Hafnium tetrafluoride did not exhibit any phase changes within the range of temperatures studied. Equipment limitations prevented extending the heat-content measurements to a temperature sufficiently high for determining the melting point and the heat of fusion of this compound.

Rubidium fluoride had one phase change, that of melting, within the temperature range studied. The results for this compound, in both solid and liquid states, appear normal in comparison with other alkali halides. The melting point was found to be 1048°K. and the heat of fusion 5490 cal. per mole.

TABLE II

HEAT CONTENTS (CAL. MOLE^{-1}) AND ENTROPY INCREMENTS (CAL. DEGREE^{-1} MOLE^{-1}) ABOVE 273.5°K.

	RbF		HfF_4	
T, °K.	$H_T - H_{273.15}$	$S_T - S_{273.15}$	$H_T - H_{273.15}$	$S_T - S_{273.15}$
298.15	305	1.06	675	1.86
400	1544	4.65	3276	9.33
450	2175	6.14	4621	12.49
500	2823	7.50	6023	15.44
550	3489	8.77	7344	17.96
600	4175	9.96	8832	20.54
650	4881	11.06	10344	22.92
700	5609	12.14	11886	25.20
750	6356	13.17	13431	27.33
800	7148	14.19	14990	29.34
850	7912	15.17	16565	31.35
900	8723	16.10	18147	33.15
950	9553	17.00	19717	34.84
1000	10408	17.88	21321	36.48
1048	11252(S)	18.70	...	...
1048	16742(L)	23.94	...	...
1050	...	...	22912	38.03
1100	17668	24.80	24529	39.54
1150	18613	25.63	...	...
1200	19554	26.43	...	...

Table II presents smooth heat-content and entropy data for the two substances at even 50° intervals in the 400 to 1200°K. range.

The heat-content equations presented below were derived by the method of least squares, using the experimental data from Table I. The average deviations are indicated by the figures in parentheses.

The heat-content equation of the solid RbF was derived to fit conditions:

$$H_T - H_{273.15} = a + bT + cT^2 + dT^{-1} \qquad (1)$$

$$C_p = b + 2cT - dT^{-2} \text{ where } C_p = 12.04 \text{ at } 283.15°\text{K.}^5 \qquad (2)$$

$$0 = a + bT + cT^2 + dT^1 \text{ at } 273.15°\text{K.} \qquad (3)$$

The heat-content equation of HfF_4 was made to fit only conditions 1 and 3, since no heat-capacity data were available at low temperatures.

Least square solutions were obtained by means of a Univac-60 electronic computer.[6] Entropy increments were calculated by means of the method suggested by Kelley.[7] The heat-content data are represented by the equations

RbF (solid)

$$H_T - H_{273.15} = -2078 + 7.966T + 4.605 \times 10^{-3}T^2 - 1.206 \times 10^5\ T^{-1} \text{ (273.15 to 1048°K.; } \pm 0.5\%)$$

RbF (liquid)

$$H_T - H_{273.15} = 61518 - 1.1303 \times 10^1 T + 4.416 \times 10^{-4}T^2 - 3.50677 \times 10^7\ T^{-1} \text{ (1048 to 1200°K.; } \pm 0.5\%)$$

HfF_4

$$H_T - H_{273.15} = -11884.9 + 3.1904 \times 10^1\ T + 3.739 \times 10^{-4}T^2 + 8.9889 \times 10^5\ T^{-1} \text{ (273.15 to 1103.3°K.; } \pm 0.7\%)$$

The data show that average deviations of the experimental heat contents from the calculated values are greater at the lower than at the higher temperatures.

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(5) J. W. Brønsted, *Z. Elektrochem.*, **20**, 554 (1914).

(6) R. W. Smith, Jr., Supervisory Mathematician, Region V, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Penna.

(7) K. K. Kelley, Bulletin 476, Bureau of Mines, U. S. Department of the Interior, Berkeley, California.

UNIVERSITY, ALABAMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW MEXICO]

Isotopic Exchange between Potassium Iodide and Benzyl Iodides. Solvent Effects[1]

BY J. A. LEARY AND MILTON KAHN

RECEIVED MARCH 12, 1959

The rates of exchange between benzyl iodide and potassium iodide and between *p*-nitrobenzyl iodide and potassium iodide, in acetone, are represented by the rate laws: $R = 9.5 \times 10^{10}e^{-13,720/RT}(\text{KI})(\text{BzI})$ and $R = 2 \times 10^{12}e^{-14,350/RT}(\text{KI})(p\text{-NO}_2\text{-BzI})$, respectively, where the units of R are mole liter^{-1} sec.$^{-1}$. The rates of exchange, at 0°, between benzyl iodide and potassium iodide in acetone–ethanol, acetone–water, acetone–phenol and acetone–carbon tetrachloride mixtures and between *p*-nitrobenzyl iodide and potassium iodide in acetone–ethanol mixtures have been studied. The inhibitory effect of the hydroxylic compounds has been correlated with their tendency to solvate the iodide ion through hydrogen-bond formation.

Introduction

The isotopic exchange between benzyl iodide and potassium iodide, in methanol and ethanol, was found to proceed *via* an S_N2 mechanism with an easily measurable rate at room temperature.[2] However, under the same conditions, the reaction appeared to be extremely rapid in absolute acetone.[(3)]

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[1] This paper is a portion of the dissertation presented by J. A. Leary in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1956. Presented before the Physical and Inorganic Division of the American Chemical Society in Atlantic City, September, 1956.

(2) P. Stillson and M. Kahn, THIS JOURNAL, **75**, 3579 (1953).

(3) P. Stillson, Doctoral Thesis, The University of New Mexico, 1951.

This paper deals with the role of the solvent in the aforementioned reaction. Isotopic exchange between benzyl iodide and potassium iodide and between *p*-nitrobenzyl iodide and potassium iodide in acetone and acetone–ethanol mixtures was investigated. Also, the effect of water, phenol and carbon tetrachloride on the rate of exchange between benzyl iodide and potassium iodide in acetone was studied. The variation of reaction rate with composition of solvent has been correlated with the tendency for the hydroxylic solvent to solvate the iodide ion through hydrogen-bond formation.

Experimental

Radioactivity.—Eight-day iodine-131, obtained from Oak Ridge, was used as tracer in all experiments. Radiochemical purity was checked by observing the decay of a silver iodide sample prepared from an aliquot of a stock solution of iodine tracer. The activity, over a 64-day period, decayed with an 8.0-day half-life in satisfactory agreement with that reported in the literature.[4] Solutions of radioactive potassium iodide in organic solvents were prepared in the described manner. Iodine-131 tracer containing a small amount of carrier iodide was oxidized to iodine with chromium(VI) in acid solution and subsequently extracted into 2 ml. of benzene. After washing the benzene phase with three 2-ml. portions of water, 5.00 ml. of an aqueous standardized solution of potassium iodide was mixed with the benzene in order to effect isotopic exchange between the iodine and potassium iodide: this operation and all subsequent ones were conducted in subdued light. The aqueous phase and water washings of the benzene phase were transferred to a 50-ml. volumetric flask and evaporated to dryness. The desired organic solvent was added to the flask, which had been allowed to cool in a vacuum desiccator and the resulting solution sparged for 2 hr. with argon that had been passed through chromous chloride, concentrated sulfuric acid and Drierite. The solution then was diluted to the mark with oxygen-free solvent and stored in the dark in a refrigerator.

Chemicals.—Benzyl iodide (BzI) and *p*-nitrobenzyl iodide (*p*-NO_2BzI) were prepared as previously reported.[2,5] J. T. Baker Chemical Company Analytical Grade potassium iodide was dried at 110° and used without further purification. Eastman Kodak phenol was fractionally distilled through a six-bulb Snyder column; the middle fraction was collected and stored in a refrigerator. Triple-distilled water was used to prepare aqueous solutions of potassium iodide.

All solvents were distilled in oven-dried glass apparatus under a purified argon atmosphere at a pressure of about 580 mm. mercury, sparged with argon over a 4 hr. period and then stored in the dark. J. T. Baker Chemical Company alcohol-free C.P. acetone was dried 48 hr. over Drierite prior to distillation in the dark. U. S. Industrial Chemicals Company absolute ethanol was dried by the method of Lund and Bjerrum[6] before distillation. Mallinckrodt Chemical Works C.P. carbon tetrachloride was dried 48 hr. over Drierite and then distilled. In all distillations only the middle fraction was retained.

Procedure.—The exchange experiments were carried out as described elsewhere.[2] It was necessary to correct the concentration of each reaction mixture for expansion or contraction of the solvent because all stock solutions were standardized at room temperature. These corrections were computed from the equations[7] for cubical expansion of the solvents.

Measurement of Radioactivity.—The γ-radiation associated with the decay of iodine-131 was measured with an anticoincidence scintillation counter employing a thallium-activated sodium iodide crystal. Liquid samples of the separated reactants were prepared by the method of Keneshea and Kahn.[8]

Results

The reactions investigated were

$$\text{BzI} + \text{KI}^* = \text{BzI}^* + \text{KI} \qquad (1)$$

$$p\text{-NO}_2\text{BzI} + \text{KI}^* = p\text{-NO}_2\text{BzI}^* + \text{KI} \qquad (2)$$

where the asterisks indicate radioactive atoms. The constant rate of exchange R of iodine atoms between organic iodide and potassium iodide in any one experiment was evaluated with the aid of the logarithmic form of the isotopic exponential exchange law.[9]

Exchange in Absolute Acetone.—If the exchange reaction between organic iodide (Org I) and potassium iodide is first order with respect to each reactant, an S_N2 type reaction, $R = k$ (Org I)(KI), and a plot of R/(Org I) *vs.* (KI) should yield a straight line passing through the origin with a slope equal to k, the specific reaction rate. Such plots of the data obtained with BzI and *p*-NO_2BzI at various temperatures indicated in each instance an S_N2 type reaction.

Rate Laws for Exchange in Absolute Acetone.—The average values for the specific reaction rate k for each reaction are summarized in Table I.

TABLE I

AVERAGE VALUES OF THE SPECIFIC REACTION RATE k IN ACETONE

Organic iodide	Temp., °C.	$\bar{k}$, l. mole^{-1} sec.$^{-1}$
BzI	0.0	0.99 ± 0.02
	17.8	4.43 ± .04
	34.2	16.7 ± .3
p-NO_2BzI	0.0	6.20 ± .04
	16.0	26.8 ± .2

The slopes of the linear semi-logarithmic plots of the values for the specific reaction rate k against the reciprocal of the absolute temperature were evaluated by the method of least squares. The experimental activation energies and their probable errors for benzyl iodide and *p*-nitrobenzyl iodide as calculated from the slopes are 13,720 ± 90 and 14,350 ± 50 cal., respectively.

For benzyl iodide, the experimental data were obtained over a temperature range from 0.0 to 34.2°, a benzyl iodide concentration range from 2.912×10^{-5} to 1.452×10^{-4} M and a potassium iodide concentration range from 1.491×10^{-5} to 4.724×10^{-4} M. The *p*-nitrobenzyl iodide experiments were conducted in the temperature range from 0.0 to 16.0°. The concentration of *p*-nitrobenzyl iodide ranged from 2.621×10^{-6} to $3.440 \times 10^{-5} M$ and that of potassium iodide ranged from 3.450×10^{-6} to 3.125×10^{-5} M. The data are well represented by the rate laws

$$R = 9.5 \times 10^{10} e^{-13{,}720/RT}\,(\text{KI})(\text{BzI}) \qquad (3)$$

$$R = 2 \times 10^{12} e^{-14{,}350/RT}(\text{KI})(p\text{-NO}_2\text{BzI}) \qquad (4)$$

where the units of R are moles liter^{-1} sec.$^{-1}$

Exchange in Acetone Mixtures.—The results of studies of the benzyl iodide exchange reaction at 0°

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(4) H. H. Seliger, L. Carallo and S. V. Culpepper, *Phys. Rev.*, **90**, 443 (1953).

(5) E. L. Purlee, M. Kahn and J. L. Riebsomer, THIS JOURNAL, **76**, 3796 (1954).

(6) H. Lund and N. Bjerrum, *Ber.*, **64**, 210 (1931).

(7) "International Critical Tables of Numerical Data. Physics, Chemistry, and Technology," Vol. III, McGraw–Hill Book Company, Inc., New York, N. Y., 1928, pp. 27–29.

(8) F. J. Keneshea, Jr., and M. Kahn, THIS JOURNAL, **74**, 5254 (1952).

(9) G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 315.

in mixtures of acetone–ethanol, acetone–water, acetone–phenol and acetone–carbon tetrachloride are summarized in Tables II, III, IV and V, respectively. Table VI contains the results of an investigation of the *p*-nitrobenzyl iodide exchange reaction in acetone–ethanol mixtures at 0°. Because the benzyl iodide exchange reaction was found to proceed *via* an S$_N$2 type reaction in acetone, methanol,[2] ethanol[2] and acetone–ethanol[3] mixtures, it is presumed that the exchange reactions in the various solvent mixtures reported here are also first order with respect to each reactant.

Table II

Results of Benzyl Iodide Exchange Experiments at 0.0° in Acetone–Ethanol Solvent Mixtures

(C_6H_3O), M	(C_2H_6O), M	(BzI), $M \times 10^3$	(KI), $M \times 10^3$	k, l. mole^{-1} sec.$^{-1}$
14.00[a]	0	.....	.....	0.99
13.73	0.351	0.2728	0.2592	.62
13.40	0.753	.2598	.2592	.42
12.60	1.75	.980	.0635	.192
7.01	8.75	12.27	6.43	.0172
7.01	8.75	12.08	6.41	.0177
5.60	10.50	5.61	7.72	.0117
4.67	11.67	8.06	8.54	.0089
0.0	17.53	22.45	12.86	.00173
0.0	17.53	15.70	12.79	.00172

[a] See Table I.

Table III

Results of Benzyl Iodide Exchange Experiments at 0.0° in Acetone–Water Solvent Mixtures

(C_3H_6O), M	(H_2O), M	(BzI), M	(KI), M	k, l. mole^{-1} sec.$^{-1}$
14.00[a]	0	....	....	0.99
13.95	0.256	0.1244	0.3120	.75
13.82	0.648	.3838	.1501	.58
13.70	1.296	.2558	.3002	.395

[a] See Table I.

Table IV

Results of Benzyl Iodide Exchange Experiments at 0.0° in Acetone–Phenol Solvent Mixtures

(C_3H_6O), M	(C_6H_6O), M	(BzI), M	(KI), M	k, l. mole^{-1} sec.$^{-1}$
14.00[a]	0	....	....	0.99
13.92	0.0661	0.2557	0.0610	.70
13.86	.1136	.2046	.0976	.60
13.60	.336	.3846	.1384	.353
13.20	.672	.2563	.2768	.188
12.38	1.345	.529	.2412	.071

[a] See Table I.

Table V

Results of Benzyl Iodide Exchange Experiments at 0.0° in Acetone–Carbon Tetrachloride Solvent Mixtures

(C_3H_6O), M	(CCl_4), M	(BzI), M	(KI), M	k, l. mole^{-1} sec.$^{-1}$
14.00[a]	0	....	....	0.99
13.29	0.531	0.2532	0.2592	1.01
12.60	1.063	.3730	.2580	1.02
11.20	2.120	.1688	.2592	0.93

[a] See Table I.

Table VI

Results of *p*-Nitrobenzyl Iodide Exchange Experiments at 0.0° in Acetone–Ethanol Solvent Mixtures

(C_3H_6O), M	(C_2H_6O), M	(BzI), M	(KI), M	k, l. mole^{-1}, sec.$^{-1}$
14.00[a]	0	.....	.....	6.20
13.66	0.416	0.0825	0.02132	3.52
13.31	0.833	.0619	.04260	2.25
12.60	1.75	.03934	.06350	1.13

[a] See Table I.

Discussion

As shown in Tables II, III, IV and V, the addition of ethanol, water or phenol to acetone decreased the value of the observed specific reaction rate k for the benzyl iodide exchange reaction considerably. Because the value of k in acetone was not significantly altered by the addition of carbon tetrachloride up to a concentration of 1.063 M (Table V), it is believed that the decrease in k with the addition of the hydroxylic compounds is a result of the inhibition of the reaction by these compounds rather than acceleration by acetone. The significant decrease in k observed in 2.12 M carbon tetrachloride is attributed to increased ion-pair formation attending the lowering of the dielectric constant of the solvent medium.

The order of increasing effectiveness of the hydroxylic compounds as inhibitors for the exchange reaction was found to be

$$\text{acetone} < \text{water} < \text{ethanol} < \text{phenol}$$

and can be correlated with the increasing tendency toward hydrogen bond formation. It is noteworthy that the relative strength of the hydrogen bonds formed with the chloride of the hydrogen chloride–ether complex in dioxane is reported to be phenol>ethanol>>acetone.[10] Also, the position of ethanol with respect to water is in accord with the intermolecular hydrogen bond energies of 6.2 and 4.5 kcal./mole, respectively.[11] Assuming, then, that the organic iodide exchanges at a much lower rate with hydroxylically solvated iodide ion than with purely acetonated iodide ion and that all species of solvated organic iodide react rapidly, the observed initial rapid decrease in the specific reaction rate k with increase in hydroxylic compound concentration can be attributed to the reversible reaction

$$I^-\cdot A_n + mH = H_m\cdot I^-\cdot A_{n-m} + mA \qquad (5)$$

where $I^-\cdot A_n$ is an iodide ion solvated by n molecules of acetone and $H_m\cdot I^-\cdot A_{n-m}$ represents an iodide ion solvated by m molecules of hydroxylic compound and $n-m$ molecules of acetone. At sufficiently low concentrations ($\stackrel{=}{<}\sim 1.4\,M$) of hydroxylic compound, m is presumed to have only values of 0 and 1. The equilibrium constant K is defined for equation 5 as

$$K = \frac{(H\cdot I^-\cdot A_{n-1})(A)}{(I^-\cdot A_n)(H)} \qquad (6)$$

where the parentheses refer to molar concentrations. It is assumed that over the aforementioned concentration range of hydroxylic compound the

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(10) P. D. Bartlett and H. J. Dauben, Jr., This Journal, **62**, 1339 (1940).

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1948, p. 333.

ratio of the activity coefficients of all the species is constant. It follows that

$$(\mathrm{I^-{\cdot}A}_n) = \frac{\Sigma(\mathrm{I^-})}{K\frac{(\mathrm{H})}{(\mathrm{A})} + 1} \qquad (7)$$

where

$$\Sigma(\mathrm{I^-}) = (\mathrm{I^-{\cdot}A}_n) + (\mathrm{H{\cdot}I^-{\cdot}A}_{n-1}) = (\mathrm{KI})$$

In line with the foregoing comments, the rate of exchange R for the benzyl iodide exchange reaction is now expressed as

$$R = k_1(\mathrm{I^-{\cdot}A}_n)(\mathrm{BzI}) \qquad (8)$$

Substitution of equation 7 into equation 8 gives

$$R = \frac{k_1}{K\frac{(\mathrm{H})}{(\mathrm{A})} + 1}(\mathrm{KI})(\mathrm{BzI}) \qquad (9)$$

and comparison of equation 3 with equation 9 reveals that

$$\frac{k_1}{k} = \frac{K(\mathrm{H})}{(\mathrm{A})} + 1 \qquad (10)$$

where k_1 is the specific reaction rate in pure acetone. Plots of k_1/k *versus* (H)/(A) proved to be linear in accordance with equation 10 and the values of K obtained from the slopes are 80, 25 and 15 for phenol, ethanol and water, respectively. The value of K for the p-$\mathrm{NO_2BzI}$ exchange reaction in acetone–ethanol mixtures turned out to be the same as that for benzyl iodide, indicating that only solvation of the iodide ion is of primary importance as previously assumed in the derivation of equation 10. The curves shown in Fig. 1 represent the variation of k with the ratio (H)/(A) as calculated from equation 10 using the values of K mentioned above; the points represent the experimentally determined values for k.

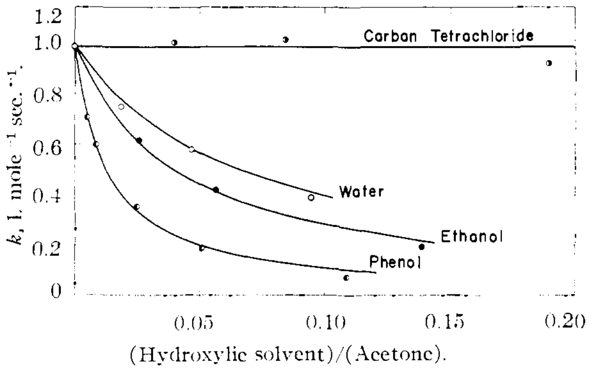

Fig. 1.—The variation of k for benzyl iodide with the ratio (hydroxylic solvent)/(acetone) as calculated from equation 10. The points are experimentally determined values for k.

Acknowledgments.—The authors are indebted to Drs. Roderick W. Spence, James Sattizahn, Alfred H. Zeltman and Mr. Gordon W. Knobeloch of the Los Alamos Scientific Laboratory for supplying equipment and facilities and to Drs. J. L. Riebsomer and E. Lee Purlee of the University of New Mexico Chemistry Department for the preparation of p-nitrobenzyl iodide.

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[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

Thermodynamics for the Extraction of Uranyl Nitrate and Nitric Acid by Esters of the Types $(\mathrm{RO})_3\mathrm{P{=}O}$ and $(\mathrm{RO})_2\mathrm{RP{=}O}$[1]

BY T. H. SIDDALL, III

RECEIVED JANUARY 8, 1959

The thermodynamic quantities, ΔH, ΔF and ΔS, were obtained for the extraction of uranyl nitrate and of nitric acid by twenty-one compounds of the types $(\mathrm{RO})_3\mathrm{P{=}O}$ and $(\mathrm{RO})_2\mathrm{RP{=}O}$. The values of ΔS suggest that a very open structure is retained by the extractant molecules when they are bound to uranyl nitrate. The strength of the bonds formed with the uranyl ion is substantially altered as substituents on the phosphorus atom are replaced by various radicals. A partial correlation with Kharasch's[2] electronegativity scale was obtained for the substituents. When ΔF for the extraction of uranyl nitrate was plotted against ΔF for the extraction of nitric acid, a straight line was obtained. However, the fit of the data to the straight line is only approximate. Evidence was obtained that an extra order–disorder transition accompanies extraction of uranyl nitrate by certain extractants, but not with others.

Introduction

The utility of tri-n-butyl phosphate (TBP) suggests that other trialkyl phosphates and possibly dialkyl alkylphosphonates might be even more advantageous in processing irradiated uranium. Burger[3] and the author[4] of this paper have published data that indicate that there are such advantageous compounds. However, these earlier data were obtained at single temperatures, and, therefore, do not permit calculation of ΔH and ΔS for the extraction reaction of uranium with the compounds that were tested.

It was felt that values for ΔH and ΔS might throw some light in a fundamental way on the effect of altering the substituents around the phosphorus atom.

Experimental

The thermodynamic quantities were calculated from the variation in the extraction coefficient for uranium over the temperature range, 0 to 50°. In two cases the range was extended to >80°.

The standard conditions chosen were 1.00 M nitric acid in the aqueous phase and 0.050 M extractant diluted with n-dodecane in the organic phase. These conditions gave extraction coefficients of conveniently measurable size. From the work of McKay and co-workers[5] and from work in

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[1] The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 769 (1955).

[3] L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958).

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[5] H. A. C. McKay and T. V. Healy, *Rec. trav. chim.*, **75**, 730 (1956).