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The Reaction of *p*-Nitrobenzyl Bromide and Chloride with Lithium Bromide[1]

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Measurements of the rates of the halogen exchange reactions of *p*-nitrobenzyl bromide and chloride with lithium bromide in acetone containing 5% methanol and 0.5% water at 0 and 30° indicate that the bromide ion reacts considerably more rapidly than the undissociated lithium bromide. The use of pile-irradiated lithium bromide permits rate measurements extending to lower salt concentrations than heretofore accessible.

Early in the present century, Acree proposed that many reactions involving ionizable substances proceed at rates which are dependent on the concentrations of undissociated molecules as well as the concentrations of ions, so that the observed rate constants k are of the form

$$k = (1 - \alpha)k_m + \alpha k_i \qquad (1)$$

where k_m and k_i are the rate constants for undissociated molecules and for ions, respectively, and α is the degree of dissociation of the ionizable substance. Acree and his collaborators[3] studied many reactions which seemed to conform to equation 1, and similar observations have been reported more recently by others.[4]

The availability of radioactive isotopes of high specific activity, prepared by pile irradiation, permits extending rate measurements pertinent to the Acree proposal to much lower concentrations than was formerly possible. The present work was undertaken to exploit this possibility. We have studied the reaction of lithium bromide with *p*-nitrobenzyl bromide and chloride, using in most experiments radioactive $LiBr^{82}$ obtained by irradiation of ordinary LiBr in the atomic pile at Oak Ridge. In none of the previous work[5] on exchange reactions between organic halides and inorganic halides has the concentration effect been explicitly considered.

During the course of this work Evans and Sugden[6] published measurements of the rate of reaction of highly active $LiBr^{82}$ with *sec*-octyl bromide at 65.5° and with *n*-butyl bromide at 26.2°, both in absolute acetone, using LiBr concentrations ranging from 0.00025 to 0.04 *M*. Their results fit the Acree equation within experimental accuracy.

Experimental

Solvent.—Redistilled acetone was diluted with methanol in the proportion 95 volumes of acetone to 5 volumes of methanol. Water was added to bring the water content as determined by the Karl Fischer reagent to 0.0055 ± 0.0003 g. per ml. A mixed solvent was employed to increase the solubility of the lithium halides; the presence of a constant small amount of water decreased the danger of erratic results caused by accidental contamination of an anhydrous solvent.

Organic Halides.—Eastman Kodak Co. White Label *p*-nitrobenzyl bromide and chloride were recrystallized twice from 95% ethanol, and dried *in vacuo*. Microscopic observation of the melting and solidifying behavior of these materials indicated them to be pure. The observed melting points were 98.5–99.0° and 72.5–73.5°, respectively.

Lithium Bromide.—Lithium carbonate was recrystallized from water, and converted to the bromide by two evaporations in a platinum dish with reagent-grade HBr. The salt was finally heated to just below the fusion point and cooled *in vacuo* over $CaCl_2$. Gravimetric determinations of bromine indicated a purity of 100.05 ± 0.04%.

Radioactive Lithium Bromide.—Approximately 0.5-g. samples, accurately weighed, of the anhydrous salt were sealed in quartz tubes of 1 mm. wall thickness. Each sample was irradiated for one week in the pile at the Oak Ridge National Laboratory, and was received 2 or 3 days after removal from the pile. This time interval was sufficient to ensure complete decay of the short-lived bromine isotopes. The sample tube was broken under a known amount of solvent in a storage bottle, and the solution thoroughly mixed. The storage bottle, adequately shielded, was fitted with a buret for dispensing the solution.

The concentration of the solution in the case of each of the five solutions prepared from irradiated samples was found to be considerably lower than expected from the known amount of LiBr originally irradiated. The discrepancy varied from 7.2% for the second sample to 21.0% for the third sample. In spite of these discrepancies, the irradiated samples were used without further purification because of the short half-life of the Br^{82} and the difficulties of manipulations of the highly radioactive material.

Counting Procedure.—All samples were counted in solution, in most cases in jacketed counters. It was shown that the counting rate for a given sample was independent of the solvent (water or benzene–acetone–methanol) in which it was dissolved. Suitable corrections for the finite resolving times of the counters were applied. All counting times were sufficiently short so that it could be assumed that the samples decayed linearly during the counting.

Half-life of Br^{82}.—During the course of this work several determinations of the half-life of Br^{82} were made. Measurements extending over a week or more (approximately 5 half-lives) were made on several different dilutions of a stock solution, and the half-life determined from the slope of the plot of logarithm of counts per ml. of stock solution *vs.* time. The closely agreeing results had a mean value of 35.3 hr. with an estimated uncertainty of ±0.3. This value agrees moderately well with the values 36.0 ± 0.1 and 36.0 ± 0.2 reported by Berne,[7] and 36.2, reported by Bither, *et al.*[5]

Kinetic Measurements.—All reactions were carried out at temperatures held constant to ±0.05° and measured by a mercury-in-glass thermometer calibrated against a Bureau of Standards certified platinum resistance thermometer. Timing was done with an electric clock with sweep second hand.

At the desired time the contents of a reaction flask were rapidly poured into a separatory funnel containing H_2O and benzene, and the mixture was vigorously shaken to quench the reaction. The reaction flask was rinsed with a small portion of solvent and three portions of water which were added to the separatory funnel. After further shaking, the water layer was drawn off into a 250-ml. volumetric flask, and the benzene layer washed with two portions of water which were added to the volumetric flask. The water extract was diluted to the mark. The benzene layer was

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[1] Based on material in a Ph.D. dissertation by S. D. Bowers, June, 1951.

[2] Sheffield Fellow, 1949-1950.

[3] See, for example, J. H. Shroder and S. F. Acree, *J. Chem. Soc.*, 2582 (1914); H. C. Robertson and S. F. Acree, THIS JOURNAL, **37**, 1902 (1915).

[4] P. J. Hardwick, *J. Chem. Soc.*, 141 (1935); S. S. Woolf, *ibid.*, 1172 (1937); J. A. Mitchell, *ibid.*, 1792 (1937); E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **45**, 167 (1949).

[5] J. B. Conant and R. E. Hussey, THIS JOURNAL, **47**, 476 (1925); T. A. Bither, J. M. Sturtevant and H. C. Thomas, *ibid.*, **67**, 1562 (1945); J. W. Hackett and H. C. Thomas, *ibid.*, **72**, 4962 (1950).

[6] C. C. Evans and S. Sugden, *J. Chem. Soc.*, 270 (1949).

[7] E. Berne, *Phys. Rev.*, **77**, 568 (1950); *Acta Polytech., Chem. Met.*, Ser. 3, No. 3, 3 (1952); (*C. A.*, **47**, 3150 (1953)).

heated on a hot plate to remove most of the water and then diluted to 250 ml.

Analyses by Radioactivity Determinations.—The radioactivity in the benzene and water layers was determined, and compared with that in a standard solution containing the same amount of radioactive LiBr as used in the reaction flask diluted to 250 ml. with water. Standard solutions containing radioactive LiBr diluted with benzene were unsatisfactory, apparently because of adsorption of the LiBr (present in very low concentration) on the walls of the volumetric flask; the apparent activity of such a solution decreased with time at a rate several times larger than expected from the known half-life of Br^{82}.

The quantities used in calculations of rates are defined as

$$Q_b = \frac{\text{counting rate of RBr in benzene layer cor. to ref. time}}{\text{counting rate of LiBr in standard cor. to ref. time}} \quad (2)$$

and

$$Q_w = \frac{\text{counting rate of LiBr in water layer cor. to ref. time}}{\text{counting rate of LiBr in standard cor. to ref. time}} \quad (3)$$

That there was no significant loss of material in the separation procedure is indicated by the fact that $Q_b + Q_w$ was closely equal to unity in all experiments.

Gravimetric Analyses.—In some of the reactions between *p*-nitrobenzyl chloride and LiBr, the reaction was followed by weighing the mixed silver halides formed by addition of $AgNO_3$ to the water layer obtained as described above. The AgBr precipitated from an equivalent amount of LiBr solution was also weighed.

Results

Reaction between *p*-Nitrobenzyl Bromide and Lithium Bromide.—There is abundant evidence[8] that reactions of this type follow second-order kinetics. The integrated rate equation can be written in the form

$$\frac{(A + B)kt}{2.303} = -\log\left[1 - \frac{A + B}{A} Q_b\right] \quad (4)$$

where k is the rate constant, A and B are, respectively, the initial concentrations of organic halide and LiBr, and t is the reaction time. Data from water layer activities are used in a similar equation with Q_b replaced by $(1 - Q_w)$. A plot of the right side of equation 4 against t should be a straight line from the slope of which the rate constant can be evaluated.

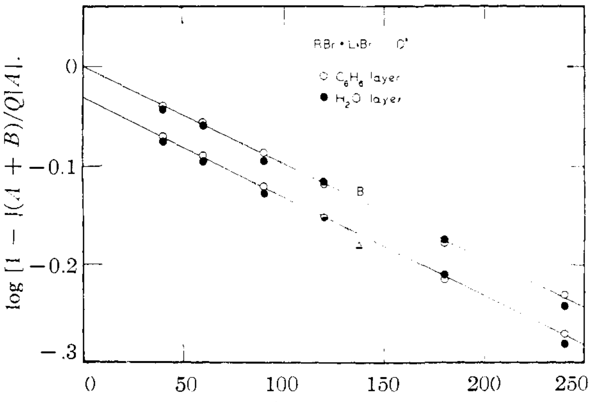

Fig. 1.—Illustrating the evaluation of rate constants by successive approximations: A, first approximation; B, second approximation.

In many of the experiments this plot gave a non-vanishing intercept, the discrepancy from equation 4 being in the direction to be expected if a constant fraction, during any one run, of the activity which should have been in the water layer appeared instead in the benzene layer, as a result, for example, of partition of LiBr between water and moist benzene. Assuming this explanation of the non-vanishing intercept to be correct, one may plot log $[1 - [(A + B)/A]Q'_b]$, where $Q'_b = Q_b + \delta(1 - Q_b)$ is the observed benzene layer activity, against t. The intercept will then give an approximate value for δ

$$\delta = (1 - I)\frac{A}{A + B} \quad (5)$$

where log I is the intercept. This value of δ is used to correct the observed readings, and a new plot is made to obtain a more accurate value of δ. When a plot is obtained passing through the origin, k is evaluated from the slope. Although this procedure is not entirely satisfactory in view of the lack of definite knowledge as to the origin of the intercept discrepancy, relatively small changes in the value of k were involved in the successive approximations.

Data for a typical experiment are given in Table I, and the method of calculation is illustrated in Fig. 1. Line A is the plot of log $[1 - [(A + B)/A]Q'_b]$ and log $[1 - [(A + B)/A](1 - Q'_w)]$ *vs.* time. The value of δ obtained from the intercept is 0.047. Revised values for Q_b and $1 - Q_w$ obtained using this δ lead to the line B which is seen to pass through the origin as required by equation 4. The slope of line B differs from that of line A by only 3%.

TABLE I

THE REACTION OF *p*-NITROBENZYL BROMIDE WITH LITHIUM BROMIDE AT 0°

$A = 0.004556\ M$, $B = 0.002128\ M$

t, min.	40	60	90	120	180	240
Q'_b	0.1018	0.1259	0.1642	0.1998	0.2660	0.3144
$1 - Q'_w$	.108	.128	.173	.199	.262	.324

Experiments were performed at 0 and 30°, the data for which are recorded in Table II. The quan-

TABLE II

THE REACTION OF *p*-NITROBENZYL BROMIDE (A) WITH LITHIUM BROMIDE (B) AT 0 AND 30°

Run no.	Temp., °C.	A, mole/l., $\times 10^3$	B, mole/l., $\times 10^3$	k, l. mole^{-1} sec.$^{-1}$, $\times 10^3$	α
1	0	4.56	0.118	8.98	0.914
2	0	4.56	0.598	8.16	.786
3	0	4.56	2.13	5.62	.624
4	0	4.56	5.81	4.42	.492
5	0	4.55	10.41	4.33	.426
6	0	4.56	21.2	3.63	.364
7	0	4.56	38.1	1.98	.320
8	30	3.48	0.122	223	.906
9	30	3.48	0.488	160	.800
10	30	3.48	1.225	134	.673
11	30	3.97	4.05	121	.516
12	30	3.97	4.27	120	.510
13	30	3.97	10.23	95.7	.408
14	30	3.97	16.51	86.2	.360
15	30	4.37	24.0	75.3	.313
16	30	3.97	33.1	76.8	.306
17	30	3.97	44.4	61.8	.290

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(8) See, for example, M. B. Neimann, G. V. Maksimova and Yu. M. Shapovalov, *Doklady Akad. Nauk SSSR*, **85**, 1289 (1952); *C. A.*, **47**, 388 (1953).

tities in the last column are the values, estimated as described below, for the degree of dissociation of the LiBr.

Reaction between *p*-Nitrobenzyl Chloride and Lithium Bromide.—This reaction

$$\mathrm{RCl} + \mathrm{LiBr} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{RBr} + \mathrm{LiCl}$$

may also be assumed to follow second-order kinetics. It can be shown that for $A > B$

$$\frac{ak_1t}{2.303} - \log(1 - M) = \log\left[\frac{M}{1 - M} + \frac{Q_{b\infty}}{Q_{b\infty} - Q_b}\right] \quad (6)$$

where $Q_{b\infty}$ is the relative activity in the benzene layer at equilibrium, and M is given by

$$M = \frac{(A + B) - \alpha}{(A + B) + \alpha} = \frac{A + B}{A} Q_{b\infty} - 1 \quad (7)$$

As in the case of the isotopic exchange reaction, in some of the experiments a plot of the right side of equation 6 *vs.* time did not give an intercept equal to $-\log(1 - M)$. In such cases a method of successive approximations similar to that outlined above was employed.

The apparent equilibrium constant for the reverse reaction is given by

$$K = \frac{k_2}{k_1} = \frac{\left(\frac{A}{B} - Q_{b\infty}\right)(1 - Q_{b\infty})}{Q_{b\infty}^2} \quad (8)$$

Two rate experiments and two additional equilibrium determinations were carried out using the gravimetric procedure outlined earlier.

In experiments at 0° the reaction is so slow that in the limited reaction time imposed by the decay of the Br^{82} it may be assumed that the reaction is irreversible. The integrated rate equation is then

$$\frac{(A - B)k_1t}{2.303} + \log\frac{A}{B} = \log\frac{\frac{A}{B} - Q_b}{1 - Q_b} \quad (9)$$

A method of successive approximations similar to that outlined above was employed where required.

Attainment of equilibrium at 0° required so long a time that it was necessary to employ an analytical procedure not involving Br^{82}. The gravimetric procedure was unsatisfactory because the extent of reaction at equilibrium was very small. The titration procedure described by Tomicek and Jansky[9] was employed and was found to give reliable results for bromide in the presence of chloride.

The results obtained for the reaction of *p*-nitrobenzyl chloride with LiBr are summarized in Tables III and IV.

TABLE III

THE REACTION OF *p*-NITROBENZYL CHLORIDE (A) WITH LITHIUM BROMIDE (B) AT 0°

Run no.	A, mole/l., $\times 10^2$	B, mole/l., $\times 10^3$	k_1, l. mole^{-1} sec.$^{-1}$, $\times 10^6$	K'_e	α
31	4.81	0.269	11.0	..	0.865
32	4.79	0.524	11.4	..	.800
33	5.07	2.69	7.19	..	.590
34	4.94	13.71	6.05	..	.400
35	5.81	30.93	6.17	..	.335
36	10.37	2.52	...	60	.600
37	10.37	12.59	...	74	.408

TABLE IV

THE REACTION OF *p*-NITROBENZYL CHLORIDE (A) WITH LITHIUM BROMIDE (B) AT 30°

Run no.	A, mole/l., $\times 10^2$	B, mole/l., $\times 10^3$	k_1, l. mole^{-1} sec.$^{-1}$, $\times 10^4$	K'_2	α
18	4.89	0.244	6.34	61.2	0.862
19	4.68	0.64	5.37	62.2	.764
20	4.68	1.62	4.30	47.5	.617
21	4.68	3.96	4.52	30.8	.520
22	4.89	4.27	5.00	27.3	.509
23	4.89	10.42	3.70	22.1	.406
24	4.68	16.3	3.28	19.4	.362
25	4.89	30.7	2.83	22.0	.312
26	4.89	33.2	2.92	21.5	.306
27[a]	4.75	63.7	2.50	19.6	.275
28[a]	4.75	65.8	2.30	18.3	.273
29[a]	4.75	63.8	..	19.8	.275
30[a]	4.24	81.7	..	20.5	.262

[a] Gravimetric method.

Discussion of Results

Variation of Rate with Concentration of Lithium Bromide.—It is evident that the rate constant in each series of experiments decreases as the concentration of LiBr increases, indicating that the exchange reactions take place primarily with bromide ions. No conductivity or other data are available for LiBr, in the solvent used here, which permit a direct evaluation of the degree of dissociation. We have therefore estimated the dissociation constant of the ion pair $\mathrm{Li}^+\mathrm{Br}^-$ from Bjerrum's[10] equation

$$\frac{1}{K} = \frac{4\pi N}{1000}\left[\frac{|Z_1Z_2|\epsilon^2}{DkT}\right]^3 Q(b) \quad (10)$$

where $b = |Z_1Z_2|\epsilon^2/aDkT$, Z_1, Z_2 are the valencies of the ions, ϵ is the protonic charge, D is the dielectric constant, k is Boltzmann's constant, T is the absolute temperature, N is Avogadro's number, and a is the distance of closest approach of the ions. $Q(b)$ is a definite integral values of which are given by Harned and Owen.[10] The dielectric constant of the solvent was estimated from the additivity of polarizations to be 24.0 at 0° and 21.0 at 30°. The sum of the crystallographic radii of Li^+ and Br^- is 2.56 Å. If we set $a = 2.5$ Å., we find $Q(b) = 5.3$, $K = 1.3 \times 10^{-3}$ at 0°, and $Q(b) = 6.3$, $K = 1.1 \times 10^{-3}$ at 30°. The dissociation constant is, if we assume unit activity coefficient for $\mathrm{Li}^+\mathrm{Br}^-$

$$K = \frac{\alpha^2 B}{1 - \alpha} y_{\pm}^2 \quad (11)$$

where, as before, B is the concentration of LiBr (strictly $\mathrm{Li}^+\mathrm{Br}^-$) and $y_{\pm}$ is the mean activity coefficient. This latter was evaluated from the Debye–Hückel theory in the form

$$\log f_{\pm} = -\frac{\frac{1.283 \times 10^6}{(DT)^{3/2}}\sqrt{2\alpha B}}{1 + \frac{35.57 \times 10^8 a}{(DT)^{1/2}}\sqrt{2\alpha B}} \approx \log y_{\pm} \quad (12)$$

From equations 11 and 12 α was evaluated as a function of B by successive approximations.

The values obtained in the case of the isotopic exchange are listed in the last column of Table II.

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(9) O. Tomicek and A. Jansky, *Coll. Czech. Chem. Comm.*, **1**, 585 (1929).

(10) N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd edition, Reinhold Publ. Corp., New York, N. Y., 1950, pp. 42, 123.

The application of this procedure in the reaction involving the organic chloride may be objected to on the ground that the LiBr is partially replaced by LiCl, having presumably a lower dissociation constant, so that the ional concentration decreases during the reaction. However, it can be shown that the extent of reaction is so small, because of the large value of K_2', that even with no consideration given to the ional concentration due to the LiCl the change in α is not significant. Furthermore, there was no significant deviation from second-order kinetics in these experiments. The values of α obtained with neglect of the change produced by the reaction are given in the last column of Tables III and IV.

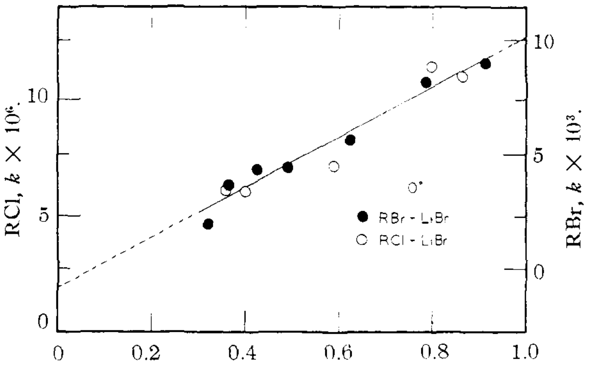

Fig. 2.—The variation of the 0° rate constants with the degree of dissociation of LiBr.

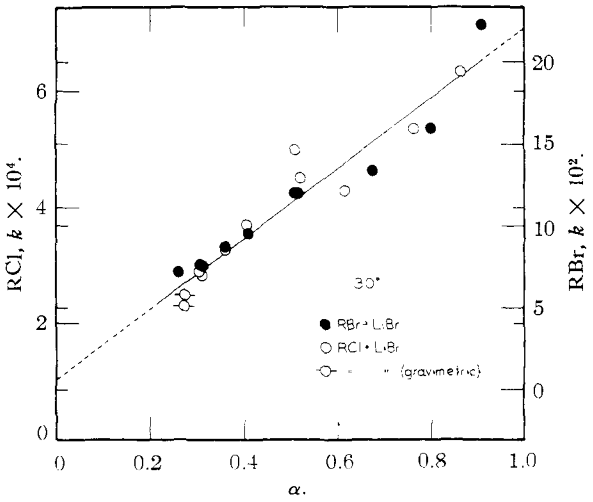

Fig. 3.—The variation of the 30° rate constants with the degree of dissociation of LiBr.

In Figs. 2 and 3 the observed rate constants are plotted as functions of α. Within the accuracy of the data, these plots are linear as expected on the basis of Acree's equation. (Since the observed rate constants were evaluated in terms of concentrations rather than activities, they should be considered as functions of the concentrations of LiBr and Br^-.) The method of least squares leads to the constants given in Table V. The mean deviations of the experimental points from the least squares lines are also listed in the table.

TABLE V

CONSTANTS IN THE ACREE EQUATION

System	Temp., °C.	k_m	k_i	Mean dev.
RBr + LiBr	0	-0.84×10^{-3}	10.12×10^{-3}	$\pm 0.39 \times 10^{-3}$
RBr + LiBr	30	$+0.66 \times 10^{-2}$	22.1×10^{-2}	$.83 \times 10^{-2}$
RCl + LiBr	0	1.92×10^{-6}	12.69×10^{-6}	$.60 \times 10^{-6}$
RCl + LiBr	30	1.06×10^{-4}	7.09×10^{-4}	$.29 \times 10^{-4}$

There is obviously a large measure of arbitrariness in these calculations. Application of the Debye–Hückel theory in a solvent of low dielectric constant at concentrations as high as 0.08 *M* is certainly an inaccurate procedure. Furthermore, considerably different values of a could be assumed without destroying the linear relation between the observed values of k and the calculated values of α. Nevertheless it is interesting that one is actually restricted to a rather narrow range of values of a by the physical requirements of the situation. In the case of the isotopic exchange reaction at 30°, calculations were carried out for three values of a, with the results given in Table VI.

TABLE VI

THE REACTION OF RBr WITH LiBr AT 30°

a, Å.	K, × 10³	k_m, l. mole⁻¹ sec.⁻¹, × 10²	k_i, l. mole⁻¹ sec.⁻¹, × 10²
2.2	0.5	0.3	23.2
2.5	1.1	.7	22.1
2.8	1.8	−3.1	22.0

The value 2.2 Å. for a is considerably less than the sum of the crystallographic radii, and therefore of doubtful significance, while the more reasonable value 2.8 Å. leads to an unacceptable negative value for k_m. The negative value for k_m given in Table V for this reaction at 0° could be made positive by the use of a value for a slightly smaller than 2.5 Å. Table VI illustrates the fact that the values of k_i derived from the present treatment are considerably less susceptible to the assumptions made in the calculations than are the values of k_m.

Activation Quantities.—Since the values of k_i, the specific rate constant for the bromide ion, are not very sensitive to the choice of the parameter a in the Bjerrum and Debye–Hückel equations, it is proper to evaluate the free energies and heats of activation for the reactions involving the ions, with the results given in Table VII. The uncertainties correspond to an uncertainty of 10% in the values of k_i.

TABLE VII

FREE ENERGIES AND HEATS OF ACTIVATION AT 25°

Reaction	$\Delta F^{\ddagger}$, cal./mole	$\Delta H^{\ddagger}$, cal./mole
$RBr + Br^-$	19,000 ± 200	16,300 ± 2000
$RCl + Br^-$	22,600 ± 200	21,500 ± 2000

Equilibrium Constants.—The apparent equilibrium constants (column 5 in Table IV) observed in the reaction between RCl and LiBr at 30° are obviously dependent on concentration. The thermodynamic equilibrium constant of interest is

$$K_2 = \frac{[RCl]_\infty\,[Br^-]_\infty}{[RBr]_\infty\,[Cl^-]_\infty} \cdot \frac{y_\pm\,(LiBr)}{y_\pm\,(LiCl)} \qquad (13)$$

An attempt could be made to evaluate K_2 using the Bjerrum and the Debye–Hückel equations to evaluate the concentrations of the ions and the activity coefficients. However, it is found empirically that K_2'/α is independent of concentration within experimental error, having the value 68 (mean deviation ± 7). One may therefore conclude with sufficient accuracy that $K_2 = 68$.

A similar calculation based on the two rough equilibrium constants determined at 0° is obviously far less significant. The result obtained is that $K_2 \approx 140$ indicating that the reaction of RCl with Br^- is endothermic.

Relative Reactivities.—The constants given in Table V indicate, as has been found in all previously reported cases, that the ion is considerably more reactive than the undissociated salt. The relatively large values for k_m found in the RCl + LiBr system seem to be significantly larger than zero, while in the RBr + LiBr system k_m appears to be indistinguishable from zero. Since the exchange reaction involves a nucleophilic attack on the carbon of the organic halide to which the halogen is bonded, it is entirely reasonable that the charged ion should more readily approach the positive end of the carbon–halogen dipole.

From the equilibrium constants evaluated in the preceding section we may conclude that for the reaction of RBr with Cl^-, k_i is 4.8×10^{-2} at 30° and approximately 1.8×10^{-3} at 0°. Thus at both temperatures the attack of Cl^- on RBr is roughly one-fifth as fast as that of Br^- on RBr, whereas the attack of Br^- on RBr is 310 times as fast as that of Br^- on RCl at 30°, and 800 times as fast at 0°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Effect of Nuclear Substitution on the Rate of Oxidation of α-Phenylethanol by Chromium Trioxide[1a]

BY HAROLD KWART AND PETER S. FRANCIS[1b]

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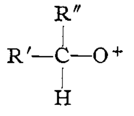
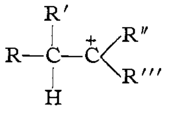
A series of *meta* and *para* substituted α-phenylethanols have been synthesized and their rates of oxidation by hexavalent chromium have been determined under acidic and basic conditions and in benzene without catalysts. Application of the data obtained to the Hammett equation gave negative reaction (ρ) constants varying from -0.37 to -1.01 for a variety of reaction conditions. Evidence is presented which suggests that the ρ constants observed in the acid- and base-catalyzed reactions are the sum of a ρ of oxidation and a ρ due to substituent activity in the initial esterification step of the reaction: $X\text{-}ArRCHOH + CrO_3 \rightleftarrows X\text{-}ArRCHOCrO_3H$.

There have been in recent years several investigations of the mechanism of oxidation of secondary alcohols by chromic acid.[2-4] The results of most of these studies lead to a mechanistic picture closely akin to the elimination reaction.[5] Mosher and coworkers have demonstrated the occurrence of cleavage products in chromate oxidation reactions under common conditions, particularly when the residual cleavage fragment has a tertiary carbon center. This occurrence is strikingly similar to numerous observations of the dehydration reaction, where the carbinol carbon is believed to sustain a large positive charge in the transition state. The suggested analogy of the respective intermediates may be represented as



$$\begin{array}{c} R'' \\ | \\ R'\text{—}C\text{—}O^+ \\ | \\ H \end{array}$$

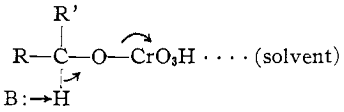
Oxidation



$$\begin{array}{c} R' \\ | \\ R\text{—}C\text{—}\overset{+}{C}\!\left\langle\begin{array}{l} R'' \\ R''' \end{array}\right. \\ | \\ H \end{array}$$

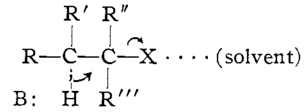
Dehydration (E_1)

Further similarity of the chromate oxidation reaction to the elimination reaction is found in the significant studies of base-catalyzed decomposition of chromate esters as reported by Westheimer and coworkers.[2c,d] Here again the analogous behavior of alcohols (as chromate ester) and halides may be explained in the terms of a common elimination mechanism



$$\begin{array}{l} \quad R' \\ \quad | \\ R\text{—}C\text{—}O\text{—}CrO_3H \cdots (solvent) \\ \quad | \\ B{:}\!\to\! H \end{array}$$

Oxidation



$$\begin{array}{l} \quad\ \ R'\ \ R'' \\ \quad\ \ \ |\quad\ | \\ R\text{—}C\text{—}C\text{—}X \cdots (solvent) \\ \quad\ \ \ |\quad\ | \\ B{:}\ \ H\ \ R''' \end{array}$$

Elimination (E_2)

Cristol and co-workers[6] have observed large and positive Hammett ρ[7] values for the base-catalyzed dehydrochlorination of substituted DDT's, indicating the rate-enhancing effects of electron-withdrawing groups in the E_2 reaction.

The foregoing deductions led to the work reported in this communication. A series of *meta* and *para* substituted α-phenylethanols were prepared and their rates of oxidation by hexavalent chromium were measured under widely varying conditions of solvent and catalysis. The purpose of these experiments was to seek further information concerning the mechanism of the reaction.

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[1] (a) Presented in part before the 126th Meeting of the American Chem. Soc., New York, N. Y., Sept., 1954; (b) Walter G. Karr Fellow of Smith, Kline and French Laboratories, 1953-1954.

[2] (a) F. Westheimer, *et al.*, *J. Chem. Phys.*, **11**, 506 (1943); (b) **17**, 61 (1949); (c) THIS JOURNAL, **73**, 65 (1951); (d) **74**, 4383 (1952); (e) **74**, 4387 (1952).

[3] H. G. Kuivila and W. J. Becker, III, *ibid.*, **74**, 5329 (1952).

[4] (a) W. A. Mosher, *et al.*, *ibid.*, **70**, 2544 (1948); (b) **71**, 286 (1949); (c) **73**, 1302 (1951); (d) **72**, 4452 (1950).

[5] Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[6] (a) S. J. Cristol, THIS JOURNAL, **67**, 1494 (1945); (b) S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, *ibid.*, **74**, 3333 (1952).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.