 ml 0.2 *m*-Na_2SO_4)	3.5×10^{-2}	7.6×10^{-7}	2.7×10^{-8}
anionic particles ..... (from 25 ml 0.1 *m*-$Ba(NO_3)_2$ and 28 ml 0.1 *m*-Na_2SO_4)	4.2×10^{-3}	6.1×10^{-6}	2.6×10^{-8}

that by ion exchange on the surface of barium sulphate, solid solutions are formed having a lower partial solubility of strontium sulphate than that of crystals of pure strontium sulphate. This explanation is confirmed by direct measurements of the partial solubilities of strontium sulphate and barium sulphate using solid solutions in the system $SrSO_4/BaSO_4$.

The rapid precipitation of strontium sulphate on the surface of solid barium sulphate, shown in Fig. 7, is very remarkable. The activation energy of the surface reaction seems to be very low in this case.

5. Applications

These investigations of the heterogeneous isotopic and non-isotopic ion exchange on the surface of ionic crystals open a new field of applications. There are analytical applications which have been mentioned already: solubilities can be lowered by adding a solid of lower solubility which is able to form solid solutions. Ions of very low concentration can be removed by heterogeneous ion exchange with suitable solids. This possibility is very important for the separation of radioactive tracers from aqueous solutions. It has been proposed by SUNDERMAN and MEINKE [5] to remove tracers of radioactive silver by shaking the solution with solid silver halides; a heterogeneous isotopic exchange takes place and the diffusion of silver ions into solid silver halides is very rapid.

The removal of radioactive ions from aqueous solutions by heterogeneous exchange of isotopic or non-isotopic ions on the surface of ionic crystals becomes effective if the following conditions are fulfilled:

(a) The solubility of the compound ought to be low.
(b) The specific area ought to be high.
(c) In the case of non-isotopic ion exchange the equilibrium constant, given by formula (3), should be high.
(d) Solution and solid ought to be easily separable.

It is most desirable to have the solid in a form suitable for filling an ion exchange column. Unfortunately most of the sparingly soluble salts cannot be used directly as column material. First it is necessary to convert them into a suitable form with high specific area. This has been made possible in the case of barium sulphate. By reactions with silica gel, a product was made containing about 50 wt. % of barium sulphate; this material can be used easily for the filling of columns. Under these conditions the barium sulphate has a specific area about ten times higher than the specific area of barium sulphate precipitated in the usual manner.

By using such a column filled with barium sulphate on silica gel, traces of Sr^{90} and other radioactive ions of strontium, barium and even calcium can be separated quantitatively from aqueous solutions by heterogeneous ion exchange. Decontamination factors greater than 10^5 can easily be achieved.

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DISCUSSION

D. Gál (Hungary) asked whether the speaker had investigated the effect of the pre-life of the precipitate on the kinetics of the isotopic exchange. In recent investigations he and his associates had found that the kinetics of the heterogeneous exchange between solid crystals and gaseous molecules depended to a very marked extent on, for example, the method of precipitation, the drying and, above all, the ageing of the crystals.

He also inquired whether the speaker had used Imre's equations—recently published in *Kolloid-Zeitschrift*—for recrystallization and pseudo-diffusion in connection with the isotopic and ionic exchange between solid surfaces and highly diluted solutions.

K. H. Lieser agreed that the kinetics of the exchange reactions depended on the precipitation method, the ageing, etc., but pointed out that, as was indicated in the paper itself, not all the results obtained had been presented therein. He and his associates had not so far applied the equations referred to.

J. Turkevich (United States of America) asked the speaker if he could give the size of the particles of $SrSO_4$ that had been used in his experiments.

K. H. Lieser said that the particle-size used ranged between 1 and 10 μm.

J. Turkevich said that "The Variation of Solubility of Strontium Sulphate *with Particle Size*"*, *described the results obtained in a study of the exchange* reaction between SO_4^{--} and $SrSO_4$, but in that study the $SrSO_4$ particles were only a few hundred Ångströms in size. A rapid exchange with the surface ions had been found and then a slow exchange corresponding to diffusion into the solid.

K. H. Lieser said he and his associates had also studied the exchange of $*SO_4$-ions, labelled with S^{35}. The results to which Mr. Turkevich had referred agreed quite well with the speaker's own results.

T. Schönfeld (Austria) said that the efficiency with which not-easily-soluble sulphates eliminated Sr^{90} from solutions depended also on kinetic factors such as recrystallization and, perhaps, self-diffusion in the crystal. He wished to know whether, in the speaker's investigations, $BaSO_4$ had proved superior to $SrSO_4$ in those respects as well as in respect of solubility.

K. H. Lieser said recrystallization had been observed in the system $*Sr^{++}$ (aq)/$BaSO_4$ as well as in the system $*Sr^{++}$(aq)/$SrSO_4$. In the case of perfect crystals, the ions entered the interior of the crystals mainly by recrystallization; the self-diffusion was much slower. Given plenty of time, the capacity of $SrSO_4$ and $BaSO_4$ would be similar. He and his associates had preferred $BaSO_4$ because of its lower solubility, although the equilibrium constant for the exchange reaction was only of the order of 0.1.

* *These proceedings* **III** 531

EMPLOI DU CARBONE-14 POUR L'ÉTUDE DE L'ÉCHANGE ÉLÉMENTAIRE DE CARBONE ENTRE LE MÉTHANE ET LES RÉSIDUS DE CHIMISORPTION DE CELUI-CI SUR FILMS MÉTALLIQUES

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Abstract — Résumé — Аннотация — Resumen

Use of carbon-14 for the study of elementary carbon exchange between methane and its chemisorption residues on metallic films. After giving the results of the most recent work done with a view to providing a rational account of the exchanges between two gases in contact with a catalyst, the authors, using C^{14}, proceed to study elementary exchange between methane and its chemisorption residues on molybdenum films.

The surface is labelled in two ways: by chemisorption of $C^{14}H_4$ at different temperatures; or by exchange between $C^{14}H_4$ with a high specific activity and a metallic film previously treated with inactive methane. The C^{14} is counted in the form of CO_2 in the Geiger region.

The results show that the exchange rate is measurable from about 100°C onwards and that it reaches a maximum at about 250°C. Furthermore, the exchange is governed by laws which vary according to the prior treatment of the surface.

On the basis of the results discussed, the authors suggest a methane displacement pattern which they compare with the CH_4 and D_2 exchange mechanisms suggested by Kemball.

Emploi du carbone-14 pour l'étude de l'échange élémentaire de carbone entre le méthane et les résidus de chimisorption de celui-ci sur films métalliques. Après avoir rappelé les résultats des derniers travaux qui conduisent à décrire un schéma rationnel des échanges entre deux gaz au contact d'un catalyseur, les auteurs, à l'aide de ^{14}C, étudient l'échange «élémentaire» entre le méthane et ses résidus de chimisorption sur films de molybdène.

La surface est marquée soit par chimisorption de $^{14}CH_4$ à différentes températures, soit par échange entre du $^{14}CH_4$ à haute activité spécifique et un film métallique préalablement traité par du méthane inactif. Le ^{14}C est compté sous forme de CO_2 suivant le principe du compteur flow.

Les résultats font apparaître que la vitesse d'échange est mesurable à partir de 100°C environ et passe par un maximum vers 250°C. De plus, l'échange obéit à des lois différentes suivant le traitement préalable de la surface.

Ces résultats discutés permettent aux auteurs de proposer un schéma de déplacement du méthane, schéma qu'ils comparent aux mécanismes proposés par Kemball dans l'échange entre CH_4 et D_2.

Применение углерода-14 для изучения элементарного обмена углерода между метаном и его остатками химической сорбции на металлических пленках. Представив результаты последных работ, которые позволяют описать рациональную схему обменов между двумя газами в контакте с катализатором, авторы изучают при помощи углерода-14 „элементарный" обмен между метаном и его остатками химической сорбции на молибденовых пленках.

Поверхность метится либо путем химической сорбции $C^{14}H_4$ при различных температурах, либо путем обмена между $C^{14}H_4$ с высокой удельной активностью и металлической пленкой, предварительно обработанной неактивным метаном. Углерод-14 измеряется в виде CO_2 в зависимости от принципа проточного счетчика.

Результаты показывают, что скорость обмена измерима, начиная с температуры около 100° С, и максимально увеличивается к 250° С. Более того, обмен подчиняется различным законам в зависимости от предварительной обработки поверхности.

Эти обсуждаемые результаты позволяют авторам предложить схему перестановки метана, которую они сравнивают с механизмами, предложенными Кембэллом для обмена между CH_4 и D_2.

Empleo del carbono-14 para estudiar el intercambio elemental del carbono entre el metano y sus residuos de quimiosorción sobre partículas metálicas. Después de presentar los resultados de los trabajos recientemente realizados con miras a establecer un esquema racional de los intercambios que tienen lugar entre dos gases en contacto con un catalizador, los autores estudian con ayuda de ^{14}C el intercambio "elemental" entre el metano y sus residuos de quimiosorción sobre películas de molibdeno.

Los autores han empleado dos métodos para marcar la superficie: por quimiosorción de $^{14}CH_4$ a diferentes temperaturas, y por intercambio entre $^{14}CH_4$ de elevada actividad específica y una película metálica previamente tratada con metano inactivo. Han contado el ^{14}C en forma de CO_2 en un contador de flujo.

Los resultados indican que la velocidad de intercambio es medible a partir de unos 100° C, alcanzando un máximo hacia los 250° C. Además, el intercambio obedece a leyes diferentes según el tratamiento térmico que la superficie haya sufrido previamente.

Estos resultados permiten a los autores proponer para el desplazamiento del metano un esquema que comparan con los mecanismos propuestos por Kemball para el intercambio entre CH_4 y D_2.

1. Introduction

Dans le cadre de l'étude des réactions hétérogènes faisant intervenir des hydrocarbures, différentes méthodes sont utilisées.

La chimisorption permet de déterminer essentiellement la composition statistique des radicaux de surface formés ainsi que l'apparition de phénomènes tels que la carburation. Par déplacement de ces radicaux de surface, il est possible de préciser la nature de ceux-ci.

Enfin, l'étude des cinétiques d'échange entre deux gaz au contact d'un catalyseur conduit à décrire un schéma réactionnel impliquant l'existence de certains radicaux en surface. Ceux-ci sont généralement considérés comme étant en équilibre d'adsorption-désorption avec la phase gazeuse. Or nous avons montré, au cours de l'étude d'échanges de radiohalogènes [1], que le catalyseur n'est pas la surface métallique seule mais bien un radical adsorbé en équilibre d'échange avec chacune des deux espèces gazeuses. Ce mécanisme permet par conséquent de décomposer l'échange «global» en ses deux étapes «élémentaires».

Récemment, nous nous sommes attachés à l'étude de la réaction du méthane sur films de molybdène. La chimisorption et le déplacement par l'acide chlorhydrique de la surface obtenue ont déjà fait l'objet d'une étude [2]. De plus, différents auteurs ont étudié les échanges «globaux» entre CH_4 et D_2 ainsi qu'entre CH_4 et CD_4 sur des films métalliques [3].

Le présent travail a pour but d'étudier l'échange «élémentaire» de carbone entre le méthane et ses résidus de chimisorption sur films de molybdène, à l'aide du carbone-14.

Partie expérimentale

Appareillage

L'appareil est divisé en deux parties: l'enceinte réactionnelle et la section d'analyse et de comptage d'activité. L'enceinte réactionnelle a déjà été décrite précédemment [3]. Rappelons cependant que les différentes sections sont isolées au moyen de vannes à mercure. La partie d'analyse est composée d'un four en quartz contenant de l'oxyde de cuivre ainsi que des ampoules de dessiccation à anhydride phosphorique et des pièges de distillation sous vide. La description de cette section, de même que celle des compteurs, est reprise en détail ailleurs [4].

Réactifs et catalyseur

Les réactifs sont les mêmes que ceux déjà utilisés [2]. Le méthane radioactif est fourni par le Centre d'Amersham à l'activité spécifique de 1 c par mole. L'évaporation sous vide d'un filament de molybdène est conduite de même que précédemment [1, 2].

Mode opératoire

Une fois l'évaporation du filament de molybdène terminée, à 0°C, le méthane est aussitôt chimisorbé. Selon les expériences, on utilise du méthane radioactif ou ce même gaz non actif. A partir de ce moment, le traitement de la surface diffère suivant les essais. Dans le cas où la surface est saturée de méthane radioactif, le film est porté à la température de traitement, soit sous vide soit en présence du gaz. Par contre, si la saturation à 0°C est effectuée avec du méthane non radioactif, le catalyseur est porté à la température de traitement en présence de ce gaz; l'ampoule est ensuite évacuée, et la surface est marquée par échange avec du méthane radioactif ou un mélange de ce gaz et d'hydrogène. Dans tous les cas, le méthane a la même concentration radiochimique. Pendant la réaction, de même qu'au cours de l'évaporation et du traitement de la surface, le piège de protection de l'enceinte est plongé dans la neige carbonique. Après réaction, les gaz sont évacués par la pompe de Tœpler. A ce moment, une prise est généralement faite pour l'analyse au spectromètre de masse. L'enceinte est alors évacuée jusqu'à une pression de 10^{-6} mm. Les gaz condensables obtenus par la combustion sur l'oxyde de cuivre à 700°C sont desséchés sur de l'anhydride phosphorique et distillés sous vide. Des analyses par spectrométrie de masse montrent qu'après ces purifications il n'y a plus que de l'anhydride carbonique.

Comptage

Le carbone-14 est compté sous forme d'anhydride carbonique suivant le principe du compteur «flow». Le remplissage du compteur s'effectue par détente d'une quantité constante d'anhydride carbonique mesurée à la jauge de Bourdon et par condensation de cette quantité dans le compteur. Le gaz de comptage est détendu alors jusqu'à une pression totale de 10 cm.

Les caractéristiques des compteurs ainsi remplis sont les suivantes:

seuil: (980 ± 20) V,
plateau: 600 V,
pente: inférieure à 2% par 100 V,
fond continu: 1,5 à 2,5 coups par seconde.

On n'observe pas d'effet de contamination, à condition d'avoir pompé sous haut vide pendant au moins deux heures avant le remplissage. Après vérification des bonnes conditions de remplissage par la mesure des caractéristiques du compteur, le comptage s'effectue dans le domaine de Geiger au potentiel constant de 1200 V. Les compteurs sont étalonnés par dilutions successives du méthane à 1 c par mole. La linéarité de la réponse du compteur en fonction de la concentration radiochimique est vérifiée entre $5 \cdot 10^{-5}$ et $5 \cdot 10^{-2}$ c/mole, compte tenu du temps mort imposé de 100 μs.

L'erreur due au comptage ne dépasse pas 2%.

Résultats

Au cours de l'étude de la chimisorption du méthane sur films de molybdène, nous avons constaté que l'évacuation de la phase gazeuse n'était accompagnée d'aucune désorption mesurable. C'est pourquoi nous admettrons que cette opération ne modifie pas la composition statistique de la surface. Par contre, à partir de 100°C, la chimisorption de méthane était accompagnée de désorption d'hydrogène [2, 5], dont la pression partielle limitait la quantité chimisorbée. De plus, nous avons montré que le remplacement du mélange gazeux obtenu par du méthane était suivi d'adsorption de nouvelles quantités de ce gaz. Au cours de ce travail, pour isoler l'échange isotopique de réactions chimiques entre le gaz et la surface, nous mettons les radicaux chimisorbés en présence de méthane seul ou d'un mélange de méthane et d'hydrogène. En effet, dans le premier cas il y a réaction chimique avec la surface, ainsi que nous l'avons fait remarquer, tandis qu'un mélange de méthane et d'hydrogène modifiera d'autant moins l'état de la surface que sa composition se rapprochera de celle du mélange gazeux après le traitement du catalyseur. Dans l'exposé des résultats, une distinction est faite selon que le film vierge est saturé, à 0°C, de méthane radioactif on non actif. Le poids du catalyseur varie de 10^{-4} à $5 \cdot 10^{-4}$ g/cm^2. Dans les tableaux, l'activité apparue en phase gazeuse est exprimée en curies par 100 mg de catalyseur. Cette manière d'exprimer les résultats se justifie par le fait, observé au laboratoire, que la quantité de méthane chimisorbée est proportionnelle au poids de catalyseur.

1. Films saturés de $^{14}CH_4$ à 0°C

Après la chimisorption, le gaz est évacué à 0°C, et l'ampoule est dégazée pendant une heure jusqu'à l'obtention d'une pression inférieure à 10^{-5} mm. A ce moment, des quantités toujours identiques de méthane inactif ($p = 20$ mm) sont mises en présence du film successivement à différentes températures pendant des temps égaux à 24 h. Les résultats sont consignés dans la colonne 2 du tableau I. Entre chaque essai, après avoir vidé l'ampoule, on porte celle-ci sous vide à la température de l'essai suivant.

TABLEAU I

ACTIVITÉ EXTRAITE D'UNE SURFACE DE MOLYBDÈNE MARQUÉE PAR CHIMISORPTION DE CH_4^{14} A 0°C, AU COURS DE LA RÉACTION AVEC CH^4 A DIFFÉRENTES TEMPÉRATURES

Température (°C)	Essai 1 (10^{-8} c par 100 mg)	Essai 2 (10^{-8} c par 100 mg)
0	—	—
100	4	—
150	38	—
200	60	—
250	38	—
350	15	—
450	0,7	15

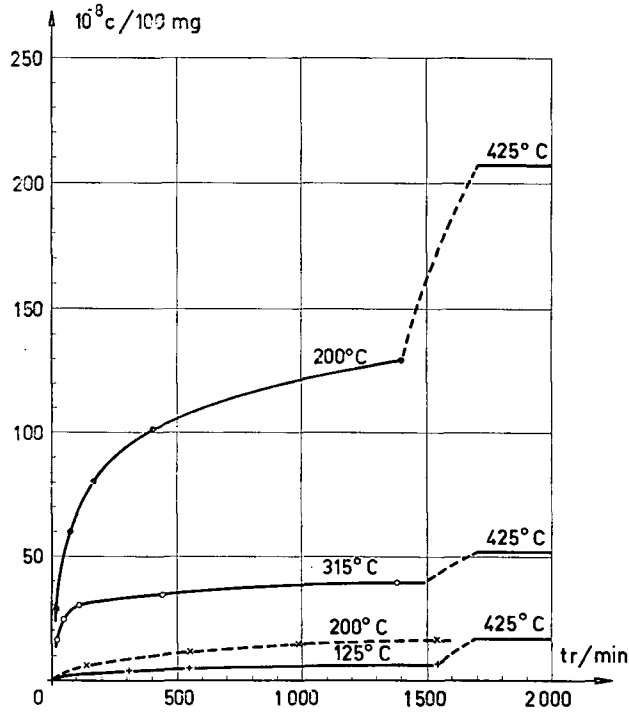

Fig. 1
Activité extraite d'une surface marquée par chimisorption de $^{14}CH_4$ à l'aide d'un mélange CH_4–H_2.

Les points expérimentaux sont établis en faisant les sommes de l'activité apparue en phase gazeuse et du temps de réaction. —La courbe en pointillé à 200°C se rapporte aux essais décrits en [5]; les temps réels sont obtenus en multipliant par 10 les valeurs lues en abscisse.

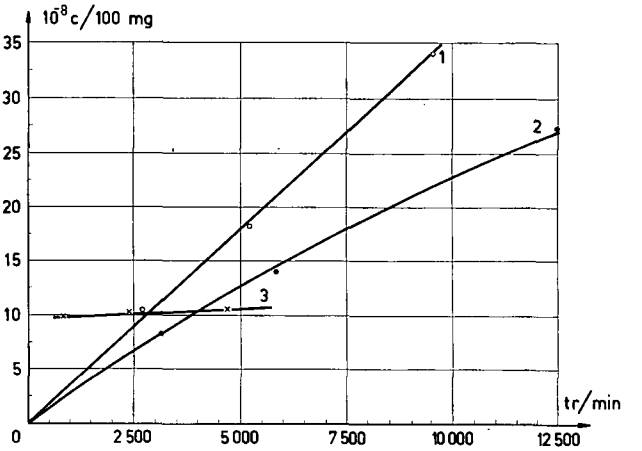

Fig. 2
Comparaison des activités extraites à 450°C par du méthane (1 et 2) ou un mélange de méthane et d'hydrogène (3) après différents traitements.
1. Film chauffé à vide à 450°C après saturation de $^{14}CH_4$ à 0°C. – 2. Film chauffé à 450°C en présence de CH_4 puis traité par du $^{14}CH_4$ à la même température. – 3. Film chauffé à 125°C en présence de $^{14}CH_4$.

2. Films chauffés sous vide à 450°C après saturation de $^{14}CH_4$ à 0°C

Cette série d'essais ne se différencie de la précédente que par un traitement à 450°C sous vide pendant 17 h avant la première introduction de méthane inactif.

Les résultats (colonne 3 du tableau I) font ressortir qu'il n'apparaît pas d'activité aux températures inférieures à celle du traitement. A cette température, une série d'essais consécutifs est réalisée de la même manière (figure 2, courbe 1).

3. Films chauffés à différentes températures en présence de $^{14}CH_4$

Après la chimisorption à 0°C, les films sont portés en présence du méthane radioactif respectivement à 125, 200 et 315°C, températures auquelles plusieurs essais consécutifs sont effectués sur un même film. Au cours des expériences à 125 et 200°C, la phase gazeuse contient 9% d'hydrogène; elle en contient 35% dans les autres expériences. La partie gauche de la figure 1 montre l'évolution de l'activité totale apparue en phase gazeuse lors des différents essais.

La partie droite du graphique représente l'activité totale extraite quand on élève la température de chaque catalyseur à 450° C pendant 24 h environ après les échanges aux différentes températures. Passé ce laps de temps, les variations d'activité en phase gazeuse sont déjà non mesurables, comme il apparaît, à titre d'exemple, sur la figure 2 (courbe 3).

4. Films saturés de CH_4 à 450°C

Après avoir vérifié qu'il n'apparaît plus d'activité, à 450°C, du film décrit en 1, on sature celui-ci à cette température par quatre additions successives de méthane. La nouvelle surface ainsi obtenue est traitée à 450°C à l'aide de méthane radioactif pendant 24 h. A ce moment, du méthane inactif est mis au contact du film à différentes températures de la même manière qu'en 1. Il

TABLEAU II

ACTIVITÉ MAXIMUM EXTRAITE A DIFFÉRENTES TEMPÉRATURES A L'AIDE D'UN MÉLANGE DE MÉTHANE ET D'HYDROGÈNE

Température (°C)	Activité en surface (10^{-8} c per 100 mg)	Activité extraite (10^{-8} c per 100 mg)
125	1600	7,5
200	3400	130
315	5000	38

n'apparaît en phase gazeuse aucune activité aux températures inférieures à 450°C. Les différents essais successifs effectués à cette température sont représentés par la courbe 2 de la figure 2.

5. Films chauffés à 200°C en présence de CH_4

Après la chimisorption, à 0°C, du méthane inactif, le film est porté à la température de 200°C en présence de ce gaz. Les résidus hydrocarbonés de surface sont alors marqués au moyen d'un mélange de méthane actif et d'hydrogène pendant 24 h. Ensuite, une série d'essais est effectuée à cette température dans les mêmes conditions qu'en 3. Les résultats apparaissent sur la figure 1 (courbe en pointillé).

Discussion

Les études de chimisorption de méthane sur film de molybdène font apparaître que la réaction du méthane avec la surface est inhibée par la présence d'hydrogène gazeux [2]. D'autre part, il existe un domaine de température où les radicaux hydrocarbonés en surface sont déplacés par l'hydrogène, avec un maximum vers 200°C, tandis que les radicaux formés à 450°C ne sont pas déplaçables, même à cette température [6]. Nous distinguerons donc deux domaines de température, selon que le déplacement de $-CH_x$ par l'hydrogène a lieu ou non.

La comparaison des courbes 1 et 2 avec la courbe 3 de la figure 2 montre la différence d'apparition d'activité à 450°C suivant que la phase gazeuse est constituée de méthane ou d'un mélange de méthane et d'hydrogène. Dans ce dernier cas, où la réaction de surface devient rapidement non mesurable, l'activité extraite tend vers une valeur limite (courbe 3). Ce fait nous conduit à relier directement l'apparition de ^{14}C en phase gazeuse à l'addition de méthane proprement dite. Nous ne voyons pas encore très bien comment expliquer cette relation. Cependant, comme l'activité extraite est faible (tableau II), il est possible que le ^{14}C apparu ne soit pas sous la forme de méthane, les analyses au spectromètre de masse n'ayant pas la précision suffisante pour détecter les faibles traces d'autres hydrocarbures, à des concentrations inférieures à 0,1%. Des analyses par entraîneurs sont actuellement en cours pour élucider ce point.

Aux températures inférieures à 450°C, auxquelles l'hydrogène déplace des radicaux hydrocarbonés, quoique les essais soient réalisés avec un mélange de méthane et d'hydrogène de manière à limiter au maximum la réaction d'addition de méthane, l'apparition d'activité est beaucoup plus importante

qu'à 450°C. Des essais sont en cours pour déterminer quantitativement l'activité *échangeable en l'absence totale d'addition complémentaire.*

Il est intéressant de constater que le domaine de température où s'observe la réaction de déplacement par l'hydrogène est le même que celui où a lieu l'«échange élémentaire» de carbone, de même que l'échange de deutérium entre CH_4 et D_2 étudié par KEMBALL [7]. Cette constatation nous permet de proposer un mécanisme unique rendant compte de chacun de ces phénomènes.

Rappelons que Kemball fait appel à deux mécanismes différents, l'un responsable de l'apparition de CH_3D, le second de celle des autres deutérométhanes selon les équations suivantes:

Formation de CH_3D:

$$\begin{array}{l} CH_4 + D \rightarrow CH_3 + HD \\ \quad\quad\;\; | \quad\quad\;\; | \\ CH_3 + D_2 \rightarrow CH_3D + D. \\ | \quad\quad\quad\quad\;\; | \end{array}$$

Formation des autres deutérométhanes:

$$\begin{array}{l} CH_4 \rightarrow CH_2 + H_2 \\ \quad\quad\;\; | \\ CH_2 \rightarrow CH + H \\ | \quad\quad\;\; | \\ H + D_2 \rightarrow D + HD. \\ | \quad\quad\;\; | \end{array}$$

Comme Kemball considère que l'étape déterminante est l'adsorption-désorption de radicaux méthylènes, on arrive rapidement à la formation de CD_4 suivant l'équation:

$$\begin{array}{l} CD_2 + D_2 \rightarrow CD_4. \\ | \end{array}$$

LAIDLER [8] a d'ailleurs sur cette base effectué le calcul du nombre de sites réagissant selon les différents mécanismes.

MIYAHARA [9], pour expliquer l'apparition des différents deutérométhanes, a établi un schéma unique reposant également sur un équilibre d'adsorption-désorption.

Contrairement à ces mécanismes, celui que nous proposons n'est pas basé sur un équilibre d'adsorption-désorption selon une réaction du type

$$\begin{array}{l} CH_4 \rightleftharpoons CH_3 + H \\ \quad\quad\;\; | \quad\quad\;\; | \end{array} \qquad (1)$$

mais bien sur une réaction de déplacement, schématisée par l'équation:

$$\begin{array}{l} CH_4 + H \underset{\leftarrow k_2}{\overset{\rightarrow k_2}{\rightleftharpoons}} CH_3 + H_2. \\ \quad\quad\;\; | \quad\quad\;\; | \end{array} \qquad (2)$$

Des CH_3 se dissocient en d'autres radicaux (CH_2, CH), avec lesquels ils peuvent être en équilibre. Statistiquement, le degré d'hydrogénation des résidus de chimisorption décroît avec leur température de formation. Il nous paraît logique de supposer que, pour être déplacé par l'hydrogène, un radical ne doit pas être trop déshydrogéné. C'est pourquoi nous ne ferons intervenir que CH_3.

Les réactions d'échange sont alors confondues avec les deux étapes de la réaction de déplacement (2), qui se décomposent comme suit:

$$\begin{array}{l} CP_4 + D \xrightarrow{\vec{k}_2} [CP_4D] \rightarrow \begin{cases} CP_3 + PD \\ CP_4 + D \\ CP_3D + P \end{cases} \end{array} \qquad (3)$$

$$\begin{array}{l} D_2 + CP_3 \xrightarrow{k'_2} [CP_3D_2]^* \rightarrow \begin{cases} CP_3 + D_2 \\ CP_2D + HD \\ CPD_2 + H_2 \end{cases} \\ \qquad\qquad \downarrow k''_2 \\ \qquad\qquad [CP_3D_2] \rightarrow \begin{cases} CP_2D_2 + P \\ CP_3D + D. \end{cases} \end{array} \qquad (4)$$

Les radicaux CH_3 de la surface penvent être en équilibre isotopique avec l'hydrogène gazeux, car la formation du complexe intermédiaire $[CH_5]^*$ ne nécessite que l'énergie d'activation E_2', alors que le déplacement implique l'énergie d'activation $\overleftarrow{E}_2 = E'_2 + E''_2$. De cette manière, nous rendons compte à l'aide d'un mécanisme unique de l'apparition à l'instant initial de CH_3D et de CD_4, avec des constantes de vitesse caractérisées par des énergies d'activation différentes.

Conclusion

L'apparition d'activité à 450°C est liée à la réaction d'addition de méthane sur le catalyseur, et l'on n'observe pas d'échange de ^{14}C au vrai sens du mot. Boreskov [10] a attiré l'attention sur les modifications apportées par la phase gazeuse à un catalyseur et sur les modifications que ces changements peuvent apporter aux réactions catalytiques. Ces modifications peuvent se produire même si les constituants de la phase gazeuse sont en équilibre chimique entre eux. La plupart des auteurs qui étudient les échanges hétérogènes entre différents gaz se placent dans ces conditions. Malheureusement, ceci n'implique pas l'absence d'une évolution lente de la surface produisant des effets difficilement décelables sur la constitution chimique de la phase gazeuse, mais importants sur l'activité du catalyseur.

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EXPERIMENTAL COMPARISON OF PRIMARY AND SECONDARY ISOTOPE EFFECTS IN TRITIUM OR CARBON LABELLED COMPOUNDS

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Abstract — Résumé — Аннотация — Resumen

Experimental comparison of primary and secondary isotope effects in tritium or carbon labelled compounds. The isotope effects (IE) in the phenylhydrazone formation of β-naphthaldehyde-(carbonyl-T), β-naphthaldehyde-(carbonyl-C^{14}), 3-phenylpropionaldehyde-1-T, β-*d*-mannose-1-C^{14} and β-*d*-mannose-1-T have been determined.

The IE in the formation of mannose-(1-C^{14})-phenylhydrazone depends on whether the reaction is carried out immediately after the mannose has dissolved or after complete mutarotation. In this reaction the IE in β-naphthaldehyde-C^{14} gives an expected value of 1.06, whereas the tritium-labelled compound has an inverse IE of about 0.78. With the 3-phenylpropionaldehyde (carbonyl-T) the IE is 1.1.

Though the IE of both tritium-labelled compounds are different in direction, the frequency shift of the carbonyl group in the infra-red spectrum of the corresponding deuterium-labelled compounds shows the same direction and magnitude.

Therefore the direction of the secondary IE cannot be predicted from the frequency shift of the reacting groups which is caused by the influence of α-substituted hydrogen isotopes.

Comparaison expérimentale des effets isotopiques primaires et secondaires dans les composés marqués au tritium ou au carbone. On a déterminé les effets isotopiques dans la formation des phénylhydrazones du β-naphtaldéhyde-(carbonyle-T), du β-naphtaldéhyde-(carbonyle-^{14}C), du phényl-3-propionaldéhyde-1-T, du β-D-mannose-1-^{14}C et du β-D-mannose-1-T.

L'effet isotopique dans la formation du phénylhydrazone-mannose-(1-^{14}C) varie selon que la réaction se produit aussitôt après la dissolution du mannose ou une fois que la mutarotation est complète. Dans cette réaction, l'effet isotopique du β-naphtaldéhyde-^{14}C a la valeur prévue (1,06), tandis que le composé marqué au tritium a un effet isotopique inverse de 0,78 environ. Pour le phényl-3-propionaldéhyde (carbonyle-T), l'effet isotopique est de 1,1.

Bien que les effets isotopiques des deux composés marqués au tritium soient de direction différente, le déplacement de fréquence du groupe carbonyle dans le spectre infra-rouge des composés correspondants marqués au deutérium a la même direction et la même importance.

De ce fait, on ne peut prédire la direction des effets isotopiques secondaires d'après le déplacement de fréquence des groupes réactifs, qui est causé par l'influence des isotopes d'hydrogène substitués en α.

Экспериментальное сопоставление первичных и вторичных изотопных воздействий в меченных тритием или углеродом составах. Были определены изотопные воздействия (ИВ) на образование фенилгидразония, исходя из бета-нафтойного альдегида — (карбонила-Т), бета-нафтойного альдегида — (карбонила-C^{14}), 3-фенилпропионового альдегида-1-Т, бета-D-маннозы-1-C^{14} и бета-D-маннозы-1-Т.

ИВ на образование маннозы-(1-C^{14}) — фенил гидразония — зависит от того, происходит ли реакция немедленно после растворения маннозы или после полного изменения направления вращения. При этой реакции ИВ на бета-фенилпропионовый альдегид-C^{14} дает ожидаемое значение 1,06, в то время как меченный тритием состав испытывает обратное ИВ, равное приблизительно 0,78. При 3-фенилпропионовом альдегиде (карбониле-Т) ИВ равно 1,1.

Хотя ИВ для обоих меченных тритием составов противоположно по направлению, смещение частоты карбониловой группы в инфракрасном спектре соответствующих меченных дейтерием составов дает то же самое направление и порядок величины.

Поэтому направление вторичного ИВ не может быть объяснено смещением частоты реагирующих групп, вызванным под влиянием α-замененных изотопов водорода.

Comparación experimental de los efectos isotópicos primarios y secundarios en compuestos marcados con tritio o con carbono-14. Los autores han determinado los efectos isotópicos (EI) en la formación de las fenilhidrazonas del β-naftaldehido-(carbonilo-T), del β-naftaldehido-(Carbonilo-^{14}C), del 3-fenilpropionaldehido-1-T, de la β-D-manosa-1-^{14}C y de la β-D-manosa-1-T.

En la formación de la fenilhidrazona de la manosa-1-^{14}C, el EI varía si la reacción se inicia inmediatamente después de disolver el azúcar o sólo una vez completada la mutorrotación. En esta reacción, el valor teórico del EI para el β-naftaldehido-^{14}C alcanza a 1,06, mientras que el compuesto marcado con tritio da un EI inverso del orden de 0,78. Por otra parte, el 3-fenilpropionaldehido-(carbonilo-T) se caracteriza por un EI de 1,1.

Anque los EI de ambos compuestos marcados con tritio tienen sentidos diferentes, los desplazamientos de frecuencia originados por el grupo carbonilo en los espectros infrarrojos de los compuestos deuterados correspondientes tienen igual sentido y magnitud.

Por consiguiente, el sentido del EI secundario no puede predecirse con ayuda del desplazamiento de frecuencia de los grupos activos, que se debe a la influencia ejercida por los isótopos del hidrógeno sustituidos en posición α.

1. Introduction

For some years, intra- and intermolecular isotope effects (IE) have been used in increasing amounts to look closer into the reaction mechanism of organic molecules. More recently, kinetic secondary isotope effects (sec. IE) are being studied.

Until now, reactions have been investigated whose mechanisms are known. On the basis of the experimental results and the ideas which had developed, valuable information was obtained about the transition states of reactions. After studying many reactions, different factors have been discussed [1] which are responsible for magnitude and direction of the effects.

By their nature, sec. IE are much smaller than primary and are only large enough to measure with hydrogen isotopes. While a satisfactory theory exists to explain the size and direction of a primary IE, or from its magnitude to obtain information of the transition state [2], this cannot be done with the same certainty with sec. IE. This is because primary IE are caused by one factor which completely overshadows all others by 1 to 2 orders of magnitude. The reason for the IE, as is well known, is the difference in frequency of a C—H and C—D or C—T bond in the ground state. Under certain circumstances there is such a difference in activation energies that the ratio of velocity constants k_H/k_D is often 4—8, or for k_H/k_T, 10—20. These differences of 400 to 2000% in the reaction

velocity between labelled and non-labelled compounds stand in extreme contrast to sec. IE, which show differences of only 1 to 25%.

Meanwhile, we have investigated the quarternization of pyridine with CH_2TI and compared the value of the IE with that of BENDER *et al.* [3] for $C^{14}H_3I$. We also determined the IE of the esterification of *p*-nitrobenzoyl-chloride with $C^{14}H_3OH$ and CH_2TOH in alkaline and neutral solution [4].

We also studied the question of how far, in a chemical reaction, the sec. IE depend on the neighbouring group. It also appeared of interest to us to make a comparison with a C^{14} and T-labelled group, because of the equal masses. We chose to investigate the phenylhydrazone formation of *β*-naphthaldehyde labelled in the aldehyde group with a C^{14} atom or a tritium atom, and 3 phenyl-propionaldehyde-1-T over a range of pH values. According to the results of JENCKS [5], the formation of the carbinolamine is rate determining (RD) in acidic pH regions, while, near neutrality, the splitting off of water from the carbinolamine is RD. The determination of the IE of a reaction, which, by changing only one factor, exhibits a changeover from one RD step to another, appeared to be of particular interest. The two T-labelled aldehydes were compared, since one might expect that differences in the magnitude and direction of the IE would appear if the tritium atom was contained in a carbonyl group in conjugation with an aromatic system in one case and not in another.

We also determined the IE of the phenylhydrazone formation of *d*-mannose-1-C^{14} and *d*-mannose-1-T, since we were interested in these experiments for analytical reasons.

2. Results and Discussion

The IE of the reaction of *β*-naphthaldehyde-T with phenylhydrazine and *p*-nitrophenylhydrazine at various pH values are shown in Table I. These results show a relatively high inverse IE. However, it was unexpected that the IE would show essentially no dependence on the pH. The corresponding effects of *β*-naphthaldehyde-C^{14} (Table II) are also nearly independent of pH, and the size and direction are those which one would expect of a primary IE for C^{14}.

TABLE I

KINETIC ISOTOPE EFFECT (IE) OF THE REACTION OF β-NAPHTHALDEHYDE-CARBONYL-T AT DIFFERENT *pH VALUES WITH PHENYLHYDRAZINE OR *p*-NITROPHENYLHYDRAZINE**

pH	Carbonyl Reagent	Conversion (%)	Starting Act. (%)	Kinetic IE (k_H/k_T)
1.3	phenylhydrazine	35.1	123.0	0.78 ± 0.02
5.0	phenylhydrazine	26.1	129.0	0.75 ± 0.02
7.1	phenylhydrazine	40.3	121.7	0.78 ± 0.02
1.0	p-nitro-phenyl-hydrazine	36.4	117.2	0.83 ± 0.02
2.8	p-nitro-phenyl-hydrazine	47.2	116.6	0.81 ± 0.03
5.0	p-nitro-phenyl-hydrazine	28.8	130.1	0.75 ± 0.02
6.9	p-nitro-phenyl-hydrazine	30.4	130.0	0.75 ± 0.02

* *p* as written in Tables II & III

TABLE II

KINETIC IE OF THE REACTION OF β-NAPHTHALDEHYDE-CARBONYL-C^{14} AT DIFFERENT pH VALUES WITH PHENYLHYDRAZINE AND SEMICARBAZINE

pH	Carbonyl Reagent	Conversion (%)	Starting Act. (%)	Kinetic IE ($k_{C^{12}}/k_{C^{14}}$
1.8	Phenylhydrazine	29.6	95.4	1.057 ± 0.005
5.0	Phenylhydrazine	15.9	95.3	1.052 ± 0.005
7.2	Phenylhydrazine	46.3	95.3	1.066 ± 0.005
5.0	Semicarbazine	29.0	94.8	1.055 ± 0.01

TABLE III

KINETIC IE BY THE REACTION OF 3-PHENYLPROPIONALDEHYDE-1-T AT DIFFERENT pH VALUES WITH PHENYLHYDRAZINE AND p-NITROPHENYLHYDRAZINE

pH	Carbonyl Reagent	Conversion (%)	Starting Act. (%)	Kinetic IE (k_H/k_T)
1.14	*p*-nitrophenylhydrazine	19.5	93.9	1.11 ± 0.01
4.75	*p*-nitrophenylhydrazine	17.4	92.0	1.10 ± 0.01
7.60	*p*-nitrophenylhydrazine	18.2	92.1	1.06 ± 0.01

TABLE IV

FREQUENCY SHIFT OF THE C—O BAND AND C—H ALDEHYDE BAND BY SUBSTITUTION OF D FOR H IN THE ALDEHYDE GROUP OF β-NAPHTHALDEHYDE AND 3-PHENYLPROPIONALDEHYDE

	νCO		$\Delta\nu$CO	ν C—H	ν C—D	ν CH—νCD
	H	D				
β-naphthaldehyde	1695	1675	20	2710	2075	635
3-phenylpropionaldehyde	1728	1709	19	2707	2074	633

Table III shows the IE values for 3-phenylpropionaldehyde-1-T. The direction of the effect is actually inverted from that observed with T-labelled naphthaldehyde. Here also, practically no dependence on the pH of the reaction solution was found. In order to determine the effect of the hydrogen isotopes on the ground state of the carbonyl group, we synthesized both aldehydes containing deuterium in the aldehyde group and measured their infra-red spectra (Table IV). The ratio of the frequency (in wave numbers) of the aldehyde C—H band to that of the aldehyde C—D band is 1.30:1, which comes quite close to the average value of 1.35:1. The carbonyl bands are shifted to longer wavelengths by a value of 19 to 20 cm^{-1}. The shifts are, in both cases, in the same direction, in contrast to the direction of the IE, and therefore offer no explanation of the differences in the latter. It can be seen from numerous previously described sec. IE that

inverse effects occur when, in the reaction, a change from the sp^2 state to the sp^3 state is rate-determining. Normal effects are observed in the opposite direction. The inverse effects, which occur in the hydrolyses of methyl halides [6], have been explained by HALEVI [7] through the increased electron donating effect of the C—D bond.

This inductive effect, if it plays a role in phenylhydrazone formation, should affect both cases in the same direction. Its effectiveness, however, depends on the properties of the surrounding groups.

The fact that the magnitude and direction of the IE in naphthaldehyde labelled with C^{14} or tritium, or with tritium-labelled 3-phenylpropionaldehyde, is independent of pH, would seem to indicate that in the pH region investigated, no change of the RD step occurs. One must make the assumption that different RD steps are affected in the same manner by the hydrogen isotopes.

Therefore, the hybridization change in the RD step of these cases cannot be decided on the basis of the IE direction. The shift of the C=O frequency under the effect of deuterium would explain the direction and magnitude of the effect on 3-phenylpropionaldehyde. The comparison of the band area of non-labelled naphthaldehyde and deuterium-labelled naphthaldehyde leads one to suspect an increase in the C=O dipole in the labelled compound; i.e., that a nucleophilic attack of base is facilitated, from which a contribution to the found inverse IE can be derived.

Fig. 1 shows a segment of the infra-red spectra of naphthaldehyde and naphthaldehyde-D. The spectra were measured in identical concentration in CCl_4. One can see the broadening of the C=O band in the deuterium-labelled naphthaldehyde. The corresponding comparison of the labelled and non-labelled 3-phenylpropionaldehydes does not allow one to determine with any certainty an increase in the band area. That the different directions of the IE of the two aldehydes cannot be explained by one effect shows clearly that in the same reaction, under certain circumstances, opposing factors can occur whose effects depend on the neighbouring groups.

TABLE V

COURSE OF THE IE BY PERIODIC REMOVAL OF THE MANNOSE-PHENYLHYDRAZONE
(The reaction was started immediately after solution of the mannose-1-C^{14} in 0.6% acetic acid)

Fraction	Conversion (%)	Activity (mMole)*	Kinetic IE
1	0—26	8.96×10^5	0.94 ± 0.008
2	26—42	8.38×10^5	0.96 ± 0.012
3	42—62	7.94×10^5	1.00 ± 0.014
4	62—75	7.79×10^5	1.03 ± 0.016
5	75—87	7.82×10^5	1.07 ± 0.030

* Initial activity of mannose-1-C^{14}: 8.47×10^5 ipm/mMole.

The IE of the phenylhydrazone formation of mannose-1-C^{14} can be seen from Table V. Here the IE shows first an inverse value and then rises with the progress of reaction. From this it can be postulated that, in comparison to the mannose phenylhydrazone formation the *β-d*-mannose undergoes a more rapid trans-

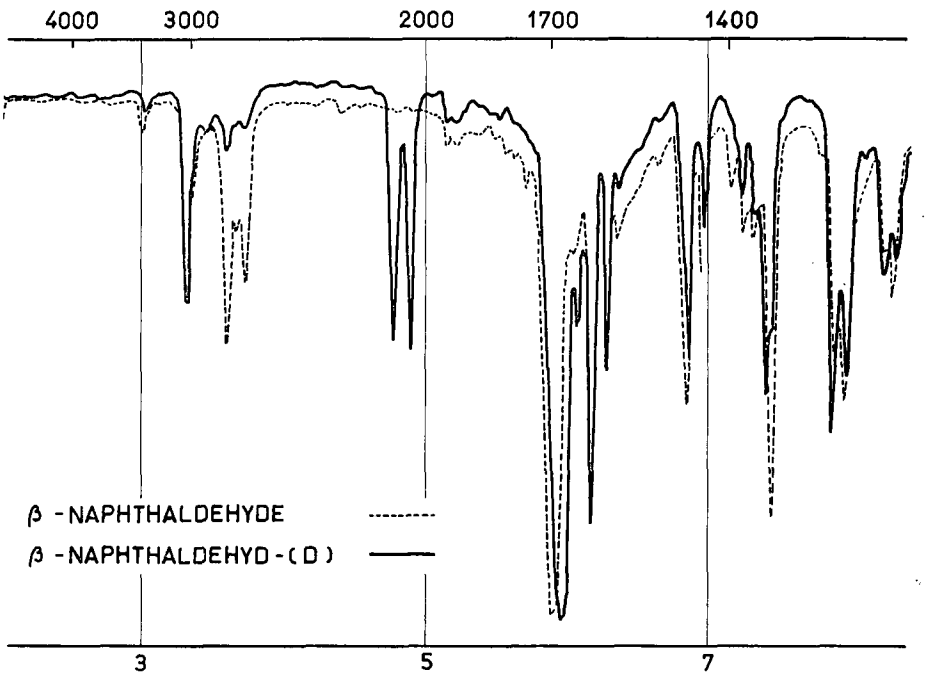

Fig. 1
Segment of the infra-red spectra of β-naphthaldehyde and β-naphthaldehyde-carbonyl-D measured in identical concn. in CCl_4.

formation to a product X with a normal IE. The inverse IE can be explained by the fact that the phenylhydrazone formation results form a mannose form in which the C^{14}-labelled mannose molecules are enriched. It must further be postulated that the above-mentioned product X forms no phenylhydrazone, or at least does so more slowly than the enriched form. This explanation is based on the fact that, according to experience, no inverse IE occur with C^{14}. If this is correct, then the phenylhydrazone formation of mannose-1-C^{14}, after equilibrium in solution, must show a constant IE. That this is actually the case can be seen in

TABLE VI

COURSE OF THE IE BY PERIODIC REMOVAL OF THE MANNOSE-PHENYLHYDRAZONE
(The solution of the mannose-1-C^{14} in 0.6% acetic acid stood for 20 h before the reaction was started)

Fraction	Conversion (%)	Activity (mMole)	Kinetic IE
1	0—24	7.87×10^5	1.09 ± 0.01
2	24—47	7.99×10^5	1.10 ± 0.01
3	47—62	8.28×10^5	1.10 ± 0.01
4	62—78	8.31×10^5	1.11 ± 0.02

Table VI. The effct is now independent of progress of the reaction, and the value is rather high.

The IE of 1.30 of the phenylhydrazone formation of β-*d*-mannose-1-T is normal, even if the reaction sets in immediately after dissolution of the mannose. Since, as we have already reported [8], an IE occurs when mannose-1-T phenylhydrazone crystallizes out of solution, this value is too complex to be compared with the others.

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DISCUSSION

R. J. Baily (United Kingdom) asked whether the experiments with mannose-1-C^{14} had been done with equilibrium muta-rotated mannose as well as with the crystalline form.

H. Simon said that two experiments had been performed. Firstly, phenylhydrazine had been added immediately after dissolving the β-*d*-mannose-1-C^{14} in 0.6% acidic solution. Secondly, the phenylhydrazine had been added after the β-*d*-mannose-1-C^{14} had been in solution for 20 h.

ВОССТАНОВЛЕНИЕ ПРОМЕТИЯ НА РТУТНОМ КАТОДЕ

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СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

Abstract — Résumé — Аннотация — Resumen

Reduction of promethium on a mercury cathode. The authors observed the separation of radioactive promethium on a mercury cathode with samarium, which showed that it can be reduced to a bivalent state.

Using radiochemically-pure Pm^{147}, the authors made a detailed study of the influence of a series of factors on the extent to which promethium passes into an amalgam.

It was shown that radioactive promethium only passes into the mercury cathode if the current is relatively dense (above 50 mA/cm²) and when rare-earth elements such as ytterbium and samarium, which have a stable bivalent state, are present in the electrolyte. Electrolytic separation of the promethium is not observable until formation of the mixed potassium and samarium amalgam. The promethium then passes into the amalgam up to 85%.

When the current is denser (100 mA/cm²), a notable difference may be observed in the transition speed of the promethium and samarium.

The promethium separation is mainly affected by the nature of the alkali metal contained in the electrolyte. With lithium, the degree of promethium transition does not depend on the presence of another rare-earth element or the citrate ion concentration. This confirms the occurence of electrolytic reduction of promethium in electrolysis with a mercury cathode at high current densities.

Separation of the promethium into the mercury cathode goes through the stage of its reduction to a bivalent state with formation of the amalgam with the alkali metal.

The authors also studied the behaviour of cerium and erbium.

From the results of this study and all the published data, the authors conclude that promethium and other elements of the cerium group can be reduced to a bivalent state under certain conditions of electrolysis.

Réduction du prométhéum sur une cathode de mercure. Les auteurs ont étudié la séparation du prométhéum radioactif sur une cathode de mercure, en présence de samarium, ce qui montre que le prométhéum peut être ramené à un état bivalent.

A l'aide de ^{147}Pm radiochimiquement pur, les auteurs ont étudié en détail l'influence d'un certain nombre de facteurs sur l'aptitude du prométhéum à s'amalgamer.

On a constaté que le prométhéum radioactif ne passe dans le mercure que si le courant est relativement intense (plus de 50 mA/cm²) et s'il y a dans l'électrolyte des terres rares — samarium ou ytterbium — dans un état bivalent stable. La séparation électrolytique du prométhéum n'intervient qu'après formation de l'amalgame potassium-samarium. Le prométhéum passe alors dans l'amalgame jusqu'à concurrence de 85%.

Lorsque le courant est plus intense (100 mA/cm²), on remarque une différence sensible dans la vitesse d'amalgamation du prométhéum et du samarium.

Le processus de séparation du prométhéum est surtout influencé par la nature du métal alcalin contenu dans l'électrolyte. Avec du lithium, le degré de transformation du prométhéum ne dépend pas de la présence d'une autre terre rare ni de la concentration des ions du citrate. Il se produit donc bien une réduction électrolytique du prométhéum lors de l'électrolyse avec cathode de mercure et sous courant intense.

Losque le prométhéum se sépare sur la cathode de mercure. il est d'abord ramené à un état bivalent avant de s'amalgamer au métal alcalin.

Les auteurs ont également étudié le comportement du cérium et de l'erbium.

En tenant compte des résultats de la présente étude et de toutes les données publiées, les auteurs arrivent à la conclusion que dans certaines conditions le prométhéum et les autres éléments du groupe du cérium peuvent être ramenés par électrolyse à l'état bivalent.

Восстановление прометия на ртутном катоде. Обнаружено явление выделения радиоактивного прометия на ртутном катоде совместно с самарием, показывающее способность прометия к восстановлению до двухвалентного состояния.

С помощью радиохимически чистого Pm^{147} детально исследовано влияние ряда факторов на степень перехода прометия в амальгаму.

Показано, что радиоактивный прометий переходит в ртутный катод только при сравнительно высокой плотности тока (свыше 50 мА/см^2) и наличии в электролите редкоземельных элементов — самария или иттербия, имеющих устойчивое двухвалентное состояние. Электролитическое выделение прометия наблюдается только после образования смешанной амальгамы калия и самария. Переход прометия в амальгаму в этих условиях достигает 85%.

При большой плотности тока (100 мА/см^2) замечено резкое различие в скорости процесса перехода прометия и самария.

На процесс выделения прометия основное влияние оказывает природа щелочного металла, присутствующего в электролите. В случае лития степень перехода прометия не зависит от присутствия другого редкоземельного элемента и концентрации цитрат ионов. Этим подтверждается наличие процесса электролитического восстановления прометия при электролизе с ртутным катодом при высоких плотностях тока.

Выделение прометия в ртутный катод проходит через стадию восстановления его до двухвалентного состояния наряду с образованием амальгамы щелочного металла.

Изучалось также поведение церия и эрбия.

На основании результатов исследования и совокупности литературных данных делается вывод о том, что при определенных условиях электролиза прометий и другие элементы цериевой группы проявляют способность к восстановлению до двухвалентного состояния.

Reducción del promecio en un cátodo de mercurio. Los autores observaron la deposición de promecio radiactivo en un cátodo de mercurio que contenía samario, lo que demostró que el promecio puede reducirse al estado bivalente.

Con ayuda de ^{147}Pm radioquímicamente puro, los autores estudiaron detalladamente la influencia de una serie de factores sobre la medida en que el promecio se incorpora a la amalgama.

Se demostró que el promecio radiactivo sólo pasa al cátodo de mercurio si la densidad de corriente es relativamente elevada (más de 50 mA/cm^2) y si en el electrólito existen tierras raras, como el samario o el iterbio, que tienen un estado bivalente estable. No se observa separación electrolítica del promecio hasta que se forma una amalgama de potasio y samario. El 85% del promecio pasa entonces a la amalgama.

Si la densidad de corriente es mayor (100 mA/cm^2), se observa una diferencia notable en la velocidad con que el promecio y el samario se incorporan a la amalgama.

La separación del promecio depende principalmente de la naturaleza del metal alcalino contenido en el electrólito. La cantidad de promecio que pasa en presencia de lítio no depende de que haya otra tierra rara ni de la concentración de iones citrato. Esto confirma la existencia de un proceso de reducción electrolítica del promecio en la electrólisis con cátodo de mercurio y elevada densidad de corriente.

En la deposición en el cátodo de mercurio el promecio pasa por una fase bivalente y otra de formación de amalgama con el metal alcalino.

Los autores estudiaron también el comportamiento del cerio y del erbio. El cerio se deposita en un cátodo de mercurio en las mismas condiciones que el promecio. Por el contrario, el erbio prácticamente no se deposita.

De los resultados de este estudio y de todos los datos publicados se deduce que, en determinadas condiciones de electrólisis, el promecio y otros elementos del grupo del cerio pueden reducirse al estado bivalente.

Высокое перенапряжение водорода на ртутном катоде позволяет осуществлять восстановление редкоземельных элементов — европия, иттербия и самария — до двухвалентного состояния и выделять их в виде амальгам при электролизе из растворов, содержащих комплексообразующие адденды [1—5].

При изучении условий отделения самария от продуктов его расщепления быстрыми протонами нами в начале 1959 года был обнаружен переход радиоактивного прометия совместно с самарием в ртутный катод при высоких плотностях тока. Этот факт был недавно подтвержден в работе [6].

Наблюдаемое явление представляет несомненный интерес для установления у прометия способности к восстановлению до двухвалентного состояния. Для решения этого вопроса большое значение имеет сопоставление степени выделения Pm и Sm на ртутном катоде. В связи с этим и было изучено поведение этих элементов в процессе электролиза.

1. Методика исследования

Электролиз проводился в сосуде типа делительной воронки с рубашкой для охлаждения. В качестве катода использовалось 200 г очищенной ртути, поверхность которой составляла 10,6 см^2; анодом служила спираль из платиновой проволоки длиной 25 см и диаметром 0,8 мм. Опыты проводились при следующих постоянных условиях: объем электролита 10 мл, pH 5,9, температура от 0 до $+2^\circ$ C, скорость перемешивания раствора и ртути 500 оборотов/мин., напряжение 10—12 в, C_{K^+}—0,35 M, C_{AC^-}—0,174 M (Ac = CH COOO$^-$), $C_{Cit^{3-}}$ — 0,116 M/Cit^{3-} = $C_6H_5O_7^{3-}$/, $C_{Sm^{3+}}$— $5{,}8\cdot10^{-2}$ M, $C^3_{Pm^{3+}}$—$1{,}10^{-9}$ M.

После окончания электролиза амальгама трижды промывалась водой, разлагалась 6 н. HCl и производилось определение прометия по активности Pm^{147}, а самария — весовым способом и по Sm^{153}.

Продажный препарат Pm^{147} отделялся от примесей радиоактивных изотопов других редких земель на хроматографической колонке, заполненной смолой КУ-2Х12 с зернением 400 меш. [7]. В качестве элюента использовался 0,33 M лактат аммония (pH 5,8). Обнаружены 3 пика, соответствующие радиоизотопам $Eu^{154, 155}$, Pm^{147} и Ce^{144}, идентификация которых производилась измерением энергии бета-излучения по поглощению в алюминиевых фольгах. (Возможная примесь Sm^{151} (E_β=0,08 Мэв) не могла быть обнаружена в условиях наших измерений.) Часть выделенного прометия подвергалась дополнительной очистке указанным выше способом. Полученная в этом случае выходная кривая, приведенная на рис. 1, свидетельствует об отсутствии примесей в препарате прометия. Радиоактивная чистота Pm^{147} была также подтверждена отсутствием гамма-излучения при измерении на люминесцентном гамма-спектрометре со 100-канальным анализатором.

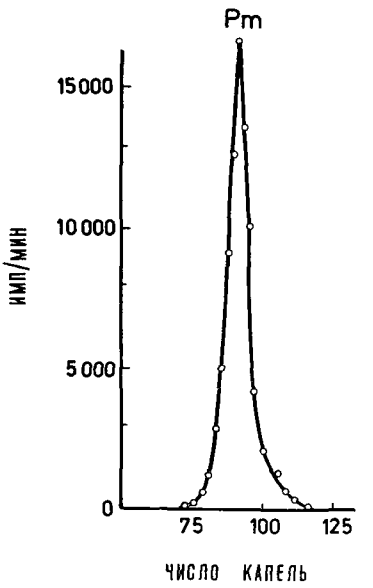

Рис. 1

Кривая вымывания прометия с катионита КУ-2, х-12 0,33 М раствором лактата аммония с pH 5,8 при температуре 90° С со скоростью 0,05 мл/мин. (2 капли/мин). Размеры колонки 150 × 2 мм.

Измерение активности производилось на установке с торцевым счетчиком МСТ-17 со статистической ошибкой счета ±3%. Вводились поправки на поглощение активности Pm^{147} ($E_{\beta-}$ = 0,22 Мэв) в веществе мишени.

2. Изучение влияния некоторых факторов на степень выделения прометия в ртутный катод

Для установления механизма процесса перехода прометия в ртутный катод представляет интерес изучение влияния ряда факторов на степень его выделения: катодной плотности тока, продолжительности электролиза, присутствия других элементов и концентрации комплексообразующего адденда.

Зависимость выхода прометия в амальгаму от величины катодной плотности тока в интервале от 25 до 100 мА/см² изучалась при продолжительности электролиза 1,5 часа. На рис. 2 представлены результаты опытов, из которых видно, что только при сравнительно высоких плотностях тока (свыше 50 мА/см²) происходит выделение прометия на ртутном катоде. При плотности тока 100 мА/см² степень его выделения достигает 85%. В отличие от прометия величина плотности тока не оказывает существенного влияния на выделение самария. Так, уже при 25 мА/см² в амальгаму переходит 90% Sm.

Зависимость степени выделения прометия в ртутный катод от продолжительности электролиза изучалась при плотности тока в 100 мА/см². Данные, представленные в виде кривых 1 и 2 на рис. 3, показывают, что

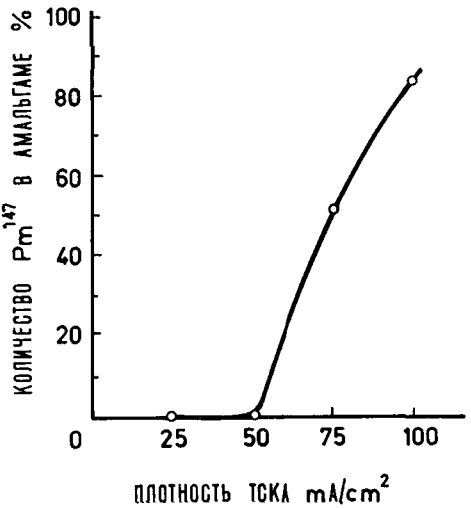

Рис. 2

Зависимость выделения прометия в амальгаму от катодной плотности тока.

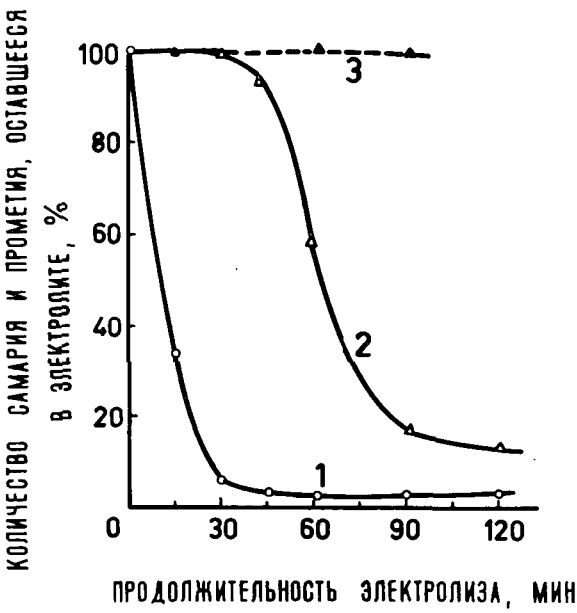

Рис. 3

Зависимость количества оставшегося в электролите самария (кривая 1) и прометия (кривые 2,3) от продолжительности электролиза. Кривая 3 получена в случае добавления цитрата калия в процессе опыта.

прометий начинает выделяться на ртутном катоде только через 30 мин. после начала электролиза, когда основное количество самария уже перешло в амальгаму.

Таблица I

ВЛИЯНИЕ ПРИРОДЫ РЕДКОЗЕМЕЛЬНОГО ЭЛЕМЕНТА НА СТЕПЕНЬ ВЫДЕЛЕНИЯ ПРОМЕТИЯ НА РТУТНОМ КАТОДЕ

(Объем раствора 10 мл, pH 5,9, Cu± 0,35 M, C_{Ac} — 0,174 M, $C_{Cit^{3-}}$ — 0,116 M, температура в интервале от 0 до + 2° C, скорость перемешивания электролита и ртути 500 оборотов/мин, плотность тока 100 мА/см², продолжительность электролиза 1,5 часа. Активность Pm^{147} 3,1 мккюри., что соответствует ~1,10⁻⁹ г/мл)

№№ опытов	Элемент	Концентрация, 10^{-2} M	Добавлено цитрата калия в процессе электролиза, M	Найдено в амальгаме, %	
				Pm	Me
1	—	—	—	0,13	—
2	La*	4,7	—	0,02	3,1
3	La	6,0	0,09	*Не обнаружено*	—
4	Sm	5,0	—	83,0	—
5	Sm	5,0	0,105	0,1	97,0
6	Sm	0,12	—	0,07	—
7	Yb	5,1	—	86,5	99,5

* В процессе электролиза образуется осадок, содержащий 80% лантана от введенного количества.

Влияние наличия в электролите других редкоземельных элементов исследовалось на примере Sm, Yb и La. Из таблицы 1 следует, что прометий переходит в ртуть только в присутствии редкоземельных металлов, имеющих устойчивое двухвалентное состояние. В случае лантана наблюдается постепенное выпадение нерастворимого осадка, по-видимому, основного ацетата или цитрата лантана, с которым соосаждается до 80% Pm^{147}. В отсутствие редкоземельного элемента или при малой его концентрации прометий практически полностью остается в растворе.

Результаты описанных выше опытов свидетельствуют о том, что в определенных условиях электролиза прометий переходит в ртутный катод даже при 10^8-кратном избытке комплексообразующего адденда. Представляет интерес и тот факт, что при дополнительном введении в процессе электролиза цитрата калия прометий полностью остается в растворе (опыт 5, таблица 1 и кривая 3, рис. 3), между тем как самарий выделяется почти количественно. Это различие в поведении Sm и Pm использовано нами для их разделения.

Для установления влияния природы щелочного металла были проведены опыты с цитратом лития. Данные таблицы 2 показывают, что в этом случае уже через 30 мин. электролиза 58% прометия переходит в ртутный катод, в то время как в присутствии ионов даже после 45-минутной продолжительности опыта выделяется только 8% прометия. Кроме того, при электролизе растворов, содержащих ионы лития, наблюдается выделение прометия как в отсутствие самария, так и при дополнительном введении цитрата лития.

Таким образом, на степень выделения прометия на ртутном катоде из ацетатно-цитратных растворов наибольшее влияние оказывают величина

Таблица II

ВЛИЯНИЕ ПРИРОДЫ ЩЕЛОЧНОГО МЕТАЛЛА И КОЛИЧЕСТВА САМАРИЯ НА ВЫДЕЛЕНИЕ Pm, Ce И Er НА РТУТНОМ КАТОДЕ

(Объем раствора 10 мл, pH 5,9, температура в интервале от 0 до +2° С. Скорость перемешивания электролита и ртути 500 оборотов/мин. Соотношение Sm^{3+}; Cit $3^- = 1:2,2$ (K) и 1:3,5 (Li). Активность Pm^{147} 0,75 мккюри/мл, Ce^{144} — 0,13 мккюри/мл, Er^{169} — 1,18 мккюри/мл, напряжение 10—12 в)

Элемент	Концентрация Sm^{3+}, 10^{-2} М	Щелочной металл в электролите	Плотность тока, мА/см²	Продолжительность электролиза, мин	Добавлено цитрата калия или лития, М	Выход Pm в амальгаму, %
Pm	5,0	K	100	90	—	83,0
	—	K	100	90	—	0
	—	K	150	90	—	0
	5,3	Li	100	30	—	58,0
	5,4	Li	100	60	0,123	89,4
	—	Li	150	90	—	72,0
	5,0	Li	100	90	—	96,8
Ce	—	K	100	90	—	0
	5,3*	K	100	90	—	94,5
	5,4	K	100	90	—	85,0
	5,8	K	100	60	0,116	0
	—	Li	150	60	—	24,2
Er**	5,4	K	100	90	—	0,25
	—	Li	150	90	—	0,01

* Содержание церия 0,05 мг.
** Содержание эрбия 0,2 мг.

плотности тока, продолжительность электролиза, природа редкоземельного и щелочного металлов, присутствующих в электролите.

Все вышеизложенные факты позволяют сделать вывод о том, что переход прометия в ртутный катод обусловлен электролитическим восстановлением. Объяснение явления выделения прометия адсорбционными процессами маловероятно. Выполненные в этом направлении опыты показали практически полное отсутствие адсорбции Pm^{147} на поверхности ртути при 1,5-часовом перемешивании ее с нитратными растворами прометия с pH 1,8; 4,8; 6—7; ацетатно-цитратными — с pH 5,8—6,0, а также с растворами, полученными после 30-минутного электролиза при плотности тока 100 мА/см², из которых, как мы видели выше, начинает выделяться прометий.

3. Поведение других редкоземельных элементов

Из литературных данных известно, что при длительном электролизе спиртовых растворов хлоридов металлов цериевой группы [8, 9], а также при взаимодействии амальгамы натрия с уксуснокислыми растворами этих элементов [10] удалось получить их амальгамы. Однако выход при этом незначителен и составляет, например, для церия 10% [8].

Представлялось интересным изучить поведение некоторых редких земель, которые не были выделены на ртутном катоде при электролизе ацетатно-цитратных растворов. Опыты проводились с церием и эрбием, как наиболее характерными представителями цериевой и иттриевой групп, в тех же самых условиях электролиза, что и для прометия. Использовались радиоактивные изотопы Ce^{144} и Er^{169}. Результаты, представленные в табл. 2, показывают, что поведение церия аналогично поведению прометия. Церий также выделяется на ртутном катоде (в присутствии цитрата калия) только при наличии в электролите самария. Концентрация церия в интервале от 5.10^{-12} до $3{,}6\ 10^{-5}$ М не оказывает существенного влияния на степень его выделения. Переход Ce^{144} в ртутный катод наблюдался недавно в работе [6], но в иных условиях электролиза.

Эрбий, напротив, не обнаруживает заметной склонности к выделению на ртутном катоде даже в присутствии ионов лития и при высокой плотности тока (150 мА/см^2).

На основании результатов настоящего исследования и совокупности литературных данных [1—6, 8—10], можно сделать вывод о том, что наблюдается резкое различие в способности к образованию амальгам для элементов цериевой и иттриевой групп.

4. Предполагаемый механизм процесса выделения прометия на ртутном катоде

При электролизе ацетатно-цитратных растворов протекают гораздо более сложные химические процессы, чем предполагалось в работах [2]. Это обусловлено наличием в электролите ионов Ac^-, H_2Cit^-, $HCit^{2-}$ и Cit^{3-}, которые образуют с катионами редкоземельных металлов комплексные ионы различного состава. Их относительное содержание зависит от pH раствора, константы нестойкости и соотношения концентраций металла и комплексообразующих аддендов. Однако состав комплексных ионов и его изменение в процессе электролиза за счет наблюдаемого в опытах уменьшения pH раствора до 4,3; 4,4 вряд ли играет большую роль, так как согласно существующим представлениям при высоких отрицательных потенциалах на ртутном катоде могут восстанавливаться как простые, так и комплексные ионы независимо от знака их заряда.

На ртутном катоде наряду с редкоземельными металлами могут восстанавливаться катионы щелочных металлов и водорода, последовательность и степень восстановления которых зависят от соотношения их потенциалов и pH раствора. В присутствии комплексообразующих аддендов потенциал восстановления редкоземельных металлов сдвигается в более отрицательную сторону, поэтому потенциал самария, о котором мы можем судить по потенциалу полуволны ($E_{1/2}=1{,}96$ в отсутствие комплексообразующего адденда), в условиях нашего опыта близок к потенциалу восстановления калия ($E_{1/2}=2{,}13$ в) [11], стр. 681. Вследствие этого калий может выделяться на ртутном катоде совместно с самарием. Действительно, в опытах было обнаружено, что через 30 минут после начала электролиза при плотности тока 100 мА/см^2 образуется амальгама, содержащая 40% калия и 94% самария от начального их содержания в растворе.

Интересно, что выделение прометия начинается только после образования амальгам такого состава, о чем свидетельствует кривая 2 рис. 3. По составу образующейся амальгамы мы рассчитали ее потенциал, который соответствует началу выделения прометия. Он оказался равным — 2,11 в. относи-

тельно насыщенного электрода (без учета поправки на температурный коэффициент).

Наличие ионов лития, имеющих по сравнению с калием более отрицательный потенциал восстановления ($E_{1/2} = -2{,}34$ в.) способствует более быстрому и полному выделению прометия. Это не противоречит высказываемому в работах [4, 6] мнению о том, что переход редкоземельных элементов в ртутный катод связан, в основном, с образованием амальгамы щелочного металла. Однако в отличие от работ [2, 4, 6] мы наблюдали выделение самария и в отсутствие калия.

Представляет несомненный интерес рассмотрение вопроса о том, происходит ли восстановление прометия на ртутном катоде через промежуточное двухвалентное состояние. Достоверность двухступенчатого восстановления европия, иттербия и самария доказывается многими фактами и, главным образом, наличием двух волн на полярограммах, полученных на капельном ртутном катоде [11], стр. 273, [12]. Кроме того, известна аналогия между способностью металлов к образованию амальгам и устойчивостью двухвалентного состояния в ряду $Eu > Yb > Sm$. Это может быть связано с тем, что двухвалентные катионы редких земель, в отличие от трехвалентных, гидролизуются при более высоких pH, что имеет очень существенное значение для процесса последующего их восстановления до металла в условиях повышенной концентрации гидроксил-ионов в прикатодном слое по сравнению с раствором.

Для большинства элементов цериевой группы в настоящее время также получены полярограммы с четко выраженными волнами, соответствующие процессам [13—16]:

$$Me^{3+} + e^- \rightleftarrows Me^{2+} \quad (1)$$

$$Me^{2+} + 2e^- \rightleftarrows Me\,(Hg) \quad (2)$$

Таким образом, переход прометия и церия в ртутный катод свидетельствует о наличии у них, так же как и у других элементов цериевой группы, двухвалентного состояния. Для элементов иттриевой группы, кроме иттербия, не обнаружено ни двухступенчатого восстановления на капельном ртутном катоде, ни перехода в стационарный ртутный катод.

5. Выводы

Установлено, что основное влияние на степень перехода прометия в ртутный катод оказывают природа редкоземельного и щелочного металлов, плотность тока ни продолжительность электролиза. При электролизе в присутствии ионов калия прометий выделяется на катоде только при наличии больших количеств самария или другой редкой земли, проявляющей устойчивое двухвалентное состояние.

Изучалось поведение церия и эрбия. Оказалось, что церий выделяется на ртутном катоде в тех же условиях, что и прометий. Эрбий, напротив, практически не выделяется.

На основании результатов настоящего исследования и совокупности литературных данных делается вывод о том, что при определенных условиях электролиза прометий и другие элементы цериевой группы проявляют способность к восстановлению до двухвалентного состояния.

Наблюдающиеся различия в поведении самария, церия и прометия позволили найти метод отделения макроколичеств самария от радиоактивных элементов цериевой группы.

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THE ADSORPTION OF HYDROGEN ON A MOLECULAR SIEVE AT —196°C AND THE OBSERVATION OF AN ISOTOPE EFFECT

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Abstract — Résumé — Аннотация — Resumen

The adsorption of hydrogen on a molecular sieve at —196°C and the observation of an isotope effect. Linde Molecular Sieve 4A has been examined as a possible means of handling small volumes of hydrogen isotopes in a vacuum system, as an alternative to the slow Toepler pump method.

The equilibrium pressure (P) was measured for various volumes (V) of hydrogen adsorbed by 1 g of Sieve at —196°C. Experiments with activated charcoal showed the superiority of the Sieve as a hydrogen adsorbent. 1 g of the Sieve in a system of vol. 500 ml will adsorb about 97% of a 1-ml sample of hydrogen. Adsorption is negligible at —78°C and desorption is quantitative and rapid at room temperature.

The possibility of an isotope effect was investigated by adsorbing measured volumes of tritium (5 μc/mole) at an equilibrium pressure of about 5 mm, pumping off the system for times up to 15 min and measuring the volume of residual hydrogen. The latter was converted quantitatively to water, thence to butane, and gas-counted. The specific activity was always higher than that of tritium which had undergone 10 cycles of adsorption and desorption without intermediate pumping off, so that there was no net loss of gas. This had the same specific activity as untreated tritium from the storage bulb. It was found that log (residual vol./ initial vol.) was proportional to 1/log (residual sp. act./ initial sp. act.) over the range investigated (0—90% of initial gas pumped off). When 90% had been removed the specific activity ratio was about 3.

Isotopic fractionation during adsorption is possible, but in these experiments about 99% of the initial hydrogen was adsorbed on the Molecular Sieve before desorption by pumping off was begun. It seems likely, therefore, that the considerable fractionation observed occurs mainly during desorption. The effect is thus not likely to be important when the Sieve is used for manipulating small volumes of hydrogen isotopes, since complete desorption by warming will usually be employed.

Adsorption d'hydrogène sur un tamis moléculaire à —196°C et observation d'un effet isotopique. L'auteur a examiné la possibilité d'utiliser le tamis à molécules Linde 4A au lieu de la méthode de pompage Toepler, qui est assez lente, pour manipuler sous vide de petites quantités d'isotopes de l'hydrogène.

La pression d'équilibre (P) a été mesurée pour différents volumes (V) d'hydrogène adsorbé par un gramme du tamis à —196°. Les expériences faites avec du charbon de bois activé ont montré la supériorité du tamis comme adsorbant d'hydrogène. Un gramme du tamis, dans un système de 500 ml, adsorbera environ 97% d'un échantillon d'un millilitre d'hydrogène. L'adsorption est négligeable à —78° et la désorption est totale et rapide à la température ambiente.

On a étudié la possibilité d'un effet isotopique en adsorbant des volumes déterminés de tritium (5 μc/mole) à une pression d'équilibre d'environ 5 mm, en vidant le système par pompages allant juspqu'à 15 minutes et en mesurant le volume de l'hydrogène résiduel. Ce dernier a été converti en eau, ensuite en butane, et compté sous forme de gaz. L'activité spécifique était toujours plus élevée que celle du tritium

ayant subi 10 cycles d'absorption et de désorption sans pompage intermédiaire, de sorte qu'il n'y avait pas de perte nette de gaz. Cette activité spécifique était la même que celle du tritium non traité provenant de l'ampoule de stockage. On a constaté que log (volume résiduel/volume initial) était proportionnel à 1/log (activité spécifique résiduelle/activité spécifique initiale) à tous les stades considérés (évacuation de 0 à 90% du gaz initial). Après évacuation de 90% du gaz, le rapport des activités spécifiques était de 3 environ.

Il est possible qu'il y ait fractionnement isotopique pendant l'adsorption mais, dans ces expériences, environ 99% de l'hydrogène initial était adsorbé sur le tamis moléculaire avant le commencement de la désorption par pompage. Il semble donc vraisemblable que le fractionnement important observé se produit surtout pendant la désorption. Cet effet isotopique ne saurait par conséquent être important lorsque le tamis est utilisé pour manipuler de petites quantités d'isotopes de l'hydrogène, étant donné qu'on procédera généralement à une désorption complète par chauffage.

Абсорбция водорода на молекулярном фильтре при —196° и наблюдение результатов действия изотопов. Испытывался молекулярный фильтр Линде 4 А в качестве возможного средства обращения с небольшими объемами изотопов водорода в вакууме, вместо применяющегося в настоящее время насоса Тоиплера.

Давление равновесия (P) измеряется различными объемами (V) водорода, абсорбируемого одним граммом фильтра при температуре —196°. Эксперименты с активированным древесным углем показывают преимущество фильтра как абсорбента водорода. Один грамм фильтра в системе с объемом в 500 мл абсорбирует около 97% одного мл образца водорода. Абсорбция незначительна при температуре —78°, и десорбция является количественной и быстро протекает при комнатной температуре.

Возможность результатов действия изотопа изучалась путем абсорбирования измеряемых объемов трития (5 милликюри/моль) при равномерном давлении около 5 мм, при этом происходило выкачивание системы в периоде до 15 минут и измерение объема остаточного водорода. Последний превращался количественно в воду, затем в бутан и газ. Удельная активность была всегда выше, чем активность трития, который проходил 10 циклов абсорбции и десорбции без промежуточного выкачивания с тем, чтобы не было никаких чистых потерь газа. Это имело такую же удельную активность, как у необработанного трития, взятого из резервной колбы. Было обнаружено, что логарифм (остаточный объем/начальный объем) пропорционален 1/логарифм (остаточная удельная активность/начальная удельная активность) в исследуемом порядке (0—90% первоначального выкаченного газа). Когда 90% газа выкачано, коэффициент удельной активности оказался приблизительно равным 3.

Изотопное фракционирование в процессе абсорбции возможно, но при этих экспериментах около 99% начального объема водорода абсорбируется на молекулярном фильтре, прежде чем начнется десорбция при выкачивании. Поэтому представляется вероятным, что наблюдаемая значительная фракционность встречается, главным образом, при десорбции. Таким образом, маловероятно, чтобы результат имел большое значение в случае применения молекулярного фильтра при манипуляции с небольшими объемами изотопа водорода, поскольку обычно будет применяться полная десорбция при подогреве.

Adsorción de hidrógeno en un tamiz molecular a —196° C y observación de un efecto isotópico. El autor ha estudiado la posibilidad de utilizar un tamiz molecular Linde 4A como medio para manejar pequeños volúmenes de isótopos del hidrógeno en un sistema de vacío, en sustitución del lento método de la bomba de Toepler.

Midió la presión de equilibrio (P) para varios volúmenes (V) de hidrógeno adsorbido por un gramo de tamiz a —196° C. Los experimentos realizados con carbono activado demuestran la superioridad de tamiz como adsorbente de hidrógeno. En un sistema de 500 ml de volumen un gramo de tamiz adsorbe alrededor del 97% de una muestra de hidrógeno de 1 ml. A —78° C la adsorción es despreciable y a temperatura ambiente la desorción es cuantitativa y rápida.

El autor investigó la posibilidad de que se produzca un efecto isotópico adsorbiendo volúmenes medidos de tritio (5 μc/mol) a una presión de equilibrio de unos 5 mm, evacuando el sistema durante períodos de hasta 15 minutos, y midiendo el volumen de hidrógeno residual. Este último se convirtió cuantitativamente en agua y después en butano, cuya actividad se determinó por recuento. La actividad específica fue siempre superior a la del tritio que había sufrido diez ciclos de adsorción y desorción sin bombeo intermedio, de forma que no hubiera pérdida neta de gas. Este último poseía la misma actividad específica que el tritio no tratado procedente de la ampolla de almacenamiento. Se comprobó que el log (volumen residual/volumen inicial) era proporcional a 1/log (actividad específica residual/actividad específica inicial) en todo el intervalo estudiado (se extrajo por bombeo de 0 a 90% de gas inicial). Después de eliminar el 90 por ciento del gas, la razón de actividades específicas era del orden de 3.

Es posible que se produzca un fraccionamiento isotópico durante la adsorción, pero en estos experimentos se adsorbió en el tamiz molecular cerca del 99% del hidrógeno inicial antes de comenzar la desorción por bombeo. Por lo tanto, parece probable que el considerable fraccionamiento observado tenga lugar principalmente durante la desorción y que el efecto carezca de importancia cuando el tamiz se emplea para manipular pequeños volúmenes de isótopos del hidrógeno ya que, por lo general, la desorción total se efectuará por calentamiento.

1. Introduction

The quantitative transfer of hydrogen in a vacuum system is difficult by normal methods involving cooling. Charcoal cooled with liquid nitrogen will only partly adsorb hydrogen, and quantitative transfer is usually carried out by repeated strokes of a Toepler pump, a slow and inflexible method. Pyrophoric uranium will quantitatively adsorb hydrogen, and is used thus during the production process for tritium [1], but the gas can be recovered only by heating the metal to above 400°C, and the material is in any case not very suitable for general use. There is still need, therefore, for a simple, rapid method for manipulating hydrogen, particularly in the tracer laboratory for dealing with small volumes of hydrogen isotopes.

The use of Molecular Sieves as gas samplers has already been described by TONGE *et al.* [2], who found, for example, that Molecular Sieves cooled with liquid air would adsorb coal gas from a low-pressure system. An examination of this material as an adsorbent for hydrogen has therefore been made and compared with a gas-adsorption charcoal. Since a useful degree of adsorption was found with the Molecular Sieve, the possibility of an isotope effect was also investigated, since such effects have already been found with several other adsorbents (for summary see [3]).

2. Materials and Methods

Molecular Sieve type 4A, in 1/16 inch pellets (Linde Air Products Company); activated charcoal, granular, "Special for Gas Absorption". Both these were obtained from The British Drug Houses Ltd.

For investigation of the adsorption of hydrogen, 1 g of the chosen adsorbent was placed in a side arm of a high-vacuum apparatus, communicating with a manometer and also, if desired, with a McLeod gauge, the volumes of these sections being calibrated. The adsorbent was degassed by heating under vacuum at about 250°C and cooled to room temperature. Hydrogen, purified by passage

through the Molecular Sieve at — 78°C, was admitted to the system, its pressure read on the manometer and the adsorbent cooled with liquid nitrogen. When apparent equilibrium had been reached, in about 3—5 min, the residual pressure was read on the manometer or McLeod gauge. This was repeated with varying volumes of hydrogen and from these figures the volume of hydrogen adsorbed for a particular equilibrium pressure could be calculated.

Isotopic fractionation was investigated by adsorbing measured volumes of dilute tritium gas (at a specific activity of about 5 μc/mole) on the Molecular Sieve at — 196°C and at an equilibrium pressure of about 5 mm. The system was then opened to the pumps for varying times up to 15 min, isolated, the adsorbent warmed to room temperature, resulting in complete desorption and the volume of tritium, representing that remaining adsorbed at — 196°C, measured.

Tritium samples were converted to water by sparking with a slight excess of oxygen at reduced pressure [4], a quantitative conversion which should give no isotope effect. The water was then converted to butane for gas-counting in the Geiger region [5], a procedure already found to give no isotope effect.

3. Results and Discussion

Fig. 1 shows isotherms for the adsorption of hydrogen on the Molecular Sieve and on activated charcoal. They are qualitatively in agreement with those found by BASMADJIAN [3], whose paper was seen after submission of the Abstract of the present work, and, like his, they are not consistent with the Freundlich or Langmuir equations over the whole pressure-range studied. In the present experiments, however, activated charcoal was found to be inferior to the Molecular Sieve, whereas Basmadjian found two other varieties of charcoal to be superior.

The capacity of the Molecular Sieve for adsorbing hydrogen is particularly valuable at low pressures (not shown in Fig. 1). Thus 1 g of Sieve at — 196°C

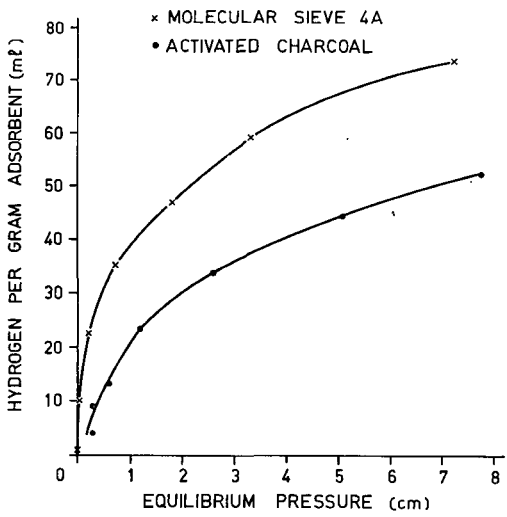

Fig. 1
Adsorption isotherms at —196°C for hydrogen on Molecular Sieve 4A and on activated charcoal.

adsorbed about 97% of one standard ml of hydrogen in a system of vol. 500 ml, while under the same conditions 10 g adsorbed more than 99%. The Molecular Sieve has been used in this way for the storage of gas remaining after microhydrogenations using tritium of high specific activity. This gas can readily be introduced, with small loss, into a storage vessel in any convenient part of the vacuum apparatus, or sealed in a break-seal tube containing the adsorbent.

As a preliminary to the isotopic fractionation experiments, a sample of the stock tritium gas used throughout was adsorbed on to the Molecular Sieve at —196° C and desorbed by warming without intermediate pumping off. This same gas was cycled in this way ten times without net loss of gas. Its specific activity was unaltered from that of the stock tritium, showing that mere contact with the Molecular Sieve does not introduce any isotope effect or dilution or exchange of tritium with hydrogen which may possibly be present in any form in the Sieve.

Results of the isotopic fractionation experiments are shown in Fig. 2. For each run, the vol. % of tritium remaining adsorbed on the Molecular Sieve after partia desorption by pumping off is plotted against the ratio of the specific activity

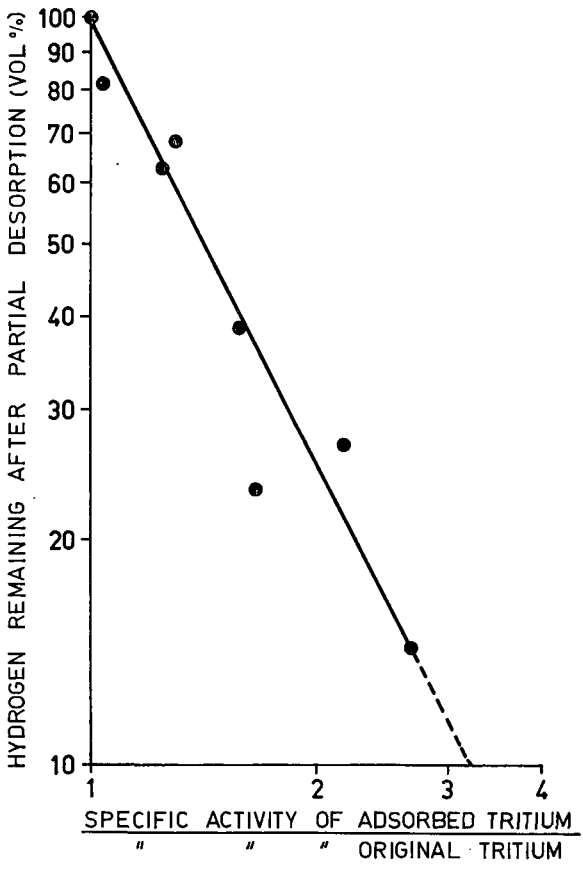

Fig. 2
Isotopic fractionation during the partial desorption of tritium gas from Molecular Sieve at —196°C.

of adsorbed tritium to the specific activity of original tritium (before adsorption and pumping off). A reasonably straight line was obtained by plotting the results on a log-log basis. Considerable fractionation was observed, the specific activity of the adsorbed fraction being some 3 times that of the original gas when only 10% remained adsorbed. This preferential adsorption of the heavier isotope is qualitatively in agreement with previous work using deuterium with other adsorbents (see [3] for a summary). In the present experiments, the labelled molecular species is virtually only HT, since the specific activity corresponds to about one tritium atom in 10^{10} hydrogen atoms.

Single component adsorption isotherms for pure hydrogen and deuterium on the Molecular Sieve [3] show that there is preferential adsorption of deuterium. However, the correlation between the volume of gas desorbed and the degree of fractionation (Fig. 2) shows that the fractionation cannot occur primarily during adsorption, since the amount of Molecular Sieve used was such that in all runs about 99% of the initial gas was adsorbed before the partial desorption by pumping off was begun.

From a practical point of view the isotope effect is not likely to be of importance when using the Molecular Sieve for manipulating small volumes of hydrogen isotopes. Under such conditions sufficient Sieve can be used to make adsorption almost quantitative, while the adsorbed gas will usually be recovered quantitatively by warming the Sieve to room temperature.

ACKNOWLEDGEMENTS

The assistance of Mr. I. C. Collie and Mr. P. J. Russell in carrying out tritium determinations is gratefully acknowledged.

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DISCUSSION

A. Melkonian (Federal Republic of Germany) asked whether any ortho-para conversion of hydrogen had been observed during adsorption on the Molecular Sieve at —196° C, as happened with charcoal.

He further inquired whether the author had considered repeating his adsorption experiments at the temperature of liquid oxygen in order to obtain the values of the adsorption energies.

W. G. Duncombe replied that the main object of the investigation was to develop a practically useful method for handling small quantities of hydrogen isotopes in a tracer laboratory. No other work on the physical chemistry of the system had been attempted.

A. H. Ward (Ghana) asked whether the threefold isotopic concentration that had been obtained in the isotopic fractionation experiments was a reproducible figure or whether it had varied appreciably depending on the conditions of the experiments.

W. G. Duncombe replied that each point in Fig. 2 was derived from a separate experiment and the results indicated that the effect should be reasonably reproducible. However, the method would not be a very economical means of concentrating tritium, since to obtain a threefold concentration about 90% of the initial material had to be pumped away.

G. M. Harris (United States of America) asked how Molecular Sieve was pretreated in order to avoid exchangeable impurities.

W. G. Duncombe said the material was heated under a vacuum at 250° C. The results quoted showed that there was no dilution of the tritium with hydrogen or water from the material.

N. A. Ghanem (United Arab Republic) asked if there was any possible explanation for the preferential adsorption of tritium on the surfaces mentioned.

W. G. Duncombe said that a detailed discussion of such isotope effects was contained in the article by Basmadjian to which he had referred in his paper.

The Chairman (P. Albert, France) asked what was the material composing the Linde Air Products Molecular Sieve which had been used in the experiments.

W. G. Duncombe said the Sieve was made of an aluminosilicate which was commercially available in a standardized form.

SOME APPLICATIONS OF RADIOISOTOPES IN PHYSICAL CHEMISTRY— TWO-PHASE EQUILIBRIA AND PACKED-COLUMN TECHNIQUES

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Abstract — Résumé — Аннотация — Resumen

Some applications of radioisotopes in physical chemistry — two-phase equilibria and packed-column techniques. One of the most effective applications of radioisotopes in physical chemistry is the study of two-phase equilibria; our own studies for a number of years have been concentrated on ion exchange reactions with commercial organic and with new types of non-siliceous inorganic exchangers. With the former, the studies were carried out in depth, covering at times most elements in the periodic table, the objective being comparison of functional relationships of many systems rather than the detailed study of a few. With the inorganic exchangers, the objective was also broad coverage of many systems, particularly comparison of large numbers of adsorbents. Since these studies required hundreds of thousands of analyses, they would have been almost impossible with conventional analytical techniques.

The feasibility of such studies can therefore be considered a direct outgrowth of the ready availability of radioactive tracers, and the steady increase in precision and convenience of counting techniques.

More recently, packed-column techniques have been developed which, with radioactive tracers and relatively simple equipment, permit ready extension of studies of two-phase equilibria and of the kinetics of interfaces to higher temperatures (at present up to 200°C). Sampling and continuous monitoring techniques were used. Through adsorption and solubility studies, information on enthalpy and entropy changes of adsorption and ion-exchange reactions is reported as well as information on heats of solution, activity coefficients in concentrated electrolyte mixtures, and on complexing reactions in high-temperature aqueous systems.

Quelques applications des radioisotopes en chimie physique: équilibres à deux phases et emploi de colonnes à garniture interne. L'une des applications les plus efficaces des radioisotopes en chimie physique est l'étude des équilibres à deux phases; les recherches effectuées par l'auteur depuis quelques années ont surtout porté sur les réactions d'échange d'ions au moyen d'échangeurs organiques que l'on trouve dans le commerce et de nouveaux types d'échangeurs minéraux non silicieux. Les travaux effectués à l'aide des échangeurs organiques ont été poussés très loin, englobant parfois la plupart des éléments de la classification périodique, car l'objectif visé était la comparaison des relations fonctionnelles entre de nombreux systèmes, plutôt que l'étude détaillée de quelques-uns d'entre eux. Les recherches faites avec des échangeurs minéraux avaient également pour objet l'étude de nombreux systèmes, et notamment la comparaison d'un grand nombre d'adsorbants. Comme il fallait pour cela des centaines de milliers d'analyses, il aurait été presque impossible de recourir aux méthodes classiques d'analyse; si les auteurs ont pu mener à bien leurs travaux, ils le doivent aussi bien à l'existence des indicateurs radioactifs qu'aux progrès constants des méthodes de comptage, de plus en plus précises et commodes.

Plus récemment ont été mises au point des méthodes utilisant des colonnes à garniture qui permettent, au moyen de radioindicateurs et d'un matériel relativement simple, d'étendre sans difficulté à des températures plus élevées (actuellement jusqu'à 200 °C) l'étude des équilibres à deux phases et celle de la cinétique des interfaces. On a utilisé à cet effet des méthodes d'échantillonnage et de contrôle continu. Par des études sur l'adsorption et la solubilité, on a obtenu des renseignements sur les modifications de l'enthalpie et de l'entropie dans les réactions d'adsorption et d'échange ionique, ainsi que sur les chaleurs de dissolution, les coefficients d'activité dans les mélanges électrolytiques concentrés et les réactions complexantes dans les systèmes aqueux à haute température.

Некоторые случаи применения радиоизотопов в физической химии — двухфазное равновесие и метод насадочной колонны. Одним из наиболее производительных способов применения радиоизотопов в физической химии является изучение двухфазного равновесия. Наши собственные многолетние изыскания сосредоточивались на реакциях обмена ионов как в имеющихся в продаже органических ионообменниках, так и в некремнистых неорганических обменниках новой конструкции. С помощью ионообменников первой группы исследования были проведены в глубину, распространяясь иногда на большую часть элементов периодической таблицы, причем целью изыскания было сопоставление функциональных взаимоотношений между многими системами, а не подробное изучение некоторых из них. При работе с неорганическими обменниками целью был также широкий охват многих систем и, в частности, сопоставление большого числа адсорбентов. Поскольку эти исследования требуют проведения анализа сотни тысяч раз, они были бы почти неосуществимы обычными методами анализа, так что осуществимость такого рода исследований может считаться непосредственным результатом появления на свет легкодоступных радиоактивных индикаторов и постоянного увеличения точности и доступности методов подсчета.

Совсем недавно были выработаны методы насадочной колонны, позволяющие при помощи радиоактивных индикаторов и относительно простого оборудования распространить исследования на двухфазное равновесие и изучить кинетику поверхностей раздела при более высоких температурах (в настоящее время до 200° С). Были использованы методы взятия образцов и непрерывного дозиметрического контроля. На основании исследований адсорбции и растворимости даются сведения об изменениях энтальпии и энтропии адсорбции и о реакциях ионного обмена; кроме того, сообщаются сведения о количестве тепла, затраченного на растворение, о коэффициентах активности в концентрированных электролитических смесях и о комплексообразующих реакциях водных систем при высоких температурах.

Algunas aplicaciones de los radioisótopos en la química física: equilibrios bifásicos y empleo de las columnas de relleno. El estudio de los equilibrios bifásicos constituye una de las aplicaciones más notables de los radioisótopos en la química física. Durante varios años el autor ha centrado sus estudios en las reacciones de intercambio iónico con intercambiadores orgánicos comerciales y con intercambiadores inorgánicos, de tipo nuevo, exentos de sílice. Los estudios realizados con los primeros fueron extensivos y llegaron a comprender a casi todos los elementos del sistema periódico; su principal propósito fue comparar las relaciones funcionales de muchos sistemas, más que estudiar detalladamente unos pocos. En el caso de los intercambiadores inorgánicos, las investigaciones persiguieron la misma finalidad, a saber, la comparación de un gran número de adsorbentes. Como estas investigaciones exigían la realización de cientos de miles de análisis, no hubieran podido llevarse a cabo con las técnicas analíticas clásicas, de modo que su realización puede considerarse una consecuencia directa de la disponibilidad de trazadores radiactivos y del constante aumento de la precisión y la facilidad de empleo de las técnicas de recuento.

En fecha más reciente, se han desarrollado técnicas basadas en el empleo de columnas de relleno que, con la ayuda de trazadores radiactivos y de un equipo relativamente

sencillo, permiten estudiar los equilibrios bifásicos y la cinética de interfases a temperaturas más elevadas (hasta 200° C). El autor empleó técnicas de muestreo y monitoraje continuos. Los estudios de adsorción y de solubilidad permitieron obtener datos sobre las variaciones de entalpía y de entropía en las reacciones de adsorción y de intercambio iónico, así como sobre los calores de disolución, los coeficientes de actividad en mezclas de electrólitos concentradas, y las reacciones de formación de complejos en sistemas acuosos a temperaturas elevadas.

Introduction

It has long been recognized that many physical-chemical studies can be greatly simplified by the use of radioisotopes. Indeed, the development of techniques for use of radioisotopes in physical chemistry closely parallels the development of the science of radioactivity. While, by necessity, early work had to be confined to the naturally-occurring radioisotopes of less than a dozen elements, this restriction no longer holds since radioactive isotopes of practically every element in the periodic table can be obtained readily and comparatively cheaply. The prediction of HEVESY and PANETH [1] has long become true that "there can be no doubt that in the future the artificial radio-elements will surpass the natural radio-elements in their importance as indicators".

The simplicity and economy of radiotracer techniques has frequently been pointed out. Even in 1938 Hevesy and Paneth could write, recommending the use of radioisotopes, that "the acquisition ... of ... artificial radioelements as indicators does not necessarily involve large monetary expenditure," and that at a time when the use of artificial radioelements implied individual irradiations and acquisition of suitable radon- or radium-beryllium neutron sources. However, the apparent need for the present Conference implies that even today radiotracers are not used to the extent they deserve to be.

The purpose of the present paper is to illustrate some of the techniques which we have used in the Oak Ridge National Laboratory in the study of two-phase equilibria, which play such a dominant role in physical chemistry. Most of this work was confined to solid-liquid (aqueous) equilibria, particularly ion-exchange studies with conventional organic exchangers, adsorption studies with amorphous or micro-crystalline inorganic solids oriented towards development of new radiation-resistant ion-exchange materials, stability studies of these materials, and solubility studies. Radiotracers seem to be almost ideally suited for such work, since large numbers of almost routine analyses are usually required, which, with the aid of tracers, may be made rapidly and with reasonable precision.

1. Techniques

(1) RADIOISOTOPES AND COUNTERS

While, in principle, any radioisotope of convenient half-life can be used in physical-chemical studies, the development of scintillation counters placed gamma-emitting isotopes in a particularly preferred position. Using well-type counters, the amount of radiotracer in a liquid sample in a convenient sample tube can be determined in a few minutes with considerable precision. If tubes of reasonably uniform bore are selected and if sample sizes do not differ widely, overall accuracies of better than $\pm 1\%$ may readily be obtained, at least with radioisotopes of γ-energies larger than 0.1 MeV. If care is taken in the canning of the crystal

(thin-walled well), substantially less energetic gamma-rays may be counted. However, there may be some sacrifice of precision unless careful attention is paid to the uniform wall thickness of the sample tubes. At low energies, the density of the solutions will, of course, also affect counting efficiency.

The overall precision obtainable with radioactive tracers and scintillation counters in the study of two-phase equilibria is illustrated in Fig. 1, where the

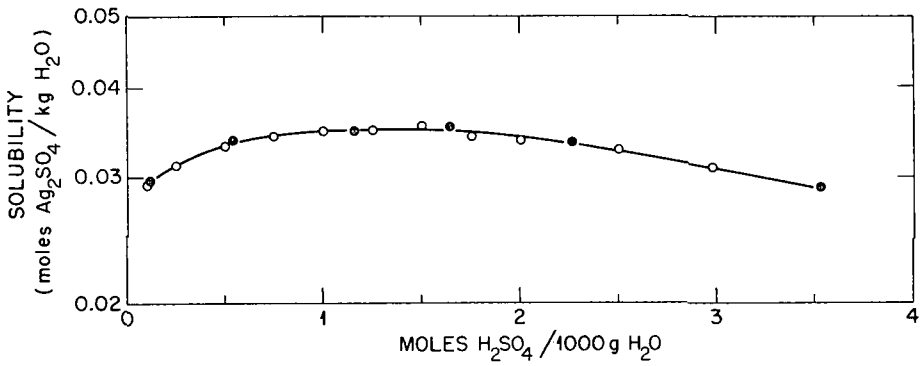

Fig. 1
Solubility of Ag_2SO_4 in H_2SO_4 at 25°C.
○ = Akerlöf and Thomas.
● = Tracer Method.

radiometrically-determined solubility of silver sulphate is compared with careful measurements in the literature [2]. Our measurements were carried out [3] with a packed bed (see Section 1. (2) below) of silver sulphate crystals precipitated from silver nitrate solutions containing a known amount of Ag^{110} tracer per *gram of silver. They were designed to yield absolute solubilities rather than* relative values. After preparation of the radioactive silver sulphate, a series of radiometric measurements ordinarily takes less than half a day, including equilibration and analysis.

The use of well-type scintillation counters for beta-emitters, even of high energy, must be considered treacherous. For these, wall thickness and solution density may become important variables and, indeed, some research workers prefer to restrict scintillation counting of beta-emitters to the bremsstrahlen produced, in spite of the fact that the efficiency of their production is very low. For accurate β-counting, as with α-counting, the more tedious method of preparing plates of dry samples is probably safer. These are then counted with a proportional counter or a GM tube.

With the present development of spectrometers which contain very large numbers of channels, physical-chemical studies involving two or more tracers in a single experiment will no doubt become more popular. In the past, we have found it usually simpler to study the components separately rather than to rely on the older, more cumbersome spectrometers.

(2) EQUILIBRATION METHODS — PACKED BEDS

With the time needed for analysis reduced to minutes, the limiting feature in the study of two-phase equilibria becomes the time necessary to reach equilibrium.

We have used various methods with ion-exchangers to good advantage [4]. Thus, as in other two-phase equilibria, small samples of solid and solution may be shaken for several hours or days with tracer originally in the aqueous phase. This method is particularly suited for simultaneous equilibration of a large number of samples. When the distribution coefficients D (amount per kg solid/amount per liter solution) are high, the necessary equilibration time may be substantially shortened by initially placing the tracer in the solid phase and allowing it to diffuse out.

When D is low, column methods may be more convenient. In the break-through method, solution (containing tracer) may be passed through the packed-bed and the volume noted at which break-through occurs. Distribution coefficients are obtained from the volume at which the effluent concentration is one-half the inflowing concentration, provided the break-through curves are not seriously distorted because of lack of equilibration. The column elution method is similar, except that in this case a thin band of the material (tracer) whose adsorbability is to be studied is added first to the column, tracer-free medium is used for elution and the volume noted at which the effluent contains the material in maximum concentration (elution maximum).

For D of the order of unity, we found a slightly different column-method more accurate. The tracer solution is passed through a small column until inflowing and outflowing solutions are of equal composition. The column is then centrifuged to remove most of the interstitial solution and the bed counted, e.g., in a well-type scintillation-counter. After minor correction for retained liquid, D is obtained from this measurement, together with the known concentration of the solution and the weight of resin in the column.

One of the most powerful packed-column techniques, however, is the one which we have called the preloaded-column method. In it, small mesh particles are initially equilibrated with the material (tracer) of interest, a column is prepared, and the solution for which the distribution coefficient is to be determined is passed through this bed. Extremely rapid equilibration occurs if D is high enough. The amount of material leaving the solid is then only a small fraction of the total and the equilibration rate is mainly determined by diffusion in the interstitial (liquid) space of the column, rather than in the solid. Completeness of equilibration can readily be checked by measuring the effluent (tracer) concentration as a function of flow rate. This method has the additional advantage that changes in composition of the solid are confined to the upper layers of the bed, final equilibration being with respect to the (constant composition) lower layers; hence, in a series of experiments, the results are obtained essentially at constant loading.

Other solid-liquid equilibria may be studied by the packed-bed method and we have used it for determining solubilities of crystalline materials and for studying ion exchange, adsorption, and stability properties of amorphous inorganic solids.

When solubility measurements are essentially diffusion-controlled, packed beds of the crystals (containing a known amount of tracer) are particularly

convenient. While the method has been used and recommended as rapid and "specially suited to precise measurements" almost 40 years ago by BRÖNSTED *et al.* [5], its great advantages seem not to have been generally appreciated and most solubility measurements are being carried out by the more cumbersome, though more familiar, shaking techniques. The packed-bed method is particularly advantageous when the solubility is low. If solubilities are high, exhaustion of the bed or channelling may occur inconveniently often.

When packed columns are used under conditions where the relative equilibrium concentration in the solution is very small, e.g., if D is very high or the materials extremely insoluble, the concentration of tracer in the solid phase will have to be high to yield an effluent of convenient counting-rate. The column may then have to be shielded. A convenient shield is obtained by inserting the active portion of the column into a snug-fitting hole in a lead brick (Fig. 2).

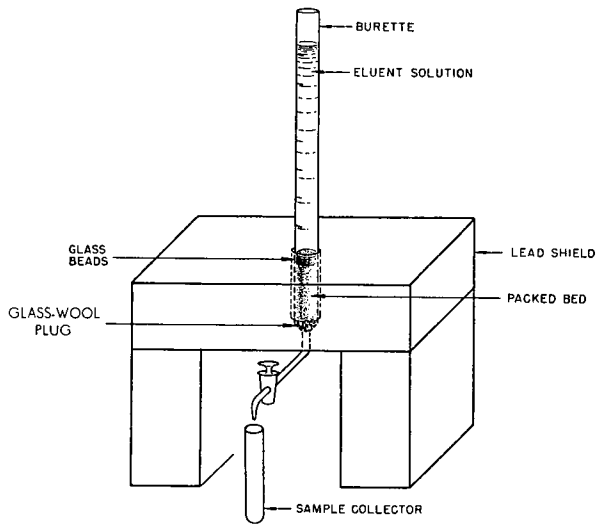

Fig. 2
Shielded column.

With packed columns, temperature control is particularly easy. For example, the column can be provided with a jacket through which vapours from a boiling liquid are passed or through which a thermostatic liquid is pumped. By utilizing capillary columns and relatively simple valves and fittings, the measurements may readily be extended to high-pressure, high-temperature systems [6].

The equipment described [6] was specifically designed for ion-exchange measurements where separation of a solid phase from the effluent at the "let-down valve," which is kept at low temperature, is no problem. An adaptation of this equipment has been developed [7] (Fig. 3) in which this is not a restriction. The effluent from the column passes through a long, jacketed capillary. It contains a larger diameter portion before the exit end which serves as the counting cell. The concentration of radioactive tracer is ascertained with a scintillation counter, located above the cell in a thermally insulated well. The crystal of the counter and the housing of the photomultiplier tube, are cooled by a continuous, slow stream

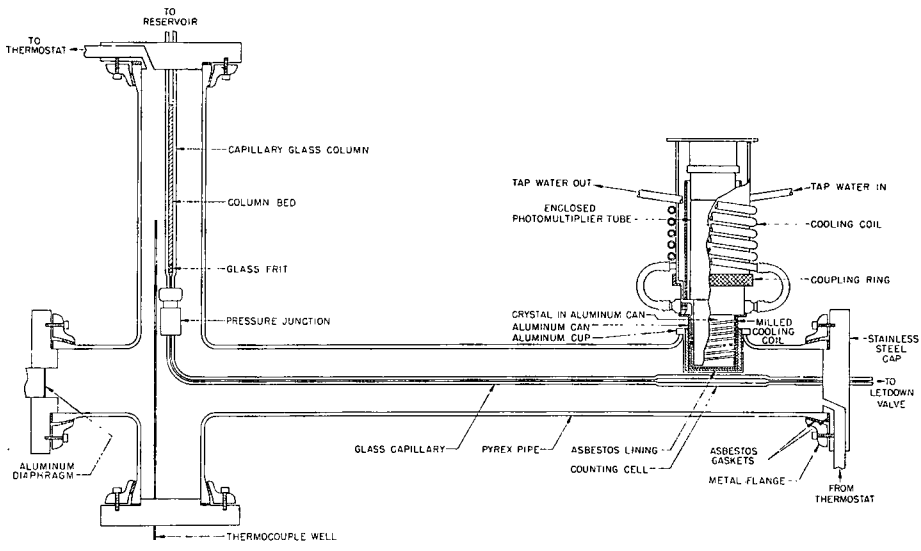

Fig. 3
High-temperature pressurized solubility-column.

of water. While a substantial distance separates the stationary counter from the capillary containing the packed bed of radioactive material, some shielding is necessary to lower the background of the counter to a convenient level. Hence, the column and its jacket are enclosed in a cylindrical lead shield containing about 2 inches of lead in a radial direction and, in addition, a barrier of lead bricks surrounds the scintillation head.

To adapt the equipment to absolute measurements of solubilities, the counting cell must be calibrated, e.g., by comparing its counting rate under steady-state conditions with that of effluent samples counted in the well-type counter used for establishing the counting rate of the original sample.

(3) Kinetics of packed beds

While in recent years a great deal of work has been done on the kinetics of chromatographic columns, we shall restrict ourselves here to a discussion of the time necessary to come to practical equilibrium in a packed bed of fine-mesh particles. If the process is controlled by diffusion through solid spherical particles, the time τ will vary with the square of the radius (R) of the particles and, inversely with the diffusion coefficient $\mathcal{D}$. The solution of the time-dependent diffusion equation [8] for spherical particles into which diffusion occurs is

$$\tau \approx R^2/\mathcal{D}\ [-0.050 - 0.233 \log \Delta] \qquad (1)$$

when Δ, the complement of the fractional attainment of equilibrium, is small. For $\Delta = 0.001$ (99.9% attainment of equilibrium), Eq. (1) becomes $\tau_{.999} \approx 0.65\, R^2/\mathcal{D}$. For 100 mesh particles ($R = 0.0075$ cm) and $\mathcal{D} = 10^{-6}$ or 10^{-7} cm^2 sec^{-1} (which is typical for many commercial ion exchange resins and relatively "fast" ions), $\tau_{.999} \approx 37$ sec ($\mathcal{D} = 10^{-6}$) or 370 sec ($\mathcal{D} \approx 10^{-7}$).

If equilibration is controlled only by diffusion in the interstitial liquid, equilibration times even in a stationary system are very much shorter, primarily because $\mathcal{D}$ is larger ($\mathcal{D}$ = approx. 10^{-5}) than in the solid. The somewhat more favourable geometry should also decrease the equilibration time. These, of course, are the underlying reasons for our preferring preloaded-column techniques for measurements of high distribution coefficients and for solubility measurements where diffusion in the solid is either negligible or non-existent.

Equilibration time controlled by diffusion in the interstitial space of a randomly packed bed is, of course, difficult to compute. Lower and upper limits for τ are presumably given by the size of the octahedral holes ($(\sqrt{2}-1)R$) in a close-packed bed of spheres of uniform radius R and by the size of the spheres themselves. Thus, presumably,

$$(R^2/\mathcal{D})\ [-0.0086 - 0.0343 \log \Delta] < \tau < (R^2/\mathcal{D})\ [-0.050 - 0.233 \log \Delta] \qquad (2)$$

An estimate of τ may also be obtained by assuming that the relatively large fractional interstitial space ($i \approx 0.38$) of a randomly packed bed compared with a close-packed bed ($i \approx 0.26$) results from imperfect packing of spheres of the type described by EYRING [9] in his theory of liquids. He considers dislocations in the second layer of a close-packed arrangement. While two types of such imperfections are feasible, we shall consider only the larger ones. These can accommodate spheres with radius $r \approx 0.62\ R$. The dislocations tend to arrange in channels and we shall assume that τ is approximated by the characteristics of an infinite cylinder of radius $r = 0.62\ R$. For this model,

$$\tau = (r^2/\mathcal{D})\ [-0.0637 - 0.398 \log \Delta] = (R^2/\mathcal{D})\ [-0.025 - 0.153 \log \Delta] \qquad (3)$$

when Δ is small. For $\Delta = 0.001$, one obtains $\tau \approx 0.43\ R^2/\mathcal{D}$, i.e., the equilibration time for the (stationary) liquid in a packed bed is perhaps two-thirds of that for equivalent spheres with radius R.

For 100-mesh particles and $\mathcal{D} = 10^{-5}$, equilibration time will be $\tau_{.999} \approx 2.4$ s. In a flowing system, the equilibration time is presumably considerable less. With τ, and hence the necessary residence time in the bed, of the order of 1 s, one may expect diffusion equilibrium to be reached, even with beds of 1 cm height, at flow rates of many centimeters per minute. Thus the packed-bed method not only permits extremely rapid equilibrations, but, together with radioactive tracers, it affords a rapid method for studying phase changes of the solid and their effects on the equilibrium concentrations in the liquid.

2. Some typical applications

(1) ADSORPTION STUDIES AND SEPARATIONS WITH ORGANIC ION EXCHANGERS

Equilibria between ion-exchange resins and solutions principally carried out with radioactive tracers as analytical tool have been studied in this laboratory for many years. These studies had three major objectives:

(1) development of useful and rapid separation producures;

(2) elucidation of the species and equilibria in aqueous solutions; and

(3) elucidation of the properties of the resins.

The objectives, of course, are interdependent and a given series of experiments usually gives information on more than one topic.

A comparative study of anion-exchange adsorbabilities in HCl of most elements in the periodic table was carried out in this laboratory some years ago [10] and the results are summarized in Fig. 4.

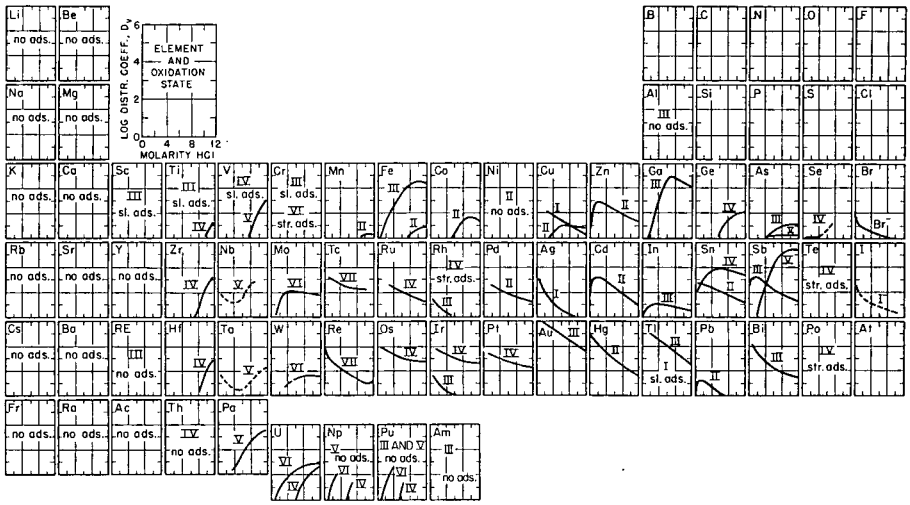

Fig. 4

Adsorption of elements from HCl solutions by an anion exchange resin.

no ads. — no adsorption $0.1 < M$ HCl < 12.

sl. ads. — slight adsorption in 12 M HCl ($0.3 \leq D \leq 1$).

str. ads. — strong adsorption $D_v >> 1$.

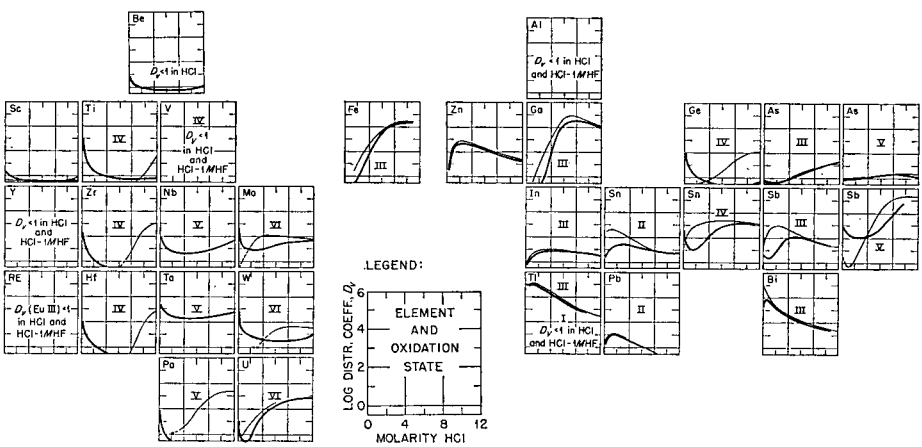

Fig. 5

Adsorption of some elements from HCl and HCl-HF solutions ($0.1 \leq M$ HCl ≤ 12).

——— Distribution coefficients in absence of HF

——— Distribution coefficients in HCl-HF mixtures (usually 1 M HF except Zr (IV), Hf (IV), Nb (V), Ta (V) and Pa (V) where M HF = 0.5)

Since then, a study in HCl–HF media (Fig. 5) was completed [11] which, though less ambitious than the HCl study, still covers most of those metallic elements whose adsorbabilities in HCl and HCl–HF are expected to differ substantially.

Equally broad studies in other mineral acids (e.g., nitrate [12] or sulphate) though desirable, have not yet been carried out, but the number of elements adsorbable from these media seems quite restricted [4]. While a limitation from some points of view, this can also be considered an advantage, since the rapid purification of the few elements which are strongly adsorbed is simplified. Thus, the relatively unique adsorbability of U(VI) from sulphate solutions by anion exchangers affords an unusually effective method for the isolation of this element from low-grade ores.

A collection of adsorption functions of many elements in various media has, of course, direct application to the development of separation methods since – barring kinetic difficulties – regions of high D can be used in the adsorption step and regions of low D in the elution step. By properly spacing eluting conditions (or continuously varying them), sequential elution of elements may be achieved.

While sufficient information seems to have been accumulated for the development of a generalized separations scheme using only ion exchangers (preferably anion exchangers), a broadly tested scheme has so far not been reported. In a cursory examination of some of the problems which might be encountered, we have attempted to develop an anion exchange scheme for the metallic elements of the first long row of the periodic table (Fig. 6).

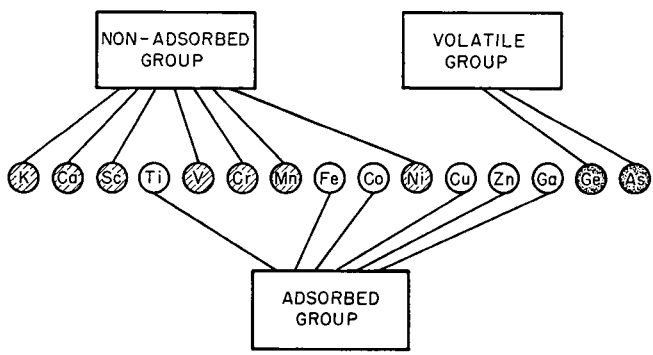

Fig. 6
Group separation in conc. hydrochloric acid.

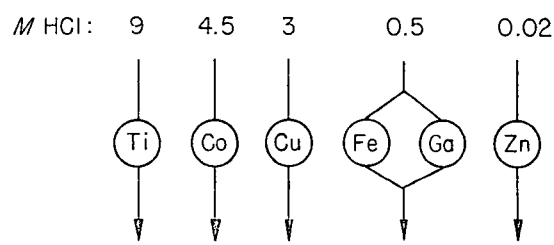

Fig. 7
Separation of elements adsorbed from 12 M HCl.

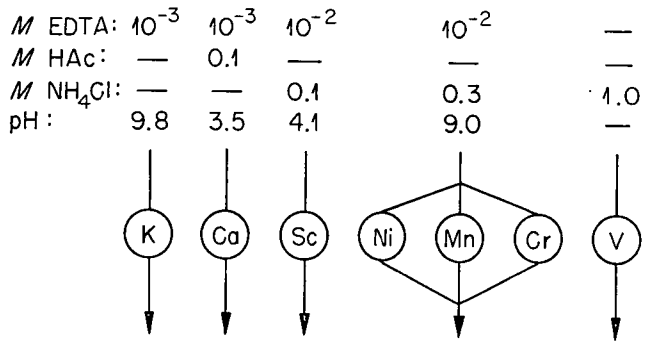

Fig. 8
Separation of elements not adsorbed from 12 *M* HCl.

Using conc HCl as the initial medium, the elements divide into three groups: volatile, adsorbable and non-adsorbable. The division, of course, is not sharp and depends on the volume of effluent collected during the adsorption and washing steps. Most of the elements of the adsorbable group can be separated from each other and isolated by sequential elution (Fig. 7). For separation of the "HCl – non-adsorbable group", we chose anion exchange adsorption and sequential elution in EDTA (ethylenediaminetetraacetic acid) [13] (Fig. 8). The volatile elements can be handled by a special technique [14].

It appears obvious that for the development of ion exchangers as a separation tool, large numbers of elements must be studied under a variety of conditions and the proposed schemes repeatedly tested. It is hard to visualize how such broad studies, involving considerably more than 100000 analyses, could be carried out without the aid of radioactive tracers and the implied simplicity of the analytical work.

(2) Properties of amorphous inorganic solids

Radiotracers may be used in a large variety of studies with inorganic materials as has been repeatedly pointed out. We have used them, in recent years, principally for a broad comparative study of the adsorption properties of various solids, their stability and, to some extent, their kinetic behaviour.

Systematic adsorption studies with amorphous hydrous oxides and insoluble acid salts such as phosphates, tungstates, molybdates, and arsenates revealed them to be excellent ion-exchange materials [15]. While the adsorptive properties of materials such as hydrous oxides had, of course, long been known and ion-exchange had been suggested as one of the mechanisms for this adsorption, their establishment as suitable ion-exchangers was delayed until a concerted attack on the problem could be carried out with radioactive tracers.

Thus, to obtain convincing evidence of the cation-exchange properties of these solids, it appeared necessary to study their behaviour with respect to cations which do not tend to precipitate or hydrolyse, e.g., the alkali metals and, to some extent, the alkaline earths. Such studies are extremely difficult by conventional analytical methods and easy by tracer techniques.

Establishment of ion exchange as a suitable description for adsorption reactions implied to us confirmation of a number of idealized relationships or at least to establish the limits under which these relationships can serve as good approxi-

mations. Thus, the linearity of the adsorption isotherms needed to be confirmed at low-loading, as did the applicability of typical expressions of ion-exchange equilibrium and the well-known log-log relationship between distribution coefficients and ionic strength.

For an exchanger to have practical utility, the rates of exchange must be rapid and the properties reasonably invariant with time. Kinetic studies need to be carried out and detailed elution curves obtained. The latter not only give important kinetic information but also establish the utility of the exchangers for separations.

It is clear that answers to any one of these, or to many other questions require enormous numbers of analyses. Without radiotracers, the resolution of these questions becomes discouragingly slow. Apart from the analytical convenience of radiotracers, their application is almost essential when the adsorptive capacity of the solids is small and operation in the linear portion of the adsorption isotherm is desired, i.e., when only a small fraction of the limited capacity is utilized. Conditions may then occur where the amount adsorbed is below the conventional analytical limits and reasonable accuracy can only be achieved with radiotracers.

It is not feasible here (but see [15]) to give illustrations of the many facets of the use of radioisotopes in the study of these materials, and we shall confine ourselves to three examples:

(a) Use of P^{32} to establish the composition of precipitated phosphates;
(b) Use of P^{32} in the study of the stability of phosphates; and
(c) Separation of Ba^{137} from Cs^{137}.

(a) *Composition of zirconium phosphate*

Addition of phosphoric acid to a solution of a soluble zirconium salt (e.g., $ZrOCl_2 \cdot 8\,H_2O$ in dilute acid) causes precipitation of a gelatinous material which we have loosely called zirconium phosphate. After drying, it has interesting ion-exchange properties. Precipitation of Zr(IV) is essentially complete even if only 0.5 mole of phosphoric acid is added per mole of Zr(IV). It was of interest to establish the P/Zr ratio of the precipitate as a function of the amount of phosphate added to a given amount of Zr(IV).

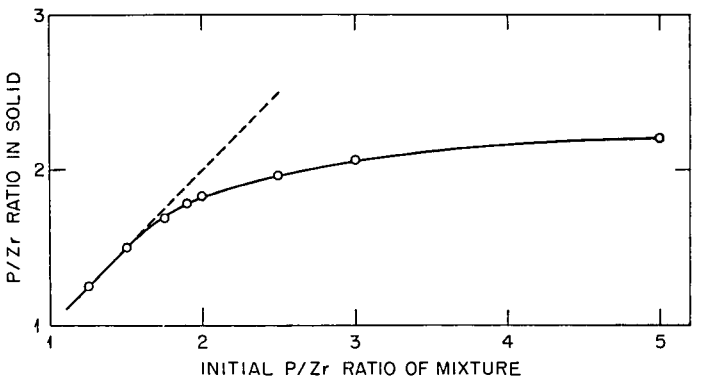

Fig. 9
Composition of Zr (IV) — Phosphate precipitates.

This compositional analysis may readily be achieved by carrying out the precipitation with P^{32}-labelled phosphoric acid and counting either the solid or the solution. The latter technique in this case is more direct since, with the analysis of the precipitate, a correction has to be made for occluded activity.

The results of the experiments are shown in Fig. 9 as a plot of the ratio P/Zr in the solid against the initial P/Zr ratio of the mixture. In this series of experiments, the initial Zr(IV) concentration was kept constant at 0.1 *M*. At low P/Zr ratios, phosphate is essentially quantitatively carried by the precipitate and the initial and final values of P/Zr are equal. The P/Zr ratio in the solid tends to level in the vicinity of 2, the value expected for the parent product of the pyrophosphate. In the presence of a large excess of phosphoric acid, this ratio seems to become slightly larger.

(b) *Stability of zirconium phosphate and titanium phosphate*

While zirconium phosphate is one of the most insoluble materials available, it was not clear whether this stability also extends to retention of phosphate by the solid in flowing streams (phosphate-free) of eluent. Stability with respect to phosphate loss may be established relatively easily by preparing P^{32}-labelled zirconium phosphate and measuring either with shaking experiments, or, preferably, with a packed bed, the extent of removal of activity by various solutions. Since zirconium phosphate has implied usefulness as an ion-exchange material at elevated temperatures, its stability in flowing streams under these conditions is of particular interest. Measurements have therefore been carried out with the high-temperature ion-exchange column [6] at 200°C. The loss of phosphate from the solid (originally dried at 200°C) was found to be less than 0.02% per column volume in such varied media as 1 *M* NH_4NO_3, 0.05 *M* HNO_3, water, and even 0.10 *M* NaOH.

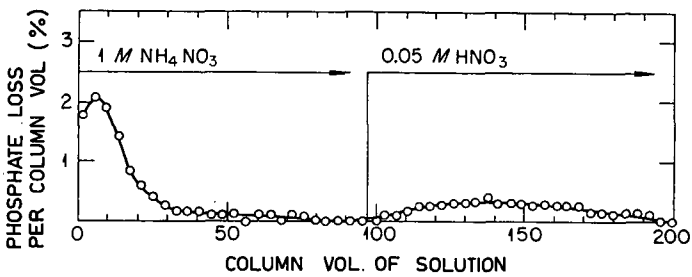

Fig. 10
Phosphate loss from "Titanium Phosphate" at 200°C.
(Drying temp. 200°C).

We may contrast this remarkable stability of zirconium phosphate with that of titanium phosphate. As shown in Fig. 10, phosphate loss from this material is substantial at 200°C.

(c) *Separation of* Ba^{137} *from* Cs^{137}

Inorganic exchangers such as zirconium phosphate not only have remarkable selectivity for various ions but this selectivity is strongly affected by the acidity of the medium in a manner not easily predictable from simple considerations.

Thus, zirconium phosphate in the ammonium form adsorbs alkaline earths such as Ba^{++} much more strongly than alkali metals such as Cs^{+}. In acidic solutions, the reverse is the case; extremely strong adsorption of Cs^{+}. may be achieved under conditions where Ba^{++} does not appreciably adsorb. Thus the elution order can be controlled easily by proper adjustment of acidity.

For the separation of the short-lived (2.6 min) Ba^{137} from Cs^{137} ($T_{1/2}=3$ yr), it is desirable to retain the caesium on the solid and allow the barium to diffuse out and enter the solution; i.e., with zirconium phosphate, acid-eluting conditions are desired. The separation is remarkably effective, at least if it is carried out within a reasonable amount of time after loading the solid with the parent activity.

A small column of zirconium phosphate (hydrogen form) was loaded with Cs^{137} tracer. The activity of the bed was monitored with a sodium-iodide scintillation-

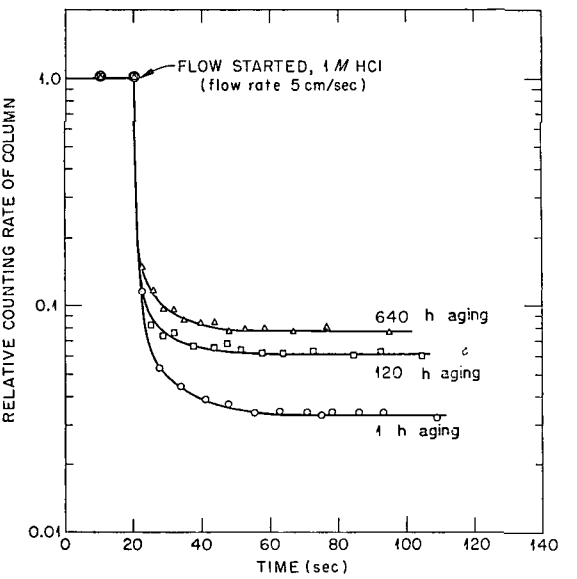

Fig. 11
Separation of 2.6 min Ba^{137} from Cs^{137}.
(Cs^{137} parent adsorbed on 1 ml 80—170-mesh zirconium phosphate).

counter, properly collimated. A 1-*M* HCl solution was pumped through this bed (flow rate 5 cm/sec). As shown in Fig. 11, immediately after starting the pump the activity of the bed decreases very rapidly; on continued pumping the activity levels off at a few per cent of the initial value. If the flow is stopped, the activity of the bed increases again practically to its initial value, the increase occurring with a half-time of about 2.6 min.

Clearly, in this medium, Ba^{137} is almost instantaneously flushed from the column when the flow is started. Since, at least in a closed system, the bed returns to practically its initial activity, there is no significant Cs^{+}-loss. Most of the residual counting rate after about 0.5 min of pumping results from a small fraction of the (continuously produced) Ba^{137} which diffuses much more slowly than the bulk of the Ba^{137}. The counting efficiency for Cs^{137} (bremsstrahlen) is very low in this system.

After many hours of aging (Fig. 11), the residual Ba^{137} content of the sample slowly rises, probably because an increasing part of the Ba^{137} is produced in sites from which it can diffuse only slowly. This type of experiment thus also offers a new type of measurement for aging phenomena. Interestingly, even after 640 h of aging, substantially over 90% of the barium content of the bed may be removed within seconds.

A Cs^{137}-loaded zirconium phosphate column in acid is therefore a very convenient arrangement for the intermittent production ("milking") of this isotope. Since the adsorbent is inorganic, it should be usuable for long times at high radiation levels. The arrangement could also from the basis of a rapidly decaying radiation source. For this purpose, one would want to concentrate the eluted Ba^{137} on another adsorbent which in this acidic medium has high selectivity for Ba^{++} but low selectivity for Cs^{+}. We have found that a packed bed of fine-mesh crystals of barium sulphate fits these requirements. These are extremely selective for Ba^{++}; Cs^{+} is not significantly held. Adsorption of the short-lived Ba^{137} activity occurs presumably through a surface exchange mechanism; there is not sufficient time for substantial diffusion through the particles. The adsorption is extremely fast as demonstrated by the fact that it is essentially quantitative, even with small beds at high flow-rates. Since barium sulphate packs very poorly it seems advisable, for practical applications, to incorporate it into another solid of larger mesh-size. We have used tantalum oxide for this purpose, though other gel-like materials would no doubt be equally effective.

(3) Solution equilibria

Measurement of two-phase equilibria is a favourite method for evaluating complexing reactions in solution. Pertinent experiments would involve measurement of either distribution coefficients or solubilities. While various techniques may be employed to obtain quantitative information on complexing reactions from these, we shall limit ourselves here to describing one example from our anion exchange and one from the solubility work.

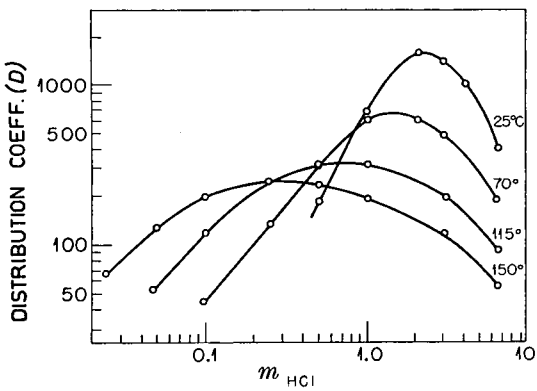

Fig. 12
Adsorption of Zn (II) from HCl solutions as a function of temp.
(Dowex — 1 × 10, Cl^{-} form).

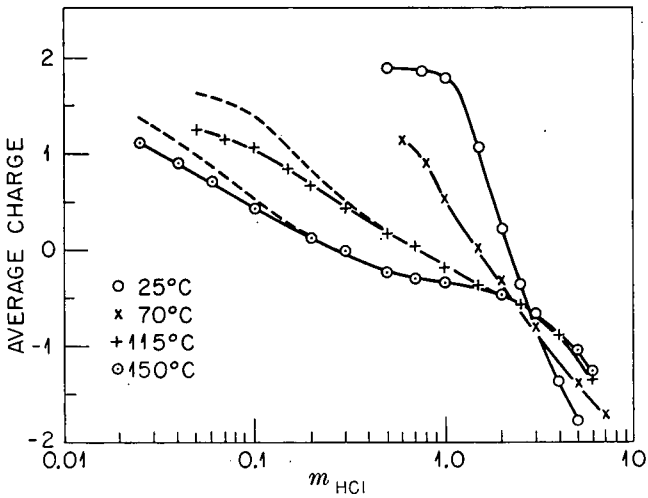

Fig. 13
Chloride complexing of Zn (II) from anion exchange data.
(Solid lines are d log D/d log m HCl; broken lines are corrected for Debye-Hückel theory.)

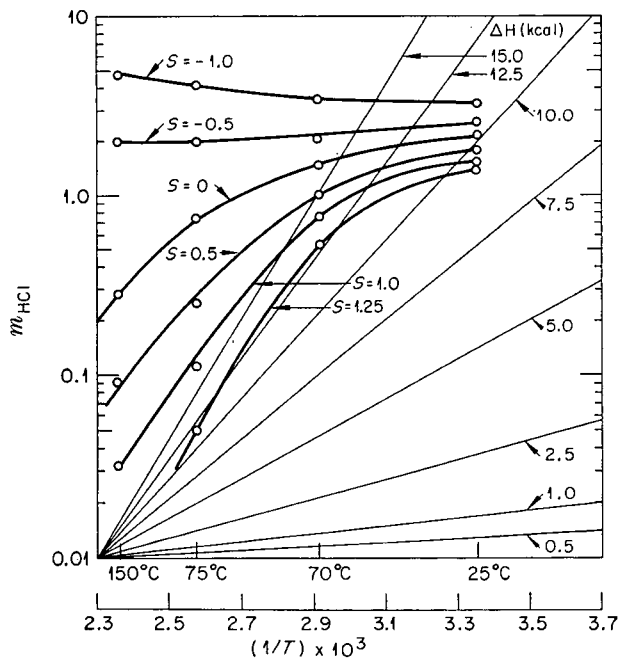

Fig. 14
Estimation of heat of complex formation [Zn (II) in HCl].

In those anion exchange studies where the supporting electrolyte also supplies the ligand, the slope of a plot of log D against log m (where m is the supporting electrolyte concn) yields the average charge $\bar{z}$ of the metal species, after correction is made for resin invasion and activity coefficient effects in both phases [16]. Once $\bar{z}$ is determined, stability constants of the complexes may be obtained. Measurements as a function of temperature yield changes of $\bar{z}$ at a constant concentration of the complexing agent or, alternatively, the change of the concentration of the complexing agent at constant $\bar{z}$ may be determined as a function of temperature. From these observations, average heats and entropies of the complexing reactions may be computed.

Such an analysis of anion exchange data [17] of Zn(II) in HCl in the range 25 to 150°C is illustrated in Figs. 12, 13 and 14. The measurements were made using the high-temperature column technique. Fig. 12 shows the rapid change in adsorbabilities which occurs with temperature. Fig. 13 gives the pertinent slopes ($\mathrm{d} \log D/\mathrm{d} \log m_{\mathrm{HCl}}$) which approximate the average charge. At high temperatures and low HCl concentrations a correction for activity coefficients was made using the Debye-Hückel theory; under these conditions the resin invasion and resin activity coefficient derivatives are negligible. Clearly, complexing increases rapidly with increasing temperature. From Fig. 14, a logarithmic plot of the HCl concentrations at which the adsorption functions have definite slopes, estimates may be deduced of the average enthalpy changes $\Delta\bar{H}$ of the complexing reactions. These are large and positive (approx. 15 kcal/mole) at high temperatures and high values of $\bar{z}$ (low average degree of complexing). Further, $\Delta\bar{H}$ decreases with $\bar{z}$ and becomes slightly negative when $\bar{z}$ is negative.

Similar information may be obtained from measurements of solubility s, except that the slopes $\mathrm{d} \log s/\mathrm{d} \log m$ give the negative of the average charge $\bar{z}$ after

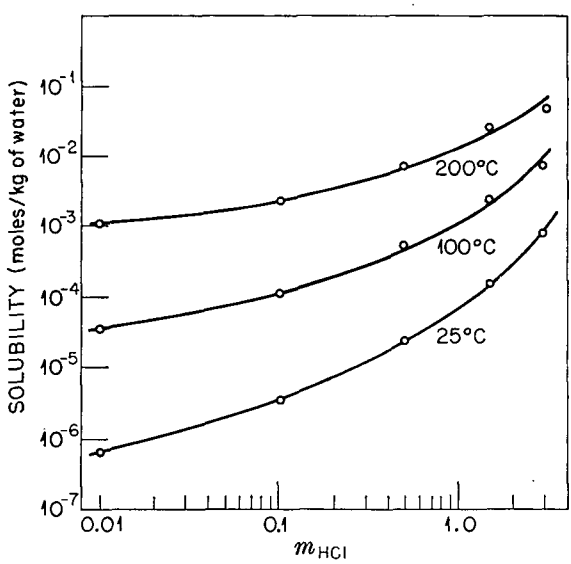

Fig. 15
Solubility of AgCl in HCl solutions at constant temperature.

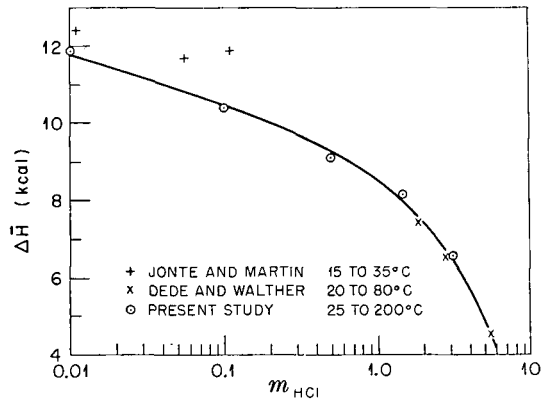

Fig. 16
Apparent heats of solution of AgCl in chloride solutions.

appropriate correction for activity coefficient derivatives. Solubility measurements are somewhat more direct than ion exchange measurements for determining $\bar{z}$ since, of course, the resin invasion and resin activity coefficient terms do not appear. On the other hand, the resin method is more general, since it is not restricted by solubility considerations.

An example [18] of the solubility of AgCl in HCl solutions at 25, 100 and 200°C is illustrated in Fig. 15. The measurements were carried out by the high-temperature column method with Ag^{110}-labelled AgCl. The shape of the solubility function changes remarkably little with temperature T, though the absolute solubilities s increase rapidly with T. Since plots of log s against $1/T$ at const. m_{HCl} are essentially linear, the apparent heats of solution are practically constant in this temperature interval. The enthalpy changes $\Delta\bar{H}$, obtained from these linear plots, are shown in Fig. 16; a comparison of these values with earlier data in the literature [19] [20] is favourable.

The slow change of shape of the solubility functions with temperature (Fig. 15) implies that the complexing reactions of AgCl at 200°C are not very different from those at 25°C. The changes are confined to a flattening of the curves with increasing temperature. Typical values of the slope at $m_{HCl}=0.1$ are 0.94, 0.70 and 0.55 at 25, 100 and 200°C respectively. Assuming that these slopes give the negative of the average charge, one concludes that the average species under these conditions are $AgCl_{1.94}$, $AgCl_{1.70}$ and $AgCl_{1.55}$. Thus AgCl is slightly less complexed by chloride ions at 200°C. The average enthalpy changes for the complexing reactions involving neutral and negative species are slightly negative, as they also were for Zn(II).

In conclusion, it is hoped that the few examples taken from work at our laboratory demonstrate again the wide applicability of tracer techniques in physical-chemical studies. We have placed considerable emphasis on the simultaneous use of packed beds and radioisotopes. These combine rapid equilibration, rapid analysis, reasonable precision and wide adaptability. These simplifications are particularly welcome in high-temperature, high-pressure aqueous systems where they make otherwise very difficult measurements relatively easy.

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DISCUSSION

A. Voigt (United States of America) asked whether the zirconium phosphate column loaded with Cs^{137} could be used repeatedly for the removal of the Ba^{137} daughter.

K. A. Kraus replied that the separation of Ba^{137} from Cs^{137} as described in the paper could be repeated at will. It was even possible to use a four-years-old sample of caesium containing zirconium phosphates; the separation was still satisfactory although in that case the Ba^{137} retention was somewhat higher than with fresher samples. The inorganic exchangers of the type of zirconium phosphate, zirconium tungstate and so on, as well as the hydrous oxides in general, had a surprisingly good reproducibility and that was of course one of the reasons for his preferring those materials.

E. Amis (United States of America) asked whether, in making the Debye-Hückel corrections, Mr. Kraus had had to use anything other than the limiting law.

K. A. Kraus replied that the activity coefficient correction which he had made in estimating the average charge of Zn (II) in HCl was limited to a modified Debye-Hückel equation: $\log \gamma = -Sz_i z_j \cdot \mu^{1}/_{2}/(1 + A\,\mu^{1}/_{2})$. The closest distance of the approach parameter A was taken as $A = 1.5$. It was assumed to be independent of temperature. Linear terms in the activity coefficient were not included although they could be of considerable importance, as he had pointed out in an earlier article [17].

T. Schönfeld (Austria) asked if the author could suggest any reason why the caesium was adsorbed so strongly on the zirconium phosphate exchanger in acid conditions.

K. A. Kraus said he would not care to put forward any theories. Any speculations should take into account the fact that the high selectivity for Cs^+ was typical of the hydrogen form of those exchangers.

D. Geithoff (Federal Republic of Germany) asked how much of the Cs^{137} was milked with the eluted Ba^{137m} under normal working conditions and under optimum conditions.

K. A. Kraus replied that the amount of Cs^{137} lost from the zirconium phosphate bed depended on the amount of fresh solution passed over the bed and on the distribution coefficient. The latter could easily be made as large as 1000, in which case only 0.1% of the caesium was removed per column volume of solution passing over the bed. If losses were to be kept to a minimum, a closed system in which the effluent was returned to the top of the bed should of course be used. The loss of caesium was then given by the distribution coefficient and the ratio of bed volume to total solution volume.

The Chairman (P. Albert, France) said he thought Mr. Kraus' work was of the utmost value, as it was very important to evolve new techniques for the separation of elements by elution with simple mineral acids like HCl, HF and HNO_3. For if a process of rapid "systematic analysis" was to be developed, it was essential not to allow ions which were too complex, or too difficult to eliminate, to accumulate in the solution. He wondered whether Mr. Kraus thought there was hope of separating many other elements by continuing his research in that direction.

K. A. Kraus said he shared the Chairman's enthusiasm for separation processes by ion-exchange with simple inorganic acids as eluents. That, in fact, had been the aim of his separation studies over the last 12 years. The separation scheme proposed in his paper for the first long row of the periodic table, while largely based on simple acids, used EDTA for the sequential separation of the elements of the "HCl-non-adsorbable group" though some of those elements could also be separated from each other by elution with inorganic liquids. He and his associates had often considered extending these studies to the separation of other inorganic ions and had drawn up a tentative programme of work based on their extensive equilibrium studies in HCl, HCl—HF, HNO_3 and H_2SO_4. However, they had not yet gone so far as to test a scheme involving all the metals in the periodic table, though that seemed the next logical objective.

APPLICATION OF RADIOISOTOPES TO THE INVESTIGATION OF THE KINETICS AND MECHANISM OF REACTIONS OF SOME INORGANIC COMPLEX COMPOUNDS

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Abstract — Résumé — Аннотация — Resumen

Application of radioisotopes to the investigation of the kinetics and mechanism of reactions of some inorganic complex compounds. Radioisotopes are invaluable tools in the study of many types of inorganic chemical reactions, particularly those involving complex ionic substances in aqueous solution. One important approach is through research on the rates and mechanisms of isotopic exchange processes. For example, a series of studies has been made of the exchange between carbon-14-labelled "free" carbonate and the ligand carbonate in octahedral complex ions of the type $CoA_2CO_3^+$, where $A = 2\,NH_3$, ethylenediamine (en), propylenediamine (pn), or trimethylenediamine (tn). These studies have led to a rather thorough understanding of the nature of this kind of ligand substitution reaction, and of the part played by the non-exchanging amine ligands in the process. Similar studies of oxalate exchange with tris-oxalato complexes of the form $M(C_2O_4)_3^{-3}$, where M = Co (III), Cr (III), or Rh (III), have been equally fruitful.

An alternative technique, applicable only when using low-atomic-weight radioisotopes such as carbon-14, is to observe the equilibrium or kinetic isotope effects in the reaction of interest. It has, for instance, been possible to interpret differences in the ligand carbonate exchange mechanism of $Coen_2CO_3^+$ and $Cotn_2CO_3^+$ on the basis of equilibrium isotope-effect measurements made on the carbonate exchange reaction. Similarly, data on the kinetic isotope effect in the acid-catalysed aquation of the $Co(NH_3)_4CO_3^+$ ion has supported deductions as to the nature of the rate-determining bond-breakage step in such reactions.

Finally, the mechanistic path of certain atoms or radicals in inorganic reactions, where a choice between alternative explanations must be made, is frequently facilitated by a radioactive tracer experiment. An example is the proof that cyanide does not appear as a rapidly exchanging intermediate in the oxidation of thiocyanate ion by hydrogen peroxide, although cyanide is an important end-product.

Application des radioisotopes à l'étude de la cinétique et du mécanisme des réactions de certains complexes inorganiques. Les radioisotopes sont particulièrement précieux dans l'étude de nombreux types de réactions de chimie minérale, notamment de réactions où interviennent des ions complexes en solution aqueuse. Les recherches sur la vitesse et le mécanisme des échanges isotopiques constituent un aspect important de ces applications. C'est ainsi qu'on a fait une série d'études sur l'échange entre du carbonate "libre" marqué au carbone-14 et le carbonate qui joue le rôle de coordinat dans les ions complexes octaédriques du type $CoA_2CO_3^+$, où A représente le $2NH_3$, ou l'éthylène-diamine (én), ou la propylène-diamine (pn) ou la triméthylène-diamine (tn). Grâce aux études ainsi effectuées, on connaît assez exactement la nature de ces réactions par substitution de coordinats, ainsi que le rôle joué par les coordinats aminés qui ne participent pas à l'échange. Des études analogues sur l'échange entre oxalates dans les complexes tri-oxaliques de forme $M(C_2O_4)_3^{3-}$, où M = Co (III), Cr (III), ou Rh (III), n'ont pas été moins fécondes en résultats.

Une autre technique, applicable seulement lorsqu'on utilise des radioisotopes de faible poids atomique comme le carbone-14, consiste à observer les effets d'équilibre ou les effets cinétiques que les isotopes exercent sur la réaction étudiée. C'est ainsi qu'il a été possible d'interpréter des différences dans le mécanisme d'échange du coordinat carbonate dans le $Coen_2CO_3^+$ et le $Cotn_2CO_3^+$, par mesure de l'effet isotopique à l'état d'équilibre dans la réaction d'échange des carbonates. De même, des données sur l'effet isotopique cinétique dans l'hydratation avec catalyseur acide de l'ion $Co(NH_3)_4CO_3^+$ ont confirmé les déductions faites en ce qui concerne l'étape à laquelle se rompt la liaison, étape qui détermine la vitesse de ces réactions.

Enfin, la détermination des positions successives de certains atomes ou radicaux, dans des réactions inorganiques pour lesquelles il faut choisir entre différentes explications, est souvent facilitée par l'emploi d'indicateurs radioactifs. C'est ainsi qu'on a pu prouver que le cyanure n'est pas un produit intermédiaire qui subit un échange rapide dans l'oxydation de l'ion thiocyanate par le péroxyde d'hydrogène, quoique le cyanure soit un produit final important de la réaction.

Применение радиоизотопов к исследованиям кинетики и механизма реакций некоторых неорганических сложных соединений. Использование радиоизотопов оказывает неоценимые услуги при исследовании химических неорганических реакций самых разнообразных видов и, в частности, реакций со сложными ионизированными веществами в водных растворах. Одним из важных методов служит изучение скорости и механизма процессов изотопного обмена. Так, например, был проведен ряд исследований обмена между т.н. „свободным" карбонатом, меченным углеродом-14, и связывающим карбонатом октоэдральных сложных ионов типа $CoA_2CO_3^+$, где $A = 2\ NH_3$, этилендиамин (en), пропилендиамин (pn) или триметилендиамин (tn). Эти исследования привели к довольно точному пониманию характера реакций этого рода по замене связи, а также роли в этой реакции неучаствующих в обмене связывающих аминовых звеньев. Аналогичные исследования обмена оксалатов, проведенные со сложными триоаксалатами типа $M(C_2O_4)_3^{-3}$, где M = Co (III), Cr (III) или Bn (III), дали столь же плодотворные результаты.

Другим методом, применимым только в случае использования радиоизотопов с малым атомным весом, как например углерода-14, может служить изучение в соответствующих реакциях равновесия или кинетического изотопного воздействия. Так, например, на основании измерения равновесия воздействия изотопов в реакциях обмена карбонатов представилось возможным истолковать различие в механизме обмена связывающих карбонатов $Coen_2CO_3^+$ и $Cotn_2CO_3^+$. Подобным же образом данные о кинетическом воздействии изотопов при кислотно-катализированной гидратации ионов $Co(NH_3)_4CO_3^+$ подтвердили выводы относительно характера этих реакций в стадии разрыва связи, определяющей скорость реакций.

Наконец, опыты с применением радиоактивных индикаторов часто облегчают изучение траектории некоторых атомов или радикалов в неорганических реакциях, при которых приходится делать выбор между двумя возможными объяснениями. Примером этого может служить доказательство того, что, по-видимому, при окислении тиоционатовых ионов перекисью водорода цианиды не являются средой быстрого обмена, хотя они и являются важным конечным продуктом.

Aplicación de los radioisótopos al estudio de la cinética y del mecanismo de las reacciones de algunos complejos inorgánicos. Los radioisótopos constituyen medios auxiliares de incalculable valor para el estudio de muchos tipos de reacciones de la química inorgánica, especialmente de aquellas en que intervienen iones complejos en solución acuosa. Uno de sus aspectos más importantes es la determinación de las velocidades de reacción y del mecanismo de los intercambios isotópicos. Por ejemplo, el autor ha realizado una serie de estudios sobre el intercambio entre carbonato "libre" marcado con carbono-14 y carbonato ligante en iones complejos octaédricos del tipo $CoA_2CO_3^+$, donde $A = 2\ NH_3$, etilendiamina (en), propilendiamina (pn) o trimetilendiamina (tn). Estos estudios han permitido comprender a fondo la natura-

leza de las reacciones de sustitución de ligantes de este tipo y del papel que desempeñan en el proceso los ligantes amino que no experimentan intercambio. Igualmente fructíferos han sido unos estudios análogos del intercambio de restos oxalato en complejos trioxálicos de fórmula $M(C_2O_4)_3^{3-}$, en la que M = Co (III), Cr (III) o Rh (III).

Otra técnica, que puede aplicarse solamente cuando se emplean radioisótopos de bajo peso atómico, tales como el carbono-14, consiste en observar los efectos de equilibrio o los efectos cinéticos que los isótopos ejercen sobre la reacción. Como ejemplo, el autor ha logrado interpretar diferencias entre los mecanismos de intercambio de los restos carbonato ligantes entre el $Coen_2CO_3^+$ y el $Cotn_2CO_3^+$ por medición del efecto isotópico, en estado de equilibrio, efectuada en la reacción de intercambio de carbonatos. De la misma manera, los datos relativos al efecto cinético de los isótopos en la hidratación del ion $Co(NH_3)_4CO_3^+$ catalizada por ácidos han corroborado las teorías sobre el carácter de la fase de ruptura de enlaces, que determina la velocidad de estas reacciones.

Por último, los experimentos con trazadores radiactivos facilitan frecuentemente el estudio de las posiciones sucesivas de ciertos átomos o radicales en las reacciones inorgánicas para las que existen diversas explicaciones teóricamente posibles. Como ejemplo puede citarse la demostración de que en la oxidación del ion tiocianato por peróxido de hidrógeno, el cianuro no es un producto intermedio que sufre un intercambio rápido a pesar de que constituye uno de los principales productos finales.

Radioisotopes have proved to be invaluable tools in the study of many types of inorganic chemical reactions, particularly those of complex ionic substances in aqueous solution. A recent review [1] has admirably summarized the possibilities of this type of research. The following approaches have proved to be unusually fruitful, and have been used repeatedly over the past several years in the present author's laboratory:

(i) Studies of the rates and mechanisms of isotopic exchange processes involving substitution reactions of co-ordinated ligands.
(ii) Determination of equilibrium and/or kinetic isotope effects in reactions in which low-atomic-weight radioisotopes such as carbon-14 are implicated.
(iii) Radioisotopic tracer investigation of the mechanistic path of specified atoms or radicals in reactions where a choice between alternatives is not readily made by any other technique.

It is the purpose of this paper to present a résumé of a number of these researches, pointing out the generalizations which have been developed on the basis of the most recent work, some of it as yet unpublished.

One series of studies has been concerned with the nature of the exchange reaction which occurs in aqueous solution between carbon-14-labelled "free" carbonate ion and the ligand carbonate of octahedral complexes of the type $CoA_2CO_3^+$. Work has been done in which the diamine ligand A was $(NH_3)_2$ [2], ethylenediamine (en) [3], trimethylenediamine (tn) [4], and propylenediamine (pn) [5]. The technique used in this type of work is to react the carbonato complex with carbon-14-labelled "free" carbonate (e.g. $Na_2C^{14}O_3$) in buffered aqueous solution for various periods of time at fixed temperature. The free carbonate is then precipitated as the barium salt and assayed for radioactivity. The plot of log (1 — fraction of exchange) against time readily enables evaluation of the rate of exchange R, which is a function of the concentrations of the various reactants. To do this, one employs the standard expression (neglecting isotope effects [6]):

$$R = \frac{0.693}{t_{\frac{1}{2}}}\left(\frac{ab}{a+b}\right).$$

In this, $t_{\frac{1}{2}}$ is the half-time of exchange; a and b are the total concentrations of the exchanging reactants, complexed and free-carbonate, respectively. The nature of the function R may then be deduced by studying its variation with change in the significant concentration factors.

On the basis of recent detailed studies of the pn_2 analogue [5], it now appears that all four of the carbonato complexes mentioned above react according to a common mechanism:

$$CoA_2CO_3^+ + H_2O \rightleftarrows CoA_2CO_3 \cdot H_2O^+ \text{ (rapid equilibration) } K_1 \quad (1)$$

$$CoA_2CO_3 \cdot H_2O^+ + H^+ \rightleftarrows CoA_2HCO_3 \cdot H_2O^{++} \text{ (rapid equilibration) } K_2 \quad (2)$$

$$CoA_2HCO_3 \cdot H_2O^{++} + HC^*O_3^- \rightleftarrows CoA_2HC^*O_3 \cdot H_2O^{++} + HCO_3^- \text{ (slow) } k_3 \quad (3)$$

$$CoA_2HCO_3 \cdot H_2O^{++} + H_2O \rightleftarrows CoA_2(H_2O)_2^{+++} + HCO_3^- \text{ (slow) } k_4 \quad (4)$$

$$CO_3^= + H^+ \rightleftarrows HCO_3^- \text{ (rapid equilibration) } K_5 \quad (5)$$

Carbonate exchange may occur either through the biomolecular substitution path of reactions (1), (2) and (3), or through the dissociative mechanisms of reactions (1), (2) and (4). Neglecting the indeterminate kinetic contribution of the aquation equilibrium of reaction (1), the rate law takes the form:

$$R = k_3\left(\frac{K_2h}{K_2h+1}\right)\left(\frac{K_5h}{K_5h+1}\right)ab + k_4\left(\frac{K_2h}{K_2h+1}\right)a$$

Here, a and b have their previous significance, h is the hydrogen ion concentration, the small k's are rate constants, and the large K's are equilibrium constants. This proposal fits the experimental data very satisfactorily for all four complexes studied. The published values [7] for K_5 are used, and in each case it is found that K_2 is smaller than, but of the same order of magnitude as, K_5. This is reasonable, since one would expect the co-ordinated carbonate to be somewhat less basic than the free ion, but not markedly so. The $(NH_3)_4$ and en_2 species are closely similar to the pn_2 complex, as might be anticipated. However, the $Cotn_2CO_3^+$ ion, in contrast, reacts much more slowly than the others, such that exchange does not become conveniently measurable until the temperature is raised to about 50°C. It has been suggested that this greater resistance to exchange is the result of more favourable geometry for hydrogen-bonding to the CO_3 oxygens in this complex [4]. Recent deuterium exchange experiments [5] involving the various carbonato complexes appear to confirm this view in that the exchange rate is about ten times greater for the en_2 analogue than for the tn_2. It is of interest that the reactant concentration-dependence of the $Co(NH_3)_5CO_3^+/C^{14}O_3^=$ exchange reaction [8] is also fitted by the proposed general mechanism. For this ion, K_2 is known to be only 2.5×10^6 at 25° [9], so that the factor $K_2h/(K_2h+1)$ reduces to K_2h at any pH over 8, leading to the much stronger dependence of this exchange on hydrogen ion concentration than is observed for the others.

Oxalate exchange studies of the series of oxalato complex ions $M(C_2O_4)_3^{\equiv}$, where M = Co (III), Cr (III) and Rh (III), have been carried out in a manner analogous to the work just described, utilizing carbon-14-labelled "free" oxalate

ion. Large differences are observed in the behaviour of the three complexes. Oxalate exchange [10] with the cobaltiate is so slow at 50°C, as to be completely masked by the concurrent, intramolecular, oxidation-reduction reaction:

$$2\ Co\ (C_2O_4)_3^{\equiv} \rightarrow Co\ (C_2O_4)_2^{=} + Co\ (C_2O_4)_3^{-4} + 2\ CO_2.$$

The chromiate, on the other hand, is completely stable in neutral or slightly acidic aqueous solution for long periods of time at 90°C, and the rate of oxalate exchange is readily measurable [10] at 75°. The data are consistent with a mechanism involving the following series of reversible reactions:

$$Cr\ (C_2O_4)_3^{\equiv} + H_2O \rightleftarrows Cr\ (C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{\equiv}\ \text{(rapid)}\ K_6 \qquad (6)$$

$$Cr\ (C_2O_4)_3^{\equiv} + H_3O^{+} \rightleftarrows Cr\ (C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{=}\ \text{(rapid)}\ K_7 \qquad (7)$$

$$Cr\ (C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{\equiv} + H_2O \rightleftarrows Cr\ (C_2O_4)_2\ (H_2O)_2^{-} + C_2O_4^{=}\ \text{(slow)}\ k_8 \qquad (8)$$

$$Cr\ (C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{=} + H_2O \rightleftarrows Cr\ (C_2O_4)_2\ (H_2O)_2^{-} + HC_2O_4^{-}\ \text{(slow)}\ k_9 \qquad (9)$$

$$Cr\ (C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{\equiv} + HC_2{}^{*}O_4^{-} \rightleftarrows Cr\ (C_2O_4)_2 \cdot OC_2{}^{*}O_3 \cdot H_2O^{\equiv} + HC_2O_4^{-}\ \text{(slow)}\ k_{10} \qquad (10)$$

$$Cr\ (C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{=} + HC_2{}^{*}O_4^{-} \rightleftarrows Cr\ (C_2O_4)_2 \cdot OC_2{}^{*}O_3H \cdot H_2O^{=} + HC_2O_4^{-}\ \text{(slow)}\ k_{11} \qquad (11)$$

It is seen that, like the carbonato cobalt complexes, two types of exchange path are offered, one by way of aquation and one by way of bimolecular oxalate substitution. A difference is that parallel acid-catalysed and non-catalysed mechanisms obtain here, so that the total rate of exchange is the sum of four contributions. Assuming continuous maintenance of the equilibria (6) and (7), and that the equilibrium constant K_7 is not too large, the rate law is:

$$R = K_6k_8a + K_6k_8ab + K_7k_9ah + K_7k_{11}abh$$

In this, the small k's are rate-determining rate constants and a, b and h represent concentrations of complexed and free oxalate and of hydrogen ion, respectively. This law interprets the experimental data very well, and has been confirmed by two further types of investigation. In the first of these [10], it was shown that the ionic strength has little effect on R when the ion-molecule reactions (6) and (8) account for most of the exchange (conditions of high pH and low free-oxalate concentration). However, R becomes strongly dependent on ionic strength when the ion-ion reaction (10) makes a major contribution to the exchange (high free-oxalate concentration). Additional support of the chromiate exchange mechanism is provided by a recent study of the acid-catalysed aquation of this complex. In this work [11], it was found that use of increasing proportions of heavy water in the solvent increased the rate of aquation quantitatively in accordance with the predictions of the Gross-Butler theory as recently revised by PURLEE [12]. This accord is to be expected only if a proton pre-equilibration of the type of reaction (7) is indeed operative.

The tris-oxalato rhodium (III) ion resembles the corresponding chromium (III) species in oxalate exchange behaviour but with two major divergencies [13]. The first of these is the markedly greater resistance of the rhodiate to oxalate substitution such that the exchange only becomes measurable in experiments done in sealed tubes at 130°C. Secondly, the bimolecular exchange path makes little, if any, contribution in this instance. A much greater resistance to breakage

of the metal-oxygen co-ordination bond can probably account for both these effects. This contrast in behaviour of the tris-oxalato-rhodium (III) and chromium (III) ions has also appeared in a study of their acid-catalysed aquation reactions. The pH-dependence differs markedly and the rate of aquation of the Rh (III) complex is only about 0.006 as great as that of the Cr (III) [13]. The contrast has also recently been noted [14] in a study of exchange of oxygen-18-labelled water between solvent and the ion Rh $(H_2O)_6^{+++}$. The latter exchanges at a rate about 0.007 as great as does the Cr $(H_2O)_6^{+++}$ under comparable conditions [15].

In all the work thus far discussed, active participation of water molecules in various reaction steps has been a feature of each mechanism. A recent study in this laboratory [16] has been aimed at evaluation of the role of solvent water in some reactions involving *cis* and *trans* forms of the complex ion Co en_2 Cl_2^+. Using, as solvent, acidified methanol containing predetermined small percentages of water, the kinetics of the *cis-trans* interconversion and of "free" chloride exchange with the *trans* form of the complex were studied. The first was done by spectrophotometry and the second by standard radiochemical procedures using chlorine-36-labelled free chloride. The results obtained required consideration of the intermediate partially aquated ion Co en_2 $Cl \cdot H_2O^{++}$, and the following mechanism was postulated to account for both reactions mentioned:

$$cis - Coen_2Cl_2^+ + H_2O \rightarrow Coen_2Cl \cdot H_2O^{++} + Cl^- \quad k_{12} \tag{12}$$

$$Coen_2Cl \cdot H_2O^{++} + Cl^- \rightleftarrows trans - Coen_2Cl_2^+ + H_2O \quad k_{13},\ k'_{13} \tag{13}$$

$$cis - Coen_2Cl_2^+ \rightarrow trans - Coen_2Cl_2^+ \quad k_{14} \tag{14}$$

The rate-law corresponding to this mechanism was confirmed by evaluation of the data by electronic computer technique, enabling the various rate constants to be determined. Very satisfactory correspondence between observed and calculated concentration/time curves was obtainable. It is noteworthy that k_{12} and k'_{13} turn out to be pseudo-first-order rate constants of magnitude proportional to the water content of the solvent, while k_{13} and k_{14} are true first-order constants. Furthermore, good agreement exists between k_{13} as obtained from *cis-trans* interconversion data and from chloride exchange data.

We shall now turn to the second general type of investigation under review, that involving isotope effects. An example of what can be deduced from equilibrium isotope-effect studies is offered by work on the exchanges:

$$CoA_2CO_3^+ + C^{14}O_3^{=} \rightleftarrows CoA_2C^{14}O_3^+ + CO_3^{=} \tag{15}$$

where A is en or tn. Earlier studies [17] [18] had shown that for the en_2 complex, practically no isotope discrimination occurs. However, the tn_2 analogue does show appreciable isotope effect [19], such that the equilibrium constant for reaction (15) is $K = 0.93$ at 50°C. This indicates that, while the CO_3 group in the $Coen_2CO_3^+$ ion differs little chemically from free carbonate ion, the same group in $Cotn_2CO_3^+$ must have an appreciably different partition function ratio for carbon-14 and carbon-12 species than does free carbonate. Such a divergence would exist if the co-ordinated CO_3 group in the tn_2 ion is largely chelated, when it resembles carbonyl compounds of the form $X_2C=O$. For the CO_3 group in monodentate form, however, with water occupying the sixth ligand position, little isotope effect would be anticipated, since the partition function of the

group$\leftarrow OCO_2$ should be very close in magnitude to that for HCO_3^- or $CO_3^=$. Application of this reasoning to the proposed mechanism of carbonate exchange (reactions (1) to (5)) suggests that reaction (1) may be essentially complete in the case of $Coen_2CO_3^+$ (K, large), but not so for $Cotn_2CO_3^+$ (K, small). Comparison of molecular models of the two ions supports this view, in that there is much more steric hindrance to the addition of a water molecule to the tn_2 complex than to the en_2.

An example of the use of kinetic isotope effect in a mechanism elucidation is the work [20] on the acid-catalysed decomposition consisting of reactions (1) and (2) above, followed by:

$$Co(NH_3)_4HCO_3 \cdot H_2O^{++} + H_3O^+ \rightarrow Co(NH_3)_4(H_2O)_2^{+++} + H_2O + CO_2 \qquad (16)$$

No isotope effect was observable in this reaction, as indicated by the fact that the CO_2 liberated on fractional decomposition of carbon-14-labelled complex ion was of constant activity irrespective of fraction of reaction. It is thus concluded that the rate-determining step does not involve carbon-oxygen bond breakage. Studies of this reaction and of the corresponding process for $Co(NH_3)_5CO_3^+$ in oxygen-18-labelled solvent water, however, indicate that the first bond to oxygen broken is probably the C-O bond [21]. It must therefore be concluded that the rate-determining step in this decarboxylation is reaction (2), which involves no bond breakages in the complex. Although this reaction is assumed to be fast relative to (3) or (4), it may very well be slow in relation to (16) in appreciably acidic solution.

The final example of radioisotope use to be discussed here is drawn from a recent study [22] of the oxidation of thiocyanate ion by hydrogen peroxide. The overall reaction in the range $4 < pH < 12$ is quite accurately given by the equations:

$$4H_2O_2 + SCN^- \rightarrow HSO_4^- + HOCN + 3H_2O \qquad (17)$$

$$HOCN + 2H_2O \rightarrow HN_4^+ + HCO_3^- \qquad (18)$$

However, small amounts of cyanide are formed in addition to the major products indicated. It was therefore of interest to determine whether the mechanisms of reactions (17) or (18) involved any step in which cyanide appeared as a short-lived, rapidly-exchanging intermediate. The reaction was therefore performed in the presence of carbon-14-labelled cyanide and the carbonate product was examined for radioactivity. Only a negligible fraction of activity appeared in this product, eliminating the cyanide intermediate possibility suggested. The path of reaction eventually deduced takes, as the rate-determining step, the reaction

$$H_2O_2 + SCN^- \rightarrow HOSCN + OH^-$$

with subsequent reactions of HOSCN leading to all the products, including the cyanide.

ACKNOWLEDGEMENTS

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SOME SOLVENT EXTRACTION STUDIES OF TRIVALENT METAL HALIDES*

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Abstract — Résumé — Аннотация — Resumen

Some solvent extraction studies of trivalent metal halides. Radiotracer techniques have made possible physical-chemical studies of the distribution of Ga (III) and In (III) between aqueous HCl and HBr solutions and the organic solvents, bis (2-chloroethyl) ether and nitrobenzene. From measurements of the extraction coefficients over a metal concentration range of greater than 10^{10} and under conditions where the coefficient varies by a factor of 10^5, the empirical behaviour of these systems has been thoroughly explored. The data have been explained in terms of ionization of the complex acid, HMX_4, in these relatively high dielectric solvents.

From the variation of the extraction coefficient with metal concentration the ionization constant has been calculated of the supporting electrolyte, HCl or HBr, in the non-aqueous phase using a method developed by Poskanzer.

Variation of the extraction coefficient with HX concentration has been used to calculate stability constants for the complex species MX_3 and MX_4^-. Since these are aqueous-phase reactions they are independent of the organic solvent used and excellent agreement is obtained for In (III)-HCl, using both bis (2-chloroethyl) ether and nitrobenzene.

Attempts to evaluate the formation constants for gallium chloride and bromide complexes failed since the complex formation occurs over a very narrow range of acid concentration. Calculation from extraction data of the fraction, $(GaCl_4^-)/\Sigma$ Ga (III), as a function of HCl concentration gave a quantitative agreement with the data obtained from ion-exchange measurement by Kraus and Nelson.

Quelques études sur l'extraction par solvant d'halogénures de métaux trivalents. Les techniques utilisant des indicateurs radioactifs ont permis l'étude physico-chimique de la distribution du gallium (II) et de l'indium (III) entre les solutions aqueuses d'HCl et d'HBr et les solvants organiques éther bis (chloro-2-éthylique) et nitrobenzène. On étudié d'une façon empirique et approfondie le comportement de ces systèmes, en se fondant sur les mesures des coefficients d'extraction pour une gamme de concentrations du métal supérieure à 10^{10} et dans des conditions où le coefficient varie selon un facteur de 10^5. Les données ont été expliquées en termes d'ionisation de l'acide complexe HMX_4 dans ces solvants à constante diélectrique relativement très élevée.

D'après la variation du coefficient d'extraction en fonction de la concentration du métal, on a calculé la constante d'ionisation de l'électrolyte de support, HCl ou HBr, dans la phase non aqueuse, en appliquant une méthode mise au point par Poskanzer.

La variation du coefficient d'extraction en fonction de la concentration d'HX a été utilisée pour calculer les constantes de stabilité, pour les espèces complètes MX_3 et MX_4^-. Etant donné que ces réactions ont lieu en phase aqueuse, elles sont

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indépendantes du solvant organique et l'on obtient une excellente concordance pour le système indium (III) — HCl en employant de l'éther bis (chloro-2-éthylique) et du nitrobenzène.

Les efforts en vue d'évaluer les constantes de formation des complexes du chlorure et du bromure de gallium ont échoué, car la formation du complexe ne se produit *qu'à l'intérieur d'une gamme très restreinte* de concentrations de l'acide. Les résultats des calculs effectués d'après les données d'extraction de la fraction $(GaCl_4^-)/\Sigma$ Ga(III), en fonction de la concentration d'HCl, correspondent quantitativement aux résultats obtenus par Kraus et Nelson au moyen des échanges d'ions.

Изучение экстракции некоторых растворителей из трехвалентных металлических галоидов. Метод меченых атомов позволил провести изучение физико-химического распределения Ga (III) и In (III) между водными растворами HCl и HBr и органическими растворителями, двойным эфиром (2-хлороэтил) и нитробензолом. На основе измерений коэффициентов экстракции при концентрации металла выше 10^{10} и при колебании данного коэффициента в пределах 10^5 тщательно было разработано эмпирическое поведение данных систем. Результаты выражались в степени ионизации сложной кислоты, HMX_4, известной в качестве растворителя с относительно высокими диэлектрическими свойствами.

По колебаниям коэффициента экстракции при различной концентрации металла была получена константа ионизации вспомогательного электролита, HCl или HBr, в неводной фазе с использованием метода, разработанного Посканцером.

Вариации коэффициента экстракции с концентрацией HX использовались для расчета констант стабильности для сложных образцов MX_3 и MX_4^-. Так как они являются реакциями водной фазы, то не зависят от использованного органического растворителя, и получена полная согласованность для In (III)—HCl при использовании двойного эфира (2-хлороэтил) и нитробензола.

Попытки проведения оценки образования констант для галлиевого хлорида и соединений брома окончились неудачей, так как сложное образование происходит в очень узком диапазоне концентрации кислоты. Расчеты на основе результатов экстракции фракции $(GaCl_4^-)/\Sigma$Ga (III) в качестве функции от концентрации HCl находятся в количественном соответствии с результатами, полученными Краусом и Нельсоном при измерении ионного обмена.

Algunos estudios de la extracción mediante disolventes de haluros de metales trivalentes. Las técnicas que emplean trazadores radiactivos permiten efectuar estudios químico-físicos de la distribución del Ga (III) y del In (III) entre soluciones acuosas del HCl y HBr, y los disolventes orgánicos éter bis (2-cloroetílico) y nitrobenceno. Los autores han examinado empíricamente el comportamiento de estos sistemas midiendo los coeficientes de extracción para concentraciones del metal que abarcan un intervalo superior a 10^{10} y en condiciones en las que el orden de magnitud del coeficiente varía en un intervalo de 10^5. Los autores explican los datos obtenidos sobre la base de la ionización del ácido complejo HMX_4 en estos disolventes, cuyas constantes dieléctricas son relativamente elevadas.

Empleando un método ideado por Poskanzer, han calculado la constante de ionización del electrolito soporte, HCl o HBr, en la fase no acuosa a partir de las variaciones que el coeficiente de extracción experimenta en función de las concentraciones del metal.

Las variaciones del coeficiente de extracción con la concentración de HX han servido para calcular las constantes de estabilidad de las especies complejas MX_3 y MX_4^-. Como se trata de reacciones en fase acuosa, las constantes son independientes del disolvente orgánico que se emplee. Para el sistema In (III)-HCl los autores obtuvieron resultados perfectamente concordantes tanto al emplear éter bis (2-cloroetílico) como nitrobenceno.

Los autores no consiguieron evaluar las constantes de los complejos de cloruro y bromuro de galio porque dichos compuestos sólo se forman en un intervalo de con-

centraciones de ácido muy estrecho. Los valores del cociente ($GaCl_4^-$)/ Σ Ga (III) en función de la concentración de HCl, calculados a partir de los datos de extracción, concuerdan con los datos que Kraus y Nelson obtuvieron por mediciones del intercambio iónico.

1. Introduction

Previously reported work from these laboratories [1] [2] gave the preliminary results of the extraction of Ga(III) and In(III) from HCl and In(III) from HBr solutions by bis(2-chloroethyl)ether. This paper reports additional results from these studies, and data and results in the systems Ga(III)-HBr-bis(2-chloroethyl) ether and Ga(III) and In(III)-HCl-nitrobenzene. These results support the hypothesis that HMX_4 is a relatively strong acid in the organic phase [3], provide values of the ionization constants of HCl and HBr in the organic phase and of the stability constants k_3 and k_4 for $InCl_4^-$ and $InBr_4^-$ and confirm the unusual behaviour of the formation of $GaCl_4^-$ reported by Kraus *et al.* [4].

2. Experimental

The solvents, bis(2-chloroethyl)ether and nitrobenzene were purified by the method previously described [2]. The ether was stored in dark containers under dry nitrogen and used within 24 h of purification. The nitrobenzene was very much less sensitive to light, air and moisture, and gave satisfactory extraction results up to a week after purification without special storage precautions.

Analytical grade acids were used for making all solutions. Carrier solutions of Ga(III) and In(III) were prepared by dissolving the metals (99.95 + % purity) in HCl or HBr.

Analytical-grade zinc chloride was dissolved in 8 *M* HCl and extracted with bis(2-chloroethyl)ether to remove traces of inactive gallium. Zinc hydroxide was precipitated, washed and ignited to the oxide for use as target material. Deuteron bombardment of 100 mg ZnO at 15 MeV for 30–40 μAh gave Ga^{66} (9.5h) and Ga^{67} (78h) plus short-lived isotopes. Carrier-free separations were effected by dissolving the oxide in 8 *M* HCl or 8 *M* HBr, extracting the radiogallium into the ether or nitrobenzene and back-extracting into the appropriate dilute acid.

Analytical-grade cadmium metal was dissolved in 8 *M* HBr and extracted with bis(2-chloroethyl)ether to remove traces of indium. Cadmium hydroxide was precipitated, washed, ignited to the oxide and 100 mg used for each cyclotron target. Bombardments were similar to those for the ZnO targets and the principle indium isotopes produced were In^{111} (2.8 d) and In^{114} (49 d). Carrier-free separations of the active indium were made by extraction from HBr solution.

For each measurement, 15 ml of organic solvent and 15 ml of an aqueous phase, containing the desired concentration of acid, metal ion and tracer activity, were placed in a 50-ml polyethylene centrifuge tube and agitated for about 25 min by a mechanical shaker in a water bath at 25°C. No variations in extraction coefficients were observed for phase contact times between 10 and 60 min. Phase separation was facilitated by centrifuging and 4-ml aliquots were withdrawn from each phase. The activity of each sample was determined by counting with a well-type NaI(Tl) scintillation crystal.

Equilibrium-phase volume ratios and HX extraction coefficients, both *versus* initial HX concentrations were determined in independent experiments. The total volume change was negligible ($<1\%$) in all systems, and $(\Delta V/V)_{aq}$ had a maximum value of ~ 0.07 for HCl and HBr with bis(2-chloroethyl)ether and ~ 0.015 for HCl with nitrobenzene. The thermodynamic activities, [HX], of the acid solutions were calculated from the activity coefficients given by ROBINSON *et al.* [5] and by BIERMANN *et al.* [6]. Corrections to these activities for dissolved organic solvent are $<4\%$ for bis(2-chloroethyl)ether and $<1\%$ for nitrobenzene. These data were used to correct all extraction coefficients to equilibrium conditions.

3. Results and discussion

The extraction coefficient, E, was determined as a function of C_M at various concentrations. E is defined as C_{M_o}/C_M where C_M represents the total metal-ion concentration, subscript o the organic phase and no subscript for the aqueous phase. These data are shown in Figs. 1—3. The lowest concentration of metal is without added carrier and is estimated as 10^{-12} to 10^{-13} M.

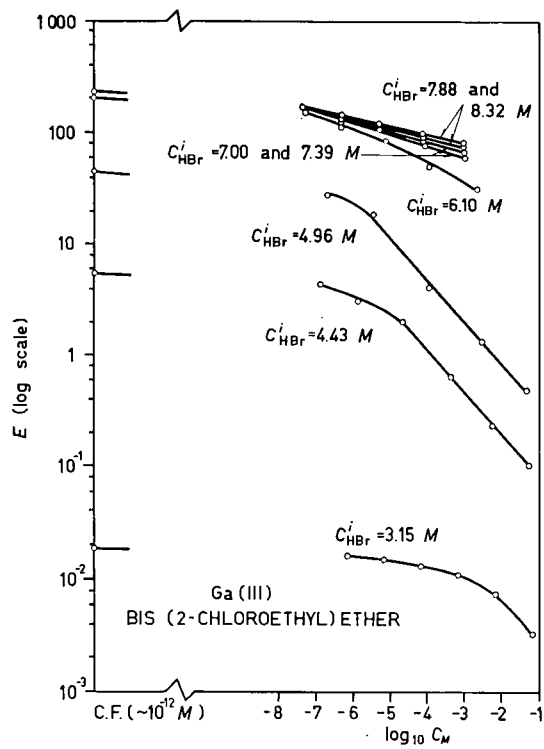

Fig. 1
Variation of extraction coefficient with equilibrium metal-ion concentration for the system HBr-Ga(III)-bis(2-chloroethyl)ether.

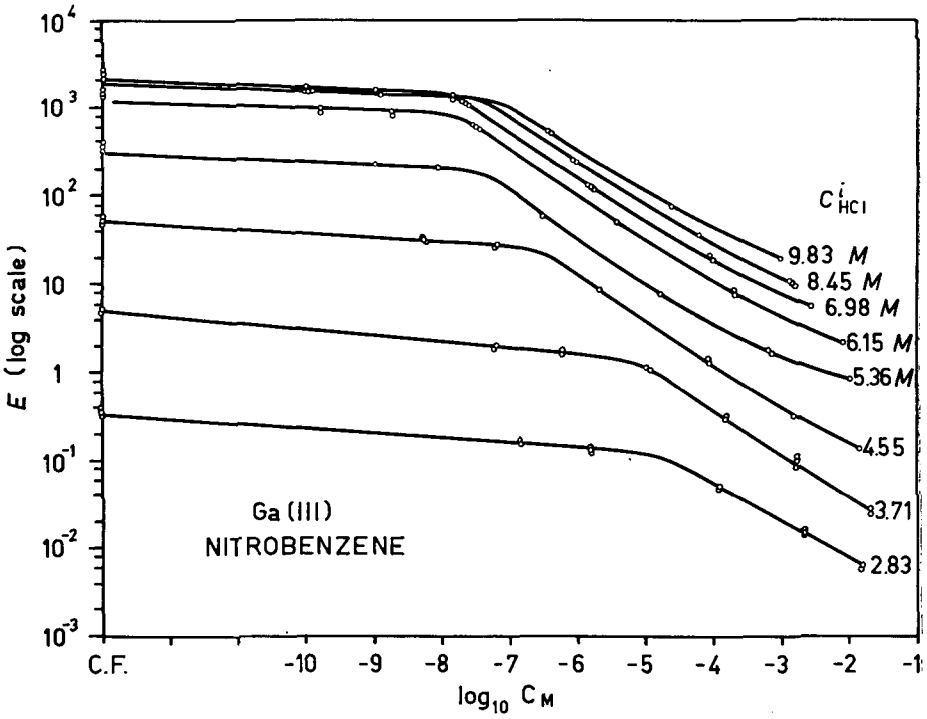

Fig. 2
Variation of extraction coefficient with equilibrium metal-ion concentration for the system HCl-Ga(III)-nitrobenzene.

The E *vs.* [HX] curves, Figs. 4—6, were obtained from the above curves by re-plotting the data at constant metal concentrations.

It is well established that the metal-containing species in the organic phase is HMX_4 or MX_4^- [7—9] and qualitative measurements of conductivity indicate that HMX_4 is a much stronger acid than HX in this phase. It is also known that water is carried into the organic phase by the complex, probably due to hydration of the proton [7]. Less well established, but highly probable, are specific solution effects depending on the basicity of the organic solvent [10]. Calculation of the absolute magnitude of E would certainly have to take into account these solution effects, but they do not enter into the relationships discussed in this work.

The dielectric constant of the solvent has a marked effect on the extraction behaviour of all HMX_4 species. Solvents with low dielectric constant, e.g., di*iso*-propyl ether ($\varepsilon = 3.88$) have E *vs.* M curves that show decreasing values of E with decreasing C_M in the range $C_M = 10^{-1}$ to 10^{-3} M [8]. At lower concentrations E becomes independent of C_M.

Solvents with high dielectric constants, e.g. bis (2-chloroethyl) ether ($\varepsilon = 19.5$) and nitrobenzene ($\varepsilon = 34.8$), show a very different behaviour of E *vs.* C_M. E increases with decreasing C_M in the range of 10^{-1} to 10^{-6} M and then becomes independent of C_M. Figs. 1—3 are typical for such solvents and HMX_4 systems.

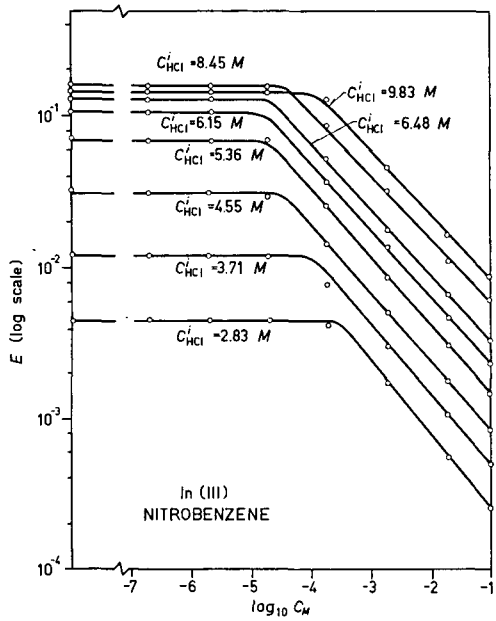

Fig. 3
Variation of extraction coefficient with equilibrium metal-ion concentration for the system HCl-In(III)-nitrobenzene.

The first satisfactory explanation of this phenomenon was given by SALDICK [3] and later elaborated by DIAMOND [11]. Their treatment was based on the postulate that HMX_4 are strong acids in the organic phase and the extraction coefficient is controlled by the hydrogen-ion activity in that phase. At high C_{M_o} the ionization of HMX_4 controls the $[H^+]$ but at low values of C_{M_o}, the $[H^+]$ is determined by the ionizations of HX which are weak acids in these solvents.

The equations of Saldick and Diamond suffer by being too explicit and involve too many thermodynamic constants to be checked by any simple set of experiments. POSKANZER [12], following the same line of reasoning, has developed a set of equations based on weight-average parameters which can be applied to the data reported here. These equations have been elaborated and extended by DIETZ [13] and MENDEZ [14].

The extraction coefficient can be related to the ionization of HX in the organic phase at low concentrations of metal where E is independent of C_M:

$$E = D_b/g_{b_o} \sqrt{K_{HX_o} C_{HX_o}}$$

where D_b is a function of the acid concentration and can be calculated from the relation

$$D_b = E^2 g^2_{b_o} C_M$$

and g_{b_o} is a Bjerrum activity coefficient calculated from theoretical considerations [15].

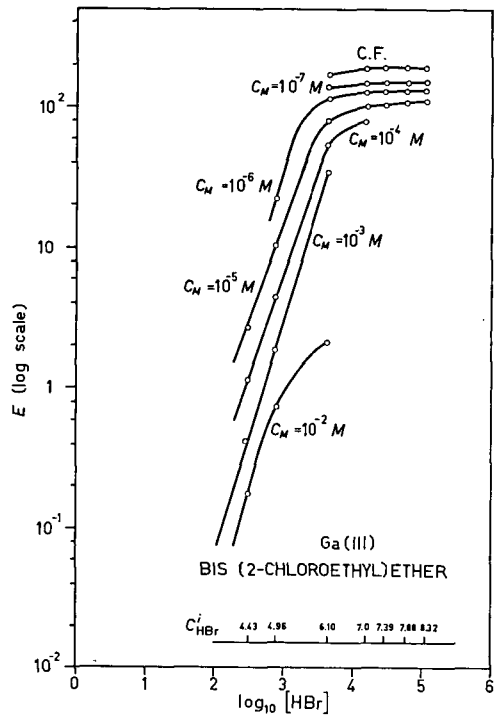

Fig. 4
Dependence of extraction coefficient on the activity of HBr for the system HBr-Ga(III)-bis(2-chloroethyl)ether.

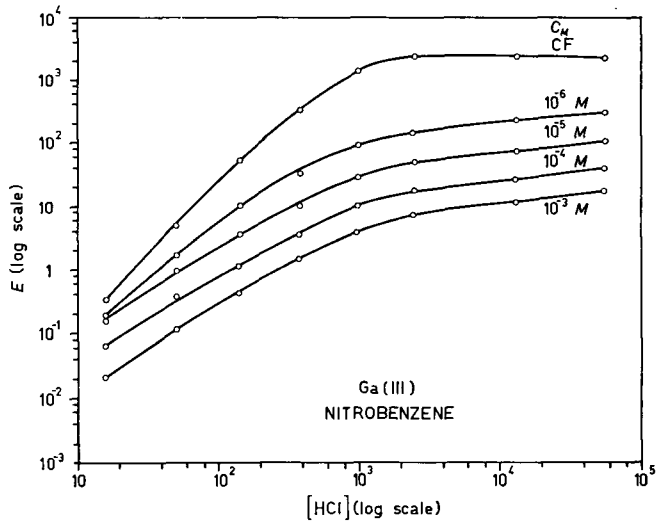

Fig. 5
Dependence of extraction coefficient on the activity of HCl for the system HCl-Ga(III)-nitrobenzene.

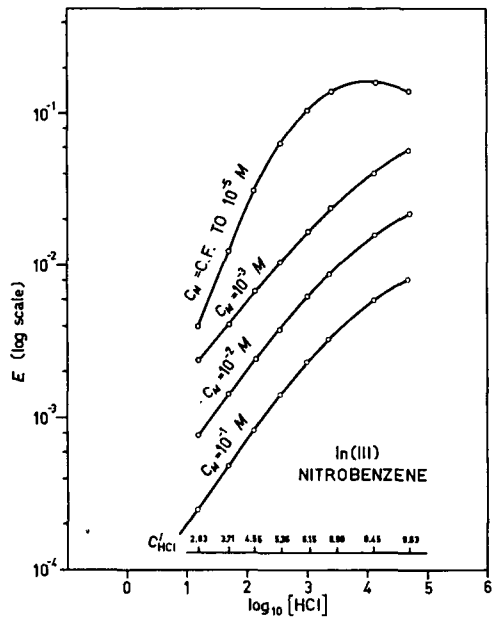

Fig. 6
Dependence of extraction coefficient on the activity of HCl for the system HCl-In(III)-nitrobenzene.

TABLE I

IONIZATION CONSTANTS OF HCl AND HBr IN BIS(2-CHLOROETHYL)ETHER AND IN NITROBENZENE

Acid	Solvent	pK_{HX_0}	Method
HCl	$(ClC_2H_4)_2O$	7.0 ± 0.1	Extn. of In (III)
HCl	$(ClC_2H_4)_2O$	7.0 ± 0.2*	Extn. of Ga (III)
HCl	$(ClC_2H_4)_2O$	7.2 ± 0.2	Conductance
HCl	$C_6H_5NO_2$	7.5 ± 0.1	Extn. of In (III)
HCl	$C_6H_5NO_2$	7.4 ± 0.1	Extn. of Ga (III)
HBr	$(ClC_2H_4)_2O$	5.1 ± 0.2	Extn. of In (III)
HBr	$(ClC_2H_4)_2O$	5.3 ± 0.1	Extn. of Ga (III)

* Recalculated from the extraction data of POSKANZER [12].

Table I lists the values of pK_{HX_0} obtained from the extraction data and includes one value determined by conductance measurement [2]. Excellent agreement of pK_{HCl} values is obtained from the data on Ga (III) and In (III), although these metals differ by several orders of magnitude in their extraction coefficients. The higher dielectric constant of nitrobenzene would suggest lower values of pK in this solvent. However, the basicity of this solvent is substantially smaller than for the ether and this apparently has an effect greater than the dielectric constant. Insufficient data are available to evaluate this effect quantitatively.

Using Poskanzer's weight-average treatment of the data of E *vs* [HX], $\bar{n}$, the average number of ligands in the metal complex, can be calculated. Since this number represents an aqueous phase phenomenon, it is independent of the organic solvent used in the extraction. Agreement between the data from bis (2-chloroethyl)ether and nitrobenzene extraction measurements is demonstrated in Fig. 7 (a). If suitable values of the first two stability constants are available

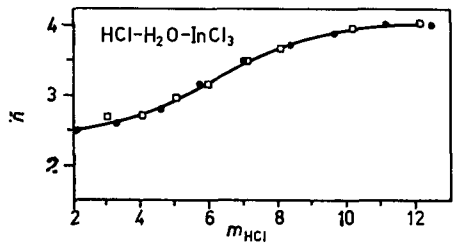

Fig. 7 (a)
Average number of ligands, $\bar{n}$, for indium as a function of the molality of HCl.
□ from nitrobenzene extraction data.
● from bis(2-chloroethyl)ether data.
— curve calculated from k_1 and k_2 of CARLESON *et al.* [16] and k_3 and k_4 from this work.

from independent measurements, k_3 and k_4 can be obtained by curve fitting. In this way values for $InCl_x$ ($k_3=0.30$; $k_4=0.055$) and $InBr_x$ ($k_3=0.06$; $k_4=0.012$) are obtained. For the chloride complex the values of k_1 and k_2 were taken from CARLESON *et al.* [16] and for the bromide from BURNS *et al.* [17].

These values of k_3 and k_4 are smaller than others reported in the literature. However, in the case of the bromide, they are consistent with the ultracentrifuge

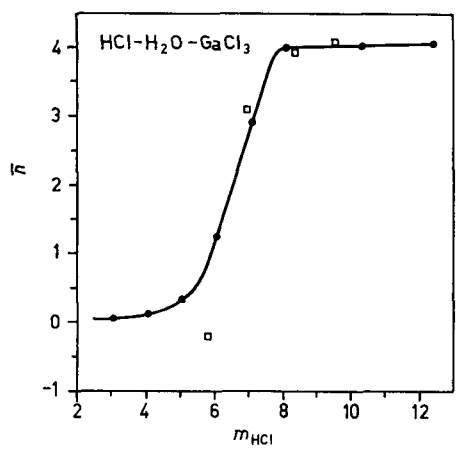

Fig. 7 (b)
Average number of ligands, $\bar{n}$, for gallium as a function of the molality of HCl.
□ from nitrobenzene extraction data.
● from bis(2-chloroethyl)ether data.

measurements of JOHNSON *et al.* [18] indicating $\bar{n}=2$ for In (III) in 2 *M* HBr. WOODWARD *et al.* [9] failed to observe the Raman spectrum of $InBr_4^-$ in aqueous solutions where the stability data of IRVING *et al.* [10] would indicate a detectable concentration of $InBr_4^-$.

Fig. 7 (b) shows $\bar{n}$ *vs.* m_{HCl} for Ga (III) and the Ga (III)-HBr curve is similar. This very steep rising curve substantiates the suggestion of KRAUS *et al.* [4] that $GaCl_2^+$ and $GaCl_3$ have extremely short stability ranges. Moreover, if the data for both the ether and nitrobenzene extraction of $HGaCl_4$ are treated in a manner analogous to that of Kraus and Nelson, and plotted as F_4 *vs.* m_{HCl} (where $F_4=(GaCl_4^-)/C_{Ga(III)}$), the experimental points fall on the curve taken from their paper. This remarkable agreement between the results of two different experimental methods applied to the same concentrated acid solution is shown in Fig. 8.

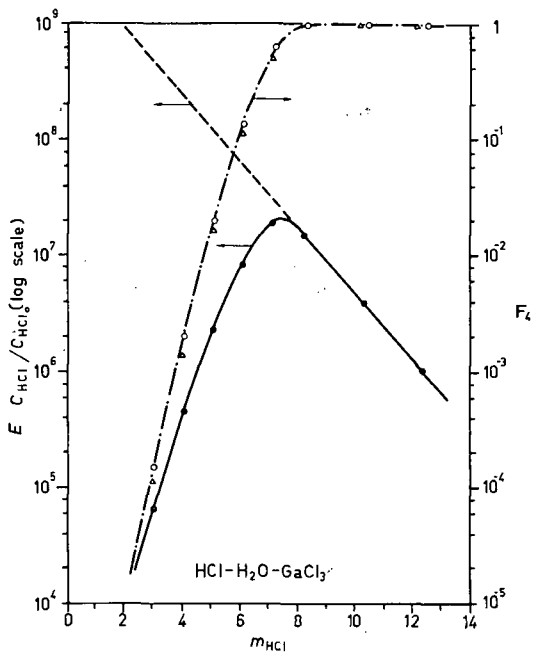

Fig. 8
Dependence of distribution function, $E \cdot C_{HCl}/C_{HCl_0}$, and ion fraction, F_4, on molality of HCl.
○ from nitrobenzene extraction data.
△ from bis(2-chloroethyl)ether extraction data.
—·—·—· curve from ion exchange measurements of KRAUS *et al* [4]..

From the consistency of the results obtained in these studies and the observed agreement, qualitative and quantitative, with independent studies based on different techniques, it is reasonable to conclude the validity of assuming that HMX_4 ionizes extensively in high dielectric solvent and that the weight-average treatment of the experimental data is effective.

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DISCUSSION

H.G. Forsberg (Sweden) inquired whether Mr. Irvine had worked with any other trivalent halides, for instance that of gold. He further asked Mr. Irvine whether he had been able to determine the ionization constants in the aqueous phase of the HMX_4 acids formed.

J. W. Irvine replied that he and his associates had done some work on the reducible species; he had mentioned iron, but they had also dealt with gold and thallium. Difficulties were caused by reduction: when measuring very low concentrations, the slightest suspicion of any reducing agent resulted in reduction of the oxidized species, and the measurements were then no longer valid. He had data on such reducible systems, but they were not reliable. He hoped that better results could be achieved by using nitrobenzene, and pointed out that most of his work had been done with bis(2-chloroethyl)ether.

In reply to the second part of Mr. Forsberg's question, he said he had no experimental data whatsoever regarding the ionization constants of HMX_4 acids in the aqueous phase, but he thought such acids would be exceedingly strong, comparable to perchloric.

THE USE OF RADIOISOTOPES FOR DETERMINATION OF COMPLEX EQUILIBRIA

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Abstract — Résumé — Аннотация — Resumen

The use of radioisotopes for determination of complex equilibria. Radioisotopes can be used for determination of complex equilibria in solution, provided this solution is in equilibrium with another phase. The most versatile systems for studying aqueous solutions use solvent-extraction and ion-exchange methods. These two methods more seen be to universally practical for determining complex equilibria than EMF, spectrophotometric and other more conventional ones.

Emploi des radioisotopes pour la détermination d'équilibres complexes. On peut utiliser les radioisotopes pour déterminer les équilibres complexes en solution, à condition que celle-ci soit en équilibre avec une autre phase. Le système le plus commode pour l'étude des solutions aqueuses est fondé sur l'extraction par solvants et sur l'échange d'ions. En fait, ces deux méthodes sont généralement plus pratiques, pour la détermination des équilibres complexes, que la méthode f.e.m., la spectrophotométrie ou les autres techniques plus classiques.

Применение радиоактивных изотопов для определения комплексных равновесий. Радиоактивные изотопы могут быть использованы для определения комплексных равновесий в растворе при условии, если этот раствор находится в равновесии с другой фазой. Наиболее многосторонняя система изучения водных растворов использует методы селективной экстракции и ионного обмена. Действительно, для определения комплексных равновесий эти два метода являются более распространенными, чем метод emf, спектрофотометрический метод или другие более обычные методы.

Empleo de los radioisótopos para la determinación de equilibrios complejos. Los radioisótopos pueden emplearse para determinar equilibrios complejos en solución siempre que ésta se encuentre en equilibrio con otra fase. Los procedimientos más adecuados para el estudio de las soluciones acuosas se basan en métodos de extracción con disolventes y de intercambio iónico. En realidad, la aplicación de estos dos métodos a la determinación de equilibrios complejos posee un carácter más general que la medición de la fuerza electromotriz, la espectrofotometría y otras técnicas tradicionales.

1. Introduction

One of the most important objects for modern inorganic chemistry is to find out how complex (or coordination) compounds are built up. Such a knowledge can be acquired in many ways, e. g. through experimental methods such as X-ray crystallographic investigations, kinetic and equilibrium studies, and through theoretical considerations. However, each gives only one part of the story. A complete and reliable picture of how a complex compound is built up is not obtained

until all the pieces of knowledge are put together and found to be consistent. One of the most important and also most widely used methods of investigation is that of studying complex equilibria in solution. The results of such investigations are not only of interest to the theoretical inorganic chemist, but are also becoming increasingly important for understanding biochemical processes. Information about complex equilibria is also of great value to the industrial chemist. This is particularly true in connection with ion-exchange and solvent-extraction studies, which are discussed in more detail below.

2. Methods of determining complex equilibria

Suppose a metal ion M with the ligand A (charges omitted) forms stepwise complexes of the type MA, MA_2, ... MA_n ... As long as no other species of M and A are present in the solution, the concentration of these species and the total concentration of metal, $[M]_{tot}$, and of ligand, $[A]_{tot}$, are related to each other through the equations

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \tag{1}$$

$$[M]_{tot} = [M] + [MA] + \ldots + [MA_n] \ldots \tag{2}$$

$$[A]_{tot} = [A] + [MA] + 2[MA_2] + \ldots + n[MA_n] \ldots \tag{3}$$

Here, β_n is the complexity constant. In practically all experimental work $[M]_{tot}$ and $[A]_{tot}$ are known. Then we have $n+2$ equations and $2n+2$ unknowns, which means that in order to determine β_n, which is our goal, we need both to determine the concentration of one more species and to obtain more relations (for $n>1$) between the variables involved. This can be achieved in many ways, e.g. through potentiometric, conductometric, polarographic, spectrophotometric, solvent-extraction, and ion-exchange measurements. None of these methods is general, and most of them involve the introduction of one or more unknown variables.

The property of radioisotopes of being easily detectable in minute amounts makes them very useful in connection with two of these methods, namely solvent-extraction and ion-exchange. It can be shown that the use of radioisotopes in solvent-extraction or ion-exchange investigations (for brevity we shall call this the "radioisotope-partition method") usually makes it very easy to determine the free-ligand concentration. The very large concentration-range of the metal which can be investigated by using radioisotopes makes it feasible to study complicated complex systems more comprehensibly than otherwise would be possible. Also, in many cases, the radioisotope-partition method is the only practical method available.*

3. Equations governing the radioisotope-partition method

In order to understand the radioisotope-partition technique, it is necessary to give a few basic equations. Let us consider a two-phase system, one phase being an aqueous solution which contains all species MA_n (though not necessarily at the same time), where $0 \leq n \leq N$, and another phase which contains only a few of

* Some other methods, particularly the potentiometric one, are usually more accurate than the radioisotope-partition method. However, in those cases where very scattered measurements have been made with the latter method, the accuracy can often be greatly increased by an improved technique.

the MA_n species (thus showing selective properties). The partition ratio Q of the metal between this "other" phase and the aqueous phase is given by the equation

$$Q = \sum_{i}^{k} \beta_n \lambda_n [A]^n / \sum_{0}^{N} \beta_n [A]^n, \tag{4}$$

where λ_n is the partition constant of the n th species between the two phases, and [A] is the concentration of free ligand in the aqueous phase. This equation is applicable to most partition systems, provided the limits i and k are correctly chosen, and that all activity factors are constant.

One of the great advantages of using radiotracers for the metal is that its presence does not affect the activity factors, and that [M] can be chosen so low that polynuclear complexes of M can be neglected. Another advantage is that, according to Eq. (3), one obtains

$$[A]_{tot} = [A] \text{ for } [M]_{tot} \ll [A]_{tot}. \tag{5}$$

If A has basic properties forming an acid HA, and A and/or HA enters the "other" phase, corrections must be made for that; since these corrections are usually simple to make, [A] can easily be found.

Of possible partition systems, we shall discuss here only the use of ion-exchange resins and solvent-extraction with an organic solvent. To simplify the following discussion, we shall assume that an uncharged complex MA_ν is formed, that all complexes with $n < \nu$ are positively charged and that all complexes with $n > \nu$ are negatively charged.

(a) Cation exchange

When only the adsorption of cations has to be considered $i = 0$ and $k = \nu - 1$ in Eq. (4). This equation can then be written

$$\sum_{0}^{N} (Q - \lambda_n) \beta_n [A]^n = 0 \quad (\lambda_n = 0 \text{ for } n \geq \nu). \tag{4a}$$

Here λ_n and β_n are unknown, while [A] is known through Eq. (5). Q is the measured distribution of radioactivity between the resin and the aqueous phase. The radioactivity in the resin phase is usually obtained as the difference between the radioactivity of the aqueous phase before and after equilibrium with the resin or, in some cases, through elution of the resin; the latter method involves some complications [21].

In Eq. (4a), λ_0 can be determined in the absence of complexing ligand ($n = 0$; $[A] = 0$). If $n > 1$, β_n and λ_n cannot be determined independently of each other except when $Q \gg \lambda_n$. Both graphical and numerical methods may be used for calculating β_n (e.g. [1] [2]).

The first investigation reported using this method was probably on the complex formation between strontium (using Sr^{89}) and citrate, where the cation exchanger Amberlite IR-1 was used [3]. Among the large number of later investigations, the very careful studies on the Ce(III) sulphate system (using $Ce^{141-144}$ and Dowex-50 resin) ought to be mentioned [4] [5].

(b) Anion exchange

When only the adsorption of anions has to be considered, $i=\nu+1$ and $k=N$ in Eq. (4). However, Eq. (4) may also be written like Eq. (4a), provided $\lambda_n=0$ for $n \leq \nu$. Under these conditions, what is said in section 3 (a) above also applies to the anion-exchange case.

It is rather common that only one negatively charged complex has to be considered, i.e. $\nu+1=N$. If this condition is introduced into Eq. (4), it can be written

$$Q = \lambda_N \beta_N [\mathrm{A}]^N / \sum_0^N \beta_n [\mathrm{A}]^n \quad (\nu + 1 = N), \tag{4b}$$

Q and [A] are obtained in the same way as for the cation-exchange case. In investigations with anion exchangers it may sometimes be difficult to keep a constant ionic strength throughout a sufficiently large concentration range of [A]. In such a case it is necessary to modify Eq. (4b) in order to take care of the Donnan equilibria [6]. Both graphical and numerical methods may be used for the calculation of λ_N and β_n (e.g. [2] [6]).

One of the first investigations using this method dealt with the complex formation between Cd(II) (using Cd^{115}) and Br^- and I^-, and Ce(IV) and acetate, using Amberlite IRA-400 resin [6]. Among other investigations one may mention the recent work on the Th(IV)-nitrate system (using Th^{234} and Dowex-1 resin) [7] and, in general, the work done by Kraus *et al.* [21].

(c) Solvent extraction: extractable complex

We shall assume that only the uncharged complex MA_ν is extracted into the organic solvent. Thus $i=k=\nu$ in Eq. (4), which then is reduced to

$$Q = \lambda_\nu \beta_\nu [\mathrm{A}]^\nu / \sum_0^N \beta_n [\mathrm{A}]^n. \tag{4c}$$

As before, [A] is obtained according to Eq. (5). Q is obtained from measurements of the radioactivity in the organic and the aqueous phase. Graphical and numerical methods have been given for the calculation of λ_ν and β_n from this equation [8—10]; a common case is obtained for $\nu=N$, when Eq. (4c) becomes equal to Eq. (4b).

The first determination of complexity constants for an extractable complex was probably made on the Th(IV)-acetylacetone system (using UX_1—UX_2 tracer and benzene as the organic solvent) [8]. A large number of investigations by this method have since been reported (e.g. [11]; experimental uncertainties are discussed in [10] and [11]).

(d) Solvent extraction; non-extractable complex

Sometimes it is of interest to study a complex between M and a ligand B, in which case no extractable MB_ν complex is formed (B may be an inorganic ligand like HSO_4^-, F^-, etc.). However, the solvent-extraction technique can still be

used if A is added to the system, and A forms an extractable complex MA_v. The pertinent equation for this case can be written

$$Q_{[A]}^{-1} = C \sum_{0}^{P} \beta_p [B]^p, \tag{4d}$$

where $Q_{[A]}$ is the measured distribution ratio at constant [A]. Since [B] is known in a manner analogous to [A] in Eq. (5), C and β_p are the unknown constants. Both graphical and numerical methods for the calculation of C and β_p have been given [10] [12] [13].

This method was probably first applied on Zr(IV) complexes with HSO_4^- and HF (using Zr^{95} as a tracer and thenoyltrifluoroacetone to form a complex extractable into the benzene phase) [12]. Among other investigations of this kind, the determination of the equilibrium constants for the Np(IV)-HSO_4^- system may be mentioned [13].

4. Concentration ranges and specific radioactivity of the metal

From Eqs. (4a—d) it is seen that complexity constants can be obtained with ion-exchange and solvent-extraction methods, provided Q, [A] and [B] can be measured. As pointed out before, the great advantage with radioisotopes is that $[M]_{tot} \ll [A]_{tot}$ (or $[B]_{tot}$), which makes it possible to use Eq. (5) instead of Eq. (3) for the determination of [A]. However, there are some practical aspects which normally limit the usable concentration ranges of $[M]_{tot}$ and $[A]_{tot}$.

It has been shown that a very low concentrations of M, say $[M] < 10^{-8}\ M$, a large fraction of the metal may be lost through adsorption on surfaces in contact with the solution; this adsorption increases with decreasing concentration and increasing charge of the metal, and varies with pH, nature of surface, etc. [14] [15]. Since this adsorption may be quite disturbing in many partition experiments, it is recommended to work with $[M]_{tot} \gtrsim 10^{-5}\ M$. At this concentration, adsorption losses rarely exceed a few per cent for tetravalent ions, and are still lower for less highly charged ions. It may be mentioned, however, that under certain circumstances much lower metal concentrations may be used.

At $[M]_{tot} \approx 10^{-5}\ M$ one has to choose $[A]_{tot} \gtrsim 10^{-3}\ M$ in order to fulfil the requirements of Eq. (5). On the other hand $[A]_{tot}$ should be $\lesssim 10^{-1}\ M$ in order to keep the activity factors in the system constant (cf. section 3 (b) above); of course, this latter requirement is by no means specific for the radioisotope-partition method.

The limitation on the concentration of the metal puts some requirements on the specific radioactivity needed. One can deduce the relation

$$S_{min} = 4{\cdot}5 \times 10^{-5} \frac{f I_B}{E A V_s [M]}. \tag{6}$$

S_{min} is the minimum specific activity (in mc/g) needed in order to cause $f I_B$ counts/min to be registered on a counter with an efficiency of E% (cpm/dpm). The volume of the sample taken out of the solution is V_s ml; in this volume, the concentration of the metal is [M] and its at. wt. is A.

In Table I, S_{min} values have been calculated for some common types of detectors, which seem suitable for the particular type of radiation. These S_{min} values are based on the assumption that $[M] = 10^{-8}\ M$ (because $[M] \gtrsim 10^{-5}$ and the

TABLE I

MINIMUM SPECIFIC ACTIVITY NEEDED FOR VARIOUS TYPES OF RADIATION AND DETECTORS AS USED IN CONNEXION WITH THE RADIOISOTOPE-PARTITION METHOD

Radiation	Detector	Efficiency (E) %	Background (I_B)cpm	Sample volume (V_S) ml	S_{min}* (mc/g)
α	external thin-wall proportional count.	~30	~ 1	~0.1	~ 7
β, E_{max} < 0.2 MeV	internal proportional counter	~50	~20	~0.1	~90
β, E_{max} 0.2–0.8 MeV	external thin wall proportional count.	~20–30	~20	~0.1–0.5	~30
β, E_{max} > 0.8 MeV	GM-counter for liquids	~20	~20	~10	~2
	scintillation counter (NaI)	~50	~300	~ 5	~27
γ	scint. count. with spectrometer	~40	~30	~ 5	~ 3

* Computed for $A = 100$, $f = 0{,}5$ and $[M] = 10^{-8}$, so that $S\text{min} = 22.5 \times I_B E \times V_S$.

measured range of Q is 10^{-3} — 10^{3}), $f = 0.5$ (as a reasonable average value) and $A = 100$. For sample volumes < 0.5 ml, it is assumed that the solvent has evaporated so that the measured sample is in dry form and does not contain any large amounts of salt.

5. Survey of available radioisotopes

If specific activities as high as those in Table I are used in ion-exchange or solvent-extraction work ([M] $\sim 10^{-5}$ M), partition ratios in the range 10^{-3} to 10^{3} can be measured with good accuracy using conventional radiochemical technique.

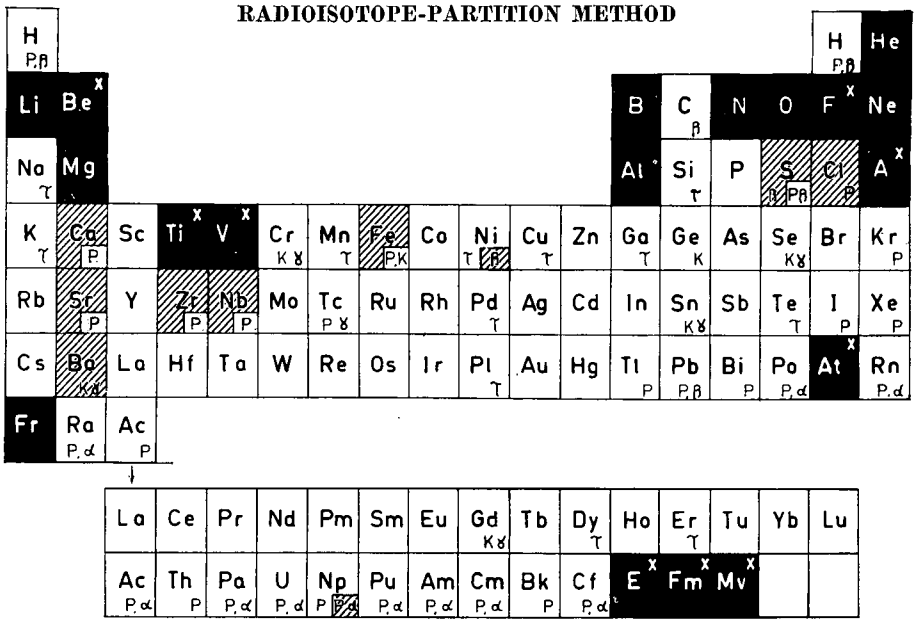
However, in most practical cases it is not necessary to use S_{min} values as high as those given in Table I, as may be found by analysing each term in Eq. (6). Here, an average S_{min} value of 5 mc/g shall be used with the meaning that elements which can easily be obtained at this or higher specific activity in millicurie amounts are, from a radiochemical point of view, well suited for complex equilibrium studies. These elements are marked by white squares in Table II [16].

For some elements it is not possible to reach specific activities of the order of 0.5 mc/g except with great difficulty. It is of little advantage to use radiotracers of these elements in complex equilibrium studies; they are marked by black squares in Table II. If an element in this group has a radioisotope with a half-life of 1 h — 1 yr, this is indicated in Table II by a cross; this isotope may be produced by high-energy nuclear reactions, though usually at a rather low total activity (μc-level or lower).

The group of elements between these two extremes are found in the shaded squares of the table. This group includes elements which, with some difficulty, can be obtained in specific activities in the range 0.5 to 5 mc/g. These elements are useful as radiotracers in partition-experiments, though with greater restrictions and difficulties than the elements in the white squares.

TABLE II

AVAILABILITY OF RADIOISOTOPES FOR INVESTIGATIONS WITH THE RADIOISOTOPE-PARTITION METHOD



All radioisotopes are obtained through reactor irradiation of natural element and decay through β-emission ($E_{max} > 0.2$ MeV) with half-lives > 24 h, with the following exceptions: α for α-emitters, β for soft β-emitters ($E_{max} < 0.2$ MeV), K for K-capture, γ for only γ-emission; τ for half-lives 2-24 h; P for processed isotope.

Sp. act. $\gtrsim$ 5 mc/g easily obtained ($\varnothing = 10^{12}$ n/cm²s; $T \lesssim 1$ month).

Sp. act. 0.5—5 mc/g obtained with some difficulty ($\varnothing = 10^{13}$ n/cm²s; $T \lesssim 6$ months).

No radioisotope suitable for ordinary chemical work (× means that radioisotopes with $\tau > 1$ h exist).

In some cases there may be a choice of isotope, e.g. with Ni, where high specific activity can be obtained with a short-lived isotope (Ni^{65}, $\tau = 2.6$ h) while a lower specific activity is obtained for an isotope with rather soft beta-radiation (Ni^{63}, E_{max} 0.06 MeV).

Higher specific activities are usually obtained if processed isotopes (marked P) are used. This means that the specific activity is not simply obtained by irradiation of the natural and stable element with slow neutrons, but that some kind of special processing is involved (which consequently makes the radioelement more expensive): for calcium it means that enriched Ca^{44} has been used; for strontium it means the isolation of fission product Sr^{89+90}; for hydrogen it means production of tritium through Li^6 (n, α) T reaction; for uranium it means U^{233} obtained through Th^{232} (n, γ) $Th^{233} \rightarrow Pa^{233} \rightarrow U^{233}$; etc.

Since most (n, γ)-produced radioisotopes are β-unstable, β decay is not specifically indicated in Table II, except when the β-energy is very low (< 0.2 MeV). Other types of decay are indicated in the table by their common symbols.

Since a short half-life is a serious complication in equilibrium studies, half-lives between 2 and 24 h have been indicated by a τ. For the rest of the radioactive elements ("grey" and "white") all half-lives are > 24 h.

6. Conclusions

From Table II, it is obvious that there are very few elements (notably Be, Mg, Al, Ti and V) which are unsuitable for complex studies by the radioisotope-partition method. In this respect, the radioisotope-partition method is probably the most general one of studying complex equilibria.

The complexes which can be investigated by it are by no means limited to the types MA_n or MB_p, which have been discussed above. Successful investigations have thus been made on mixed complexes of the type MA_nB_p, polynuclear complexes like M_mA_n, acid complexes like HMA_n and complexes with organic solvents (molecular symbol Org) like $MA_n Org_s$ (e.g. [17—20]).

Investigations with the radioisotope-partition method not only yield information about how complex compounds are built up, but also about how ion-exchange and solvent-extraction processes operate. This is particularly important to the atomic energy industry, which to a large scale uses these methods for preparing their products, as for example pure uranium and plutonium. Of course, this is one of the main reasons why nuclear- and radiochemists have become interested in this specific field and made such important contributions to it during the last 15 years that one talks about a new era in modern inorganic chemistry. However, continued research along these lines will probably not only be important to the nuclear industry but in the long run also to the chemical industry as a whole.

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ИССЛЕДОВАНИЕ ПРИ ПОМОЩИ РАДИОАКТИВНОЙ СЕРЫ КИНЕТИКИ ПРОЦЕССА $SO_2+0{,}5\ O_2 \rightleftarrows SO_3$, НАХОДЯЩЕГОСЯ В СОСТОЯНИИ ХИМИЧЕСКОГО РАВНОВЕСИЯ, НА ПЛАТИНОВОМ КАТАЛИЗАТОРЕ

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Abstract — Résumé — Аннотация — Resumen

Study with radio-sulphur of the kinetics of the process $SO_2+0.5\ O_2 \rightleftarrows SO_3$ in a state of chemical equilibrium on a platinum catalyst. The authors describe an attempt to use radioisotopes in the study of the kinetics of heterogeneous catalytic processes in a state of equilibrium.

The investigation was carried out by the circulation method. After establishment of equilibrium, a small amount of $S^{35}O_2$ was introduced into the system as a tracer and its conversion rate into $S^{35}O_3$ was measured. From that rate the speed of the direct and inverse processes of oxidation of SO_2 on the catalyst was calculated. Possible sequence patterns for the process are suggested and discussed.

Etude, à l'aide du soufre radioactif, de la cinétique de la réaction $SO_2+0{,}5\ O_2 \rightleftarrows SO_3$ en équilibre chimique, en présence d'un catalyseur de platine. Le mémoire expose un essai d'application des radioisotopes à l'étude de la cinétique des réactions catalytiques hétérogènes en équilibre chimique.

Les recherches ont été effectuées par la méthode à circulation. Après établissement de l'équilibre, on a introduit comme indicateur une petite quantité de $^{35}SO_2$ et mesuré la vitesse de sa transformation en $^{35}SO_3$. En partant de cette vitesse, on a calculé celle du processus d'oxydation directe et inverse du SO_2 sur le catalyseur. Les auteurs proposent et étudient différentes formules selon lesquelles la réaction peut se dérouler.

Исследование при помощи радиоактивной серы кинетики процесса $SO_2+0{,}5\ O_2 \rightleftarrows SO_3$, находящегося в состоянии химического равновесия, на платиновом катализаторе. Излагается опыт применения радиоактивных изотопов для изучения кинетики гетерогенных каталитических процессов, находящихся в состоянии равновесия.

Исследование проводилось циркуляционным методом. После установления равновесия в систему вводилось в качестве метки малое количество $S^{35}O_2$ и измерялась скорость перехода его в $S^{35}O_3$. Из этой скорости вычислялась скорость прямого и обратного процессов окисления SO_2 на катализаторе. Предложены и обсуждены возможные схемы протекания процесса.

Estudio, con ayuda de azufre radiactivo, de la cinética de la reacción $SO_2+0{,}5\ O_2 \rightleftarrows SO_3$ en equilibrio químico en presencia de un catalizador de platino. Los autores describen un experimento sobre el empleo de radioisótopos en el estudio de la cinética de procesos catalíticos heterogéneos en estado de equilibrio.

La investigación se llevó a cabo por el método de circulación. Una vez establecido el equilibrio, se introdujo en el sistema una pequeña cantidad de $^{35}SO_2$ como trazador y se midió su índice de conversión en $^{35}SO_3$. De dicho índice se dedujo la velocidad de los procesos directo e inverso de oxidación del SO_2 en presencia del catalizador. Los autores proponen y examinan diversos tipos posibles de cinética para el proceso.

Применение метода меченых атомов позволяет изучать скорости прямого и обратного процессов обратимых реакций, находящихся в состоянии равновесия, и зависимость этих скоростей от концентраций, температуры и других факторов. Подобные исследования представляют интерес для выяснения механизма процессов. То обстоятельство, что в состоянии равновесия суммарного процесса все его стадии обратимы и также находятся в равновесии, значительно ограничивает выбор возможных схем процесса из числа формально удовлетворяющих наблюдаемым кинетическим закономерностям. Сопоставляя, далее, кинетику в равновесных условиях с наблюдаемой при удалении от равновесия, можно судить о лимитирующих скорости стадиях процессов.

В настоящей работе мы подвергли подобному исследованию процесс каталитического окисления сернистого газа кислородом на платиновой сетке с применением в качестве метки радиоактивного изотопа серы S^{35}.

Принцип метода заключается в следующем. В сосуд, содержащий катализатор и равновесную смесь SO_2, SO_3 и воздуха, вводят столь небольшое количество радиоактивного $S^{35}O_2$, чтобы равновесие реакции не могло заметно нарушиться, и, обеспечив хорошее перемешивание смеси, наблюдают скорость перехода радиоактивной серы из SO_2 в SO_3. Полагая, что этот переход обязан процессу

$$2\,S^*O_2 + O_2 \rightleftarrows 2\,S^*O_3,$$

легко связать наблюдаемую скорость изотопного обмена со скоростью химического процесса окисления SO_2 или равной ей скоростью обратного процесса диссоциации серного ангидрида (W).

Пусть V_{SO_2} — количество SO_2 в сосуде,

V_{SO_3} — количество SO_3; y и x — молярные доли S^{35} соответственно в SO_2 и в SO_3 ко времени τ, y_0 — в начальный момент ($x=0$).

Тогда
$$-\frac{dy}{d\tau} V_{SO_2} = W(y - x),$$

или, т. к.
$$x = (y_0 - y)\frac{V_{SO_2}}{V_{SO_3}},$$

$$\frac{dy}{d\tau} = \frac{W}{V_{SO_3}}[y_0 - y(\lambda + 1)], \text{ где } \lambda = \frac{V_{SO_2}}{V_{SO_3}},$$

интегрируя от y_0 до y и от 0 до τ, получаем:

$$\ln \frac{\lambda y_0}{(1+\lambda)y - y_0} = \frac{W(\lambda+1)}{V_{SO_3}}\tau, \text{ откуда } W = \frac{2{,}3\,V_{SO_3}}{\tau(\lambda+1)} \lg \frac{\lambda y_0}{(1+\lambda)y - y_0}.$$

Т. к. на опыте мы измеряем не непосредственно молярные доли радиоактивной серы в SO_2 или в SO_3, а пропорциональные им удельные радиоактивности осадков $BaSO_4$, образованных, соответственно, из SO_2 и SO_3 (I_{SO_2} и I_{SO_3}), заменим y через $\alpha\, I_{SO_2}$, а y_0 через $\alpha\,(J_{SO_2} + J_{SO_3}) = J_{SO_0}$.

Тогда $$W = \frac{2{,}3\ V_{SO_3}}{\tau(\lambda+1)} \lg \frac{\lambda J_0}{(\lambda+1) J_{SO_2} - J_0}.$$

Еще удобнее пользоваться безразмерным параметром $J' = \frac{J_{SO_2}}{J_{SO_3}}$. При этом уравнение приобретает вид: $W = \frac{2{,}3\ V_{SO_3}}{\tau(\lambda+1)} \lg \frac{\lambda}{(\lambda+1)\frac{J'}{J'+1} - 1}$. Изменяя начальные соотношения SO_2 и воздуха, а, следовательно, равновесные соотношения SO_2 и SO_3, можно было исследовать зависимость W от концентраций реагентов и вычислить константы скорости прямого и обратного процессов (K_1 и K_2). Изменяя температуру, можно найти соответствующие теплоты активации.

1. Постановка эксперимента

Исследование проводилось в циркуляционной установке, изображенной на рис. 1. Цикл состоял из кварцевого реакционного прибора, циркуляционного насоса мощностью 5 литров в минуту, блочной печи, дизирующего устройства для введения меченого SO_2 и пробоотборника для анализа реакционной смеси. Сернистый газ и воздух, пройдя соответствующую очистку

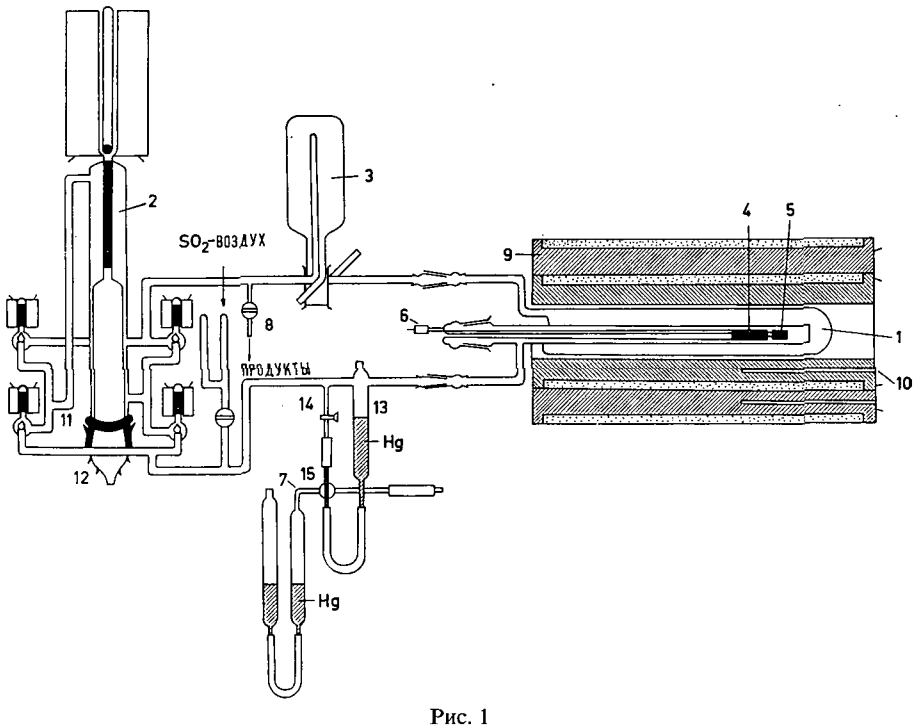

Рис. 1

Циркуляционная установка для изучения кинетики в состоянии равновесия.
1 — реакционный сосуд из кварца; 2 — стеклянный циркуляционный насос; 3 — пробоотборник; 4 — вспомогательный платиновый катализатор; 5 — рабочий платиновый катализатор; 6 — проволока для перемещения вспомогательного катализатора в холодную часть прибора; 7 — бюретка с радиоактивным SO_2.

поступали в смеситель, откуда направлялись в цикл. Технический сернистый газ осушался серной кислотой, воздух пропускался через колонку с плавленой щелочью, хлористым кальцием и через ловушку, охлаждаемую жидким воздухом.

Катализатор — платиновая сетка весом около 0,2 г — неподвижно закреплялся на маншоне для термопары, проходящем по оси реакционного сосуда. Удельная геометрическая поверхность проволочек сетки составляла 16 $см^2/г$. Для ускорения достижения равновесия имелся, кроме того, вспомогательный катализатор из такой же сетки (вес 2 г), который после достижения равновесия перемещался при помощи прикрепленной к нему платиновой проволоки в холодную часть прибора. Введение в цикл радиоактивного SO_2 производилось следующим образом: бюретку 7 (рис. 1) наполняли радиоактивным SO_2, поворотом дозирующего крана „К" вводили его в цикл, приведя предварительно ртуть в бюретке и в уравнительной склянке к одному уровню. Поднимая затем склянку 13, доводили ртуть вплотную до крана 14, вытеснив весь объем введенного SO_2 в цикл, после чего закрывали этот кран.

Радиоактивный SO_2 получали сжиганием радиоактивной серы в струе кислорода. Полученный так $S^{35}O_2$ конденсировался при охлаждении жидким воздухом в стеклянной ловушке, откуда переводился для хранения в стальной баллончик.

Агрессивность среды и чувствительность ее к следам влаги заставили работать без смазки, на сухих, тщательно притертых шлифах и кранах. В циркуляционном насосе металлическая пружина была заменена подушкой из битого стекла-11, причем ток в катушке был подобран так, чтобы поршень, как правило, не падал на подушку, а зависал в нижнем положении и вновь подхватывался при повышении силы тока.

Смесь SO_2 и SO_3 выдувалась из пробоотборника десятикратным объемом сухого воздуха последовательно через трубку, заполненную сухим NaCl для связывания SO_3 [1] и затем через ловушку с титрованным раствором йода для связывания SO_2. Образовавшийся в первой трубке $NaCl \cdot SO_3$ после растворения в воде титровали раствором NaOH, раствор J_2 оттитровывался гипосульфитом. Так определялось содержание SO_2 и SO_3 в пробоотборнике.

Затем ионы $SO^2{}_4^-$, образовавшиеся из SO_2 и из SO_3, осаждали порознь хлористым барием, осадки $BaSO_4$ фильтровали, промывали, наносили при помощи кисточки на предварительно взвешенные стеклянные пластинки диаметром 1,9 см, высушивали, взвешивали и радиометрировали на торцевом счетчике.

Для изучения кинетики в неравновесных условиях использовалась обычная проточно-циркуляционная установка. Скорость циркуляции 4—5 л/мин, скорость протока 0,2 л/мин.

2. Исследование кинетики в состоянии равновесия

После нагрева реактора до заданной температуры систему продували реакционной смесью в течение часа. Затем систему замыкали на 1—2 часа (в зависимости от температуры опыта) для установления химического равновесия. Время, достаточное для этого при каждой температуре, определялось предварительными опытами. По достижении равновесия вспомогательный катализатор перемещали в холодную часть прибора и в прибор вводилось

через дозирующее устройство 0,3 мл радиоактивного SO_2. (Общий объем цикла составлял 1650 мл). По истечении заданного времени (8—12 мин), анализировали содержание SO_2 и SO_3 в нем описанным выше способом. Всякий раз при анализе измерялась температура пробоотборника и вводилась поправка на содержащийся в нем объем газовой смеси. Благодаря хорошей циркуляции газовой смеси и небольшому подогреву электрической лампочкой циркуляционного насоса, температура в цикле нигде не опускалась ниже 30° С, что обеспечивало поддержание всех компонентов смеси в газовой фазе.

Результаты одной из серий опытов, в которых варьировалась начальная концентрация SO_2 при постоянной температуре, приведены в табл. I.

Все данные для скорости реакции отнесены к 1 г катализатора.

В табл. II приведены данные по исследованию зависимости скорости реакции от температуры.

Таблица I

ЗАВИСИМОСТЬ СКОРОСТИ ОКИСЛЕНИЯ СЕРНИСТОГО ГАЗА ОТ СОДЕРЖАНИЯ SO_2 В ИСХОДНОЙ СМЕСИ (α_{SO_2})

Температура 650° С

α_{SO_2}, %	τ, мин	P_{SO_2}, ат.	P_{SO_3}, ат.	P_{O_2}, ат.	$\lambda = \frac{P_{SO_3}}{P_{SO_2}}$	J_{SO_2}	J_{SO_3}	$J' = \frac{J_{SO_2}}{J_{SO_3}}$	W, $\frac{\text{мл}}{\text{мин. г}}$
3,60	10	0,0114	0,0246	0,191	2,14	14,0	10,3	1,36	1,051
3,71	8	0,0117	0,0254	0,189	2,17	38,0	17,2	2,20	0,844
3,89	8	0,0120	0,0269	0,189	2,24	28,2	11,7	2,40	0,800
6,13	8	0,0184	0,0429	0,176	2,33	15,7	9,3	1,69	1,72
6,19	8	0,0184	0,0435	0,175	2,36	18,7	8,6	2,17	1,33
7,33	9	0,0223	0,0510	0,169	2,29	15,8	9,2	1,71	1,83
8,40	10	0,0234	0,0606	0,163	2,59	8,5	5,1	1,66	1,73
9,04	10	0,0280	0,0624	0,161	2,23	8,3	5,5	1,51	2,32

Таблица II

ЗАВИСИМОСТЬ СКОРОСТИ РЕАКЦИИ $SO_2 + {}^1/_2 O_2 \rightleftarrows SO_3$ ОТ ТЕМПЕРАТУРЫ

τ во всех опытах = 8 мин, за исключением опыта при 650° С, в котором τ = 6 мин.

t, ° C	P_{SO_2}, ат	P_{SO_3}, ат	J'	W, $\frac{\text{мл}}{\text{мин. г}}$
600	0,0105	0,0377	4,40	0,375
606	0,0115	0,0382	3,98	0,450
625	0,0151	0,0356	2,74	0,846
625	0,0145	0,0386	2,50	0,889
650	0,0169	0,0276	2,50	1,440
655	0,0172	0,0267	1,82	1,558
674	0,0205	0,0289	1,43	2,470

3. Исследование кинетики реакции при удалении от равновесия

Исследование проводилось в установке такого же типа, как и при исследовании в условиях равновесия, но проточно-циркуляционным методом. Скорость циркуляции поддерживалась 4—5 л/мин; скорость потока 0,2 л/мин. Вес катализатора — платиновой сетки — 0,9512 г.

Нагрев реактор до заданной температуры, продували систему исходной смесью SO_2 и воздуха, состав которой устанавливался по реометрам. Через 20—30 минут приступали к химическому анализу смеси на выходе из реактора. Для этого на выходе подсоединялись последовательно ловушка с хлористым натрием для связывания SO_3, промывалка с титрованным раствором йода для определения SO_2 и сосуд Мариотта для определения общего объема смеси, взятой для анализа. Заданные условия (температуру, концентрации SO_2 на входе) выдерживали до тех пор, пока установившаяся степень превращения сохраняла свое значение в течение 1,5—2 часов.

Варьирование концентраций в цикле производилось изменением начальной концентрации SO_2 (α_{SO_2}). Наблюдаемая скорость превращения, получаемая произведением концентрации SO_3 на выходе на скорость протока, представляла собою разность скоростей прямой и обратной реакций ($W_1 - W_2$).

Результаты одной из серий опытов, в которой степень превращения составляла около 70%, приведена в таблице III.

В таблице IV приведены результаты исследования влияния температуры на скорость реакции.

Таблица III

ЗАВИСИМОСТЬ СКОРОСТИ РЕАКЦИИ ОТ ИСХОДНОЙ КОНЦЕНТРАЦИИ SO_2. Т-ра 587° С

α_{SO_2}, %	Скорость потока мл/мин.	P_{SO_2}, ат	P_{SO_3}, ат	P_{O_2}, ат	$W_1 - W_2$, мл/мин. г
2,69	204	0,0114	0,0155	0,197	3,32
3,46	206	0,0150	0,0197	0,194	4,27
3,39	206	0,0150	0,0189	0,194	4,08
5,74	210	0,0258	0,0316	0,182	6,98
6,26	210	0,0289	0,0346	0,180	7,65

Таблица IV

ЗАВИСИМОСТЬ СКОРОСТИ РЕАКЦИИ ОТ ТЕМПЕРАТУРЫ

t, ° С	P_{SO_2}, ат.	P_{SO_3}, ат.	$W_1 - W_2$ мл/мин. г	t, ° С	P_{SO_2}, ат.	P_{SO_3}, ат.	$W_1 - W_2$, мл/мин. г
600	0,0237	0,0356	7,68	500	0,0342	0,0214	4,62
600	0,0233	0,0339	7,22	510	0,0338	0,0216	4,66
575	0,0242	0,0324	6,97	450	0,0465	0,0109	2,36
550	0,0254	0,0320	6,91	450	0,0438	0,0109	2,36
550	0,0252	0,0316	6,80	420	0,0410	0,0070	1,42

4. Обработка и обсуждение результатов

В наших опытах концентрация кислорода изменялась очень мало и в первом приближении ее можно было принять постоянной. Для выяснения формы зависимости W от концентраций SO_2 и SO_3 полученные значения W (табл. I) были представлены на графике как функции этих концентраций (рис. 2 и 3).

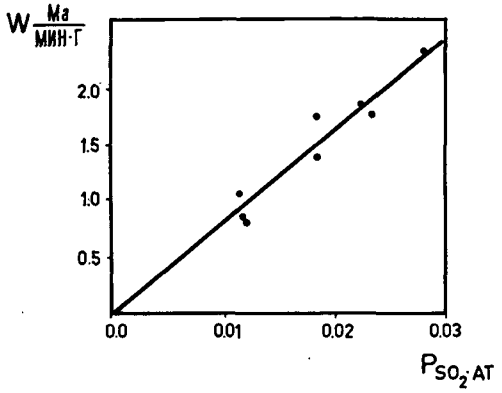

Рис. 2
Зависимость скорости прямой реакции от парциального давления SO_2.

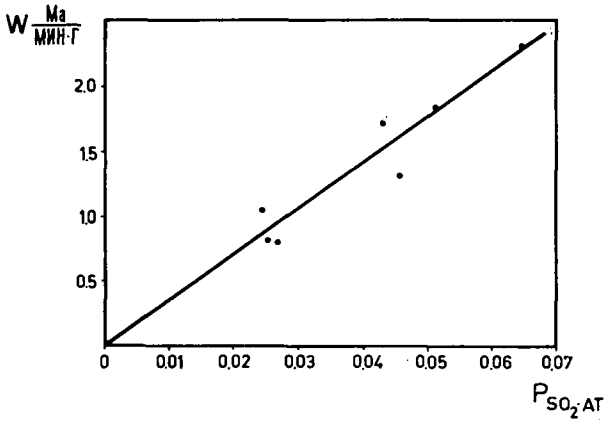

Рис. 3
Зависимость скорости обратной реакции от парциального давления SO_3.

Как видно из графиков, значения W могут быть достаточно удовлетворительно представлены либо уравнением $W=k'P_{SO_2}$, либо $W=k''P_{SO_3}$. Очевидно, первое из них отвечает кинетике прямого, второе — обратного процесса. Таким образом, в элементарном акте окисления SO_2 на платине принимает участие 1 молекула SO_2, в обратном — 1 молекула SO_3. Это соответствует выводу Борескова [2] о мономолекулярности процесса $\nu=1$.

Линейность зависимостей указывает, далее, на слабую адсорбируемость SO_2 и SO_3 (область Генри).

При трактовке кинетики реакций, протекающих в условиях равновесия, с позиций того или иного предполагаемого механизма следует, как уже указывалось в начале статьи, отбросить все те механизмы, которые предполагают отсутствие равновесия хотя бы в одном из звеньев реакции. Так, очевидно, непригоден для этого подход М. И. Темика (принцип полуравновесий), который был применен Боресковым [3] для вывода кинетического уравнения рассматриваемого процесса. В этом случае предполагается от-

сутствие равновесия между газообразной и адсорбированной SO_2. Действительно, выведенные им выражения для скоростей прямого и обратного процессов

$$W_1 = k_1 \cdot P_{O_2}^{0,25} \cdot P_{SO_2} \cdot P_{SO_3}^{-0,5}$$
$$W_2 = k_2 \cdot P_{O_2}^{-0,25} \cdot P_{SO_3}^{0,5}$$

не соответствуют полученным нами линейным зависимостям от P_{SO_2} и P_{SO_3}. Также, очевидно, нельзя предполагать цепную схему протекания процесса, т.к. в ее основе лежит предположение о накоплении активных радикалов в концентрациях, превышающих равновесные.

С другой стороны, в условиях установившегося равновесия, когда нет ограничения во времени, SO_3 может образовываться по всем возможным параллельным путям, даже если некоторые из этих путей требуют высокой энергии активации. Наблюдаемая кинетика окисления будет в этом случае определяться кинетикой той частной реакции, которая протекает быстрее других параллельных реакций, по которой, следовательно, образуется основное количество SO_3.

В качестве возможных механизмов реакции, отвечающих полученным экспериментальным данным и, в то же время, принципу детального равновесия, можно предположить следующие:

I.* 1) $\underline{O_2} \rightleftarrows 2\underline{O}$
2) $\underline{O} + \underline{SO_2} \rightleftarrows \underline{SO_3}$

II. 1) $\underline{SO_2} + \underline{O_2} \rightleftarrows \underline{SO_3} + \underline{O}$
2) $\underline{O} + \underline{SO_2} \rightleftarrows \underline{SO_3}$
3) $2\,\underline{O} \rightleftarrows \underline{O_2}$

Для выбора между этим вариантами на основании кинетических данных необходимо детальное исследование зависимости скорости реакции от концентрации кислорода, т.к. в отношении вида зависимости от концентрации SO_2 и SO_3 оба варианта неотличимы. Поэтому наши данные не могут быть использованы для этой цели. Для дальнейших расчетов мы приняли условно 1-ый вариант, как простейший и соответствующий к тому же литературным данным** о большой скорости адсорбции кислорода платиной, сопровождающейся полной или частичной диссоциацией.

Общая схема процесса, отвечающая 1-му варианту, изображена на рис. 4.

Кинетические уравнения для скорости прямого и обратного процессов, соответствующие этому варианту:

$$W_1 = k' \, \theta_{SO_2} \, \theta_0,$$
$$W_2 = k'' \, \theta_{SO_3},$$

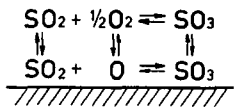

Рис. 4
Схема процесса окисления SO_2 на поверхности платины.

* Черточкой под формулами веществ условно обозначено нахождение этих веществ в адсорбированном состоянии.

** Обстоятельный обзор литературы по этому вопросу см. в цитированной выше монографии Г. К. Борескова.

где θ — доля каталитически активной поверхности, занятой данным компонентом. Приняв на основании наших экспериментальных данных

$$\theta_{SO_2}=\alpha_{SO_2}\ P_{SO_2},\ \theta_{SO_3}=\alpha_{SO_3}\ P_{SO_3}$$

и, условно $\theta_0=\sqrt{\alpha_{O_2}\cdot P_{O_2}}$, получаем

$$W_1=k_1\cdot P_{SO_2}\cdot\sqrt{P_{O_2}};\ W_2=k_2\cdot P_{SO_3}. \qquad (1)$$

В таблице V приведены значения k_1 и k_2 для разных температур, вычисленные по этим уравнениям из данных таблицы II.

На рисунках 5 и 6 приведены графики $\lg k_1 \Big/ \frac{1}{T}$ и $\lg k_2 \Big/ \frac{1}{T}$.

Таблица V

ЗАВИСИМОСТЬ КОНСТАНТ СКОРОСТЕЙ РЕАКЦИИ $SO_2 + {}^1/_2\ O_2 \rightleftarrows SO_3$ В УСЛОВИЯХ РАВНОВЕСИЯ ОТ ТЕМПЕРАТУРЫ

t, ° C	600	606	625	625	650	655	674
K_1	82,5	92,0	132,0	144,0	196,8	209,0	279,0
K_2	9,95	11,80	23,80	23,00	52,30	58,25	85,60

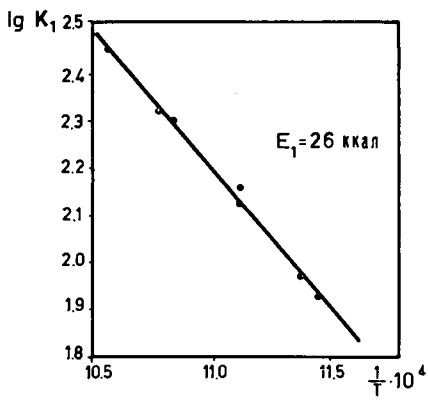

Рис. 5

График $\lg K_1 \Big/ \frac{1}{T}$

Наблюдается хорошее соответствие уравнению Аррениуса. Вычисленные из наклона прямых теплоты активации для прямого процесса $E_1=26$ ккал/моль, для обратного — $E_2=49$ ккал/моль; значение разности $E_2 - E_1=23$ кк. согласуется с известным значением топлоты реакции.

Энергетическая схема предполагаемого механизма реакции изображена на рис. 7.

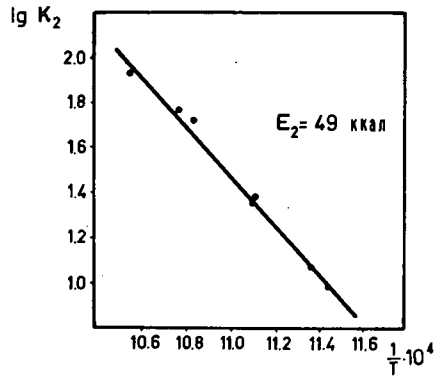

Рис. 6
График $\lg K_2 / \frac{1}{T}$

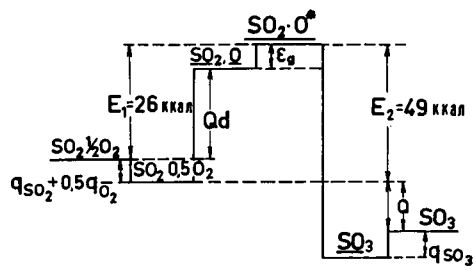

Рис. 7
Энергетическая схема пути реакции:

E_1 и E_2	— наблюденные теплоты активации;
Q	— теплота реакции $SO_2+{}^1/_2O_2 \rightarrow SO_3$;
q_{SO_2}, q_{SO_3}, q_{O_2}	— теплоты адсорбции SO_2, SO_3, O_2;
Qd	— теплота реакции $0{,}5O_2 \rightarrow O$;
ε_O	— собственная высота активационного барьера.

Из этой схемы следует, что теплота превращения молекулярного газообразного кислорода в адсорбированный атом

$$Q\,d = -(E_1 - E_0) = -(26 - E_0).$$

Т.к. величина E_0, учитывая радикальный характер 0, должна быть небольшой (в пределах 10 ккал/моль [4]), значение $Q\,d$ можно приближенно оценить величиной — 20 ккал/г-атом. Учитывая, что теплота диссоциации O_2 на газообразные атомы равна — 59 ккал/г-атом, энергия связи адсорбированного атома кислорода с платиной должна иметь величину около 40 ккал/г-атом, что достаточно правдоподобно.

При удалении от равновесия последнее будет нарушаться в первую очередь в стадиях, протекающих наиболее медленно. Если таковой является элементарная реакция на поверхности, скорость реакции будет определяться разностью скоростей этой поверхностной реакции, равновесия же между адсорбированными газообразными участниками реакции будут сохраняться. В этом случае (кинетика Лэнгмюра-Шваба) следует ожидать, что общая

кинетика будет описываться, как разность скоростей W_1 и W_2, где каждая из этих скоростей может сохранить ту же форму зависимости от концентраций, которая наблюдалась в состоянии равновесия. Если наиболее медленной стадией является адсорбция одного из участников реакции, равновесие на поверхности будет сохраняться, а скорость реакции будет определяться скоростью адсорбции этого вещества (кинетика Темкина). В этом случае вид кинетики будет иным, напр. соответствующим ур-нию Борескова.

Для сопоставления с равновесной схемой рис. 4 оба эти случая изображены аналогичным образом на рис. 8.

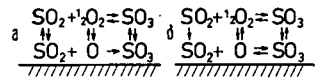

Рис. 8
а) кинетика Лэнгмюра-Шваба; б) кинетика Темкина-Борескова.

Таблица VI

СОПОСТАВЛЕНИЕ КОНСТАНТ СКОРОСТЕЙ, ВЫЧИСЛЕННЫХ ПО УРАВНЕНИЮ ДЛЯ РАВНОВЕСНЫХ УСЛОВИЙ И ПО УРАВНЕНИЮ БОРЕСКОВА. t = 587° С

a_{SO}, %	2,69	3,46	3,39	5,74	6,26
$K_1 = \dfrac{W_1 - W_2}{P_{O_2}^{0,5} \cdot P_{SO_2} - \dfrac{P_{SO_3}}{Kp}}$	894	880	824	844	860
$K_1 = \dfrac{W_1 - W_2}{P_{SO_2} \cdot P_{O_2}^{0,25}\left(1 - \dfrac{P_{SO_3}}{Kp \cdot P_{SO_2} \cdot P_{O_2}^{0,5}}\right)}$	73,4	81,5	75,4	97,8	104,0

В таблице VI приведены значения K_1, вычисленные по данным $W_1 - W_2$ таблицы III по уравнениям:

$$K_1 = \frac{W_1 - W_2}{P_{O_2}^{0,5} \cdot P_{SO_2} - \dfrac{P_{SO_3}}{Kp}},$$

соответствующему кинетическому уравнению в состоянии равновесия, и

$$K_1 = \frac{W_1 - W_2}{P_{SO_2} \cdot P_{O_2}^{0,25}\left(1 - \dfrac{P_{SO_3}}{Kp \cdot P_{SO_2} \cdot P_{O_2}^{0,5}}\right)},$$

соответствующему уравнению Борескова.

Из таблицы видно, что уравнение Борескова приводит к значительному систематическому росту K_1, в то время, как K_1, вычисленная по первому уравнению, практически не зависит от концентрации SO_2 и SO_3.

Таким образом и при удалении от равновесия сохраняется, по-видимому, тот же механизм и та же кинетика, что и в состоянии равновесия.

В таблице VII приведены значения констант K_1 для разных температур, вычисленные по первому уравнению и данным таблицы IV.

Таблица VII

ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ КОНСТАНТЫ СКОРОСТИ K_1 ОТ ТЕМПЕРАТУРЫ

t, ° C	600	575	550	500	450	420
K_1	686 635	440	362 358	200 202	97,8 97,8	58,9

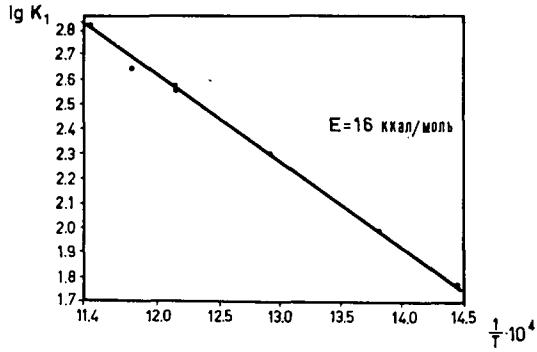

Рис. 9

График $\lg k_1 \Big/ \frac{1}{T}$ (в неравновесных условиях).

На рис. 9 приведен график зависимости $\lg k_1 \Big/ \frac{1}{T}$, из которого видно хорошее согласие температурной зависимости с уравнением Аррениуса. Теплота активации, вычисленная из наклона прямой $E_1 = 16$ ккал/моль.

При сопоставлении результатов обработки данных, полученных в условиях равновесия и при удалении от него, обращает на себя внимание тот факт, что при сохранении тех же кинетических зависимостей и, по-видимому, того же механизма реакции, наблюдается резкое различие в абсолютных значениях констант: константы скорости в состоянии равновесия много ниже, а величины теплот активации значительно выше величин, вычисленных при протекании реакции вне равновесных условий.

Эти несоответствия можно объяснить, если предположить, что при взаимодействии кислорода с платиной, кроме способных к реакции атомов O, может образовываться другое какое-то поверхностное соединение, которое мы условно обозначим как $Pt\ldots O_2$, очень медленно реагирующее с сернистым газом. В условиях равновесия к процессам, изображенным в схемах по 1-му или 2-му вариантам, прибавятся, следовательно, еще равновесные стадии:

$$O_2 + Pt \rightleftarrows Pt\ldots O_2$$

$$Pt\ldots O_2 + 2\,SO_2 \rightleftarrows Pt + 2\,SO_3.$$

Если принять, что эти процессы текут очень медленно по сравнению с процессами, учитываемыми ранее, количество SO_3, образующееся этим путем, ничтожно и им можно пренебречь. Однако наличие этих стадий

приводит к уменьшению свободной поверхности платины и к снижению, таким образом, величин K_1 и K_2.

Если принять, далее, что химический потенциал $Pt\ldots O_2$, как это свойственно поверхностным соединениям, зависит от степени покрытия поверхности, отношение $\frac{Pt}{Pt\ldots O_2}$ будет увеличиваться с повышением температуры (процесс $Pt+O_2 \rightarrow Pt\ldots O_2$, очевидно, экзотермичен) и константы скорости реакции окисления SO_2 будут возрастать не только за счет увеличения вероятности взаимодействия SO_2 с O_2 на данной поверхности активной платины, но и за счет увеличения доли свободной поверхности, что проявляется в виде повышенных значений наблюдаемых теплот активации [5].

При удалении от равновесия, как уже отмечалось выше, прежде всего, будут нарушены равновесия наиболее медленных параллельных частных реакции, к которым относятся рассматриваемое взаимодействие кислорода с платиной. Равновесие сдвинется далеко влево, поверхность платины освободится, константы скорости резко возрастут. Повышение температуры теперь уже не сможет дать увеличение значений K_1 и K_2 за счет освобождения поверхности платины, благодаря чему наблюдаемые теплоты активации примут нормальные значения, более низкие, чем в условиях равновесия.

Отравляющее влияние кислорода на платиновые катализаторы отмечалось многими исследователями [6]. Все же мы поставили специальный опыт для подтверждения развитой здесь гипотезы. Активный катализатор обрабатывали при 550—600° С воздухом (без SO_2) в течение 2 часов, после чего проверили его активность при той же температуре. Оказалось, что действительно активность его после этой обработки резко снизилась: степень превращения до обработки была 57,9%; 51,2%; после обработки воздухом — 9,2%; 8,8%. Потребовалось 3 часа работы катализатора на газо-воздушной смеси, чтобы активность его постепенно поднялась до исходного значения. Таким образом, действительно существует такой тип взаимодействия кислорода с платиной, который приводит к отравлению контакта, причем как этот процесс, так и процесс освобождения поверхности контакта при катализе — очень медленные процессы.

Выводы

1. Измерены при помощи метода меченых атомов скорости прямой и обратной реакций окисления SO_2 на платиновой сетке в зависимости от концентраций SO_2 и SO_3 при разных температурах. Показано, что молекулярность процессов $\nu=1$. Найдены кинетические уравнения, согласующиеся с экспериментальными данными, и предложены возможные схемы процесса, удовлетворяющие найденным кинетическим зависимостям и принципу детального равновесия. Вычислены теплоты активации прямого и обратного процессов.

2. На таком же катализаторе проведено исследование кинетики при удалении от равновесия. Данные укладываются в те же кинетические уравнения, которые были получены в состоянии равновесия. Это позволяет распространить предложенный механизм и на протекание процесса вне равновесия и сделать вывод, что лимитирующей стадией является поверхностная реакция SO_2 с кислородом, а не процессы взаимодействия какого-либо из компонентов реакции с катализатором.

3. Вместе с тем установлено, что в состоянии равновесия вычисленные *константы скорости значительно меньше по своей абсолютной величине*, а наблюдаемые теплоты активации выше соответствующих величин, найденных при протекании процесса вне равновесия. Дано объяснение этому факту наличием медленного обратимого взаимодействия кислорода с платиной, приводящего к образованию малореакционноспособного поверхностного соединения, уменьшающего активную поверхность платины. Показано, что это отравление должно проявляться главным образом в условиях равновесия и практически не сказывается при удалении от него. Предположение об отравляющем воздействии кислорода на платину и медленности этого процесса подтверждено специальным экспериментом.

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ADSORPTION STUDIES AT IONIZED SURFACE LAYERS BY MEANS OF HOT ATOMS

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Abstract — Résumé — Аннотация — Resumen

Adsorption studies at ionized surface layers by means of hot atoms. Adsorption of ions at the surface of solutions of ionic surface-active substances can directly be studied using hot atoms. Extremely small amounts of suitable radioactive ions, or ions liable to undergo induced nuclear transformations *in situ*, are added to such solutions, replacing some of the normal counter ions coadsorbed at the primary-adsorbed organic ions. Hot atoms with energies from about 100 keV down to a few electron volts give ranges in water from about 1000 Å down to monomolecular layers. This makes them suitable for sensitive surface layer studies. The hot atoms ejected from the surface are collected and counted.

Among α-disintegration recoils, the system Bi^{212}/Tl^{208} has proved to be suitable. Now, by refining the method, valuable information about adsorption conditions at sodium dodecyl sulphate surface layers could be found. The kinetics of adsorption was studied by following in time the collected recoil activity caused by Bi-ion adsorption. Adsorption isotherms of Bi-ions as a function of the bulk concentration of the surface-active substance under varying conditions of ionic strength, pH and Bi^{212} activity were measured.

By comparing these isotherms with those obtained by measuring the surface tension of the solutions and calculating the surface excess with the aid of a suitably modified Gibbs' isotherm, the adsorption of Bi^{+++} and Pb^{++} relative to that of Na^+ and H_3O^+, and by this the extent of ion exchange in the adsorbed layer could be determined.

As the method measures the adsorption of charged species, surface reactions transforming primary-adsorbed organic anions to a non-ionic state could be followed. Conclusions could be drawn about the formation of a non-ionized acid soap in the surface and about micelle formation in the bulk under various experimental conditions.

Etude, à l'aide d'atomes excités, de l'adsorption dans des couches superficielles ionisées. L'adsorption d'ions à la surface de solutions de substances ioniques tensioactives peut être étudiée directement si l'on utilise des atomes excités. Des quantités extrêmement faibles d'ions radioactifs appropriés, ou d'ions capables de subir *in situ* des transformations nucléaires induites, sont ajoutées à ces solutions, en remplacement de certains contre-ions coadsorbés sur les ions organiques adsorbés initialement. Des atomes excités dont l'énergie va de 100 keV à quelques électrons volts seulement ont dans l'eau un parcours compris entre 1000Å et des valeurs correspondant aux couches monomoléculaires. On peut donc s'en servir pour des études très sensibles sur les couches superficielles. Les atomes excités qui sont expulsés de la surface sont séparés et comptés.

Pour obtenir des particules de recul par désintégration α, le système $^{212}Bi/^{208}Tl$ s'est révélé satisfaisant.

En améliorant cette méthode, on a pu obtenir des renseignements utiles sur les conditions d'adsorption en couches superficielles de dodécyl-sulfate de sodium. On a étudié la cinétique de cette adsorption en suivant dans le temps l'activité des particules de recul formées par adsorption d'ions Bi. On a mesuré les isothermes d'ad-

sorption des ionsBi en fonction de la concentration globale de la substance tensioactive sous différentes conditions de force ionique, de pH et d'activité ^{212}Bi. En comparant ces isothermes avec ceux obtenus par mesure de la tension superficielle des solutions et en calculant l'excès de surface à l'aide d'un isotherme de Gibbs convenablement modifié, on a pu déterminer l'adsorption de Bi^{+++} et de Pb^{++} par rapport à celle de Na^+ et de H_3O^+ et, à partir de ces données, l'importance de l'échange ionique dans la couche adsorbée.

Etant donné que cette méthode permet de mesurer l'adsorption des espèces ionisées, on a pu suivre les réactions de surface transformant les anions organiques primaires adsorbés en un état non ionique. On a pu en tirer des conclusions sur la formation de savons acides non ionisés en surface et sur certaines formations de micelles dans la masse de la solution dans les différentes conditions expérimentales.

Исследование при помощи горячих атомов адсорбции на ионизированных поверхностных слоях. С помощью горячих атомов можно непосредственно исследовать явления адсорбции ионов на поверхности растворов активных веществ с ионизированной поверхностью. К таким растворам добавляются чрезвычайно малые количества соответствующих радиоактивных ионов или ионов, могущих подвергнуться на месте наведенным ядерным преобразованиям: эти ионы заменяют обычные служащие для отсчета ионы, адсорбированные вместе с первичными органическими ионами. Горячие атомы с энергией приблизительно от 100 кэв и вплоть до нескольких электронвольт дают в воде слои толщиной приблизительно от 1000 ангстремов и вплоть до одномолекулярных. Это делает их пригодными для изучения чувствительного поверхностного слоя. Горячие атомы, выталкиваемые с поверхности, собираются и подвергаются отсчету.

Среди отдач, испытывающих альфа-распад, оказалась подходящей система Bi-212/TI-208.

Путем дальнейшей разработки этого метода могли быть получены ценные сведения относительно условий адсорбции на поверхностных слоях сернокислого натрия додециловой кислоты. Кинетика адсорбции была изучена наблюдением во времени за активностью собранной отдачи, вызванной адсорбцией ионов висмута. Были замерены изотермы адсорбции ионов висмута в функции от массовой концентрации поверхностного активного вещества в различных условиях ионной интенсивности, а также pH и активность Bi-212.

Путем сопоставления этих изотерм с изотермами, полученными измерением поверхностного напряжения растворов и путем подсчета поверхностного избытка при помощи надлежащим образом измененной изотермы Гиббса, удалось определить адсорбцию Bi^{+++} и Pb^{++} по отношению к адсорбции Na^+ и H_3O^+ и тем самым установить степень ионного обмена в адсорбированном слое.

Так как этот метод позволяет измерять адсорбцию заряженных частиц, то можно было проследить за поверхностными реакциями, превращающими первичные поглощенные органические анионы в неионное состояние. Из этого можно было вывести заключение относительно образования неионизированного кислотного мыла на поверхности и относительно образования ницеллы в массе раствора при различных экспериментальных условиях.

Estudios, con ayuda de átomos excitados, de la adsorción en capas superficiales ionizadas. Los átomos excitados permiten estudiar directamente la adsorción de iones en la superficie de soluciones de sustancias tensoactivas iónicas. Para efectuar tales estudios se añaden a esas soluciones cantidades muy pequeñas de iones radiactivos adecuados, o de iones susceptibles de experimentar transformaciones nucleares inducidas *in situ*, que sustituyen a algunos de los contra-iones coadsorbidos en los iones orgánicos adsorbidos inicialmente. El alcance en agua de los iones excitados cuyas energías están comprendidas entre unos 100 keV y algunos electrón-voltios oscila entre 1000 Å y valores del orden del espesor de capas monomoleculares. Por ello, permiten realizar estudios muy sensibles de las capas superficiales. Los átomos excitados expulsados de la superficie se separan para proceder a su recuento.

Para obtener partículas de retroceso por desintegración alfa, puede utilizarse, entre otros, el sistema $^{212}Bi/^{208}Tl$.

Perfeccionando el método, los autores han podido reunir datos interesantes sobre las condiciones de adsorción en capas superficiales de soluciones de dodecilsulfato sódico. Estudiaron la cinética de la adsorción registrando en función del tiempo la actividad de las partículas de retroceso formadas por adsorción de iones Bi, y determinaron las isotermas de adsorción de los iones Bi en función de la concentración total de la sustancia tensoactiva en diversas condiciones de fuerza iónica, de pH y de actividad del ^{212}Bi.

Comparando estas isotermas con las obtenidas al medir la tensión superficial de las soluciones, y calculando el exceso de superficie con ayuda de una isoterma de Gibbs convenientemente modificada, pudieron determinar la adsorción del Bi^{3+} y del Pb^{++} con respecto al Na^+ y al H_3O^+; de estos datos, derivan el grado de intercambio iónico en la capa adsorbida.

Como este método mide la adsorción de las especies ionizadas, fue posible seguir las reacciones superficiales por las que los aniones orgánicos adsorbidos inicialmente pasan al estado no iónico. Los autores pudieron deducir la formación de un jabón ácido no ionizado en la superficie y llegar a conclusiones sobre la formación de micelas en la masa de la solución, en diversas condiciones experimentales.

1. Introduction

Various direct and indirect methods have been developed for studying the adsorption of solutes at the liquid/gas interface. In the last few years radioactive methods have been introduced, as they seemed to be promising.

In these methods the amounts of radioactively tagged adsorbed-soap-molecules or secondarily adsorbed radioactive-ions at the surface of a solution were measured with a G-M tube, mounted closely on the surface [1—3].

It turned out that the ranges of the radioactive disintegration particles usually employed were large in comparison with the "thickness" of the surface phase studied, and so most of the outcoming radiation originated in the bulk of the solution, while only a small fraction of it represented the actual adsorbed layer.

TABLE I

VARIOUS RADIONUCLIDES USED AND THEIR SUITABILITY FOR ADSORPTION MEASUREMENTS

Nuclide	Disintegration fragment used	E_{max} (MeV)	$T_{1/2}$	Range in water (Å)	$\frac{A_s}{A_s + A_i}$
Na^{22}	β^+	0.542	2.6 yr	$\sim 1.96 \times 10^7$	~ 0.006
Ca^{45}	β^-	0.260	164 d	6.5×10^6	0.018
S^{35}	β^-	0.169	87.1 d	3.4×10^6	0.035
C^{14}	β^-	0.156	5570 yr	3.0×10^6	0.034
Ni^{63}	β^-	0.065	85 yr	$\sim 6.7 \times 10^5$	~ 0.12
H^3	β^-	0.0179	12.46 yr	6.0×10^4	0.64
Po^{210}	α	5.30	138.4 d	3.2×10^5	0.058
Bi^{212}	α-recoil atom Tl^{208}	0.117	60.5 min	800 ± 30	0.95
	β-recoil atoms	1—50 eV		a few atomic layers	0.98—1.00

The most common radionuclides which have been used are summarized in Table I. The last column gives the ratio between the radiation from the surface and the total outcoming radiation, i.e., radiation-from-surface plus radiation-contributed-by-the-bulk, which depends on the length of the range. The figures in this column are for typical adsorption conditions, namely, a surface concn of 10^{-10} mole/cm^2 and a bulk concn of 10^{-3} mole/l. The values presented are partly based on data by ANIANSSON [2]. As may be seen from Table I, tritium, being the softest β-emitter, allows the maximum representation of the surface layer that can be achieved by the above-mentioned methods. Employing this emitter, NILSSON [4] measured the adsorption of tritiated sodium-dodecyl-sulphate at its solution surface with a windowless, high-humidity gas, flow-proportional counter. In this way about 2/3 of the measured radiation represented the investigated surface region.

It is evident that higher sensitivity could be achieved by using particles of still lower penetrating power. Hot atoms with energies from about 100 keV down to a few electron volts give ranges in water from about 1000 Å down to monomolecular layers. It seemed, therefore, that their use for this purpose would be very suitable. This is especially the case when studying ionized surface layers formed at the surface of an aqueous solution of a surface-active substance. The primary-adsorbed surface-active ions charge the surface electrically, giving rise to an electrical double layer. In this way counter-ions of opposite sign are coadsorbed at the surface.

Extremely small amounts of suitable radioactive ions, or ions liable to undergo non-spontaneous nuclear transformations *in situ*, added to such solutions will replace some of the normal counterions coadsorbed at the primary-adsorbed organic ions. A part of the hot atoms resulting is ejected from the surface and collected by a suitable collector placed above the solution, mostly applying a direct electric field. The recoiling atoms should themselves be radioactive and can thus be easily detected and counted.

The possibility of using α-disintegration recoils for adsorption studies has been pointed out by ANIANSSON [2]. A suitable method has been worked out in detail by STEIGER and ANIANSSON [5] making use of the α-disintegration of Bi^{212} resulting in the Tl^{208}-recoil, and taking into account all possible interfering factors. By refining this method in the work presented below, new information could be obtained on adsorption conditions at sodium-dodecyl-sulphate surface layers.

2. Experimental

METHOD

The experimental method used consisted of collecting Tl^{208}-ions which recoil out from the surface of an aqueous solution of sodium-dodecyl-sulphate, at which Bi^{212}-ions had been coadsorbed as counter-ions. The collection of the recoiling Tl^{208}-ions was performed on a negatively-charged stainless-steel plate placed at a distance of 3 mm from the surface of the solution. A negatively charged collimating ring was placed between the collector and the solution at a distance of 1 mm from it. The potential between solution and collector was several hundreds of volts in order to ensure saturation collection, whereas the potential of the ring with respect to the solution was always one third, thus maintaining a homogeneous field.

Sodium-dodecyl-sulphate was dissolved in nitric acid solutions containing $[Pb^{212}]^{++}/[Bi^{212}]^{+++}$ and all its other disintegration products in transient equilibrium. This solution was prepared by dissolving the activities of the collecting cathode of a Th-emanation chamber.

Each recoil collection above the solution was continued until secular equilibrium between the collected Tl^{208} activity (3.1 min) and the equilibrium activity of the solution was reached. After removal of the collector, its integral activity was measured over a definite time-interval. A normalized recoil activity (A_D), for a certain reference time, was calculated from the integral measurement, taking into consideration the decay of solution activity, the specific activity used, correction for coincidence losses, and other experimental factors. Finally, the surface concentration of $[Bi^{212}]^{+++}$ could be calculated from A_D considering all the physical factors and experimental conditions.

The bulk concentration of the bismuth ions was obtained by two different methods: the measurement of the α-activity in a 2π-flow gas counter and measurement of the β-activity by a thin-window G-M counter in a known geometry.

The experiments were performed in an air-thermostat at a temp. of 25°C.

Surface active substance

An extremely pure sample of sodium-dodecyl-sulphate was synthesized by a method similar to that of Dreger *et al.* [6] from lauryl alcohol free from homologues, given by Prof. E. Stenhagen of the University of Upsala, and pure chloro-sulphonic acid. The sodium-dodecyl-sulphate was further purified by means of diethylether in a Sohxlet for 250 h, and kept in a vacuum desiccator. When measuring the surface-tension against concentration, it was found that the bend of the critical micelle concn (CMC) curve is at 8 mM/l. Conductivity measurements gave the same results.

The water used was distilled three times, and the nitric acid was of analytical grade, diluted with three volumes of distilled water.

3. Results and discussion

By means of the α-recoil method the following problems concerning ion adsorption at the surface of solutions could be investigated: adsorption kinetics, relative coadsorption of various counterions, surface reactions transforming primary-adsorbed organic-anions into a non-ionic state, and micelle formation.

Parallel to the α-recoil measurements, surface-tension measurements were made versus concentration of surface-active substance.

The range of Tl^{208} in water

The range of Tl^{208} in water was calculated, assuming additivity of the atomic stopping powers of the recoil in a compound $S = A_x B_y$ as follows:

$$R_S = \frac{M_S}{\varrho_S \left[x \frac{M_A}{R_A \varrho_A} + y \frac{M_B}{R_B P_B} \right]}$$

where: R = range of the recoil,
M = molecular or atomic weight and
ϱ = density.

When using the ranges of Tl^{208} in air and hydrogen, as measured by Baulch and Duncan [7], a value of 800 ± 30 Å was obtained for its range in water. This

range is of the same order as the investigated diffuse surface layer, the thickness of which can be estimated within some tens to some hundreds of Ångström.

Kinetics of adsorption

The kinetics of adsorption was studied by following in time the collected recoil activity caused by Bi-ion adsorption. Fig. 1 shows the results for different concentrations of the surface-active substance, ranging from 10^{-5} to 10^{-2} mole/l.

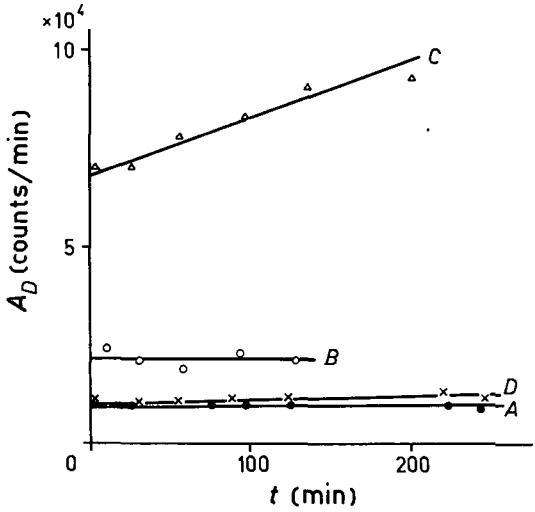

Fig. 1
Adsorption kinetics of $[Bi^{212}]^{+++}$ at pH = 2.
$A = 10^{-2}$ mole/l sodium-dodecyl-sulphate; $B = 10^{-3}$; $C = 10^{-4}$; $D = 10^{-5}$.

Since the coadsorption of the Bi-ions at the surface layer is mainly dependent on the primary adsorption of the dodecyl-sulphate ions, the measurement of recoil activity as a function of time gives a certain indication of the primary adsorption. It can be seen that at higher sodium-dodecyl-sulphate (SDS) concentrations the kinetics is faster than at lower ones. In previous measurements with a less purified sample of SDS, which was probably contaminated with higher ionic homologues, it was found that the equilibrium was reached much more slowly.

Various adsorption isotherms

It is a well-known fact that the ionic strength of a solution of an ionic surface-active substance influences markedly the extent of primary adsorption, and consequently also the extent of coadsorption. Furthermore, the CMC is influenced, and the ratio changed between the different cations liable to undergo coadsorption. The ionic strength of the solutions under investigation was controlled by addition of sodium nitrate; thus no new species were added to the system. The $[Bi^{212}]^{+++}$ concentration was always kept constant, due correction being made for radioactive disintegration. In Fig. 2 a series of adsorption isotherms is given with ionic strength as parameter.

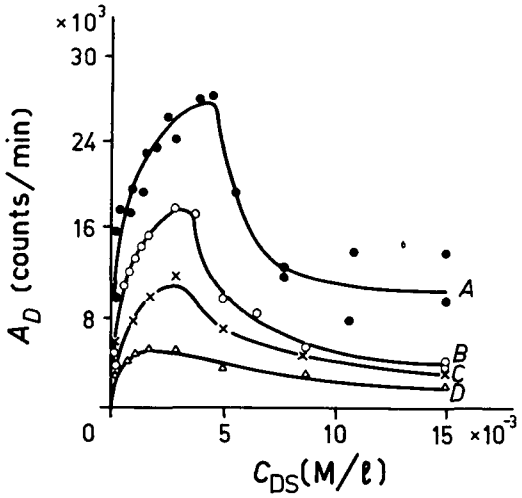

Fig. 2
The $[Bi^{212}]^{+++}$ coadsorption at various ionic strengths at pH = 2.
A = ionic strength (μ) = 2.5×10^{-2} mole/l;
$B = 4.0 \times 10^{-2}$; $C = 5.5 \times 10^{-2}$; $D = 7.0 \times 10^{-2}$.

Comparison with corresponding conventional surface-tension/concn curves shows that the CMC values in these curves can be related to the adsorption maxima in Fig. 2. As expected, these maxima move to lower SDS concentrations with increasing ionic strength. The decrease of the $[Bi^{212}]^{+++}$ coadsorption with increasing ionic strength is brought about by the decrease of the $[Bi^{212}]^{+++}/[I^+]$ ratio in the solution, which is much more pronounced than the total increase of adsorption caused by the increase of the ionic strength. $[I^+]$ represents the sum $[Na^+] + [H_3O^+]$. Following VAN OS [9], the adsorption characteristics of Na^+ and H_3O^+ were assumed to be approximately equal.

As the DS^- ion exhibits an equilibrium with the acid form:

$$HDS + H_2O \rightleftarrows H_3O^+ + DS^-$$

$$K_a = [H_3O^+]\,[DS^-]/[HDS]$$

it is evident that at different hydrogen-ion concentrations different amounts of the still more surface-active species HDS are formed, especially in the surface, owing to the higher ion concentrations existing there. As the recoil method measures the adsorption of charged species, the transformation of the primary adsorbed DS^- anions into the non-ionic acid state could be followed.

In Fig. 3 adsorption isotherms for two pH values at constant ionic strength are shown. It is seen that, at higher hydrogen-ion concentration (curve A), the $[Bi^{212}]^{+++}$ adsorption maximum shifts to higher SDS molarity. This may be qualitatively explained by taking into consideration the difference in ionic activities between Na^+ and H_3O^+ resulting from the different size of their radii. Furthermore, at pH = 2, more hydrogen ions are consumed, thus reducing the ionic strength, and the $[Bi^{212}]^{+++}/[I^+]$ ratio is increased; this explains the fact that curve A is higher than curve B.

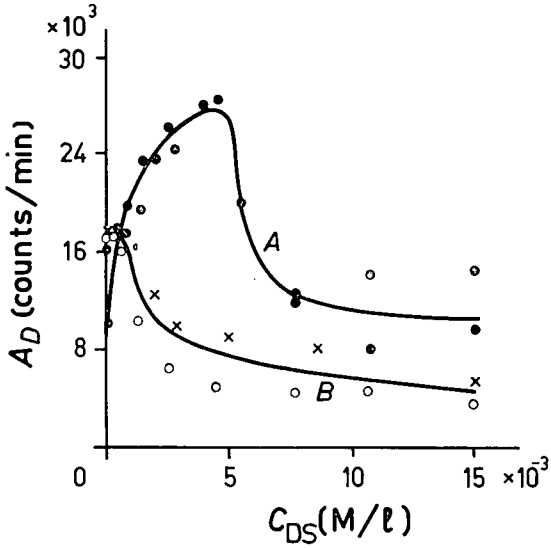

Fig. 3
The $[Bi^{212}]^{+++}$ coadsorption at two different pH values and constant ionic strength 2.5×10^{-2} mole/l.
A = pH = 2; B = pH = 3.

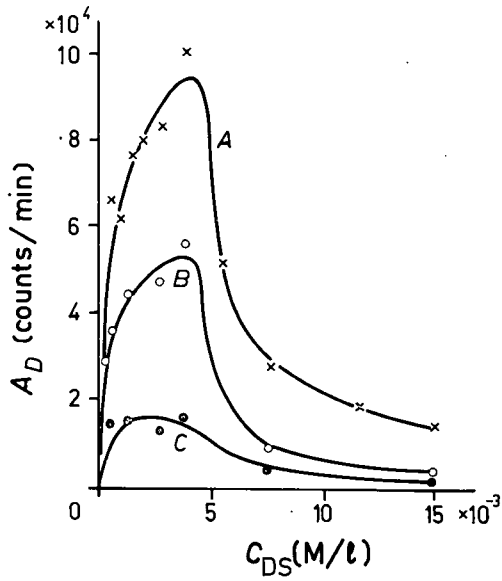

Fig. 4
$[Bi^{212}]^{+++}$ adsorption isotherms with $3Bi^{+++}/I^{+}$ ratio as parameter.
pH = 2; $\mu = 2.5 \times 10^{-2}$ mole/l;
$A = 3Bi^{+++}/I^{+} = 11.9 \times 10^{-10}$; $B = 3Bi^{+++}/I^{+} = 4.30 \times 10^{-10}$;
$C = 3Bi^{+++}/I^{+} = 1.51 \times 10^{-10}$.

The relative adsorption of the small trivalent Bi^{+++} ion in comparison with that of the monovalent ions is dependent on their ratio in the bulk. It was, therefore, of interest to investigate the influence of the Bi-ion concentration on its relative adsorption, keeping the concentration of the monovalent ions constant. Fig. 4 shows adsorption isotherms for different Bi-ion concentrations. These results will be discussed later on.

SUPPLEMENTARY MEASUREMENTS

The possible influence of the electrical collecting field on the ionic coadsorption was investigated by exerting the usual electrical field on a solution of SDS containing a small amount of Po^{210}. A brass net was used instead of the collector, and a G-M tube served as a detector for the α-particles passing through the net. No significant influence of the electrical field on the adsorption could be detected.

In all the experiments the ratio 3 $[Bi^{212}]^{+++}/2[Pb^{208}]^{++} + 2\ [Pb^{212}]^{++}$ was kept constant. In order to estimate the participation of Pb^{++} ions in the coadsorption two adsorption isotherms were measured, differing only as to the amount of $[Pb^{208}]^{++}$. The results are shown in Fig. 5.

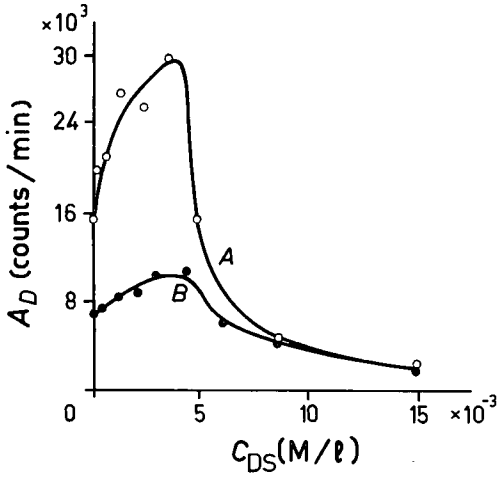

Fig. 5
$[Bi^{212}]^{+++}$ adsorption isotherms with $3Bi^{+++}/2Pb^{++}$ ratio as parameter.
pH = 2; $\mu = 2.5 \times 10^{-2}$ mole/l; $3\ [Bi^{212}]^{+++} = 1.2 \times 10^{-11}$ equivs./l;
$A = 3Bi^{+++}/2Pb^{++} = 7.5 \times 10^{-3}$; $B = 3Bi^{+++}/2Pb^{++} = 5.0 \times 10^{-4}$

While following the recoil activity of the collector over a period large enough for the Tl^{208}-activity to disappear, a small fraction of a longer-living component was detected and identified as Bi^{212} (60.5 min). This nuclide, which is the disintegration product of Pb^{212}, could leave the surface of the solution as a β-recoil only. It can be supposed that a fraction of those β-recoils which succeeded in leaving the surface reached the collector: the neutral β-recoils by a diffusion mechanism and the charged ones by the aid of the electrical field. Comprehensive results on the penetration of β-recoils through such an adsorption layer are given elsewhere [8]. Experiments concerning the application of the use of β-recoils

as well as experiments applying radiative capture recoils for surface-layer studies are under preparation.

PREFERENTIAL ION ADSORPTION

The surface excess of the dodecyl-sulphate species (DS) can be calculated with the aid of a suitably modified Gibbs adsorption equation from surface tension measurements, thus obtaining the sum:

$$\Gamma_{DS} = \Gamma_{DS^-} + \Gamma_{HDS}$$

where Γ represents the surface excess in the adsorption layer in mole/cm². An approximate value of the dissociation constant of HDS was found by a series of pH measurements ($K_a \sim 10^{-2}$ mole/l), and thus the surface concentration of DS^- was calculated (Γ_{DS^-}). As the total amount of the polyvalent radioactive ions is extremely negligible, it can be assumed that, according to the electroneutrality of the surface layer, $\Gamma_{DS^-} = \Gamma_{I^+}$. Up to moderate hydrogen-ion concentrations the approximation $\Gamma_{DS} \simeq \Gamma_{I^+}$ is justified.

From the surface concentration of the bismuth ions, which could be obtained directly by the recoil method, their surface excess could be deduced, taking into consideration the concentration of the bismuth ions in the bulk. From these results the preference factor for adsorption of the bismuth ion to the monovalent ions at the soluble ionized surface layer in comparison with their bulk concentration could be calculated:

$$f_p = (\Gamma_{Bi^{+++}}/C_{Bi^{+++}})/(\Gamma_{I^+}/C_{I^+})$$

Fig. 6 shows the Γ/C values for bismuth and monovalent ions as a function of the DS^- concentration.

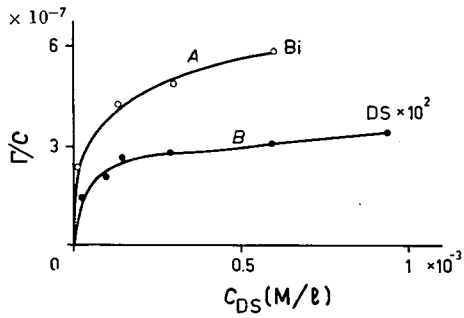

Fig. 6
The Γ/C values for bismuth and monovalent ions as a function of the DS^- concn.

When the dependence of the preference factor on the extent of ionic adsorption was investigated, it was found that f_p increases with the decrease of the ionic adsorption. This can be explained by the fact that with the decrease of the number of ionic adsorption sites, the competition between the counterions to be coadsorbed increases and the preference of coadsorption of the smaller trivalent bismuth ions becomes more pronounced. Except for the very low primary ionic-adsorption region, where f_p increases steeply with decreasing adsorption, this preference is of the order of 300.

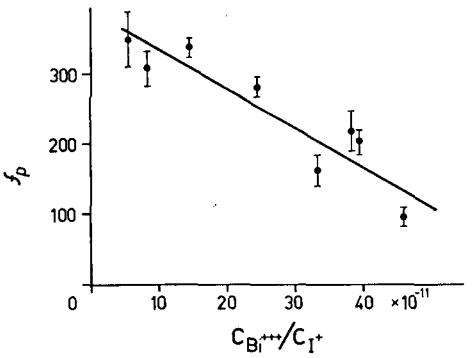

Fig. 7
Bismuth ion adsorption preference as function of the ion concn ratio ${}_BC_i{}^{+++}/C_I{}^+$. $\mu = 2.5 \times 10^{-2}$ mole/l; $\Gamma_{DS} = 3.25 \times 10^{-10}$ mole/cm².

Fig. 7 shows the influence of the ion concentration ratio $C_{Bi}{}^{+++}/{}_IC^+$ on the preference factor at constant ionic adsorption. The ratio was changed by varying the specific activity of the solution, i.e., the bismuth ion concentration.

These results agree qualitatively with those obtained by van Os [9] when discussing ion exchange between monovalent and divalent ions in a diffuse double layer at a negatively charged plane wall in equilibrium with a solution containing these ions. The calculations were based on Gouy's model of the diffuse double layer, where any specificity of the ions, except their valency, is neglected, although, in a more rigorous treatment, the size of the ions should be taken into consideration.

For studying the influence of the hydrogen-ion concentration on the formation of the non-ionic species HDS, adsorption isotherms at constant ionic strength

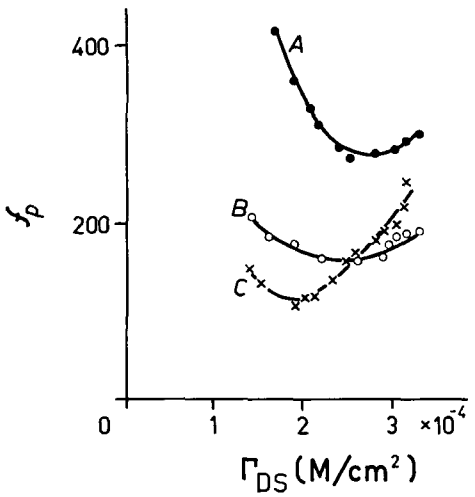

Fig. 8
Dependence of the preference factor on the primary adsorption at different pH values. $\mu = 11 \times 10^{-2}$ mole/l; A = pH = 2; B = pH = 1.5; C = pH = 1.0.

with varying pH were measured. The preference factor f_p was worked out from these results, using an approximated value for Γ_{I^+} (i.e., Γ_{DS}), which was justified at low hydrogen-ion concentrations. On the other hand, at low pH values a deviation arises, being more pronounced the lower the pH value. This was confirmed experimentally, as shown in Fig. 8. The higher the hydrogen-ion concentration, i.e., the more that non-ionic species are present in the surface layer, the lower is the preference factor.

On studying Fig. 5, which shows adsorption isotherms of $[Bi^{212}]^{+++}$ differing as to their $3Bi^{+++}/2Pb^{++}$ ratio, an approximate value for the preferential adsorption of bismuth to lead ions can be deduced. The concentration of the two

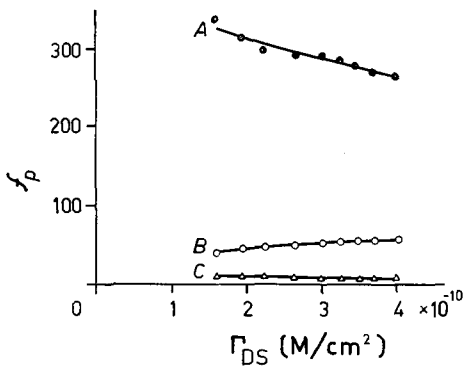

Fig. 9
Preference at ionic coadsorption.
pH = 2; $\mu = 2.5 \times 10^{-2}$ mole/l;
A = Preference of Bi^{+++} to I^+;
B = Preference of Pb^{++} to I^+;
C = Preference of Bi^{+++} to Pb^{++}.

isotopic lead ions in the solution was calculated on the basis of their genetic relations and the experimental conditions. Accordingly, the preference factor of bismuth to lead ions was found to be of the order of 6, while that of lead to the monovalent ions was about 50. The results are summarized in Fig. 9.

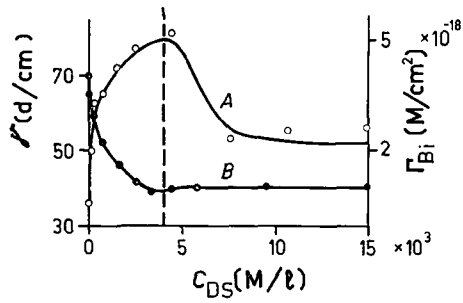

Fig. 10
Change of recoil activity (A = right ordinate) and of surface tension (B = left ordinate) with DS concentration. pH = 2; $\mu = 2.5 \times 10^{-2}$ mole/l.

MICELLE FORMATION

When comparing isotherms obtained by the α-recoil method with surface-tension/DS-concentration curves, it can be seen that the maxima of the recoil curves coincide with the critical micelle concentration, as shown in Fig. 10. Starting from the CMC, the bismuth ion adsorption decreases with increasing DS concentration, which implies that the primary ionic adsorption at the air/water interface decreases. As the surface tension remains nearly constant, it must be concluded that a fraction of the ionic surface-active species at the surface is replaced by the non-ionic HDS, and thus the micelles are built up mainly of the ionic species DS^-.

4. Conclusions

The α-recoil method has proved to be a sensitive tool for adsorption studies at ionized surface layers. The method allows an easy distinction between primary ionic and non-ionic adsorption, supplies information on adsorption conditions at the surface after the beginning of micelle formation and on micelle structure, and gives the extent of ionic exchange in the double layer as a function of the charge and radii of the ions.

A more comprehensive publication concerning surface studies by means of hot atoms will be published elsewhere.

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DISCUSSION

B. E. Gordon (United States of America), referring to Table I, expressed some surprise at the low values shown for the calculated increase in concentrate with adsorption as a function of the energy of the radiation. For C^{14} the value of 3.4% seemed too low.

In his own work he had found that when a G-M tube was immersed in the solution—i.e., if he understood correctly, in conditions similar to those described by Mr. Steiger— the increase of signal over background depended largely on the concentration of the labelled surfactant, its specific activity and its surface activity. That being so, increases of 20—50% in count rate could easily be obtained if a tightly packed monolayer was adsorbed from a dilute solution. The technique described in the paper had greater applicability, therefore, than was suggested by Table I.

N. H. Steiger replied that the figures shown in the last column of Table I were relative figures for a particular set of adsorption conditions. It was, however, clear that the shorter the range of the particles used, the more they would represent the actual layer.

THE USE OF RADIOISOTOPES IN RADIATION CHEMISTRY: THE EFFECT OF RADIATION ON TOLUENE*

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Abstract — Résumé — Аннотация — Resumen

The use of radioisotopes in radiation chemistry: the effect of radiation on toluene. The radiation chemistry of organic compounds can often be studied more effectively and in greater detail using compounds labelled with radioisotopes. Use of this approach permits observation of products not otherwise detectable and provides information about the processes by which they are formed.

The versatility of this technique is illustrated by results obtained in a study of the radiation chemistry of toluene. Toluene labelled in the methyl group with tritium (one atom per 600 mol.), was prepared and was exposed in the vapour phase to gamma-radiation (1.46 eV/mol.). The product was fractionated and the volatile fractions were injected into a gas fractometer equipped with an ionization chamber to permit simultaneous recording of radioactivity and thermal conductivity. Concentrations of tritium in the various products were determined from relative areas under peaks in the two curves.

From the concentrations of tritium in these products it can be deduced that the methane is formed exclusively from the methyl group of toluene and that the xylenes are formed by attack of methyl radicals on toluene.

Oxidation of the recovered toluene showed that transfer of tritium from the methyl group to the benzene ring had occurred to some extent during the irradiation. The benzoic acid contained one tritium atom per 140 000 molecules, corresponding to a G value of 0.3 for the "exchange" reaction. This appearance of tritium in the ring could result either from abstraction of methyl hydrogen by a tolyl radical or from reconversion of a symmetrical intermediate, such as the tropylium ion to toluene. To provide information on this point the irradiation of toluene labelled with carbon-14 is being investigated.

Emploi des radioisotopes en radiochimie: effet des rayonnements sur le toluène. On peut souvent étudier d'une manière plus efficace et plus détaillée les réactions induites par les rayonnements dans les composés organiques en utilisant des composés marqués au moyen de radioisotopes. Cette méthode permet d'observer des produits qui, autrement, ne seraient pas décelables et fournit des renseignements sur les processus de formation de ces produits.

Les possibilités d'application de cette technique sont illustrées par les résultats obtenus en étudiant les effets chimiques des rayonnements sur le toluène. On a préparé du toluène marqué au tritium (un atome pour 600 mol.) dans le groupe méthyle et on l'a exposé à des rayonnements gamma (1.46 eV/mol.) en phase vapeur. Après fractionnement du produit, les fractions volatiles ont été injectées dans un fractomètre de gaz, muni d'une chambre d'ionisation afin d'enregistrer simultanément la radioactivité et la conductivité thermique. Les concentrations du tritium dans les différents produits ont été déterminées d'après les surfaces relatives correspondant aux maximums des deux courbes.

* Work performed under the auspices of the United States Atomic Energy Commission.

D'après la concentration du tritium dans ces produits, on peut considérer que le méthane est formé exclusivement à partir du groupe méthyle du toluène et que les xylènes se forment par attaque du toluène par des radicaux méthyle.

L'oxydation du toluène récupéré a montré que pendant l'irradiation il y avait transfert d'une partie du tritium du groupe méthyle à l'anneau benzénique. L'acide benzoïque contenait un atome de tritium pour 140000 mol., ce qui correspond à une valeur de G de 0,3 pour la réaction "d'échange". La présence du tritium dans l'anneau peut être due soit à la fixation d'hydrogène du groupe méthyle par un radical tolyle, soit à la reconversion en toluène d'un produit intermédiaire symétrique, tel que l'ion tropyle. Pour obtenir des renseignements à ce sujet, on étudie actuellement l'irradiation du toluène marqué au carbone-14.

Использование радиоизотопов в радиационной химии: воздействие радиации на толуол. Исследования в радиационной химии органических сложных соединений часто могут проводиться более эффективно и более детально при помощи использования сложных соединений, меченных радиоизотопами. Этот метод дает возможность вести наблюдения над продуктами, присутствие которых не может быть обнаружено никакими другими способами, и вместе с тем он дает указания относительно самих процессов образования этих продуктов.

Многосторонность этого метода видна из результатов, полученных при изучении толуола с точки зрения радиационной химии. Был приготовлен и подвержен в газообразном состоянии облучению гамма-радиации (1,46 эв на молекулу) содержащийся в метиловой группе толуол, меченный тритием. Продукт был подвергнут дробной перегонке, и летучие фракции подавались в газовый фракционный измеритель, снабженный ионизационной камерой для одновременного замера радиоактивности и теплопроводности. Концентрации трития в различных продуктах определялись на основании соотношения площадей, охваченных пиками на двух кривых.

На основании концентраций трития в этих продуктах можно заключить, что метан образуется исключительно из метиловой группы толуола и что ксилон образуется в результате воздействия радикалов метила на толуол.

Окисление полученного толуола показало, что перенесение трития из метиловой группы в бензоловое кольцо происходит в некоторой мере в процессе облучения. Бензойная кислота содержала один атом трития на 140.000 молекул, что соответствует значению $G = 0{,}3$ для реакции „обмена". Это появление трития в кольце может являться результатом или извлечения водорода из метила радикалом толила, или же обратным превращением симметричного промежуточного соединения, как например, иона тропилия в толуол. Для выяснения этого вопроса в настоящее время производится облучение толуола, меченного углеродом-14.

Empleo de los radioisótopos en el estudio de los efectos químicos de las radiaciones: efectos de las radiaciones sobre el tolueno. Con frecuencia, las reacciones inducidas por las radiaciones en los compuestos orgánicos pueden estudiarse en forma más eficaz y detallada cuando se emplean compuestos marcados con radioisótopos. Este medio de investigación permite observar productos que de otro modo no serían detectables, y obtener datos sobre los procesos a los que se debe su formación.

Las posibilidades de aplicación de esta técnica quedan ilustradas por los resultados obtenidos en el estudio de los efectos químicos que las radiaciones ejercen sobre el tolueno. El autor sintetizó tolueno marcado con tritio en el grupo metilo (un átomo por cada 600 moléculas) y lo expuso a radiaciones gamma (1,46 eV/mol.) en fase vapor. Seguidamente fraccionó el producto e inyectó las fracciones volátiles en un fractómetro de gases, equipado con una cámara de ionización a fin de registrar simultáneamente la radiactividad y la conductividad térmica. Las concentraciones del tritio en los diversos productos se determinaron midiendo las áreas relativas correspondientes a los máximos de las dos curvas.

De las concentraciones de trotio de estos productos, puede deducirse que el metano se forma exclusivamente a partir del grupo metilo del tolueno, y que los xilenos se forman por el ataque del tolueno por radicales metilo.

La oxidación del tolueno recuperado demostró que, durante la irradiación, parte del tritio del grupo metilo se había transferido al anillo bencénico. El ácido benzoico contenía un átomo de tritio por cada 140000 moléculas, lo que corresponde a un valor de G de 0,3 para la reacción de "intercambio". La presencia del tritio en el anillo puede deberse a la fijación de hidrógeno del grupo metilo por un radical toluilo o a la reconversión en tolueno de un producto intermedio simétrico, como el ión tropilio. El autor está investigando la irradiación de tolueno marcado con carbono-14 con objeto de aclarar este punto.

1. Introduction

The radiation chemistry of toluene is a subject of considerable interest. It is of practical interest because toluene is a more readily studied analogue of materials used as moderators in nuclear reactors. Theoretical interest arises, in part, from the fact that toluene is potentially a more revealing analogue of benzene. It is rather surprising, therefore, that the radiation chemistry of toluene has received so little attention. One group of workers, BURTON *et al.* [1] has contributed most of the information available. Their investigations have been confined to the liquid phase, however, and their attention directed toward determining the yields of "polymer" and of products (H_2, CH_4, C_2) volatile at —120°C.

Further studies of the radiation chemistry of toluene have been started at Argonne National Laboratory to investigate the possible occurrence of other products, to compare irradiation of liquid and vapour, and to acquire some understanding of the reactions which lead to the various products. In particular, evidence was sought for the possible participation of the tropylium ion, $C_7H_7^+$, recently observed [2] in mass spectrometry of toluene. In this connection, toluene labelled in the methyl group with tritium was irradiated and the distribution of tritium in recovered toluene was determined. The appearance of tritium in the aromatic nucleus after the irradiation supports the view that a symmetrical intermediate is involved, but this conclusion cannot be drawn with certainty since alternative, though less likely, explanations are possible. Concentrations of tritium in other products of the radiolysis were also determined, by radioactive scanning in gas chromatographic analysis. The results lead to interesting conclusions about the processes by which the various products are formed.

2. Experimental

The tritiated toluene was prepared by reaction of tritiated water (5 mmole, 10 c/ml) with an excess of benzyl magnesium chloride in diethyl ether. Solvent and product were removed from the reaction mixture in a vacuum system. The toluene was isolated from the mixture and purified by repeated distillations through a series of traps cooled to —30°, —65° and —78°C. The concentration of tritium in the product was 48 mc/mM, equivalent to one tritium atom per 600 mol.

The chemical and radiochemical purity of the toluene was demonstrated by gas chromatography in a unit (Perkin-Elmer Corporation, Model 154) modified, by addition of an ion-chamber, to permit concurrent determination of mass and radioactivity. The ion chamber, vol. 6 cm^3, was contained within the heated

chamber of the fractometer and was coupled closely with the thermal conductivity cell. The ion current was measured, as the voltage drop across a resistance of 10^9 or 10^{11} Ω, by a vibrating-reed electrometer (Applied Physics Corporation, Model 30). Chemical and radiochemical peaks were registered simultaneously on synchronized recording potentiometers.

The irradiations were carried out at a flux of 1 to 3×10^6 r/h. in the High-Level Gamma-Irradiation Facility at Argonne National Laboratory. The gamma flux in this facility is provided by the fission products in spent reactor fuel elements; its average energy is 0.75 MeV. Chemical dosimetry, by ferrous sulphate, is used.

The cell used for irradiation of toluene vapour was a cylindrical Pyrex vessel (7.5 cm diam, 20 cm long) with a volume of 700 cm^3. Two arms were attached, one constricted for sealing after introduction of the toluene, the other containing a break seal for removal of products into a vacuum system. Before introduction of the toluene, the reaction vessel was evacuated to 10^{-5} mm and flamed. Toluene vapour was admitted to a pressure of 21 mm by expansion from a sample of the liquid maintained at 19.5°C. The vapour was condensed at —195°C and the vessel was re-evacuated before being sealed. The quantity of toluene in the vessel, calculated by gas laws, was 73.0 mg. The vessel was irradiated at 27°C for 83 h with a gamma flux of 1.1×10^6 r/hr. The energy input was determined by reference to the polymerization of acetylene at equivalent electron density in an identical reaction vessel. The 100-eV yield [3] for polymerization of acetylene was taken to be 72. Energy absorbed by toluene was calculated to be 7.0×10^{20} eV, which corresponds to 1.46 eV absorbed per molecule.

After the irradiation, the vessel was attached to a vacuum system and cooled to 0°C. The break-seal was opened and the products volatile at 0° were removed and separated according to volatility. Three fractions were collected: (1) volatile at —195°C; (2) volatile at —140°C, condensable at —195°C; (3) volatile at 0°C, condensable at —140°C. The third fraction (largely toluene) was distilled into a tared tube and weighed to determine loss of toluene during the irradiation. The toluene recovered weighed 67.6 mg. Non-volatile products, recovered by rinsing the reaction vessel with benzene, weighed 4.6 mg.

The volatile fractions were analysed by gas chromatography in the instrument described above. Fractions (1) and (2) were examined on a 2-m column of silica gel at temperatures of 34°C and 100°C, respectively. For analysis of Fraction (3) a 2-m column coated with silicone oil and maintained at 100°C was used. Toluene, the bulk of Fraction (3), was recovered from the effluent gas by condensation in a trap cooled to —80°C. A 13-fold dilution was made gravimetrically.

Components of the fractions were identified by comparison of their retention volumes with those of known compounds under the same conditions. The quantity of each product was determined from the amount of known compound required to reproduce the observed thermal-conductivity response. The radioactivity of each product was determined from the area under its peak in ion current, using a calibration factor established by the response of compounds with known tritium content.

For the liquid-phase irradiation of toluene, a small break-seal tube, 9 mm diam., vol. 2 cm^3, was used. Toluene, 101.2 mg, was introduced by distillation and the vessel was evacuated to 10^{-5} mm before being sealed. The toluene was irradiated at 27°C for 32 h with a gamma-flux of 2.9×10^6 r/hr. The energy input

was 5.9×10^{20} eV, or 0.89 eV/mol. After the irradiation, toluene was separated from the non-volatile products by distillation at 0°C.

Toluene samples recovered from the liquid-phase and vapour-phase irradiations were diluted gravimetrically with a ten-fold quantity of reagent-grade toluene. Similar dilutions were made of tritiated toluene which had been sampled in the same way and at the same time as the irradiated samples. An aliquot of each dilution was oxidized with alkaline permanganate and the samples of benzoic acid produced were recrystallized to constant activity from water and from hexane. The benzoic acid samples corresponding to the vapour-phase irradiation were converted to 3.5-dinitrobenzoic acid by treatment with a mixture of sulphuric and nitric acids. Another aliquot of the dilutions corresponding to the vapour-phase irradiation was treated with fuming nitric acid at —30°C and the reaction products were oxidized with alkaline permanganate. Pure *p*-nitrobenzoic acid was obtained by repeated recrystallization from aqueous alcohol.

Tritium analyses of samples other than those processed by gas chromatography were performed by ion-current measurements [4] on gas samples prepared by the zinc fusion technique [5].

3. Results and discussion

Products observed in the vapour-phase irradiation of tritiated toluene are listed in Table I. Also presented in this table are their yields, tritium contents and relative specific activities (referred to parent toluene). Of the products listed, hydrogen, methane, ethylene, acetylene and polymer have been observed in irradiation of liquid toluene. Although benzene and the xylenes had not previously been observed in the radiolysis of toluene, their occurrence had been predicted [6] from their formation as tritiated products in the exposure of toluene to tritium gas. Their appearance here supports the view [7] that identification of radiolysis products can be facilitated by examination of labelled by-products formed in the presence of tritium gas.

TABLE I

YIELD AND RADIOACTIVITY OF PRODUCTS FROM TOLUENE-7-*t* BY IRRADIATION IN THE VAPOUR PHASE*

Product	Yield, (μ mole)	*G* value	Tritium content, (μ c)	Relative specific activity, (toluene = 1)
Hydrogen	3.7	0.32	36	0.20
Methane	1.25	.11	56	0.94
Ethane	0.40	.035	20	1.04
Ethylene	0.37	.032	5.2	0.29
Acetylene	5.4	.46	39	0.15
Benzene	1.16	.10	8.3	0.15
Ethylbenzene, *m*, *p*-Xylene	0.63	.054	62	2.0
o-Xylene	0.11	.009	11	2.1
"Polymer"	> 50**	> 4.3**	2400	1.0

* Toluene-7-*t*, 73 mg, 48 mc/mmole, irradiated in 700-cm³ vessel at 27°C to 7.0×10^{20} eV with gamma-radiation of 0.75 MeV average energy.

** Possibility of incomplete rinse from reaction vessel and of loss on evaporation of solvent. On basis of recovered toluene, G (— M) = 5.0.

The determination of yields was not the primary aim of this investigation; a more complete study of yields in the liquid and vapour state will be reported later. In passing, however, it might be noted that decomposition of toluene, particularly to C_2, is greater than in the liquid state, where G values observed [1d] in irradiation with 1.5 MeV electrons are: H_2, 0.13; CH_4, 0.0077; C_2, 0.0043; polymer, 0.92. The effect is similar to that reported [8] for irradiation of benzene in the liquid and vapour states.

Despite the fact, *v.i.*, that 99.98% of the tritium in the toluene was initially contained in the methyl group, all of the products contain substantial concentrations of tritium. The relative specific activity of each product, in Table I, indicates the average number of tritium atoms/mol. that have been derived from the methyl group of the toluene. For products formed without rupture of any of the methyl hydrogen bonds, the relative specific activity is simply the number of methyl groups per molecule that have been derived intact from toluene.

The value for methane, 0.94, thus indicates that this product is formed predominantly, if not exclusively, from the methyl group of toluene.

Similarly, the value of 2.0 for ethylbenzene and the xylenes is a clear indication that the second methyl group in these molecules is transferred intact from a toluene molecule, most probably by combination of methyl radicals with benzyl or tolyl radicals. The value of unity for ethane, on the other hand, indicates that a combination of methyl radicals cannot, as might have been expected, be the sole source. The appearance of tritium in acetylene indicates that it is formed, at least in part, from the methyl group as such, or from an intermediate possessing some symmetry. Because hydrogen-transfer reactions are involved in their formation, no definite conclusions concerning the precursors of the other products can be drawn from these data alone. When rupture of a methyl hydrogen bond occurs, statistical factors and isotope effects come into play, and the relative specific activity of the resulting product bears no simple relationship to the number of hydrogen atoms lost or gained.

Some indication that a symmetrical intermediate may occur in radiolysis of toluene was obtained by investigating the distribution of tritium within the toluene molecule before and after irradiation. Activities of benzoic acid and two nitrated benzoic acids prepared from toluene irradiated in the vapour phase and from a control sample are shown in Table II. Also shown are the activities of benzoic acid prepared from toluene, irradiated in the liquid phase, and from a corresponding control sample.

It is evident from the data in Table II that 99.98% of the tritium in the toluene samples was initially in the methyl group, and it is also clear that some transfer of tritium to the aromatic nucleus occurred during the irradiations. The amount transferred in the vapour phase, during irradiation to 1.46 eV/mol., was 0.41% of that in the methyl group. Transfer of tritium in the irradiation of liquid toluene amounted to 0.056% of that in the methyl group for an energy input of 0.89 eV/mol. Values of G_T, the number of tritium atoms transferred per 100 eV absorbed, are 0.28 and 0.063 for the vapour and liquid phases, respectively. From the data in Table II it can also be calculated that transfer of tritium to an ortho, meta, or para position during irradiation in the vapour phase occurs in the ratio 1:0.77:0.70.

Although the absence of tritium from the aromatic nucleus would have provided conclusive evidence against the hypothesis that a symmetrical intermediate reverts to toluene, the presence of tritium does not provide conclusive evidence for it. Conceivably, the effect might also be accounted for by reaction of a tolyl

TABLE II

TRITIUM CONTENT OF DERIVATIVES FROM IRRADIATED AND CONTROL SAMPLES OF TRITIATED TOLUENE [a]

Derivative	Tritium content, (μc/mM)	
	Irradiated (a)	Control
Vapour-phase irradiation (c)		
Benzoic acid	210	11.0
4-Nitrobenzoic acid	175	9.1
3,5-Dinitrobenzoic acid	135	7.8
Liquid-phase irradiation (d)		
Benzoic acid	39.3	12.4

(a) Activity of toluene was 48000 μc/mM.
(b) At 27°C with gamma-radiation of 0.75 MeV.
(c) Energy input, 1.46 eV/mol.
(d) Energy input, 0.89 eV/mol.

radical with a tritium atom attached to, or already separated from, the methyl group of a toluene molecule. It is rather unlikely, however, that such reactions would lead to a distribution as unselective as that observed. Further, the magnitude of the transfer is greater than might be expected if such reactions were the sole source of the effect. Since the number of tolyl radicals acquiring a hydrogen atom might easily be an order of magnitude greater than those acquiring a tritium atom, an improbably high yield of tolyl radicals would have to be postulated.

The irradiation of toluene labelled in the methyl group with carbon-14 is being investigated to provide more conclusive evidence for the existence of a symmetrical intermediate. It is hoped that this study will also lead to additional conclusions regarding the source of the various products.

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DISCUSSION

A. Voigt (United States of America) referred to some similar experiments which he and his colleagues had been carrying out in analysing isobutane-1-C^{14} and isobutane-2-C^{14} which had been subjected to Co^{60} gamma-radiation in the gas and liquid phases.

In general the results had been as expected. For example, no $C^{14}H_4$ was obtained when isobutane-2-C^{14} was irradiated and the activity yield of $C^{14}H_4$ from isobutane-1-C^{14} was one third the yield of methane, as calculated on the basis of the thermal conductivity measurements. That was what might be expected, seeing that only one of the three methyl groups in isobutane was active.

Similarly, the yields of 2 and 3 carbon compounds had been as expected. An interesting phenomenon was that neopentane (tetra-methyl methane) was produced in larger quantity than isopentane (2-methyl butane) even though in attack by a methyl group an isobutane molecule had many more positions from which the isopentane might be expected. The rearrangement of isobutyl radicals to tertiary butyl radicals was a logical explanation.

D. S. Urch (United Kingdom) asked the speaker what was the relevance of the observed ring-tritium distribution in irradiated toluene ($o:m:p = 1.0:0.8:0.7$) to the rearrangement mechanism.

K. E. Wilzbach replied that if tritium only appeared in the aromatic nucleus *via* a symmetrical intermediate, one would expect the same concentration at ortho, meta and para positions. The different G values for transfer of the isotope which had been observed for tritium, and C^{14}-labelled toluene indicated, however, that there must be an additional mechanism for the transfer of tritium to the ring. In his view, it was that second process which accounted for the non-statistical distribution observed.

ÉTUDE DE LA RADIOLYSE DU PENTANE ET DU CYCLOPENTANE AU MOYEN D'IODE RADIOACTIF

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Abstract — Résumé — Аннотация — Resumen

Study of pentane and cyclopentane radiolysis with the aid of radioactive iodine. Irradiation of hydrocarbons by ionizing radiation such as Co^{60}gamma-rays produces, *inter alia*, free radicals. Analysis of these radicals may lead to at least a partial explanation of the phenomena occurring.

For analysis, the "isotopic dilution" method is used: the iodine used for taking up the radicals is labelled with iodine-131, resulting in a whole series of labelled iodides when the reaction is completed. Separation is affected by means of distillation on a microcolumn after inactive carriers have been added and the mineral iodine has been extracted. The activity of each fraction is measured directly it leaves the column. A control is used to obtain absolute G values from the counting. Precautions are taken to prevent isotopic exchange during separation.

This method has been applied to cyclopentane and *n*-pentane and has yielded a detailed radiolysis spectrum.

Etude de la radiolyse du pentane et du cyclopentane à l'aide d'iode radioactif. Les hydrocarbures irradiés par des rayonnements ionisants tels que les γ du cobalt-60 produisent entre autres entités des radicaux libres, dont l'analyse peut amener à découvrir une explication au moins partielle des phénomènes.

Pour effectuer cette analyse, on utilise la technique de la «dilution isotopique»: l'iode servant de capteur est marqué par de l'iode-131, ce qui a pour résultat de donner toute une série d'iodures marqués en fin de réaction. La séparation se fait par distillation sur une microcolonne, après addition d'entraîneurs inactifs et extraction de l'iode minéral. L'activité de chaque fraction est mesurée directement à la sortie de la colonne. Un témoin permet l'obtention de valeurs absolues de G à partir des comptages. Des précautions sont prises pour éviter l'échange isotopique en cours de séparation.

Appliquée au cyclopentane et au *n*-pentane, cette méthode a permis d'obtenir un spectre détaillé de radiolyse.

Исследование радиолиза пентана и циклопентана с помощью радиоактивного йода. Углеводороды, облученные ионизирующими лучами, такими, как гамма-лучи кобальта-60, среди других веществ дают свободные радикалы. Анализ этих радикалов может привести к частичному объяснению явлений.

Чтобы осуществить этот анализ, применяют метод „изотопного разбавления": йод, служащий уловителем, метят йодом-131, что приводит к тому, что в конце реакции получается целая серия меченых йодидов. Разделение осуществляется перегонкой на микроколонном аппарате после добавления неактивных носителей и извлечения свободного йода. Активность каждой фракции измеряется прямо после выхода из колонки. Знак дает возможность получить абсолютные значения G от начала счета. Были приняты меры предосторожности, чтобы избежать изотопного обмена во время разделения.

Этот метод применялся к циклопентану и к n-пентану и позволил получить подробный спектр радиолиза.

Estudio de la radiólisis del pentano y del ciclopentano con ayuda de yodo radiactivo. La exposición de los hidrocarburos a la acción de radiaciones ionizantes tales como los rayos gamma del ^{60}Co da lugar a la formación de radicales libres. Es posible que el análisis de estos radicales permite explicar, por lo menos parcialmente, los fenómenos observados.

El autor efectúa el análisis por «dilución isotópica»: el yodo empleado como receptor se marca con yodo-131, por lo que al final de la reacción se obtiene toda una serie de yoduros marcados. Lleva a cabo la separación por destilación en una microcolumna después de haber añadido portadores inactivos y extraído el yodo inorgánico. La actividad de cada fracción se mide directamente a la salida de la columna. Los valores absolutos del coeficiente G se determinan por recuento de la actividad de una muestra testigo. El autor adopta las precauciones necesarias para evitar el intercambio isotópico durante la separación.

El método se aplicó al ciclopentano y al n-pentano, habiéndose obtenido un espectro de radiólisis detallado.

Généralités

L'action des rayonnements ionisants sur les hydrocarbures conduit, par l'intermédiaire d'états ionisés ou excités, à une rupture des molécules. La scission, qui peut s'effectuer de plusieurs façons, produit des molécules stables ou des radicaux libres qui se stabilisent par réaction sur le substrat ou recombinaison [1].

Pour élucider le mécanisme de la radiolyse, il est intéressant de pouvoir fixer les radicaux sous une forme facilement analysable avant qu'ils n'aient réagi sur le substrat: ce résultat est obtenu grâce aux techniques d'interception.

Suivant la méthode mise au point par Williams et Hamill [2], nous avons employé comme intercepteur de l'iode, marqué par son isotope 131, qui capte les radicaux par les réactions

$$\begin{cases} R. + I_2 \rightarrow RI + I. \\ R. + I. \rightarrow RI \end{cases}$$

Ces réactions transforment chaque radical en l'iodure radioactif correspondant.

Pour ne pas trop perturber le milieu, l'intercepteur doit se trouver en faible concentration; mais au-dessous d'environ $2 \cdot 10^{-4}$ $M(I_2)$ tous les radicaux ne sont plus captés, ce qui limite la dose totale que peut subir la solution. Par ailleurs, l'emploi d'une faible dose totale rend négligeable les actions secondaires du rayonnement sur des produits de radiolyse déjà formés et permet d'éviter une perturbation du mécanisme primaire par ces produits. Il est aussi souhaitable d'irradier sous faibles intensités: on permet ainsi aux radicaux formés de diffuser, ce qui les empêche d'atteindre localement de fortes concentrations, qui favoriseraient les recombinaisons aux dépens de l'interception.

En contrepartie, l'emploi de faibles doses totales complique le problème analytique: il faut doser chaque iodure dans un mélange complexe où il ne figure qu'à faible concentration. L'utilisation d'iode radioactif permet de mener à bien cette analyse. Sachant à priori, grâce à des considérations structurales, quels sont les iodures qui peuvent se former lorsqu'on irradie un hydrocarbure donné, on peut ajouter, après radiolyse, tous les entraîneurs inactifs correspondants. Il suffit alors de fractionner le mélange et de mesurer l'activité de chaque fraction pour pouvoir déterminer quels sont les iodures effectivement formés et quels en sont les rendements. Si l'on néglige les perturbations que peuvent provoquer les échanges isotopiques entre les iodures, la sensibilité de cette méthode

d'analyse est pratiquement illimitée: si faible que soit son rendement, un radical sera décelé et dosé pouvu que l'activité mise en œuvre au début de la radiolyse soit suffisante.

Nous avons choisi d'étudier la radiolyse du cyclopentane et du n-pentane liquides. Ces deux hydrocarbures ont un nombre d'atomes de carbone suffisamment élevé pour que le mécanisme de leur radiolyse soit susceptible d'être généralisé à d'autres alcanes ou cyclanes. Ils sont cependant suffisamment légers pour que, pratiquement, tous les iodures pouvant se former par radiolyse en présence d'iode soient assez facilement séparables par distillation. Le cyclopentane possède en outre l'avantage de ne présenter dans sa molécule que deux types distincts de liaisons (C–C cyclaniques et C–H secondaires), ce qui limite le nombre des ruptures à envisager. Le cas du n-pentane est un peu plus complexe, puisqu'on y trouve des liaisons C–C 1–2 et 2–3 et des liaisons C–H primaires et secondaires.

La littérature nous apprend que la radiolyse procède en particulier par rupture des liaisons C–H, dans le cas des alcanes et des cyclanes.

$$RH \rightsquigarrow R. + H.$$

L'atome d'hydrogène, étant l'analogue d'un radical, devrait être capté par l'iode et donner de l'acide iodhydrique. Comme en général il est impossible de repérer, dans les produits de radiolyse, une grande quantité de cet acide, on se heurte à des difficultés d'interprétation. Dans un travail récent, MESHITSUKA et BURTON [3] ont démontré qu'en fait le rendement radiochimique d'acide iodhydrique est élevé, mais que ce composé disparaît, pendant ou après la radiolyse, probablement par addition sur les alcènes engendrés sous rayonnement par les processus suivants:

$$R - CH_2 - CH_2 - R' \rightsquigarrow R - CH = CH - R' + H_2$$

ou

$$R - CH_2 - CH_2 - R' \rightsquigarrow R - CH_2 - CH - R' + H.$$

$$R - CH_2 - CH - R' + H. \rightarrow R - CH = CH - R' + H_2$$

Pour confirmer cette hypothèse, nous avons essayé de fixer l'acide iodhydrique au fur et à mesure de sa formation. Dans ce but, quelques essais de radiolyse ont été effectués en présence d'un «capteur» d'acide iodhydrique. Il s'agissait soit de carbonate de calcium solide subissant la réaction

$$CO_3Ca + 2IH \rightarrow CaI_2 + CO_2 + H_2O$$

soit d'un alcène convenablement choisi, c'est-à-dire additionnant l'acide iodhydrique pour donner un iodure n'existant pas ou existant peu, dans les produits normaux de radiolyse. Nous espérions, grâce à cette compétition entre un «capteur» volontairement ajouté et les alcènes d'origine radiochimiques vis-à-vis de l'addition de IH, repérer les iodures dont la formation, en partie ou en totalité, relève de la réaction

$$R - CH = CH - R' + IH \rightarrow R - CHI - CH_2 - R'$$

car les rendement de ces iodures doivent être abaissés par la présence du «capteur».

Enfin, à côté de l'étude, au moyen d'iode radioactif, de la partie radicalaire de la radiolyse du n-pentane et du cyclopentane, nous avons cherché à déterminer certains rendements en produits moléculaires. Mais cette partie du travail ne relève pas de l'emploi des isotopes et ne sera pas discutée ici.

Partie expérimentale

Produits utilisés

Le n-pentane et le cyclopentane sont repurifiés par lavages répétés à l'acide sulfurique concentré et à la soude diluée. Ils sont distillés sur du pentoxyde de phosphore et conservés sur sodium ou sur mercure. Leur purification est contrôlée par les spectres ultraviolet.

L'iode marqué est préparé, au moment de l'emploi, par acidification d'une solution d'iodure et d'iodate de sodium purs, de titre connu, additionnée du volume désiré de solution d'iodure de sodium ^{131}I Na.

Les iodures inactifs entraîneurs sont utilisés sans purification ultérieure, mais conservés sur cuivre à l'abri de la lumière. L'iodocyclopentane n'étant pas un produit commercial, nous l'avons préparé à partir de cyclopentène, par reflux en présence d'un mélange d'iodure de potassium, d'acide phosphorique pur et de pentoxyde de phosphore.

Des carbures éthyléniques ont été utilisés comme capteur d'acide iodhydrique.

Préparation des solutions à irradier

L'iode marqué précipité de la solution aqueuse est extrait dans l'hydrocarbure voulu. Les volumes mis en œuvre sont tels qu'on atteint une solution organique $5{,}2 \cdot 10^{-3}$ M (I_2) dont l'activité est de l'ordre de 0,2 mc/cm^3.

Chaque essai à irradier est formé de 5 cm^3 de solution organique d'iode, distillés sous vide en présence de pentoxyde de phosphore dans une ampoule de «Pyrex». Après dégazage du liquide, l'ampoule est scellée sous vide. Un essai témoin, qui ne sera pas irradié, est préparé de façon identique.

Dans les expériences de fixation de l'acide iodhydrique, nous avons utilisé soit 10 mg environ de carbonate de calcium ajoutés dans les ampoules avant distillation sous vide de la solution organique, soit des concentrations de l'ordre de $5 \cdot 10^{-3}$ M d'alcènes dans l'hydrocarbure de départ, réalisées avant extraction de l'iode marqué (cyclopentène dans le n-pentane, n-pentène dans le cyclopentane).

Irradiations

La source de rayonnement consiste en environ 12 c de cobalt-60. Les irradiations sont effectuées à des intensités de 200 à 250 r/min (dosimétries au sulfate ferreux G $[Fe^{3+}]=15{,}5$) jusqu'à des doses totales de $2 \cdot 10^6$ à $2{,}5 \cdot 10^6$ r; ainsi, la concentration finale d'iode est de l'ordre de $5 \cdot 10^{-4}$ M et l'interception reste efficace. Lorsque du carbonate de calcium est utilisé comme capteur d'acide iodhydrique, sa décantation est évitée par une rotation de l'ampoule pendant l'irradiation.

Analyse

Le liquide de l'ampoule témoin est extrait au thiosulfate concentré: l'activité restant en phase organique renseigne sur le pourcentage d'autoradiolyse, et la somme des activités des deux phases permet d'établir la relation concentration-activité nécessaire au calcul absolu des rendements.

De la solution irradiée on extrait l'acide iodhydrique libre (ou l'iodure de calcium si l'on a opéré en présence de carbonate) par de l'eau distillée. La phase organique restante est additionnée à un mélange de 5 cm^3 de chacun des iodures suivants: iodométhane, iodoéthane, 1- et 2-iodopropanes, 1- et 2-iodobutanes, 1- et 2-iodopentanes, iodocyclopentane (sauf dans le cas du n-pentane pur), diiodométhane, 1,5-diiodopentane. L'iode libre est alors extrait au thiosulfate concentré, et le mélange d'iodures est distillé en présence de pentoxyde de phosphore.

Distillation

Le fractionnement du mélange d'iodures est délicat: il faut éviter les décompositions et les échanges isotopiques possibles, tout en séparant avec précision des fractions de faible volume.

Pour rendre négligeable les décompositions et les échanges, il faut distiller à l'abri de la lumière, ajuster la pression pour ne jamais atteindre des températures trop élevées [4, 5, 6] et éviter le contact des vapeurs d'iodure avec des pièces métalliques [7].

Pour séparer de faibles volumes, la colonne de distillation doit posséder une faible rétention tout en conservant une efficacité élevée. Nous nous sommes donc orientés vers l'emploi d'une colonne à bande tournante.

Partant des travaux de ROUSSEAU [8] et de NERHEIM [9], nous avons mis au point un appareil répondant aux caractéristiques imposées. La colonne de séparation est constituée par un tube de verre de 550 mm de long sur 5,5 mm de diamètre, dans lequel tourne jointivement un cylindre de téflon portant un pas de 400 du type «vis à bois». Le sens de rotation correspond au dévissage du pas. La colonne possède une enveloppe vidée et argentée, dont l'extérieur peut être réchauffé par un four. Un système de pompage muni d'un régulateur et d'un manomètre permet d'ajuster la pression. La forme de l'élément tournant, déterminée après de nombreux essais, donne à cette colonne une grande efficacité: environ 40 plateaux théoriques à reflux total, sous pression atmosphérique, pour une vitesse de rotation de 3500 tr/min. La colonne conserve cependant la faible rétention caractéristique des appareils de distillation dynamiques.

Grâce à cette installation, la séparation du mélange d'iodures est effectuée dans de bonnes conditions: deux fractions dont les points d'ébullition sont distants de 6°C peuvent, sous pression atmosphérique, être séparées sur une charge totale de 10 cm^3.

Il existe cependant une possibilité de légers échanges isotopiques ou d'entraînements physiques susceptibles de perturber les fractions de faible activité, si bien que les rendements en iodure inférieurs à 1% du total seront douteux. D'autre part les décompositions ne peuvent être évitées s'il existe, dans les produits de radiolyse, des iodures instables (diiodures vicinaux, iodures allyliques ou de type tertiobutyle).

Les conditions de distillation employées lors de la séparation du mélange d'entraîneurs sont les suivantes:

Vitesse de rotation de l'élément:	3000 tr/min
Prélèvement:	env. 3 cm³/h
Reflux:	de l'ordre de 40/1
Pressions:	atmosphérique jusqu'au 2-iodopropane
	≃ 170 mm Hg jusqu'au 1-iodobutane
	≃ 50 mm Hg jusqu'au diiodométhane.

Il faut cependant noter que la séparation par distillation est lente et fastidieuse. Elle est d'autre part limitée: on ne peut fractionner deux iodures dont les points d'ébullition diffèrent de ≃ 4°C. Il serait certainement avantageux de la remplacer par la chromatographie en phase vapeur, méthode plus rapide et ayant un pouvoir de séparation plus élevé; cela permettrait en outre l'utilisation de volume d'entraîneurs très faibles ou même nuls, avantage non négligeable car ces produits sont rares et chers. Des problèmes analogues au nôtre ont d'ailleurs été étudiés par chromatographie en phase vapeur [10, 11].

Mesures d'activité

Nous avons employé une cellule de mesure formée par une spirale capillaire de «Pyrex», entourant un compteur Geiger-Müller à cathode de plomb. Ce système permet des mesures d'activité directement à l'état liquide sur 0,5 cm³ d'une fraction. Seuls les γ émis par l'iode-131 sont comptés, les β étant absorbés dans les parois de la cellule (épaisseur 2 mm).

Pendant la distillation du mélange d'iodures, la cellule de mesure d'activité est branchée directement à la sortie de la colonne et fonctionne en semi-continu, si bien qu'on peut tracer la courbe d'activité en fonction du volume distillé de 0,5 cm³ en 0,5 cm³.

Tous les comptages étant effectués dans la même celulle, il suffit, pour obtenir des valeurs comparables, de les ramener au même volume de base et à la même origine de temps, puis de les corriger du mouvement propre et de la perte par coïncidence.

Calcul des rendements

Les valeurs de la dose reçue et de l'activité des diverses fractions, et la connaissance, grâce au témoin, de la relation concentration/activité et du pourcentage d'autoradiolyse, permettent de calculer les valeurs absolues des rendements radiochimiques radicalaires. Nous exprimerons ces rendements sous la forme habituelle:

G = nombre de molécules formées pour 100 eV absorbés.

Précision

L'erreur sur les valeurs relatives des divers rendements ne peut dépasser $\pm$ 5% que dans les cas défavorables: faibles rendements, volatilité élevée, mauvaise séparation par distillation.

Les valeurs absolues des rendements, qui supportent en outre l'erreur sur la dose et sur la concentration d'iode au départ, sont moins précises: l'erreur peut atteindre 10 à 15%. Le but de notre travail étant d'établir un spectre des produits radicalaires de radiolyse aussi complet que possible, nous avons souvent dû sacrifier la précision à la possibilité de mesurer, sur un même essai, le plus grand nombre possible de rendements.

Résultats

La figure 1 présente un exemple typique des courbes de distillation obtenues. Elle se rapporte au cas du n-pentane. On y voit en 1 la variation des points d'ébullition en fonction du volume distillé, en 2 la variation correspondante de l'activité.

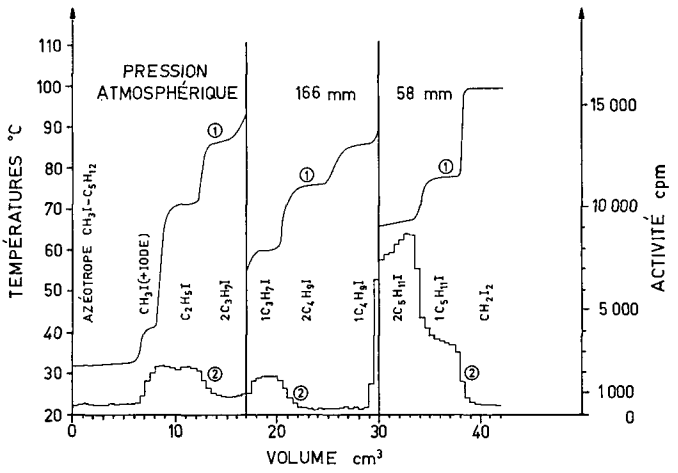

Fig. 1
Radiolyse du n-pentane liquide en présence d'iode-131 — Distillation des iodures formés.
1. Courbes de la température d'ébullition en fonction du volume distillé. — 2. Courbe de l'activité en fonction du volume distillé.

Cas du cyclopentane

Le tableau I donne les rendements mesurés sur le cyclopentane liquide en présence d'iode, avec ou sans capteur d'acide iodhydrique. Sans vouloir interpréter ici ces résultats, nous allons cependant en dégager quelques aspects importants.

a) Le rendement de disparition d'iode G (—I) est de l'ordre de 4,9. En étudiant spectroscopiquement la disparition d'iode (non radioactif) au cours de la radiolyse du cyclopentane, nous avons obtenu G (—I) = 5,1 ; pour des cas analogues comme celui du cyclohexane, la littérature fournit des valeurs encore plus élevées [12, 13].

Nous pensons pouvoir expliquer cela par la fixation réversible de l'iode sur les doubles liaisons formées lors de la radiolyse, qui conduit à des diiodures vicinaux. Ces produits sont peu stables et, suivant les conditions de mesure, on déplace plus ou moins leur équilibre de dégradation. La valeur de G (—I) peut donc varier dans d'assez larges limites.

Les diiodures vicinaux ne sont d'ailleurs pas entièrement détruits et, au cours de la distillation, dès que la température du bouilleur atteint 60 à 70°C, la décomposition s'achève et l'iode formé est entraîné par la tête de la fraction idioéthane. Il en résulte un pic parasite d'activité, de hauteur variable, qui peut perturber un

TABLEAU I

RADIOLYSE DU CYCLOPENTANE ET DU n-PENTANE LIQUIDES EN PRÉSENCE D'IODE-131
(Rendements absolus et relatifs)

Corps irradié →	Cyclopentane + iode		Cyclopentane + iode + # 10 mg CO_3Ca		Cyclopentane + iode + # $5 \cdot 10^{-3}$ n-pentène		n-Pentane + iode		n-Pentane + iode + # $5 \cdot 10^{-3}$ M cyclopentène	
Produits analysés (1) ↓	*G*	% du total des iodures	*G*	% du total des iodures	*G*	% du total des iodures	*G*	% du total des iodures	*G*	% du total des iodures
Iode disparu (en atomes d'iode)	4,92		4,85		4,92		5,10		5,75	
Iodométhane(2)	0,21	4,75	0,24	5,55	0,25	5,4	0,46	9,5	0,52	10,75
Iodoéthane	0,065	1,45	0,075	1,75	0,11	2,35	0,48	9,8	0,48	9,65
2-iodopropane	0,05	1,2	0,045	1,0	0,05	1,15	0,16	3,4	0,065	1,3
1-iodopropane	0,04	0,95	0,055	1,25	0,06	1,25	0,40	8,25	0,40	8,3
Total iodopropanes	*0,09*	*2,15*	*0,10*	*2,25*	*0,16*	*2,35*	*0,56*	*11,65*	*0,465*	*9,6*
2-iodobutane	0,01	0,25	0,02	0,5	0,02	0,5	0,04	0,8	0,03	0,6
1-iodobutane	0,025	0,55	0,035	0,75	0,035	0,7	0,06	1,25	0,065	1,35
Total iodobutanes	*0,035*	*0,8*	*0,055*	*1,25*	*0,055*	*1,2*	*0,10*	*2,05*	*0,095*	*1,95*
2-iodopentane (et 3-)	0,10	2,3	0,055	1,2	0,06	1,3	2,10	43	1,78	36,8
1-iodopentane	0,22	5,15	0,27	6,25	0,24	5,1	0,83	17	0,48	9,95
Total iodopentanes(3)	*0,32*	*7,45*	*0,325*	*7,45*	*0,30*	*6,4*	*2,93*	*60*	*2,26*	*46,75*
Iodocyclopentane	2,86	66,0	2,31	53,4	2,62	56,4	—	—	—	—
Diiodométhane	0,075	1,75	0,13	2,9	0,11	2,35	0,045	0,9	0,06	1,2
Résidu	0,25	5,75	0,20	4,7	0,23	4,9	0,03	0,6	0,05	1,0
Acide iodhydrique (sous toutes ses formes)	0,11	2,5	0,56	13,05	0,53	11,3	0,20	4,0	0,82	17,0
Total iodures(4)	*4,34*	—	*4,33*	—	*4,65*	—	*4,87*	—	*4,84*	—
Perte	0,58	—	0,52	—	0,27	—	0,23	—	0,91	—

(1) Chaque fraction comprend l'iodure cité et ceux dont le point d'ébullition est voisin ($\Delta E < 4°C$).
(2) Rendement calculé à partir des caractéristiques de l'azéotrope : 63,5 % en moles d'iodure.
(3) [Et iodopentènes ?] dans le cas du n-pentane.
(4) Dans cette somme, les rendements de diiodures comptent double.

peu la valeur du rendement d'iodure d'éthyle. Cette activité n'est pas comptée dans la somme des rendements radicalaires G (RI), ce qui explique que cette dernière valeur soit notablement inférieure à G (—I).

b) L'iodocyclopentane est le produit majeur de la radiolyse. Il peut se former par deux mécanismes principaux:

$$\text{Cyclo } C_5H_{10} \begin{cases} \sim\sim\sim\rightarrow \text{cyclo } C_5H_9. + H. \\ \sim\sim\sim\rightarrow \text{cyclo } C_5H_8 + H_2 \end{cases}$$

$$\text{Cyclo } C_5H_9. + \underset{\text{(ou I)}}{I_2} \rightarrow \text{cyclo } C_5H_9I + I.$$

$$\text{Cyclo } C_5H_8 + IH \rightarrow \text{cyclo } C_5H_9I \text{ (inhibée lorsqu'on fixe IH).}$$

La radiolyse s'attaque donc principalement aux liaisons C—H et on peut comparer la radiorésistance du cycle en C_5 à celle du cycle en C_6 [14, 15].

c) Le cycle peut cependant s'ouvrir, comme le montre la présence d'un rendement non négligeable d'iodopentanes linéaires. Cette ouverture se fait certainement suivant un mécanisme complexe, car, partant d'une molécule de formule C_5H_{10}, on arrive à un radical C_5H_{11}.

Comme la formation de 2- et 3-iodopentane semble tendre vers 0 lorsqu'on fixe IH sur un capteur, on peut l'attribuer à la réaction:

$$n\ C_5H_{10} + IH \rightarrow C_5H_{11}I \text{ secondaire}$$

cette addition se faisant dans le sens prévu par la règle de Markovnikov s'il s'agit de pentène 1.

Quant au pentène, il proviendrait du réarrangement du radical $.C_5H_{10}.$ formé par ouverture du cycle [16].

Il est moins facile d'expliquer la présence du 1-iodopentane, et il faudrait peut-être faire intervenir une réaction avant neutralisation entre l'ion parent du cyclopentane, qui semble linéaire [17], et une molécule de cyclopentane:

$$C_5H_{10}^+ + \text{cyclo } C_5H_{10} \rightarrow C_5H_{11}^+ + \text{cyclo } C_5H_9$$

$$C_5H_{11}^+ + e^- \rightarrow C_5H_{11}. \text{ (primaire ?)}$$

d) Le rendement élevé d'iodure de méthyle est aussi difficile à interpréter. On peut penser à une rupture de l'ion parent cyclopentane, analogue à celles qui se produisent en spectrographie de masse [17]:

$$C_5H_{10}^+ \rightarrow CH_3. + C_4H_7^+$$

$$C_4H_7^+ + e^- \rightarrow C_4H_7. \text{ (radical éthylénique ?)}$$

L'iodure formé à partir de $C_4H_7.$ serait instable (allylique) ou réagirait avec IH pour donner un diiodure, ce qui expliquerait la quasi-inexistence de monoiodures en C_4.

e) Lorsqu'on capte l'acide iodhydrique, on constate une diminution des rendements d'iodocyclopentane et de 2-iodopentane. Les résultats de plusieurs essais

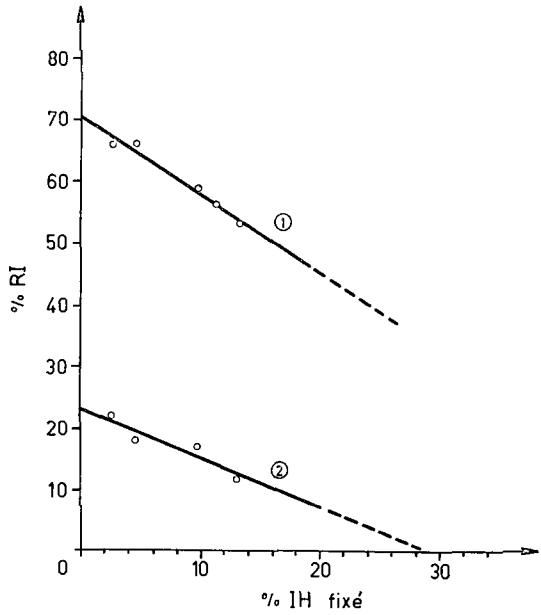

Fig. 2
Fixation de l'acide iodhydrique par un capteur dans la radiolyse du cyclopentane liquide en présence d'iode-131.
1. Variation du rendement relatif d'iodo-cyclopentane en fonction de la quantité d'acide iodhydrique fixé. — 2. Variation du rendement relatif (× 10) du 2-iodopentane en fonction de la quantité d'acide iodhydrique fixé.

ont permis de tracer les courbes de la figure 2, qui rendent possible une extrapolation des rendements au cas où tout l'acide iodhydrique serait fixé sur des alcènes d'origine radiochimique.

$$\left.\begin{array}{l} G\ (\text{cyclo}\ C_5H_9\ I) = 2{,}98 \\ G\ (2\ C_5H_{11}\ I) = 0{,}10 \end{array}\right\} \text{ pour un } G\ (\text{RI}) \text{ moyen de } 4{,}40.$$

Grâce à certaines hypothèses, on pourrait aussi extrapoler dans l'autre sens pour déterminer le palier des rendements correspondant à une formation exclusivement radicalaire des iodures en question; le résultat obtenu serait assez douteux.

Cas du n-pentane

Cet hydrocarbure a été moins étudié que le précédent. Les résultats donnés dans le tableau I montrent cependant certains points intéressants.

a) La valeur de G (—I) est inférieure à celles qui existent dans la littérature, comme dans le cas du cyclopentane [13]. Sans doute les diiodures vicinaux sont-ils ici moins stables, car on constate en outre que le pic d'activité parasite dû à la décomposition de ces produits pendant la distillation est de faible importance. La différence entre G (RI) et G (—I) est donc petite.

Evidemment, lorsque la radiolyse est faite en présence de cyclopentène, la perturbation due aux diiodures apparaît.

b) Nous pouvons comparer les résultats de la radiolyse du n-pentane, en l'absence de capteur d'acide iodhydrique, à ceux de DEWHURST [18] sur le n-hexane et à ceux de MACCAULEY sur le n-butane [19]. Dans les trois, cas, les liaisons C-H se montrent les plus touchées par la radiolyse.

En formant le rapport

$$Rn = \frac{\text{nombre de radicaux en Cn secondaires}}{\text{nombre de radicaux en Cn primaires}}$$

qui compare le nombre des ruptures C—H secondaires et C—H primaires observées et le rapport

$$Hn = \frac{\text{nombre d'hydrogènes secondaires du carbure}}{\text{nombre d'hydrogènes primaires du carbure}}$$

qui indique la probabilité théorique des ruptures primaires et secondaires, on obtient:

pour le n-butane, $R_4 = 1{,}9$ $H_4 = 0{,}67$

pour le n-pentane, $R_5 = 2{,}5$ $H_5 = 1$

pour le n-hexane, $R_6 = 3{,}7$ $H_6 = 1{,}33$.

Ces chiffres indiquent que les liaisons C—H secondaires sont les plus fragiles.

Si nous calculons le rapport R_5 dans le cas où un capteur d'acide iodhydrique a été ajouté, nous trouvons une valeur de 3,7, sans doute beaucoup plus proche du rapport réel entre les radicaux pentyle secondaire et primaire formés par la radiolyse, puisque dans ce cas on élimine une bonne partie des iodures formés à partir d'alcènes.

c) La fixation de l'acide iodhydrique par le cyclopentène abaisse les rendements d'iodopentanes et du 2-iodopropane. La décroissance du rendement de 1-iodopentane est assez étonnante, car elle implique la formation d'une partie de cet iodure par une addition d'acide iodhydrique sur du pentène-1 en sens inverse de celui que prévoit la règle de Markovnikov. Mais peut-être s'agit-il d'iodopentènes qui ont un point d'ébullition voisin de celui du 1-iodopentane.

Il faut aussi remarquer qu'en empêchant en partie la formation du 2-iodopropane par addition d'acide iodhydrique, nous arrivons à obtenir une égalité approchée entre la formation des radicaux en C_3 et en C_2. Il en résulte que ces radicaux se forment sans doute par coupure simple de la chaîne du pentane normal.

d) Enfin, comme pour le cyclopentane, nous retrouvons beaucoup plus de radicaux méthyle que de leur complément en C_4. La formation des radicaux méthyle n'est donc pas le résultat de la coupure simple:

$$C_5H_{12} \rightarrow CH_3\cdot + C_4H_9\cdot$$

Les travaux déjà cités de Dewurst et de MacCauley montrent une anomalie analogue, ainsi d'ailleurs que ceux de WAGNER [20] sur la radiolyse du n-pentane en absence d'iode.

Conclusions

Les résultats que nous venons de présenter sont encore partiels, et il serait prématuré de pousser leur interprétation plus avant. Le but de cet exposé était plutôt de montrer que, par l'emploi de l'iode-131 comme intercepteur, il semble possible d'établir une partie du mécanisme de radiolyse des hydrocarbures étudiés. Ce travail devra être complété par l'examen des produits moléculaires engendrés par l'irradiation. La méthode utilisée nous a permis, en particulier, de mettre en évidence les réactions purement chimiques qui se produisent à côté de la radiolyse, et dont il faut tenir compte pour déterminer, à partir des résultats obtenus en présence d'un intercepteur, un schéma du comportement des carbures purs sous irradiation.

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NOTE. Depuis la rédaction du présent mémoire, les résultats qui y sont donnés ont fait l'objet de quelques corrections, et le travail sur le sujet a été développé dans la thèse soutenue par l'auteur le 12 juin 1961 devant la Faculté des sciences de Paris. Cette thèse a été publiée en octobre-novembre 1961 dans le *Journal de chimie-physique* (Paris).

TECHNIQUE FOR THE STUDY OF HALOGEN ATOM REACTIONS

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Abstract — Résumé — Аннотация — Resumen

Technique for the study of halogen atom reactions. A technique has been developed for measuring the rates of gas phase reactions involving halogen atoms. The technique utilizes the effect of the nuclear (n, γ) reaction to generate radioactive atoms which then react with a substrate.

Under certain conditions the atoms formed by the (n, γ) reaction do not undergo hot recoil reactions, but react only as normal thermal atoms. The kinetics of the reactions of the atoms may be evaluated by using a competing reaction whose kinetics are well established. The method depends for its successful application upon various conditions given in the paper.

When those conditions are fulfilled the technique is very much simpler than photolysis. With a small laboratory-neutron source the concentration of the labelled atoms can be made so small that the direct recombination of the labelled halogen atoms can be ignored, so that accurate measurements of the radiation absorbed and the quantum yield for the production of the atoms are unnecessary, as are a knowledge of the recombination rate, or the use of a sector technique to measure this rate. The method has possible applications to the study of the reactions of halogen atoms with radicals, but this possibility has not so far been explored.

The technique has been developed in the study of the thermal exchange reaction between iodine atoms and methyl iodide, the exchange reaction between iodine atoms and molecules being

$$I^{128} + I_2 \qquad\qquad II^{128} + I$$

used as a competing reaction. From the rate constant for this exchange, the rate constant and activation energy for the exchange with methyl iodide have been determined, and the values confirmed by direct measurement.

Technique pour l'étude des réactions d'atomes d'halogènes. Un procédé a été mis au point pour mesurer la vitesse des réactions en phase gazeuse dans lesquelles interviennent des atomes d'halogènes. On utilise l'effet de la réaction nucléaire n, γ pour former des atomes radioactifs qui réagissent ensuite avec un substrat.

Dans certaines conditions, les atomes formés par la réaction (n, γ) ne subissent pas de réactions caractéristiques des particules de recul excitées, mais réagissent seulement comme des atomes thermiques normaux. On peut évaluer la cinétique de ces réactions atomiques par comparaison avec une réaction dont l'équation cinétique est connue. Le succès de l'opération dépend de diverses conditions données dans le texte.

Lorsque ces conditions sont remplies, le procédé est beaucoup plus simple que celui de la photolyse. Si l'on utilise une petite source de neutrons de laboratoire, la concentration des atomes marqués est si faible qu'on peut négliger la recombinaison directe des halogènes marqués et se dispenser de mesurer exactement la quantité de rayonnement absorbée et le rendement quantique lors de la production des atomes, outre qu'il est inutile de connaître la vitesse de recombinaison ou d'utiliser une technique de mesure par secteurs pour déterminer cette vitesse. La méthode décrite

pourrait être appliquée à l'étude des réactions entre des atomes d'halogènes et des radicaux, mais cette possibilité n'a pas encore été explorée.

Les auteurs ont perfectionné cette nouvelle méthode en étudiant la réaction d'échange thermique entre atomes d'iode et iodure de méthyle, la réaction d'échange entre atomes d'iode et molécules ayant servi de réaction témoin. D'après la constante de vitesse de cet échange, les auteurs ont pu déterminer la constante de vitesse et l'énergie d'activation pour l'échange avec l'iodure de méthyle; les valeurs obtenues ont été confirmées par des mesures directes.

Метод изучения реакций галоидных атомов. Был разработан новый метод измерения скорости связанных с галоидными атомами реакций газовой фазы. В этом методе используется действие ядерной реакции (n, γ) для производства радиоактивных атомов, которые затем вступают в реакцию с субстратом.

При некоторых условиях атомы, образованные в результате реакции (n, γ), не участвуют в высокоактивных реакциях отдачи, а реагируют только как нормальные тепловые атомы. Кинетика реакций атомов может быть установлена при помощи использования конкурирующей реакции, кинетика которой хорошо известна. Для успешного проведения этого метода необходимо соблюдение различных данных в тексте условий. При соблюдении этих условий данный метод много проще, чем фотолиз. С помощью небольшого лабораторного источника нейтронов можно свести концентрацию меченых атомов до такой малой величины, что это позволит пренебречь непосредственной рекомбинацией меченых галоидных атомов, так что точные измерения поглощенного света и выхода квантов для производства атомов становятся излишними, так же как и необходимость знания скорости рекомбинации или использование секторного метода для измерения этой скорости. Этот метод может быть применен к изучению реакций между галоидными атомами и радикалами, но до сих пор эта возможность еще не была исследована.

Этот метод был выработан в процессе изучения тепловых реакций обмена между атомами йода и иодида метила. В качестве конкурирующей реакции была использована реакция обмена между атомами йода и молекулами, и из постоянной для скорости этого обмена была выведена постоянная для скорости и энергия активации для обмена с иодидом метила; полученные значения были подтверждены непосредственными измерениями.

Procedimiento para estudiar las reacciones de átomos de halógeno. Los autores han perfeccionado un nuevo procedimiento para medir la velocidad de las reacciones en fase gaseosa en las que intervienen átomos de halógeno. En este procedimiento se utiliza el efecto de la reacción nuclear (n, γ) para formar átomos radiactivos, que reaccionan luego con un sustrato.

En determinadas condiciones, los átomos formados por la reacción (n, γ), no experimentan reacciones características de las partículas de retroceso excitadas, sino que reaccionan simplemente como átomos térmicos normales. La cinética de esas reacciones atómicas puede evaluarse por comparación con una reacción cuya ecuación cinética se conozca con exactitud. Para obtener resultados satisfactorios con este método, se han de cumplir varias condiciones.

En los casos en que se cumplen estas condiciones, este procedimiento es mucho más simple que el de fotólisis. Al utilizar una pequeña fuente neutrónica de laboratorio, la concentración de los átomos marcados es tan reducida que la recombinación directa de los halógenos marcados puede despreciarse y no resulta necesario, al revés de lo que ocurre con la fotólisis, proceder a una medición exacta de la cantidad de luz absorbida ni del rendimiento cuántico en la producción de los átomos; tampoco es preciso conocer la velocidad de recombinación ni recurrir a una técnica de sector para medir esta velocidad. El método puede aplicarse al estudio de las reacciones de halógenos atómicos con radicales, pero esta posibilidad no ha sido explorada aún. Los autores han perfeccionado el procedimiento estudiando la reacción de intercambio térmico entre átomos de yodo y yoduro de metilo.

El intercambio entre átomos y moléculas de yodo fue utilizado como reacción de competición y, a partir de la constante de velocidad de este intercambio, se determinó la constante de velocidad y la energía de activación para el intercambio con yoduro de metilo; los valores obtenidos pudieron confirmarse por medición directa.

1. Introduction

To study the reactions of halogen atoms in the gas phase the atoms are usually generated by photolytic or thermal dissociation of the halogen or an alkyl halide. The steady-state concentrations of the halogen atoms can be measured directly by spectrophotometry, or the mean lifetimes of the atoms obtained from measurements with a rotating sector; the rate constants obtained from such experiments are normally independent of other kinetic data. Analysis of the products of the reaction has in many cases been simplified by the use of radioisotopes. Labelled halogen molecules or alkyl halides have been photolysed and the activity of the reaction products used to determine their concentrations, and to allow an accurate identification of products present in very low concentrations.

The method to be described combines the inherent analytical advantages of the tracer technique with a highly specific action; only labelled halogen atoms would be generated in the ideal case, and secondary reactions can be avoided. The nuclear (n, γ) reaction is used to generate radioactive halogen atoms which then react with a substrate. The source of the halogen may be this substrate or some other halogen-containing molecule. The reactions which occur can be followed by an analysis with known kinetics of the labelled products and rate constants obtained by the use of competing reactions.

The technique has some advantages, although corresponding disadvantages may limit its usefulness in many cases. It is simple, and it is not necessary to prepare a labelled compound. As the number of halogen atoms generated is much smaller than is usual in photolysis, the homogeneous gas phase recombination of the atoms can be neglected and determination of the stationary-state concentrations of the atoms may be unnecessary. The analysis of the products of the reaction is simplified by the radioactive labelling. The very specific generation of the labelled atoms has advantages over the photolysis of a labelled compound. For example, if labelled iodine atoms are generated by photolysis of a labelled organic iodide, say RI^{131},

$$RI^{131} \xrightarrow{h\nu} R + I^{131}$$

a large number of unlabelled iodine atoms and organic radicals R will also be produced, and these may result in competing secondary reactions.

The experimental conditions are restricted somewhat by the disadvantages of the technique. The complications of the initial generation of the labelled atoms from a nuclear reaction restrict the technique to the study of gas-phase reactions. Two main requirements are the absence of 'hot' reactions of the atoms (i.e. of reactions occurring when an atom has an energy above thermal energies) and of interference by reactions with the atoms or radicals produced by the gamma-rays nearly always associated with neutron sources. The use of a suitable competition reaction with known kinetic characteristics is also necessary, and in some cases a suitable reaction may be hard to find.

The technique has been successfully employed to measure the rate of exchange between iodine atoms and methyl iodide

$$CH_3I + I^* \rightarrow CH_3I^* + I$$

in the gas phase. The rate constant and energy of activation obtained are compared, using conventional methods, with values from the direct measurement of the rate of the exchange.

2. The general technique

The method depends on the production of radioactive halogen atoms by the nuclear (n, γ) reaction. For halogens these reactions have large cross-sections for thermal neutrons, and the product atoms have relatively short half-lives, so that sufficient activity for accurate analysis can be produced by small neutron fluxes in short irradiation times, minimizing unwanted interference by gamma-radiolysis. Three conditions must be fulfilled for the successful application of the method.

The radioactive halogen atoms generated by the (n, γ) reaction must not undergo 'hot' reactions. The atoms are produced with energies considerably in excess of thermal energies, and must lose the excess energy by collision with the medium. They may react before losing all of this excess energy; such 'hot' reactions occur in liquids and solids [1] and will obviously interfere with the study of thermal reactions. In addition, the atoms are initially charged, and may be able to undergo ion-molecule reactions. Both ion-molecule reactions and 'hot' reactions must be shown to be unimportant, or allowance made, if possible, for their occurrence.

The gamma-rays associated with a neutron source such as a radium-beryllium mixture or a nuclear reactor must not produce radiolysis of the reaction mixture sufficient to cause interference either by reactions of the ions and radicals produced with the radioactive halogen atoms or with the products of the reaction being studied. In the gas phase the extent of the radiolysis can be checked by the direct measurement of the rate of ion production by the gamma-radiation by performing the irradiation in an ion-chamber. The rate constants for the reactions of halogen atoms with organic radicals such as CH_3 in the gas phase are either known or can be estimated, and the stationary-state concentrations of the atoms and radicals can be calculated. The extent of any expected interference by the radicals can then be assessed.

The method depends on being able to use a competition reaction to obtain the rate constant for the unknown reaction. For two competing reactions

$$A + X \rightarrow P_1 \qquad k_1 \tag{1}$$

$$B + X \rightarrow P_2 \qquad k_2 \tag{2}$$

in the steady-state conditions when (X) is independent of time

$$\frac{\mathrm{d}(P_1)}{\mathrm{d}t} = k_1(A)(X)$$

$$\frac{\mathrm{d}(P_2)}{\mathrm{d}t} = k_2(B)(X)$$

where k_1 and k_2 are the rate constants for reactions (1) and (2). Under most conditions with small neutron fluxes (X) is very small indeed and as little as 1 mol. in 10^{10} of A and B reacts. The concentrations of A and B are therefore constant, and on integration and rearrangement,

$$\frac{(P_1)}{(P_2)} = \frac{k_1(A)}{k_2(B)}$$

If k_2 is known, k_1 may be found. The competition reaction must be of the same order in halogen-atom concentration as the reaction being studied, to allow the halogen-atom concentration to cancel from the final expression. The rate of the competition reaction should be of about the same order of magnitude as that of the unknown reaction, so that the ratio of the concentration of the products will be about unity, when it can be found with greatest accuracy. When halogen atoms are radioactive, the products will be labelled, and the ratio of the concentrations will be the ratio of the specific activities. The restrictions against 'hot' reactions will apply to the reactant added to undergo the competition reaction.

3. Application to the exchange reaction

Experimental procedure

The methyl iodide was carefully purified to remove free iodine and unsaturated organic compounds. After purification it was stored in the dark over mercury, and distilled *in vacuo* before use. The purity was checked by gas chromatography. All other chemicals were of 'Analar' purity.

An antimony-124/beryllium neutron-source was used for the irradiations. The source was supported in a tank of water, the temperature of which could be controlled to ± 0.02°C. The gases were irradiated in sealed soda-glass bulbs for periods from 30 min to 24 h.

After irradiation, the contents of the bulb were frozen into a side-arm and the bulb opened. A solution of methyl iodide and iodine in carbon tetrachloride was then added. When the bulbs contained gases such as argon, they were attached to the vacuum line through a break seal, the seal was opened, and the contents passed slowly through cooled spiral traps which retained the methyl iodide. The activity in the organic and inorganic forms was separated by extracting the solution with 0.1 *M* sodium sulphite solution. Two further portions of the carrier solution were similarly added to the bulb and extracted.

The organic and inorganic fractions were counted in 10-ml liquid Geiger counters. Corrections were made to the observed activities for the decay of the iodine-128 and for the different counting efficiencies of the aqueous and carbon tetrachloride solutions. The percentages of the total iodine-128 activity present in the two fractions have been designated the organic and inorganic yields.

Experimental results

It was important to identify the individual organic compounds contributing to the organic yield. Both carrier distillations and gas chromatography were used. The only organic compound found to contain iodine-128 after the irradiations was methyl iodide. Methylene iodide, which is produced in about 10% yield in the neutron irradiation of liquid methyl iodide [3] [4] does not contribute more than 0.5% to the total yield in the gas phase.

The organic yield was shown to be the result of thermal, not 'hot' reactions by irradiating mixtures of methyl iodide and inert gases. Argon, nitrogen and helium were used. At sufficiently high inert gas pressures there will be a high probability that the iodine atoms will have lost all their excess energy before encountering a methyl iodide molecule. With argon this probability was as

high as 0.5 for some experiments, but no change in the organic yield was observed. These results imply that 'hot' reactions are unimportant at the pressures used, and further evidence for this conclusion is the temperature dependence of the methyl-iodide yield.

The organic yield was independent of a ten-fold variation in the gamma-ray flux associated with the neutron source, and of the length of the irradiation (from 30 min to 24 h). The independence suggests that the yield is not the result of a reaction between radicals produced by gamma-ray and the iodine atoms. Support for this conclusion is given by the difficulty of formulating a plausible reaction-scheme involving such radicals which will give the correct dependence of the organic yield upon methyl-iodide pressure. Irradiations performed in an ion-chamber where the ion current during irradiation was measured, enabled the steady-state concentration of gamma-produced radicals and atoms to be estimated. This was so low that provided the reaction of the iodine atoms leading to the organic yield had a rate constant greater than about 10 cm^3/moles, reaction between the radicals from the gamma radiolysis and the iodine atoms could contribute less than 1% to the total organic yield. In fact the rate constant for the exchange reaction is much greater than this.

Both nitric oxide and oxygen are well known scavengers for methyl radicals and can compete effectively with iodine atoms. The organic yields from mixtures of nitric oxide or oxygen and methyl iodide at pressures where the scavengers should have been 500 to 1000 times as effective as the iodine atoms in reacting with methyl radicals, were unchanged. All the evidence therefore supports the view that the organic yield is not due to the reaction of the iodine atoms with radicals.

The labelled methyl iodide might have been produced by an ion-molecule reaction, the ions coming from the initial nuclear reaction or from the gamma-radiolysis. Unequivocal evidence for the occurrence of ion-molecule reactions in the present system is hard to find. Ion-molecule reactions should be influenced by the addition to the reacting system of gases with ionization potentials less than the electron affinities of the reacting ions. This technique has been used [2] to demonstrate the existence of the reaction $CH_4 + I^+ \rightarrow CH_3I^+ + H$. As methyl iodide has a lower ionization potential than atomic iodine, in the present experiments it is probable that charge transfer will occur in pure methyl-iodide. Certainly nitric oxide which also has a lower ionization potential than iodine atoms, did not change the organic yield. The application of electric fields of about 500 V/cm across the gas during irradiations did not change the yields. In the absence of positive evidence, ion-molecule reactions are not believed to play an important part in determining the yield of the labelled methyl-iodide.

The organic yield increased with increasing methyl-iodide pressure in the range 20 to 250 mm Hg. The increase in the yield is shown in Table I. In the pressure-range covered, the ratio of the organic yield to the inorganic yield is a linear function of the methyl-iodide pressure (Fig. 1). The linear pressure dependence is expected in the labelled methyl-iodide and arises from the exchange

$$CH_3I + I^* \rightarrow CH_3I^* + I \; k_3, \tag{3}$$

while the inorganic iodine (which cannot be precisely, as most inorganic iodine compounds exchange rapidly) arises from a reaction which can be written

$$I^* \rightarrow \text{Inorganic products} \; k_4. \tag{4}$$

Reaction (4) probably involves two steps, the adsorption of the iodine atoms

on the surface followed by heterogeneous combination. If k_3 and k_4 are the rate constants of the two reactions, then

$$\mathrm{d}\,(CH_3I^*)/\mathrm{d}t = k_3\,(CH_3I)\,(I^*)$$

and

$$\mathrm{d}\,(\text{Inorganic product})/\mathrm{d}t = k_4\,(I^*).$$

As the concentration of the methyl iodide is so much larger than the iodine-atom concentration, it is effectively constant, and in the steady state, on integrating and re-arranging we have

$$(CH_3I^*)/(\text{Inorganic product}) = k_3\,(CH_3I)/k_4,$$

that is $R_0 = \text{Organic yield/Inorganic yield} = k_3\,(CH_3I)/k_4$, which is the relationship obtained experimentally.

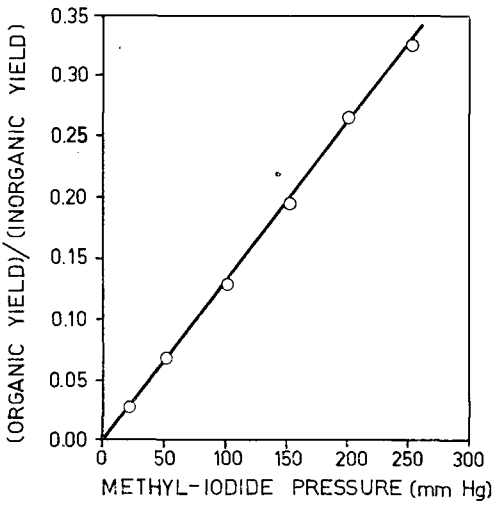

Fig. 1
The dependence of the ratio of the organic yield to the inorganic yield upon pressure, in pure methyl iodide at 20°C.

TABLE I

DEPENDENCE OF THE ORGANIC YIELD UPON METHYL-IODIDE PRESSURE

CH_3I pressure (mm Hg)	Organic Yield (%)	Inorganic Yield (%)	R_0/CH_3I pressure
20	2.5	97.5	1.30×10^{-3}
50	6.3	93.7	1.34×10^{-3}
100	11.3	88.7	1.28×10^{-3}
150	16.3	83.7	1.30×10^{-3}
200	21.0	79.0	1.33×10^{-3}
250	24.6	75.4	1.31×10^{-3}

The organic yield increased with temperature during the irradiation. The function log R_o is linearly dependent on the reciprocal of the absolute temperature (Fig. 2). The slope of the straight line corresponds to the difference in the activation energies of reactions (3) and (4). This difference is 14.3 ± 0.5 kcal/mole. The linear dependence of Fig. 2 is further evidence for the absence of 'hot' reactions. The heat of adsorption of iodine atoms upon glass is probably small, and if so, reaction (4) will be temperature-dependent only to the extent of the term in RT in the collision expression. The activation energy of reaction (3) would then be about 14.8 ± 0.5 kcal/mole.

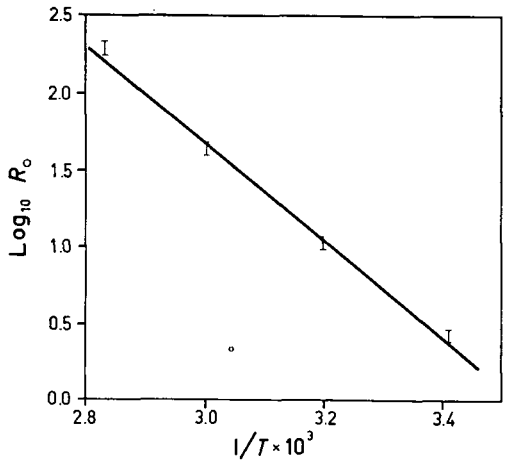

Fig. 2
Temp. dependence of log (Organic yield)/(Inorganic yield) at 200 mm Hg methyl-iodide pressure.

To obtain the rate constant of reaction (3) a competing reaction is needed. In the present case it is preferable for this reaction to lead to an inorganic product, as the separation of the products of the reactions will be the same as that in the absence of competition. Iodine is a suitable reactant, which will remove labelled iodine-atoms by the exchange reaction

$$I^* + I_2 \rightarrow II^* + I \quad k_5. \tag{5}$$

The concentration of the iodine molecules is so very much greater than that of the iodine atoms that the reverse reaction can be ignored. The labelled molecular iodine is produced in such low specific activity that no observable reaction occurs with atoms or radicals in the system. The rate constant of reaction (5) has not been measured in the gas phase, but in hexane solution it is $8 \pm 4 \times 10^{10}$ cm^3/mole s at 25°C [5]. The rate in the gas phase should be much the same for a reaction involving such simple collisions. Mixtures of iodine and methyl iodide have a much lower organic yield than pure methyl-iodide (Table II). In the presence of added iodine the rate expressions will be

$$\mathrm{d}(CH_3I^*)/\mathrm{d}t = k_3 (CH_3I)\ (I^*)$$

and

$$\mathrm{d}(\text{Inorganic product})/\mathrm{d}t = k_4 (I^*) + k_5 (I_2)\ (I^*).$$

Integrating and arranging as before we have

$$1/R_I = (\text{Inorganic product})/(CH_3I^*) = k_4/k_3\,(CH_3I) + k_5\,(I_2)/k_3\,(CH_3I).$$

The term $k_4/k_3\,(CH_3I)$ is the ratio of the inorganic yield to the organic yield at the same methyl-iodide pressure in the absence of iodine, i.e. $1/R_O$. In the presence of added iodine therefore

$$1/R_I - 1/R_O = k_5\,(I_2)/k_3\,(CH_3I)$$

and at constant methyl-iodide pressure $1/R_I - 1/R_O$ should be a linear function of the added iodine concentration; this is shown in Fig. 3, and from the slope of the line and the value of k_5, k_3 may be found.

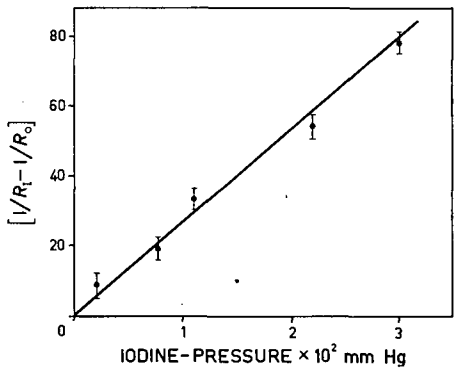

Fig. 3
Dependence of the function $[1/R_I - 1/R_O]$ upon added iodine pressure at 200 mm Hg methyl-iodide pressure.

TABLE II

DEPENDENCE OF THE ORGANIC YIELD UPON IODINE PRESSURE AT 200 mm Hg METHYL-IODIDE PRESSURE

I_2 pressure (mm Hg)	Organic Yield (%)	$1/R_I$	$[1/R_I - 1/R_O]/I_2$ pressure
0	21.0		
2.0×10^{-3}	9.6	9.4	28.0×10^2
7.8×10^{-3}	4.2	22.8	24.4×10^2
1.1×10^{-2}	2.6	37.4	30.5×10^2
2.2×10^{-2}	1.7	57.8	24.5×10^2
3.0×10^{-2}	1.2	82.3	26.2×10^2

If the value of k_5 given above is used, the rate constant for the exchange reaction (3) is found to be $10 \pm 6 \times 10^4$ cm³/mole s at 25°C. The greatest part of the uncertainty in the value arises from that in the value of k_5.

4. Direct measurement of the exchange rate

To confirm the values of the rate constant and the activation energy given above it was necessary to measure the exchange rate directly, under substantially the same conditions. The exchange rate was measured by irradiating mixtures

of methyl iodide and iodine (labelled with iodine-131) with 5461 Å light. Under these conditions the following reactions occur:

$$I_2 \xrightarrow{h\nu} I + I \tag{6}$$

$$CH_3I + I \rightarrow CH_3I + I \quad k_3 \tag{3}$$

$$I + I + M \rightarrow I_2 + M' \quad k_7. \tag{7}$$

The exchange was followed in the usual way by extracting the organic and inorganic activities and measuring the specific activities in order to calculate the fraction exchange. To determine k_3, the stationary-state concentration of the iodine atoms under the experimental conditions is needed. The iodine-atom concentration could have been measured by using a sector method, but for simplicity the value of the recombination rate-constant k_7 was assumed. This rate-constant has not been measured in the presence of methyl-iodide as a third body. It has been assumed that methyl-iodide will have much the same efficiency for energy removal as ethyl-iodide, where the rate of recombination has been measured [6] [7]. In methyl-iodide the second-order value of k_7 has been taken to be 2×10^{12} cm^3/mole s at 25°C and 200 mm Hg methyl-iodide pressure. The exchange rate constant k_3 is not markedly dependent on the value of k_7 chosen, as the iodine atom concentration depends only upon the square root of k_7.

The rate constant for the exchange obtained from these direct measurements is $5 \pm 0.5 \times 10^3$ cm^3/mole s at 25°C; the activation energy is 15.2 ± 0.5 kcal/mole. From a few experiments in liquid methyl-iodide, the rate-constant under these conditions is 20 cm^3/mole s at 25°C.

5. Discussion

The new technique described has yielded values for the rate constant and energy of activation of the exchange reaction

$$CH_3I + I^* \rightarrow CH_3I^* + I$$

which must be compared with the values from the direct measurement. Both values depend on other data, and in view of the uncertainty in this, the agreement between the two methods is believed to be satisfactory. The activation energies, which are independent of other data, agree within the experimental error. This agreement indicates that the assumptions made about the nature of the reactions of the recoil iodine atoms were correct. The precision of the results would be increased by using a competing reaction with a more accurately known rate-constant.

Although several reports on the exchange reaction between methyl iodide and iodine appear in the literature, the results are not generally comparable with those obtained in the present work. Recently Noyes [8] has measured the exchange between iodine and methyl-iodide at temperatures between 150° and 200°C in hexachlorobutadiene, and interprets the results in terms of exchange between iodine atoms and methyl iodide. Extrapolated to room-temperature the rate-constant for the exchange is about 100 cm^3/mole s and the activation energy is about 30 kcal/mole. The rate is in substantial agreement with the value found in liquid methyl-iodide in the present work. The difference in the

rate constants in the gas and liquid phases is accounted for by the difference in the activation energies, and this may point to the presence of heterogeneous effects in the gas phase, such as have been observed by SCHMIED *et al.* [9] in the thermal exchange of iodine with methyl iodide in the gas phase. MILLER *et al.* [10] also seem to have found heterogeneous exchange in the gas phase.

ACKNOWLEDGEMENT

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DISCUSSION

H. Elias (Federal Republic of Germany) asked the speaker whether he had considered the reverse exchange reaction between inactive iodine atoms and active methyl-iodide.

G. S. Laurence said the concentrations of the reactants had been such as to make that unnecessary. The methyl-iodide had been at a concentration of about 10^{18} mol./cm^3 while the iodine atom concentration had only been about 10^5 atoms/cm^3.

B. Dzantiev (USSR) asked what were the conditions in which the experiment had taken place, and in particular to what extent the iodine atoms were "hot".

G. S. Laurence said that presumably all the I^{128} atoms were "hot" immediately after the nuclear reaction. It did not seem, however, that, in the experiments described, they reacted above thermal energies. That result seemed surprising. He and his associates could only assume that in the gas phase the iodine atoms could not form stable products until they reached thermal energies.

VAPOUR-PRESSURE DETERMINATIONS ON TRITIUM-LABELLED ORGANIC COMPOUNDS

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Abstract — Résumé — Аннотация — Resumen

Vapour-pressure determinations on tritium-labelled organic compounds. The recent thermochemical interest in organo-metallic compounds requires the measurement of very low sublimation heats and vapour pressures. For this purpose a radio-tracer technique may be used to advantage, tritium being especially suitable.

The authors describe experiments with tetraphenyl lead and tin, labelled with tritium yielding high specific activities per exposure. The paper describes the technique employed and the damage caused to the target material by irradiation.

Vapour pressures as low as 10^{-10}—10^{-11} mm Hg can be determined with accuracy, using a modified Knudsen effusion technique. The paper describes the effusion cell and the results of assaying tritium in a proportional counter.

The experimental values of the vapour pressures and latent heat of sublimation in the range 20°C—40°C are given.

Déterminations des tensions de vapeur utilisant des composés organiques marqués au tritium. Dans la thermochimie des composés organo-métalliques, il est nécessaire de mesurer des chaleurs de sublimations et de tensions de vapeur très basses. Ceci peut être fait en utilisant des traceurs radioactifs et plus particulièrement le tritium.

Les auteurs décrivent des expériences réalisées avec du tétraphényl de plomb et d'étain, marqués au tritium avec de fortes activités spécifiques par procédé de contact. Le mémoire expose la technique utilisée et traite des dommages causés à la cible par irradiation.

Les tensions de vapeur, mesurées au moyen d'une technique d'effusion de Knudsen modifiée, sont déterminées avec précision jusqu'à 10^{-10} à 10^{-11} mm de Hg. La description de la cellule d'effusion, les résultats du comptage du tritium par compteur proportionnel sont donnés.

Enfin, les auteurs fournissent les valeurs expérimentales des tensions de vapeur et des chaleurs latentes de sublimation entre 20°C et 40°C.

Определение упругости пара на органических соединениях, меченных тритием. В термохимии металлоорганических соединений необходимо измерять очень низкую теплоту сублимации и упругость пара. Это можно сделать, используя радиоактивные индикаторы и в первую очередь тритий.

Авторы описывают опыты, проведенные с тетрафениловым свинцом и оловом, меченными тритием с большой удельной активностью при помощи контактного способа. В докладе излагаются использованные методы и рассматривается повреждение, причиняемое мишени облучением.

Упругость пара, измерявшаяся при помощи измененного метода Кнудсеновской эффузии, определяется с точностью до 10^{-10}—10^{-11} миллиметра ртутного столба. Даются описания эффузионной камеры и результаты счета трития в пропорциональном счетчике.

Наконец, авторы дают экспериментальные значения упругости пара и скрытой теплоты сублимации между 20° С и 40° С.

Determinación de las tensiones de vapor de compuestos orgánicos marcados con tritio. El estudio termoquímico de los compuestos organometálicos exige la medición de calores de sublimación y de tensiones de vapor muy bajas. Estas determinaciones se pueden realizar empleando indicadores radiactivos y, en especial, el tritio.

Los autores describen experimentos efectuados con tetrafenil plomo y tetrafenil estaño marcados con tritio por el procedimiento de contacto hasta alcanzar actividades específicas muy elevadas. La memoria describe las técnicas utilizadas y trata de los daños causados en el blanco por irradiación.

Empleando el método de efusión de Knudsen modificado se pueden determinar las tensiones de vapor con una precisión que llega hasta 10^{-10} ó 10^{-11} mm de Hg. La memoria describe la célula de efusión y los resultados de la valoración del tritio por medio de un contador proporcional.

Por último, los autores dan los valores experimentales de las tensiones de vapor y de los colores latentes de sublimación en un intervalo comprendido entre 20° C y 40° C.

1. Introduction

The versatility of organo-metallic compounds in the reactions which they undergo has led to much interest being aroused in their thermochemistry. A knowledge of their heats of formation is useful since the heats of formation of other compounds can be found and, in addition, an estimate can be made of the mean energies of the metal-carbon bonds within these compounds.

The mean dissociation energy of the metal-carbon bonds in the organo-metallic compound MR_4 containing a tetravalent metal M, and a monovalent organic radical R, is given by:

$$\overline{D}\,(\mathrm{M}-\mathrm{C}) = \frac{1}{4}\{4\,\Delta H^\circ_{\mathrm{f}}\,(\mathrm{R},\mathrm{g}) + \Delta H^\circ_{\mathrm{f}}\,(\mathrm{M},\mathrm{g}) - \Delta H^\circ_{\mathrm{f}}\,(\mathrm{MR}_4,\mathrm{g}).\},$$

where $\Delta H^\circ_{\mathrm{f}}\,(x, \mathrm{g})$ is the conventional symbol representing the standard heat of formation, from the elements, of the compound within the brackets. The quantity in the above expression which is of vital interest is the standard heat of formation of the organo-metallic compound, MR_4, in the gaseous state. Calorimetry will yield data which are relevant to the standard state of the compound, i.e. that state which is stable at 25°C; this is usually solid or liquid and often no reliable data are available either on latent heats of sublimation or on vaporization.

The latent heat of sublimation of a solid can be found from the way in which the vapour-pressure varies with temperature. Usually it is desirable to determine the latent heat of sublimation in the region of 25°C, but at this temperature the vapour-pressures of solids are often below 10^{-3} mm Hg. The vapour-pressure of sulphur has been measured as 4×10^{-7} mm at 15°C by BRADLEY [1], but this seems to represent the lower limit of the conventional Knudsen effusion-technique. Dynamic methods depend on the ability to detect a mass of material collected in a known time interval and, below 10^{-6} g, conventional techniques become specialized and difficult to use. However, by making a solid radioactive, it is possible to detect much less than a microgram of material, and in recent years this modification to the conventional techniques for measuring very low vapour-pressures has been used successfully by many researchers. Reviews of this type of work appear elsewhere [2] and will not be discussed in this paper.

The compounds under study are tetraphenyl tin and tetraphenyl lead, the heats-of-combustion of which are known, but there are no reliable data available about latent heat-of-sublimation.

2. Tritium labelling

The particular labelling isotope used in the compound under examination plays an important part in the general experimental techniques used in the determination of its latent heat-of-sublimation. In the particular organo-metallic compounds being studied, labelling of the metal, carbon, or hydrogen atoms may be undertaken, but only tritium-labelling was found to be practicable. Synthesis of tetraphenyl tin from radioactive tin, C^{14}- or H^3-labelled materials is impractical due to the low specific activities attainable with these isotopes in the final compounds and also to the low synthetic yields of the Grignard reaction needed to produce these compounds. A similar state of affairs applies to the production of labelled tetraphenyl lead by the above methods. The availability of sources of tritium of high specific activity suggests that labelling of the hydrogen atoms on the phenyl groups would be the best method of producing a compound with a specific activity high enough for the required measurements.

Two main methods are available for producing tritium-labelled compounds, namely:

(a) Tritium "recoil" labelling.

(b) Tritium gas-exchange labelling.

The first of these methods, that of WOLFGANG [3], involves the irradiation in the neutron flux of a nuclear reactor of an intimate mixture of a lithium salt and the material to be labelled. Recoil tritons are produced by the Li (n, α) reaction and recoil through the medium which produces excited organic species and which can recombine with tritons whose energies have been reduced to the thermal value. Thus the exchange of hydrogen atoms with tritium atoms produces a labelled molecule, but concomitant with this are two factors which render this method unsuitable, namely:-

(a) serious radiation damage to the material caused by the high fast-neutron and γ-ray flux in the reactor, and

(b) the production of undesirable tin isotopes which would render the compound radiochemically impure.

The second method, that of WILZBACH [4], utilizes the fact that the exposure of organic compounds to tritium gas yields tritiated products of high specific activity without, in favourable cases, extensive radiation damage. Subsequent work [5] has shown that aromatic, rather than aliphatic, hydrogen-replacement takes place. A similar preference for ring-tritiation was found when using the recoil method [6]. Since the compounds being studied each contain twenty aromatic-bonded replaceable hydrogen atoms per molecule, the Wilzbach method would seem to be a useful one to apply.

EXPERIMENTAL

The specific activity of the product is a maximum when the smallest amount of material is used that can completely absorb the radiation. Since the maximum range of tritium β's is $\sim$0.6 mg/cm^2, the material to be labelled was distributed at this thickness over the walls of a small vessel. The irradiation vessel in which labelling took place was made from Pyrex glass and had a surface area of approx. 70 cm^2, so that 50 mg of material could be exposed to tritium gas each time. The solid material to be labelled was thinly spread over the inside walls of the vessel by evaporating a benzene solution of the material from each face in turn. The vessel was then transferred to a vacuum line where it was evacuated and

5 c of tritium gas (2.00 ml at NTP 97% isotopic abundance) were pumped into it from a reservoir by means of a Toepler pump.

The period of irradiation used was 7 d, after which time the tritium gas was pumped back to storage and the material was removed from the cell for purification.

In order to devise a suitable purification-scheme for these metal-aryls, an attempt was made to determine the radioactive products formed during the tritium irradiation. At the end of the 7-d irradiation, the material in the cell was discoloured and this indicated that some decomposition had taken place. A reasonable possibility, in view of the stability of the aromatic ring to such radiation, is that rupture of the metal-carbon bonds had occurred and likely products are labelled benzene, diphenyl, and some polymerized diphenyl tin derivatives. To retain the volatile irradiation products, the cell was frozen down in liquid nitrogen and tritium gas removed as before. Labelled benzene produced during the irradiation was removed by distillation *in vacuo* into a cold trap. Labelled benzene trapped in the lattice of the material was removed by dissolving the contents of the cell in benzene and then distilling off the benzene into a cold trap. This was repeated and all the benzene distillates were combined and made up to a known volume with analar benzene. The solid product from the cell was repeatedly recrystallized from absolute ethanol, the mother liquors being retained. Finally a few milligrams of inactive diphenyl carrier were added to the system to remove any active diphenyl present. Samples of material were removed at the end of each purification step for specific activity checks and the recrystallizations were continued until this was constant. The "benzene" activity was assayed by preparing the 2-4 dinitro derivative, using accepted methods of nitration. The active diphenyl was recovered from the recrystallization mother-liquors by repeated recrystallization of inactive metal-aryl, which would remove from the system any active metal-aryl. Infra-red spectra and combustion analyses yielded no evidence of impurities in the final products. An assay of tritium-labelled material was undertaken using a flow proportional counter of conventional type with methane as the flow gas.

RESULTS

(1) Specific activity of purified samples:

Crude tin tetraphenyl	2053 ± 30 counts/min/10^{-8} g
after 1st recrystallization	1570 ± 20 counts/min/10^{-8} g
after 2nd recrystallization	1411 ± 18 counts/min/10^{-8} g
after 3rd recrystallization	1450 ± 21 counts/min/10^{-8} g

The yield of pure, labelled tin tetraphenyl was 32 mg.

Crude lead tetraphenyl	8540 ± 100 counts/min/10^{-8} g
after 1st recrystallization	15720 ± 110 counts/min/10^{-8} g
after 2nd recrystallization	23600 ± 300 counts/min/10^{-8} g
after 3rd recrystallization	23804 ± 310 counts/min/10^{-8} g

The yield of pure labelled lead tetraphenyl was 21.1 mg.

(2) The distribution of activity:

Table I shows the distribution of activity found for both tetraphenyl tin and tetraphenyl lead, assuming that all the activity produced is retained in these three fractions.

TABLE I

DISTRIBUTION OF ACTIVITY IN THE PRODUCTS FROM TRITIUM IRRADIATIONS

	"C_6H_6" (%)	"M $(C_6H_5)_4$" (%)	"$(C_6H_5)_2$" (%)
Sn $(C_6H_5)_4$	61.5 ± 0.4	31.9 ± 0.5	6.50 ± 0.04
Pb $(C_6H_5)_4$	59.7 ± 0.2	37.2 ± 0.1	3.05 ± 0.01

CONCLUSIONS

These results show that a large amount of activity appears in the tritium-labelled by-products formed by the rupture of the metal-carbon bonds and that the purification scheme is sufficiently rigorous to yield a pure labelled product of specific activity high enough to allow the measurement of the very low vapour-pressures expected for this type of compound.

3. Vapour-pressure determinations

In view of the experience gained in this department on the use of a modified Knudsen effusion technique for determining the very low vapour-pressures of radioactive solids, this method was chosen for the proposed measurements.

The apparatus used was essentially that used by CARSON *et al.* [7] with an improved effusion cell and a considerable modification in effusate-collection technique to make it suitable for use with a flow proportional counter.

Basically the principle of the method is to allow a small proportion of the gas molecules which are in equilibrium with the solid to pass through a small hole into a highly evacuated space. KNUDSEN [8] has derived an equation:

$$G = pA\sqrt{M/2\pi RT}$$

containing the weight G grams of the vapour of mol. wt. M, in equilibrium with its condensed phase at a pressure p and at a temperature T^0K, which passes through an orifice of area A cm^2 into an evacuated space in unit time.

EXPERIMENTAL

The apparatus used is shown in Fig. 1. The effusion cell, machined from Nilo-K, an alloy whose coefficient of linear thermal expansion is close to that of Pyrex glass, was mounted in a ground-glass Pyrex socket at one end of a glass tube. This could be evacuated through a side-arm and had a second socket at the upper end into which was fitted a cone carrying the target tube or probe. The probe was internally silvered in order to minimize heat radiation between the target surface and the effusion cell. The target surface was cooled by placing liquid nitrogen in the probe.

In order that the effusate could be assayed in a flow proportional counter, the effusate was collected on a nickel planchet attached to the lower surface of the target tube and, held in position by a polythene ring, made to fit tightly to the bottom of the target tube. Many surfaces were tested with a view to finding one which would strongly absorb the effusate, and the most satisfactory one was

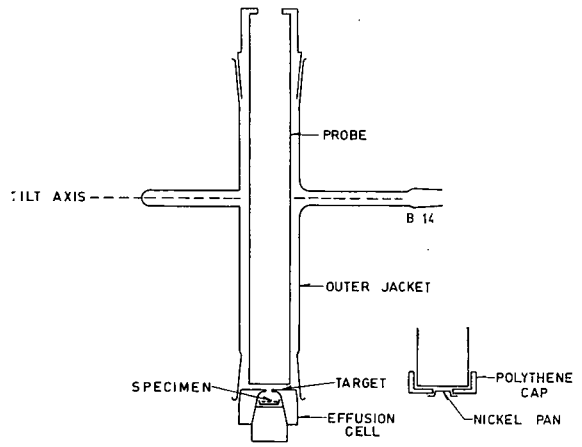

Fig. 1
The target assembly.

a thin coating of graphite spread over a nickel planchet. The surface was prepared by slowly evaporating 0.3 ml of a colloidal solution of graphite in alcohol on the surface of a nickel planchet. After a period of up to 3 h, less than 1% of the effusate was found to have evaporated. This was satisfactory, since counting was usually completed in periods ranging up to a maximum of 30 min.

In a typical run, the effusion cell was thoroughly evacuated and the effusion hole closed before the target tube was introduced. The apparatus was then evacuated to a hard vacuum and the effusion started by tilting the effusion assembly about the tilt axis allowing the effusion hole, incorporated in the cover slip, to move into position over the large hole in the upper surface of the effusion cell.

At the end of the effusion, the assembly was tilted so that the cover-slip sealed off the system in the effusion cell. Dry air was admitted to the system and the nickel planchet removed from the target tube with tweezers, and placed in the proportional counter. After a few minutes, during which the dry methane flowing through the counter had de-frosted the sample, the count was taken until a total of 50000 counts had been recorded. Before each count, a check was made with a standard tritium source to allow for day-to-day variations in counter sensitivity, and corrections were made to the count for background. For duplicate runs the counting rates of effusates collected in equivalent effusion times agreed within the limits of statistical counting error and the heat of sublimation of the material could be calculated from the results at different temperatures. The estimation of the absolute vapour-pressure requires an exact measurement of the mass of effusate on the target. This can be calculated from the observed specific activity of the prepared sample.

Results

The results shown in Table II have been obtained using a sample of tritium-labelled tetraphenyl tin of specific activity 7615 counts/min/10^{-8} g.

TABLE II

TEMPERATURE VARIATION OF THE VAPOUR-PRESSURE OF Sn $(C_6H_5)_4$

Temperature (T°K)	$\sqrt{T}$	Sn $(C_6H_5)_4$ effusing per minute ($=G$ counts/min)	$G\sqrt{T}$	Log $G\sqrt{T}$	$\frac{10^3}{T}$
313	17.692	974.7 ± 4.8	17244 ± 85	4.236 ± 0.003	3.1948
308	17.550	505.1 ± 4.5	8864 ± 79	3.947 ± 0.004	3.2467
308	17.550	492.8 ± 4.5	8648 ± 79	3.936 ± 0.004	3.2467
303	17.407	255.0 ± 2.5	4448 ± 44	3.648 ± 0.004	3.3003

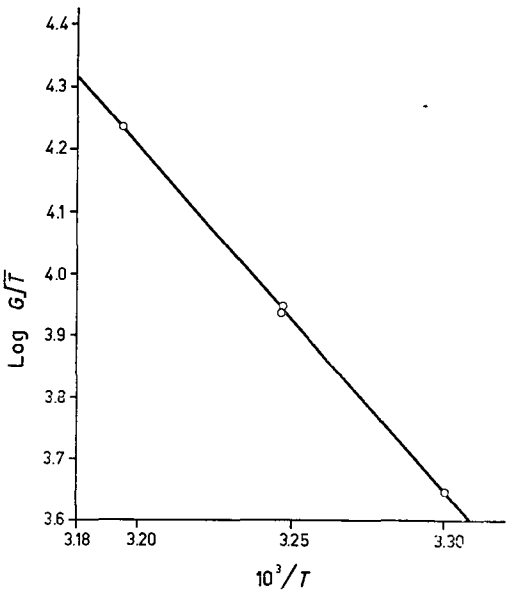

Fig. 2
The latent heat of sublimation of tetraphenyl tin in the temp. range 30°C to 40°C.

The Knudsen equation may be written:

$$p = G/A\sqrt{2\pi R\, T/M} = \text{constant}\ G\sqrt{T}$$

A plot of $\log_{10} G\sqrt{T}$ *versus* $10^3/T$ is shown in Fig. 2, the slope of which indicates that the latent heat of sublimation of tetraphenyl tin in the temperature range 30°C—40°C is 15.8 ± 0.3 kcal/mole. The saturated vapour-pressure can be cal-

culated from the Knudsen equation above by substituting the experimental conditions. Hence at 35°C, $p = 2.88 \pm 0.03 \times 10^{-8}$ mm Hg.

Further work has shown that the value of the vapour-pressure of tetraphenyl tin is 6.34×10^{-9} mm Hg at 25°C.

Similar work on tetraphenyl lead leads to a value of 18.96 ± 0.65 kcal/mole for the latent heat of sublimation and a vapour-pressure of 6.72×10^{-10} mm at 25°C.

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THE ELUCIDATION OF A SECONDARY CHEMICAL INTERACTION IN AN ION-EXCHANGE RESIN BY A RADIOISOTOPE-DILUTION METHOD

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Abstract — Résumé — Аннотация — Resumen

The elucidation of a secondary chemical interaction in an ion-exchange resin by a radioisotope-dilution method. The purpose of the paper is to estimate the dissociation constants of the acid and mildly alkaline forms of the iminodiacetate functional groups linked to the copolymer matrix of the chelating resin Dowex A-1.

The dissociation constants can be estimated by studying the controlled neutralization of the resin by means of a Na^{22}-labelled solution of NaOH in 0.1 *M* NaCl. The concentration of Na^+ and H^+ (or H_3O^+) ions in the resin and solution phases at equilibrium are evaluated from the pH of the solution and the observed distribution of Na^{22} between the two phases, and the dissociation constants are estimated accordingly.

The dissociation constant of the acid form is found to be about 1.2×10^{-3} and that of the alkaline form about 10^{-14}. An unexpected acidic property of the resin, attributable to the nitrogen of the functional group, appears to be demonstrated from these data.

Clarification d'une interaction chimique secondaire dans une résine d'échange d'ions par un méthode de dilution radio-isotopique. L'objet de ce mémoire est l'évaluation de la constante de dissociation de la forme acide et de la forme faiblement basique des groupes fonctionnels iminodiacétate, liés à la matrice de copolymère de la résine chélatante Dowex A-1.

Cette évaluation est faite en étudiant la neutralisation contrólée de la résine au moyen d'une solution marquu au ^{22}Na de NaOH dans du NaCl (0,1 M). A l'équilibre, les constantes de dissociation sont obtenues à partir des mesures des concentrations en H^+ (ou H_3O^+) et en Na^+ dans la résine et la solution. Ces mesures sont faites d'après le pH de la solution et la répartition du ^{22}Na entre les deux phases.

D'après ces travaux, la constante de dissociation de la forme acide serait égale à environ $1{,}2 \cdot 10^{-3}$, et celle de la forme basique de l'ordre de 10^{-14}. Ces données semblent démontrer que la résine possède un caractère acide inattendu attribuable à l'azote du groupe fonctionnel.

Разъяснение вторичного химического взаимодействия в ионообменной смоле методом радиоизотопного растворения. Цель настоящего доклада сводится к оценке константы диссоциации кислотной формы и слабо основной формы функциональных иминодиацетатных групп, связанных с матрицей сополимера циклической смолы Dowex A-1 цепью, замкнутой координационными связями концевых атомотов.

Эта оценка осуществляется путем изучения контролируемой нейтрализации смолы при помощи раствора Na OH в Cl (0,1 M), меченного $Na^{22}Na$. При равновесии константы диссоциации получаются при помощи измерения концентраций H^+ (или H_3O^+) и Na^+ в смоле и растворе. Эти измерения делаются по pH раствора и распределению Na^{22} между 2 фазами.

Согласно этим работам константа диссоциации кислотной формы равна приблизительно $1{,}2 \times 10^{-3}$, а константа диссоциации основной формы — порядка 10^{-14}. Эти данные, как кажется, показывают, что смола приобретает неожиданное кислотное свойство за счет присутствия азота функциональной группы.

Estudio, por dilución radioisotópica, de una interacción química secundaria en una resina de intercambio iónico. La finalidad de la presente memoria es evaluar las constantes de disociación de la forma ácida y de la forma débilmente básica de los grupos funcionales iminodiacetato ligados a la matriz de copolímero de la resina quelante Dowex A-1.

La evaluación se efectúa estudiando la neutralización controlada de la resina por medio de una solución de NaOH, marcada ^{22}Na, en NaCl (0,1 M). En el estado de equilibrio, las constantes de disociación se obtienen midiendo las concentraciones de H^+ (o H_3O^+) y de Na^+ en la resina y en la solución. Las mediciones se efectúan determinando el pH de la solución y la distribución del ^{22}Na entre las dos fases.

Según esos experimentos la constante de disociación de la forma ácida es del orden de $1{,}2 \cdot 10^{+3}$, y la de la forma básica, del orden de 10^{-14}. Estos datos parecen demostrar que la resina posee un carácter ácido inesperado, que puede atribuirse al nitrógeno del grupo funcional.

1. Introduction

The initial object of this research was to evaluate the dissociation constant of the acidic form of the imino-diacetate functional groups attached to the styrene-divinyl benzene copolymer matrix of the Dowex Chelating Resin A-1 [1]. Comparison of this constant with those obtained for similar water-soluble systems was expected to provide some insight on the value of the dielectric constant within the resin gel phase.

The dissociation constant of the acid form of a weakly acidic ion-exchange resin can be evaluated from careful study of the controlled neutralization of the resin with standard alkali, if the following assumptions are made:

(1) the functional groups of the acid from of the resin are so weakly acidic that there are essentially no H_3O^+ ions in the gel-phase; and

(2) the salt form is completely ionized.

The standard mass-action expression [2] for the reaction of the acid form of a resin with Na^+ ion

$$H_3O^+{}_r + Na^+{}_s = Na^+{}_r + H_3O^+{}_s \tag{1}$$

is given by

$$K_1 = \frac{(H_3O^+)_s\,(Na^+)_r}{(H_3O^+)_r\,(Na^+)_s} \tag{2}$$

The subscript symbols "s" and "r" represent the solution and resin phases, respectively, the brackets are used to denote the activity of each substituent that is involved in the reaction, and K_1 is the thermodynamically based equilibrium-constant. When the acid form of the resin is weakly dissociated, the activity of H_3O^+ ion in the resin phase is expressed by

$$(H_3O^+)_r = K_{HR}\,(HR)/(R^-), \tag{3}$$

where K_{HR} is the dissociation constant of the weakly acidic resin form and (HR) and (R^-) are the activities of the acid and salt forms of the resin. Substituting (3) in (2),

$$K_1 = \frac{(H_3O^+)_s\,(Na^+)_r}{[K_{HR}\,(HR)/(R^-)]\,(Na^+)_s}\,. \tag{4}$$

From the two assumptions already mentioned, it follows that

$$C_{R^-} = C_{Nar^+} \tag{5}$$

and

$$C_{HR} = R - C_{Na_r^+} \tag{6}$$

C representing concentration and R representing resin capacity. Then

$$K_1 = \frac{(H_3O^+)_s\,[C_{Na_r^+}\,\gamma^{\pm}_{Na^+R^-}]^2}{K_{HR}\,(R - C_{Na_r^+})(\gamma_{HR})\,(Na^+)_s} \tag{7}$$

where $\gamma^{\pm}_{Na^+R^-}$ is the mean activity coefficient of $Na^+\ R^-$, the ionized salt form of the resin, and γ is the activity coefficient of the undissociated acid-resin form. Rearranging Eq. (7),

$$K_{HR} = \frac{(H_3O^+)_s\,[C_{Na_r^+}\,\gamma^{\pm}_{Na^+R^-}]^2}{K_1\,(R - C_{Na_r^+})\,(\gamma_{HR})\,(Na^+)_s} \tag{8}$$

when the standard states of the various components in the resin and solution phases are defined exactly the same, K_1 becomes equal to unity and

$$K_{HR} = \frac{(H_3O^+)_s\,[C_{Na_r^+}\,\gamma^{\pm}_{Na^+R^-}]^2}{(R - C_{Na_r^+})\,(\gamma_{HR})\,(Na^+)_s} \tag{9}$$

Only the mean activity-coefficient values for the ionized-salt form of the resin and the activity coefficient for the undissociated hydrogen-resin form are not easily available. Osmotic coefficients can, however, be determined for each resin system studied and may be used to calculate these activity coefficient values [3–5]. Measurement of the equilibrium pH with the standard glass electrode approximates the activity of H_3O^+ ion in solution. The activity of NaCl in solution can be accurately evaluated from the activity-coefficient values which have been compiled for NaCl in the literature.

The ~2.6-yr Na^{22} nuclide was employed in equilibration experiments to facilitate this study. In the course of the investigation, a discrepancy was observed between the exchange of Na^+ ion for H_3O^+ in the resin analysed by isotope dilution and the degree of neutralization of the OH^- ion added in an experiment. The lack of stoichiometric exchange was assumed to demonstrate the existence of a second equilibrium attributable to a weakly basic property of the resin. The unshared pair of electrons associated with the nitrogen of the iminodiacetate active groups, which are attached to the styrene-divinyl benzene copolymer matrix of the resin, apparently coordinate with the hydrogen of the water molecule.

2. Experimental

Preparation of resin samples

The acid form of the Dowex Chelating Resin A-1 was prepared from the Na^+-ion form by conversion with M HCl. The resin was then washed free of absorbed HCl with distilled H_2O and was stored in an atmosphere due to 6 M HCl.

Analysis on resin samples

Before an experiment, representative and weighed samples of the resin were placed in *M* NaCl and were titrated with standardized NaOH. The course of the neutralization reaction was followed by pH measurements with a glass electrode, previously calibrated with standard buffer solutions selected to include the pH range of the titration. Aliquot portions of weighed resin-samples were also dried to constant weight at 105°C to evaluate their moisture content.

Equilibration procedure

Weighed samples of resin were added to a solution which was eventually diluted to a definite volume (10.0 ml or 50.0 ml, respectively, in different runs) until 0.1 *M* in NaCl. A measured amount of the 2.6-yr Na^{22}-nuclide was always present. Predetermined quantities of NaOH were added before dilution to provide the desired conversion of the acid form of the resin to the salt form. The stoppered samples were gently shaken at the ambient room temperature for at least 24 h until equilibrium was reached.

Analysis of equilibrium mixtures

The concentrations of H_3O^+ ion in solution and Na^+ ion in both phases at equilibrium were evaluated from the solution pH and the observed distribution of Na^{22} between the resin and solution phases.

The pH measurements were made before phase separation with the solution still in contact with the resin. A stream of nitrogen covered the surface of the solution when the pH of the solution was expected to exceed 4, so as to eliminate any possibility of pH change due to solution of CO_2 from the atmosphere.

The resin and solution phases in a typical equilibrium were first separated to facilitate analysis of Na^+-ion concentration in both phases. The resin was next quantitatively transferred to a glass cylinder fitted with a fritted glass disc. Adherent supernatant solution was completely removed by centrifugation-filtration into a 50-ml conical centrifuge-tube which contained the fritted cylinder. Para-film was used to cover the centrifuge tube to avoid evaporation during centrifugation. The centrifugation was continued for a 30-min interval until constant weight of the fritted cylinder and the resin it contained was achieved. The resin was transferred quantitatively once again to a test tube, which had been previously weighed together with its polyethylene stopper. The stoppered test-tube was then reweighed and the Na^{22} activity which entered the resin phase during the ion-exchange reaction was measured in a $1^1/_4$ in $\times 2$ in well-type sodium-iodide, thallium-activated, gamma-ray scintillation crystal-detector. The resin sample, after activity measurement was finally dried to const. wt. at 105°C to determine its moisture content. This centrifugation-filtration method of resin-solution separation has been fully described by other researchers [6].

A 2.0-ml aliquot portion of the separated solution phase of each equilibrated sample was placed in another test tube and the Na^{22} activity contained therein was measured in the crystal well-counter for comparison with the activity initially present, before equilibration, in a 2-ml aliquot portion of the solution.

Chloride analysis of the equilibrated solutions with standardized $Hg(NO_3)_2$ and *s*-diphenyl carbazone indicator [7] was conducted in several instances to check the discrepancy between removal of Na^+ and OH^- ions from the solutions.

3. Results

The data that were obtained in the experimental programme are presented below in Tables I, II and III together with the pertinent information derived from these data. The quantities of solvent, solute, resin and Na^{22}-activity that were employed at the start of each experiment are also included in the Tables.

The initial and equilibrium composition of resin and solution phases are given in Table I. The number of each experiment is designated in Column 1 of this Table. Columns 2 and 4 give, respectively, the weight of the resin sample employed and the total milliequivalents of replaceable hydrogen corresponding to this weight of resin: the resin capacity is based upon the titration of representative samples with standard 0.1 *M* NaOH to a solution pH of 7.0. A typical titration curve is shown in Fig. 1.

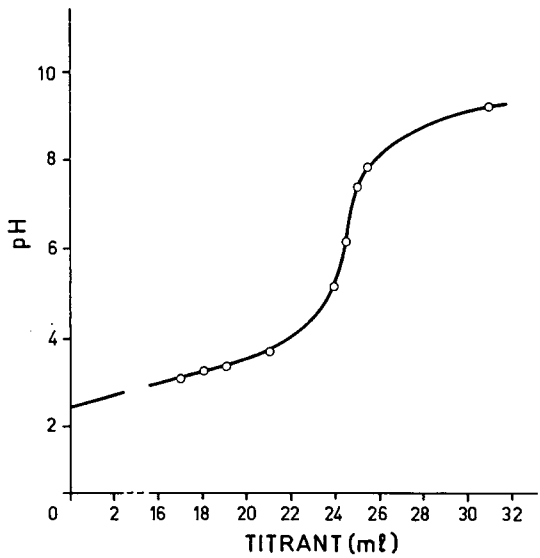


Fig. 1
A typical titration curve for the determination of resin capacity.
1.0691 g of wet resin H form; 0.112 *N* NaOH, NaCl added.

The milliequivalents of NaOH employed in an experiment are given in Column 3. The amount of solvent contained within the resin at equilibrium is presented in Column 7 and is based upon the difference in resin-sample weight measured before and after drying to const. wt. at 105°C. The solution pH value observed at equilibrium is given in Column 10. Column 8 reports the H_3O^+-ion composition of the solution computed from the pH measurement without correction for small deviation from the actual concentration at the ionic strength of the system. The Na^+ ion concentration of the solution at equilibrium is given in Column 9 and is calculated from the Na^+ ion-exchange data that are reported in Table II. The molalities at equilibrium of the undissociated acid-forms and Na^+ salt-forms of the resin are given in Columns 5 and 6, respectively.

The radioactivity measurement data are in Table II. Column 1 of this Table designates the number of the experiment. The total Na^{22} activity in the initial

TABLE I

SUMMARY OF Na^+—H_3O^+ ION EXCHANGE DATA

Run D: aqueous vol. 10.0 ml; Run F: aqueous vol. 50.0 ml; NaCl concn = 0.100*M*

Exp.	Initial Composition			Equilibrium Composition					pH
	H_2R (wet g)	NaOH (meq)	F.F.* (meq)	H_2R (mole × 10^3 g H_2O_r)	Na^+_r (mole × 10^3 g H_2O_r)	H_2O_r (g)	$H_3O^+_S$ (mole/l)	Na^+_S (mole/l)	
D-0	0.1690	0.0000	0.4428	6.14	0.461	0.0561	5.48×10^{-3}	9.74×10^{-2}	2.26
D-1	0.2106	0.0552	0.5518	4.91	0.305	0.0885	3.79×10^{-3}	1.01×10^{-1}	2.42
D-2	0.2205	0.1155	0.5777	3.97	0.401	0.1103	1.35×10^{-3}	1.07×10^{-1}	2.87
D-3	0.1809	0.1422	0.4740	3.20	0.72	0.1008	4.68×10^{-4}	1.07×10^{-1}	3.33
D-4	0.2483	0.2602	0.6505	2.11	0.852	0.1836	3.01×10^{-4}	1.10×10^{-1}	3.52
D-5	0.2804	0.3673	0.7346	1.42	0.935	0.2571	1.99×10^{-4}	1.13×10^{-1}	3.70
D-6	0.2249	0.3535	0.5892	0.95	1.04	0.2471	1.07×10^{-4}	1.10×10^{-1}	3.97
D-7	0.1757	0.3207	0.4582	0.60	1.10	0.2284	5.47×10^{-5}	1.07×10^{-1}	4.26
D-8	0.1102	0.2310	0.2887	0.344	1.18	0.1506	2.94×10^{-5}	1.05×10^{-1}	4.53
D-9	0.1861	0.4388	0.4876	0.168	1.26	0.2893	9.5×10^{-6}	1.07×10^{-1}	5.02
F-0	2.8270	0.0000	7.1240	6.01	0.00515	0.975	1.4×10^{-2}	1.00×10^{-1}	1.86
F-1	3.1239	0.8099	8.0990	5.91	0.0905	1.129	5.24×10^{-3}	1.15×10^{-1}	2.28
F-2	2.3814	1.2053	6.0263	4.77	0.32	0.983	1.31×10^{-3}	1.19×10^{-1}	2.88
F-3	2.2577	1.7068	5.6894	3.26	0.541	1.24	6.29×10^{-4}	1.23×10^{-1}	3.20
F-4	2.7853	2.8076	7.0190	1.94	0.763	2.150	4.15×10^{-4}	1.28×10^{-1}	3.38
F-5	2.6552	3.3456	6.6911	1.14	0.842	2.815	2.88×10^{-4}	1.25×10^{-1}	3.54
F-6	2.7311	4.1294	6.8824	0.854	0.873	3.505	1.90×10^{-4}	1.30×10^{-1}	3.72
F-7	2.9945	5.2823	7.5461	0.813	0.877	3.505	2.50×10^{-4}	1.53×10^{-1}	3.60
F-8	3.3736	6.8012	8.5015	0.202	1.13	5.61	1.0×10^{-5}	1.20×10^{-1}	5.01
F-9	2.5245	5.7255	6.3617	0.1345	1.15	4.22	1.77×10^{-5}	1.26×10^{-1}	4.93

* Resin capacity (1st exchangeable H_3O^+ ion) = 2.62 meq/wet g H_2R; water content = 0.18 g/wet g.

** The H_3O^+ ion composition values are calculated from the observed pH and approximate activities; computations of dissociation-constant values use these numbers later.

TABLE II

RADIOACTIVITY MEASUREMENT DATA

Experiment	Initial Solution	Equilibrium Solution				Na^+ Ion Exchanged	
	Observed Activity (counts/min × Aliquot Factor)	Observed Activity (counts/min × Aliquot Factor)	Corr. Act. (counts/min)	H_2O pick-up (g)	Resin Observed Activity (counts/min)	Solution (%)	Resin (%)
D-0	118965	119450			3071		2.58
D-1		116470			3047		2.56
D-2		115860			4723		3.97
D-3		118150			7545		6.35
D-4		106530			14810	10.5	12.4
D-5		101890			20922	14.3	17.6
D-6		100280			22413	15.8	18.8
D-7		98625			22673	17.2	19.1
D-8		102705			17119	13.6	14.4
D-9	118965	90485			30253	24.0	25.4
F-0	190910	190750		0.475	1952		1.2
F-1		188300		0.57	3351		1.75
F-2		182450		0.55	9690		5.07
F-3	190910	172200		0.84	19045		10.0
F-4	199725	154125	149040	1.65		21.0	
F-5		141775	135310	2.33		28.3	
F-6		134050	125390	3.23		33.5	
F-7	188725	140750	132400	2.96		29.9	
F-8	185650	44650	85185	5.00		54.1	
F-9	185650	110000	101600	3.77		45.8	

and equilibrated solutions is given in Columns 2 and 3 and is based upon the activity measured in a 2.00-ml aliquot sample. The sorption of water by the resin during equilibration is significant only in the F series of experiments because of the large resin samples that were employed. A correction for this volume loss is included in the activity values given in Column 4 for this set of experiments. The correction is not shown for the first few F-runs since these activity data were not employed in the calculation of per cent Na^+ exchange.

The grams of water pick-up that were observed in each of these cases are given in the next column. Column 6 gives the total activity measured directly in the resin phase. Blank spaces in this column indicate the absence of a measurement because of the poor sample geometry, which resulted from the considerable expansion of the resin during equilibration. Values for per cent Na^+ ion-exchange that were computed from the observed Na^{22} activity in the solution and resin phases, respectively, are given in Columns 7 and 8. The resin-based per cent exchange-values are employed in preference to the solution-based values when both measurements are available, so as to limit dependence upon numbers calculated from the difference of two large numbers. For this reason the Na^+ ion-concentration values in the resin phase that are reported in Tables I and III for the D-series of experiments are based on the direct measurement of the Na^{22} activity in the resin phase.

TABLE III

MATERIAL BALANCE STUDY

Exp.	Initial		Equilibrium				Exchange			Stoichiometry Discrepancy		
	Na^+ (meq)	OH^- (meq)	Na^+_r (meq)*	Na^+_r (meq)**	Cl^-_s (meq)	$H_3O^+_s$ (meq)	ΔCl^-_s (meq)	ΔNa^+_s (meq)	ΔH_r*** (meq)	$(\Delta H_r - \Delta Na)$ (meq)*	$\frac{(\Delta H_r - \Delta Na)}{(H_2R)\ (meq/wet)}$	$\frac{(\Delta Cl_s)}{(H_2R)\ (g\ H_2R)^*}$
D-0	1.00	0.00	0.0258			0.055		0.0258	0.055	0.029	0.17	
D-1	1.0552	0.0552	0.027			0.038		0.0270	0.0932	0.046	0.22	
D-2	1.1155	0.1155	0.0442			0.014		0.0442	0.129	0.085	0.38	
D-3	1.1422	0.1422	0.0726			0.0047		0.0726	0.147	0.074	0.41	
D-4	1.2602	0.2602	0.156	0.132		0.0030		0.156	0.263	0.107	0.43	
D-5	1.3673	0.3673	0.240	0.195		0.0020		0.240	0.369	0.128	0.45	
D-6	1.3535	0.3535	0.256	0.214		0.0011		0.256	0.355	0.098	0.44	
D-7	1.3207	0.3207	0.252	0.227		0.00055		0.252	0.321	0.068	0.39	
D-8	1.2310	0.2310	0.177	0.167		0.00029		0.177	0.231	0.053	0.49	
D-9	1.4388	0.4388	0.365	0.345		0.000095		0.365	0.439	0.073	0.39	
F-0	5.00	0.00	0.050		5.92	0.70	0.91	0.050	0.70	0.65	0.23	0.32
F-1	5.8099	0.8099	0.102		6.12	0.26	1.11	0.102	1.07	0.97	0.31	0.34
F-2	6.2053	1.2053	0.314		5.94	0.065	0.93	0.314	1.27	0.96	0.40	0.39
F-3	6.7068	1.7068	0.671		5.97	0.0031	0.96	0.671	1.71	1.04	0.46	0.42
F-4	7.8076	2.8076		1.64	6.20	0.0021	1.19	1.64	2.81	1.17	0.42	0.43
F-5	8.3456	3.3456		2.36	6.12	0.0014	1.11	2.36	3.35	0.98	0.37	0.42
F-6	9.1294	4.1294		3.06	5.84		0.83	3.06	4.13	1.07	0.39	0.30
F-7	10.2823	5.2823		3.07	6.64		1.63	3.07	5.28	2.21	0.74	0.54
F-8	11.8012	6.8012		6.37	6.01		1.00	6.37	6.80	0.43	0.13	0.30
F-9	10.7255	5.7255		4.87	5.93		0.92	4.87	5.72	0.85	0.36	0.34

(*) Calculated from activity measured in resin phase.
(**) Calculated from activity measured in solution phase.
(***) Sum of meq OH^- added initially and meq H_3O^+ observed at equilibrium.

The material balance data are presented in Table III and lead to the disclosure that more OH^- ion is neutralized during equilibration than can be accounted for by the production of H_3O^+ ion due to Na^+ ion-exchange. Substantiation of this discrepancy in the stoichiometry is provided by the observation of an increase in Cl^- ion-concentration of the solutions during their equilibration in the F-series of experiments.

Column 1 of Table III designates the number of an experiment. The milliequivalents of Na^+ and OH^- ions in the solution at the start of an experiment are given in Columns 2 and 3. The milliequivalents of Na^+ ion in the resin and of Cl^- and H_3O^+ ions in solution at equilibrium are given in Columns 4 to 7.

The Na^+ ion composition of the resin phase that is reported in Column 4 is based upon the per cent Na^+ ion exchange data that were obtained from direct measurement of Na^{22} activity in the resin phase; the values reported in Column 5 are due to measurements of the Na^{22} activity in the solution phase.

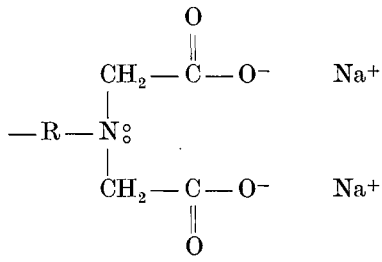
The observed change of the Cl^- and Na^+ ion concentrations in solution and the exchangeable hydrogen in the resin phase during equilibration is given in Columns 8, 9 and 10, respectively. The change in exchangeable hydrogen is calculated from the sum of milliequivalents of OH^- consumed and the H_3O^+ ions eventually entering the solution at equilibrium. The difference between Na^+ ion exchange and net hydrogen removal from the resin is given in Column 11. These data should be compared with the observed values for the increase in Cl^- ion that are presented in Column 8. A more convenient comparison of the stoichiometric discrepancy observed in these two different measurements is presented on a unit-weight basis in Columns 12 and 13. The agreement between the measurements where comparison is made is fair except in experiments F–0, F–6, F–7 and F–8.

Careful scrutiny of the material balance data shows that the stoichiometric discrepancy that is observed in the D series of experiments, increases asymptotically with neutralization of the acid-form of the resin to a value of about 0.43 meq/g of wet hydrogen-form resin. Scattering of the data upon reaching this value is due to the fact that this number is the difference between two larger numbers associated with Na^+ ion-removal and the appearance of H_3O^+ in solution. Small errors in the direct measurement of Na^+ ion entry into the resin, the determination more susceptible to error, are thus magnified and reflected in the values obtained.

The same general behaviour of the data is observed in the F series of experiments until run R-5. Up to this point the data based on Cl^- ion-analysis are in reasonably good agreement with the less direct and less accurate analysis employed in the D series of experiments. Beyond this point, however, there is too much scattering of the data and little agreement between the two methods of stoichiometric analysis. The scatter of the data may be due to the fact that the resin samples employed in these particular experiments were not uniform and contained variable amounts of physically sorbed HCl. The resin was stored in an open beaker that was contained in a desiccator partially filled with 6 *M* HCl. An HCl sorption-gradient varying with the depth of the resin in the beaker probably existed once the first resin samples were removed. Even though the resin was stirred in the beaker before sampling, the much larger samples employed in the F-series of experiments may have exposed this non-uniformity. The reason for internal disagreement is not known.

4. Discussion

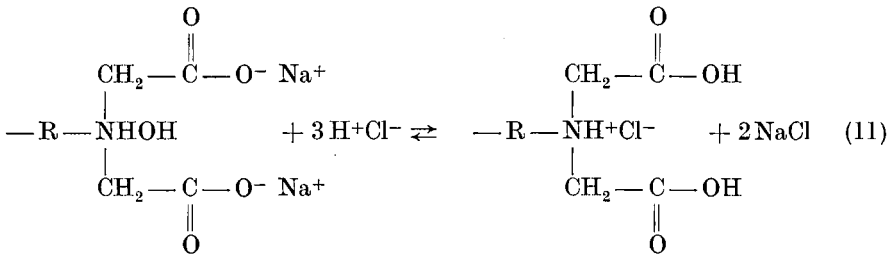
The Dowex Chelating Resin A-1 has been described as having imino-diacetate functional groups attached to a styrene-divinyl benzene copolymer matrix and its sodium salt has been depicted as follows:



(10)

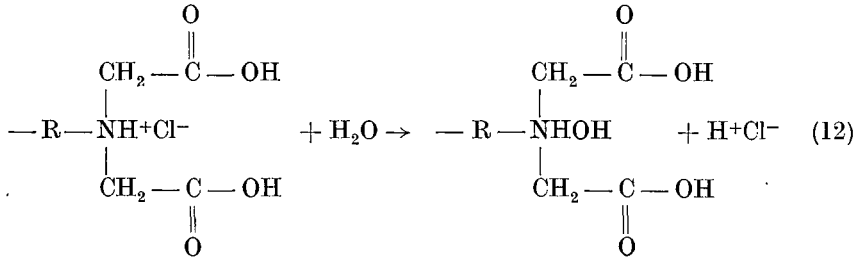
the symbol R being used to represent the polymer matrix. However, on the basis of the experimental data presented in the previous section, the resin appears to exhibit "zwitter – ion" properties and the unshared pair of electrons on the N atom is undoubtedly coordinated with the hydrogen of the water molecule. The following operational view of the resin appears to correlate well with its observed behaviour.

When the disodium salt of the resin is reacted with HCl, the weakly basic portion of the resin is converted to the hydrochloride salt while the diacidic form of the resin is concurrently produced.



(11)

Washing the diacidic form of the resin with H_2O then results in the hydrolysis of the hydrochloride salt and eventually complete conversion to the weak base.



(12)

The extra HCl that was observed to be associated with the resin in the experiments discussed previously is thus due to the hydrochloride salt form of the weakly basic portion of the resin as well as to Donnan absorbed acid originating in the HCl atmosphere to which the resin was exposed during its storage. The

Cl^- ion of the resin is removed during agitation with 0.1 *M* NaCl solution until equilibrium is achieved between the resin and the resultant HCl – NaCl aqueous solution. Equilibration of the resin with increasing quantities of OH^- ion eventually results in the complete hydrolysis of the hydrochloride salt, as is evidenced by the eventual constancy of the stoichiometric discrepancy between the entry of Na^+ ion into the resin and H_3O^+ and/or the appearance of Cl^- ion in the solution that is observed in experiments D-4 to D-9 inclusively.

This interpretation of the data is supported by the results of the brief experiment described below. Approximately six 1.0-g samples of the hydrogen form of the resin were washed with distilled water until there was no Cl^- ion in the wash solution. The 6 samples were then equilibrated with 0.0100 *M*, 0.0300 *M*, and 0.100 *M* HCl and NaCl solution, respectively. Chloride analysis of each supernatant solution then showed that considerably less sorption of NaCl than HCl had occurred. The ratio of HCl to NaCl sorption at the three concentration values was 34, 8.5, and 7.2.

Evaluation of dissociation constants for the weak base and first acid of the resin

The equilibrium composition data that were obtained from the series of experiments D-4 to D-9 and F-4 to F-9 have been used in Eq. (9) to calculate the first acid dissociation constant of the resin. Data obtained from the D-0 to D-3 and F-0 to F-3 experiments are not included in these calculations because of the complicating presence of free Cl^- ion in the resin phase and because the assumption of negligible H_3O^+ ion-concentration in the resin phase is not valid when the resin is essentially in the acid form, as it was in these experiments. Furthermore, the activity coefficient values $\gamma_{Na^+}{}_r$, $\gamma_{R^-}{}_r$, and $\gamma_{Na^+}{}_s$ are not employed in the calculation.

The results of these calculations are presented in Table IV together with the necessary data. Except for experiment F-8, which has produced consistently anomalous results throughout, the constant that is calculated is uniformly constant in both sets of experiments. The average value that is calculated is about 1.2×10^{-3}, excluding the F-8 result.

Table IV

FIRST ACID-DISSOCIATION CONSTANT
($H_2R \rightarrow HR^- + H^+$)

Experiment	H_2R (mole/10^3g H_2O)	$HR^- = Na^+{}_r$ (mole/10^3g H_2O)	$H^+{}_s$ (mole/l)	$Na^+{}_s$ (mole/l)	$K_1 \times 10^{-4}$
D-4	2.11	0.852	3.01×10^{-4}	1.10×10^{-1}	9.4
D-5	1.42	0.935	1.99×10^{-4}	1.13×10^{-1}	10.9
D-6	0.95	1.04	1.07×10^{-4}	1.10×10^{-1}	11.1
D-7	0.60	1.10	5.47×10^{-5}	1.07×10^{-1}	10.3
D-8	0.344	1.18	2.94×10^{-5}	1.05×10^{-1}	11.3
D-9	0.178	1.26	9.50×10^{-6}	1.07×10^{-1}	8.4
F-4	1.94	0.763	4.15×10^{-4}	1.28×10^{-1}	9.8
F-5	1.14	0.842	2.88×10^{-4}	1.25×10^{-1}	14.6
F-6	0.854	0.873	1.90×10^{-4}	1.30×10^{-1}	13.1
F-7	0.813	0.877	2.50×10^{-4}	1.53×10^{-1}	15.4
F-8	0.202	1.13	1.00×10^{-5}	1.20×10^{-1}	5.4
F-9	0.132	1.15	1.77×10^{-5}	1.26×10^{-1}	17.2

Using this value, the dissociation constant of the weak base has been estimated to be of the order of 10^{-14}. The data from experiments D-0 to D-3 and F-0 to F-2 have been employed for this computation in the following manner.

The dissociation of the weak base may be depicted as

$$RNHOH \rightleftarrows RHN^+ + OH^- \tag{13}$$

and

$$K_b = (RNH^+)\ (OH^-)/RNHOH. \tag{14}$$

Assuming the hydrochloride salt-form to be completely ionized, the concentration of Cl^- ion in the resin must be equal to the concentration of RNH^+. The Cl^- ion-concentration at equilibrium for this calculation is taken to be equal to the difference between its initial concentration-level (0.43 meq/g of wet hydrogen-form resin $\times$ initial weight of resin) and the observed increase of Cl^- ion-concentration in the solution at equilibrium (ΔCl^-).

The OH^- ion-concentration of the resin may then be estimated from the H_3O^+ ion-concentration in the resin-phase evaluated from the first acid-dissociation constant as shown below

$$H_3O^+ = K_a\,(H_2R)/(HR^-). \tag{3}$$

The value of H_3O^+ ion so obtained, though it will suffice for an estimate of this order of magnitude, is only approximate since the value of HR^- is based upon the assumption that $HR^- = Na^+$. However, the HR^- ion-concentration due to dissociation of H_2R, is not negligible when it is predominantly in the acid form.

Assuming the dissociation constant of H_2O, K_w, to be unchanged in the resin phase,

$$OH^- = K_w/H_3O^+. \tag{15}$$

Finally, the concentration of RHNOH can be estimated from the experimentally determined values for the concentration of the undissociated acid-form of the resin, the concentration of the salt-form, and the concentration of the Cl^- ion in the resin. The total molal capacity of the basic form of the resin is independent of the dissociation of the first acid and

$$RNHOH = H_2R + HR^- \tag{16}$$

TABLE V

DISSOCIATION CONSTANT OF BASIC RESIN FORM

Experiment	Cl^-_r	H_2R	HR^-_3	RNHOH	OH^-_r	K_D
	(molality; mole/10^3 g solvent)					
D-0	0.78	6.14	0.461	5.79	6.2×10^{-13}	0.8×10^{-14}
D-1	0.50	4.91	0.305	4.70	5.1×10^{-13}	5.5×10^{-14}
D-2	0.088	3.97	0.401	4.28	8.3×10^{-13}	1.7×10^{-14}
D-3	0.038	3.20	0.72	3.88	1.9×10^{-13}	1.8×10^{-14}
F-0	0.308	6.01	0.051	5.75	7.1×10^{-14}	0.4×10^{-14}
F-1	0.204	5.91	0.091	5.80	1.3×10^{-13}	0.4×10^{-14}
F-2	0.092	4.77	0.32	5.00	5.6×10^{-13}	1.0×10^{-14}

When the hydrochloride salt-form exists,

$$RNHOH = H_2R + HR^- — RNH^+$$

or

$$RNHOH = H_2R + HR^- — Cl^-_r \qquad (17)$$

The pertinent data and the estimated values for the dissociation constant of the weak base are presented in Table V. The dissociation constant of the weakly basic form of the Dowex-Chelating Resin A-1 is about 10^{-14}.

ACKNOWLEDGEMENT

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SOLUBILITY OF METALLIC MERCURY IN ORGANIC SOLVENTS*

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Abstract — Résumé — Аннотация — Resumen

Solubility of metallic mercury in organic solvents. The solubilities of metallic mercury at 25°C in the solvents carbon tetrachloride, 2, 2, 4-trimethylpentane, *n*-decane, benzene, toluene, nitrobenzene, chlorobenzene and bromobenzene have been determined by the use of Hg^{203} tracer. Measurements were made either by shaking mercury metal of known specific activity with the solvent, or by measuring the distribution coefficient of the metal between the solvent and water and combining this measurement with the solubility of mercury in water, or by both methods. Radioactivity was measured by counting precipitated samples with a GM counter or liquid aliquots with a well-type scintillator counter. All solubilities were in the range (4.6 to 16)$\times 10^{-6}$g atoms/l. For *n*-decane, toluene and chlorobenzene, the temperature dependence of the solubility was determined over the range 0 to 45°C.

The Hildebrand-Scott theory of solubility has been applied to these systems for comparison. For the aliphatic hydrocarbons, the solubilities predicted by theory are within 35% of those observed, but for the other solvents, the predicted values are 4 to 18 times larger than those observed. Modification of the theory gives better agreement for some solvents but poorer agreement for others.

Curves of log C (solubility) *vs.* $1/T$ were straight lines with slopes similar to those obtained from the Hildebrand-Scott theory but displaced from those curves. The slopes of the curves were used for the calculation of heats and entropies of solution. Entropies were also calculated from curves of log C *vs.* log T. The two sets of entropy values were in agreement with each other and were within one to four entropy units of the ideal entropies of mixing.

Solubilité du mercure métallique dans les solvants organiques. Les auteurs ont déterminé la solubilité du mercure métallique à 25°C dans les solvants suivants: tétrachlorure de carbone, triméthylpentane 2, 2, 4, *n*-décane, benzène, toluène, nitrobenzène, chlorobenzène et bromobenzène en utilisant le mercure-203 comme radioindicateur. Ils ont fait les mesures soit en mélangeant du mercure métallique d'une activité spécifique connue avec le solvant et en agitant, soit en mesurant le le coefficient de distribution du métal entre le solvant et l'eau et en combinant cette mesure avec la solubilité du mercure dans l'eau, soit en employant simultanément les deux méthodes. Ils ont mesuré la radioactivité en comptant soit des échantillons de précipité avec un compteur de Geiger-Muller, soit des liquides aliquotes avec un compteur à scintillations à puits. Toutes les valeurs de solubilité étaient comprises entre $4{,}6 \cdot 10^{-6}$ et $16 \cdot 10^{-6}$ atomes g/l. Pour le *n*-décane, le toluène et le chlorobenzène, ils ont déterminé l'influence de la température sur la solubilité, de 0 à 45°C.

Ils ont appliqué à ces systèmes la théorie de Hildebrand-Scott sur la solubilité, à des fins de comparaison. Pour les hydrocarbures aliphatiques, les valeurs de la solubilité prévues par la théorie sont égales à 35% des valeurs observées; en revanche, pour d'autres solvants les valeurs prédites sont 4 à 18 fois plus élevées que les valeurs

* Work performed in the Ames Laboratory of the US Atomic Energy Commission.

observées. En modifiant la théorie, on obtient une meilleure concordance pour certains solvants, mais la concordance est moins bonne pour d'autres.

Les courbes de log C en fonction de $1/T$ (C étant la solubilité) sont des droites dont la pente est la même que celle des droites obtenues par la théorie de Hildebrand-Scott, mais déplacées par rapport à celles-ci. Les auteurs ont utilisé les pentes des courbes pour calculer les quantités de chaleur et d'entropie de la solution; ils ont également calculé les quantités d'entropie à partie des courbes de log C en fonction de log T. Les deux séries de quantités d'entropie concordent l'une avec l'autre et diffèrent de une à quatre unités d'entropie de la quantité d'entropie idéale du mélange.

Растворимость металлической ртути в органических растворителях. Определялась растворимость металлической ртути при температуре 25°C с помощью индикатора Hg^{203} в растворителях четыреххлористого углерода, 2,2,4-триметилпентана, *n*-декана, бензола, толуола, нитробензола, хлорбензола и бромбензола. Измерения осуществлялись либо путем взбалтывания металлической ртути известной удельной активности с растворителем, либо измерением коэффициента распределения металла между растворителем и водой и объединением этого измерения с растворимостью ртути в воде или и тем и другим методом. Радиоактивность измерялась подсчетом осажденных образцов счетчиком Гейгера-Мюллера или жидких расслоений сцинтилляционным счетчиком типа колодца. Все растворимости были порядка (4,6 до 16) $\times 10^{-6}$ грамм-атомов/л. Температурная зависимость растворимости для *n*-декана, толуола и хлорбензола определялась порядком от 0 до 45°C.

Для сравнения к этим системам применялась теория растворимости Хильдебранда-Скотта. Для углеводородов алифатического ряда предсказанные теорией растворимости составляют 35% тех, которые удалось наблюдать, но для других растворителей предсказанные величины являются в 4—18 раз больше тех, которые пришлось наблюдать. Изменение теории дает лучшее согласование для одних растворителей и худшее для других.

Кривые log C (растворимость) против $1/T$ были прямыми линиями с наклонами, которые сходны с наклонами теории Хильдебранда-Скотта, но со смещением от этих кривых. Наклоны кривых использовались для вычисления тепла и энтропии раствора, а энтропии также вычислялись из кривых log C против log T. Две серии значений энтропии согласовывались друг с другом, а также находились в пределах от одного до четырех единиц энтропии наилучшего смешения энтропии.

Solubilidad del mercurio metálico en solventes orgánicos. Usando ^{203}Hg como trazador, los autores han determinado la solubilidad del mercurio metálico, a 25 °C, en los siguientes solventes: tetracloruro de carbono; 2,2,4-trimetilpentano; *n*-decano; benceno; tolueno; nitrobenceno, clorobenceno y bromobenceno. Las mediciones se efectuaron sea agitando mercurio metálico de actividad específica conocida con el solvente, sea determinando el coeficiente de distribución del metal entre el solvente y el agua y combinando esta determinación con la de la solubilidad del mercurio en agua, sea aplicando los dos métodos sucesivamente. La radiactividad se determinó recontando las muestras del precipitado con un contador Geiger-Müller, o recontando partes alícuotas del líquido con un contador de centelleo del tipo de pozo. Los valores de la solubilidad resultaron del orden de 4,6 a 16×10^{-6} átomos g/l. En el caso del *n*-decano, del tolueno y del clorobenceno, se determinó la relación de dependencia entre la solubilidad y la temperatura desde 0 hasta 45 °C.

Para comparar los resultados se aplicó a estos sistemas la teoría de la solubilidad de Hildebrand-Scott. En el caso de los hidrocarburos alifáticos, los valores de la solubilidad calculados teóricamente no se alejan más de un 35% de los observados, pero para los otros solventes los valores teóricos son de 4 a 18 veces mayores que los observados. Modificando la teoría se obtiene una concordancia mayor para unos solventes y menor para otros.

Determinando el log C (solubilidad) en función de $1/T$ se obtienen líneas rectas cuya inclinación es análoga a las de las curvas obtenidas con la teoría de Hildebrand-Scott, pero que no coinciden con estas últimas. Las inclinaciones de las curvas se utilizaron para calcular los calores y las entropías de la solución; estas últimas se calcularon también partiendo de las curvas de log C en función de log T. Las dos series de valores de la entropía concuerdan entre sí y sólo se alejan de 1 a 4 unidades entrópicas de los valores ideales de la entropía de las mezclas.

1. Introduction

That mercury dissolves to some extent in various liquids was noticed in 1908 by CHRISTOFF [1] who detected mercury in water, aqueous solutions of potassium hydroxide and sulphuric acid and in organic liquids such as alcohol and benzene. BONHOEFFER *et al.* in 1929 [2] demonstrated conclusively by means of ultraviolet absorption that free mercury was present in water after equilibration and estimated its solubility to be roughly that of a noble gas. Later they studied [3] [4] the absorption spectrum of mercury dissolved in water, methanol and hexane as a function of temperature. STOCK *et al.* [5] measured the solubility of mercury in air-free water as a function of temperature and in dilute potassium hydroxide, potassium chloride, benzene, blood and egg albumen. The solubility in water was found to be 0.02 $\mu g/cm^3$ at 30°C, 0.3 $\mu g/cm^3$ at 85°C and 0.6 $\mu g/cm^3$ at 100°C. MOSER [6] used radioactive tracers to measure the solubility of free mercury in several organic liquids. His results and methods will be discussed later in this work.

The use of tracers to measure solubilities was first proposed and tried by HEVESY *et al.* [7] who measured the solubility of PbS and $PbCrO_4$ with Pb^{210} (RaD) and suggested that tracers might prove a useful tool for this purpose, especially for slightly soluble salts. Since then, a number of reviews of the use of tracers for determining solubility have appeared [8–11].

In the present work, solubility measurements were made by a direct determination of the specific activity of the solution. In a second method the solubility was inferred from studies of the distribution of mercury between the organic liquid and dilute nitric acid. The measured distribution coefficients and solubility of mercury in dilute nitric acid were used to calculate the solubility of mercury in the organic phase. The two methods of measurement gave comparable results.

2. Experimental

To carry out a determination, a globule of mercury containing Hg^{203} was placed in about 50 ml of organic solvent in a 100-ml volumetric flask and agitated in a constant-temperature water-bath. Samples were taken for analysis until the solution appeared to be at equilibrium. Analyses were made by GM-counting solid precipitates or by scintillation-counting liquid aliquots.

In the solid-sample technique, aqueous mercuric-nitrate-carrier solution was added to a 0.5-ml aliquot of the organic liquid. Enough acetone was added to make the system homogeneous and the solution was allowed to stand for 15 to 30 min to ensure complete exchange between the carrier and radioactive mercury.

Preliminary experiments had indicated that 6 to 10 min would be sufficient. The acetone and organic solvent were evaporated with a stream of warm air and the mercury was precipitated with ammonium sulphide and centrifuged. After careful decantation, a few drops of dilute aqueous sodium hydroxide solution were added to form a slurry which was transferred to a stainless steel planchet, evaporated to dryness and counted. The method was standardized by applying the same procedure to the original radioactive mercuric nitrate solution. This solution had previously been standardized by precipitation with sulphide and by titration with potassium thiocyanate. Details of this method of analysis are given by MOSER [6].

In the second method, a 0.5-ml aliquot of the solution was delivered with a rinse to a 5-ml volumetric flask. The flask was filled to volume with benzene and the solution transferred to a scintillation-counting tube with a rinse which gave a total volume of 7 ml. This method of analysis was calibrated by employing the same procedure with the original radioactive mercuric-nitrate solution but diluting it with water.

In this measurement, the 0.28 MeV γ-radiation of the Hg^{203} was counted. The amount of this radiation absorbed in the small liquid sample would be only a few per cent of the total. A change in the density of the solution from that of water to benzene would lead to a small change in the amount absorbed, but this would affect the counting rate by considerably less than 1% and, thus, would not introduce any observable error. This conclusion was demonstrated by measuring a sample of the Hg^{203} in solutions of densities ranging from 0.875 to 1.463.

In the extraction experiments, 15 ml each of aqueous phase and Hg-saturated organic phase were put into flasks. The aqueous phase was 0.1 *M* in nitric acid and 0.007 *M* in hypophosphorous acid. The flasks were agitated in the constant-temperature water-bath and both phases were analysed by one of the above methods. Samples were taken until the distribution coefficient remained at a constant value.

Previous experiments had shown that mercury slowly undergoes reactions other than simple solution in pure water; most probably oxidation and hydrolysis processes. However, a small amount of hypophosphorous acid, to keep a reducing atmosphere, and dilute acid, to prevent hydrolysis, gave reproducible results for the solubility. Constant values of 3×10^{-7} mole/l were obtained over a range of hypophosphorous acid concn from 10^{-3} to 10^{-1} *M*. This value for the solubility in water was multiplied by the distribution coefficients to obtain the indirect measurement of the solubilities in the organic liquids.

MATERIALS

Benzene was repurified by stirring with repeated portions of conc. sulphuric acid and then redistilling. The nitrobenzene was steam-distilled from a dilute sulphuric-nitric acid solution and redistilled.

Research grade toluene and 2, 2, 4- trimethylpentane (*iso*octane) and *pure* grade *n*-decane were used without further repurification.

Bromobenzene was found to cause a black deposit on the surface of the mercury after a few hours and, after a few days a white, finely divided precipitate. Re-

purification consisted of shaking with stannous chloride and redistilling. Chlorobenzene was used without further treatment.

Carbon tetrachloride was shaken with an aqueous solution of sodium sulphate, dried by passing it through a silica gel column, and redistilled.

The mercuric nitrate containing Hg^{203} had a half-life of 47.0 d, which agrees with published values. Finely divided metal, obtained by adding a few drops of hypophosphorous acid to the solution, was coagulated into a globule by stirring with conc. hydrochloric acid. The globule was washed and dried.

3. Experimental results

Studies at 25°C

The solubilities of mercury at 25°C in the various solvents are listed in Table I. The second column contains values obtained from measurements of the distribution coefficient for the organic-aqueous systems. The third column lists values as measured by Moser [6]. The agreement between the two methods of measurement, and between the previous values and those obtained in the present study is quite satisfactory.

Variation of solubility with temperature

The solubilities of free mercury as a function of temperature over the range 0–45°C in toluene, chlorobenzene, and *n*-decane are given in Table II and Fig. 1.

Table I

THE SOLUBILITY OF MERCURY AT 25°C

Solvent	Concn (mole/l) × 10^6		
	Direct Measurement	Indirect Measurement	Moser
carbon tetrachloride	7.5 ± 0.1	7.5	7.5 ± 0.3
*iso*octane (trimethylpentane)	4.6 ± 0.1	4.7	
n-decane	7.0 ± 0.1		
benzene	11.4 ± 0.3	11.1	12.0 ± 0.6
toluene	13.4 ± 0.1		12.5 ± 0.5
nitrobenzene		8.8	9.3 ± 0.7
chlorobenzene	12.5 ± 0.1		
bromobenzene	16.0 ± 0.3		

From the slopes of the curves of log x *vs.* $1/T$ (Fig. 1), the partial molal enthalpies of solution were calculated using the relation:

$$\Delta \bar{H}_1 = -2.303\, R\, (\Delta \log x / \Delta\, 1/T).$$

These values are listed in Table II for the three solvents.

TABLE II

THE SOLUBILITY OF MERCURY AS A FUNCTION OF TEMPERATURE

Temp. (°C)	Concn (mole/l) × 10^6		
	n-decane	toluene	chlorobenzene
0	2.1 ± 0.1	3.4 ± 0.1	2.8 ± 0.1
10	3.0 ± 0.1	5.1 ± 0.1	5.0 ± 0.1
15	4.5 ± 0.1	6.6 ± 0.1	6.8 ± 0.1
20	4.9 ± 0.1	8.5 ± 0.1	8.4 ± 0.1
25	7.0 ± 0.1	13.4 ± 0.1	12.5 ± 0.1
30	8.6 ± 0.1	14.4 ± 0.1	
35	9.6 ± 0.1	16.5 ± 0.1	19.3 ± 0.1
45	13.3 ± 0.1	26.9 ± 0.2	
$\Delta \bar{H}_1$	$+7570 \pm 360$	$+8380 \pm 400$	$+9500$ ± 290 cal/mole

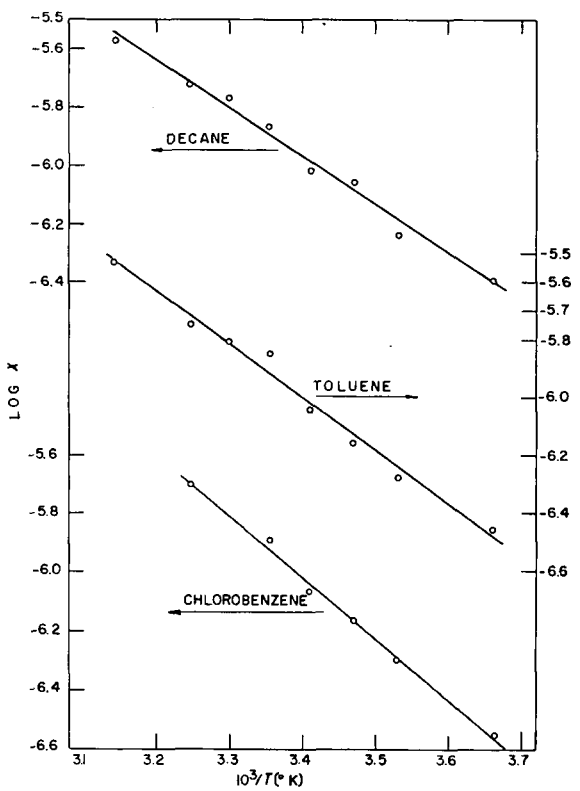

Fig. 1

Effect of temperature on the solubility of mercury in *n*-decane, toluene and chlorobenzene.

4. Theory of Hildebrand and Scott

It was interesting to attempt to correlate the above results with the "solubility parameter" theory of HILDEBRAND *et al.* The theory was introduced by papers in 1927 [12] and 1929 [13], in which the simplifying assumption was made that the molecules in a regular solution were distributed randomly, leading to an essentially ideal entropy of mixing, which was then calculated for such a random arrangement.

The justification of this assumption of an ideal entropy of mixing, and its consequences are discussed thoroughly in the HILDEBRAND-SCOTT monograph on solubility [14] and will not be treated here. The ideal entropy of mixing can be expressed as:

$$\Delta S = -R(n_1 \ln x_1 + n_2 \ln x_2) \tag{1}$$

if the free volumes of the two components are assumed to be the same. As shown by FLORY [15] and HUGGINS [16], the entropy change for components of widely differing volumes becomes:

$$\Delta S = -R(n_1 \ln \varphi_1 + n_2 \ln \varphi_2) \tag{2}$$

f the free volumes are assumed to be proportional to the molar volumes. In these expressions, n represents the number of moles, x the mole fraction, and φ the volume fraction.

Eq. (1) has been found to be generally applicable when the molar volumes of solvent and solute are similar. Since these usually lie between 60 and 150 ml, this is justified in general. In the present system the molal volumes of the solvents are 6 to 13 times that of the solute, so that a test of the two equations can be made under rather extreme conditions.

The heat of mixing for a solute randomly distributed in a solvent was studied by SCATCHARD in 1931 [17]. He assumed:

(1) that the mutual energy of two molecules depends only on the distance between them and on their relative orientation and not on the nature of the other molecules between or around them, or on the temperature;
(2) that the distribution of the molecules in position and in orientation is random; and
(3) that the change of volume on mixing at constant pressure is zero.

HILDEBRAND [14 p. 123] pointed out that the first assumption is essentially that of the additivity of the energies of molecular pairs, which although not exactly true for dispersion forces, has been quite successful as the basis for nearly all theories of liquids and solutions. The second assumption ignores the ordering effect of molecular shapes and differences in intermolecular potentials.

These assumptions lead to an expression for the "cohesive energy" of a mole of liquid mixture:

$$-U_m = (c_{11} V_1^2 x_1^2 + c_{22} V_2^2 x_2^2 - 2c_{12} V_1 V_2 x_1 x_2)/(V_1 x_1 + V_2 x_2), \tag{3}$$

and for pure components:

$$-U_1 = c_{11} V_1; \quad -U_2 = c_{22} V_2. \tag{4}$$

The energy of mixing is then:

$$\Delta U^m = U_m - U_1 - U_2 = (x_1 V_1 + x_2 V_2)(c_{11} + c_{22} - 2c_{12})\, \varphi_1 \varphi_2. \tag{5}$$

With the assumption that c_{12} is the geometric mean of c_{11} and c_{22},

$$\Delta U^{M} = (x_1 V_1 + x_2 V_2)\left[c_{11}^{\frac{1}{2}} - c_{22}^{\frac{1}{2}}\right]^2 \varphi_1 \varphi_2. \tag{6}$$

The cohesive energy times c_{11} and c_{22} are expressed in terms of their square roots and given the symbol, δ, called a solubility parameter. This has been evaluated in several ways, but the most successful has been by assuming that the vapour above the liquid is ideal so that $-U$ becomes ΔU^{V}, the energy of vaporization. Thus:

$$\delta = c^{\frac{1}{2}} = \left(\frac{\Delta U^{V}}{V}\right)^{\frac{1}{2}}$$

and Eq. (6) becomes:

$$\Delta U^{M} = (x_1 V_1 + x_2 V_2)(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2. \tag{7}$$

From this the partial molal energy of mixing can be derived as

$$\Delta \bar{U}^{M} = V_1 \varphi_2^2 (\delta_1 - \delta_2)^2. \tag{8}$$

Since it has been assumed that the volume change on mixing is zero,

$$\Delta \bar{H}_1 = \Delta \bar{U}_1 + p\Delta V = \Delta \bar{U}_1.$$

By using the partial molal-entropy change for a regular solution, $\Delta \bar{S}_1 = -R ln x_1$, the partial (Gibbs) free energy of mixing can be expressed as:

$$\Delta \bar{G}_1^{M} = RT ln a_1 = V_1 \varphi_2^2 (\delta_1 - \delta_2)^2 + RT ln x_1. \tag{9}$$

From this, the solubility can be calculated in terms of the molal volume and the solubility parameters. If the maximum or Flory-Huggins value of the entropy change is used (Eq. 2) the partial molal entropy becomes:

$$\Delta \bar{S}_1^{M} = -R\{ln \varphi_1 + \varphi_2 [1 - (V_1/V_2)]\}, \tag{10}$$

which reduces to:

$$\Delta \bar{S}_1^{M} = -R\left[\ln x_1 + \ln \frac{V_1}{V_2} + 1 - \frac{V_1}{V_2}\right] \tag{11}$$

for small values of x_1, giving for the free energy:

$$\Delta \bar{G}_1 = V_1 \varphi_2^2 (\delta_1 - \delta_2)^2 + RT\left(\ln x_1 + \ln \frac{V_1}{V_2} + 1 - \frac{V_1}{V_2}\right). \tag{12}$$

In spite of all of the assumptions which have been made in deriving Eq. (9), it has been used with marked success in estimating vapour-pressures of solutions, immiscibilities of metals, solubilities of both liquids and solids in liquids and a number of other properties. The simple theory fits most free energy data on binary systems of non-polar non-electrolytes to within 10 – 20% of thermal energies or to within experimental uncertainty of the solubility parameter itself. Unfortunately this uncertainty can be quite significant.

5. Calculations

From Eq. (8), with subscript 1 referring to solutes, one obtains for a saturated solution:

$$\ln x_1 = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{13}$$

from which the concentration in mole/l can be calculated. From the molal volumes and solubility parameters the expected solubility of mercury in the organic liquids can be calculated.

Of the different methods given by HILDEBRAND [14, Chapter 23] of evaluating δ, the best seems to be the calculation from heats of vaporization. At low vapour-pressures $-U=\Delta U^V=\Delta H^V-RT$. The heat of vaporization can be evaluated from calorimetric measurements or from the Clausius-Clapeyron equation, and the molal volume can readily be obtained from density measurements. In the present work, δ values were calculated from calorimetric measurements of ΔH^V when possible or from the appropriate relation of vapour-pressure with temperature [18] [19]. In all cases the values of δ so obtained agreed well with those quoted by HILDEBRAND [14]. Comparison of the calculated and experimental values for the solubility are given in Table III. A second set was calculated using the maximum entropy-change, Eq. (12), and is given in Column 4 of Table III. The agreement of the latter values with the measured solubilities is considerably poorer than it is for those based on the assumption that the entropy-change is ideal, but this assumption also predicts solubilities considerably higher than those observed.

TABLE III

COMPARISON OF CALCULATED AND OBSERVED SOLUBILITIES OF MERCURY AT 25°C

Solvent	δ[1]	V_c[2]	Solubility (mole/l) × 10^4			
			H-S Theory[3]	F-H Entropy[4]	Reed[5]	Observed
CCl_4	8.5	276	41.5	116	11.3	7.5
*iso*octane	6.8	490	3.3	15	0.54	4.6
n-decane	7.8	602	9.2	4.8	0.81	7.0
benzene	9.1	256	86	225	25	11.4
toluene	8.9	316	58	175	12	13.4
nitrobenzene	10.0		193	569		9
chlorobenzene	9.7	308	144	422	26	12.5
bromobenzene	9.5	323	112	335	20	16.0
mercury	30.8	56.3				

[1] *Solubility parameter* $=(\Delta U^V/V)^{1/2}$

[2] Critical volume

[3] Calculated from $\Delta \overline{G}_1 = V_1 (\delta_1 - \delta_2)^2 + RT \ln x_1$ — Eq. (9)

[4] Calculated from $\Delta \overline{G}_1 = V_1 (\delta_1 - \delta_2)^2 + RT \{\ln \varphi_1 + [1 - (V_1/V_2)]\}$ Eq. (12)

[5] Calculated from $\Delta \overline{G}_1 = V_1 [(\delta_1 - \delta_2)^2 + 2 \delta_1 \delta_2 (1 - f)/d)] + RT \ln x_1$

Similarly the measured solubility *vs.* temperature curves for *n*-decane, toluene and chlorobenzene were compared with curves calculated from values of δ using Eq. (13). The fact that $\ln \delta$ is a linear function of temperature was used to interpolate values of δ between the temperatures for which it could be calculated from measured values of ΔH^V. For the cases of toluene and chlorobenzene, the calculated curves were not quite straight lines over this temperature range, but the curvatures were slight and the average slope agreed well with the slope of the observed curve. For *n*-decane the slope differed appreciably. In all three cases the calculated curves were higher than the observed curves by considerable factors: 1.25 for decane, 4 for toluene and 10 for chlorobenzene.

6. Modifications of the Hildebrand equation

A modification of the Hildebrand solubility equation has been published by REED [20]. Eq. (6) is valid only if the partial molal volumes are equal to the molal volumes and if the cohesive energy-density of a solution is the geometric mean of those of the pure components. By considering that the only attractive forces operative in a non-polar system are the London dispersion forces and including a partial molal-volume term, Reed obtained the following equation for the c_{12} term in Eq. (2):

$$c_{12} = (c_{11}c_{22})^{\frac{1}{2}} \left[\frac{V_1}{\overline{V}_1}\right]\left[\frac{V_2}{\overline{V}_2}\right]\left[\frac{2\,(d_{11}{}^0 d_{22}{}^0)^{\frac{1}{2}}}{d_{11}{}^0 + d_{22}{}^0}\right]^3\left[\frac{2\,(I_1 I_2)^{\frac{1}{2}}}{(I_1 + I_2)}\right] \tag{14}$$

In this, d^0 is the distance from the centre of a molecule to the first maximum in the density distribution of other molecular centres located around the first molecule and I is the ionization potential of the molecule. Since it was not possible to evaluate the partial molal volumes in the present work, the simplifying assumption was made that $\overline{V} = V$. The bracketed terms in Eq. (14) can be separated as factors:

$$f_d = \left[\frac{2\,(d_{11}{}^0 d_{22}{}^0)^{\frac{1}{2}}}{d_{11} + d_{22}}\right]^3$$

$$\text{and } f_I = \left[\frac{2\,(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2}\right]$$

and substituted into Eq. (4) to obtain:

$$\Delta \overline{U}_1 = V_1 \varphi_2{}^2\,[(\delta_1 - \delta_2)^2 + 2\,\delta_1\,\delta_2\,(1 - f_I f_d)]. \tag{15}$$

The effect of the f_I and f_d terms on the predicted solubilities can then be evaluated. From published values for ionization potentials [21–23], the quantity f_I was found to all intents to be unity for all cases.

The distance parameter can be evaluated from viscosity data or from values of the second virial coefficient, but it was not possible to obtain a consistent set of the necessary values to calculate f_d by either of these methods. In order to evaluate f_d consistently for all the solvents, it was assumed that d^0 is proportional to the cube root of the critical volumes of mercury and the solvents. Published values of the critical volumes [18] [24] [25] were used for the calculations, the results of which are listed in Table III.

7. Calculation of entropy of solution

The solubility data and parameters can be used to calculate the partial molal entropy of mixing as a way of testing the various assumptions. The results of these calculations are listed in Table IV under the symbols given in the following discussion. By using the measured solubility directly in the expression $\Delta \overline{S}_1 = R \ln x_1$ the ideal partial entropy of solution can be calculated (A). Eq. (10) for the maximum entropy can also be used (B).

The solubility *vs.* temperature data can be used to calculate entropy changes for the three solvents used in that study. A relation proposed by HILDEBRAND [26] [27]:

$$\overline{S} - S_0 = R\left(\frac{\delta \ln a_1}{\delta \ln x_1}\right)_T \left(\frac{\delta \ln x_1}{\delta \ln T}\right)_{\text{sat}} \tag{16}$$

TABLE IV

CALCULATED PARTIAL MOLAL ENTROPIES OF SOLUTION AT 25°C

Solvent	(A)	(B)	(C)	(D)
CCl_4	28.1	30.1		
isooctane	28.0	31.0		
n-decane	26.8	30.1	25.8	25.4
benzene	27.4	29.3		
toluene	26.7	29.0	28.4	28.1
nitrobenzene	27.6	29.8		
chlorobenzene	27.0	29.1	32.8	31.9
bromobenzene	26.4	28.6		

(A) $\Delta \overline{S}_1 = -R \ln x_1$

(B) $\Delta \overline{S}_1 = -R \{\ln \varphi_1 + 1 - (V_1/V_2)\}$

(C) $\Delta \overline{S}_1 = R (\delta \ln x / \delta \ln T)_{sat}$

(D) $\Delta s_1 = -\frac{R}{T} \left(\frac{\delta \ln x}{\delta 1/T}\right)_{sat}$

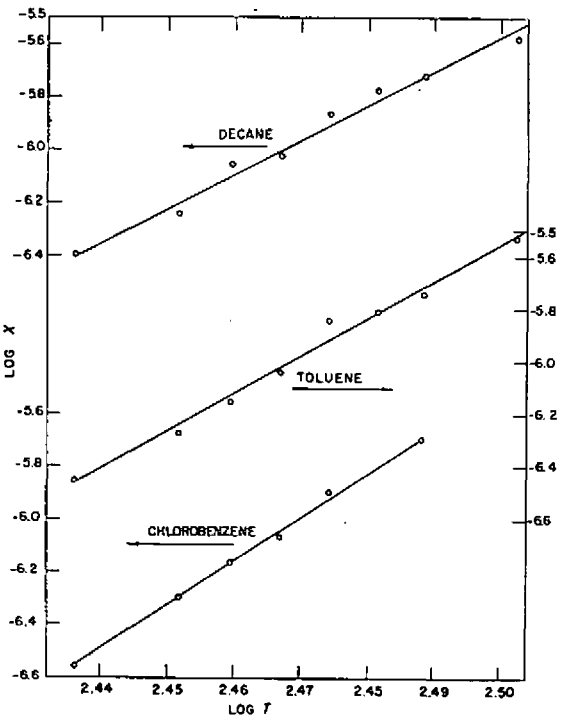

Fig. 2

Temperature dependence of solubility of mercury in *n*-decane, toluene and chlorobenzene.

shows that the slope of a $\log x$ *vs.* $\log T$ curve can be equated to $\Delta S^M/R$ if the function $\delta \ln a_1/\delta \ln x_1$ is essentially unity. For highly dilute solutions such as these, this function should be very close to 1 so that the slope of a $\log x$ *vs.* $\log T$ plot should give a reasonable value for $\Delta \bar{S}^M$. From such plots shown in Fig. 2, it can be seen that the dependence is linear. Entropy changes calculated from these are given as (C) in Table IV.

Another method of using the data on solubility *vs.* temperature is to evaluate $\Delta \bar{H}$ at the temperature of interest and divide by T, since if $\Delta \bar{G}$ is zero at saturation, $\Delta \bar{H} = T \Delta \bar{S}$. These values for the entropy obtained from Fig. 2 are given as (D) in Table IV.

The most reliable values for ΔS are probably those for *n*-decane, toluene and chlorobenzene from the $\log x$ *vs.* $\log T$ graph. In two cases out of three, these are higher than the values from $-R \ln x$. The latter expression can probably be used to give reasonable estimates of the entropy change in the absence of data over a temperature range. The Flory-Huggins entropy appears to be too high in each case.

8. Conclusions

Metallic mercury possesses a solubility in organic liquids which is measurable by radiotracer technique using direct solution methods or distribution studies between the solvent and water coupled with measurements of the solubility of mercury in water. In general, the solubility in organic liquids is considerably less than would be predicted by the Hildebrand theory if heat of vaporization data were used to evaluate the solubility parameters. The use of the Flory-Huggins equation for entropy, which was derived to cover the situation in which the molecular volumes of solvent and solute were very different, gave even poorer agreement with the observed solubilities. A modification due to Reed of the Hildebrand theory predicted solubilities which were in better agreement with results for some solvents but in poorer agreement for others.

Partial molal entropies of solution were calculated by a number of different methods using the observed data and predictions from theory. The entropy calculated on an ideal model seemed to be closer to reality than that calculated using the Flory-Huggins model.

Solubility *vs.* temperature measurements were used to calculate enthalpies and entropies of solution for three solvents. Entropies obtained in this way by two different methods of calculation are in fair agreement with the ideal entropy for two solvents and are somewhat higher for the third.

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THE VARIATION OF SOLUBILITY OF STRONTIUM SULPHATE WITH PARTICLE SIZE

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Abstract — Résumé — Аннотация — Resumen

The variation of solubility of strontium sulphate with particle size. Radioactive sulphur was used to study the variation of solubility of strontium sulphate with particle size. Synthetic methods were used to control the particle size ($d = 160—1000$ Å) and the size distribution was determined by electron microscopy. The separation of phases was carried out by sedimentation and the supernatant liquid was examined with the electron microscope to check for existence of peptized particles. The concentration of the dissolved $SrSO_4$ was determined by evaporation of an aliquot of the supernatant and determining the sulphur activity.

The results were found to follow the Ostwald-Freundlich equation for solubility with the smallest particles in a given distribution determining the solubility. From the solubility data an interfacial tension of 84 ± 8 erg/cm^2 was obtained, a value much lower than previously reported in the literature.

The Ostwald-Freundlich equation was extended to crystals of any geometry. Using this extended equation the interfacial tension of the different faces of strontium sulphate was calculated.

The data on variation of solubility with particle size and on the synthesis of particles of $SrSO_4$ were used to determine the size of the nucleus of $SrSO_4$.

Semiquantitative observations showed that the rate of solubility is much faster than the rate of growth.

Variation de la solubilité du sulfate de strontium selon la dimension des particules. Les auteurs ont utilisé du soufre radioactif pour étudier les variations de la solubilité du sulfate de strontium en fonction de la dimension des particules. Ils ont eu recours à des méthodes synthétiques pour contrôler la dimension des particules ($d = 160$ à 1000 Å) et ont déterminé leur granulométrie par microscopie électronique. Ils ont séparé les phases par sédimentation et examiné le liquide surnageant au microscope électronique pour voir s'il contenait des particules peptisées. La concentration du $SrSO_4$ dissous a été déterminée par évaporation d'une partie aliquote du liquide surnageant et mesure de l'activité du soufre.

Les résultats obtenus sont conformes à l'équation de solubilité formulée par Ostwald-Freundlich; la solubilité est déterminée dans une distribution donnée par les plus petites particules. A partir des données obtenues sur la solubilité, les auteurs ont calculé une tension interfaciale de 84 ± 8 erg/cm^2 — valeur beaucoup plus faible que celle qui est mentionnée dans diverses publications.

L'équation d'Ostwald-Freundlich a été étendue aux cristaux de toute géométrie; on a pu ainsi calculer la tension interfaciale des différentes faces des cristaux de sulfate de strontium.

Les données sur la variation de la solubilité selon la dimension des particules et sur la synthèse des particules de $SrSO_4$ ont été employées pour déterminer les dimensions du noyau du $SrSO_4$.

Des observations semi-quantitatives ont montré que la vitesse de dissolution est beaucoup plus grande que la vitesse de croissance.

Изменения растворимости сульфата стронция в зависимости от размера частиц. Для изучения изменений растворимости сульфата стронция в зависимости от размера частиц была использована радиоактивная сера. Для измерения размеров частиц ($d = 160-1000$ Å) были использованы синтетические методы, а распределение частиц разных размеров было определено при помощи электронной микроскопии. Отделение фаз производилось при помощи седиментации, и для проверки наличия пептизированных частиц поверхностная жидкость изучалась под электронным микроскопом. Концентрация растворенной соли $SrSO_4$ была определена посредством выпаривания аликвотного образца поверхностного слоя и определения активности серы.

В отношении растворимости при данном, определяющем растворимость распределении частиц было обнаружено, что для наименьших частиц результаты соответствуют уравнению Освальда-Фрейндлиха. Из данных относительно растворимости была выведена величина межповерхностного напряжения, оказавшаяся равной 84 ± 8 эрг/см^2, что является гораздо меньшей величиной, чем ранее сообщавшаяся в технической литературе.

Уравнение Освальда-Фрейндлиха было распространено на кристаллы любой геометрической формы. При помощи этого добавочного уравнения были подсчитаны межповерхностные напряжения различных граней сульфата стронция.

Данные относительно растворимости в зависимости от размера частиц, а также данные относительно синтеза частиц $SrSO_4$ были использованы для определения размера ядра $SrSO_4$.

Полуколичественные наблюдения показали, что растворимость увеличивается скорее, чем скорость образования сульфата стронция.

Variación de la solubilidad del sulfato de estroncio según el tamaño de las partículas. Los autores emplearon azufre radiactivo para estudiar la variación de la solubilidad del sulfato de estroncio en función del tamaño de las partículas. Recurrieron a métodos de síntesis para controlar el tamaño de las partículas ($d = 160-1000$ Å) y determinaron su granulometría por microscopia electrónica. Efectuaron la separación de las fases por sedimentación y examinaron con el microscopio electrónico el líquido sobrenadante para comprobar la ausencia de partículas peptizadas. Determinaron la concentración del $SrSO_4$ por evaporación de una parte alícuota del líquido sobrenadante y medición de la actividad del azufre.

Los resultados que obtienen obedecen a la ecuación de solubilidad de Ostwald-Freundlich; las partículas de menor tamaño en una cierta distribución son las que determinan la solubilidad. A partir de los datos obtenidos acerca de la solubilidad, calcularon una tensión interfacial de 84 ± 8 erg/cm^2, esto es, un valor considerablemente inferior al que figura en la bibliografía.

Los autores extendieron la aplicación de la ecuación de Ostwald-Freundlich a los cristales de cualquier geometría, y emplearon esta ecuación ampliada para calcular la tensión interfacial en las diversas caras de los cristales de sulfato de estroncio.

Utilizaron los datos relativos a la variación de la solubilidad según el tamaño de las partículas y a la síntesis de partículas de $SrSO_4$ para determinar las dimensiones del núcleo de $SrSO_4$.

Las determinaciones semicuantitativas realizadas demuestran que la velocidad de disolución es muy superior a la velocidad de crecimiento.

1. Statement of problem

The variation of solubility of solids with particle size is one of the basic problems of physical chemistry. Although it is generally and rightly assumed that the solubility increases with decreasing particle size, there is no satisfactory experimental examination of this increased solubility. The problem has many ramifications. Once the thermodynamic equation of OSTWALD [6] and FREUNDLICH [7] is experimentally substantiated, the surface tension between

the solid and the liquid can be determined. This, coupled with the knowledge of the concentration of the solid just necessary to produce a precipitate, permits the calculation of the size of the nucleus of the solid necessary for the crystallization of the solid from the liquid.

The experimental difficulties involved in the problem are the following: procurement of samples of narrow particle-size distribution in the sub-micron range, the contacting of these particles with the solvent to obtain equilibrium, a clean separation of the solid from the liquid phase, the determination of the concentration in solution and the determination of the particle-size distribution of the solid *in equilibrium with the saturated solution*.

The problem of variation of solubility of solids with particle size can be attacked more effectively by using radioactive tracers as sensitive methods of measuring the concentration of the material in the dissolved state and the electron microscope as a means of determining the particle size of the solid in equilibrium with the liquid.

2. Historical introduction

As early as 1813, WOLLASTON [1] and in 1885 CURIE [2] pointed out that finely divided solids should have a greater solubility than the larger crystals. The problem was treated theoretically in the nineteenth century by a number of scientists. GIBBS [3] gave a rigorous but implicit statement of the relation. THOMSON [4] and HELMHOLTZ [5] obtained a solution to a similar problem: the vapour pressure of small droplets. However, the analogy to the solubility of small particles of solids was overlooked for a considerable length of time.

OSTWALD [6] gave the first equation for the excess solubility of small spheres and his equation was later corrected by FREUNDLICH [7].

The first experimental investigation to test the Ostwald relationship between supersaturation and particle size, was carried out by HULETT [8] at Princeton University using 0.3-μm particles of $CaSO_4 \times 2\ H_2O$ and 0.1-μm particles of $BaSO_4$. The size was measured by an optical microscope and the concentration in the aqueous phase conductometrically. The solid/liquid interfacial tension was calculated using the incorrect Ostwald equation. The interfacial tensions so obtained were recalculated by JONES [9] who took into account the electrolytic dissociation of the dissolved salts. The corrected values for $CaSO_4 \times 2\ H_2O$ were 1050 and for $BaSO_4$, 1300 erg/cm^2.

HULETT's experiments [8] were repeated by DUNDON and MACK [10] [11] and were extended to $SrSO_4$, PbF_2, PbI_2, Ag_2CrO_4 and CaF_2. Measurable supersaturation was obtained in each case. For instance 26% supersaturation was observed for the 0.25-μm-diam. $SrSO_4$. The interfacial tensions were 370 for $CaSO_4 \times 2\ H_2O$, 1400 for $SrSO_4$ and 1250 erg/cm^2 for $BaSO_4$.

Experiments carried out later by COHEN et al. [16] and BALAREV [17] apparently invalidated the results of Hulett and Dundon *et al.* Cohen *et al.* investigated the solubilities of samples of $BaSO_4$ of various size. The solubility was determined by conductometric and polarographic method while the size of the particle was measured by optical microscopy. They reported no effect of size on the solubility, but it appears from their paper that the systems they investigated did not contain any particles smaller than 1 μm.

BALAREV [17] was not able to observe any change in solubility on washing with water for 10 to 14 yr particles of $BaSO_4$, $CaSO \times 2\ H_2O$, $SrSO_4$, BaF_2, PbF_2

and CaF_2. These particles ranged in diam. from 0.1 to 300 μm and the determination of the particle size was made by use of the Stokes law of sedimentation.

TOURKY *et al.* [20] measured the solubility of fine silver-oxide particles. The particle size was determined by sedimentation and the concentration of the ions in solution by an EMF measurement. Although these authors report a considerable increase in the silver ion concentration accompanying the decrease in particle size, it is impossible to obtain a consistent value for the interfacial tension. The internal inconsistency of their data was ascribed by Tourky *et al.* to the adsorption of the hydroxyl ions by the silver-oxide particles.

VAN HOOK *et al.* [21] found an excess solubility of small sucrose crystals over that of the large ones giving the value of 12 erg/cm² for the interfacial tension. The concentration of the dissolved sucrose was determined by a refractometer.

Recently, ALEXANDER [22] measured the solubility of amorphous silica of various specific surface-area and found a 300% excess solubility for material of 600 m²/g. Alexander obtained agreement with the Ostwald-Freundlich type of equation and calculated from this a value of 46 erg/cm² for the silica/water interfacial tension.

VAN ZEGGEREN *et al.* [23] studied the solubility in alcohol of sodium chloride specimens of varying specific surface. The specimens were prepared by electrostatic precipitation and their specific surface, as determined by the BET method using nitrogen adsorption, covered the range from 1.2 to 42.5 m²/g. The concentration in the liquid phase was determined by the conductometric method. A 6.7% excess-solubility was obtained for material of 42.5 m²/g area, corresponding to an average particle size of 650 Å. Fairly good formal agreement was obtained with the theory and a value of 171 erg/cm² was calculated for the surface tension.

For as long as there has been a problem of the solubility varying with particle size, the reliability of many experimental results was questioned. Thus, the electric charge on dispersed particles [12] [13], the geometry of the particles, the specific effects of edges and corners of crystals [9] [14] were believed to complicate the problem. BALAREV [15] has attributed the observed increase in the conductivity of the barium sulphate solution when in contact with small crystals of barium sulphate observed by DUNDON *et al.* [10] [11] as due to adsorbed barium chloride and to the mechanical effect of the grinding which appears to have been used by the early researchers to reduce the particles to the desired size. ALEXANDER *et al.* [18] discuss the possible effect of the electric charge and seem to believe that impurities that lower the interfacial tension by adsorption are the main cause for the failure to detect excess solubility of the smaller particles. A number of theoretical and experimental difficulties in treating fine particles have been pointed out by HARBURY [19] who considered the interfacial tension values obtained from the solubility measurements as empirical rather than fundamental quantities. Harbury pointed out that a serious source of error is the presence of particles too small to be detected by ordinary optical microscopes. Probably the reason for the controversial results of the early researchers lies in this uncertainty. There are definite limitations in the experimental approach which determines the average particle size from the specific surface area. This approach assumes, without experimental evidence, that the particles are all of uniform size. If the sample has a particle-size distribution, as most real samples do, the system is unstable with the smaller particles disappearing and the larger ones growing. It should be expected when such a solid sample is dispersed in a solution saturated with respect to the larger particles, that the concentration in the solution would first

rise and then fall. This behaviour has been observed by previous workers. At maximum concentration, which was assumed to be the equilibrium concentration, the effective particle size which satisfied the solubility concentration is somewhere between the minimum and the maximum values of the particle-size distribution curve. In the absence of any knowledge of the size distribution, it is impossible to assess the magnitude of this uncertainty. Furthermore in investigations where the particle size is determined by the specific surface, this quantity is measured on the original solid and this is considered to be identical with that of the solid in equilibrium with the solution.

It is the purpose of the present investigation to obtain new experimental data, paying attention to the difficulties previously presented and taking advantage of recent advances in experimental technique. The fine particles of varying particle size were obtained by synthesis instead of by grinding large crystals. Not only the average size but the size distribution of the particles in equilibrium with the solution were determined by electron microscopy. The concentration of the dissolved material was determined by a radioactive tracer technique, thus avoiding the possible interference of adsorbed ions that use of the conductometric method may involve. The system chosen was strontium sulphate-water, partly because it is one of the systems associated with experimental contradictions and partly because the present investigation is part of a programme of studying the behaviour of fine particles of strontium compounds in connection with the Sr^{90} fall-out.

3. Theoretical treatment

MOILLIET *et al.* [24] obtained a relation for the excess solubility of small crystalline solids to the particle size and the interfacial tension which is both quite general and rigorous. However, in their treatment of the solubility of a parallel piped with three different crystalline faces having three different interfacial tensions, they used the geometric mean of these interfacial tensions, the physical meaning of which is difficult to interpret. Furthermore they dealt with ideal solutions of non-electrolytes.

Solutions of electrolytes have been treated by VAN ZEGGEREN *et al.* [23] but their treatment suffers from the limitation to one type of crystal face with one interfacial tension and from the unnecessary use of the internal pressure of a solid.

Therefore we would like to present an independent derivation of a more general equation of the variation of the solubility of a solid with particle size.

Consider a single crystal of any geometry having any number of type of surfaces in equilibrium with the solution phase. Let s_i and γ_i be the area and interfacial tension associated with the ith type of surface, and assume that γ_i is independent of crystal size and composition of the solution phase. At constant temp. and pressure we have

$$\mathrm{d}F = \mu_0 \,\mathrm{d}n + \sum_i \gamma_i \,\mathrm{d}s_i \tag{1}$$

where F is the Gibbs free energy, μ_0 is the bulk chemical potential of this crystal and n is the number of moles it contains. Dividing this expression by $\mathrm{d}n$ we get the overall chemical potential of the crystal:

$$\mu = \mu_0 + \sum_i \gamma_i \frac{\mathrm{d}s_i}{\mathrm{d}n}. \tag{2}$$

If v is the volume, ϱ is the density of the crystal and M is the molecular weight, then (2) can be written as

$$\mu = \mu_0 + \frac{M}{\varrho} \sum_i \gamma_i \frac{\mathrm{d}s_i}{\mathrm{d}v}. \tag{3}$$

According to the Gibbs boundary condition [p. 321 of Ref. 3] a crystal which is in equilibrium with a solution phase assumes a constant geometric shape during dissolution or growth. If x is any characteristic dimension—e.g. length, width, depth, etc.—of the crystal, it follows, therefore, that

$$s_i = k_i\, x^2 \tag{4}$$

for each type of surface, and

$$v = l\, x^3, \tag{5}$$

where k_i and l are geometric constants independent of x. k_i is characteristic for each type of surface and l is characteristic for the geometry of the whole crystal. From (4) and (5) we get

$$\mathrm{d}s_i/\mathrm{d}v = \frac{2}{3}(s_i/v). \tag{6}$$

Substituting (6) into (3) we obtain

$$\mu = \mu_0 + (2M/3\varrho\, v) \sum_i \gamma_i s_i. \tag{7}$$

If we define a "mean interfacial tension" by

$$\bar{\gamma} = \sum_i \gamma_i s_i \Big/ \sum_i s_i. \tag{8}$$

which is simply the total surface free-energy divided by total surface, from (7) and (8) we get

$$\mu = \mu_0 + \frac{2M \sum_i s_i}{3\varrho\, v} \bar{\gamma}. \tag{9}$$

This equation is the general form of Eq. (15) of VAN ZEGGEREN *et al.* [23] and Eq. (40) of MOILLIET *et al.* [24]. Going back to Eqs. (4) and (5), from (9) we obtain

$$\mu = \mu_0 + \frac{2M\alpha}{3\varrho} \frac{\bar{\gamma}}{x}, \tag{10}$$

where α is a characteristic geometric factor of the crystal shape, and given by

$$\alpha = \sum_i k_i \Big/ l. \tag{11}$$

If the substance under consideration is an electrolyte, its chemical potential μ' in the solution is given by

$$\mu' = \mu'_0 + \nu\, RT \ln a, \tag{12}$$

where μ'_0 is the standard chemical potential, ν is the number of ions produced by dissociation of one mole of electrolyte, R is the gas constant, T is the temperature and a is the mean activity of the electrolyte in the solution. Equating μ

to μ' as required by the condition of equilibrium between the crystal and the solution, from Eqs. (10) and (12) we get

$$\mu_0+(2M\alpha/3\varrho)(\bar{\gamma}/x)=\mu'_0+\nu\,RT\ln a. \tag{13}$$

When x is effectively large, the second term in the left-hand side of (13) vanishes and the saturation activity a assumes its normal value a_0 given by

$$\mu_0=\mu'_0+N\,RT\ln a_0. \tag{14}$$

Finally, from (13) and (14) we obtain

$$\mathrm{Log}_{10}\,a/a_0=\frac{2/3\,M\,\alpha\,\bar{\gamma}}{2.303\,N\,RT\,\varrho\,x}. \tag{15}$$

If geometry of the crystal is known, α can easily be calculated since, as will be seen from (4), (5) and (11), it is the ratio of the total surface area to the volume of a crystal of unit x. For instance, for a cube, if x is the length of one edge, $\alpha=6$. In the case of a sphere of diameter x, α is also 6. In this case (15) becomes equivalent to the Ostwald-Freundlich equation. Alternatively, α can also be calculated from x and the specific surface even if the specific surface is determined with a sample of non-uniform size, provided that distribution of x is established. Indeed, it can be shown from the above definition of α that for a population of geometrically similar particles

$$\alpha=\varrho\,(\sigma\Sigma x^3/\Sigma x^2) \tag{16}$$

where σ is the specific surface.

4. Experimental programme

In the present work we have determined the solubility of fine $SrSO_4$ particles of various sizes in water at 25.0°C. The experimental method was so designed as to eliminate the sources of error which might have existed in the previous investigations, as discussed in section 2, as far as possible. Namely we (a) synthesized the fine particles instead of grinding large crystals, (b) determined the solubility by a radioactive-tracer technique using S^{35} as sulphate, instead of by a conductometric method to avoid possible interference of chlorides adsorbed (*cf.* section 2), and (c) measured the size of the particles in equilibrium with the solution by electron microscopy.

5. Preparation of $SrSO_4$ particles

We have investigated the precipitation of $SrSO_4$ from aqueous solutions at various reactant concentrations and the precipitates formed. We have observed, by mixing equivalent amounts of $SrCl_2$ and Li_2SO_4 solutions, that the minimum $SrSO_4$ concentration which initiates precipitation (in approx. 10 h) is 0.015 *M*. The particles formed in aqueous solutions had exactly the same spindle shape as $BaSO_4$ particles which can be seen in electron micrographs in a recent publication by TAKIYAMA [25]. The particles so obtained were not only too large for the solubility studies, but were also compound crystals with scales around them, as was revealed by the electron microscope at high magnifications. They were, therefore, unsuitable for the present work.

However, we were able to obtain primitive and small enough crystals of $SrSO_4$ by precipitation from alcoholic solutions, as mentioned by WEISER [26]. By mixing equivalent amounts of aqueous $SrCl_2$ and Li_2SO_4 solutions together, we found that no precipitation takes place in 21 h in a solution which contains 0.01 *M* $SrSO_4$. If the reactant solutions contain 20 vol. % of methanol, precipitation takes place in 1 min. The crystals so formed are large and similar to those precipitated from aqueous solutions as described above. At 30% methanol concn the same large crystals precipitate in approx. 30 s followed by formation of fine particles in approx. 3 min in small quantity. At 50% methanol concn, fine particles are formed abundantly in approx. 15 s with no formation of large crystals. At methanol concentrations higher than 50%, the higher the methanol concentration the smaller the particles formed. We have also observed that precipitation can be affected by adding a small amount of methanol after mixing the aqueous reactants of the same concentrations presumably due to local formation of relatively few particles and their subsequent growth. The particles so obtained are much larger than those formed at 50% methanol concentration.

Making use of these observations, we prepared three different samples of radioactive $SrSO_4$ particles of various size-ranges using the same Li_2SO_4 stock-solution which contained S^{35} as sulphate. The recipes of these batches are given in Table I.

TABLE I

RECIPES OF THREE SAMPLES OF RADIOACTIVE $SrSO_4$ PARTICLES

Batch	A (ml)	B (ml)	C (ml)	
0.5 *N* $SrCl_2$	3	3	10	I
H_2O	—	147	500	I
CH_3OH	300	600	—	I
0.5 *N* Li_2SO_4 (S^{35})	3	3	10	II
H_2O	—	147	500	II
CH_3OH	300	600	—	II

Reactants I and II were mixed at room temperature by pouring II into I which was vigorously stirred. In the case of Batch C, 20 ml methanol was added after mixing. The colloidal $SrSO_4$ so formed coagulates in a short time under these conditions. It was then allowed to settle and 24 h later the bulk of the supernatant was decanted off. The residue was centrifuged, decanted and washed with 6 ml distilled water, 5 times discarding the washings by centrifuging. It was observed that the first three washings eliminated effectively the bulk of chloride ion. However, further washings could not remove a persistent trace of chlorides from the solid. Similar behaviour has been reported by BALAREV [17] in the case of $BaSO_4$.

Large crystals of active $SrSO_4$ to be used as standard were also prepared by a method similar to that described by LEWIN *et al.* [27], by using the same Li_2SO_4 solution as follows: a solution consisting of 10 ml 0.5 *N* $SrCl_2$ and 40 ml water was mixed with 10 ml 0.5 *N* Li_2SO_4 (S^{35}) + 40 ml water, which were preheated, kept at 100°C for 1 h and the supernatant was decanted off. The precipitate was washed with water three times, dissolved in hot azeotropic hydrochloric acid, evaporated slowly to dryness in a beaker placed on a steam bath and covered

with a watch glass, washed with water until no chloride could be detected and then dried in an oven at 175°C. The crystals obtained in this manner were about 0.1 mm in size.

6. Solubility measurements

Samples A, B, C and the standard sample were dispersed in 500 ml distilled water in 1-liter volumetric flasks thermostatically set at 25.0°C and stirred by magnetic stirrers. With the aid of an electron microscope we have observed that all particles in these suspensions were in the form of aggregates which settled quantitatively in less than 18 h after stopping the stirrers, and that the supernatant sampled at that moment at a depth of 1 cm from the surface contained no particles. In this manner 1-ml samples were drawn from the supernatants when required, weighed in counting planchettes, evaporated and their radioactivities were determined by a GM counter provided with an end-window GM tube of 1.9 mg/cm^2 window-thickness, which was found suitable for counting soft β-emissions of S^{35}.

Saturation of the solution with the standard large crystals took about 8 d of continuous stirring, as revealed by the supernatant activity, whereas the equilibrium could be established in less than 24 h in the case of fine particles unless the amount of solid phase was very small compared to the volume of the solution phase.

The supersaturation ratio, in terms of concentration, C/C_0 in systems A, B and C were calculated by taking the ratio of the counts of the samples drawn from these systems to the count of the standard measured at the same time and corrected for the sample weights. These were 1.50, 1.33 and 1.11, respectively, and did not change during several days of stirring.

Later, 227 ml of suspension B was diluted drop-wise with 100 ml water in 1 h (system B) while stirring vigorously. Similarly, system C was diluted with 325 ml water in 1.5 h (system C'). C/C_0 was then determined in these diluted systems B' and C', after equilibration, as described above and found to be lower than those of B and C, respectively (see Table II).

TABLE II

SOLUBILITY AND PARTICLE-SIZE MEASUREMENTS

System	$C/C_0 \pm 0.01$	$\mathrm{Log}_{10}\, a/a_0$	$\Sigma x^2/\Sigma x$ (Å)	$x_{\min}$ (Å ± 10 Å)
A	1.50	0.154 ± .003	247	96
A'	1.41	0.130 ± .003	269	130
A''	1.32	0.106 ± .003	388	155
B	1.33	0.109 ± .003	541	168
B'	1.18	0.063 ± .004	629	252
C	1.11	0.040 ± .004	1260	378
C'	1.08	0.029 ± .004	1660	500

We kept the suspension A stirring continuously, measured C/C_0 2 months after the first dispersion and found it to have dropped to 1.41, apparently because of particle growth (system A'). Subsequently we gradually diluted this system also with 100 ml water in 45 min (system A'') and determined C/C_0 again. All these C/C_0 values are given in Table II together with the estimated standard errors.

7. Particle-size measurements

Before each solubility determination, just before turning off the stirrer, 5-ml samples were taken from the suspensions and shaken vigorously for 5 min after adding one drop of 0.1% fresh gelatine solution as a dispersing agent to break up the particle aggregates. In this manner colloidal dispersions were obtained. A small drop from this dispersion was then transferred on to an electron microscope grid covered with collodion film. About one minute later the liquid

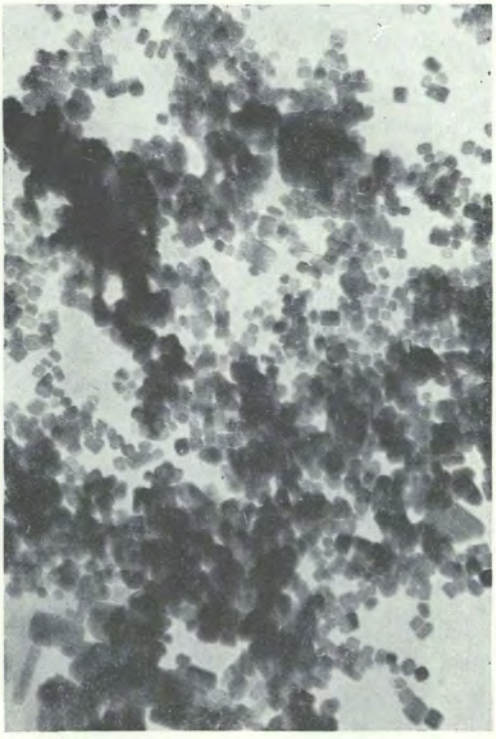

Fig. 1
Strontium sulphate particles.

was drawn by a piece of filter paper off the grid in the usual manner [28] and electron micrographs of the particles adhering to the collodion film were taken with an electron microscope at suitable magnifications. Fig. 1 is a typical electron micrograph of fine $SrSO_4$ particles. (It was taken using particles from system B.)

The micrographs were analysed and corresponding number-particle size-distributions were established. The apparent width of the orthorhombic parallelipiped crystals was taken as the characteristic dimension x (see section 3). Fig. 2 shows the particle-size distributions of the populations in equilibrium in the systems investigated.

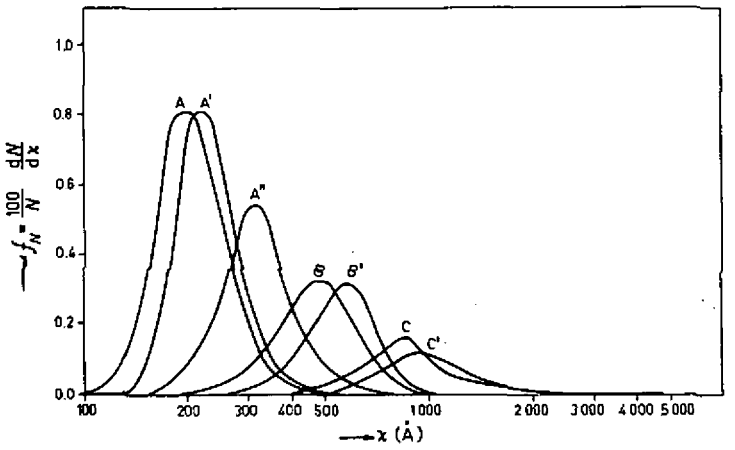

Fig. 2
Size distribution curves of $SrSO_4$ particles.

8. Estimation of the geometric factor

In order to estimate the geometric factor α of the particles from Eq. (16) we determined the specific surface of an inactive $SrSO_4$ sample, prepared in the same manner as Batch B but in larger quantity, by isotopic ion exchange method as described by one of us elsewhere [29]. For this purpose 1.1215 g of dry sample was dispersed in 100 ml of 0.01 M Li_2SO_4 solution containing some S^{35} as sulphate, and stirred at 25.0 °C. Activity of the supernatant was measured each time by taking 2 ml sample, centrifuging, weighing, evaporating and counting 1 ml of supernatant in a planchette. Fig. 3 shows the activity of 1 g of the supernatant sampled at various times but measured at the same time. The initial and extrapolated equilibrium counting rates of the solution were 3011 and 1965 cpm/g, respectively. From these values the specific surface σ was calculated as $(3.39 \pm 0.16)\ 10^5$ cm^2/g, taking 1.09×10^9 cm^2/mole for the molar surface of $SrSO_4$.

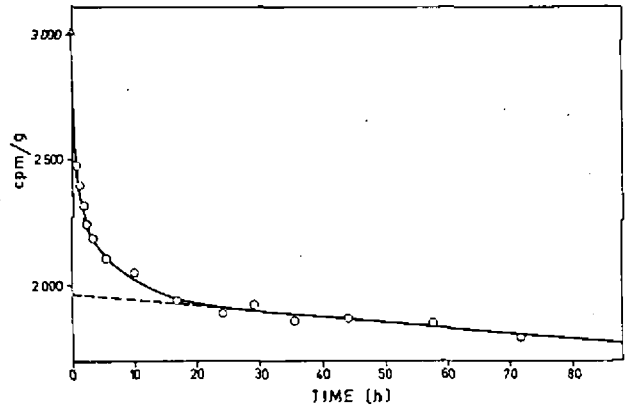

Fig. 3
Activity of supernatant *vs.* time.

At the end of this experiment, a sample was taken from the suspension and the size distribution of the particles was determined as described in section 7. The quantity $\Sigma x^3/\Sigma x^2$ calculated from these measurements was 5.2×10^{-6} cm. Using this value, the specific surface and $\varrho = 3.96$ g/cm^3, the geometric factor α was calculated from Eq. (16) as 7.0 ± 0.3.

9. Charge effect

As mentioned in section 6, microscopic examinations showed that, if no dispersing agent were present, all $SrSO_4$ particles in suspensions were in the form of aggregates. This indicates the absence of electrical charge on particles in the present system to interfere with the solubility, as discussed by some authors [12] [13].

10. Shifts in size distribution

Let us first consider the case of system A, which exhibited a significant shift in particle-size distribution to the bigger size, as is shown in Fig. 2, over a period of 2 months, and a corresponding drop in solubility, as mentioned in Section 6. The shift has taken place in such a manner that the minimum particle-size of the population has also increased. This is, clearly, a typical crystal growth called "Ostwald ripening" i.e., the growth of the larger crystals at the expense of smaller ones, as predicted by the theory.

Similar but more pronounced shifts were observed by gradual dilution of the systems A', B and C (see Fig. 2) which show the preferential solubility of the smaller particles. This behaviour also gives us a clue as to the effective particle size which controls the solubility of the present system, as will be discussed in the next paragraph.

11. Solubility and particle size

To take into account the deviation of the solution from the ideal, we converted the concentration ratios C/C_0 to activity ratios a/a_0 by using the activity coefficients of $SrSO_4$ calculated from the Debye-Hückel equation. $\mathrm{Log}_{10}\, a/a_0$ values so obtained are given in the third column of Table II with the corresponding standard errors.

In order to test the theoretical equation (15) a plot of $\mathrm{Log}_{10}\, a/a_0$ must be made against the reciprocal of particle size. However, as mentioned in Section 1, we were confronted with the difficulty of which particle size to use, since the particles were far from being uniform in size (Fig. 2). The first attempt was to use as the effective size various average sizes such as the number average, the surface average and the volume average. The peak values of the number, width, surface and volume distribution curves were also used. The ratio $\Sigma x^2/\Sigma x$ was also considered and this ratio can be shown to be the effective size if the amount of solid to be dissolved reversibly per unit surface area is irrespective of the particle size. Finally, the ratio $\Sigma x^3/\Sigma x^2$, equal to the average size calculated from the specific surface (*cf.* Eq. (16)) was calculated. This is the ratio used in the treatment of VAN HOOK *et al.* [21] and that of ALEXANDER [22] and is virtually that used by VAN ZEGGEREN *et al.* [23]. In all cases, as predicted by Eq. (15), reasonable straight-line relationship was obtained for all points except those of system B. On the basis of the plot, no preference could be made between these various

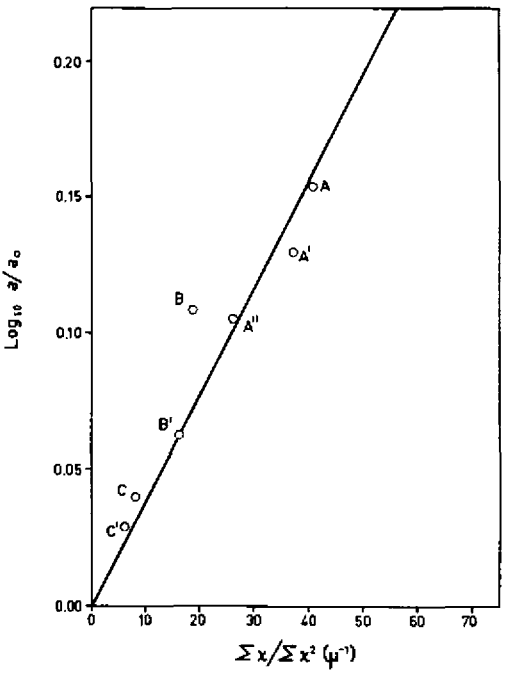

Fig. 4
$\mathrm{Log}_{10}\ a/a_0$ plotted against the reciprocal of particle size.

ratios characterizing the particle size. The numerical values of these variables, one must observe, are very close to each other. One of these plots, i.e. using $\Sigma x^2/\Sigma x$ as variable, is shown in Fig. 4. The values of $\Sigma x^2/\Sigma x$ are given in the fourth column of Table II.

At this stage our attention was drawn to the behaviour of systems A″ and B. It will be seen from Fig. 2 and Table II that, despite the considerable difference between the particle-size distributions in these systems, the solubilities are practically the same. But, it is interesting to note that these systems have another common feature, i.e. their minimum particle sizes are also practically the same. This observation coupled with the disappearance of the smallest particles on dilution, as mentioned in the preceding paragraph, suggested that the solution was in equilibrium with the smallest particles rather than any larger ones, or in other words, *the effective size was the minimum particle size.*

This suggestion became a conviction when we made the following experiments: a solution which was equilibrated with fine particles showed no change in concentration when stirred with large crystals 0.1 mm in size for 24 h. The concentration of a solution which was equilibrated with large crystals, however, increased substantially when stirred with fine particles for the same period of time. This meant that the larger particles in the population of graded sizes were not in thermodynamic equilibrium with the solution and, therefore, had no influence on the solubility. In other words, the solution was in equilibrium with the smallest particles, and in a supersaturated state with respect to any larger

particles. This is, undoubtedly, because of the low rate of crystallization, as indicated by very slow Ostwald ripening and a constant supersaturation for a considerable time (Section 6) compared to the rate of solution. This was also reported by DUNDON [11]. This result is, of course, neither new nor surprising. It is a well-known fact that the persistence of supersaturation is observed far more often than undersaturation. But it brings out once more the fundamental difference between the mechanism of dissolution and crystallization phenomena. In the case of fine particles the manifestation of this difference is more striking, since the smaller particles have not only greater solubility but also a greater rate of solution per unit surface area, as shown by ROLLER [30].

The case of $CaSO_4 \cdot 2\ H_2O$ appears to be somewhat different. DUNDON *et al.* [10] report that the solubility first increases on dispersing fine gypsum particles, then falls to its normal value indicating a rapid crystal growth in contrast to $SrSO_4$ and $BaSO_4$[11]. This difference in the rate of crystallization can perhaps be attributed to the fact that $CaSO_4$ is linked with $2\ H_2O$, whereas $SrSO_4$ and $BaSO_4$ crystals have no water of crystallization. Probably, in the latter cases the hydrated ions in solution require a high activation energy to be freed from all hydrating H_2O molecules before they can be accommodated in the crystal lattice, thus reduce the rate of crystallization.

In the light of the foregoing discussion, we can conclude that the effective particle-size which satisfies Eq. (15) is the minimum size of the population for the present system. Accordingly, we plot $\log_{10} a/a_0$ in Fig. 5 against the reciprocal of minimum size which is given in the fifth column of Table II for each system. Comparing Fig. 5 with Fig. 4, it will be seen that a better agreement with Eq. (15) is obtained this way, which is as much as can be expected. The equation of the best straight line drawn from the origin through the points in Fig. 5 is

$$\log_{10} a/a_0 = 16/x \tag{17}$$

which represents the solubility of $SrSO_4$ particles at 25.0°C within $\pm 8.4\%$ standard deviation in $\log_{10} a/a_0$, where x is the width of the smallest crystals measured in Å.

Having established the relationship between the solubility of $SrSO_4$ and its particle size, it is appropriate here to compare the present data with the results reported in the literature, and to discuss and give reasons for the controversial results of the earlier workers mentioned in Section 2. Since the size of the smallest particles controls the solubility, we can safely attribute these contradictions to the failure in detection of these small particles rather than to any experimental error involved in solubility measurements. The 26% supersaturation reported by DUNDON [11] for 0.25-μm particles appears to be too high when compared with the present data given in Table II. It is reasonable to believe that Dundon had much smaller particles in his $SrSO_4$ sample which could not be detected by an ordinary microscope, and that the particles investigated by BALAREV [17] were not small enough to produce measurable supersaturation.

Probably the same argument applies to the case of other substances studied by the earlier researchers [8] [10] [11] [16] [17]. For instance, it is very likely that Balarev's prolonged washing has eliminated (*cf.* section 10) the particles of $BaSO_4$ smaller than 0.1 μm which were present but not detected in the suspensions used by HULETT [8] and DUNDON [11]. The particles of $BaSO_4$ investigated by COHEN *et al.* [16] were definitely too coarse (see section 2) to produce supersaturation.

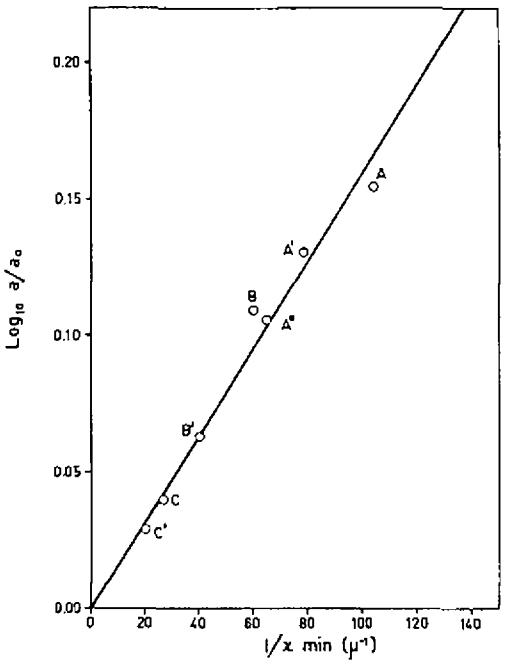

Fig. 5
$\mathrm{Log_{10}}\ a/a_0$ plotted against the reciprocal of minimum size.

12. Interfacial tension

Substituting $\nu=2$, $\alpha=7.0$ (section 3) for $SrSO_4$ and the values of the other constants in Eq. (15), from Eqs. (15) and (17) we obtain $\overline{\gamma}=84\pm8$ erg/cm^2 for solid $SrSO_4$/solution mean-interfacial-tension at 25.0°C. The value 1400 erg/cm^2 calculated by DUNDON [11] from his results appears to be much too high. This is merely because of the fact that his estimated particle size must have been much larger than the size of the smallest particles which were actually present in the system investigated (paragraph 11). Although Dundon's calculation was based on the Ostwald-Freundlich equation which is applicable to spherical particles, this is not expected to make an appreciable difference in $\overline{\gamma}$ calculated, since, as pointed out in section 3, the Ostwald-Freundlich equation corresponds to the use of a geometric factor 6 in our treatment instead of 7 (or perhaps even 6.24, as will be discussed below) for $SrSO_4$ crystals.

It is interesting to note that the order of magnitude of the solid/liquid interfacial-tension values given by the early researchers [8] [10] [11] who used an ordinary microscope for particle-size measurements is significantly bigger than that of values obtained by recent research workers [21—23] who have calculated actually or virtually the particle size from the specific surface determined by surface phenomena. This is because of the fact that the particle size determination by the latter method takes care of the submicroscopic particles. Although the specific surface method gives a more realistic estimate of particle size and, therefore, of interfacial tension, the particle size so obtained is an average value and

the question of how close this average is to the effective size (section 2) is still open. However, the interfacial-tension values obtained by a specific surface method is expected to be at least of the right order of magnitude. Indeed, the values 46 erg/cm² for silica/water, 171 erg/cm² for NaCl/alcohol obtained by ALEXANDER [22] and VAN ZEGGEREN *et al.* [23] respectively, appear to be reasonable estimates when compared with 84 erg/cm² for the present system. The value 12 erg/cm² given for sucrose/solution by VAN HOOK *et al.* [21] is also a reasonable figure for the surface tension of a molecular lattice measured against a conc. solution.

MOILLIET *et al.* [24] derive relationships between the three interfacial tensions of a parallelipiped, from the GIBBS boundary condition [3], which in the case of rectangular parallelipiped crystals of $SrSO_4$ reduce to

$$\gamma_1 bc = \gamma_2 ac = \gamma_3 ab, \tag{18}$$

where a, b and c are the dimensions of such a crystal and γ_1, γ_2 and γ_3 are the interfacial tensions associated with 100, 010, 001 faces, respectively. We also have from Eq. (8), by definition

$$\overline{\gamma}\,(ab+bc+ac) = \gamma_1 bc + \gamma_2 ac + \gamma_3 ab. \tag{19}$$

From (18) and (19) we get

$$\begin{aligned}
\gamma_1 &= \frac{1}{3}\overline{\gamma}\left(1 + \frac{a}{b} + \frac{a}{c}\right),\\
\gamma_2 &= \frac{1}{3}\overline{\gamma}\left(1 + \frac{b}{a} + \frac{b}{c}\right),\\
\gamma_3 &= \frac{1}{3}\overline{\gamma}\left(1 + \frac{c}{a} + \frac{c}{b}\right).
\end{aligned} \tag{20}$$

Electron micrographs suggest that the dimensions of the primitive orthorhombic crystals of $SrSO_4$ are in the same proportions as the unit cell dimensions 8.36, 5.36, 6.84 Å [34]. This can be seen from Fig. 1 showing such $SrSO_4$ crystals which expose their 010 faces. Therefore, assuming a, b, c to be in the same proportion as the unit cell dimensions and substituting $\overline{\gamma} = 84$ erg/cm² in Eqs. (20) we obtain $\gamma_1 = 106$, $\gamma_2 = 68$, $\gamma_3 = 87$ erg/cm².

13. Geometric factor

If we calculate the geometric factor α, by assuming that $SrSO_4$ crystals have the same geometry as the unit cell and taking the dimension c as the characteristic dimension x (see section 3), we find $\alpha = 6.24$. The experimental value 7.0 appears, therefore, a little too big. We believe this is due to the fact that some crystals in the specimens mounted for electron micrography were slightly tilted with respect to the electron beam, because of surface irregularities of the collodion substrate, in such a way that the measured width x of the image so obtained was on the average bigger than actual c by a factor of 7.0/6.24. Thus, α calculated from (16) was also overestimated by the same factor. However, in spite of this we used 7.0 for α in calculating $\overline{\gamma}$ since errors in α and x originating from this source eventually cancel in Eq. (15).

14. Size of nuclei

As mentioned in section 5, our estimate of the minimum $SrSO_4$ concentration which initiates precipitation on mixing equivalent amounts of $SrCl_2$ and Li_2SO_4 solutions is 0.015 *M*. Taking 114 mg/l* for the normal solubility of $SrSO_4$, this corresponds to a supersaturation ratio of 24.2 against 13—26 reported by FIGUROVSKY *et al.* [31]. LUCCHESI [32] claims, however, that he was able to get precipitate at a concn of 0.001 *M*. LA MER *et al.* [33], on the other hand, have reported a value of 2.95 for the limiting supersaturation ratio in terms of activities. If we convert our figures and those of LUCCHESI [32] to activity ratios, using the Debye-Hückel equation for the activity coefficients, we find 7.53 and 1.41, respectively. Therefore, both Lucchesi's and La Mer *et al.*'s figures appear to be too low compared to ours, which is in agreement with the result obtained by Figurovsky *et al.*

Substituting $a/a_0=7.53$ in Eq. (17) we find $x=18$ Å, which can be considered as the width (i.e. *c* dimension) of $SrSO_4$ nuclei. This is about 3 times the *c* dimension of the unit cell 6.84 Å (*cf.* section 12.) It can be concluded, therefore, that a nucleus consists of $3^3=27$ unit cells.

By similar calculations LA MER *et al.* [33] arrive at a value of 100 Å for the size of $BaSO_4$ nuclei from their experimental results. Nevertheless, in their calculation they use HULETT's value (1500 erg/cm²) [8] for the interfacial tension of $BaSO_4$, which we consider too high (*cf.* sections 12 and 2). If we can assume that the *c* dimension of a $BaSO_4$ nucleus is also 3 times that of a unit cell, i.e. 7.14 Å [34], using La Mer *et al.*'s value of 21.5 for the critical a/a_0 and α calculated from the unit cell dimensions [34], we obtain from Eq. (15) $\bar{\gamma}=150$ erg/cm² for $BaSO_4$/solution mean-interfacial-tension.

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* This figure is given in "Handbook of Chemistry and Physics" (1956-57) for 30°C which agrees with our estimate of solubility of $SrSO_4$ crystals 0.1 mm in size, using a tracer method.

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DISCUSSION

K. H. Lieser (Federal Republic of Germany) said the experiments carried out in his laboratory and reported in detail in other papers had led to similar conclusions regarding the change in particle size of precipitates. He had been studying the precipitation of barium sulphate by an exchange method and had calculated the total surface area and the mean particle size of the crystals as a function of time during the precipitation reaction. The surface area increased as a result of crystal growth, and then decreased as a result of Ostwald ripening. Both crystal growth and Ostwald ripening were governed by the same surface reaction, which had a rather high activation energy. At a certain moment a metastable particle-size distribution had been reached, and at constant temperature a very slow but continuous recrystallization process could be observed. If the system were brought to a higher temperature, however, a new ripening process started and the surface area decreased fairly rapidly until a new particle-size distribution was reached—and so on.

In determining the particle-size distribution, using the same technique, he had found two sources of error:

(1) The size distribution could easily be altered by a sedimentation effect while the specimens were being prepared for the electron microscope;
(2) If the isotope exchange method was used to determine the surface area, the results obtained might vary by a factor of 2 or more, depending on the surface structure, as could be seen from the measurements of Stow and Spinks.

He asked whether Mr. Turkevich had been able to avoid these sources of error.

J. Turkevich said the particle size had been determined by a technique developed in his laboratory for preparing specimens for the electron microscope, namely the addition of gelatine to the solution before mounting. That method gave satisfactory particle-size distribution curves. An important feature of the investigation he and Mr. Enüstün had carried out was that they had used particle-size distribution curves instead of average sizes. They had thus been able to take advantage of the changes in the tail of the distribution curve on the small particle size. The effect of surface structure did not seem very important, since all the $SrSO_4$ samples had been prepared in the same way and the results for different samples were consistent.

RADIOISOTOPES IN THE PHYSICAL CHEMISTRY OF CORROSION PROCESSES AND THEIR INHIBITION

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Abstract — Résumé — Аннотация — Resumen

Radioisotopes in the physical chemistry of corrosion processes and their inhibition. The fundamental study of the electrochemical processes of corrosion and inhibition involves various factors, including in particular: (a) adsorption phenomena of different types; (b) ion-exchange properties of passive films; and (c) the electrochemical kinetics of both anodic and cathodic processes across the interface between a metal and its corrosive environment. The availability of radioisotopes has made possible certain studies of these phenomena that could not be made previously with conventional techniques.

The element technetium, a homologue of manganese in the periodic system, has been found uniquely suited to certain of these studies by reason of its nuclear properties. The chemical properties of technetium compounds are summarized and contrasted with those of corresponding Cr^{51} compounds and those of molybdenum and tungsten, so much used in studies of inhibition.

Selected experimental studies are given as examples of the uses to which technetium has already been put in this type of work. Among these are empirical studies of its action as a very efficient inhibitor of the corrosion of iron, together with the results of long-term observations of surface activity. Other studies with both Tc^{99} and I^{131} have demonstrated the significance of competitive adsorption of ions in the determination of the kinetics of the corrosion and inhibitory processes. Finally, the author shows how the unique properties of technetium have permitted a clear discrimination between the relative contributions of oxygen and the oxidizing inhibitor in the maintenance of passivity.

Les radioisotopes dans la chimie physique des processus de corrosion et de leur inhibition. Parmi les facteurs qui entrent en jeu dans l'étude fondamentale des processus électrochimiques de corrosion et d'inhibition on relève notamment: *a)* différents types de phénomènes d'adsorption; *b)* les propriétés d'échange ioniques des films passifs; *c)* la cinétique électrochimique des processus tant anodiques que cathodiques qui se produisent dans l'interface entre un métal et le milieu corrosif. Avec les radioisotopes, on peut maintenant entreprendre sur ce sujet certaines recherches impossibles avec les moyens classiques.

Le technétium, homologue du manganèse dans la classification périodique, s'est révélé l'élément de choix pour certaines de ces recherches. Ses propriétés nucléaires sont extrêmement intéressantes à cet égard. Le mémoire résume les propriétés chimiques des composés du technétium, qu'il oppose à celles des composés correspondants du chrome-51, ainsi qu'à celles du molybdène et du tungstène, d'usage répandu dans les recherches sur l'inhibition.

L'auteur décrit ensuite quelques études expérimentales à titre d'exemples des emplois que le technétium a déjà trouvés dans les travaux de ce genre. Il mentionne notamment certains études empiriques sur l'action du technétium en tant qu'inhibiteur très efficace de la corrosion du fer, ainsi que les résultats d'observations faites pendant une longue période sur l'activité de surface. D'autres recherches au moyen

du technétium-99 et de l'iode-131 ont montré l'importance de l'adsorption compétitive d'ions dans l'étude cinétique des processus de corrosion et d'inhibition. Enfin l'auteur montre comment les propriétés spéciales du technétium ont permis de faire une distinction nette entre la part de l'oxygène et celle de l'inhibiteur oxydant dans le maintien de la passivité.

Применение радиоизотопов в физической химии процессов коррозии и их торможения. Среди факторов, входящих в фундаментальное изучение электрохимических процессов коррозии и торможения, выделяются в частности следующие: a) различные виды адсорбционных явлений; b) ионообменные свойства пассивных пленок; c) электрохимическая кинетика как анодных, так и катодных процессов, происходящих между металлом и коррозийной средой. Теперь при помощи радиоизотопов можно провести некоторые исследования этих явлений, которые невозможно осуществить обычными средствами.

Технеций, гомолог марганца в периодической системе, оказался весьма подходящим для некоторых этих исследований. Его ядерные свойства крайне интересны в этом отношении. В докладе кратко излагаются химические свойства соединений технеция, противопоставленные свойствам соответствующих соединений хрома-51, молибдена и вольфрама, обычно использующихся при изучении процессов торможения.

Далее автор описывает некоторые экспериментальные исследования в качестве примеров использования технеция в работах подобного рода. В частности, он упоминает некоторые эмпирические исследования действия технеция как весьма эффективного средства торможения коррозии железа, а также результаты многочисленных наблюдений над активностью поверхности. Другие исследования при помощи как технеция-99, так и йода-131 показали важность сравнительной адсорбции ионов в кинетическом изучении процессов коррозии и торможения. Наконец, автор показывает, как особые свойства технеция позволили провести четкое разграничение между долей кислорода и долей замедлителя окисления при сохранении пассивности.

Los radioisótopos en la química física de los procesos de corrosión y de inhibición. Algunos de los factores que intervienen en los estudios fundamentales de los procesos electroquímicos de corrosión e inhibición son los siguientes: *a)* fenómenos de adsorción de diversos tipos, *b)* propiedades de intercambio iónico de las películas pasivas, y *c)* la cinética electroquímica de los procesos anódicos y catódicos que tienen lugar en la fase que separa un metal del medio corrosivo. Los radioisótopos han hecho posible ciertos estudios de estos fenómenos que antes no podían llevarse a cabo con los métodos clásicos.

Se ha comprobado que el tecnecio, un homólogo del manganeso en el sistema periódico, es particularmente adecuado para algunos de estos estudios. Las ventajas de este elemento estriban en sus propiedades nucleares. La memoria resume las propiedades químicas de los compuestos de tecnecio y las compara con las de los compuestos correspondientes de ^{51}Cr, de molibdeno y de wolframio, que con tanta frecuencia se emplean en el estudio de la inhibición.

La memoria describe seguidamente ciertos estudios experimentales como ejemplo de los usos a que se ha destinado el tecnecio en los trabajos de este tipo. Entre ellos menciona estudios empíricos de su acción como eficaz inhibidor de la corrosión del hierro, y observaciones de la actividad de superficie realizadas durante períodos largos de tiempo. Otros estudios efectuados con ^{99}Tc y con ^{131}I han demostrado la importancia de la adsorción competitiva de iones en la determinación de la cinética de los procesos de corrosión y de inhibición. Como tercer ejemplo, describe cómo las propiedades excepcionales del tecnecio han permitido distinguir claramente las contribuciones relativas del oxígeno de las del inhibidor oxidante en el mantenimiento de la pasividad.

1. Introduction

The study of the phenomenon of corrosion began as an essentially empirical measurement of rates of attack and, later, of the effect of added substances in stimulating or retarding such attack. Since the time of Faraday it has been recognized that peculiar conditions existing at the boundary between a metal and its corrosive environment may produce very great changes in the rate or distribution of the reaction. Thus, we have the phenomenon of passivity, which Faraday ascribed to a film of oxygen held in some unknown manner in the boundary. There are also effects on the distribution of attack over the surface, such as the pitting type of corrosion which is induced by chlorides in certain circumstances.

With the recognition that corrosion involves a combination of two or more electrochemical processes, the over-all free-energy change of which is negative, it becomes apparent that corrosion is determined primarily by kinetic parameters. Hence, all those properties of the total interface that affect transport of electric charges across this interface are significant for the phenomena in question. The total interface must be considered to include a thin skin of the metallic phase, any non-metallic film on the surface, and a thin layer of the solution phase, from which reactants or adsorbed species may arise.

The complexity of the process is emphasized by the recognition that it involves several branches of physical chemistry and solid-state physics. First, there are the principles of electrolytic solutions and their bearing on the theory of electrochemical kinetics. Included in this category are the various factors that determine diffusion phenomena and local activities at the solution side of the interface. Next, there are the two-phase interactions between the solution and solid phase, which may be metallic or non-metallic. These interactions, in turn, may be either reversible or irreversible, in the thermodynamic sense. Such interactions include, among others, adsorption, ion-exchange, and precipitation or dissolution processes. Thirdly, the kinetic effects associated with any solid, non-metallic interphase may depend upon its defect structure, the multiple valency of its constituents, and other properties related to transfer of charges (ions, electrons, or defects) through it. Finally, the thin outer skin of the metal is to be considered, since the energy levels and structural features there may differ from those in the interior for various reasons, and, further, because there are often epitaxial relationships at the metal-film interface which have an important bearing on the stability of the film. From this summary, it may be seen that many phases of modern physical science must be applied to the study of the phenomena associated with corrosion. Several such studies have been made already by use of radioisotopes. The present paper will be devoted chiefly to work done in this laboratory with fission-product technetium, with brief reference to use of other isotopes.

2. Properties of technetium compounds

In 1952, consideration of possible mechanisms of the action of certain ions of the XO_4^{n-} type led the author to predict that the pertechnetate ion, TcO_4^-, should be an inhibitor of the corrosion of iron. The expectation was fulfilled [1], and several studies of different phases of the problem have been made [2]. The nuclear and chemical properties of technetium compounds make it extremely advantageous to use them in such studies. The element is produced in the fission

of U^{235} with a yield of Tc^{99} of somewhat over 6%. It is normally recovered in the form of the pertechnetate ion, TcO_4^-. Being in the seventh group of the periodic system, the element bears a close relation to rhenium, though there are important differences. The principal oxidation states and corresponding oxidation-reduction couple potentials are as follows [3—5]:

$$Tc(OH)_4 + 4\,H^+ + 4e^- \rightleftarrows Tc + 4\,H_2O;\ E^\circ = 0.266\ V$$

$$TcO_4^- + 8\,H^+ + 7e^- \rightleftarrows Tc + 4\,H_2O;\ E^\circ = 0.468\ V$$

$$TcO_4^- + 4\,H^+ + 3e^- \rightleftarrows Tc(OH)_{4(ppt)};\ E^\circ = 0.738\ V.$$

An unstable TcO_3 and complexes derived from the 5+ valence are also known. Since the $CrO_4^=$ ion has been used so extensively in studies of inhibition, it may be noted that in 10^{-3} *F* solutions of TcO_4^- and $CrO_4^=$, both at pH = 6, the reversible potentials for reduction to $Tc(OH)_4$ or $Cr(OH)_3$ are 0.20 and 0.59 V, noble to the normal hydrogen electrode, respectively. The pertechnetate ion is therefore considerably milder as an oxidizing agent. The acid, $HTcO_4$, is a strong acid, hence the ion TcO_4^- does not have the buffering action associated with the equilibrium, $CrO_4^= + H^+ \rightleftarrows HCrO_4^-$. Furthermore, the known salts of pertechnic acid are rather soluble, with the exception of the silver salt. In its valence, oxidizing power and solubility-relationships the pertechnetate ion therefore provides a research tool quite different from the much-used chromate ion.

The pertechnetate ion has a strong and distinctive absorption spectrum which is very useful for analytical purposes. Suitable maxima of absorption occur at 2440 and 2875 Å, where the molar extinction coefficients are 6080 and 2310, respectively, as measured on a Beckman spectrophotometer (Model DU). The ratio of the absorption at these two wavelengths is useful as a test of purity, the best value being 2.63_5. The element may be determined also by polarographic analysis [6].

The chief isotope, Tc^{99}, is a beta-emitter with a maximum energy of $0.29 \pm \pm 0.01$ MeV and a half-life of $2.15 \pm 0.05 \times 10^5$ yr [7]. These properties make autoradiography and counting techniques very convenient for experimental purposes, without necessitating precautions against radiation from the small quantities of material required. The half-life is particularly advantageous for long-term studies in comparison with chromate ions containing Cr^{51}, the half-life of which is only 27.8 d. Tc^{99} is now available for research purposes through the Isotopes Division of the Oak Ridge National Laboratory.

3. Inhibition by the pertechnetate ion

After simple qualitative tests had demonstrated that the pertechnetate ion inhibits the corrosion of iron very effectively, a series of experiments was conducted to delimit the conditions of concentration, acidity and temperature which control its action. A primary purpose of these experiments was to gain evidence bearing on the alternative hypotheses that have been developed to account for the inhibitory action of chromates, molybdates and tungstates, all of which derive from relatively weak acids of varying oxidizing power. When the pertechnetate ion reacts with active iron, a surface film containing $Tc(OH)_4$ and iron oxides (or hydrated oxides) is formed. By counting the beta-activity of well-washed specimens after treatment with an aerated pertechnetate solution, it was found that the surface film might contain very different amounts of

technetium according to the activity of the iron surface. Under suitable conditions, the specimen might remain passive with no visible film and much less technetium than would suffice, if uniformly distributed, to form a monomolecular layer. On the other hand, very large deposits might be formed under other circumstances without passivation. The experiments made it clear that the mere formation of a film of reaction products is not a sufficient condition for inhibition. It was further found that whatever amount of film is present, inhibition is maintained only if a certain minimum concentration of pertechnetate ions remains in solution. With a low-carbon steel, this amount was approximately 5 ppm ($5 \times 10^{-5} f$) in solutions containing no other electrolytes and a pH approximating 6. Such a concentration was found effective even at 250°. Higher concentrations were required when other electrolytes were present in low concentration.

Measurements of beta-activity are continuing on two specimens that have been under observation in aerated solution since January 1953. The activity shows that there has been no detectable consumption of inhibitor since the system stabilized within the first month. Over the 7-yr period, the total beta-count of a specimen kept in 4×10^{-4} *F* TcO_4^- with 10 ppm of Cl^- has corresponded to 2×10^{14} atoms/cm^2, of which approximately one third is localized in a tiny flaw in the metal. The properties of $Tc(OH)_4$ make it possible to distinguish a pure product arising from a localized cathodic process from one formed in admixture with iron oxides resulting from an anodic process. A freshly precipitated cathodic product may be reconverted to TcO_4^- almost quantitatively either by an anodic treatment or by two brief washes in ammoniacal or acidic hydrogen peroxide [8]. If the deposit arises from associated anodic processes, decontamination efficiencies in the peroxide treatment are usually in the neighbourhood of 30—40%.

Another series of experiments was conducted with radioisotopes to test the possibility that the inhibitory properties of the pertechnetate ion are associated with its radiations or radiolytic products arising from them. Advantage was taken of the fact that rhenium is available in both stable and radioisotopic forms [9]. It was found that natural $KReO_4$ failed to produce significant inhibition at any concentration at temperatures from near 0° to 95°. The natural compound was then irradiated in the graphite reactor to give Re^{186} and Re^{188}, along with K^{42}. When mixtures of natural and radioactive $KReO_4$ were prepared to give β-activities equivalent to those of inhibiting pertechnetate solutions, still no inhibition was obtained.

Since the experiments have demonstrated that $Tc(OH)_4$ precipitated on the surface is not the primary source of inhibition, the alternative is that unreduced TcO_4^- ions held on the surface in some way alter the kinetics of the dissolution process. By means of electrochemical measurements, as well as by observations of corrosion, it was shown that the state responsible for inhibition is sensitive to the addition of low concentrations of several anions, including the sulphate ion. This suggests that an adsorbed species must be maintained by having sufficient TcO_4^- in the solution, and also that this equilibrium is displaced by the addition of sulphate or other anions which do not inhibit. There is much evidence to indicate that the activity counted on a well-washed specimen arises only from any $Tc(OH)_4$ that may be held on the surface. Attempts to determine the adsorption by measuring the decrease in concentration of a pertechnetate solution upon insertion of a bundle of fine iron-wires gave no significant results. Some pertechnetate is always reduced at active sites, but the total removal on a carefully cleaned surface, including both reaction product

and adsorbed species, was just at the limit of accuracy of the counting procedure. It is evident that the adsorption which occurs is labile with respect to washing or displacement by other anions.

In view of the results reported by KRAUS *et al.* [10], there is the further possibility that the passive film holds pertechnetate ions that are removable only by an ion-exchange process. This has been investigated [11] by use of carbonyl iron-powder, fine iron-wire, and also by examination of a piece of sheet-steel that had been passivated in an aerated pertechnetate solution for 15 months. When the inhibited specimens were first washed with water and then with NH_4OH (which exchanges $CrO_4^=$ from bulk oxides), the TcO_4^- released, if any, was at the most a small fraction of a monolayer. When the 4-cm² specimen was extracted with 6-*N* NH_4OH after 15 months in the pertechnetate solution (15 ppm Tc), the beta-activity was as follows: before NH_4OH, 4370 counts/min; after NH_4OH, 4350 counts/min. On this specimen, removal of a monolayer of TcO_4^- should have reduced the count by 16% or 700 counts/min. Hence, it must be concluded

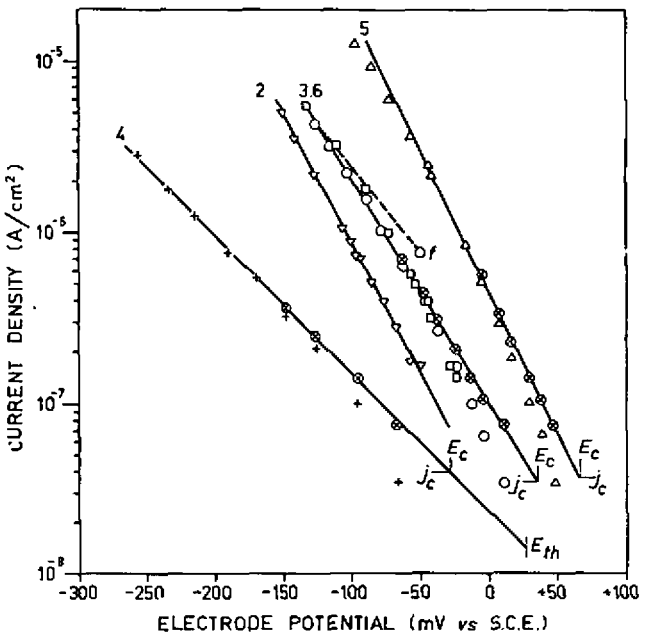

Fig. 1

Successive cathodic polarizations of passive iron in phthalate or pertechnetate solutions (0.0100 *f* at pH 5.6 — 5.9), to determine the effects of oxygen and of precipitated $Tc(OH)_4$ in the surface film.

Curves represent the following conditions:

(2) oxygenated phthalate;
(3) oxygenated pertechnetate;
(4) pertechnetate in helium;
(5) oxygenated pertechnetate with $Tc(OH)_4$ left on film;
(6) same after removal of $Tc(OH)_4$ by anodic polarization.

At lowest current-densities data points require correction for an anodic current-density of 4×10^{-8} A/cm². Corrected points are shown by ⊠.

that the pertechnetate ion does not interact significantly with the passive film by anything resembling an ion-exchange process.

Another problem which is currently being investigated concerns the comparative roles of oxygen and reducible inhibitors in maintaining the passivity of iron [12]. The use of Tc^{99} as inhibitor makes it possible to determine the amount on the electrode and to remove the $Tc(OH)_4$ by brief anodic polarization. In this way, any effect of $Tc(OH)_4$ in the film upon the rate of cathodic processes may be established. Fig. 1 shows the results of one series of experiments. Curve 2 represents the second of duplicate cathodic polarizations of an iron electrode that had been passivated in an oxygenated phthalate buffer-solution. Curve 3 shows the moderate acceleration of the cathodic processes in 0.0100 *F* $KTcO_4$. These two curves represent polarization of oxygenated solutions. In curve 4, the result of polarizing the electrode again in the 0.0100 *F* pertechnetate solution in an atmosphere of essentially oxygen-free helium is shown. It is seen that the current density at any chosen potential is much higher in the oxygenated solution. Curve 5 was obtained by another polarization in the presence of oxygen, the $Tc(OH)_4$ formed during the previous polarization in helium having been left on the electrode. Curve 6 was obtained from another polarization in oxygen after removal of the $Tc(OH)_4$ by a brief anodic treatment. The experiments demonstrate that oxygen is the chief cathodic reactant when present along with the pertechnetate ion, and that a considerable acceleration of the cathodic processes is induced by any $Tc(OH)_4$ on the electrode. In similar potentiostatic studies it was found that the polarization over-voltage was considerably reduced by amounts of $Tc(OH)_4$ equivalent to less than a complete monolayer.

4. The use of $Fe^{55,59}$ and Cu^{64} in studies of passivation

In connection with studies on the passivation of stainless steel, the iron radioisotopes have been used to determine the relation of dissolved iron ions to the passivation process [13]. It is well known that iron (III) ions are an effective passivator in this system. Four similar electrodes were immersed in 0.10-*N* H_2SO_4 at 85° with air passing through the solution. While the electrodes were corroding at an active potential, the tracer iron solution was added. Two of the electrodes were allowed to passivate spontaneously, while the other two were kept slightly below the corrosion potential by a sufficient cathodic polarization. After a time the electrodes were removed, washed and counted. It was shown that the iron activity was 3 to 5 times as great on the electrodes which passivated. This excess activity was removed when the electrodes were returned to the solution and polarized back to the active potential. The experiment shows a definite contribution of dissolved iron ions to the passivation process. A similar effect was found in the passivation of electrolytic iron in an aerated benzoate solution to which iron-ions were added.

Similar participation of copper (II) ions in the passivation of stainless steel has been demonstrated by use of Cu^{64} [14]. Here it was shown that some copper species passes into the surface film when the passive electrode is cathodically polarized in solutions of sulphuric acid to which increasing amounts of copper (II) sulphate are added. Upon reducing the concentration of copper ions, the potential diminishes (for constant current density), but the activity of Cu^{64} on the electrode does not decrease. A possible mechanism was developed to account for the results.

5. The use of I^{131} in studies of inhibition

The radioisotope I^{131} has been used by KOLOTYRKIN *et al.* [15—18] in studies of adsorption on metallic surfaces. In this laboratory it has been used as an inhibitor for the dissolution of electrolytically deposited iron in sulphuric acid [19]. It was shown that iodide ions in concentrations of 10^{-3} F or above increase slightly the overvoltage for evolution of hydrogen, but exert a much greater effect on the anodic dissolution of iron. From polarization measurements at different concentrations and pH values, the dependence of the anodic polarization curve upon these variables was established. It was shown that the inhibited system becomes essentially unpolarizable above a certain potential, which is a function of the concentration of iodide and hydrogen ions. I^{131} was then used to determine the amount of iodide removed from solution as a function of concentration and current-density in the steady state. It was found that the adsorption at the open-circuit potential is reversible and varies with concentration in accordance with either a Langmuir or a Temkin isotherm. The amount adsorbed decreased when anodic current-densities exceeding 1 mA/cm^2 were applied. The results have been tentatively accounted for by assuming an adsorption process depending upon concentration and area available, and a desorption process depending both on surface coverage and on current density.

From these selected illustrations it may be seen that radioisotopes may be used as valuable tools in studying phenomena related to corrosion. However, many opportunities for the further application of radioisotopes remain, since the full significance of adsorption and films for the kinetics of corrosion is still not clear. Thus, the work of FEITKNECHT *et al.* [20] on the exchange of tritium with film-forming hydrated oxides and the demonstrated mobility of protons in organic and inorganic materials are examples of phenomena which have been little investigated, but doubtless have important implications for the study of corrosion.

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DISCUSSION

K. H. Lieser (Federal Republic of Germany) asked whether Mr. Cartledge had ever observed a direct exchange between iron ions in solution and metallic iron atoms without applying external potential.

G. H. Cartledge said that the effect had been observed only with film ions, particularly in conditions where stainless steel was in process of becoming passive. The iron dropped off when the specimens were reduced cathodically. A similar effect had also been observed in the case of passivation by oxygen in a benzoate solution; in that case the process was greatly accelerated by the addition of iron ions. The experiments had been carried out on an open circuit, except for the cathodic reduction.

RADIO-TRACER TECHNIQUES IN THE STUDY OF CORROSION BY MOLTEN FLUORIDES

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Abstract — Résumé — Аннотация — Resumen

Radio-tracer techniques in the study of corrosion by molten fluorides. When Inconel or Inor-8 alloys are exposed to a molten fluoride mixture containing reducible material, chromium is selectively oxidized and removed from the alloy.

By the use of radio-tracer Cr^{51}, the self-diffusion coefficients for chromium in Inconel and Inor-8 and the applicability of these values to alloys under corrosive conditions have been evaluated.

Overall coefficients have been obtained (1) by measuring depletion of Cr^{51} (charged as CrF_2) for non-corrosive fluoride melts in alloy capsules and (2) by comparison of measured total radioactivity of exposed alloy specimens with that of the salt to which they were exposed. In addition, coefficients were obtained from measurement of tracer concentration profiles through successive electropolishings of the specimens. The overall coefficients and those obtained from electropolishing experiments agree very well for Inconel at high temperatures and for Inor-8 at all temperatures. For temperatures below 750°C, coefficients obtained by electropolishing Inconel specimens are higher than the overall values; the bulk diffusion process is not uniform for this case. In all cases, good agreement was found between the overall diffusion coefficients and those extrapolated from published data at higher temperature with generally similar Cr-Ni alloys.

Duplicate, polythermal loops of Inor-8 were used to circulate a non-corrosive fluoride melt containing Cr^{51} (as CrF_2). One of these loops was sacrificed to evaluate take-up of Cr^{51} by the alloy; the second was used to circulate a melt containing FeF_2 to obtain measurable removal of Cr from the alloy. Good agreement between observed behaviour and that predicted from the measured diffusion coefficients was obtained; this agreement suggests that the self-diffusion coefficient for Cr is insensitive to changes in chromium content of the Inor-8 alloy.

Etude, à l'aide d'indicateurs radioactifs, de la corrosion provoquée par les fluorures fondus. Lorsqu'on soumet les alliages Inconel ou Inor-8 à l'action d'un mélange de fluorures fondus contenant des substances réductibles, le chrome est oxydé sélectivement et éliminé de l'alliage.

En utilisant comme radioindicateur le chrome-51, les auteurs du mémoire ont évalué les coefficients d'autodiffusion du chrome dans l'Inconel et l'Inor-8 et vérifié dans quelle mesure les valeurs obtenues sont applicables aux alliages exposés à la corrosion.

Les auteurs ont calculé les coefficients globaux: 1) en mesurant le passage du chrome-51 (employé sous forme de CrF_2) des capsules d'alliage aux fluorures non corrosifs fondus; 2) en comparant la radioactivité totale mesurée des échantillons d'alliage exposés avec celle du sel auquel ils avaient été exposés. Ils ont calculé en outre des coefficients en mesurant les profils de concentration de l'indicateur par polissages électrolytiques successifs des échantillons. Les coefficients globaux et ceux qui ont été obtenus par polissage électrolytique concordent parfaitement pour l'Inconel à des températures élevées et pour l'Inor-8 à toutes les températures. Pour les températures inférieures à 750°C, les coefficients obtenus par polissage électrolytique de l'Inconel sont supérieurs aux coefficients globaux; dans ce cas, le processus de diffusion

dans la masse n'est pas uniforme. Il y a toujours concordance satisfaisante entre les coefficients globaux de diffusion et les coefficients obtenus par extrapolation des données publiées au sujet d'alliages Cr-Ni généralement analogues, à des températures plus élevées.

Les auteurs se sont servis de deux anneaux polythermiques d'Inor-8 pour faire circuler une masse de fluorures fondus non corrosifs contenant du chrome-51 (sous forme de CrF_2). Ils ont sacrifié l'un des circuits pour évaluer la quantité de ^{51}Cr absorbée par l'alliage, et utilisé l'autre pour faire circuler un mélange fondu contenant du FeF_2 et mesurer l'élimination du chrome de l'alliage. Les résultats obtenus concordent assez bien avec les données fournies par les coefficients de diffusion mesurés expérimentalement; il est permis d'en conclure que le coefficient d'autodiffusion du chrome est insensible aux modifications de la teneur en chrome de l'alliage Inor-8

Применение методов радиоактивных индикаторов при изучении коррозии, причиняемой расплавленными фтористыми соединениями. Когда „инконель" или „инор-8" подвергаются действию расплавленных фтористых смесей, содержащих восстанавливающие вещества, хром избирательно окисляется и удаляется из сплава.

С помощью радиоактивного индикатора Cr^{51} были установлены коэффициенты самодиффузии хрома в „инконеле" и „иноре-8", а также была изучена применимость значений этих коэффициентов к сплавам в коррозийных условиях.

Суммарные коэффициенты были получены путем следующих замеров: 1) обеднения в Cr^{51} (загруженного в виде CrF_2) некоррозийных фтористых расплавов в легированных капсулах и 2) соотношения между измеренной общей радиоактивностью обработанных солью образцов сплава и радиоактивностью соли, действию которой образцы были подвергнуты. Помимо этого, коэффициенты были получены путем замера графика концентрации индикатора при последовательной электрополировке образцов. Суммарные коэффициенты, а также коэффициенты, полученные опытами электрополировки, очень близко совпадают для „инконеля" при высоких температурах и для „инора-8" при всех температурах. Для температур ниже 750° С коэффициенты, полученные при помощи электрополировки образцов "инконеля", превышают значения суммарных коэффициентов; в этом случае процесс диффузии в массе не однообразен. Во всех случаях наблюдалось хорошее совпадение между суммарными коэффициентами диффузии и коэффициентами, полученными путем экстраполяции данных, опубликованных обычно для аналогичных сплавов хрома и никеля при более высоких температурах.

Двойные политермические петли „инора-8" были использованы для циркуляции некоррозийного фтористого расплава, содержащего Cr^{51} (в виде CrF_2). Одна из этих петель была пожертвована для определения усвоения Cr^{51} этим сплавом; вторая петля была использована для циркуляции расплава, содержащего FeF_2, для получения измеримого устранения Cr из сплава. Было получено хорошее совпадение между фактически наблюдавшимися явлениями и прогнозом, сделанным на основании измеренных коэффициентов диффузии. Из этого совпадения можно заключить, что коэффициент самодиффузии хрома нечувствителен к изменениям содержания хрома в сплаве „инор-8".

Estudio con indicadores radiactivos de la corrosión ocasionada por fluoruros fundidos. Si se someten el Inconel o el Inor-8 a la acción de una mezcla de fluoruros fundidos, que contenga sustancias reducibles, el cromo sufre una oxidación selectiva y es extraído de la aleación.

Con ayuda del indicador radiactivo ^{51}Cr, los autores han evaluado los coeficientes de autodifusión del cromo en el Inconel y en el Inor-8, y han comprobado que los datos obtenidos son válidos para las aleaciones expuestas a la corrosión.

Han calculado los coeficientes globales 1) midiendo el paso del ^{51}Cr de las cápsulas de aleación (empleado en forma de CrF_2) a los fluoruros no corrosivos fundidos, y 2) comparando la radiactividad total medida en las muestras de aleación expuestas con la radiactividad de la sal a cuya acción fueron sometidas. Además, calcularon los coeficientes midiendo los perfiles de concentración del indicador por pulidos electrolíticos sucesivos de las muestras. Los coeficientes globales y los obtenidos

por pulido electrolítico concuerdan satisfactoriamente para el Inconel a temperaturas elevadas, y para el Inor-8 a todas las temperaturas. Los valores obtenidos por pulido electrolítico del Inconel tratado a temperaturas inferiores a 750° C superan a los valores globales; en este caso, el proceso de difusión másica no es uniforme. Los coeficientes medios de difusión encontrados concuerdan siempre con los que se calculan por extrapolación de los valores publicados, que fueron obtenidos con aleaciones de Cr-Ni similares, a temperaturas más elevadas.

Los autores se sirvieron de un par de bucles politérmicos de Inor-8 para hacer *circular una masa* de *fluoruros* no corrosivos fundidos que contenían ^{51}Cr (en forma de CrF_2). Sacrificaron uno de estos bucles para evaluar la cantidad de ^{51}Cr absorbida por la aleación; el segundo se utilizó para hacer circular una mezcla fundida que contenía FeF_2 y medir la eliminación del cromo de la aleación. Los resultados obtenidos concuerdan satisfactoriamente con los que se calculan con ayuda de los coeficientes de difusión determinados experimentalmente; esta concordancia indica que el coeficiente de autodifusión del Cr no es afectado por las variaciones de la concentración de cromo en la aleación Inor-8.

1. Introduction

The results of recent studies [1] have shown that when Inconel* or INOR-8** is exposed to molten fluoride mixtures containing reducible materials, chromium is selectively oxidized and removed from the alloy. These alloys are of particular interest as they are suitable for molten-salt reactor applications [2]. When UF_4 serves as the oxidant in a polythermal test system the temperature-sensitive equilibrium

$$2UF_4 + Cr^\circ \rightleftarrows 2UF_3 + CrF_2$$

provides a mechanism by which the alloy at high temperature is depleted and the alloy at low temperature is enriched in chromium.

On the other hand, reactions of the type:

$$MF_2 + Cr^\circ \rightarrow M^\circ + CrF_2$$

with easily reducible substances such as FeF_2 or NiF_2, are essentially complete at all temperatures [3]. In either case, corrosion is controlled by rates of diffusion of chromium *within the alloy*.

Accordingly, a thorough knowledge of solid-state diffusion of chromium in the alloys is an important phase of corrosion studies. Initial studies and reviews revealed that several investigations related to solid-state diffusion have been reported in the literature, but only a portion of the reported work covered cases in which molten salts and chromium alloys were involved.

A large number of the chromium diffusion coefficients available in the literature were applicable only at temperatures above 900°C [4]. However, extrapolation of this information to temperatures of reactor interest (600° to 900°) could be misleading if the diffusion mechanism were to change within the extrapolated region.

An experimental investigation was performed using Cr^{51} to determine self-diffusion coefficients of the radio-tracer in systems composed of molten NaF-ZrF_4 mixtures in contact with either Inconel or INOR-8, under non-corrosive conditions. The validity of the use of the self-diffusion coefficients under corrosive conditions was also experimentally evaluated.

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* Nominal composition: 15% Cr, 5% Fe, balance Ni
** Nominal composition: 7% Cr, 16% Mo, balance Ni

2. Experimental

Materials

Chromium tracer

Chromium tracer was introduced to the alloy-salt systems as Cr^{51}-labelled chromous fluoride for all the experiments mentioned in this report. The method of preparation has been described in detail elsewhere [5].

Molten fluoride solvent

The molten fluoride mixtures were prepared from reagent-grade materials and purified in a closed system of nickel at 800°C by alternate flushing with anhydrous HF and H_2. The apparatus and procedure were identical with those described in a previous publication [6].

Alloys

Information regarding the chromium content, type of alloy, and pre-test treatments of the alloy specimens studied may be found in Table I.

Counting techniques

A well-type scintillation counter was employed for all count-rate determinations involving chromium-51. Undesirable geometry and shielding effects which might introduce counting errors were eliminated or minimized as described previously [7].

Theory of experimental techniques

Wall exchange-reaction

If consideration is given to a semi-infinite isothermal system wherein an alloy containing metallic chromium (Cr°) is in contact with a molten salt containing a fixed amount of CrF_2, the net rate of transfer of Cr between the metal and the salt must be zero at equilibrium, although a random dynamic exchange of Cr takes place [8] [9]. If a small amount of the CrF_2 is removed and replaced by an equal amount of labelled Cr^*F_2, the dynamic exchange can be studied by following the exchange rate of the labelled Cr^*F_2. The expression which relates the quantities of interest in terms of the surface exchange-reaction or "wall reaction",

$$Cr^\circ + Cr^*F_2 \rightleftarrows Cr^{++}F_2 + Cr^{*\circ}, \ (\Delta F = 0) \tag{1}$$

is

$$K_{\text{wt. frac.}} = [Cr^{*\circ}]\,[CrF_2]/[Cr^\circ]\,[Cr^*F_2] \tag{2}$$

where $K_{\text{wt. frac.}}$ = equilibrium quotient in terms of weight fractions of the constituents.

The equilibrium of Eq. (1) is established within a short period of time at the surface after the Cr^*F_2 is added. Since the equilibrium constant

$$K_a = 1 \cong K_{\text{wt. frac.}} \tag{3}$$

the concentration of $Cr^{\circ *}$ at the surface ($x = 0$) of the alloy at any temperature is given by:

$$C[_{Cr^{*\circ}}]_{x=0} = \varrho_m\,[Cr^\circ]\,[Cr^*F_2]/[CrF_2]. \tag{4}$$

TABLE I

SUMMARY OF EXPERIMENTS TO DETERMINE OVER-ALL DIFFUSION COEFFICIENTS

Experiment Group Number	Type of Experiment	Chromium Content of Alloy (wt. %)	Solvent Composition (mole %)	Alloy Material and Dimensions	Alloy Pretreatment or Annealing Conditions	Remarks
I	Isothermal capsule (depletion)	16.0	NaF-ZrF_4 (50-50)	Inconel: sides, $^3/_8$-in tubing; bottom, plate	Welding temp., then normalized under H_2 for 4 h at 900°C	Previously uncorrelated data obtained from Ref [9] at 3 temps.
II	Poly-thermal capsule (depletion)	14.4	NaF-ZrF_4 (53-47)	Inconel: capsules machined from bar stock $^3/_8$-in outer diam., $^5/_{16}$-in inner diam, $^{25}/_{64}$-in inside length	Annealed under H_2 for 8 h at 1150°C	Experiment performed to verify and augment Group I results
III	Constant potential	15.2	NaF-ZrF_4 (53-47)	Inconel: $^1/_4$-in tubing, 0.035-in wall	Annealed under H_2 for 2 to 4 h at 1150°C	Several groups of isothermal experiments performed to verify Eq. (6) and to evaluate the experimental method
IV	Constant potential	15.1	NaF-ZrF_4 (53-47)	Inconel: $^1/_4$-in tubing, 0.035-in wall	Annealed under He for 2 to 4 h at 1150°C	Single 1-day exposure time; experiments performed to show effects of H_2 *vs.* He annealing
V	Constant potential	14.8	NaF-ZrF_4 (53-47)	Inconel: $^1/_4$-in tubing 0.035-in wall	Annealed under H_2 for 8 to 12 h at 800°C	Single 2-week exposure-time experiments performed to show effects of lower annealing temp. and to provide specimens for electropolishing experiments
VI	Constant potential	7.03	NaF-ZrF_4 (53-47)	INOR-8: $^1/_4$-in tubing 0.028-in wall	Annealed under H_2 for 8 to 12 h at 800°C	Single 2-week exposure-time experiments performed to obtain preliminary INOR-8 over-all coeff. comparable to Inconel coeff.

where

$C[Cr^{*\circ}]_{x=0}$ = concn (g/cm³) of labelled chromium at the surface of the alloy and

ϱ_m = density of alloy (g/cm³).

The $Cr^{\circ *}$ initially distributed on the wall surface diffuses into the metal as time progresses; this tends to deplete both the $Cr^{\circ *}$ at the surface and the Cr^*F_2 in the salt, unless Cr^*F_2 is added to the system at a rate equal to the diffusion rate.

Depletion method

If Cr^*F_2 is not added to the salt after time-zero and the subsequent depletion of the Cr^*F_2 activity in the salt (corrected for time decay) is measured as a function of time, a diffusion coefficient for chromium in the metal may be calculated by means of the following relationship:

$$(b_{t=0} - b_t)/(b_{t=0}) = 1 - \exp(a^2 t)\ \mathrm{erfc}\ (a\sqrt{t}), \tag{5}$$

where

t = time, sec,

$b_{t=0}$ = counts/g min at t of a filtered salt sample taken at t_0,

b_t = counts/g min at t of a filtered salt sample taken at t, and

$$a = \frac{A}{V}\frac{[Cr^\circ]}{[CrF_2]}\frac{\varrho_{metal}}{\varrho_{salt}}\sqrt{D}\left(\sec^{-\frac{1}{2}}\right),$$

where

$\frac{A}{V}$ = ratio of the salt-exposed area of Inconel to the salt vol. (cm^{-1}),

$\frac{[Cr^\circ]}{[CrF_2]}$ = weight-fraction ratio of chromium in Inconel to chromous fluoride (as Cr^{++}) in the salt,

$\frac{\varrho_{metal}}{\varrho_{salt}}$ = density ratio of metal to salt,

D = diffusion coefficient (cm²/sec).

Eq. (5) was utilized in the correlation of data obtained in capsule experiments as will be explained later.

Constant potential method

If the concentration of the Cr^*F_2 in the molten salt is kept constant during the exposure period, alloy specimens immersed in the salt absorb labelled chromium under conditions of constant surface potential. That is, the concentration of labelled chromium at the surface remains constant with time. The ratio of the corresponding $Cr^{\circ *}$ transfer to the activity of the salt is given [10] by:

$$\frac{y}{z} = 2A\,\varrho_m\frac{[Cr^\circ]}{[CrF_2]}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \tag{6}$$

where

y = total counts/min of the entire specimen at t,

z = counts/g min of the salt at t.

The variable y is a measure of the total amount of tracer gained by the specimen; z is an indirect measure of the tracer concentration which is maintained on the specimen surface during immersion.

Electropolishing method

After constant potential exposure, self-diffusion coefficients were also determined by measuring the tracer concentration profile through successive removal

and analysis of thin layers of alloy. An electropolishing technique previously described [11] was used in the present investigation. An integral method [12] was employed to correlate the data. The electropolishing experiments were conducted as follows: after salt exposure, the specimens were counted, polished, recounted, polished again, etc. until less than 10% of the original activity remained in the alloy. The percentage of activity remaining after each polishing was plotted as a function of the cumulative penetration distances (wall thickness—sum of polishing increments). The experimental plot was compared to a generalized plot of an equation applicable to the experimental procedure. For a constant-potential, semi-infinite system, with initial tracer-concentration at zero, the equation is:

$$F(x) = 100\sqrt{\pi}\int_{x}^{\infty} \operatorname{erfc} u \, du \tag{7}$$

where

$F(x)$ = per cent of original activity remaining at penetration x (cm) and

$$u = \left(\frac{x}{2\sqrt{Dt}}\right).$$

Values of $\int_{u}^{\infty} \operatorname{erfc} u \, du$ are available in tabular form in the literature [13].

Procedures for determining diffusion coefficients

Capsules

A detailed description of the procedures utilized to perform capsule (depletion) experiments has been given by Evans *et al.* [7] [9]. Briefly, suitable quantities of prepurified frozen salt containing concentrations of CrF_2 and of Cr^*F_2 were enclosed in a number of identical alloy capsules of known dimensions which were sealed in a helium atmosphere and placed in a furnace. For the isothermal experiments [9] the furnace was kept at constant temperature and at various time-intervals a single capsule was removed until the entire series had been transferred. For the polythermal experiments, a thermal gradient block [14] was used and the entire group of capsules was heated for an identical period but over a known temperature range. After exposure, the depletions were determined for the various capsules.

Eq. (5) was used to correlate data from the two types of capsule experiments. Isothermal depletions were determined as a function of time in one experiment [9], whereas depletions as a function of temperature (at identical molten-salt exposure-times) were determined in the second type of experiment.

The ratio

$$\left(\frac{A}{V}\right)\frac{[Cr_0]}{[CrF_2]}\frac{\varrho_m}{\varrho_s}(D)^{\frac{1}{2}}(\sec)^{-\frac{1}{2}}$$

was held constant in both cases. The corrected depletions were plotted against the independent variable measured and this curve was compared to a plot of the function $1-e^{u^2}\operatorname{erfc}(u)$ against u, where u was considered to be $(a\sqrt{t})$. Values of a and D were readily calculated by this method.

Constant-potential experiments

A description in detail of the experimental procedures followed to obtain alloy samples which had absorbed Cr* under conditions of a constant surface

potential may be found elsewhere [7]. In general, the alloy specimens employed were small (1/4-in outer diam. thermocouple wells) and were immersed in a relatively large volume of salt (200 cm³). Furthermore, the salt was contained in a vessel of the same alloy material which, prior to the introduction of the sample, had been heated in contact with the solution to high temperatures (about 950°C) and had absorbed Cr* for some time. After this pretreatment, the temperature of the system was lowered to the temperature of interest and the specimens were introduced. In this manner, not only the salt but also the walls of the vessel served as reservoirs of Cr*. Experimentally, the Cr^*F_2 concentration in the solution could be maintained constant throughout the duration of the specimen exposure.

Four series of experiments were performed by means of the constant-potential method. Three series involved Inconel specimens which had been subjected to three types of pretreatment conditions; the fourth series involved INOR-8 specimens.

Loop experiments

Experiments of longer duration using INOR-8 were performed using thermal-convection loops. Thermal-convection loops similar to the ones employed have been described in detail previously [1]. The complete experimental procedures followed in the present experiment may be found elsewhere [15], where duplicate polythermal loops of INOR-8 were used. Two loops were started with non-corrosive fluoride solutions containing Cr^*F_2 and were operated for 500 h and 1056 h, respectively. After 500 h the first loop was drained and sacrificed to obtain diffusion coefficients under non-corrosive conditions. After 792 h of operating the second loop under non-corrosive conditions, a corrosive agent, (FeF_2), was added without otherwise disturbing the operation. After 264 h of additional operation under corrosive conditions, the second loop was shut down for analysis.

The data of the first loop were correlated using Eqs. (6) and (7). The data of the second loop were correlated using the following equations [10]:

$$\frac{y}{z} = 2A\varrho m \frac{[\mathrm{Cr}^\circ]}{[\mathrm{CrF}_2]} \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left[(t')^{\frac{1}{2}} - (t' - t_0)^{\frac{1}{2}}\right] \tag{8}$$

and

$$F(x) = \frac{100\sqrt{\pi}\left[(t')^{\frac{1}{2}} \int_w^\infty \operatorname{erfc} w\,dw - (t' - t_0)^{\frac{1}{2}} \int_u^\infty \operatorname{erfc} u\,du\right]}{(t')^{\frac{1}{2}} - (t' - t_0)^{\frac{1}{2}}} \tag{9}$$

where all symbols have the same significance as those in Eqs (6) and (7), but in addition:

t' = total time of exposure,
t_0 = time at which FeF_2 was added,
$w = x/2\,(Dt')^{1/2}$, and
$u = x/2\,[D\,(t' - t_0)]^{1/2}$.

3. Results and discussion

The experimental methods previously mentioned provide two types of diffusion coefficients for a given specimen. One coefficient is based on the measurement of the over-all amount of tracer which diffused into the specimen under a known

potential, such as provided in the depletion and in the constant-potential methods. The results obtained by these methods will be discussed under the classification of "over-all diffusion coefficients". The second coefficient is based on the tracer concentration-profile within the specimen, such as obtained by the electropolishing method, and will be discussed under the heading of "concentration-profile diffusion coefficients. In addition, the results obtained using INOR-8, where no difference was noted between the "over-all" and the "profile" coefficients, will be discussed under the classification of "loop experiments".

Over-all diffusion-coefficients

Over-all coefficients, as a function of temperature and grain size, were obtained from six series of experiments. The experiments could be conveniently grouped according to experimental method, alloy pretreatment, and type alloy. For brevity of presentation, these groupings are shown in Table I.

Experimental points for groups I—IV and reported high-temp. values for a similar alloy are plotted on Fig. 1.

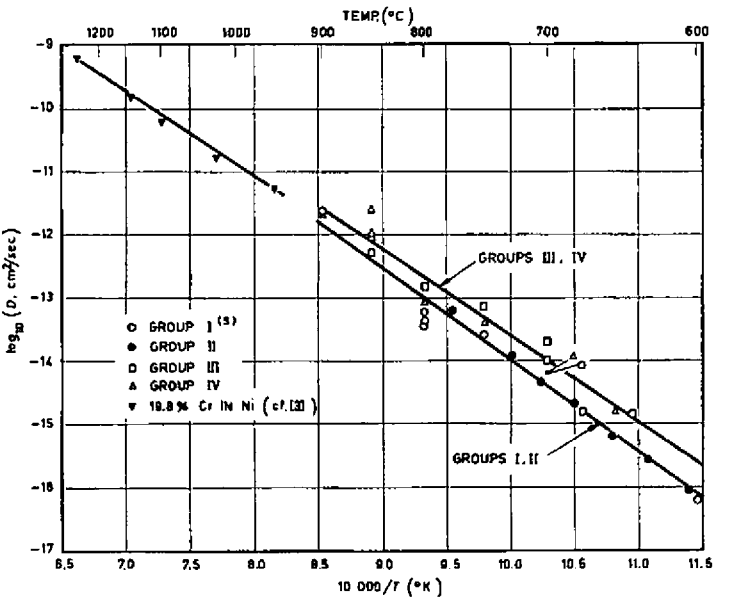

Fig. 1
Experimental results for 1150°C annealed Inconel (over-all coefficients).

References [5] and [3] should read respectively [9] and [4].

It should be mentioned that an isothermally determined over-all coefficient depends on the measurement, control, or knowledge of ten variables. Seven of these variables are squared in the final equation; also, the coefficient changes approx. 4%/deg C at 700°C. The maximum contribution from accumulated experimental uncertainties is believed to be ± 0.4 cycle on Figs. 1 and 2. This estimate excludes the effects of grain-size variations.

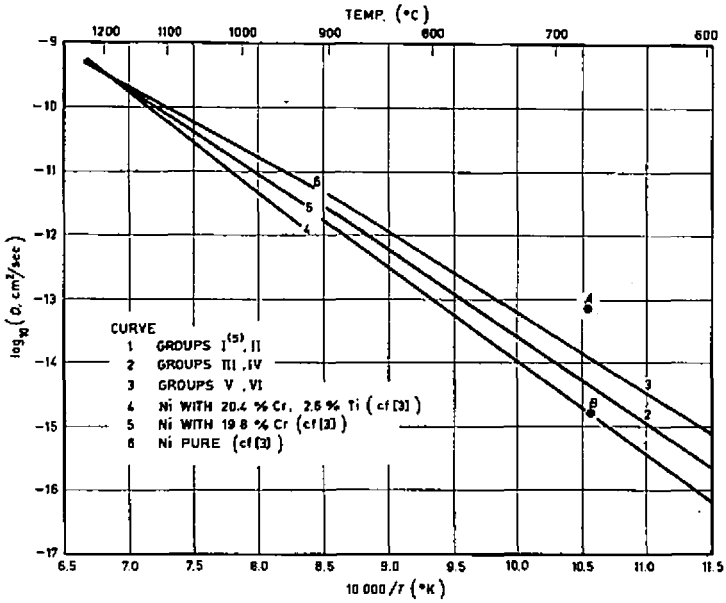

Fig. 2
Chromium-51 diffusion coefficients in nickel-base alloys. Over-all values.

References [5] and [3] should read respectively [9] and [4].

In view of the over-all precision involved, the most realistic summary of the results might be a comparison of the average curves for all of the available data. Such a comparison is presented in Fig. 2.

A comparison of the results obtained with an unannealed Inconel specimen (point A, Fig. 2) and those obtained with three annealed specimens (point B, Fig. 2) presents an illustration of effects associated with grain size. Photomicrographs showing the grain size of the actual specimens may be found in Fig. 3. All of these specimens were exposed to the same salt solution at the same temperature. The same trend was shown by all the experimental results in that increases in the time and temperature of the pretreatment increased the grain size and decreased the over-all coefficient. It was concluded that effects associated with grain size had a marked influence on the over-all diffusion coefficient at the lower temperatures.

An encouraging feature of the results shown on Fig. 2 is the relatively good agreement between the high and low temperature data. A "break" in the over-all curves indicating a change in mechanism was not found for the Inconel specimens. The breaks in other systems (generally obtained from concentration profiles) result in relatively low negative slopes in low temperature regions.

Coefficients presented in Fig. 2 represent alloys with chromium contents ranging from 0 to 20.4 wt. %. In view of the precision of the measurements and grain-size effects, it was concluded that the over-all coefficients above 700°C did not depend on the chromium concentration in the alloys. The amount of diffusion did depend on the concentration in a manner predicted by Eqs. (5) and (6).

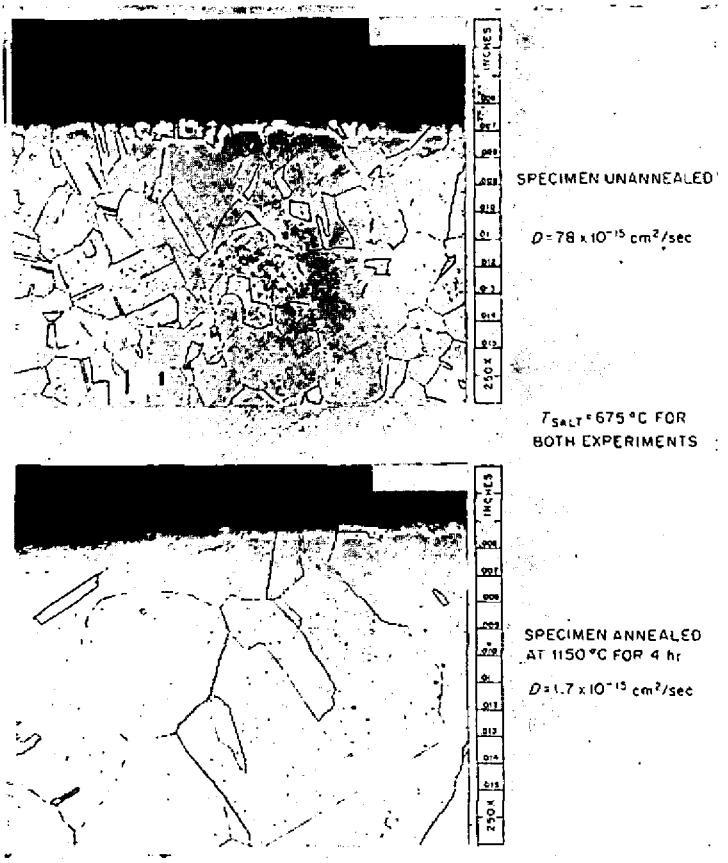

Fig. 3
Photomicrographs of Group III Inconel specimens after diffusion experiments.

Concentration-profile diffusion-coefficients

Electropolishing experiments were performed on duplicate specimens obtained from 13 separate experiments mentioned in the preceding section (see Group V). The final results are presented on Fig. 4 (open circles) immediately above the average curve, which represents the over-all coefficients obtained with the same specimens. It was interesting to note that the deviations exhibited by these data were faithfully reproduced by the over-all values on the lower curve. In addition, electropolishing data available from depletion experiments (see Group I) were also plotted and compared with the corresponding over-all values. Since the Group I experiments were depletion experiments, the integral of the concentration profile is given only approximately by Eq. (7). However, the approximate equation accurately described a major portion of the experimental profiles as shown in Fig. 5.

The results shown in Fig. 4 show that at temperatures below 750°C the profile diffusion-coefficients for Inconel are higher and show a lower temperature depend-

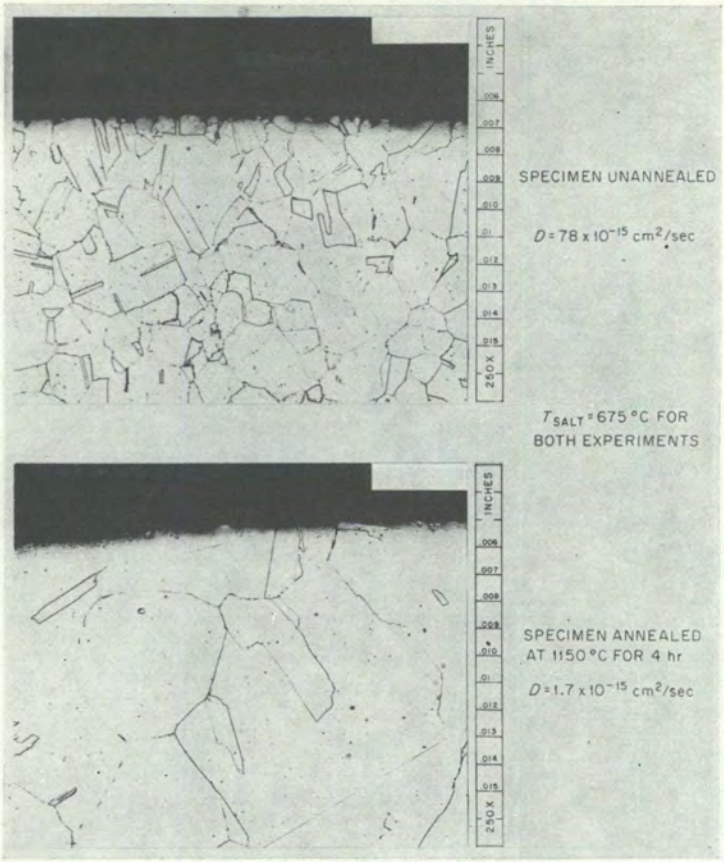

Fig. 3
Photomicrographs of Group III Inconel specimens after diffusion experiments.

Concentration-profile diffusion-coefficients

Electropolishing experiments were performed on duplicate specimens obtained from 13 separate experiments mentioned in the preceding section (see Group V). The final results are presented on Fig. 4 (open circles) immediately above the average curve, which represents the over-all coefficients obtained with the same specimens. It was interesting to note that the deviations exhibited by these data were faithfully reproduced by the over-all values on the lower curve. In addition, electropolishing data available from depletion experiments (see Group I) were also plotted and compared with the corresponding over-all values. Since the Group I experiments were depletion experiments, the integral of the concentration profile is given only approximately by Eq. (7). However, the approximate equation accurately described a major portion of the experimental profiles as shown in Fig. 5.

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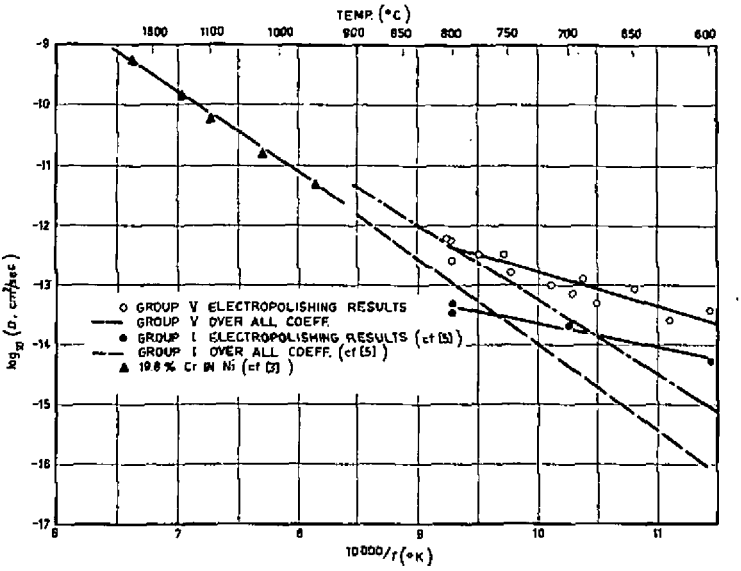

Fig. 4
Chromium diffusion coefficients for Inconel based on electropolishing data.
References [5] and [3] should read respectively [9] and [4].

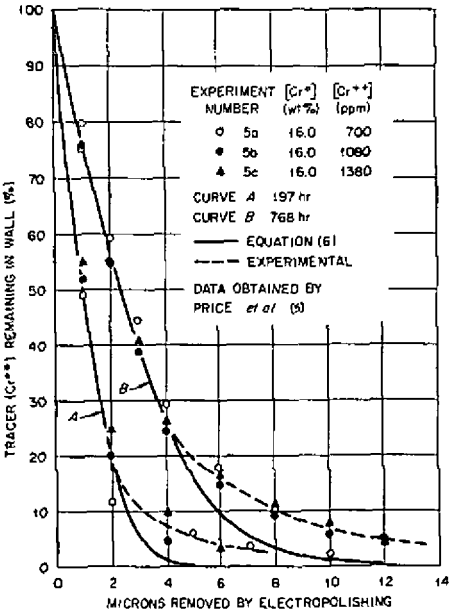

Fig. 5
Concentration profiles in 800°C deplotion capsules.
References [6] and [5] should read respectively [7] and [9].

ence than the corresponding over-all coefficients. At high temperatures, the over-all and the profile coefficients appear to have the same value for Inconel. It is presently believed that the equality of coefficients is indicative of homogeneous diffusion. The break observed in Fig. 4 is probably due to a change in mechanism of the diffusion process in Inconel from homogeneous or "volume" at high temperatures to "channel" or "grain-boundary" at low temperatures. Similar effects have been observed previously [16].

The above, when considered together with the previously mentioned annealing effect, leads to the speculation that two coefficients, e.g., volume and grain boundary, controlled the migration rates. A treatment of a similar case by FISHER [16] revealed that the time dependence of the penetration relationships would be altered when both mechanisms are combined. Such was not the case in this investigation, however, at any temperature studied. The data appeared to follow the equations presented. These equations were based on phenomenological coefficients which could be used to represent a homogeneous diffusion process taking place in an isotropic medium.

Loop experiments

Loop experiments offer several advantages over the small-scale experiments used to obtain the data on Inconel. The greater uniformity of the alloy specimens from loops leads to more consistent results. In loops, all the alloy specimens are exposed to the same salt solution, and the experience in the performance of loop experiments acquired over many years in other studies has led to much better control of the experimental variables over prolonged periods of time than could be easily achieved in small-scale experiments. In addition, longer exposures gave consequently greater penetrations which could be measured with improved precision. Furthermore, the larger loop specimens could be manipulated with

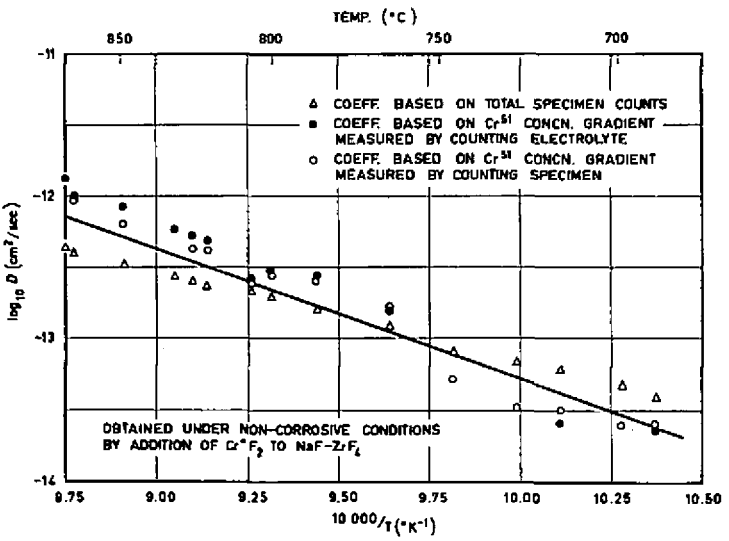

Fig. 6
Self-diffusion coefficients for chromium-51 in INOR-8; loop 1248.

equal ease in the same types of radiochemical and chemical analyses with no loss of precision as compared to the small-scale samples.

In the present investigation, two polythermal loops of INOR-8 were used, as mentioned previously. The experimental results for the first loop (No. 1248) are shown in Fig. 6. A small difference was observed between the values obtained by the various methods used; the coefficients obtained on total specimen counts tended to be low at high temperatures and *vice versa*. The reason for this trend is not immediately apparent and is presently ascribed to small systematic errors well within the over-all experimental precision of ± 0.4 cycle as explained previously.

In order to determine the validity of the self-diffusion coefficients determined in loop 1248 for predicting chromium diffusion-rates under corrosive conditions, loop 1249 was allowed to absorb chromium under non-corrosive conditions as described above. It must be noted that operation in the presence of FeF_2 in the solution causes the total chromium concentration at the surface to be reduced practically to zero. The reaction (3)

$$Cr^\circ + FeF_2 \rightleftharpoons CrF_2 + Fe^\circ$$

has an equilibrium quotient of 1.5×10^4 at 600° and this is greater at higher temperatures. Accordingly, these operating conditions represent very drastic corrosive conditions which are just short of disturbing the Ni-Mo matrix of the alloy. In Fig. 7, the results obtained with a specimen of loop 1249 are compared with the results obtained with the corresponding specimen of loop 1248. It is

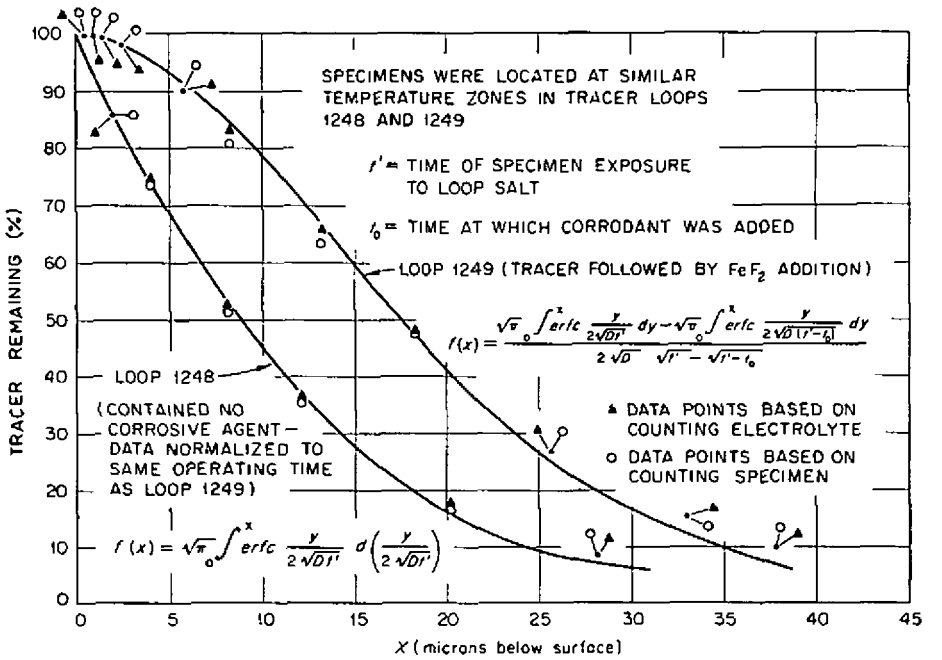

Fig. 7
Per cent of tracer remaining as a function of depth removed from specimen surface.

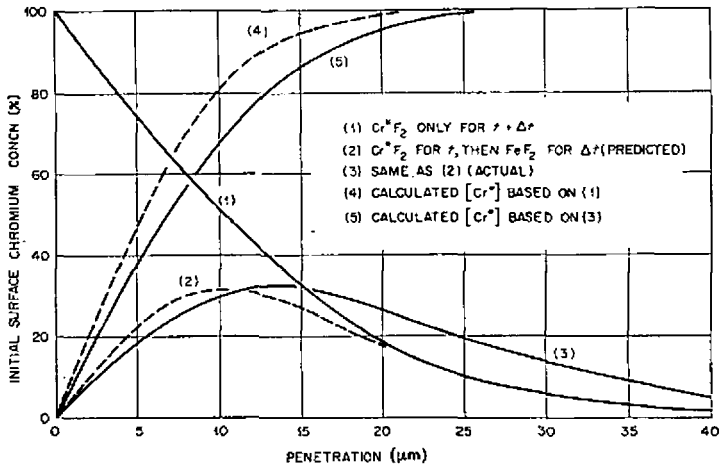

Fig. 8
Various chromium concentration profiles in 813°C, INOR-8, loop specimens.

observed that for both specimens the experimental points agree well with the calculated curves.

Fig. 8 shows the concentration profiles in the specimens as calculated from the corresponding diffusion coefficients obtained from the experimental data. Curve 1 gives the concentration of tracer for the longest period of operation (1056 h) using the diffusion coefficient obtained from the average line in Fig. 6. Curve 2 represents the tracer concentration-profile in the specimen of loop 1249 as predicted by the value of the diffusion coefficient used to calculate Curve 1. Curve 3 shows the tracer concentration-profile in the same specimen calculated by the diffusion coefficient obtained from Eq. (8), using the ratio of the actual activity of the corroded specimen to that of the salt. Some deviation occurs particularly as the penetration reaches about 25 μm. The source of the deviation is apparent from the last three experimental points of Fig. 7. Since at these penetrations only about 25% of the tracer remains, the experimental techniques employed have, by then, lost a substantial degree of precision and it is not possible to ascertain at present if the effect is real even if it is of a minor nature. However, in many other specimens the experimentally determined tracer concentrations at the greater penetrations were found to be greater than calculated. The deviations are within the experimental uncertainty but the trend is always in the same direction, which suggests that the effect is real. Although this effect was interesting, it was ignored in view of the minor contribution of this effect to the over-all diffusion rates. Curves 4 and 5 of Fig. 8 represent the total chromium concentration-profile.

4. Conclusions

As a result of the present investigation the following conclusions are apparent:

1. Self-diffusion coefficients of chromium in nickel-base alloys in the temp. range 600—900°C were conveniently determined (a) by monitoring the total intake of Cr^{51} by the alloys exposed to salt solutions containing Cr^*F_2

and (b) by measuring the tracer concentration-profiles through successive electropolishing of the specimens.

2. The self-diffusion coefficients of chromium in Inconel were found to be strongly dependent on annealing conditions at low temperatures. Conditions leading to large grains led to low diffusion coefficients and *vice versa* within this temperature range.
3. For Inconel, at temperatures above 800°C the magnitudes of the self-diffusion coefficients of chromium obtained by the different techniques were the same. At lower temperatures, the diffusion coefficients calculated from the concentration profiles were higher and had a lower temperature-dependence than those obtained by direct monitoring of the intake of Cr^{51}.
4. For INOR-8, no differences were found, over the temperature range studied, between the values of the diffusion coefficients obtained by the different experimental techniques.
5. At temperatures above 800°C the observed self-diffusion coefficients of chromium in INOR-8 and Inconel were found to be the same.
6. The values of the self-diffusion coefficients of chromium in INOR-8 were valid for the prediction of tracer diffusion-rates and concentration profiles induced under actual corrosive conditions.

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RADIOISOTOPES AS TRACERS FOR REACTIONS IN MOLTEN FLUORIDE MEDIA

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Abstract — Résumé — Аннотация — Resumen

Radioisotopes as tracers for reactions in molten fluoride media. Chemical reactions which may be useful for removing certain constituents from molten fluoride solution have been examined by use of appropriate radioisotopes and standard counting procedures. Classes of reactions studied have included

(1) isotopic exchange between solute tracer and insoluble compound,
(2) partition of solute between the melt and a solid solution of a similar compound, and
(3) precipitation of the radioisotope as insoluble compound.

In typical experiments, radiotracer LaF_3 in LiF-NaF melts was shown to exchange rapidly with inactive La_2O_3. A similar rapid exchange in this solvent occurred between radiotracer CeF_3 and inactive CeO_2; the electron transfer required in the latter case is apparently no barrier to the reaction. Addition of inactive CeF_3 to each system increased the radiotracer content of the solution in accordance with the mass-action principle.

When certain LiF-BeF_2 melts containing CeF_3 and rare-earth fluorides are cooled the primary phase is a solid solution of the trifluorides. Equilibria, between molten solution and solid solution, have been evaluated for various fluoride pairs. No significant deviations from the simple mass-action principle have been observed.

Separations of various species by selective precipitation of oxides from molten fluoride solutions have also been demonstrated.

Les radioisotopes comme indicateurs des réactions se produisant dans des milieux de fluorures fondus. Les auteurs ont étudié, au moyen de radioisotopes appropriés et des procédés de comptage habituels, les réactions chimiques qui peuvent contribuer à l'élimination de certains constituants en solution dans des fluorures fondus. Les catégories de réactions étudiées comprenaient

1. L'échange isotopique entre indicateurs dissous et composés insolubles;
2. La répartition du soluté entre la masse fondue et la solution solide d'un composé analogue;
3. La précipitation du radioisotope comme composé insoluble.

Des expériences caractéristiques ont montré que, dans les échantillons de LiF-NaF, il se produit un échange rapide entre l'indicateur radioactif LaF_3 et le La_2O_3 non actif. Dans le même solvant, il se produit aussi un échange rapide entre l'indicateur radioactif CeF_3 et le CeO_2 non actif; le transfert d'électrons nécessaire dans ce dernier cas ne fait apparemment pas obstacle à la réaction. L'addition de CeF_3 non actif à chacun de ces systèmes augmente la concentration de radioisotopes dans la solution, conformément à la loi d'action des masses.

Lorsque l'on refroidit certains mélanges fondus de LiF et BeF_2 contenant du CeF_3 et des fluorures de terres rares, la phase primaire est une solution solide des trifluorures. Des équilibres entre la solution fondue et la solution solide ont été évalués pour diverses paires de fluorures. On n'a observé aucune dérogation significative à la loi d'action de masse.

Les auteurs du mémoire ont réussi à séparer diverses espèces par précipitation sélective des oxydes à partir de solutions de fluorures fondus.

Использование радиоизотопов в качестве индикаторов для реакций в расплавленной фтористой среде. Путем использования соответствующих радиоизотопов и стандартных методов отсчета были изучены химические реакции, которые могут оказаться полезными для удаления некоторых составных частей из расплавленных фтористых растворов. Были изучены следующие категории реакций:

1) изотопный обмен между растворенным индикатором и нерастворимыми сложными веществами;

2) распределение растворенного индикатора между расплавом и раствором аналогичного сложного вещества в твердом состоянии и

3) осаждение радиоизотопа в качестве нерастворимого сложного вещества.

В типичных экспериментах наблюдалось, что радиоактивный индикатор LaF_3 в расплавах LiF-NaF быстро обменивается на неактивный La_2O_3. В этом растворителе аналогичный быстрый обмен происходит между радиоактивным индикатором CeF_3 и неактивным CeO_2; требуемое в последнем случае перенесение электрона очевидно не препятствует этой реакции. В соответствии с принципом массового действия добавление к каждой из этих систем неактивного CeF_3 увеличивало содержание радиоактивного индикатора в растворе.

При охлаждении некоторых расплавов ZiF-BeF_2, содержащих CeF_3, и редких земель в качестве первичной фазы образуется твердый раствор трифтористых соединений. Для различных пар фтористых соединений наблюдались равновесия между расплавленным и твердым растворами. Значительных отклонений от простого принципа массового действия не наблюдалось.

Была показана возможность извлечения при помощи избирательного осаждения окисей различных групп из растопленных фтористых растворов.

Los radioisótopos como indicadores de las reacciones que tienen lugar en un medio de fluoruros fundidos. Los autores han estudiado las reacciones químicas que pueden contribuir a la eliminación de ciertos constituyentes disueltos en fluoruros fundidos. Para ello han empleado radioisótopos adecuados y técnicas corrientes de recuento. Las reacciones estudiadas incluyen:

1) el intercambio isotópico entre indicadores disueltos y compuestos insolubles,
2) la partición del soluto entre la fase fundida y una solución sólida de un compuesto similar y
3) la precipitación del radioisótopo como compuesto insoluble.

Algunos experimentos típicos revelan que en las muestras de LiF-NaF el LaF_3 utilizado como indicador radiactivo se intercambia rápidamente con el La_2O_3 inactivo. En el mismo disolvente se observa también intercambio rápido entre el CeF_3 radiotrazador y CeO_2 inactivo; aparentemente, la transferencia de electrones necesaria en este último caso no impide la reacción. La adición de CeF_3 inactivo a cada uno de los sistemas produce un aumento de la concentración de radioisótopos en la solución, de conformidad con la ley de acción de masas.

Cuando se enfrían ciertas mezclas de LiF y BeF_2 fundidas que contengan CeF_3 y fluoruros de las tierras raras, la fase primaria consiste en una solución sólida de los trifluoruros. Los autores han evaluado los equilibrios entre la solución fundida y la solución sólida, para diversos pares de fluoruros. No han observado ninguna desviación notable respecto de la ley de acción de masas.

Los autores logran la separación de diversas especies por precipitación selectiva de los óxidos a partir de soluciones de fluoruros fundidos.

1. Introduction

A circulating molten-fluoride solution containing uranium tetrafluoride is a promising fuel for a high-temperature nuclear reactor [1–4]. One large potential advantage of a fluid fuel is that a side stream may be removed for continuous processing. The work described in this paper is related to the development of

methods for removing fission products and other components from molten fluoride solutions.

Rare-earth fission products formed in a reactor fuelled with a molten fluoride solution may be expected to account for a significant neutron loss. The appreciation of this fact has motivated studies of solubilities and chemical reactions of rare-earth fluorides which would be pertinent to the design and operation of such a reactor. The feasibility of several processes by which rare-earths could be extracted or removed from molten fluoride solutions depends substantially on the solubility relations among rare-earth fluorides. This same information is also of interest with regard to the maintenance of homogeneity of the fuel, since precipitation of a rare-earth fluoride in the fuel circuit of the reactor might interfere with its satisfactory operation.

This report presents some of the data obtained on:

(1) the solubility of LaF_3, CeF_3, SmF_3 and YF_3 in a variety of solvents,

(2) the partition of rare-earth solute between the melt and a solid solution,

(3) the separation of uranium and of thorium from rare-earths by selective precipitation of oxide phases from the molten fluoride solution, and

(4) isotope exchange between solute tracer and insoluble compound.

Most of the results to be presented were obtained using radioisotopes as tracers which proved most helpful in the analysis of the complex mixtures investigated.

2. Rationale

Rare-earth fluoride solubility and exchange

The rare-earth elements, notably samarium, europium, and gadolinium, account for about one-half the neutron absorption by non-volatile fission products. These elements will be present in very low concentration as trivalent fluorides in the fuel of a molten-fluoride nuclear reactor. The possibility of removing the rare-earth poisons by exchange with cerium through formation of a solid solution with an excess of cerium fluoride was studied in some detail. A process of this sort was envisaged as an extraction of a compound from a liquid by means of a solid extractant. Accordingly, the solubility-behaviour of various rare-earth trifluorides, both individually and in pairs, was determined in possible fuel melts over a 350°C range. The experimental data was correlated by fairly simple assumptions and calculations of the type commonly employed in solvent extraction processes. It was possible to calculate partition coefficients between the solid and liquid solvents, as will be discussed later.

Separation by oxide precipitation

The separation of uranium from soluble fission products in molten fluorides has been studied rather extensively. The method utilizes a selective precipitation of oxide phases from the solution upon the gradual addition of a suitable precipitating agent. Results on the separation of uranium, as UO_2, of thorium, as ThO_2, from fission products such as rare earths, alkaline earths, alkali metals, and halogens have been successfully demonstrated and some typical results are presented below, which employ a variety of precipitating agents, such as CaO, BeO, H_2O and others.

Isotopic exchange-reactions

A systematic programme of investigation is in progress to determine the feasibility of removing trace amounts of fission products from solutions of molten fluorides by isotopic exchange and/or adsorption on the surface of insoluble solids. The list of proposed solids includes oxides, carbides, silicides, silicates, nitrides, metals, and intermetallics. The results of some experiments using oxides are presented.

3. Experimental

Materials

Molten fluoride solvent

The molten fluoride mixtures were prepared from reagent grade materials and purified in a closed system of nickel at 800°C by alternate flushing with anhydrous HF and H_2. The purification technique was identical with that described in a previous publication [5].

Labelled rare-earth fluorides

The labelled rare-earth fluorides were prepared by mixing a few millicuries of the most suitable available radioisotope, in the form of an aqueous solution, with inactive, rare-earth chloride solution. From the resulting solution, the rare-earth fluoride was precipitated with aqueous hydrofluoric acid. This precipitate, after centrifuging, washing, and recentrifuging, was dried in a vacuum oven. More detailed information about the preparation of the labelled materials may be found elsewhere [6–9]. The isotopes used were: Ce^{141} (half-life, 32 d), La^{140} (half-life, 40 h), Sm^{153} (half-life, 47 h), and Y^{91} (half-life, 58 d). Although yttrium is not strictly a rare earth, it behaves in many instances like a rare earth and may advantageously be studied with the rare earths.

Apparatus and procedure

The apparatus used in this study has been described in detail previously [6]. The molten solution was contained in a thin-walled cylindrical vessel of nickel inserted as a liner in a heavy-walled flanged reaction-vessel, also of nickel. The lid of the reaction vessel contained a thermocouple well and a gas-inlet tube, both extending into the molten charge, a gas-outlet line, and a port, closed by a screw cap with a Teflon gasket, through which samples could be drawn. Closure of the reaction vessel was effected by bolts and a gasket of copper.

The solvent with an excess of rare-earth fluorides, which contained suitable radio-tracer rare-earth isotopes, was heated to 800–900°C and allowed to equilibrate with stirring by bubbling dry helium for about 1 hour. For solubility measurements, the temperature was lowered step by step to about 800, 700, 600, and 500 or 550°C. After equilibration at each temperature, a sample of liquid was withdrawn by inserting a filtering tube of sintered nickel or copper. The concentration of the rare earth was obtained by comparing the counting rate of the sample with that of suitable standards.

A very similar procedure was employed in the studies of the selective precipitation of oxides from molten fluorides. To the melt containing the species to be studied, weighed portions of precipitating agent were added; samples of liquid were obtained after each addition. The concentrations of solutes remaining in

the liquid were obtained by radiochemical and chemical analyses of the filtrates. In the cases where water vapour was used as precipitating agent, samples of the liquid were obtained at different stages of the reaction as indicated by monitoring the quantity of HF liberated.

For the investigation of exchange reactions, the radio-tracer was generally dissolved in the solution and allowed to equilibrate with solid, insoluble samples of the corresponding inactive isotope which were added to the solution during the course of the experiment. Samples of liquid were obtained and analysed in the same manner as previously explained.

4. Results and discussion

Rare-earth fluoride solubility and exchange

The solubilities of yttrium, lanthanum, cerium, and samarium trifluorides in $NaF\text{-}ZrF_4\text{-}UF_4$ (50–46–4 mole %) solvent and the solubilities of lanthanum, cerium, and samarium trifluorides in $LiF\text{-}BeF_4\text{-}UF_4$ (63–36–1 mole %) solvent are shown in Fig. 1. Cerium trifluoride is considerably less soluble in the latter solvent; the solubility in either case, however, seems sufficiently low to make the extraction process attractive.

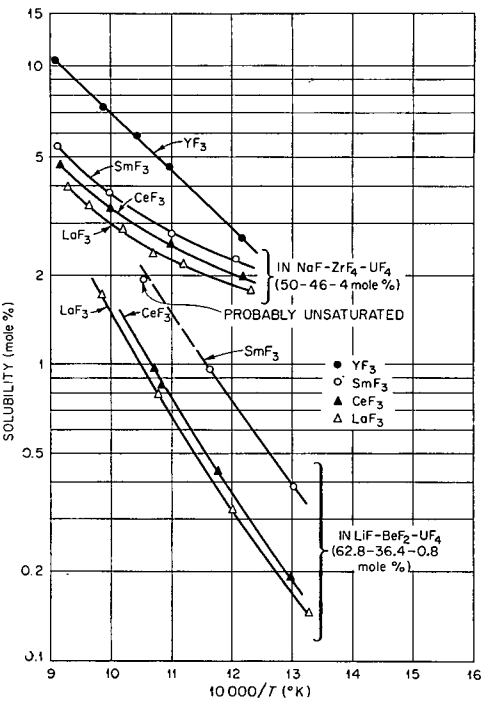

Fig. 1
Additive solubilities of YF_3, SmF_3, CeF_3 and LaF_3 in $NaF\text{-}ZrF_4\text{-}UF_4$ (50-46-4 mole %) and in $LiF\text{-}BeF_2\text{-}UF_4$ (62.8-36.4-0.8 mole %).

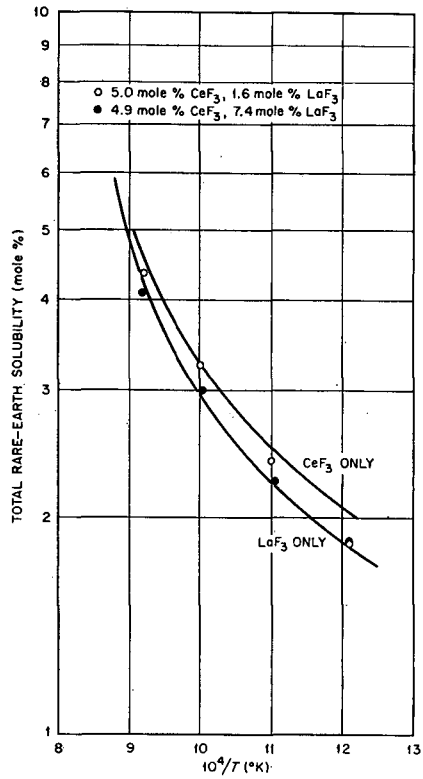

Fig. 2
Additive solubilities of CeF_3 and LaF_3 in NaF-ZrF_4-UF_4 (50-46-4 mole %).

Experiments which measured the solubilities of lanthanum and cerium trifluorides, when both were present in the NaF-ZrF_4-UF_4 solvent, yielded the data shown in Fig. 2. As anticipated, the sum of the solubilities of the two components lies essentially between the values obtained when each was present alone. Similar data were obtained when cerium and samarium trifluorides were examined. Results of corresponding experiments in the LiF-BeF_2-UF_4 solvent are shown in Figs. 3 and 4. In each case, the solubility of each trifluoride of the pair could be closely approximated by multiplying the solubility it would have shown when present alone ($S°$) by its mole fraction in the solid phase.

The equilibrium which is established can be represented for a typical case by

$$CeF_3\,(ss) + SmF_3\,(d) = CeF_3\,(d) + SmF_3\,(ss)$$

where (d) indicates that the rare-earth fluoride is dissolved in the liquid solvent, and (ss) that it is in solid solution. With suitable restrictive conditions, the equilibrium constant for this reaction can be shown to be approximately equal to a simple solubility ratio [6]:

$$K_N = \frac{N_{CeF_3\,(d)} \times N_{SmF_3\,(ss)}}{N_{SmF_3\,(d)} \times N_{CeF_3\,(ss)}} = \frac{S°_{CeF_3}}{S°_{SmF_3}}$$

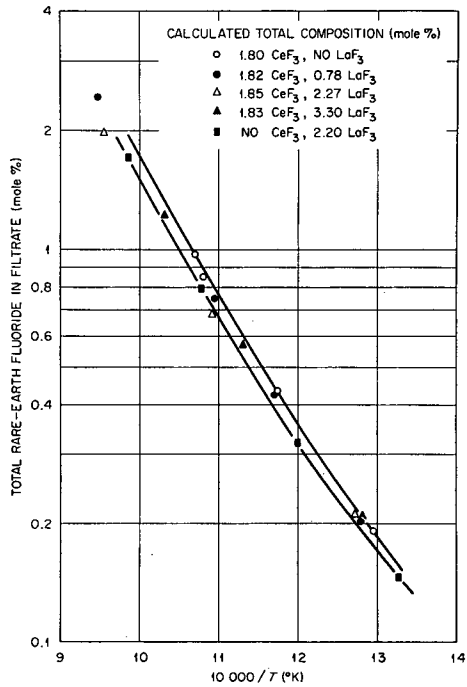

Fig. 3
Additive solubilities of CeF_3 and LaF_3 in $LiF\text{-}BeF_2\text{-}UF_4$,

where N is the mole fraction of the given species in the specified phase and $S°$ is the mole fraction of the given species in a saturated solution in the absence of the other rare-earth fluoride, all at the same temperature. Tables I, II, and III show the calculated extraction coefficients along with those based on the experimental results in various systems. There appear to be some systematic differences between the calculated and the experimental coefficients. A possible reason for these differences may be the lack of homogeneity of composition in the solid solutions due to the very low diffusion rates in the solid phase. However, the agreement between the calculated and the experimental results appears to be entirely adequate for purposes of fuel-reprocessing calculations.

No evidence of precipitation of uranium tetrafluoride in any of these solids has been observed. It therefore appears that a useful decontamination process based on extraction of rare-earth fluorides in cerium fluoride should be possible.

Separation by oxide precipitation

Selective precipitation of oxides appears to be useful in the development of suitable schemes for the reprocessing of molten-salt reactor-fuels. In general, the method may have possible applications in the separation of uranium and of thorium from the majority of fission products by selective precipitation from molten fluoride solutions. Such solutions are not uncommon and are obtained by the dissolution of spent, solid-fuel elements by hydrofluorination in molten

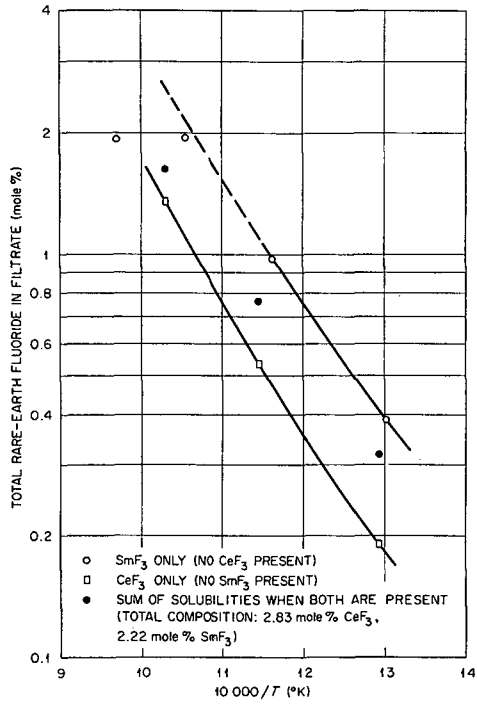

Fig. 4
Additive solubilities of CeF_3 and SmF_3 in LiF-BeF_2-UF_4.

TABLE I

SOLID-SOLVENT EXTRACTION COEFFICIENTS FOR LaF_3-CeF_3 IN NaF-ZrF_4-UF_4 (50-46-4 MOLE %)

Temp. (°C)	Calculated K_N ($S°CeF_3/S°LaF_3$)	Experimental K_N*	
		6.1 % CeF_3 1.9 % LaF_3	5.7 % CeF_3 8.4 % LaF_3
815	1.09	1.0	1.2
724	1.10	1.0	1.0
634	1.13	1.0	1.0
553	1.12	0.9	1.0

* $K_N = \dfrac{N_{LaF_3(ss)} N_{CeF_3(d)}}{N_{CeF_3(ss)} N_{LaF_3(d)}}$

fluorides as in the first step of the volatility process [10]. Accordingly, relative solubilities of the metallic oxides in question and some selective precipitation reactions were studied in a variety of solvents. A number of different precipitating agents were used. The difference in solubilities of the oxides involved appears to be a determining factor in the completeness and feasibility of separation. Some experimental results are illustrated in Figs. 5—11.

TABLE II
SOLID-SOLVENT EXTRACTION COEFFICIENTS FOR SmF_3-CeF_3 IN NaF-ZrF_4-UF_4 (50-46-4 mole %)

Temp. (°C)	Calculated K_N ($S°SmF_3/S°CeF_3$)	Experimental K_N*	
		5.3 % SmF_3 4.1 % CeF_3	1.5 % SmF_3 4.0 % CeF_3
846	1.18	1.2	
745	1.12	1.4	1.2
652	1.10	1.4	1.3
561	1.08	1.5	1.4

* $K_N = \dfrac{N_{CeF_3\,(ss)}\, N_{SmF_3\,(d)}}{N_{SmF_3\,(ss)}\, N_{CeF_3\,(d)}}$

TABLE III
SOLID-SOLVENT EXTRACTION COEFFICIENTS FOR CeF_3-LaF_3 IN LiF-BeF_2-UF_4 (62.8-36.4-0.8 mole %)

Temp. (°C)	Calculated K_N ($S°CeF_3/S°LaF_3$)	Experimental K_N*		
		1.82 mole % CeF_3 0.78 mole % LaF_3**	1.85 mole % CeF_3 2.27 mole % LaF_3**	1.83 mole % CeF_3 3.30 mole % LaF_3**
700	1.14	0.97	1.55	1.18
600	1.15	1.18	1.82	1.38
500	1.09	1.52	2.28	1.68

* $K_N = \dfrac{N_{CeF_3\,(d)}\, N_{LaF_3\,(ss)}}{N_{LaF_3(d)}\, N_{CeF_3\,(ss)}}$

** Total composition in container.

Mixtures of alkali metal-fluorides constitute the simplest type of molten fluoride solvent for studies of oxide precipitation-reactions, since the alkali metal-oxides are soluble in such solvents [11]. Figs. 5, 6 and 7 illustrate reactions carried out in simple solvents using CaO as a precipitating agent. Fig. 5 shows

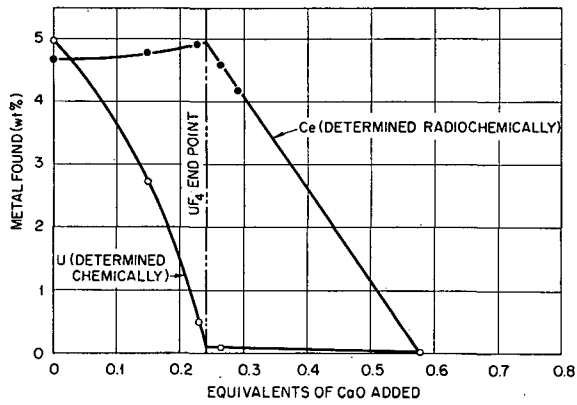

Fig. 5
Titration of CeF_3 and UF_4 with CaO in LiF-KF (50-50 mole %).

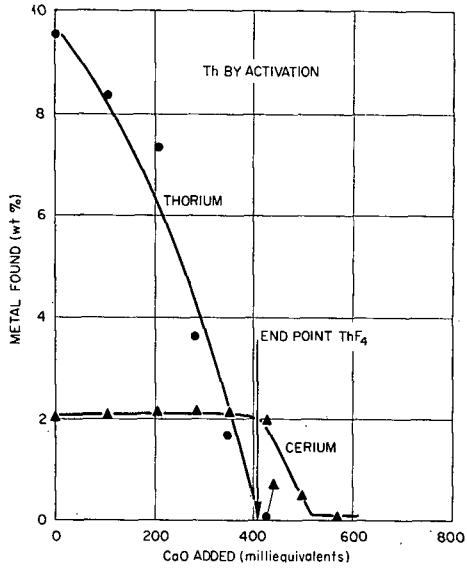

Fig. 6
Reaction of CaO with ThF_4 and CeF_3 in LiF-NaF (60-40 mole%) at 750°C.

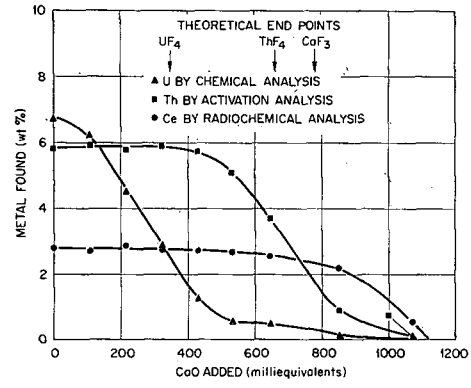

Fig. 7
Reaction of CaO with UF_4, ThF_4, and CeF_3 in LiF-NaF (60-40 mole%) at 750°C.

that when CaO was added incrementally to a solution of LiF-KF initially containing UF_4 and CeF_3 as solutes, uranium was precipitated quantitatively as UO_2 before any of the Ce_2O_3 was formed. Fig. 6 shows the corresponding separation of thorium from cerium. Fig. 7 shows the reaction of calcium oxide with UF_4, ThF_4 and CeF_3 in the same solution.

The use of calcium oxide as a precipitating agent is objectionable since the solvent becomes contaminated with calcium. Inasmuch as potential fused-salt reactor-fuel might contain beryllium fluoride as a constituent, the disadvantage of contaminating the solution can be avoided in solvents containing BeF_2 by

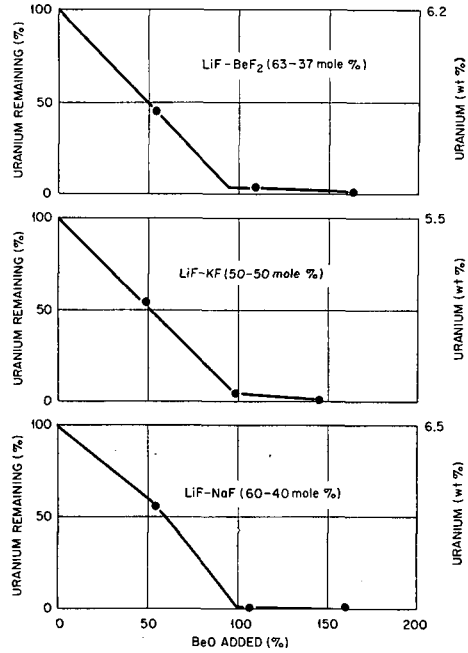

Fig. 8
Reaction of BeO with UF_4 in molten fluorides.

using BeO as a precipitating agent. Reactions of UF_4 in various solvents with BeO are shown in Figs. 8 and 9. Fig. 9 shows that the extraction of uranium originally present in minute concentrations from solutions containing thorium is feasible by surface precipitation on beryllium oxide. This behaviour might provide the basis for a processing scheme to recover uranium from the blanket of a molten-salt breeder-reactor. Further experiments are scheduled to study the extraction of trace quantities of protactinium from similar molten fluoride solutions by this process.

Fig. 10 shows the separation of uranium from cerium in LiF-BeF_2 (63—37 mole %) by the use of water vapour as the precipitating agent. The use of water vapour as a precipitating agent has the advantage of producing a volatile by-product, HF, which can be removed continuously.

Fig. 11 shows the reaction of thorium dioxide with UF_4 in LiF-BeF_2, which might be of interest in the reprocessing of molten-salt breeder-reactor blanket-solutions.

It appears from the foregoing, and from other results on studies of separation by oxide precipitation, that it is possible by rather simple procedures to separate uranium and thorium from fission products such as rare-earths, alkaline earths, alkali metals, and halogens.

Isotopic exchange reactions

The possibility of removing certain isotopic species from molten fluoride solutions by isotopic exchange has been considered and a systematic programme

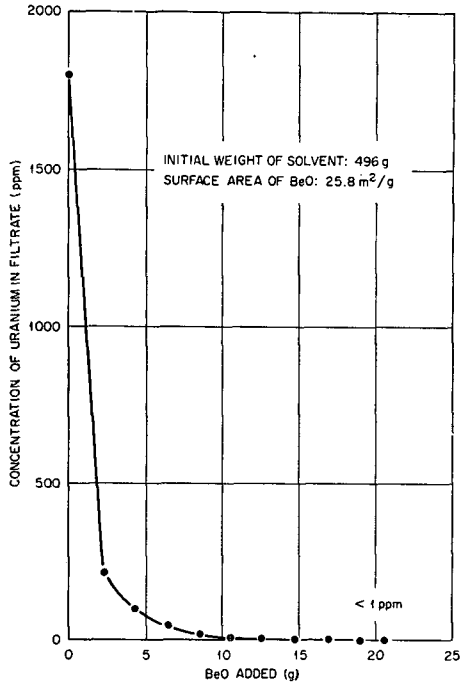

Fig. 9
Extraction of uranium from LiF-BeF_2-ThF_4 (67-18-15 mole %) at 650°C.

of investigation to determine the feasibility of this method is in progress. The results of some experiments using solid oxides are illustrated in Figs. 12—14. Fig. 12 shows that Ce^{141}, present in solution as the trifluoride, exchanges with the inert CeO_2 in accordance with the mass-action principle. The exchange took place readily and the electron transfer apparently presented no barrier. Fig. 13 shows the exchange of La^{140} with inert La_2O_3. It also shows, however, that cerium and lanthanum exchange—at least when both are in the trivalent state. Unfortunately, CeO_2 reacts readily with UF_4, ThF_4 or BeF_2. Fig. 14 illustrates the unfavourable effect of the presence of ThF_4 or BeF_2 on the removal of radiotracer cerium from solution by exchange with CeO_2.

These and other experiments show that simple isotopic-exchange reactions with oxide solids for reprocessing molten-salt reactor fuels are in many cases adversely affected by the presence of essential constituents in the fuel.

The interference with the simple exchange appears to arise from chemical reactions between the solid oxides used as exchangers and some constituents of the fuel that produce more stable oxides. Where chemical reactions are absent, the simple isotopic exchange reactions appear to be well suited for the limited removal of certain specific isotopes from solution. Additional investigations are planned in an effort to find solids that will be more inert than the oxides and which may widen the applicability of the method.

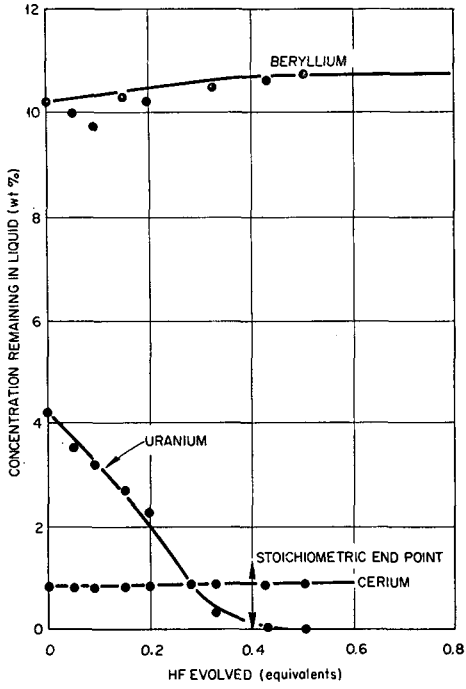

Fig. 10
Reaction of H_2O with UF_4 in LiF-BeF_2 (63-37 mole%).

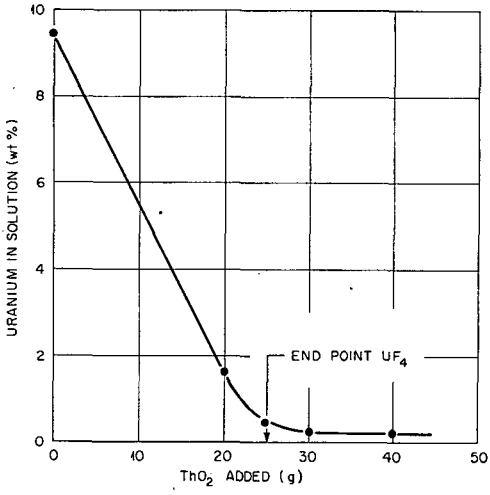

Fig. 11
Reaction of ThO_2 with UF_4 in LiF-BeF_2 (63-37 mole%) at 700°C.

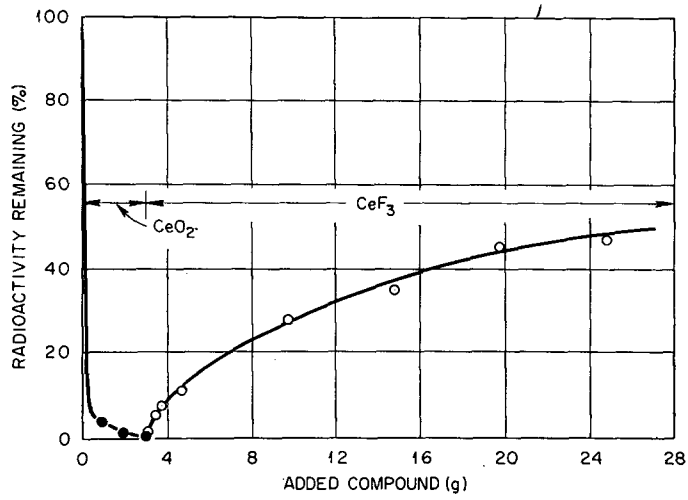

Fig. 12
Isotopic exchange of Ce^{141} with CeO_2.

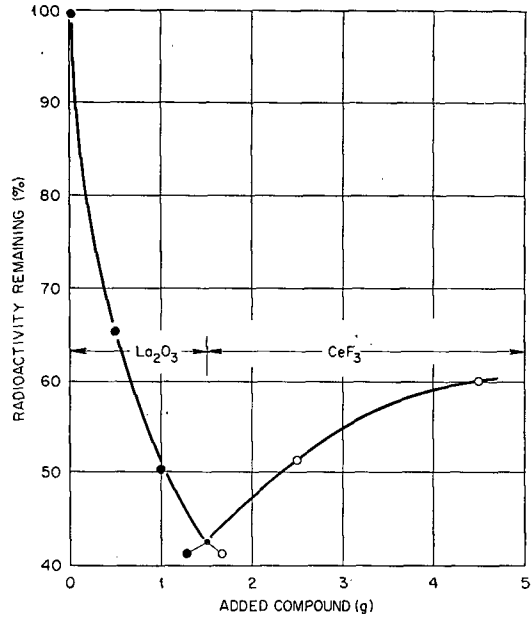

Fig. 13
Isotopic exchange of La^{140} with La_2O_3.

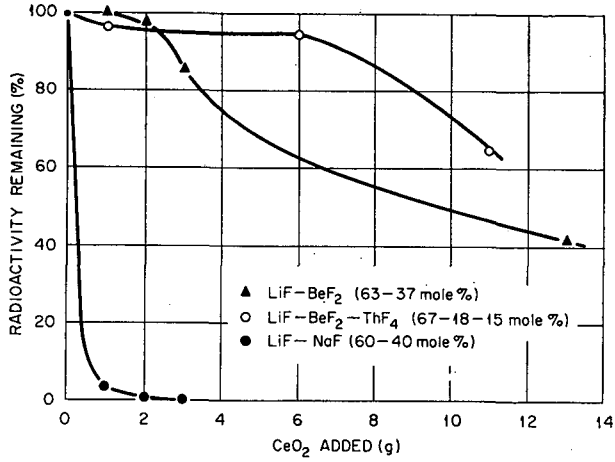

Fig. 14
Isotopic exchange of radio-tracer cerium with CeO_2 in the presence of ThF_4 or BeF_2.

5. Conclusions

As a result of the present investigation the following conclusions are apparent:

1. The use of radioisotopes as tracers greatly facilitated studies of the chemical behaviour of fission products in molten fluoride mixtures in the temp. range from 500 to 900°C.
2. The solubilities of rare-earth fluorides in various molten fluoride mixtures of potential use as nuclear fuels were determined and found to be quite high enough for reactor operation.
3. The depletion of rare-earth nuclear poisons from solution was shown to be possible by exchange with cerium, which is, from the standpoint of cross-section, relatively innocuous to thermal neutrons. The rare-earth poisons can be extracted from solution by cerium fluoride acting as a solid solvent into which the rare-earth fluorides dissolve to form solid solutions. The partition coefficients for the extraction process can be calculated from the individual solubilities of the rare-earth fluorides involved.
4. Selective precipitation of polyvalent cations from fluoride melts by the addition of oxides has been successful in laboratory-scale experiments. By this technique, separation of uranium, as UO_2, and thorium, as ThO_2, from fission products such as rare-earths, alkaline earths, alkali metals and halogens has been successfully demonstrated.
5. Isotopic exchange reactions between solids and solutes in molten fluorides were found useful for the extraction of specific isotopic species from solution, whenever chemical reactions with some fuel components did not interfere.

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AUTHOR INDEX

Boldface roman numerals refer to the volume.
Boldface arabic numerals denote the first page of a paper in these Proceedings.
Italic numerals indicate the page on which a contribution to the discussion of papers occurs.
Ordinary numerals denote literature and other references. Where necessary, the reference numbers are given in square brackets after the page number.

Aanderaa, I. **II**, 110 [5], 126
Abd el-Hafez, F. A. **III**, 201 [8], 203
Abe, K. **I, 387**
Abeles, R. H. **III**, 100 [7], 102
Abson, W. A. **II**, 295 [8], 303
Achter, M. R. **I**, 150 [10], 155, 156
Adamson, A. W. **III**, 113 [1] [2] [3], 122, 271 [1] [2], 272 [2], 276 [2], 278 [2], 280
Adda, Y. **I**, 185 [9], 192, *215*
Adkins, H. **III**, 247 [10], 253
Aebersold, P. C. **I**, *404*, *431*, **II**, 67 [1] [2], 79
Ahrens, R. W. **III**, 5 [2], 10, 45 [7], 65
Aitken, M. J. **I**, *121*, **II**, *21*, *175*, **261**
Akerlöf, G. **III**, 390 [2], 405
Albert, Ph. **I**, 208 [3], 210 [4], 215, **II**, **243**, 244 [2] [3], 245 [4], 246 [6], 254 [6] [7], 257, 258, *258-9*, *275*, *424*, **III**, *385*, *406*
Alberts, F. **II**, 153 [10], 155
Aldrich, L. T. **I**, 39 [1], 42 [1], 43
Alekseev, F. A. **I, 519**, 521 [1] [2], 530
Alexander, A. E. **III**, 534 [18], 547
Alexander, G. B. **III**, 534 [22], 542, 545 [22], 546 [22], 548
Alexander, L. T. **I**, 60 [6], 65
Alexander, T. K. **II**, 458 [15], 462
Alfvén, H. **I**, 4, 11
Aliprandi, B. **II**, 388 [100], 391, 466 [4], **III**, 44 [3], 65
Allen, R. A. **II**, *209-10*
Allison, G. M. **II**, 362 [6]
Allison, S. K. **I**, 315 [2], 326, **II**, 43 [7], 52, 58 [5], 63
Al-Salih, H. A. **II**, 456 [2], 462
Amis, E. S. **III**, **301**, 302 [2], 303 [4], 305 [6] [7], 307 [7], 309 [9], 310 [9] [10] [11], 311 [4], 312 [4], 313, *313-4*, *405*
Anbar, M. **II**, *323*, **III**, *11*, *313*, *324*
Anders, E. **II**, 504 [3], 509
Anderson, B. M. **III**, 363 [5], 367
Anderson, E. C. **I**, 92 [2] [9], 93 [9], *98*, *99*, *435* [*10*] [*11*], 445 [29] [31], 450
Anderson, G. W. **III**, 317 [2], 323
Anderson, H. **I**, 24 [15]
Anderson, R. C. **II**, 382 [45], 389
Andreeva, O. **II**, *430*, **III**, **111**, *122*
Andrew, E. R. **II**, 388 [97], 391
Andrews, H. L. **II**, 235 [3], 240
Andrysek **III**, 126 [7], 129
Anfimova, E. A. **I**, 495 [15], 496 [15], 498
Angus, P. J. **I**, 371 [2], 380
Aniansson, G. **III**, 451 [2], 452, 461
Anker, H. S. **III**, 77, 82
Ansell, H. V. **I**, *431*
Apers, D. J. **II**, 384 [64], 390
Ardaillon, E. **II**, 265, 268
Arefieva, T. V. **III**, *376* [*11*], 377 [11], 378
Argyle, A. A. **III**, 451 [1], 461
Arkharov, V. I. **I**, 154 [13], 156
Arkharova, V. V. **I**, 376 [10], 377 [10], 380
Arlman, J. J. **I**, *465*
Arnold, I. R. **I**, 92 [8] [9], 93 [9], 98, 99
Arnold, J. **II**, 456 [2], 462
Arnold, J. R. **I**, 449 [37], 450
Arnold, R. G. **III**, 107 [6], 108 [6], 109
Arnold, W. C. **I**, 345 [2], 352
Arrol, W. J. **I**, *367*, **II**, 159, 163, *163-4*, **III**, 85 [6], 90
Arslanov, Kh. A. **I**, 93 [13], 99
Artemyev, V. V. **I, 91**
Ashmore, P. G. **III**, 354 [5], 355 [5], 360
Aten, A. H. W., Jr. **I**, *44*, **II**, *20*, *188*, *275*, 384 [62], 390, *417*, **III**, *298*, **325**, *336*
Atkins, D. H. F. **II**, 279 [4], 289
Aubertin, C. **II**, 386 [77], 390, 398 [2], 400 [2], 405
Audinot, M. **III, 145**
Audrieth, L. F. **II**, 474 [6], 491
Augustiniak, W. M. **I**, 275 [8] [11], 286
Aukerman, L. W. **I**, 283 [20] [22], 286
Avdulov, G. I. **III, 255**
Avrahami, M. **III, 449**
Axelrod, J. **III**, 419 [7], 425

Azarov, K. P. II, 529 [3], 540
Azuma, R. E. II, 202, 209

Baarli, J. III, 487 [4], 493
Baas, L. W. II, 306 [3], 308
Baba, H. I, **533**, 535 [8], 537 [10], 542
Babicky III, 126 [8], 129
Badger, R. G. III, 475 [4], 482
Badin, E. J. III, 247 [8], 253
Baes, C. F. II, 544 [7] [8], 553
Bagotsky, V. S. I, 486 [8], 498
Baily, R. J. III, *367*
Bair, L. R. III, 147 [2], 155
Bajusz, E. III, 94 [8], 96
Bak, T. I, 161, 167
Bakalar, I. D. I, 188 [10], 192
Baker, R. I, 18 [34], 27, II, 454
Balaceanu, J. C. III, 250 [13], 254
Balandin, A. A. III, **245**, 246 [1] [3] [4], 247 [5] [11], 248 [3] [11], 249 [1] [5] [11], 250 [12], 253 [3] [refs], 254
Balandina, V. V. II, 529 [3], 540
Balarev, D. III, 533, 534, 538, 544 [17], 547
Balashova, N. A. III, 556 [17] [refs], 557
Ballou, N. E. I, 49, 50, 56, II, 362 [5], 366 [5], 367 [5], 544 [1], 553
Baluffi, R. W. I, 142 [4], 143 [7], 144, 146 [3] [5], 155, 156
Bamford, A. W. B. III, 185, 186
Bamford, C. H. III, 479 [16], 482
Baranov, V. I, *99*
Barber, W. C. II, 110 [4], 126
Bardeen, J. I, 162 [4], 168
Barendsen, G. I, 92 [3], 98
Baret, C. III, **145**, 147 [4], 155
Barkalov, I. M. III, **27**
Barker, S. A. III, **97**, 101 [8], 102
Barnes, R. C. M. II, 300 [16], 303
Barnett, R. I. III, 94 [10], 96
Barnevik, W. II, 497 [2], 509
Barr, D. W. I, 9, 11, 18 [32], 27
Barr, L. W. I, **137**, 140 [2], 143 [5], 144, 146, 156
Barrault, F. II, **177**, *188*, *189*
Bartholomew, G. A. I, 281 [16], 286, II, 387 [90], 390
Barton, C. J. III, 565 [14], 574
Barton, D. III, 411 [13], 414
Barton, L. A. I, 501 [7], 509
Bascom, W. D. I, 371 [1], 380
Basmadjian, D. III, 381 [3], 382, 384 [3] [refs], 385
Bassani, F. I, 297 [5], 299
Bassham II, 338 [10] [refs]
Bate, L. C. II, 283 [25] [26], 289

Batzel, R. E. I, 18 [33], 27
Bauer, C. A. I, 14 [1], 26
Bauer, H. F. III, 99 [4], 102
Bauer, R. W. I, 311 [3], 312
Baulch, D. L. III, 453, 461
Bauman, W. C. III, 504 [2], 515
Baus, R. A. I, 46 [6], 47 [5], 56
Bayly, R. J. II, **305**
Beamer, W. H. II, 68 [5], 79
Beauchamp, E. E. II, 408 [2], 409 [2], 413 [5], 417
Becker, R. A. II, 421, 424
Beetem I, 438 [16], 443 [16], 449 [16], 450
Begemann, F. I, 16, 17, 21, 26, 27, 435 [5], 449, 513 [2], 516
Bell, P. R. II, 236 [4], 240
Bell, R. E. II, 202, 209
Bell, R. N. II, 474 [6], 491
Belluco, U. III, 113 [5], 122
Bender, M. L. III, 363 [3], 367
Ben-Efraim, D. A. III, 201 [9], 203
Benjamin, B. M. III, **195**, 196 [2], 201 [2], 203
Bennett, W. E. III, 417 [1], 425
Benson, G. C. III, 534 [23], 535 [23], 536 [23], 542 [23], 545 [23], 546 [23], 548
Bentz, D. R. 417 [1], 425
Berdnikova, N. G. III, 212 [10], 216
Bergenstal, D. M. III, 77 [6], 82
Berggren, A. II, 456 [4]
Berman, I. L. II, 157 [3], 163
Berman, S. S. II, 367
Bernas, R. II, **453**
Bernelin, B. I, 371 [3] [4], 380
Bernert, T. II, *189*
Bernhard, F. II, 111 [11], 127
Bernstein, W. III, 172 [19], 177
Berry, P. F. I, **467**, 473 [5], 474 [6], 475, *475*, II, 29 [4], 32 [4], 38 [4], 39, 49 [9], 52
Berson, J. I, 201, 203
Berthelot, A. II, 113 [12], 127
Berthelot, M. III, 332 [6], 336
Berthold, R. II, 130 [5], 136
Besnard, S. I, **207**, 213 [5], 215 [5] [refs], *216*
Beswick, C. K. I, 429 [6], 430
Bettis, E. S. III, 576 [2] [4], 590
Bezborodko, M. D. I, 236 [3], 247, 376 [10], 377 [10], 380
Bhabha, H. S. I, 303-5, 308, 309, 310, 311
Bichsel, H. I, **303**, 306 [1], 312
Bickel, P. W. I, 283 [23], 286
Biehl, A. II, 237 [7], 240
Bien, G. S. I, 69 [5], 73
Biermann, W. J. III, 418, 425
Bietiechtin, A. G. I, 125 [13], 134

Bigeleisen, J. III, 226 [4], 231, 233, 237 [2], 242, 362 [2], 367
Bill, P. T. III, 419 [9], 425
Binkley, II, 326 [2], 338
Binks, J. H. III, 241 [8], 242 [9] [refs]
Birchanall, C. I, 201 [7], 206
Bird, P. M. I, 445 [28], 450
Birkelund, O. R. II, **471**
Bisby, H. II, **291**, 297, 303
Bizzell, O. I, *116*, II, **63**
Bjerrum, N. III, 420 [15], 425
Bjornholm, S. III, 296 [9], 298
Blackburn, D. A. I, **137**, 140 [2], 144, **145**, 146 [4], 156, 157
Blake, C. A. II, 544 [7], 553
Blanchard, A. A. III, 272 [11], 280
Blanchard, R. L. I, 449 [38], 450
Bleaney, B. I, 332, 335, 339
Blekkingh, J. J. A. III, 533 [16], 544 [16], 547
Blifford, I. M., Jr. I, 46 [6], 47 [5], 56
Bloch, K. III, 77 [4] [5], 78 [7], 82
Block, P. II, 213 [1], 223
Block, S. I, 177 [10], 178
Bloecher, F. M. I, 496 [17], 498
Blokh, G. A. II, 151 [7], 155, III, 33 [2], 40
Blood, C. M. III, 561 [3], 574
Blumentritt, G. II, 111 [11], 127
Bochkarev, V. II, *463*
Bockris, I. O. M. I, 170 [1], 171 [6] [7], 175 [7], 178 [7], [refs]
Boehm, F. II, 429 [13], 430
Bogar, L. C. III, 417 [1], 425
Bogdanov, N. I. II, 68 [3], 79, **527**, 529 [2], 537 [19], 538 [18] [19], 540, *540*
Bogdanova, O. K. III, 246 [1] [3], 247 [5], 248 [3], 249 [1] [5], 250 [12], 253 [3] [refs]
Boguslavsky, D. B. II, 152 [8], 155
Bohr, A. I, 329, 330, 338 [2], 339
Bojesen, E. III, 132 [1], 137 [1], 138
Bokshtein, S. Z. I, 146 [7], 156, 181 [2], 192, **193**, 195 [1] [2], 203 [8], 206
Boltaks, B. I. I, 288 [2], 289 [6], 292 [2], 293, 294
Bolton, J. R. II, 385 [69], 390
Bond, F. C. I, 398 [2] [7], 404
Bonhoeffer, K. F. III, 59, 519 [2] [3] [4], 528
Bonner, N. A. III, 338 [2], 348, 519 [10], 528
Booker, G. R. I, 218 [1] [2], 223
Boreskov, G. K. III, 250 [16], 254, 359, 360, 441 [2] [3], 442, 445, 447 [5] [6], 448
Borg, D. C. II, 201, 209
Borisov, E. A. II, 380 [31] [32], 389
Borisova, M. S. III, 250 [16], 254
Borland, J. W. II, 384 [63], 390
Boulenger, R. I, **45**
Bourne, E. J. III, 101 [8], 102
Bourquelot II, 332 [4], 338
Bowden, F. B. I, 364 [3], 367
Bowen, V. T. I, **57**, 58 [1] [2] [3] [4], 60 [2] [3], 65
Bowers I, 262 [1], 264 [1], 267
Bowers, K. D. I, 331 [5], 332 [5], 339
Bowie, S. H. U. II, 299 [11], 302 [11], 303
Boyd, G. E. II, 383 [55], 384 [55], 390, 398 [1], 403 [1], 405, III, 552 [3] [7], 556
Boyle, J. E. III, 409 [4], 410 [4], 412 [19], 414
Boytsova, V. F. III, 258 [6], 267
Bozóky, L. I, 478, 479 [2], 480 [2], 481
Bradley, R. S. III, 496, 502
Bradlow, H. L. II, 381 [39], 389
Brain, L. R. I, 426 [5], 430
Brannon, H. R. I, 78, 89
Brauer, G. II, 456 [10], 462
Braun, W. J. I, **343**, 345 [2], 352
Bray, P. J. II, 388 [95], 391
Bresesti, M. II, **455**
Briant, J. I, 371 [4], 380
Briant, R. C. III, 576 [1], 590
Briesmeister, A. C. II, **431**
Briggs, G. A. I, 501 [8], 509
Briggs, G. H. II, 112 [10], 127
Brillant, S. II, 56 [1], 63
Brinner III, 126 [6], 129
Broadbank, R. W. C. III, **179**, 184, 185 [3], 186
Broatch, W. H. III, 189 [9], 194
Brody, J. K. II, 362 [10], 363 [10]
Broecker, W. S. I, 69 [6] [9], 70 [6] [9] [11], 71 [9], 72, [9], 73, 76, 89
Broida, H. P. III, 259 [7], 267
Bromley, D. A. II, 458 [13], 462
Brönsted, J. N. III, 392, 405
Brooks, G. T. III, 84 [2], 85, 90
Brookshank, W. A. II, 235 [2], 240
de Brouckère, L. III, **187**
Brousaides, F. J. II, 353 [3], 354 [7], 355 [7], 360
Brown, A. F. I, **137**, **145**, 146 [4], 156, *156*, *157*
Brown, B. R. III, 226 [1], 233

Brown, C. J. **III**, 108 [9], 109
Brown, H. **I**, 31 [7], 32 [12] [13], 36
Brown, K. B. **II**, 544 [7], 553
Brown, M. **II**, 202 [6], 209
Brown, P. E. **III**, 137 [6], 138
Brown, R. M. **I**, 514, 516, 527 [4], 530
Brown, W. G. **II**, 381 [38], 389, **III**, 24 [11], 25, 467 [5], 469, 497 [6], 502
Brown, W. L. **I**, 275 [8] [11], 286
Brownell, G. L. **I**, 258 [6], 260, **II**, 219 [8], 222 [11], 223
Brownell, G. M. **II**, 300 [17], 303
Brownell, L. E. **II**, 10, 20, 441 [6]
Brownlee, J. L., Jr. **II**, 284 [27], 285 [27], 289
Brucer, M. **I**, 258 [7], 260
Brudewold, F. **II**, 322 [2] [refs]
Brueckner, K. **III**, 333 [7], 334, 336
Brukl, A. **III**, 377 [13], 378
Bruna, M. **III**, 113 [5], 122
Brunello, C. C. **II**, 382 [44], 389
Brunton, D. C. **II**, 154 [12], 155
Brustad, T. **III**, 487 [4], 493
Bryant, G. T. **I**, 443 [18], 449 [18], 450
Bube, R. H. **I**, 501 [7], 509
Buchanan, D. N. E. **I**, 282 [18], 286
Buchanan, J. D. **II**, 457, 462
Buchanan, R. F. **II**, **361**, 362 [8] [10], 363 [10], 366 [8], *371*, **III**, 396 [12], 405
Buchwald, H. **I**, 375 [6], 380
Buffington, F. S. **I**, 188 [10], 192
Bulashevich, Yu. P. **I**, **101**, 105, 109, *116*, 128 [10], 134, *431*
Bunney, L. R. **II**, 362 [5], 366 [5], 367 [5]
Burch, P. R. J. **I**, 445 [28], 450
Burckhardt, C. **I**, *116*, **III**, *155*
Burger, K. **III**, 321 [9], 324
Burhop, E. H. S. **III**, 161 [6], 177
Burke, W. H. **I**, 78, 89, 92 [6], 98
Burns, E. **III**, 423, 425
Burton, I. A. **I**, 288 [1], 292 [1], 293
Burton, M. **III**, 16 [3], 22 [3], 24, 59 [27], 66, 465, 469, 472 [1], 473, 482
Burttschell, R. H. **I**, 448 [33], 450
Busch, M. **III**, 95 [13], 96
Buser, W. **III**, 556 [20], 557
Busey, R. H. **III**, 552 [5], 556
Bush, I. E. **III**, 94 [9], 96
Butement, F. D. S. **II**, 426 [3] [5], 429 [5], 430
Butler, T. A. **II**, **407**, 411 [4], 417, *417*, *418*
Butomo, S. V. **I**, **91**, 93 [12], 99
Bykov, A. G. **II**, 529 [2], 540

Cabiddu, S. **II**, 468 [8], 469
Cacace, F. **II**, 382 [48] [49], 388 [100], 389, 391, 466 [4], 468, **III**, 44 [3], 65
Cadotte, J. E. **III**, 99 [6], 102
Cairo **III**, 60 [28], 66
Cali, J. P. **II**, 273, 275
Callaway, J. **I**, 298 [6], 299
Calvin, M. **II**, 332 [3], 338 [10] [refs], 388 [101], 391
Camagni, P. **I**, 297 [5], 299
Cameron, J. F. **I**, *99*, *116*, *451*, **467**, 473 [5], 474 [6], 475, *517*, **II**, **23**, 29 [4], 32 [4] [6] [8], 38 [4], 39, 49 [9], 52, *53*, 56 [3], 58 [3], 63, *91*, 139 [3], 146, *146*, *230*, *290*, 312 [3], 316
Campbell, D. O. **III**, 582 [10], 590
Campbell, I. G. **II**, 379 [25] [26], 380 [35], 383 [51], 385 [51], 387 [88], 389, 390
Campbell, R. B. **I**, **235**, 248, **355**, 362 [1], 363 [2], 366 [5], 367
Cannan, R. K. **II**, 307 [6], 308
Cannings, F. R. **III**, 155, **205**
Cantwell, T. **II**, 293 [7], 303
Carleson, B. G. F. **III**, 423, 425
Carlson, T. A. **III**, 397 [15], 398 [15], 405, 554 [10], 556
Caron, M. **II**, 244 [2], 245 [4], 257
Carslaw, H. S. **III**, 565 [13], 574
Carson, A. S. **III**, **495**, 499, 502
Carter, P. E. **II**, 529 [1], 540
Cartledge, G. H. **III**, **549**, 551 [1] [2], 552 [4], 553 [8] [9], 554 [11], 555 [12] [13] [14], 556 [19] [refs], 557 *557*
Case, L. **III**, 105 [4], 109
Cason, J. **III**, 228, 233
Cathey, W. J. **II**, 467 [7], 469
Cederlund, J. **II**, 30 [5], 39, 42 [4], 52
Certaine, J. **I**, 126 [8], 127 [8], 134
Chabert, J. **I**, 465
Chackett, K. **I**, *326*
Chadwick, G. B. **II**, 458 [15], 462

Chadwick, J. **II**, 159 [4], 163
Chalmers, B. **I**, 142, 144 [3] [refs]
Chamberlain, T. K. **I**, 465
Chapeville, F. **III**, **139**, 140 [2] [3] [4] [5], 141 [6]
Charlesby, A. **II**, 525 [6] [refs]
Chatelain, G. **III**, 149 [7], 155
Chaudron, G. **I**, 208 [3], 215, **II**, 244 [1], 257
Chauvin, R. **II**, 5 [6], 13 [6], 20, 42 [3], 52, 69 [9], 79
Chen, C. **III**, 93 [6], 96
Chen Chao-tung **III**, 207 [6], 214 [6], 216
Cheronis, N. D. **III**, 93 [7], 96, 228, 233
Chesalova, V. S. **III**, 447 [6], 448
Chiang, R. S. H. **II**, 479 [8], 491
Chiarotti, G. **I**, 297 [5], 299
Chleck, D. J. **II**, **351**, 352 [2], 353 [3] [4] [5] [6], 354 [7], 355 [7], 360, *360*, 522 [2], 525
Chmutov, K. **II**, 399 [3], 405
Chopoorian, J. A. **III**, 297 [12], 298
Choppin, G. R. **III**, **283**, 285 [2], 287 [2] [6], 297 [12], 298, *298*, *299*
Chovin, P. **III**, 146 [1], 155
Christensen, N. H. **III**, **131**
Christoff, A. **III**, 519, 528
Churchill, R. V. **III**, 564 [10], 566 [10], 574
Cieri, L. **II**, 382 [49], 389, **III**, 44 [3], 65
Ciranni, G. **II**, 466 [4], 468
Clarey, D. H. **II**, 68 [5], 79
Claridge, R. F. C. **II**, 384 [57], 390
Claycomb, C. K. **II**, 467 [7], 469
Clayton, C. G. **I**, *116*, *121*, *450-1*, **499**, 501 [8], 509, *509*, **II**, *80*, *289*
Clayton, G. D. **I**, 449, 450
Cleland, J. W. **I**, **269**, 271 [3], 272, 274 [3], 275 [3] [10], 276 [12], 282 [19], 284 [19], 285, 286
Cobble, J. W. **II**, 383 [55], 384 [55], 390, 398 [1], 403 [1], 405, **III**, 552 [3], 556
Cochran **I**, 262 [1], 264 [1], 267
Coekelbergs, R. **II**, **193**, 194 [1], 197 **III**, **351**, 352 [1] [2], 353 [1] [2] [4], 354 [2], 360
Cohen, D. **III**, 302 [2], 313
Cohen, E. **III**, 533, 544, 547
Cohen, M. **I**, 188, 192
Coleman, C. F. **II**, 544 [8], 553
Coleman, E. W. **II**, 10 [8], 20
Collie, B. **III**, 535 [24], 536 [24], 546 [24], 548
Collins, C. J. **III**, **195**, 196 [2], 201 [2], 203
Compaan, K. **I**, 162 [5], 168
Compton, A. H. **I**, 315 [2], 326, **II**, 43 [7], 52, 58 [5], 63
Conn, P. K. **II**, 379 [29], 389
Connick, R. E. **III**, 430 [4], 431 [12], 434 [18] [refs]
Conwell, E. H. **I**, 280 [15], 286
Cook, G. B. **II**, 56 [2], 60 [6], 63, 72 [4], 74, 75, 79, 216 [5], 223, 456 [9], 462
Cooke-Yarborough: *see under* Yarborough
Cooper, G. R. **III**, 303 [5], 313
Cooper, R. **III**, **495**
Corbett, J. W. **I**, 282 [18], 286
Cordeiro, S. C. **I**, **465**
Corey, R. B. **II**, 308 [8] [refs]
Cornuet, R. L. **II**, 110 [3], 116 [3], 126
Corse, J. **III**, 197 [3], 202 [3], 203
Coryell, C. D. **III**, 417 [2], 422 [2], 425
Cotterill, P. **II**, 315 [6], 316
Cotton, F. A. **III**, 271 [9], 278 [9], 280
Coulomb, P. **I**, 190 [11], 192
Courtel, R. **I**, 374 [5], 380
Courtois, G. **I**, **405**, **453**, **II**, *21*, *188*
Cowan, C. L., Jr. **I**, 444 [23] [24], 445 [23], 450
Cowper, G. **II**, 456 [5], 462
Cox, J. D. **III**, 85 [6], 90
Crahmer, H. **III**, 201 [7], 203
Cram, D. J. **III**, 201 [8], 203
Crank, J. **II**, 161 [8], 163
Crawford, J. H., Jr. **I**, **269**, 271 [3], 274 [3], 275 [3] [10], 276 [12], 282 [19], 284 [19], 285, 286, *286*
Criddle, W. J. **II**, **325**, 337 [8], 338
Croatto, U. **II**, 382 [47], 389
Crooks, R. N. **I**, 46 [10], 56, 71 [14], 73
Cross, A. S. **II**, 215 [3], 223
Crowdle, J. H. **III**, 108 [10], 109
Crucq, A. **II**, 194 [1], 197
Cruikshank, A. J. **II**, 456 [5], 462
Cuevas, M. **I**, 280 [13], 286
Curie, P. **III**, 533, 547
Curran, S. C. **I**, 444 [25], 450
Currie, L. A. **I**, 18 [26] [27], 23, 26, 27

Czubek, J. **I, 123**, 126 [7], 128, 130 [3], 134

Dabbs, J. W. T. **I, 329**, 331 [6], 332 [6] [8], 334 [10], 336 [14], 338 [6] [15], 339 [16] [refs] 340

Dahl, J. B. **II, 471**, 472 [3], 473 [3], 474 [3], 491, *492*, *493*

Dakin, H. D. **II**, 306 [1], 308

Damburg, N. A. **II**, 537 [19], 538 [19], 540

Danby, C. J. **III**, 235-7, 238 [5], 242 [5] [refs]

D'Angeli, F. **III**, 105 [2], 109

Danon, J. **II**, 366 [18], 368 [26] **III**, 430 [7], 434

Danyluk, S. S. **I**, 92 [11], 99

Darbee, L. R. **III**, 475 [5], 482

Darby, J. B., Jr. **I**, 143, 144, 146, 155

Dauphin, J. **III, 471**

Davenport, A. N. **II**, 219 [7], 223

Davey, W. **I**, 376 [11], 380

Davidsson, J. **I**, 465

Davies, A. S. **I**, 170 [1], 178

Davis, E. W. **I**, 398, 404

Davis, J. R. **I**, 17 [22], 26

Davis, R., Jr. **I, 3**

Davison, W. H. **II**, 110 [7], 126

Davison, W. H. T. **I, 251**

Day, R. A., Jr. **III**, 397 [13], 405

De, A. K. **II**, 286 [30], 289

De Bruyn, P. L. **I**, 496 [18], 498

Debuchy, D. **III, 123**

Debye, P. P. **I**, 280 [15], 286

Decot, J. **III, 351**, 352 [2], 353 [2], 354 [2], 360

De Croës, M. **II**, 110 [8], 127

Dede, L. **III**, 404 [20], 405

De Felice, J. **I**, 17 [20] [25], 18 [25], 26

Dekhtyar, I. Y. **III**, 565 [12], 574

De Long, W. A. **II**, 480 [11], 491

Delpoux, A. **II, 177**

Demildt, A. **II, 425**, 430, *430*

Demuynk, J. **II**, 429 [14], 430

Denton, C. A. **III**, 140

Derbentsev, Y. I. **III**, 246 [4], 253

Desty **III**, 155

Deutsch, M. **I**, 311, 312

De Van, J. H. **III, 559**, 565 [11], 566 [15], 574

Devell, L. **III**, 64 [35], 66

Dever, R. F. **I**, 60 [6], 65

Devirts, A. L. **I**, 76 [1] [2] [3], 83 [1], 89, 92 [7], 96 [7], 99

Devoe, J. R. **II**, 281 [16], 289

Dewhurst, H. A. **III**, 16 [2], 24, 479 [14] [15], 481 [18], 482

De Witt, B. J. **I**, 227 [4], 231 [4], 233

Diamond, R. M. **III**, 420, 425

Dibbs, H. **I**, *404*

Trotman-Dickenson, A. F. **III**, 169 [14], 177

Dickinson, R. G. **III**, 317 [3], 323

Diethorn, W. A. **I**, 78, 89

Dietz, R. J., Jr. **III, 415**, 417 [1] [2], 420, 422 [2], 425, 434 [20] [refs]

Dinegar, R. H. **III**, 547 [32], 548

Dixon, J. K. **III**, 451 [1], 461

Dobkina, E. I. **I**, 76 [1] [2] [3], 83 [1], 89, 92 [7], 96 [7], 98

Dodson, R. W. **II**, 262 [2], 268, 375, 388

Dolkey, E. S. **I**, 78 [17], 89

Dominey, D. A. **III**, 235-7, 238 [5], 242 [5] [refs]

Donohue, J. **II**, 308 [8] [refs]

Dorfman, A. **III**, 100 [7], 102

Dorfman, L. M. **II**, 378 [12], 389 **III, 3**, 5 [6], 10, 45, 55, 56, 60, 65, 163, 177, 466 [3], 469

Douglas, D. L. **I**, 412

Douis, M. **II**, *492*

Doumani, T. F. **III**, 16 [4], 22 [4], 24

Doumerc, J. **II**, 253 [8], 254 [8], 258

Downes, A. M. **III**, 228 [14], 233

Drapchinsky, L. V. **I**, 95 [15], 99

Drefahl, G. **III**, 201 [7], 203

Dreger, E. E. **III**, 453, 461

Drever, R. W. P. **I**, 444 [25], 450

Driscoll, W. J. **II, 339**, 343 [3], 349, 543 [6], 544 [2] [6], 545 [11], 550 [6] [11], 552 [6], 553

Drozdoz, N. G. **II**, 158 [7], 163

Drozhzhin, V. M. **I, 91**

Dubinin, M. M. **II**, 399 [4], 405

Du Bois, R. E. **I**, 500 [4], 509

Dubsky, J. V. **III**, 506 [7], 515

Dudley, H. W. **II**, 306 [1] [2], 308

Dudley, R. A. **II**, 219 [8], 221 [10], 222, 223

Dumond, J. W. M. **II**, 429 [13], 430

Duncan, J. F. **II**, 216 [5], 223, **III**, 453, 461

Duncombe, W. G. **II**, *188* **III, 379**, *384*, *385*

Dundon, M. L. **III**, 533, 534, 544 [10] [11], 545 [10] [11], 547

Dunham, C. L. **I**, 60, 65

Dunn, F. J. **II**, 432 [1], 438

Dushman, S. **II**, 434 [3], 438

Dutton, H. J. **III**, 147 [2], 155

van Duuren, K. **I**, 444 [27], 450

Duyckaerts, G. **II**, *371*, 512 [1] [6], 520
III, 476 [11], 482
van Dyken, A. R. **III**, 16 [4], 22 [4], 24, 467 [4], 469
Dyrssen, D. **II**, 544 [5] [10], 552 [5], 553
III, 297 [10], 298, 430 [9], 434 [19] [refs]
Dzantiev, B. G. **III**, **13**, **27**, *41*, *254*, *493*
Dziekoński, T. **II**, 168, 174, 175
Dzisko, V. A. **III**, 250 [16], 254
Dziunikowski, B. **I**, **123**, 126 [7], 130 [3], 134

Eakins, J. N. **I**, 465
II, 159 [4], 163
Eberhardt, P. **I**, 27
Ebert, K. H. **I**, 24 [46], 27
Ebihara, H. **II**, 386 [78] [79], 390
Eccleston, B. H. **II**, 138 [1], 146
Edwards, E. D. **I**, 236 [1], 247, 365 [4], 367, 376 [11], 380
Eekhaut, Z. **II**, 270 [3], 274
Egloff, G. **III**, 525 [19], 529
Ehman, W. D. **I**, 17 [23], 26
Ehrenberg, L. **III**, 52 [18], 62, 66
Eichholz, G. G. **I**, **397**, 399 [8], 404
Eichorn, J. **III**, 504 [2], 515
Eigner **III**, 22 [7], 24
Eirich, F. R. **III**, 189 [5], 194
Eisen, F. H. **I**, 283, 286
Eisenbud, M. **I**, 71 [13], 73
Eisenstein, J. C. **I**, 335 [11], 339 [11], 340
Elias, H. **III**, *11*, *122*, *493*
Elliot, J. S. **I**, 236 [1], 247, 248, 365 [4], 367
Ellis, W. R. **I**, 417 [1] [2], 418 [3], 426 [5], 430
El-Sayed, M. A. **II**, 377 [3], 388
III, 169 [13], 177
El-Wakkad, S. E. S. **III**, 534 [20], 548
Elyashevich, M. A. **III**, 262 [12], 263 [12], 267
Emeléus, V. M. **II**, **261**, 262 [3], 268
Emelyanov, V. S. **I**, 203 [9], 205 [9], 206
Enander, B. **III**, 6 [8], 10, 45 [10] [12], 58 [10], 60 [10], 65, 66
Enge, H. A. **II**, 110 [5], 126
Engorov, U. N. **II**, 158 [7], 163
Enüstün, B. V. **III**, **531**, 541 [29], 548
Eremenko, O. M. **I**, 227 [5], 231 [5], 233
Eremenko, V. N. **I**, 227 [5], 231 [5], 233
Ergen, W. K. **III**, 576 [3], 590

Ernest, E. P. **II**, 157 [3], 163
Erwall, L. G. **II**, 208 [9], 209
Esin, O. A. **I**, 170 [2], 178
Estermann, J. **III**, 519 [8], 528
Estrup, P. J. Z. **II**, 377 [3], 378 [6] [7], 388
III, 169 [13], 177
Evans, C. **II**, 159 [4], 163, *198*, **309**, 313 [4], 316, *316*
III, *129*, 184, 186
Evans, D. E. M. **III**, 19 [5], 24
Evans, J. B. **III**, 476 [10], 482
Evans, R. B. **III**, **559**, 562 [7], 565 [7], 566 [7], 574
Evans, R. D. **II**, 12, 20, 113 [13], 127
Eyring, H. **III**, 58, 59 [23], 66, 394, 405

Falting, V. **I**, 78, 89
Fan, H. Y. **I**, 283 [20], 286
Fan, S. **III**, 247 [9], 253
Fara, H. **I**, 142 [4], 144
Faris, J. P. **II**, **361**, 362 [3] [8] [10], *363* [10] [15], 365 [3], 366 [8], **III**, 396 [12], 405
Fassbender, H. **III**, 79, 82
Fateeva, Z. M. **II**, 489 [14], 491
Fayram, R. **II**, 237 [7], 240
Fechtig, H. **I**, 25 [48], 27
Federov, G. B. **III**, 561 [4], 574
Fedorov, T. B. **I**, 203 [9], 205 [9], 206
Feitknecht, W. **III**, 556 [20], 557
Felinger, A. K. **II**, **93**
Fergusson, G. J. **I**, 69 [1], 70 [10], 73, 78, 89, 92 [4], 98, 435 [7], 450
Ferraro, J. R. **II**, 543 [12], 552 [12] [14] [15], 553, 554
Ferreira, R. C. **II**, 308 [10] [refs]
Ferris, S. W. **I**, 345 [1], 352
Fessenden, R. W. **III**, 477 [12], 482
Field, F. H. **III**, 161 [7] [8], 170 [7] [8], 173 [8], 177
Figurovsky, N. A. **III**, 547, 548
Filonov, V. A. **I**, 521 [1] [2], 530
Filosofo, I. **II**, **3**, 28 [3], 30 [3], 39
Findeis, A. F. **I**, **433**
Fineman, I. **II**, 208 [9], 209
Fineman, O. **I**, *353*
II, *164*
Fink, R. W. **III**, 493 [9] [refs]
Finkelstein, A. **II**, 148 [4], 155
Finkelstein, Y. B. **I**, 521 [1] [2], 530
Fireman, E. L. **I**, 16, 17 [20] [25], 18 [31] [6], 18 [25], 23, 24, 26, 527 [5], 528 [5], 530
Firsov, E. N. **I**, 95 [15], 99

Fischer, J. **II**, 202, 209
Fisher, A. **III**, 155, **205**
Fisher, C. **II**, *540*
Fisher, D. E. **I**, 18, 19, 20, 23, 26, 27
Fisher, E. M. **I**, 46 [10], 56, 71 [14], 73
Fisher, J. C. **I**, 147, 156, 181, 182, 190, 191, 192
Fisher, J. S. **III**, 571 [16], 574
Fisher, M. E. **I**, 429 [6], 430
Fiskell, J. G. A. **II**, 480 [11], 491
Fithian, E. J. **I**, 350 [3], 352
Flerov, G. N. **I**, **117**, *121*, *122*, *531*
Florkowski, T. **II**, *21*, *106-7*
Flory, P. J. **III**, 523, 524, 528, 529
Flynn, K. F. **I**, 39, 42 [4], 43
Fogelström-Fineman, I. G. A. **II**, 496 [1], 497 [2], 509
Fokin, A. V. **II**, 529 [2], 540
Foner **I**, 262 [1], 264 [1], 267
Foos, R. A. **II**, 427 [9], 430
Forberg, S. R. **II**, **495**, 496 [1], 497 [2], 506 [7], 509, *509*
Ford, J. F. **III**, *155*, 155, **205**, *233*
Forestieri, A. F. **I**, 143 [8], 144, 146, 150, 155
Forsberg, H. G. **II**, 208 [9], 209, **III**, *425*
Foster, E. **II**, 362 [11]
Foster, G. L. **II**, 307 [5], 308
Foti, S. **II**, 362 [5], 366 [5], 367 [5]
Fouarge, J. **II**, *230*, **511**, 512 [1] [6] [7], 520
Fowler, E. E. **II**, 67 [2], 79
Fowlie, C. G. **II**, 157 [2], 163
Fox, C. J. **II**, 10 [8], 20
Franck, J. **II**, 379 [21], 389
Frank **III**, 60 [28], *66*
Franklin, J. L. **III**, 161 [7], 170 [7], 177
Fraser, J. S. **I**, 336 [13], 340
Frauenfelder, H. **I**, 311, 312, 315 [6], 319 [6], 326
Fred, M. **II**, 364 [16]
Fremlin, J. H. **II**, **317**, 318 [1], 322
Frennet, A. **II**, **193**, 194 [1], 197 **III**, **351**, 352 [1] [2], 353 [1] [2] [4], 354 [2], 360
Freundlich, H. **III**, 531-2, 533, 537, 545, 547
Frevel, L. K. **I**, 486 [5], 498
Freyermuth, H. B. **III**, 107 [7], 109
Friedlander, G. **I**, 18 [34], 27, **II**, 454
Friedlander, H. N. **II**, 271 [7], *275*
Friend, J. Newton **III**, 330 [3], 332 [3], 336
Frisch, H. L. **III**, 189 [5] [6], 194
Fritzsche, H. **I**, 280, 286
Fromageot, P. **III**, **139**, 140 [2] [4] [5], 141 [6], *143*
Fronaeus, S. **III**, 296, 298, 429 [1], 430 [5] [6], 434
Frost, A. A. **III**, 231 [15], 233
Frumkin, A. N. **I**, 486 [8], 498
Frush, H. L. **III**, 99 [1], 102
Frynta, Z. **I**, **381**
Fryxell, R. E. **III**, 419 [8], 425
Fu I-bei **III**, 371 [4] [6], 376 [4] [6], 377 [4] [6], 378
Fukai, R. **II**, 284 [28], 289
Fukushima, D. K. **II**, 381 [39], 389 **III**, 77, 82
Fumi, F. G. **I**, 297 [5], 299
Funabashi, K. **III**, 173 [21], 177
Funke, V. F. **II**, 68 [3], 79
Funt, B. L. **I**, 92 [10] [11], 93 [10], 99
Fürstenak, W. **I**, 496 [19], 498
Furukawa, M. **II**, 383 [54], 390

Gaittet, J. **II**, **243**, 246 [6], 254 [6], 258
Gál, D. **III**, **217**, 220, 224, *224*, *254*, *348*
Gale, M. M. **III**, 94 [9], 96
Gallagher, T. F. **III**, 77 [3], 82
Gant, P. L. **II**, 378 [17], 389 **III**, 45 [6], 56 [6], 65, 161 [3] [4], 168 [3] [4], 169, 172 [4], 177
Gardner, D. E. **II**, 322 [2] [refs]
Gardner, M. E. **I**, 418 [3] 430
Garms, W. I. **I**, 398 [4], 404
Garnett, J. L. **II**, 381 [38], 389 **III**, 24 [11], 25, 497 [6], 502
Garrison, W. M. **II**, 426 [1], 430
Garrod, J. **II**, 153 [9], 155
Gaudin, A. M. **I**, 496 [17] [19], 498 **II**, 293 [6], 299 [14], 300 [14], 303
Gavrilov, V. M. **III**, 259 [9], 267
Gaylord, N. G. **III**, 108 [10], 109
Gebauhr, W. **I**, *542*
Geiss, J. **I**, 16 [7] [12], 21 [7], 26, 27, **29**, 32 [15] [17], 36
Geissmann, T. A. **III**, 92, 96
Geithoff, D. **II**, *275*, *463*, *492* **III**, *406*
Gelles, E. **III**, 226 [3], 233
Gelman, N. **III**, 33 [3], 37 [3], 40
Gentner, W. **I**, 16, 25 [48], 26, 27
Gerasimov, Y. I. **I**, 227, 231 [6], 233
Gerhart, J. B. **I**, **303**, 306 [1], 312
Gerling, E. K. **I**, 17 [21], 18 [21], 26

Gertsriken, S. D. I, 154, 156, 191, 192 III, 565 [12], 574
Geyderikh, V. A. I, 227 [3], 233
Geyer, J. C. I, 443 [18], 449 [18], 450
Gfeller, C. I, 27
Ghanem, N. A. II, *163* III, **43**, 45 [11] [12], 52 [18] [19], 60 [11], 64 [33] [34] [35] [36], 66, *67*, *177*, 177, *385*
Giacomello, G. II, 382 [46] [47] [48], 386 [84], 388 [100], 389, 390, 391, 466 [4], 468
Gibbons, D. II, *240*, *241*, **269**, *275*, *276*, 279 [5], 289
Gibbs, W. J. III, 524, 533, 535, 536, 546, 547
Gibert, A. I, 465
Gibson, A. F. I, 276 [12], 286
Gifford, A. T. I, 500 [4], 509
Girammi, G. III, 44 [3], 65
Girifalco, L. A. I, 143 [8], 144, 146, 150 [2], 155
Girelli, A. I, 376 [12], 380
Gittelman, B. I, 311 [3], 312
Glascock, R. F. III, 382 [4] [5], 384
Gleason III, 126, 129
Glembotsky, V. A. I, 495 [13] [14], 498
Glendenin, L. E. I, 39, 42 [4], 43 II, 449 [10]
Glocker, G. III, 377 [12], 378
Glockler, G. III, 59, 66
Glueckauf, E. III, 505 [3], 515
Goble, A. G. III, 211, 212 [7] [8], 213, 215, 216
Godlewski, Z. II, **165**
Goebel, K. I, **13**, 18 [29], 21 [36] [37] [38], 22 [41], 23, 27, *27*
Goel, P. S. II, 456 [3], 462
Gofstein, R. III, 92 [1] [4], 95
Golbek, G. R. I, **519**
Goldberg, E. D. I, 32 [12] [13], 36
Golden, A. S. I, 443 [19], 450
Golden, G. S. III, 417 [1], 425
Goldenberg, N. III, 310 [10], 313
Goldman, A. III, 317 [7], 324
Goldstein, S. I, 439, 442, 443 [17], 450
Gordon, B. E. I, *99*, *248*, *352*, *368*, *516* II, *136*, *210*, *229*, *275*, *290*, *323* III, *11*, *72*, *143*, *194*, *461*
Gordon, S. III, 16 [4], 22 [4], 24, *465* [*1*], *469*
Görlich, P. II, 116 [15], 127
Gorter, C. J. I, 331 [3], 339
Gosselain, P. III, 352 [1], 353 [1], 360
Gossick, B. R. I, 271 [3], 274 [3], 275 [3], 285
Gosztonyi, T. III, **91**, 95 [16], 96
Gottlieb, M. B. I, 26
Gould, R. G. III, 77 [6], 82
Gradsztajn, E. II, **453**
Grapengiesser, B. III, 64 [36], 66
Gray, A. J. III, 162 10], 177
Gray, J., Jr. I, 69 [2], 71 [2], 73
Gray, P. R. II, 68 [5], 79
Graziano, F. D. III, 411 [10], 414
Greania, E. C. II, 130 [6], 136
Green, J. H. II, 385 [72] 390
Greendale, A. E. II, 282 [18], 289
Greenfield, M. A. I, 435 [12], 450
Greenwood, C. T. III, 189 [9], 194
Gregory, J. N. I, *116*, *353*, **415**, *431*, *451* II, *304*, *463* III, *11*
Griffith, W. P. III, 271 [4] [5] [6] [7] [8], 279 [6], 280
Grimes, W. R. III, **559**, 562, [6], 574, **575**, 578 [5] [8], 590
Grjebine, T. I, *27*, *56*, *37*
Grodzins, L. I, 311 [3], 312
Groshev, L. V. II, 387 [906]
Grosse, A. V. I, 435 [4], 449
Grouzine: *voir* Gruzin
Grubb, H. M. III, 465 [2], 469
Grummitt, W. E. I, 514, *516*, 527 [4], 530 II, 456 [5], 462
Grunberg, L. I, **235**, *247-8*, 248, *249*, **355**, 362 [1], 366 [5], 367, *367*
Grunwald, E. III, 197 [3], 202 [3], 203
Gruverman, I. J. II, 456 [8], 462
Gruzin, P. L. I, 181 [3], 191, 192, 203 [9], 205 [9], 206, 406 [3], 412 [3] [refs] III, 561 [4], 574
Guarino, A. II, 466 [4], 468
Gubareva, M. A. I, **193**
Guczi, L. III, **217**
Gudkova, T. I. I, 146 [7], 156, 203 [8], 206
Guermont, J.-P. III, **145**, 154 [9], 155
Guertsriken: *see* Gertsriken
Guillaume, M. II, 388 [99], 391 III, 44, 65, **69**, *72*
Guinn, V. P. I, 513 [1], 516
Guiraldenq, P. I, **179**
Guizerix, J. M. II, **81**, *91*, *92*, 110 [3], *116* [3], *126*
Gusev, N. II, 533 [14], 540
Guthrie, A. I, 471 [1], 475

Gutmann, H. R. II, 307 [7], 308
Gvion, R. II, **439**

Haag, W. O. III, 207 [6], 214 [6], 216
Hagee, G. R. I, 443 [19], 450
Hagemann, F. I, 69 [2], 71 [2], 73
Hahn, R. B. II, 440 [2]
Haissinsky, M. III, 431 [15], 434
Hale, D. K. III, 506 [6], 515
Hale, F. H. I, *116*
II, **291**, *304*
Halevi, E. A. III, 365, 367
Hall, C. E. III, 540 [28], 548
Hall, D. II, 387 [92], 391
Hall, E. T. II, **261**
Hall, G. R. I, 332 [7], 335 [7], 339
Halpern, A. II, 385 [71], 390
Hamermesh, M. I, 326 [11] [refs]
Hamill, W. H. III, 171, 173 [20] [22], 177, 472, 482
Hamilton, J. G. II, 426 [1], 430
Hamilton, L. A. I, 377 [13], 380
Hamoda, G. H. I, 60 [6], 65
Hanauer, S. H. I, **329**, 332 [8], 339
Hanawalt, I. D. I, 486 [5], 498
Handley, T. H. II, 429 [12], 430
Hanna, C. G. I, 445 [30], 450
Hanna, S. S. I, *44*, *312*, **313**, *326-7*
II, 457 [11], 462
Hanngren, Å. III, 61 [29], 66
Hans, R. II, 56 [1], 63
Hansch, C. III, 207, 214 [1], 216
Hanson, A. O. I, 311 [4], 312
Haq, S. III, 99 [5], 102
Harbottle, G. II, **375**, 383 [52], 384 [58] [68], 385 [52], 386 [85], 389, 390
Harbury, L. III, 534, 547
Hardwick, J. L. II, **317**, 318 [1], 322
Hardy, E. P., Jr. I, 60 [6] [7], 63 [7], 65
Harhash, A. H. E. III, **179**
Harned, H. S. III, 410 [7], 414
Harriden, G. S. I, 363 [2], 367
Harris, G. M. III, *224*, 228 [14], 233, *254*, *281*, *385*, **407**, 409 [2] [3] [4] [5] [6], 410 [4] [5], 411 [10] [11] [13], 412 [14] [16] [19], 413 [20] [22], 414, 475 [5], 482
Harris, W. E. II, 380 [34], 389
Harrison, D. C. III, 219, 224
Harrison, F. B. I, 444 [23], 445 [23], 450
Harrison, R. I, *466*
Hart, H. II, 117 [18], 127
Harvey, B. G. II, 387 [91], 390

Harwitz, N. H. I, 260 [8] [refs]
Hauffe, K. I, 245, 247
Hauptmann, H. III, 95, 96
Hauser, C. R. III, 227 [6], 233
Haven, Y. I, 162 [5], 168
Hawton, J. J. II, **455**
Hayes III, 126 [6], 129
Hayes, F. N. I, 92 [9], 93 [9], 99, 435 [10], 450
Heath, R. L. II, 237 [9], 240
Hefley, J. D. III, 305 [7], 307 [7], 310 [11], 313
van der Heijde, H. B. III, 326 [2], 336
Hein, R. E. II, 379 [29] [30], 389
Heine, K. II, 384 [65], 390
Helmholtz, H. L. F. III, 533, 547
Henchman, M. J. II, 378 [8], 381 [8], 389
Henisch, H. K. I, 272 [6], 285
Henley, R. II, 237 [7], 240
Henneberke, G. I, *509*
Hennig, G. II, 399 [5], 405
Henri, V. P. III, 468 [8], 469
Henry, P. S. H. II, 157 [1], 161, 163
Henry, R. II, 386 [77], 390, 398 [2], 400 [2], 405, *438*
III, **123**, 124 [2], 129
Henry, R. J. III, 271 [9], 278 [9], 280
Hentz, R. R. III, 465 [1], 469
Herber, R. H. III, 417 [1], 425
Herczeg III, 124 [2], 129
Herington, E. F. G. III, 207, 213, 214 [4], 215 [4], 216
Hérissey II, 332 [4], 338
Hermsen, J. I, 444 [27], 450
Herr, W. I, *11*, 27, **29**, 30 [3], 31 [4] [5] [6], 32 [14] [15] [17], 36, *36*
II, 380 [33], 384 [65], 389, 390
Herring, C. I, 162 [4], 168
Herrington, J. II, **309**
Herron, P. W. II, 504 [4], 509
Herz, R. H. II, 215, 223
Herzog, E. I, 208, 215
Hess, D. G. I, 16 [7] [12], 21 [7], 26, 27, 31 [11], 36
Heusler, K. E. III, 556 [19], 557
Heuzel, M. I, **453**
Hevesy, G. V. II, 130 [7], 136
III, 389, 405, 519, 528
Heyman, S. C. I, 126 [8], 127, 134
Heyne, W. III, 371 [5], 376 [5], 378
Hibbin, B. C. III, 199 [6], 203
Hicks, H. G. II, 426 [4], 427 [8], 430

Hieber, W. III, 272 [12] [13], 280
Higgs, L. A. I, 281 [16], 286
II, 387 [90]
Hild, W. III, 337
Hildebrand, J. H. III, 523 [12] [13] [14], 525, 526, 528, 529
Hill, D. L. I, 330, 331 [4], 335 [4], 338 [1], 339
Hill, O. F. II, 474 [6], 491
Hill, W. L. II, 384 [63], 390
Hincks, E. P. I, 445 [30], 450
Hindman, J. C. III, 302 [2], 313, 431 [13], 434
Hine, G. J. II, 219 [8], 222 [11], 223
Hintenberger, H. I, 16 [9], 17 [24], 26, 30 [3], 31 [4], 36
Hintrop, R. I, 406 [2], 412
Hirai, N. III, 394 [9], 405
Hirschfelder, J. O. III, 58, 59 [23], 66
Hirt, B. I, **29**, 32 [15] [17], 36
Hitchcock, N. E. F. I, 236 [1], 247, 248, 365 [4], 367
Hodnett, E. M. III, **225**, *233*
Hoeg, D. F. III, 363 [3], 367
Hoff, W. J. III, 22 [9], 25
Hoffman, D. C. III, 285 [3], 298
Hoffman, R. E. I, 146 [6], 156, 181 [5], 192
Hoffmeister, W. I, **29**, 32 [14], 36
II, *316*
Hofmann III, 51 [17], 66
Hofstra, A. I, **511**
Holcomb, D. L. III, 392 [6], 399 [6], 405
Holden, J. S. III, 409 [3], 414
Holland, R. E. I, 324 [10], 326
Hollander, J. M. II, 112 [9], 127, 202 [7], 209, 236 [5], 240, 456 [1], 462, 497 [6], 509
III, 432 [16], 434
Holm, L. W. III, **283**, 287, 298
Holmes, P. D. III, 155, **205**, 212, 216
Holt, B. D. II, 310 [2], 316
von Holt, C. III, 5 [3], 10
von Holt, L. III, 5 [3], 10
Holzhey, J. I, 406 [4], 412
Hommel, C. II, 354 [7], 355 [7], 360
Honig, R. E. I, 291 [9], 294
III, 526 [22], 529
Hope, E. III, 227 [7], 233
Hopkins, B. E. I, 238 [4], 245 [4], 247
Hopkins, J. C. I, **303**, 306 [1], 312
Hoste, J. II, 270 [3], 274, *276*, *322*, **425**, 426 [7], 429 [11], 430
Houben-Weyl III, 92 [5], 96, 132 [2], 138
Hours, R. I, **405**, 408, 412, *413-4*, 456 [5], 465, *516-7*
II, *164*
Hours, R. M. I, 444 [21] [22], 450
Houtermans, F. G. I, 27, **29**, 32 [17], 36, 78, 89, 444 [26], 450
Howes, J. E., Jr. I, **343**, 352
Howl, D. A. I, 474 [6], 475
Huber, G. III, 99 [4], 102
Hucher, I. II, **541**, 553 [16], 554
Hudis, R. I, 18 [34], 27
II, 454
Huffman, E. H. II, 368 [25]
Huggins, M. L. III, 523, 524, 528, 529
Hughes, D. J. II, 270 [4], 271 [5], 274, 459 [18], 461 [18], 462
Hughes, E. D. III, 199 [6], 203
Hughes, H. K. II, 139 [2], 146
Hughes, J. P. II, 362 [8], 366 [8]
Hulett, G. A. III, 533, 544 [8], 545 [8], 547 [8] [refs]
Hull, D. E. I, 464, 465
Hull, D. J. II, 479 [7], 491
Hume, D. N. III, 423 [17], 425
Hummel, D. III, *230*
Humphreys, R. F. II, 5 [3], 13 [3], 20 [3] [refs], 42 [2], 52
Hunt, J. P. III, 413 [21], 414
Hunter, H. F. I, 49, 50, 56
Husain, S. A. II, 68 [6], 79
Huster, E. I, 39, 42 [2], 43
Hutchens, T. T. II, 467 [7], 469
Hyde, E. K. II, 512 [4], 520

Ichimiya, T. I, **533**
Ignatkov, V. D. I, **287**
Ignatowicz, S. I, 171 [7], 175 [7], 178 [7] [refs]
Ikeda, N. II, 386 [78], 390
Iliceto, A. III, 105 [2], 109
Ilyinsky, V. P. III, 258 [6], 267
Immergut, E. H. III, 189 [7], 194
Indelli, A. III, 305 [6], 309 [9], 310 [9], 313
Inghram, M. G. I, 16 [11], 26, 31 [7], 36
Ingleman, B. II, 456 [4], 462
Ingold, C. K. III, 199, 203
Ingram, D. J. E. II, 388 [96], 391
Inman, D. L. I, 465
Inman, M. C. I, 143 [5] [6], 144, *156*
Iofa, Z. A. I, 486 [8], 498
Iredale, P. II, 299, 303

Irvine, J. W., Jr. **III**, **415**, 417 [1] [2], 422 [2], 425, *425*, 434 [20] [refs]
Irving, H. M. **III**, 419 [10], 423 [16], 424, 425
Irving, R. J. **III**, 271 [3], 280
Isaac, S. **II**, 322 [2] [refs]
Isagulyants, G. V. **III**, **245**, 246 [1] [3] [4], 247 [5], 248 [3], 249 [1] [5], 250 [12], 253 [3] [refs]
Isbell, H. S. **II**, 340 [1], 349 **III**, 99 [1] [2], 102
Iya, V. K. **II**, *492*
Izrailevich, E. A. **III**, 258 [5], 261 [10], 267

Jach, J. **II**, 384 [68], 390
Jacobs, R. B. **II**, 130 [2] [6], 136
Jacquesson, R. **I**, 253, 260
Jaeger, J. C. **III**, 565 [13], 574
Jaffry, P. **I**, **453**, 456 [5], 465, *465-6*
Jámbor, B. **III**, 94 [8] [11] [12], 96
James, A. T. **III**, 154 [8], 155
James, H. I. **I**, 58 [4], 65
Jarmie, N. **II**, 458 [14], 462
Jaspers, A. M. J. **I**, 444 [27], 450
Jatkar, S. K. K. **III**, 247 [17], 250 [17], 254
Jeanes, J. K. **III**, 227 [10], 233
Jen **I**, 262 [1], 264 [1], 267
Jencks, W. P. **III**, 363, 367
Jenkins, E. N. **II**, 270 [2], 271 [8], 275
Jerchel, D. **III**, 92 [2], 95
Jerlov, N. G. **I**, 64, 65
Jesse, W. P. **III**, 57 [22], 66
Jeżowska-Trzebiatowska *see under* Trzebiatowska
Jha, S. **II**, 456 [3], 462
Johnson, J. S. **III**, 397 [15], 398 [15], 405, 424, 425, 554 [10], 556
Johnson, P. **III**, 534 [18], 547
Johnston, W. H. **I**, **433**, 435 [1] [4] [9], 444 [20], 450
Jones, J. **III**, 404 [19], 405
Jones, W. D. **III**, 533, 534 [9], 547
Jones, W. M. **III**, 46 [15], 66
Jordan, R. H. **I**, 60 [6], 65
Jorgensen, M. **III**, 296 [9], 298
Josephson, B. D. **I**, 324 [9], 326
Jost, W. **I**, 291 [11], 292 [11], 294
II, 522 [3], 525
III, 393 [8], 405
Junod, E. **III**, **123**, *129*
Jurkiewicz, L. **I**, **123**, 125 [1] [2], 126 [2] [7], 130 [3], 134

Kabanov, B. N. **I**, 486 [8], 498
Kabara, J. J. **III**, 77 [6], 82
Kacl **III**, 126 [8], 129
Kahn **III**, 125, 129
Kahn, M. **III**, 317 [6], 324
Kaiser, D. G. **II**, 285 [29], 289
Kalinechenko, V. R. **III**, 256 [3] [4], 257 [3], 261 [3], 265 [4], 267
Kamen, M. **III**, 113 [4], 122
Kanchanalai, S. **III**, **179**
Kannuna, M. M. **II**, 32 [6], 39, 139 [3], 146
Kaplan, L. **III**, 467 [4] [5], 469
Kaplunov, M. Y. **II**, 153 [11], 155
Kappelman, F. A. **II**, 413 [6], 417
Karl-Kroupa, E. **II**, 473, 491
Karmarkar, S. S. **III**, 94 [10], 96
Karstens, E. **II**, 117 [18], 127
Kasanski: *see under* Kazansky
Kataev, G. V. **II**, 529 [5], 540
Kaufman, S. **I**, 371 [1], 380, 527 [3], 528 [3], 530, **II**, 380 [36], 389
Kaufman, W. J. **I**, 444 [21] [22], 450
Kay, J. **II**, 377 [4], 381 [4], 388
Kazansky, B. A. **III**, 207 [3], 214, 216
Kê, T. S. **I**, 148, 156
Keil, K. D. **III**, 367 [8] [refs]
Keim, G. I. **III**, 453 [6], 461
Keith, M. C. **III**, **97**
Kelley, M. T. **III**, 552 [6], 556
Kelman, F. N. **III**, 438 [1], 448
Kemball, C. **III**, 351-2, 354 [5], 355 [5], 358, 360
Keneshea **III**, 125, 129
Keriakes, J. G. **II**, 5 [4] [5], 13 [4] [5], 20, 42 [5], 52, 69 [8], 73 [7], 74, 79
Kesser, G. **II**, 368 [23]
Kessler, W. J. **II**, 124 [23], 127
Keston, A. S. **II**, 307 [6], 308
Ketchen, E. E. **II**, 411 [4], 417
Ketelaar, J. **II**, *230*, *322*, *360*
Keynes, R. **II**, 270 [1], 274
Keys, J. D. **I**, **397**
Khald, A. **I**, 96 [16], 99
Khau van Kien, L. **III**, 140 [3]
Khazhinskaya, G. N. **I**, **483**, 487 [9] [10], 498
Khokhlov, S. F. **I**, 170 [5], 178 [5] [refs]
Khol, F. **I**, **381**
Khomenko, L. A. **I**, **287**, 290 [8], 292 [8], 294
Kida, K. **II**, 293 [5], 303
Kiehn, N. M. **II**, 122 [19], 127
Kilmartin, E. J. **III**, 534 [21], 542 [21], 545 [21], 546 [21], 548
Kilner, A. E. **III**, **83**
Kim, C. K. **II**, 281 [16], 289

Kinchin, G. H. I, 275 [7], 282 [7], 286
King, J. A. III, 226 [5], 233
King, P. I, 46 [6], 54, 56
King, R. I, 142, 144 [3] [refs]
Kinsey, B. B. I, 281, 286
Kipfer, P. **I, 45**
Kiriakov, A. K. I, 170 [2], 178
Kirianenko, A. I, 185 [9], 192
Kishkin, S. T. I, 146 [7], 156, 181 [2], 192, **193**, 195 [1] [2], 203 [8], 206
Kistner, G. I, 27
Kitaygorodsky, I. I. II, 529 [6], 540
Kitchener, I. A. I, 170 [1], 171 [6] [7], 175 [7], 178 [7] [refs]
Kitt, G. P. III, 137 [6], 138
Klehr, E. H. **III, 517**
Klein, C. A. I, 282 [17], 286
Klein, S. I, 60 [7], 63 [7], 65
Klimanek, L. **II, 147**
Klinker, B. III, 296 [9], 298
Klippert, T. II, 28 [3], 30 [3], 39
Klontz, E. E. I, 275 [10], 286
Klyucharev, A. P. I, 496 [20], 498
Knapp, L. F. III, 534 [13], 542 [13], 547
Knudsen III, 495-6, 499, 501, 502
Koehler, J. S. II, 387 [89], 390
Koerner, E. L. II, 427 [10], 430
Kogan, D. I. I, 486 [6], 498
Kohman, T. P. I, 17 [23], 26
Kohn, A. II, 253 [8], 254 [8], 258
Koldaev, B. G. II, 489 [14], 492
Kolesov, G. M. III, **369**, 371 [7], 378
Kolotyrkin, Y. M. III, 556 [15] [16] [refs]
Kolthoff, I. M. II, 478 [9], 491
Kolthoff, J. M. II, 444 [9],
Komarevsky, V. I. III, 219, 224
Komarova, A. III, 247 [6] [7], 253
Kondratenko, E. S. III, 547 [31], 548
Koontz, R. L. I, 93 [14], 99
Kopecký, V. I, 435 [12], 450
Körber, F. **I, 381**
Korneychuk, G. P. I, 227 [2], 233
Körös, E. **III, 435**
Kosenko, V. E. III, **315**, *324*
Kostikova, G. I. I, **287**, 290 [7] [8], 292 [8], 294
Kostromina, N. A. **III, 111**
Kourim, V. III, 377 [16], 378
Kovner, M. A. II, 440 [5], 441 [5], 445 [5]
Kraayeveld, P. III, 262 [13] [14], 267
Kraft, G. R. I, 444 [27], 450
Krall, R. II, 69 [8], 79
Krasner, J. III, 85 [5], 88 [5], 90
Krašove, F. **III, 503**, 505 [5], 515
Krasovec, F. III, 434 [19] [refs]
Kraus, K. A. II, 544 [10], 553
II, 362 [1] [4], 368 [24]
III, 307 [8], 313, **387**, 390 [3], 391 [4], 392 [6] [7], 395 [10], 396 [4] [11], 397 [13] [14] [15], 398 [15], 399 [6], 403 [16] [17], 405 [refs], *405*, 405 [17], *406*, 415-7, 417 [4], 424 [4] [18], 425, 429 [21], 430 [21], 434, 554, 556
Krebs, A. T. II, 5 [4] [5], 13 [4] [5], 20, 42 [5], 52, 69 [8], 73 [7], 74, 79
Krishnamurty, K. V. III, 411 [11], 414
Kruger, G. III, 277 [14], 280
Kruger, P. II, 456 [8], 462
Kruissink, C. A. III, 189 [2] [3], 193 [2], 194
Krumhansl, J. A. **I, 295**
Kruse, H. W. I, 444 [23], 445 [23], 450
Kryukov, S. N. I, 201 [5], 206
Kryukova, T. A. III, 376 [11], 377 [11], 378
Krzuk, J. **I, 123**, 125 [1] [2], 126 [2] [7], 130 [3], 134
Kuba, J. II, 154 [14], 155
Kubaschewski, O. I, 238 [4], 245, 247
Kucera, E. T. II, 368 [23]
Kuchkarev, A. B. I, 93 [14], 99
Kudahl, J. N. **II, 317**, *322-3*
Kuhn, R. III, 92 [2], 95
Kulichenko, V. V. **II, 527**, 529 [2], 540
Kurchatov, B. V. **II, 395**
Kurchatova, L. N. **II, 395**
Kurnakov, N. S. II, 530 [9] [11], 540
Kuroyanagi, T. II, 421 [2], 422 [2], 424
Kusakov, M. M. I, 236 [2], 247
Kuykendall, W. E. **II, 233**
Kuyper, E. **I, 511**, *516*, *517*
Kuznetsov, V. V. I, 18 [28], 23, 27
Lacombe, P. **I, 179**, 180 [1], 181 [4], 185 [9], 191 [12], 192
Laidler, K. J. III, 358, 360
Lal, D. II, 456 [3], 462
Lamb, A. B. III, 410 [9], 414
Lamb, E. **II, 407**, 408 [2], 409 [2], 417
Lamb, W. E. I, 315, 326
Lambe, J. **I, 261**
La Mer, V. K. III, 392 [5], 405, 547, 548
Lamm, O. III, 451 [3], 461

Lampe, F. W. **III**, 161 [8], 170 [8] [15], 173 [8], 177
Lampe, H. W. **II**, 474 [5], 491
Lamprecht, W. **III**, 227, 233
Landecker, K. **III**, 162 [10], 177
Landsberg, G. S. **III**, 258 [5], 267
Lane, J. A. **III**, 561 [2], 574
Langham, W. H. **I**, 445 [31], 450
Langhoff, J. **I**, **29**, 32 [14], 36
Lapidus, G. **III**, 409 [5], 410 [5], 414
Lapp, R. E. **II**, 235 [3], 240
Larbre, J. **I**, 374 [5], 380
Lark-Horovitz, K. **I**, 272 [4] [6], 280 [13], 283 [20], 285, 286
Larson, Q. V. **III**, 505 [4], 515, 552 [7], 556
Latyshev, V. K. **II**, **93**, *107*
Laurence, G. S. **III**, **483** *493*
Laverlochère, J. **II**, *241*, *290*
Lavrukhina, A. K. **III**, **369**, 371 [7], 378
Lazarus, D. **I**, 151 [12], 153 [12], 154 [12], 156, *156*, **159**
Lbov, A. A. **I**, 201 [6], 206
Lebbe, J. **III**, 146 [1], 155
Le Claire, A. D. **I**, 162 [6], 168
Leddicotte, G. W. **I**, 449, 450
II, 235 [1] [2], 240, 283 [25] [26], 289
Lederer, M. **II**, 512 [8], 520
Lee, C. H. **I**, 143 [9], 144, 146, 155
Lee, J. K. **II**, 377 [2] [5], 380 [2a], 388
III, 22 [8], 25
Lee, T. D. **I**, 303-5, 306, 311, 312
Lee, W. **II**, 283 [24], 289
van Leemput, R. **III**, **187**
Lejia, I. **I**, 498
Leliaert, G. **II**, 270 [3], 274
Lemieux, R. M. **III**, 99 [4], 102
Leming, H. E. **III**, 168 [12], 177
Lemmon, R. M. **II**, 378 [13], 388 [101], 389, 391
III, 5 [4], 6 [4], 10, 11, 45, 56, 66
Lemonnier **III**, 126 [5], 129
Le Roy, G. V. **III**, 77, 82
Letaw, H. **I**, 294
Leth Pedersen, H. **III**, *11*
Le Trahon, J. Y. **II**, 49 [10], 52
Leussing, D. L. **III**, 219, 224
Levene, P. A. **II**, 306 [3] [4], 308
Lévêque, P. **II**, 5 [6], 13 [6], 20, 42 [3] [6], 52, 56 [1], 63, 69 [9], 79
Levey, G. **III**, 487 [3], 493
Levi, H. **I**, 435 [11], 450
Levine, N. **I**, 311 [4], 312
Levine, R. **III**, 227, 233
Levine, S. **III**, 317 [8], 324
Levsky, L. K. **I**, 17 [21], 18 [21], 26
Lewin, E. **I**, 177 [10], 178
Lewin, S. Z. **III**, 538, 548
Lewis, D. T. **III**, 526 [25], 529
Lewis, G. M. **II**, 202, 209
Lewis, J. **III**, 271 [3] [4] [5] [6] [7] [8], 279 [6], 280
Lewis, J. E. **II**, 253 [8], 254 [8], 258
Lewis, L. G. **II**, 130 [2], 136
Lewis, W. C. McC. **III**, 534 [12], 542 [12], 547
Lewskij, L. K.: *see* Levsky, L. K.
Leymonie, C. **I**, **179**, 180 [1], 181 [4] [6], 185 [9], 191 [12], 192
Libby, W. F. **I**, 18 [26], 26, 30 [1] [2], 36, 46 [3] [4], 51, 56, 76, 89, 92 [1] [2], 98, 435 [4] [5], 449 [36] [refs], 450, 513 [2], 516, 527 [3], 528 [3], 530
II, 379 [23], 384 [61], 385 [23] [61], 389, 390
III, 44 [2], 65
Liberman, A. L. **III**, 214, 216
Licht, F. R. **I**, 406 [5], 412 [5] [refs]
Lichtenberg, J. J. **I**, 448 [32], 450
Lidén, K. V. H. **II**, 5 [1], 20, 30 [5], 39, 42 [4], 52
Lidiard, A. B. **I**, 162 [6], 168, 297 [5], 299
Liebster **III**, 123-4, 126 [7] [8], 129
Liénard, G. **II**, **193**, 194 [1], 197, *197*, *198*
III, **351**, 352 [2], 353 [2] [4], 354 [2], 360
Lieser, K. H. **III**, **337**, *348*, *349*, *548*, *557*
Lind, S. C. **III**, 57, *59*, 62, *66*
Lindner, L. **II**, 384 [59], 390
Lindner, R. **II**, *258*, *349*, *360*, *371*, *492*, *509*, *525*
III, *298*, *336*
Lindroth, H. **III**, *6* [8], 10, 45 [10], 58 [10], 60 [10], 61, 64 [36], 65, 66
Lindsay, R. **III**, 57 [21], 66
Linenberger, G. **II**, 237 [7], 240
List, R. J. **I**, 60 [6], 65
Little, E. C. S. **II**, *216* [4], 223

Litton, F. B. **I**, 534 [6], 542
Livingston, R. S. **II**, 456 [6], 462
Livingstone, A. C. **I**, 500 [3], 502, 503, 509
Ljunggren, K. **I**, *431* **II**, *163*, **199**, 208 [9] [10], 209, *209*, *210*
Llewellyn, A. **III**, 365 [6], 367
Llewellyn, P. M. **I**, 332 [7], 335 [7], 339
Lockhart, L. B., Jr. **I**, 46 [6], 47 [5], 54, 56
Loeb, L. **III**, 44, *58*, 66
Loferski, J. J. **I**, 275 [9], 286
Lokshin, V. Y. **II**, 529 [4], 536 [4], 540
Love, D. L. **II**, 282, 289
Loveridge, B. A. **II**, 279 [5], 289
Lowe, L. F. **II**, 273 [9], 275
Löwenherz, R. **III**, 277 [14], 280
Lu, C. **II**, 379 [22], 380 [22], 389
Lucchesi, P. J. **III**, 547, 548
Ludwig, G. W. **I**, 321, 326
Ludzack, F. J. **I**, 443 [19], 450
Lukashevich, V. O. **III**, 133 [5], 138
Lundgren, S. **II**, 506 [7], 509
Lvov, B. V. **III**, 259 [8], 267
Lynch, F. J. **I**, 324 [10], 326
Lyon, D. W. **I**, 534 [1], 542
Lyon, W. S. **II**, 429 [12], 430
Mabis, A. J. **II**, 474 [5], 491
McBryde, W. A. E. **II**, 367 [21] [22]
McCabe **II**, 326 [2], 338
McCallum, K. J. **II**, 385 [69] [70], 390
McCarty, M. **I**, 267 [3] [refs]
McCarty, S. **II**, 544 [11] [13], 545 [11], 550 [11], 553, 554
MacCauley, C. E. **III**, 475 [6] [7], 481, 482
McCoy, H. N. **III**, 371 [1], 376 [1], 378
McDonald, F. B. **I**, 26
McFadden, W. **II**, 380 [34], 389
McGuire, A. D. **I**, 444 [23], 445 [23], 450
McHenry, R. E. **II**, 413 [7], 416 [9], 417
Machlin, J. L. **II**, 140
Machta, L. **I**, 60 [6], 65, 69 [2], 71 [2], 73
McInteer, B. B. **II**, *431*
McIntosh, R. G. **II**, 380 [34], 389
Mack, E. **III**, 533, 544 [10], 545 [10], 547
McKay, C. **II**, 377 [3], 388
Mackay, C. S. **III**, 44 [2], 65
MacKay, H. A. C. **III**, 317 [1], 323
MacKay, J. W. **I**, 275 [10], 286
MacKenzie, A. **III**, 196 [1], 199 [5], 201 [5], 203
Mackenzie, A. J. **II**, 384 [63], 390
Mackenzie, I. D. **I**, 170 [6], 178
Mackenzie, R. A. **II**, 385 [70], 390
Mackintyre, W. J. **I**, 260 [9] [refs]
Mackliet, C. A. **I**, 167 [9], 168
McLaren, H. R. **I**, 252 [1], 260
MacMahon, R. E. **III**, 215, 216
MacNair, A. **I**, **37**
MacNamara, J. E. **III**, 412 [17], 414
Macq, P. C. **II**, 202, 209
McVey, W. H. **III**, 431 [12], 434
Maddin, R. **I**, 143 [9], 144, 146, 155
Maddock, A. G. **II**, 379 [28], 382 [47] [50], 383 [53] [56], 384 [57] [64], 389, 390
Maddock, R. S. **II**, 280 [9], 281 [9], 284 [9], 285 [9], 289
Madison, R. K. **III**, 317 [2], 323
Magee, J. L. **III**, 59 [27], 66, 173 [21], 177
Magnusson, F. S. **III**, 272 [11], 280
Mahlman, H. A. **II**, 235 [2], 240
Maier, J. L. **II**, 544 [2], 553
Maier-Huser, H. **III**, **139**
Mainhardt, R. **II**, 237 [7], 240
Makin, S. M. **I**, **217**, 219 [3], 220 [4], 223 [5] [refs]
Malkin, V. I. **I**, **169**, 170 [3] [4] [5], 177 [4], 178 [4] [5] [refs]
Malling, G. F. **II**, 415 [8], 417
Malsan, R. P. **II**, 377 [4], 381 [4], 388
Manchot, W. **III**, 272 [10], 280
Mandel, L. **II**, 119 [17], 127
Manion, J. P. **III**, 465 [1], 469
Manly, W. D. **III**, 561 [1], 566 [1], 574
Mann, C. A. **I**, 474 [6], 475
Manning, J. R. **I**, 162, 168
Marcus, Y. **II**, 369 [27] [28]
Margulies, S. **I**, 315 [6], 319 [6], 326
Marinsky, J. A. **III**, **503**, 505 [5], 515
Mark, H. F. **III**, 189 [7], 194
Markham, M. C. **III**, 358 [8], 360
Markova, N. G. **I**, 76 [1] [2] [3], 83 [1], 89, 92 [7], 96 [7], 98
Marnier, P. **II**, 429 [13], 430
Marsh, J. **III**, 375 [10], 376 [10], 378
Marshall, J. **II**, 202, 209
Marshall, R. R. **I**, 31 [11], 36
Marshall, W. **I**, 315 [3], 326
Martell, E. A. **I**, 46 [8], 48 [8], 51 [8], 56, 71 [12], 73
Martin, A. J. P. **III**, 154 [8], 155
Martin, D. **III**, 404 [19], 405
Martin, D. S. **II**, 426 [2], 430

Martin, G. R. **I**, 16 [3], 23, 24 [3], 26, 27
Martin, J. A. **II**, 456 [6], 462
Martinelli, P. **II**, 5 [6], 13 [6], 20 **41**, 42 [3], 49 [10], 52, *53*, 56 [1], 63 69 [9], 79 **129**, *136*
Martishchenko, L. G. **I**, 76 [1] [2] [3], 83 [1], 89, 92 [7], 96 [7], 98
Márton, J. **III**, **91**, 95 [16], 96, *103*
Mashkevich, V. **II**, 533 [14], 540
Masironi, R. **III**, 44 [3], 65
Mason, L. H. **III**, 147 [2], 155
Mason, G. W. **II**, **541**, 543 [6] [12], 544 [2] [3] [4] [6] [9] [11] [12] [13], 545 [11], 550 [6] [11], 552 [6] [12] [14] [15], 553 [16] [refs], 554
Massey, H. S. W. **III**, 161 [6], 177
Matlack, G. M. **II**, 69 [10], 80
Mathews, D. M. **III**, 303 [4], 305 [7], 307 [7], 311 [4], 312 [4], 313
Mattok **II**, 326 [1], 338 [1] [refs]
Maugest, J. **II**, 109
Maxia, V. **II**, **465**, 466 [5] [6], 468 [8], 469
Maxwell, C. R. **III**, 468 [8], 469
May, S. **II**, 56 [1], 63
Maydebor, V. N. **I**, **519**
Mayer, S. W. **III**, 430 [4], 434
Mayne, K. I. **I**, 16 [2] [4], 18 [2], 23 [44], 26, 27
Mazelev, L. Y. **II**, 531 [12], 540
Mazzetti, F. **II**, 388 [101], 391
Meadows, J. W. T. **II**, 69 [10], 80
Medvedieva, L. A. **III**, 556 [15] [refs]
Mehl **I**, 201 [7], 206
Meinke, W. W. **II**, *209*, *223*, 245, [5], 258, **277**, 279 [1] [2] [3], 280 [7] [8] [9], 281 [9] [13] [14] [16], 283 [23], 284 [8] [9] [28] 285, [9] [29], 286 [30], 289, *289-290*, **511**
III, 347 [5], 348
Meinschein, W. C. **I**, 78 [13], 89, 92 [6], 98
Meisel, J. **III**, **91**, **103**
Meisels, G. C. **III**, 173 [20], 177
Melkonian, A. **III**, *384*
Mellish, C. E. **II**, 32 [9], 39, 49 [8], *52*, **55**, 56 [2], 60 [6], 63, *63*, 72 [4], 74, 75, 79, 271 [6], 274, 456 [7], 462
Melton, C. E. **III**, 238 [6], 240 [7], 242
Melton, S. L. **III**, 305 [6], 313
Mendez, J. **III**, **415**, 420, 425, 434 [20] [refs]
Mercer, L. **I**, 151, 153, 154, 155, 156
Meredith, L. H. **I**, 26
Merz, E. **I**, 31 [5] [6], 32 [15] [17], 36
Merz, H. **III**, 105 [1], 109
Meshitsuka, G. **III**, 473, 482
Metz, C. F. **II**, 362 [7]
Meyers, G. E. **III**, 505 [4], 515
Meyerson, S. **III**, 465 [2], 469
Michelson, D. C. **III**, 390 [3], 405
Middleton, F. M. **I**, 448 [32] [33] [34], 450
Miedreich, W. **III**, 277 [14], 280
Migeal, J. **I**, *413*, *414*
III, *72*
Miklukhin, G. I. **III**, 33 [2], 40
Milenković, S. M. **II**, 508 [5], 509
Miles, G. D. **III**, 453 [6], 461
Millar, C. H. **I**, 445 [30], 450
Miller, D. R. **I**, 18 [33], 27
Miller, H. H. **III**, 552 [6], 556
Miller, J. M. **I**, 18 [34], 27
II, 384 [66], 385 [66], 390, 504 [3], 509
Miller, V. B. **III**, 493 [10] [refs]
Miller, W. H. **III**, 317 [2], 323
Millett, R. J. **II**, 279 [5], 289
Milman, M. **II**, 379 [24], 389
Milne, A. A. **I**, **355**
Milne, J. M. **I**, 474 [6], 475
Milner, G. W. **II**, 299 [12] [13], 302 [13], 303
Milton, J. C. D. **I**, 336 [13], 340
Minozzi, G. **II**, 382 [43], 386 [83], 389, 390
Minushkin, B. **I**, 126 [8], 127 [8], 134
Miselyuk, E. G. **I**, *286*, **287**, 290 [8], 292 [8], 294
Miskel, J. **I**, 9, 11
Mitchell, J. E. **III**, 126 [6], 129
Mitchell, J. J. **III**, 207 [5], 216
Mitchell, L. **III**, 88 [7], 90
Miyahara, K. J. **III**, 358, 360
Moeller, J. E. **I**, 398 [6], 404
Moellers, D. W. **I**, 449 [38], 450
Mogutnov, B. M. **I**, **169**
Moilliet, J. L. **III**, 535, 536, 546, 548
Moline, S. W. **II**, 544 [3] [4], 553
Moljk, A. **I**, 444 [25], 450
Moller, T. W. **I**, 471 [3], 475
Mollison, P. L. **II**, 386 [74], 390
Monchamp, R. R. **III**, 271 [9], 278 [9], 280
Monnier, D. **II**, *258*

Montariol, F. **II**, 244 [2], 245 [4], 257
Montefinale, G. **II**, 382 [48], 389
Montgomery, H. **II**, 237 [7], 240
Moody **II**, 326 [1], 333 [6] [7], 338 [1] [6] [7] [9] [refs]
Moore, R. L. **II**, 450 [11]
Moreau **III**, 126 [5], 129
Morelowski, M. **II**, 166 [2], 175
Morinaga, H. **I**, *327*
II, **419**, 421 [2], 422 [2], 424, *424*, *509*
Morowitz, H. I. **III**, 259 [7], 267
Moroz, L. M. **I**, 181 [2], 192, **193**, 195 [1] [2], 206
Morozova, O. E. **I**, 236 [3], 247
Morris, G. **II**, 157 [2], 163
Morrison, G. H. **II**, 258
Morrison, J. D. **III**, 526 [23], 529
Morse, B. K. **III**, 197 [3], 202 [3], 203
Morrison, P. **I**, 4, 11
Moser, H. C. **II**, 379 [30], 389
III, 519, 520, 521, 528
Moses, A. J. **II**, 426 [2], 430
Mosley, J. R. **II**, 432 [1], 438
Moss, J. H. **III**, 137, 138
Moss, M. **I**, **295**, 297 [1], 299
Mössbauer, R. L. **I**, 313, 314, 315, 326, 327
Mott, N. F. **I**, 280, 286
Motta, E. E. **III**, 552 [7], 556
Moussebois, G. **III**, 476 [11], 482
Moy, D. **III**, **283**
Moyer, J. D. **II**, 340 [1], 349
Možišek, M. **II**, **147**, 151 [6], 155
Mullen, J. G. **I**, 159
Muller, H. **II**, 383 [53], 390
Muller, R. **II**, 5 [7], 13 [7], *20*
Müller, D. C. **II**, 68 [14], 77, 80
Müller, R. H. **II**, **65**, 68 [12] [13], 76 [15], 77 [11], 80, *80*
Mulvey, D. **I**, 371 [2], 380
Münnich, K. O. **I**, 69 [3], 71 [15], 72 [17], 73 [17] [refs]
Murray, A., III **III**, 125 [4], 129, 132 [3], 133 [4], 138, 227, 233
Murray, J. J. **II**, 429 [13], 430
Murray, R. L. **II**, 456 [6], 462
Murrenhoff, A. **II**, 262 [1], 268
Musgrave, B. **II**, 377 [2] [5], 380 [2a], 388
III, 22 [8], 25
Muspratt **III**, 51 [17], 66
Muxart, M. R. **II**, 512 [5], 520
Muxart, R. **II**, 382 [44], 389
Muzyukin, L. M. **I**, **101**, 110, 115
Myasnikova, G. A. **I**, 496 [20], 498
Myers, O. E. **III**, 562 [8], 574
Myerscough, L. C. **I**, *36*, *414*
II, *21*, 529 [1], 540
Mysels, K. **III**, 410 [9], 414
Nachlas, M. M. **III**, 94 [10], 96
Nachtrieb, N. H. **II**, 364 [16]
III, 419 [8], 425
Nagy, G. A. **II**, 386 [76], 390
Nakajima, K. **I**, **387**
Naldrett, S. N. **I**, 30, 36
Nast, R. **III**, 272 [12] [13], 280
Natalis, P. **III**, 479 [17], 482
Natarajan, N. T. **III**, 52 [18], 66
Natsume, H. **I**, *542*
Nauman, D. **III**, 371 [5], 376 [5], 378
Nauta, H. **I**, *327*, **511**, *531*
III, *11*, *72*
Nece, R. E. **I**, 500 [4], 509
Nehemias, J. V. **II**, 10 [8], 20
Neher, H. V. **I**, 24 [15] [17], 26
Neider, R. **I**, *223*, *396*
II, *80*, *175*
Neiman *see under* Neyman
Nelson, F. **II**, 362 [1] [4], 368 [24], 369 [27]
III, 307 [8], 313, **387**, 391 [4], 395 [10], 396 [4] [11], 397 [13] [14], 403 [16], 405, 415-7, 417 [4], 424 [4], 425, 429 [21], 430 [21], 434
Nelson, G. B. **II**, 69 [10], 80
Nelson, J. A. **III**, 107 [6], 108 [6], 109
Nerheim, A. G. **III**, 475, 482
Nernst, W. **III**, 303, 313
Nesmeyanov, A. N. **I**, *178*
II, 380 [31] [32], 386 [86], 389, 390
III, **13**, *25*
Nesmeyanov, H. **III**, 496 [2], 502
Neuberg **II**, 332 [5], 338
Neville, O. K. **III**, 228 [13], 233, 241 [8], 242
Newby, G. **II**, 237 [7], 240
Ney, E. P. **I**, 24 [45], 27
Neyman, M. B. **III**, 217-8, 221, 224, 246 [1] [2], 247 [5], 248 [3], 249 [1] [2] [5], 250 [12], 253 [3] [refs], 254, 493 [10] [refs]
Nicholson, A. J. C. **III**, 526 [23], 529
Nier, A. O. **I**, 32 [16], 33, 36
Niewodniczanski, J. **I**, **123**, 126 [7], 130 [3], 134
Nikolaev, A. V. **II**, 532 [13], 540
Nikolskaya, A. V. **I**, 231 [6], 233

Nilsson, G. **III**, 451 [3], 452 [4], 461
Nilsson, R. **II**, 456 [4], 462
Noddack, W. **III**, 377 [13], 378
Nolte, I. **III**, 5 [3], 10
Norbury, J. **I**, 218 [1] [2], 223
Norquist, D. E. **I**, 398 [6], 404
Norrish, R. G. W. **III**, 479 [16], 482
Noscicki, W. **I**, 77 [21], 89
Novacek, I. **I**, *116*
Novikova, L. A. **III**, 258 [5], 267
Noyes, R. M. **III**, 317 [3] [4] [5] [7] [8], 323, 324, 490 [5], 492, 493
Nozaki, T. **I**, **533**, 539 [11], 542
Nussim, M. **III**, 365 [7], 367
Nydal, R. **I**, 78, 89
von Obermayer, A. **II**, 162 [9], 163
O'Bern, M. **II**, 218 [6], 223
Öbrink, K. J. **II**, 204, 209
Obvintsev, G. **II**, 533 [14], 540
Ochert, N. **I**, 471 [2], 475
O'Connor, D. **II**, 387 [88], 390
Oelsen, W. **I**, 227 [2], 233
Oepik, E. J. **I**, 25, 27
Oeschger, H. **I**, 27, 78 [18] [19], 89, 444 [26], 450
Ofer, S. **II**, 387 [93], 391
Okolovich, A. M. **I**, 495 [13], 498
Oliver, W. F. **II**, 480 [11], 491
Olson, E. A. **I**, 69 [9], 70 [9] [11], 71 [9], 72 [9], 73
Olsson, I. **I**, 78, 89
Onstott, E. J. **III**, 371 [3], 376 [3], 378
Orlandini, K. A. **II**, 362 [8], 366 [8]
Orman, Z. **I**, **477**
Orr, P. B. **II**, 413 [5], 417
van Os, G. A. J. **III**, 455, 459, 461
Osmond, R. G. D. **I**, 46 [10], 56, 71 [14], 73
Ostwald, W. **III**, 531-2, 533, 537, 542, 544, 545, 547
O'Sullivan, D. A. **III**, 95 [14], 96
Oswalt, R. L. **II**, 368 [25]
Ottinger, C. L. **II**, 413 [5], 417
Otvos, J. W. **II**, 130 [1], 136
Otvös, L. **III**, **103**
Owen, J. **I**, 331 [5], 332 [5], 339
Owen, R. B. **II**, 295 [9], 303
Owsiak, T. **I**, 125 [1] [2], 126 [2], 130 [3], 134
Pahissa Campa, J. **I**, *11*, *116*, *475*, *482* **II**, *424*
Paiss, Y. **III**, 431 [15], 434
Paleari **I**, 376 [12], 380
Palin, D. E. **III**, 84 [2], 90
Palm, D. **III**, **361**, 363 [4], 367
Palmer, A. R. **II**, *418*
Pals, D. T. F. **III**, 189 [2], 193 [2], 194
Paneth, F. A. **I**, 16, 18, 26 **II**, 130 [7], 136 **III**, 338, 340, 348, 389, 405, 519 [7], 528
Park, G. **II**, *198* **III**, *67*, *194*
Parker, F. L. **I**, 438 [15], 443 [15], 449 [15], 450
Parker, G. W. **I**, **329**, 331 [6], 332 [6] [8], 336 [14], 338 [6] [15], 339, 340
Parker, W. **II**, 110 [8], 127
Parks, B. H. **II**, *175*
Pascaul, J. **II**, 362 [5], 366 [5], 367 [5]
de Pasquali, G. **I**, 311 [4], 312, 315 [6], 319 [6], 326
Pataki, L. **III**, **315**
Patrick, W. M. **III**, 16 [3], 22 [3], 24
Patterson, C. **I**, 31 [7] [8], 36
Patterson, P. D. **II**, 148 [3], 154
Patterson, R. L., Jr. **I**, 47 [5], 56
Patty, F. A. **I**, 449 [37], 450
Pauling, L. **III**, 279 [16], 280
Pauncz, P. **III**, 365 [7], 367
Payne, B. R. **I**, *530*
Payne, J. A. **II**, 32 [9], 39, **55**, 56 [2], 60 [6], 63, 72 [4], 74, 75, 79, 456 [7], 462
Peacock, R. N. **I**, 315 [6], 319 [6], 326
Pearson, P. B. **III**, 140
Pearson, R. G. **III**, 231 [15], 233
Pease, R. S. **I**, 275 [7], 282 [7], 286
Pederson, K. **III**, 392 [5], 405
Pegg, R. E. **I**, *368* **II**, **137**, *146*, *229*
Peirson, D. H. **II**, 263, 268
Pelc, S. R. **II**, 221 [10], 223
Penning **II**, 227
Peppard, D. F. **II**, **541**, 543 [6] [12], 544 [2] [3] [4] [6] [9] [11] [12] [13], 545 [11], 550 [6] [11], 552 [6] [12] [14] [15], 553 [16] [refs], 554
Pepper, K. W. **III**, 506 [6], 515
Peregudov, G. V. **III**, 258 [5], 267
Perette, J. **II**, 109
Perey, M. **II**, 512 [2] [3], 520
Périssé, A. C. de M. **III**, 95, 96
Perkin, W. H., Jr. **III**, 227 [7], 233
Perlman, I. **II**, 236 [5], 240 **III**, 432 [16], 434
Perlman, M. L. **I**, 9, 11
Perlow, G. J. **I**, **313**
Perrings, J. D. **I**, 445 [31], 450

Person, E. P. I, 78 [17], 89
Persson, R. III, 52 [19], 66
Petch, H. E. II, 202, 209
Peterson, D. C. III, 468 [8], 469
Pfeiffer, H. III, 95 [13], 96
Phillips, G. II, 362 [11]
Phillips, G. O. II, **325**, 326 [1], 333 [6] [7], 337 [8], 338 [1] [6] [7] [9] [refs]
Phillips, H. O. III, **387**, 397 [15], 398 [15], 405, 429 [21], 430 [21], 434, 554 [10], 556
Picciotto, E. I, **45**, 47 [9], 56
Pichat, L. III, **145**, 147 [4], 148 [6], 149 [7], 154 [9], *155*, *155*
Pick, H. I, 297 [4], 299
Picon, M. III, 330 [4], 336
Piehl, F. J. II, 130 [2], 136
Pigg, J. C. I, 272 [4], 285
Pijck, J. II, *259*
Pikus, F. W. I, 181 [5], 192
Pines, H. III, 207 [6], 214, 216
Pinkerton, D. M. II, 385 [72], 390
Pirie, N. W. III, 219, 224
Pisarevsky, A. N. I, 95 [15], 99
Pitkethly, R. I, *248*
III, *40*, *224*
Plaksin, I. N. I, **483**, 485 [1] [11], 486 [3] [11], 487 [3] [9] [10] [11], 495, [12] [13] [14] [15], 496 [15], 497, 498
Plane, R. A. III, 412 [15], 414
Pleasonton, F. III, 168 [12], 177
Pliskin, Y. S. II, **93**
Plumb, R. C. II, 253 [8], 254 [8], *258*
Plumb, W. III, 412 [14], 414
Pobereskin, M. I, 350 [3], 352
Poczynajlo, A. II, 379 [26], 389
Poe, A. J. II, 426 [5] [6], 429 [5] [6], 430
Pohl, R. O. I, **295**, 297 [2], 298 [2], 299
Point, J. II, *241*
Pokidyshev, V. V. I, 170 [4], 177 [4], 178 [4] [refs]
Polak, P. S. I, 126 [9], 134
Pollock, J. S. II, **137**
Poluektoff, N. S. II, 440 [1]
Pomerance, H. L. I, 272, 285
Poole, A. G. III, 62 [31], 66
Popov, D. K. II, 386 [82], 390
Popov, E. I. III, 246 [1] [3] [4], 247 [5], 248 [3], 249 [1] [5], 250 [12], 253 [3] [refs]
Porat, D. I. II, 110 [6], 126
Porter, G. III, 492 [7], 493
Portnoy, W. I, 294
Posey, F. A. III, 413 [21], 414, 555 [14], 556
Posey, J. C. II, 413 [7], 416 [9], 417
Poskanzer, A. M. III, 415-6, 417 [2], 420, 422 [2] [12], 423, 425
Possagno, E. II, 466 [4], 468
Potter, R. M. II, **431**, 432 [1], 438
Pottie, R. F. III, 173 [22], 177
Pound, R. V. I, 315 [5], 319 [5], 324 [8], 326, 331 [3], 339
Powell, H. M. II, 15 [10], 20, 308 [9] [refs], 522, 525
Pozdeev, V. V. III, **13**
Prądzyński, A. I, **477**, *482*
Pratt, T. H. II, 388 [98], 391
III, 5 [7], 10, 11, 44, 65, **159**
Prenner, J. S. I, 285 [24], 286
Prentice, T. K. I, 398, 399 [3], 401, 403, 404
Presnyakov, A. A. I, 146 [7]
Pressly, R. S. II, 413 [5], 417
Preston, R. S. I, 78, 89
Price, R. P. III, 562 [9], 563 [9], 565 [9], 574
Price, W. C. III, 526 [21], 529
Price, W. J. II, 237 [8], 240
Prigogine, I. I, 161 [3], 167
Pringle, R. W. I, 92 [10] [11], 93 [10], 99
Proschel, E. III, 272 [12] [13], 280
Protopopov, Kh. V. I, 93 [12], 99
Pryce, M. H. L. I, 332 [7], 335 [7] [11] [12], 339 [11] [refs], 340
Przewlocki, K. I, **123**, 125 [1] [2], 126 [2] [7], 130 [3], 134
Puig, J. R. II, **521**, *525*
Purlee, E. L. III, 411, 414
Purushottam, A. III, 377 [15], 378
Putman, J. L. I, *27*, 465
II, *290*
Quimby, O. T. II, 474 [5], 491
Raben, M. S. II, 340 [2], 349
Rabinowitch, E. II, 379 [21], 389
Radhakrishna, P. II, 456 [3], 462
Radwan, M. II, 168, *175*
Rafters, T. A. I, 435 [7], 450
Raghava Rao, B. S. V. III, 377 [15], 378
Rahmel, A. I, 245 [5], 247
Raiford, L. C. III, 107 [7], 109
Rama II, 456 [3], 462
Ramavataram, K. II, 110 [6], 126
Ramsey, N. I, 264 [2], 265 [2], 267
Ranby, B. G. III, 189 [7], 194
Randall, J. II, 237 [7], 240
Rankin, M. II, 456 [6], 462

Ransley, C. E. II, 315, 316
Rapoport, M. B. I, 126 [9], 134
Rappaport, P. I, 275 [9], 286
Raridon, R. J. III, 392 [6] [7], 399 [6], 403 [17], 404 [18], 405 [17] [refs]
Rasmussen, J. O., Jr. I, 336 [13], 340
Rauch, G. III, 75 [2], 82
Rausch, W. I, 39, 42 [2], 43
Rauscher, H. E. II, 384 [66], 385 [66], 390
Ray, R. C. II, 220 [9], 223
Razumovskaya, E. A. I, 236 [2], 247
Reas, W. H. III, 434 [18] [refs]
Reasbeck, P. I, 16 [2] [4], 18 [2], 26
II, **157**, 163, 164
Rebinder, P. A. I, 486 [7], 498
Rebka, G. A., Jr. I, 315 [5], 319 [5], 324 [8], 326
Ree, T. III, 394 [9], 405
Reed, R. I. III, 226 [3], 233
Reed, T. M. III, 526, 528, 529
Rees, A. L. G. I, 485 [2], 497
Rehberg, H. III, 227 [8], 233
Reichardt, H. III, 519 [2] [3] [4], 528
Reichenberg, G. III, 506 [6], 515
Reid, A. II, 379 [27], 389
Reiffel, L. II, **3**, 5 [2] [3], 10 [2], 13 [2] [3], 17 [11], 20 [2] [3] [refs], 42 [1] [2], 52, 72 [16], 80, 82, 91
Reilly, E. M. II, 273 [9], 275
Reilly, J. III, 95 [14], 96
Reines, F. I, 444, 445 [23], 450
Rekasheva, A. F. III, 33 [2], 40
Rempel, S. I. I, 478, 479 [1], 480 [1], 481
Renard, G. II, *21*
Renault III, 126 [5], 129
Rennecke, A. III, 105 [1], 109
Reppe, W. III, 147 [3], 148 [5], 155
Reuter: *see under* Royter
Reynolds, F. L. II, 388 [101], 391
Reynolds, S. A. II, 235 [1], 240, 429 [12], 430
Rhodes, J. R. II, **23**, 29 [4], 32 [4] [8], 38 [4], 39, 49 [9], 52, 56 [3], 58 [3], 63
Ribe, F. L. II, 459 [17], 462
Ricci, M. H. II, **129**
Richardson, A. C. III, 199 [5], 201 [5], 203
Richter, J. W. III, 430 [3], 434
Richtmyer, R. D. I, 4, 11
Rideal, E. K. III, 207, 213, 214 [4], 215 [4], 216
Riedel, O. II, *198*, *230*
Riesebos, P. II, 384 [62], 390
Riesz, P. III, 161 [2], 177
Riley, R. F. III, 79 [10], 82
Rimshaw, S. J. II, 415 [8], 417
Rinn, H. W. I, 486 [5], 498
Rittenberg, D. II, 307, 308
III, 77 [4], 78 [7], 82
Roberts, D. L. II, 122 [21], 127
Roberts, F. P. II, 362 [9], 366 [9]
Roberts, L. D. I, **329**, 331 [6], 332 [6] [8], 334 [10], 336 [14], 338 [6] [15], 339 [16] [refs], 340, *340*
Robertson, R. E. III, 365 [6], 367
Robinson, E. S. II, **431**, *438*
Robinson, G. W. I, 267 [3] [refs]
Robinson, R. A. III, 418, 425
Rochlin, R. S. II, 458 [16], 462
Rockstein, M. II, 504 [4], 509
Rodden, C. J. II, 362 [12]
Rode, S. Y. II, 530 [11], 540
Roe III, 126 [6], 129
Roemer, E. I, 406 [2], 412
Roger, R. III, 196 [1], 203
Rogers, G. T. I, 220 [4], 223 [5] [refs], *223*
Rollefson, G. K. III, 238 [4], 242 [4], [refs]
Roller, P. S. III, 544, 548
Rollier, M. A. II, **465**, 466 [1] [5] [6], 467 [2], 468 [8] [refs], 469
Romanova, E. N. I, **91**
Rona, E. III, 302, 308, 313
Ronzio, A. R. III, 105 [3], 109
Ropp, G. A. III, **235**, 235-7, 238 [3] [5] [6], 240 [7], 242 [5] [refs], 242
Rose, A. I, 501 [6], 509
Rose, M. E. I, 331 [3], 332, 339, 340
Roseman, S. III, 100 [7], 102
Rosen, A. A. I, 448 [33] [34], 450
Rosenblum, C. II, 378 [14], 389
III, 519 [9], 528
Ross, J. III, 453 [6], 461
Ross, L. E. II, 368 [23]
Rossi, A. I, 311 [4], 312
Rossini, F. D. III, 525 [18], 526 [18], 529
Rossotti, F. J. C. III, 419 [10], 424 [10], 425
Rota, A. I, *340*
Rousseau, M. III, 475, 482
Rovinsky, M. S. I, 110
Rowell, M. II, 366 [19]
Rowland, F. S. I, 18 [31], 27
II, 377 [2] [3] [4] [5], 380 [2a], 381 [4] [37] [40], 388 [98] [refs], 389, 391
III, 5 [7], 10, 11, 22 [7] [8] [9], 24, 25,

44 [2] [4], 65, 161 [5], 177
Rowton, R. L. **III, 225**
Roy, J. C. **II, 455**, *463*
Royter, V. A. **III, 435**
Rubin, B. **I,** 537 [9], 542
Rudenko, S. I. **I, 91**
Rudolph, P. S. **III,** 238 [6], 242
Rudorf **II,** 404 [6], 405
Rudzitis, E. **III,** 417 [2], 422 [2], 425
Ruggles **I,** 438 [16], 443 [16], 449 [16], 450
Rummel, T. **III,** 60 [28], 66
Rumyantsev, Y. M. **III, 13**
Rupp, A. F. **II, 407,** 408 [1], 409 [1] [3], 417
Rush, R. M. **II,** 362 [4]
III, 396 [11], 405
Rusinova, N. P. **III,** 258 [6], 267
Russell, K. E. **III,** 492 [6], 493
Rutenberg, A. C. **III,** 413 [21], 414
Rutenberg, A. M. **III,** 92 [1] [4], 95
Rutledge, A. R. **II,** 458 [13], 462
Ryabchikov, D. I. **III,** 371 [2], 375 [8], 376 [8], 377 [2], 378
Ryabova, G. G. **I,** 203 [9], 205 [9], 206
Ryan, J. L. **II,** 362 [13] [14], 366 [13]
Rydberg, B. **III,** 431 [14], 434
Rydberg, J. **III,** 61 [29], 66, *314*, **427,** 429 [2], 430 [2] [8] [10] [11], 431 [10] [14], 434 [17] [refs]
Rylander, P. N. **III,** 465 [2], 469
Sadauskis, J. **III,** 57 [22], 66
Saito, N. **II,** 383 [54], 384 [67], 385 [67], 390
Sakharov, B. A. **III,** 375 [9], 376 [9], 378
Saldick, J. **III,** 417 [3], 420 [3], 425
Salley, D. J. **III,** 317 [2], 323, 451 [1], 461
Salmon, L. **II,** 253 [8], 254 [8], 258
Samsahl, K. **II,** 472 [1] [2], 491
Sandell, E. B. **II,** 367 [20], 478 [9], 491
Sandier, J. **II,** 56 [1], 63, **521**
Sanin, P. I. **I,** 236 [2] [3], 247
Sano, H. **II,** 384 [67], 385 [67], 390
Santeler, D. J. **I,** 471 [3], 475
Santema, P. **I,** 465
Santoro, V. **II,** 382 [42] [43], 386 [83], 389, 390
Sata, T. **I,** *248*, **387,** *396*
Sato, T. R. **II,** 384 [60], 390
Sauer, M. C., Jr. **II,** 378 [10], 389
III, 5 [2], 10, 45 [7], 65
Sauerwein, K. **I,** *404*
Sawle, D. **II,** 237 [7], 240
Sayed, M. F. **III,** 22 [6], 24
Sayre, E. V. **II,** 262 [1] [2], 268
Scadden, E. M. **II,** 544 [1], 553
Scatchard, G. **III,** 523, 529
Schaeffer, H. J. **III,** 196 [2], 201 [2], 203
Schaeffer, O. A. **I, 3,** 9 [6], 10 [6], 11, *11*, 16 [10], 17 [22], 18 [30] [35], 19, 20, 23 [30] [35], 26, 27, *36*
III, 161 [9], 171 [9], 173 [9], 177
Schaffer, R. **III,** 99 [2], 102
Scharpenseel, H. W. **II,** 378 [15], 389
Schenkel, H. **III,** 226, 233
Schenkel-Rudin, M. **III,** 226 [2], 233
Scheppers, A. **I,** 406 [5], 412 [5] [refs]
Scheurer, W. **I,** 253 [3], 260
Schiavon, G. **III,** 113 [5], 122
Schiff, H. J. **III,** 23 [10], 25, 65 [37], 66, 67
Schiffer, J. **I,** 315 [3], 326
Schiffman, L. **III,** 519 [11], 528
Schildknecht, H. **III, 73,** 74 [1], 75 [2], 82 [11] [refs]
Schindewolf, U. **II,** 281 [12], 282, 284 [12], 289
Schintlmeister **II,** 111 [11], 127
Schissler, D. O. **III,** 59 [24], 66
Schlegelmilch, F. **III, 73,** 74 [1], 75 [2], 82
Schmid, H. **III,** 272 [10], 280
Schmidlin, P. **I, 13,** 21 [36] [37] [38], 27
Schmidt, F. **II,** 380 [33], 389
Schmidt, F. H. **I, 303,** 306 [1], 312
Schmidt-Küster, W.-J. **II, 225**
Schmied, H. **III,** 493 [9] [refs]
Schmitt, R. A. **II,** 386 [80] [81], 387 [81]
Schöberl, A. **III,** 219 [1] [2], 224
Scholes, S. R., Jr. **III,** 410 [7], 414
Schomaker, V. **II,** 308 [8] [refs]
III, 317 [3], 323
Schon, M. **I,** 283 [20], 286
Schönfeld, T. **I,** *121*
II, *164*, *492-3*
III, *298*, *299*, *349*, *406*
Schreiber, K. C. **III,** 197 [3], 202 [3], 203
Schroeter, G. **III,** 105 [5], 109
Schubert, J. **III,** 430 [3], 434
Schubert, M. P. **III,** 219, 224
Schuch, R. L. **I,** 445 [29] [31], 450
Schuk, R. **III,** 272 [12], 280

Schulek, E. **III**, **315**, 321 [9], 324 [9] [refs]
Schuler, R. H. **III**, 477 [12] [13], 480 [13], 482
Schulman, I. N. **I**, 498
Schultze, G. R. **I**, *247*, *353* **II**, *163*, **225**
Schulz **II**, 404 [6], 405
Schumacher, E. **I**, 34 [18], 36 **II**, 282, 289
Schwartz, H. A. **III**, 171, 177
Schwartz, R. **II**, 270 [4], 274, 459 [18], 461 [18], 462
Schwarzer, D. **I**, 16 [6], 18 [6], 26, 527 [5], 528 [5], 530
Schwarzschild, A. **II**, 387 [93], 391
Schweckendieck, W. J. **III**, 147 [3], 155
Schweers, W. **III**, *11*
Schweinler, H. C. **I**, 271, 272, 281, 285
Schweitzer, G. K. **I**, 60 [8], 65
Scott, B. F. **I**, *404*, **II**, *197*, **339**, 343 [3], 349, *349*
Scott, F. L. **III**, 95 [14], 96
Scott, H. M. **I**, 248
Scott, J. M. W. **III**, 365 [6], 367
Scott, R. F. **II**, *230*
Scott, R. L. **III**, 523 [14], 529
Scott, T. R. **I**, 534 [3], 542
Seaborg, G. T. **I**, 18 [33], 27 **II**, 112 [9], 127, 202 [7], 209, 236 [5], 240, 456 [1], 462, 497 [6], 509 **III**, 432 [16], 434
Seagrave, D. J. **II**, 458 [14], 462
Seagren, H. E. **II**, 408 [2], 409 [2], 417
Secci, M. **II**, **465**, 468 [8], 469
Seibel, G. **I**, 181 [6], 192 **II**, **41**, 49 [10], 52, 56 [4], 63, *223*
Seidell, A. **II**, 523 [4], 525 [5] [refs]
Seitz, F. **I**, 161 [1], 167 **II**, 387 [89], 390
Selgin, M. **III**, 259 [7], 267
Seligman, A. M. **III**, 92 [1] [4], 94 [10], 95, 96
Seligman, H. **I**, *121*
Sellei, H. **I**, 377 [14], 380
Sellers, P. A. **II**, 384 [60], 390
Seltz, H. **I**, 227 [4], 231 [4], 233
Selwood, P. W. **III**, 278 [15], 280
Semenov, N. N. **III**, 444 [4], 448
Semenova, N. K. **III**, **255**
Sen Sarma, R. N. **II**, 504 [3], 509
Senko-Bulatny, I. N. **I**, 114
Seren, L. **II**, 271 [7], 275
Setser, D. W. **II**, 379 [30], 389
Sevier, K., Jr. **II**, 110 [8], 127
Seymour, F. D. **II**, 32 [7], 39
Shafeev, R. S. **I**, **483**, 485 [11], 486 [11], 498
Shaffer, J. H. **III**, **575**, 583 [11], 590
Shangin, N. N. **I**, **519**
Sharp, R. A. **II**, 386 [80] [81], 387 [81]
Shashkin, W. L. **I**, 128 [11], 134
Shatenshteyn, A. I. **III**, 121 [6], 122, 256 [1] [2] [3] [4], 257 [3], 258 [5], 261 [3] [10], 265 [4], 267
Shatunovskaya, N. **II**, 399 [3], 405
Shaw, E. N. **II**, 110 [1] [2], 117 [1], 126
Shaw, P. F. D. **II**, 379 [24], 389
Shaw, T. M. **III**, 59 [26], 66
Shcheglova, A. P. **III**, 247 [5], 249 [5], 253
Shedlovsky, L. **III**, 453 [6], 461
Sherwin, J. **II**, 237 [7], 240
Shibata, N. **II**, 386 [75], 390
Shilov, N. **II**, 399 [3], 405
Shiner, V. J., Jr. **III**, 362 [1], 367
Shipko, F. J. **III**, 466 [3], 469
Shneerova, R. N. **I**, 376 [7] [8], 377 [7], 378 [7], 380
Shoemaker, D. P. **II**, 308 [8] [refs]
Shor, G. I. **I**, **369**, 376 [7] [8], 377 [7], 378 [7], 380
Short **II**, 258
Shuikin, N. I. **III**, 207 [3], 212, 216
Shulyatyev, S. A. **I**, 105
Shumilovsky, N. N. **II**, 537 [15], 540
Shuttleworth, R. **I**, 142, 144 [3] [refs]
Shvartsman, L. A. **I**, 170 [3] [5], 178 [5] [refs]
Shvedov, V. P. **III**, 371 [4], 376 [4], 377 [4], 378
Sibbet, D. J. **III**, 317 [5], 323
Sidua, A. **II**, 379 [26], 389
Siegbahn, K. **II**, 456 [4], 462
Siekierska, K. E. **II**, 379 [25], 389
Sigmond, R. S. **I**, 78 [11], 89
Signer, P. **I**, 32 [15], 36
Siksna, R. **III**, 57 [21], 66
Sillén, L. G. **III**, 297 [10], 298, 430 [9], 434
Silva, R. **III**, 287 [6], 298
Simha, R. **III**, 189 [5] [6], 194
Simon, H. **III**, **361**, 363 [4], 367 [8] [refs], *367*
Simonnet, G. **III**, 141 [6]
Simons, J. **III**, 492 [6], 493
Šimorda, J. **II**, **147**
Simpson, G. **II**, 262 [3], 268
Simpson, H. **II**, **269**
Simpson **I**, 438 [16], 443 [16], 449 [16], 450
Singleterry **I**, 371 [1], 380
Siniramed, S. **I**, 376 [12], 380
Sinnott, M. J. **I**, 150 [11], 156, 191, 192

Sinyakova, S. I. **III**, 376 [11], 377 [11], 378
Sironen, R. J. **II**, 543 [6], 544 [6] [9], 550 [6], 552 [6], 553
Skala, J. **I**, *178*
Sklyarenko, Y. S. **III**, 371 [2], 375 [9], 376 [2] [9], 377 [2], 378
Slack, G. A. **I**, **295**, 297 [3], 299
Slinko **III**, 447 [6], 448
Slivkin, L. **I**, 294
Smales, A. A. **II**, 270 [2], 271 [8], 275, 279 [4], 289
Smibert, J. A. **II**, 218 [6], 223
Smith, D. B. **I**, *44*, *116*, 465, *517* **II**, *164*
Smith, F. **III**, 99 [6], 102
Smith, F. A. **II**, 322 [2] [refs]
Smith, H. L. **III**, 285 [3], 298
Smith, L. G. **III**, 172 [18], 177
Smith, N. V. **II**, 130 [1], 136
Smith, R. S. **III**, 155, **205**, 211, 212 [7] [8], 213, 215, 216
Smith, S. E. **II**, 124 [23], 127
Smith, W. T., Jr. **III**, 552 [3], [4], 556
Smitz, M. **II**, 427 [10], 430
Smoluchowski, R. **I**, 150 [10], 156
Snell, A. H. **III**, 168 [12], 177
Sobotovich, E. V. **I**, 31 [10], 36
Sokolov, M. M. **I**, 108
Sokolova, N. P. **III**, 247 [11], 248 [11], 249 [11], 253
Sokolovsky, E. V. **I**, **519**
Sokolowska, A. **II**, 379 [25], 389
Soldano, B. **III**, 505 [4], 515
Solodovnikov, S. P. **III**, 493 [10] [refs]
Sonesson, A. **III**, 287 [4] [5], 297 [4], 298
Sowden, J. C. **III**, 99 [3], 102
Soyfer, V. N. **I**, **519**, 521 [1] [2], 530
Spangenberg, K. R. **I**, 472 [4], 475
Speecke, A. **II**, 426 [7], 429 [11], 430
Speer, R. J. **III**, 227, 233
Spiers, J. A. **I**, 332 [9], 340
Spinks, J. **III**, 340, 348, 548
Spracklen, D. **II**, **211**
Sprenkel, E. L. **I**, 17 [19], 23, 26
Spriestersbach, D. **III**, 99 [6], 102
Spriggs, A. S. **III**, 99 [3], 102
Sproull, R. L. **I**, **295**, 297 [1], 299
Stacey, M. **III**, **97**
Starfelt, N. **II**, 5 [1], 20, 30, 39, 42 [4], 52
Starik, J. E. **I**, 31 [10], 36, **91**, 93 [13], 99
Staroba, J. **II**, **147**
Staudinger, H. **III**, 108 [8], 109
Staverman, A. J. **III**, 189 [1] [2], 193 [2], 194
Steacie, E. W. R. **III**, 23 [10], 25, 29 [1], 36 [1], 37 [1], 40, 65, 66, 67
Steckelmacher, W. **I**, 471 [2], 475
Steiger, N. H. **III**, **449**, 452, 457 [8], 461, *461*
Stein, R. **III**, **187**, *194*
Steiner, H. **III**, 207, 214 [2], 216
Stepanov, B. I. **III**, 262 [12], 263 [12], 267
Stepanova, N. P. **III**, 258 [6], 267
Stevens, G. W. W. **II**, *189*, **211**, 213 [1], 219 [7], 220 [9], 223, *223*
Stevens, J. L. **I**, 398 [4], 404
Stevenson, D. P. **III**, 59 [24], 66, 172, 177
Stevenson, P. C. **II**, 427 [8], 430
Stewart, D. C. **III**, 285 [1], 298
Stewart, N. G. **I**, 46 [10], 56, 71 [14], 73
Stiennon-Bovy, R. **II**, **439**
Stock, A. **III**, 519, 528
Stöcklin, G. **II**, 380 [33], 389
Stoenner, R. W. **I**, **3**, 31 [9], 36
Stokes, R. H. **III**, 418 [5], 425
Stolle, R. **III**, 109 [11] [refs]
Stone, C. A. **II**, **3**, *21*, *91*
Stonehocker, V. T. **I**, 345 [2], 352
Stow, R. **III**, 340, 348, 548
van der Straaten, H. **II**, 384 [62], 390
Strain, H. H. **II**, 384 [60], 390
Stranks, D. R. **III**, 326 [1], 336, 409 [1] [2], 410 [8], 412 [18], 413 [20], 414, **483**, **495**, 499 [7], 502
Straub, C. P. **I**, 443 [19], 450
Strehlow, R. A. **III**, **575**
Streiff, H. J. **II**, 282 [19] [20] [21], 289
Stroganova, N. S. **III**, 371 [2], 376 [2], 377 [2], 378
Strohmeier, W. **II**, 378 [13], 389, **III**, 5 [4], 6 [4], 10, 11 [Lemmon *et al.*], 45 [14], 56 [14], 66
Strominger, D. **II**, 112 [9], 127, 202 [7], 209, 456 [1], 462, 497 [6], 509
Stroth, J. **I**, **303**, 306 [1], 312
Stroud, D. B. E. **III**, **97**
Strub, W. **I**, *52*
Stukanovskaya, N. A. **III**, **435**
Sturm, B. J. **III**, 562 [5], 574
Suen, T.-J. **III**, 247 [9], 253
Suess, H. E. **I**, 69 [5], 73, 78, 89, 92 [5], 98, 435 [6], 450
Sugden, S. **II**, 379 [20], 389
II, 379 [22], 380 [22], 389
III, 184 [2], 186

Sugihara, T. T. **I, 57**, 58 [1] [2] [3] [4], 60 [2] [3], 65
Sullivan, J. C. **III**, 302 [2], 313, 430 [10], 431 [10] [13], 434
Sullivan, W. **II**, 353 [3], 360
Sullivan, W. H. **II**, 236 [6], 240
Sunderman, D. N. **I, 343**, 345 [2], 350 [3], 352, *352*, *353*, *414*
II, 281 [13] [14], 289
III, 347 [4] [5], 348
Sunyar, A. W. **I**, 311 [3], 312
Suthers, J. **II**, 318 [1], 322
Sutin, N. **II**, 379 [28], 384 [66], 385 [66], 386 [85], 389, 390
Suttle, A. D. **I**, 30 [2], 36
Svasek, J. N. **I**, 465
Swalin, R. A. **I**, 289 [5], 292 [5], 294
Swanton **III**, 155
Sward, E. L. **III**, 412 [16], 414
Swift, E. H. **III**, 419 [7], 425
Sworski, T. J. **III**, 465 [1], 469
Szabó, Z. G. **III**, 220, 224
Szekely, G. **I**, 534 [7], 542
Szwarc, M. **III**, 241 [8], 242 [9] [refs]

Tabor, D. **I**, 364 [3], 367
Takiyama, K. **III**, 537, 548
Taksar, I. M. **II**, 537 [15], 540
Talbot, J. **I, 207**, 208 [2] [3], 213 [5], 215 [5] [refs]
II, 244 [2], 245 [4], 257
Tamir, I. **III**, 457 [8], 461
Tan Siao-en **III, 369**
Tannhauser, D. S. **I**, 173 [8], 178
Tardif, H. P. **I**, 253, 260
Tasgart, M. S. **I**, 78 [10], 89
Taube, H. **III**, 412 [15], 413 [21], 414
Tauber, H. **I, 67**, 69 [8], 70 [8], 72 [17], 73 [17] [refs], *73-4*, 76, 89
Taugbøl, K. **II**, 472 [1], 491
Taylor, D. **II**, 116 [16], 127
Taylor, G. I. **I**, 438 [14], 442, 450
Taylor, H. S. **III**, 58, 59 [23], 66, 215 [12], 216
Taylor, T. I. **III**, 352 [3], 353 [3], 360
Teal, G. K. **I**, 534 [4], 542
Tegart, W. J. McG. **I**, 139, 144
Teller, E. **I**, 4, 11
Terentieva, E. A. **III**, 375 [8], 376 [8], 378
Teterin, P. K. **I**, 253 [3], 260
Tewell, H. E. **III**, 93 [6], 96
Tharmalingam, K. **I**, 162 [6], 168
Theophilus Presbyter **II**, 173 [4], 175
Theuerer, H. C. **I**, 534 [5], 542
Thietmari **II**, 166 [1], 174
Thilo, E. **II**, 480 [10], 491
III, 277 [14], 280
Thomas, D. J. **III, 83**
Thomas, H. C. **III**, 390 [2], 405
Thomason, P. F. **III**, 552 [6], 556
Thommeret, J. **II**, *197*
Thompson **III**, 288 [7], 298
Thompson, H. D. **II**, 273 [9], 275
Thompson, S. J. **I**, 23 [44], 27
Thompson, S. O. **III**, 161 [9], 171 [9], 173 [9], 177
Thomson, J. O. **I**, 336 [14], 340
Thomson, W. **III**, 533, 547
Thon, D. M. **I**, 24 [45], 27
Thornhill, A. R. **III**, 212 [9], 216
Tilton, G. **I**, 31 [7], 36
Timmermans, J. **III**, 526 [24], 529
Timmermans, O. E. B. **I**, 398 [5], 404
Timms, D. G. **III**, 381 [2], 384
Timnick, A. **III**, 377 [12], 378
Tishkin, P. A. **III**, 259 [9], 267
Tolbert, B. M. **II**, 378 [13], 389
III, 5 [4], 6 [4], 10, 11 [Lemmon *et al.*], 45, 56, 66
Tomilin, I. A. **I, 225**
Tominaga, T. **II**, 384 [67], 385 [67], 390
Tomita, I. **II**, 383 [54], 390
Tomizuka, C. T. **I**, 143 [7], 144, 146 [3], 151 [12], 153 [12], 154 [12], 155, 156, 163, 168
Tomkins, F. S. **II**, 364 [16]
Tomlinson, J. W. **I**, 171 [7], 175 [7], 178 [7] [refs]
Tompkins, E. R. **II**, 365 [17]
Tonge, B. L. **III**, 381, 384
Tooley, F. V. **II**, 489 [13], 491
Topchieva, K. V. **III**, 250 [14] [15], 254
Tourky, A. R. **III**, 534, 548
Treacy, P. B. **II**, 387 [94], 391
Trifanov, V. **I**, 95 [15], 99
Trocker, J. **II**, 441 [7]
Troianello, E. J. **I**, 58 [4], 65
Trotman-Dickenson: *see under* Dickenson
Trtelek, J. **III**, 506 [7], 515
Trumbore, F. A. **I**, 288 [3], 293
Jeżowska-Trzebiatowska, B. **III, 269**, *281*
Tsai, L. **III**, 113 [4], 122
Tsitsiliano, P. **I**, 191 [13], 192
Tsutsui, M. **II**, 381 [39], 389
Tumulkan, A. D. **II**, 537 [19], 538 [19], 540
Tupitsyn, I. F. **II**, *417*, **III, 255**, *267*
Turchinetz, W. **I**, 92 [10] [11], 93 [10], 99
Turckevick, A. **I**, 69 [2], 71 [2], 73

Turkel, S. H. **II**, 271 [7], 275
Turkevich, J. **III**, 215 [12], 216, *267*, *348*, *349*, **531**, *548*
Turnbull, D. **I**, 146 [6], 156, 199 [4], 206
Turton, C. N. **II**, 381 [40], 389, 466 [3], 467, 468 [3] [refs] **III**, 45, 62, 65
Turton, N. **III**, 5 [5], 10
Tykachinsky, I. D. **II**, 529 [5], 540
von Ubisch, H. **II**, 497 [2], 509
Udenfriend, S. **II**, 307 [6], 308
Ulfendahl, H. R. **II**, 204, 209
Ullberg, S. **III**, 47 [16], 51 [16], 66
Ulyanova, A. V. **I**, 236 [2] [3], 247
Umblia, E. **I**, 176 [9], 178
Umstatter, H. **II**, 130 [3], 136
Upthegrive, W. R. **I**, 191 [14], 192
Urch, D. S. **II**, 377 [3], 378 [8] [9], 381 [8], 388, 389 **III**, 15 [1], 24, *25*, *41*, *470*
Ustevsky, L. M. **I**, 227 [1], 233
Valade, J. **II**, 386 [77], 390, 398 [2], 400 [2], 405
del Val Cob, M. **II**, 382 [50], 390 **III**, *129*
Valeton, J. J. P. **III**, 534 [14], 547
Van Allen, F. A. **I**, 26
Van Bruggen, J. T. **II**, 467 [7], 469
Vance, J. E. **III**, 538 [27], 548
Van Dilla, M. A. **I**, 445 [29], 450
Van Hook, A. **III**, 534, 542, 545 [21], 546, 548
Van Zeggeren, F. **III**, 534, 535, 536, 542, 545 [23], 546 [23], 548
Vargas, J. I. **II**, 383 [56], 390
Varley, J. H. O. **II**, 385 [73], 390
Varshavsky, Y. M. **III**, 256 [3] [4], 257 [3], 261 [3] [11], 265 [4], 267
Vasichev, B. N. **II**, **93**
Vasilyeva, N. A. **I**, **519**
Vaysberg, S. E. **III**, 261 [11], 267
Veall, N. **II**, 386 [74], 390 **III**, 183, 186
Vecher, A. A. **I**, 227 [3], 231 [6], 233
van der Velde, B. **II**, 429 [14], 430
Veljković, S. R. **II**, 508 [5], 509
Verbanc, J. J. **III**, 107 [6], 108 [6], *109*
Vereskunov, V. G. **II**, 529 [2], 540
Verhaeghe, J. **II**, 429 [14], 430
Verkerk, B. **I**, *156*, *414*
Vervier, J. F. **II**, 202, 209
Vestal, M. **I**, **433**
Vickery, R. C. **III**, 297 [11], 298
Vilcsek, E. **I**, 17 [13], 23 [13], 26
Vinet, R. **II**, **177**
Vink, H. **III**, 189 [4], 194
Vinogradov, A. P. **I**, **75**, 76 [1] [2] [3], 77 [7], 83 [1], 89, 92 [7], 96 [7], 98
Vinogradov, G. V. **I**, 236 [2] [3], 247, 376 [9] [10], 377 [9] [10], 380
Vinogradov, S. L. **III**, 246 [4], 253
Violi, A. **III**, 332 [5], 336
Vogel, J. C. **I**, 69 [3], 71 [15], 73
Voice, E. W. **I**, 406 [1], 412
Voigt, A. F. **III**, *25*, *405*, *470*, **517**, 519 [6], 520 [6], 521 [6], 528
Volk, W. **I**, 500 [1], 509
Volkenshteyn, M. V. **III**, 262 [12], 263 [12], 267
Volkert, H. **III**, 82 [11] [refs]
Volkova, E. V. **II**, 529 [2], 540
Volpe, M. **III**, 113 [1], 122, 271 [1], 280
Vorwerk, W. **III**, 338 [1], 340 [1], 348
Vosburgh, W. C. **III**, 303, 313
Voshage, H. **I**, *16* [9], 17 [24], 26, 30 [3], 31 [4], 36
Voskoboynikov, G. M. **I**, **101**
Voyvodic, L. **II**, **3**, 28 [3], 30 [3], 39
Vozzhennikov, G. S. **I**, 110
de Vries, A. E. **III**, *233*
de Vries, H. **I**, 69 [4], 72 [16], 73 [16] [refs], 92 [3], 98
de Vries, N. I. **I**, 78 [8], 89
Vyazemsky, V. O. **I**, 95 [15], 99
de Waard, H. **I**, *312* **II**, *21*
Wagner, A. **III**, 219, 224
Wagner, C. D. **I**, 513 [1], 516 **III**, 481, 482
Wahl, A. C. **III**, 338 [2], 348, 519 [10], 528, 562 [8], 574
Wahl, R. **II**, *240*
Wahlgren, M. **II**, 281 [12], 284 [12], 289
Wahlig, M. A. **II**, 110 [5], 126
Wainerdi, R. E. **II**, **233**, *240*, *241*
Waite, T. R. **I**, 275 [11], 286
Wajda, E. S. **I**, 183 [8], 192
Wakerling, R. K. **I**, 471 [1], 475
Walde, N. **III**, 64 [33] [34], 66
Waling, C. H. **III**, 36 [4], 40
Walker, H. **I**, 199 [3], 206
Walker, R. M. **I**, 271, 282 [18], 285, 286
Walker, W. H. **I**, 281 [16], 286
Wall, M. C. **III**, 358 [8], 360

Walter, F. J. **I**, **329**, 334 [10], 336 [14], 340
Walther, T. **III**, 404 [20], 405
Walton, A. **I**, 69 [6], 70, 73, 76 [4], 89
Walton, G. N. **II**, 387 [92], 391
Wang, F. Y. **II**, 489 [13], 491
Wänke, H. **I**, 16 [8], 17 [13], 18, 23, 24 [46] [13], 26, 27
Ward, A. H. **II**, 122 [20], 127
III, *385*
Ward, R. A. **I**, 181 [5], 192
Ward, W. T. **III**, **575**, 578 [6] [7] [9], 580 [6], 590
Wardle, G. **I**, 23 [44], 27
Warner, B. F. **II**, 441 [8], 450 [8]
Warren, J. B. **II**, 458 [15], 462
Wartenberg, H. V. **I**, 534 [2], 542
Watkins, G. D. **I**, 282 [18], 286
Watson, G. M. **III**, **559**, **575**
Watson, J. **II**, 122 [22], 127
Watson, N. E. **III**, 247 [17], 250 [17], 254
Wear, J. O. **III**, 303 [4], 311 [4], 312 [4], 313
Weaver, B. S. **II**, 413 [6], 417
Webb, J. W. **I**, **499**
Webb, R. J. **II**, 292 [2], 303
Webber, W. R. **I**, 26
Weber, H. **I**, 297 [4], 299
Wedekind, E. **III**, 92 [3], 95
Weick, C. F. **II**, 262 [1], 268
Weinberg, A. M. **III**, 576 [1], 590
Weinstock, H. **I**, 297 [1], 299
Weiser, H. B. **III**, 538, 548
Weiss, J. **III**, 172 [19], 177
Weissberg: *see under* Vaysberg
Weisz, P. **III**, 95 [16], 96
Weith, A. J. **III**, 451 [1], 461
Welker, H. **I**, 283 [20], 286
Welker, J. P. **III**, 113 [1] [2], 122, 271 [1] [2], 272 [2], 276 [2], 278 [2], 280
Wench, G. **I**, 199 [3], 206
Werbin, H. **III**, 77 [6], 82
Werner, Z. **I**, **123**, 126 [7], 130 [4], 134
Wert, C. **I**, 289 [4], 292 [4], 294
Wertheim, G. K. **I**, 282 [18], 286
Wesolowski, K. **II**, 168, 175
West, H. L. **III**, 238 [4], 242 [4] [refs]
Westermark, E. G. T. **II**, 496 [1], 509
Westermark, T. **II**, 148 [2], 150 [2], 154, **495**, 497 [2], 509
III, 6 [8], 10, **43**, 45 [10] [11], 52 [19], 58 [10], 60 [10] [11], 61 [30], 62 [32], 64 [35] [36], 65 [30], 65, 66, 177
Wetherill, G. W. **I**, 39 [1], 42 [1], 43
Wexler, S. **II**, 379 [18], 389, 398 [1], 403 [1], 405
Weygand, F. **III**, 92 [5], 96, 367 [8] [refs]
Whaling, W. **II**, 155 [14], 127
Wheeler, J. **III**, 93 [6], 96
Wheeler, J. A. **I**, 330 [1], 338 [1], 339
Wheelwright, E. J. **II**, 362 [13], 366 [13]
Whelan, W. J. **III**, 99 [5], 102
Whipple, F. L. **I**, 24 [47], 27
Whisman, M. L. **II**, 138 [1], 146
White, D. F. **II**, *164*, *198*
White, R. M. **II**, 381 [37], 389
White, W. C. **III**, 468 [8], 469
Whitsett, C. R. **I**, 283 [21], 286
Whittemore, I. M. **II**, 378 [13], 389
III, 5 [4], 6 [4], 10, 11 [Lemmon *et al.*], 45 [14], 56 [14], 66
Wiberg, K. **III**, 237 [1], 242
Wieland, T. H. **III**, 105 [1], 109
Wier, O. E. **II**, 69 [8], 79
Wiesner, L. **I**, *122*
II, **225**, *229-230*
Wiik, H. B. **I**, 10, 11
Wilezewski, J. W. **II**, 139 [2], 146
Wilford, J. **III**, 22 [9], 25
Wilgain, S. **I**, **45**
Wiljelm, H. A. **II**, 427 [9], 430
Wilkins, R. G. **III**, 326 [1], 336, 409 [1], 414
Wilkinson, G. **II**, 426 [4], 430
III, 271 [3] [4] [5] [6] [7] [8], 279 [6], 280
Willard, J. E. **II**, 378 [10], 389, 479 [8], 491
III, 5 [2], 10, 45 [7], 65, 476 [10], 482, 486 [1], 487 [3], 493
Williams, A. O., Jr. **II**, 388 [95], 391
Williams, D. D. **III**, 227 [9], 233
Williams, D. L. **III**, 105 [3], 109, 125 [4], 129, 132 [3], 133 [4], 138
Williams, F. E. **I**, 285 [24], 286
Williams, K. **II**, 293 [3], 303
Williams, L. A. **II**, 368 [25]
Williams, M. **I**, 78 [10], 89
Williams, R. R., Jr. **III**, 171, 173 [20], 177, 472, 482
Williams, W. S. **I**, 298 [7], 299
Willis, E. H. **I**, 69 [7], 71 [7], 72 [17], 73 [17] [refs]
Wills, G. O. **III**, 196 [1], 199 [5], 201 [5], 203
Wilmshurst, B. **III**, 499 [7], 502
Wilson, A. T. **III**, 79, 82

Wilson, E. J. **I, 467**
II, 159 [4], 163
III, 381 [1], 384
Wilson, H. W. **I, 37**, *44*
Wilson, I. R. **III**, 413 [22], 414
Wilzbach, K. E. **II**, 378 [11] [12], 389, 466 [1], 468
III, 3, 5 [1] [6], 10, *11*, 44, 45, 51, 55, *56*, 57, 60, 62, 65, 159-160, 161 [1] [2], 176, 177, **463**, 467 [4] [5] [6] [7], 469, *470*, 497 [4] [5], 502
Winchell, A. N. **I**, 486 [4], 498
Winstein, S. **III**, 197 [3], 202 [3], 203
Wise, E. N. **II**, 77 [11], 80
Wish, L. **II**, 366
Wohlgemuth **II**, 332 [5], 338
Wojcik, B. **III**, 247 [10], 253
Wolf, A. P. **II**, 378 [16], 382 [45], 386 [16] [87], 388 [16], 389, 390
III, 44 [2], *65*
Wolfgang, R. L. **I**, 18 [26] [34], 26, 27, 435 [4], 449
II, 377 [3], 378 [6] [7] [8] [9], 381 [8] [40], 388 [98] [refs], 389, 391
III, 5 [7], 10, *11*, 15 [1], 22 [7], 24, 44 [2] [4], 65 *66-7*, 124, 129, **159**, *161* [5], 169 [13], 177, *177*, 497, 502
Wolfrom **II**, 326 [2], 338
Wolfsberg, M. **III**, 226 [4], 233, 237 [2], 242, 362 [2], 367
Wolkenstein, *see under* Volkenshteyn
Wollaston, W. H. **III**, 533, 547
Wood, J. L. **II**, 307 [7], 308
Wood, L. G. **I**, 375 [6], 380
Woodbury, H. H. **I**, 321, 326
Woodman, H. E. **II**, 306 [2], 308
Woods, W. W. **I**, 377 [13], 380
Woodward, L. A. **III**, 419 [9], 425
Worster, R. C. **I**, 500 [2], 502, 503, 509
Wright, H. W. **II**, 429 [12], 430
Wright, K. H. R. **I, 355**
Wright, P. G. **III**, 354 [5], 355 [5], 360
Wright, W. B. **III**, 113 [2], 122, 271 [2], 272 [2], 276 [2], 278 [2], 280
Wu, C. S. **II**, 26, 39
Wyard, S. J. **II**, 26 [2], 39
Wyatt, E. I. **II**, 429 [12], 430
Wychoff, R. W. G. **III**, 546 [34], 547 [34], 548
Wyttenback, A. **III**, 556 [20], 557
Yaffe, R. P. **III**, 555 [14], 556
Yakubson, S. I. **III**, 377 [16], 378
Yamayta, N. **II**, 440 [3] [4], 444 [3] [4]
Yamasaki, R. S. **III**, 418 [6], 425
Yang, C. N. **I**, 303-5, 306, 311, 312
Yang, K. **II**, 378 [17], 389
III, 45 [6], 56 [6], 65, 161 [3] [4], 168 [3] [4], 169, 172 [4], 177
Yang, P. S. **II**, 306 [4], 308
Yanko, J. A. **III**, 189 [8], 194
Yankwich, P. E. **III**, 412 [17], 414
Yanushkovsky, V. A. **II**, 537 [15] [19], 538 [19], 540
Cooke-Yarborough, E. H. **II**, 300 [16], 303
Yoshihara, K. **II**, 386 [75] [79], 390
Youden, W. J. **III**, 231 [16], 233
Young, D. A. **II**, 387 [92], 391
Young, R. C. **III**, 271 [9], 278 [9], 280
Yukawa, S. **I**, 150 [11], 156
Yungers, J. C. **III**, 250 [13], 254
Yun-pin, K. **III**, 250 [14] [15], 254
Zakharova, K. P. **II, 527**, 538 [18], 540
Zähringer, J. **I**, 9 [6], 10 [6], 11, 16 [5] [10], 18 [30], 21 [37], 22 [41], 23 [43] [30], 24, 25 [48], 26, 27, 31 [9], 36
Zaidel, A. N. **II**, 310 [1], 316
Zaitseva, S. N. **I, 483**
Zamith, A. A. L. **II**, 368 [26]
Zarinsky, V. A. **III**, 377 [14], 378
Zaslavsky, Y. S. **I**, *248*, *249*, *352*, **369**, 376 [7] [8], 377 [7], 378 [7], 380
Zeltmann, A. H. **III**, 317 [6], 324
Zemsky, S. V. **I**, 406 [3], 412 [3] [refs]
Zener, C. **I**, 161, 167
Zeuer, C. **I**, 289 [4], 292 [4], 294
Zharkov, A. P. **I**, 93 [13], 99
Zhukhovitsky, A. A. **I**, 146 [7], 156, 201 [5], 203 [8], 206
Ziegler, C. A. **II, 351**, 352 [2], 353 [3] [4] [5] [6], 354 [7], 355 [7], 360, 522 [2], 525
Zifferero, M. **II**, 466 [4], 468
III, 44 [3], 65
Zimakov, P. V. **II, 527**, 529 [2], 540
Zimmerman, J. **III**, 490 [5], 493
Zingaro, R. A. **II**, 544 [8], 553

Ziółkowski, J. **III**, **269**
Zlatski **III**, 155
Zuber, A. **I**, **123**, 126 [7], 130 [3], 134
Zvara, I. **II**, 379 [19], 380 [31], 382 [41], 385 [41], 389

TRANSLITERATION INDEX

Азаров	Azarov	Дзисько	Dzisko
Алексеев	Alekseev	Добкина	Dobkina
Андреева	Andreeva	Драпчинский	Drapchinsky
Анфимова	Anfimova	Дроздоз	Drozdoz
Арефьева	Arefieva	Дрожжин	Drozhzhin
Арсланов	Arslanov	Дубинин	Dubinin
Артемьев	Artemyev	Ельяшевич	Elyashevich
Архаров(а)	Arkharov(a)	Емельянов	Emelyanov
Багоцкий	Bagotsky	Енгоров	Engorov
Баландин(а)	Balandin(a)	Еременко	Eremenko
Балашова	Balashova	Есин	Esin
Баранов	Baranov	Жарков	Zharkov
Баркалов	Barkalov	Жуковицкий	Zhukovitsky
Безбородько	Bezborodko	Заицева	Zaitseva
Бердникова	Berdnikova	Заринский	Zarinsky
Блох	Blokh	Заславский	Zaslavsky
Богданов(а)	Bogdanov(a)	Захарова	Zakharova
Богуславский	Boguslavsky	Звара	Zvara
Бойцова	Boytsova	Земский	Zemsky
Бокштейн	Bokshtein	Зимаков	Zimakov
Болтакс	Boltaks	Игнатков	Ignatkov
Бороскоv	Boreskov	Израилевич	Izrailevich
Борисов(а)	Borisov(a)	Ильинский	Ilyinsky
Бочкарев	Bochkarev	Иофа	Iofa
Булашевич	Bulashevich	Исагулянц	Isagulyants
Бутомо	Butomo	Кабанов	Kabanov
Быков	Bykov	Казанский	Kazansky
Вайсберг	Vaysberg	Калинеченко	Kalinechenko
Варшавский	Varshavsky	Каплунов	Kaplunov
Васильева	Vasilyeva	Катаев	Kataev
Васичев	Vasichev	Кельман	Kelman
Верескунов	Vereskunov	Кирьяков	Kiriakov
Вечер	Vecher	Китайгородский	Kitaygorodsky
Виноградов	Vinogradov	Кишкин	Kishkin
Возженников	Vozzhennikov	Климанек	Klimanek
Волкова	Volkova	Ключарев	Klyucharev
Волькенштейн	Volkenshteyn	Ковнер	Kovner
Воскобойников	Voskoboynikov	Коган	Kogan
Вяземский	Vyazemsky	Колдаев	Koldaev
Гаврилов	Gavrilov	Колесов	Kolesov
Гейдерих	Geyderikh	Колотыркин	Kolotyrkin
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