64. *Exchange Reactions and Electrolytic Dissociation in Non-aqueous Solvents.*

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It has been found that the velocity coefficient for the exchange reaction between lithium bromide and alkyl bromides in anhydrous acetone varies with dilution. The similar reaction between sodium iodide and alkyl iodides in methyl alcohol shows no effect on dilution. These results are correlated with the degree of dissociation deduced from conductivity measurements.

In the course of work on exchange reactions of the type $RBr + Br^{*\prime} \rightleftharpoons RBr^{*} + Br^{\prime}$ (where Br^{*} represents a radioactive bromine atom) it was found, with anhydrous acetone as solvent and lithium bromide as the source of bromine ion, that the bimolecular rate constant increased with decreasing concentration of bromide ion. By using radio-bromine activated in the pile at Harwell, it was possible to carry these measurements into very dilute solutions. The first observations were made with *sec.*-octyl bromide at 65·5° and are shown in Table I. In these measurements a = [RBr] was kept nearly constant at 0·044—0·047 g.-mol./l.; b represents [LiBr] in the same units; k_2 is the bimolecular rate coefficient given by

$$k_2 = \frac{1}{t(a+b)} \log_e \frac{1}{1 - x(1 + b/a)/c} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where the symbols have the meanings used in earlier papers in exchange reactions (*J.*, 1939, 1279).

Table I.

sec.-*Octyl bromide in anhydrous acetone with lithium bromide at* 65·5°.

10^4b	2·61	3·02	8·61	15·7	78·0	89·0	150	250	390
10^3k_2	7·21	7·05	4·94	4·15	2·34	2·64	1·59	1·34	1·14

Dippy's observations (*J.*, 1939, 1386) on the conductivity of lithium bromide in anhydrous acetone at 25° indicate that in this solvent lithium bromide is a weak salt with a dissociation constant of the order of 5×10^{-4}. It therefore seemed possible that the effect was due to a more rapid rate of reaction of the bromide ion than the undissociated lithium bromide molecule [later (below) it appeared that the reaction with the undissociated molecule was too slow to be measurable at the temperatures employed]. A series of rate measurements was then made on *n*-butyl bromide and lithium bromide in acetone at 26·2°. This reaction goes at a convenient rate at this temperature and the results can be compared with the conductivity measurements at 25°. In Table II, b = [LiBr], and α was calculated by using $K_{\text{therm.}} = 5{\cdot}22$ (see Appendix). The ratio $10^3k/\alpha$ is roughly constant over a range of concentrations of nearly 400-fold. It has a mean value of 4·6 with a probable error of ±0·3.

If the value of k is expressed as a linear function of α, the method of least squares gives

$$10^3k = 0{\cdot}12 \pm 0{\cdot}05 + (4{\cdot}41 \pm 0{\cdot}17)\alpha$$

This is a test of the " dual mechanism " hypothesis of Acree and his collaborators (see Robertson and Acree, *J. Amer. Chem. Soc.*, 1915, **37**, 1902). The constant term measures the rate of reaction of the undissociated molecule; it appears to be small, and more accurate data are required to determine whether it is significant or not.

Table II.

Velocity coefficient and degree of dissociation.

(*n*-Butyl bromide + lithium bromide in acetone at 26·2°.)

10^4b.	α.	10^3k.	$10^3k/\alpha$.	10^4b.	α.	10^3k.	$10^3k/\alpha$.	10^4b.	α.	10^3k.	$10^3k/\alpha$.
0·504	0·925	3·93	4·3	3·10	0·741	3·57	4·8	79·4	0·314	1·44	4·6
0·595	0·916	3·69	4·0	4·38	0·696	3·48	5·0	153·4	0·257	1·08	4·2
1·28	0·848	3·99	4·7	17·1	0·497	2·56	5·2	191·0	0·241	1·07	4·4
1·53	0·831	4·13	5·0	22·7	0·457	2·22	4·9				Mean 4·6 ± 0·3
2·49	0·774	3·13	4·0	43·4	0·378	1·84	4·9				

As a contrast with this system, the reaction of ethyl iodide with sodium iodide in methyl alcohol at 25° was investigated. This was made possible by the generous gift of 8-day iodine (^{131}I) by the National Institute for Medical Research.

The conductivity of sodium iodide in methyl alcohol at 25° was measured by Thomas and

Marum (*Z. physikal. Chem.*, 1929, **143**, 191). For complete dissociation the Onsager equation gives

$$\Lambda_0 = (\Lambda + b\sqrt{c})/(1 - a\sqrt{c}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Λ is the conductivity at a concentration c. The numerical coefficients were computed by using dielectric constant $D_{25^\circ} = 32{\cdot}7$ (Abegg and Seitz, *ibid.*, 1899, **29**, 242) and viscosity $\eta_{25^\circ} = 4{\cdot}99 \times 10^{-3}$ (I.C.T.); these gave $a = 0{\cdot}8469$, $b = 166{\cdot}2$. This formula is applied to the data of Thomas and Marum in Table III. From the constancy of Λ_0 (calc.) it is concluded that sodium iodide is completely dissociated in methyl alcohol over the range of concentrations studied.

TABLE III.

Limiting conductivity of sodium iodide in methyl alcohol.

10^5c.	Λ.	Λ_0 (calc.).	10^4c.	Λ.	Λ_0 (calc.).	10^4c.	Λ.	Λ_0 (calc.).
0·220	108·6	109·8	1·979	105·3	108·9	3·301	104·0	108·7
0·396	108·2	109·8	1·979	105·2	108·8	8·909	101·3	109·0
0·540	107·9	109·8	2·699	104·5	108·7	10·66	100·9	109·3
1·320	106·2	109·2						

The small drift in the values of Λ_0 (calc.) is probably due to experimental error; if it is interpreted as an incomplete dissociation, $K_{\text{Ost.}}$ is greater than 10^{-1}, which at $c = 10^{-2}$ gives $\alpha = 0{\cdot}96$.

The kinetic measurements are given in Table IV. It will be seen that the velocity constant does not vary with the concentration of sodium iodide. To test whether this reaction is subject to a salt effect, an experiment was carried out with [EtI] = 0·044M, [NaI] = $4{\cdot}26 \times 10^{-4}$N, and [$NH_4ClO_4$] = 0·059N. This gave $10^5k = 8{\cdot}24$. From the simple form of the Brönsted theory this reaction involving a neutral molecule should not show a salt effect. This conclusion needs modification when charge distribution in the transition state and orientation of solvent dipoles are considered. Experimentally it would appear that at the concentrations concerned in Tables IV and II salt effects are vanishingly small.

TABLE IV.

Sodium iodide and ethyl iodide in methyl alcohol at 25°.

[C_2H_5I] = 0·044 for all solutions; [NaI] = b.)

10^4b	2·50	4·60	4·67	9·06	9·10	17·6	22·0	66·5	232
10^5k	8·19	7·61	8·35	8·05	7·91	8·09	8·49	7·90	7·44
									Mean 8·0

The reaction of *sec.*-octyl bromide in acetone at 65·5° was studied over a wider range of concentrations than those recorded in Table I. The results are represented fairly well by computing α with $K_{\text{therm.}} = 2{\cdot}40 \times 10^{-4}$

$$\log_{10}f^2 = 2\left(23{\cdot}0\alpha c - \frac{4{\cdot}420\sqrt{\alpha c}}{1 + 2{\cdot}116\sqrt{\alpha c}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and then taking $10^3k = 11{\cdot}0\alpha$. The coefficients of $\sqrt{\alpha c}$ in the activity-coefficient expression were computed from the dielectric constant at this temperature. Table V shows how well this represents the observed data.

TABLE V.

Rate of reaction of LiBr *with* sec.*-octyl bromide in acetone at* 65·5°.

[LiBr] × 10^4.	α, calc.	10^3k, calc.	10^3k, obs.	Diff., obs. — calc.	[LiBr] × 10^4.	α, calc.	10^3k, calc.	10^3k, obs.	Diff., obs. — calc.
2·61	0·643	7·07	7·21	+0·14	150·0	0·161	1·77	1·53	−0·24
3·02	0·622	6·84	7·05	+0·21	250	0·130	1·43	1·37	−0·06
8·61	0·460	5·06	4·94	−0·12	250	0·130	1·43	1·27	−0·16
15·7	0·379	4·17	4·15	−0·02	390	0·106	1·17	1·14	−0·03
58·0	0·234	2·57	2·34	−0·23	660	0·0822	0·90	0·83	−0·07
78·0	0·209	2·30	2·34	+0·04	760	0·0773	0·85	0·83	−0·02
89·0	0·198	2·18	2·64	+0·46	1390	0·0573	0·63	0·77	+0·14

This can only be regarded as giving a rough estimate of the degree of dissociation of lithium bromide in acetone at 65·5°, but it is of interest since it enables an idea to be obtained of the order of magnitude of the correction which has to be made to the activation energies previously found for exchange reactions with lithium bromide in this solvent.

Writing $k_{\text{obs.}} = \alpha k$, and if E' and E are respectively the uncorrected and the corrected activation energy, we have then

$$E = E' - \mathrm{d}\ \log_e \alpha/\mathrm{d}(1/T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Values of α at the two temperatures and at $c = 10^{-2}$ and 10^{-1} were computed. These gave

$$\Delta\ \log_e\alpha/\Delta(1/T) = 784 \text{ cals. at } c = 10^{-2} \text{ and } 633 \text{ cals. at } c = 10^{-1}$$

In the concentration range used in most of these exchange reactions the correction is probably less than 1 kcal.

EXPERIMENTAL.

For *sec.*-octyl bromide the rate measurements were made by the method described previously (*J.*, 1939, 1279). For the more volatile butyl bromide and ethyl iodide a modified technique was used. A series of small, sealed ampoules containing known concentrations of reactants was placed in the thermostat and one was removed after a time (t_1) sufficient for it to have attained the desired temperture. Other ampoules were removed at times t_2, t_3, etc. All were treated as follows. The contents of the ampoule, after being cooled in solid carbon dioxide–alcohol, were washed into a flask, cooled in ice-water, and acetone and the alkyl halide removed under vacuum. This required about 20 minutes, and the temperature fell to $-20°$, so that any reaction during this operation could be neglected. The residual lithium bromide (or sodium iodide) was dissolved in a known volume of water, and its radioactivity determined with the solution as an annulus around a thin-walled Geiger–Muller counter connected to a scaling circuit. For the bromide reaction, let a = [RBr], b = [LiBr], x = [RBr*], c = [Br*] initially, then

$$k = \frac{1}{(t_2 - t_1)(a + b)} \log_e \frac{1 - (x_1/c)(1 + b/a)}{1 - (x_2/c)(1 + b/a)}$$

The absolute magnitudes of x and c are not known, but the ratio x/c is given directly by the ratio of the counts, and it is this ratio only which is required. Where necessary correction was made for radioactive decay.

APPENDIX.

Discussion of Conductivity Data.—The first difficulty encountered in the computation of α from conductivity data is the choice of the limiting conductivity Λ_0. We have attempted a detailed analysis of the available data on the following lines.

For a uni-univalent electrolyte in acetone at 25° the Onsager equation may be written

$$\Lambda_{\text{Ons.}} = \Lambda_0 - (1{\cdot}677\Lambda_0 + 338{\cdot}2)\sqrt{\alpha c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the Debye–Hückel approximation for the activity coefficient

$$\log_{10} f \pm = -3{\cdot}732\sqrt{\alpha c}(0{\cdot}1 + 1{\cdot}92\sqrt{\alpha c}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The numerical coefficients in these equations were computed using dielectric constant $E_{25°} = 20{\cdot}98$ (Graffunder, *Ann. Physik*, 1923, **70**, 225), and viscosity $\eta_{25°} = 0{\cdot}00307$ poise (Thorpe and Rodger, *Phil. Trans.*, 1895, *A*, **185**, 397). In equation (6) the distance of closest approach of the ions was taken as 3×10^{-8} cm. (the sum of the crystal radii is $2{\cdot}96 \times 10^{-8}$). Taking $\alpha = \Lambda/\Lambda_{\text{Ons.}}$, we have

$$\Lambda_0 = (\Lambda/\alpha + 338{\cdot}2\sqrt{\alpha c})/(1 - 1{\cdot}677\sqrt{\alpha c}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The only unknown in this equation is α which was computed as follows :

$$\alpha^2 c/(1 - \alpha) = K_{\text{Ost.}} = K_{\text{therm.}}/f^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$K_{\text{therm.}}$ was known to be of the order of 5×10^{-4}, and f^2 can be obtained from equation (6). This equation, however, involves α, so with $K_{\text{therm.}} = 5{\cdot}0 \times 10^{-4}$, an approximate value of α was inserted in (6) to obtain f. This was used to calculate $K_{\text{Ost.}}$ and thence α for a particular value of c. The value of α thus found was inserted in (6) and the series of calculations repeated. This method of successive approximations was continued until the value found for α did not change with further repetitions. The final value of α was inserted in (7) to calculate Λ_0. These calculations were made for the six most dilute solutions measured by Dippy for three values of $10^4 K_{\text{therm.}}$, *viz.*, 4·0, 5·0, 6·0. The results are shown graphically in the figure, where the value of Λ_0 calculated is plotted against $\sqrt{c}$. It would be expected that at high dilutions errors introduced by the wrong choice of $K_{\text{therm.}}$ or by inadequacy of the expression for f would in the first approximation vary linearly with $\sqrt{c}$. The straight lines in the figure were obtained by the method of zero sum from the calculated values of Λ_0; the equations to them are :

$$10^4\,K_{\text{therm.}} = 4{\cdot}0;\ \Lambda_0 = 160{\cdot}3 + 480\sqrt{c};\ \text{mean deviation} \pm 0{\cdot}7$$
$$10^4\,K_{\text{therm.}} = 5{\cdot}0;\ \Delta_0 = 160{\cdot}3 + 64\sqrt{c}\quad ,,\quad ,,\quad \pm 0{\cdot}9$$
$$10^4\,K_{\text{therm.}} = 6{\cdot}0;\ \Lambda_0 = 159{\cdot}5 - 174\sqrt{c}\quad ,,\quad ,,\quad \pm 0{\cdot}8$$

From these results it was concluded that $\Lambda_0 = 160{\cdot}0 \pm 0{\cdot}5$ and that $K_{\text{therm.}}$ is a little greater than $5{\cdot}0 \times 10^{-4}$.

This value of Λ_0 was used to compute $K_{\text{therm.}}$ for a more extended series of concentrations, with the results shown in Table VI. The value of α was calculated by successive approximations in the usual manner from the measured conductivities, and the values of $K_{\text{therm.}}$ in col. 4 were computed by using the values of f^2 given by the expression at the head of the Table. Two observations by Blokker (*Rec. Trav. chim.*, 1935, **54**, 975) are included; these are marked with an asterisk. The other observations are due to Dippy (*loc. cit.*). The principal object of these calculations was to determine α. The values of α calculated for $K_{\text{therm.}} = 5{\cdot}22 \times 10^{-4}$ are given in the last column; it will be seen that they are in good agreement with the values deduced from the conductivities up to concentrations of approximately 2×10^{-2}.

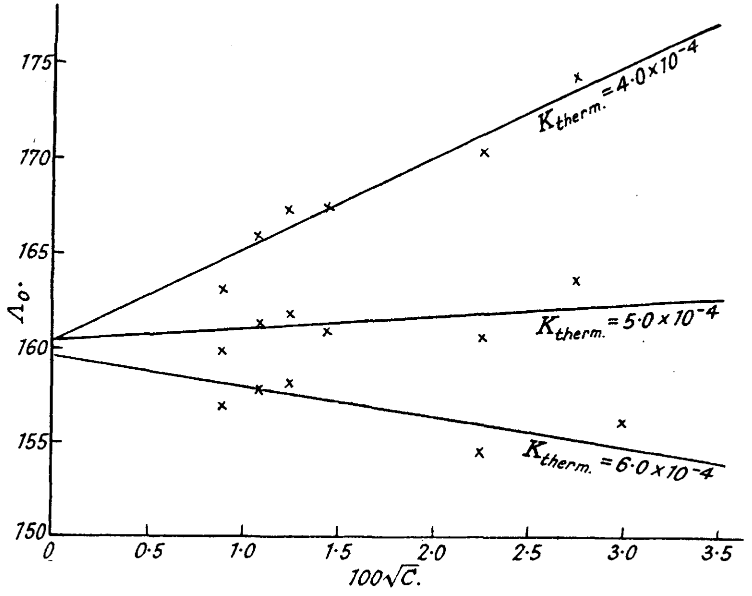

TABLE VI.

Dissociation of lithium bromide in acetone at 25°.

$$E_{\text{Ons.}} = 160{\cdot}0 - 596{\cdot}5\sqrt{\alpha c};\ f^2 = 7{\cdot}464\sqrt{\alpha c}/(1 + 1{\cdot}92/\sqrt{\alpha c}).$$

10^4c.	Λ.	α, cond.	$10^4K_{\text{therm.}}$.	α, calc.	10^4c.	Λ.	α, cond.	$10^4K_{\text{therm.}}$.	α, calc.
0·7663	138·0	0·890	(4·80)	0·897	8·025	88·70	0·604	5·14	0·607
1·148	132·7	0·861	5·18	0·860	20·07	70·4 *	0·499	(5·97)	0·475
1·525	128·0	0·835	5·33	0·832	24·11	62·39	0·444	5·04	0·449
2·057	121·1	0·796	5·13	0·797	33·23	55·51	0·402	4·99	0·409
5·096	100·0	0·671	5·36	0·674	171·7	30·7 *	0·254	5·41	0·250
7·561	91·52	0·622	5·42	0·616					

Mean value of $10^4K_{\text{therm.}}$ (excluding figures in parentheses) = 5·22.

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