

857. *Effect of Solvent Composition on the Kinetics of Reactions between Ions and Dipolar Molecules. Part I.*

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The influence of small amounts of water upon the rate at which iodide ions react with *n*-butyl bromide in acetone has been investigated. Changes in rate observed cannot, however, be satisfactorily explained in terms of changes in dielectric constant alone, even when allowance is made for incomplete dissociation of the electrolyte. A specific interaction between iodide ions and water molecules has, therefore, been postulated and its consequences considered quantitatively.

THE rates of certain reactions between ions and dipolar molecules in acetone solution are known to be appreciably retarded by small amounts of water. In the reaction between bromide ions and *n*-butyl bromide, for example, Le Roux and Sugden¹ found that the rate of bromine exchange in anhydrous acetone was nine times that in acetone containing 5% by volume of water. Further increases in the proportion of water had, however, less effect on the reaction rate, which was reduced by a half when the water content was increased from 5% to 10%. Requisite experimental data for the interpretation of such changes in rate with solvent composition are not available; we therefore studied systematically the effect of small amounts of water, from 0 to 5M, on the kinetics of a typical ion-dipolar molecule reaction, namely, that between iodide ions and *n*-butyl bromide, lithium iodide providing the iodide ions because with this reagent the reacting system remained homogeneous. The reaction was followed chemically by determining the concentration of inorganic iodide. In selected experiments, the total concentration of lithium halides was also determined and found to remain constant for the duration of the exchange reaction, from which we concluded that hydrolyses and eliminations are negligible under our conditions.

Reactions between *n*-alkyl halides and halide ions are of the first order with respect to each reactant.^{1,2,3} The rate of the reversible reaction $\text{Bu}^n\text{Br} + \text{I}^- \rightleftharpoons \text{Bu}^n\text{I} + \text{Br}^-$ is therefore

$$dx/dt = k_2(c - x)(d - x) - k_{-2}x^2 \quad \dots \quad (1)$$

where k_2 and k_{-2} are the rate constants for the forward and backward reactions, c and d are the initial concentrations of lithium iodide and *n*-butyl bromide, and x is the concentration of lithium bromide at time t . On integration eqn. (1) gives

$$k_2t = \frac{2.303}{2B(K^{-1} - 1)} \log_{10} \frac{1 + x/(B - A)}{1 - x/(B + A)} \quad \dots \quad (2)$$

Where $A = (d + c)/[2(K^{-1} - 1)]$, $B = [(d - c)^2 + 4dc/K]^{1/2}/[2(K^{-1} - 1)]$, and $K = k_2/k_{-2} = x_{\infty}^2/[(c - x_{\infty})(d - x_{\infty})]$. Second-order rate constants, calculated by means of eqn. (2) from measurements at three temperatures, are summarised in Table 1; they have been corrected for thermal expansion of the solvent. Concentrations of water and of lithium iodide quoted in Table 1 have been similarly corrected and the dielectric constants ϵ given have been interpolated from Åkerlöf's data.⁴ The initial concentration of *n*-butyl bromide was 0.035M.

Most theoretical treatments of reactions between negative ions and dipolar molecules predict that $\log k_2$ will decrease linearly as $1/\epsilon$ decreases.^{5,6} The way in which $\log k_2$ varies with $1/\epsilon$ for the reaction of iodide ions with *n*-butyl bromide is illustrated in Fig. 1, the same

¹ Le Roux and Sugden, *J.*, 1939, 1279.

² Le Roux and Swart, *J.*, 1956, 2110.

³ Moelwyn-Hughes, *Trans. Faraday Soc.*, 1949, 45, 167.

⁴ Åkerlöf, *J. Amer. Chem. Soc.*, 1932, 54, 4125.

⁵ Laidler and Landskroener, *Trans. Faraday Soc.*, 1956, 52, 200.

⁶ Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 2nd edn., p. 120.

pattern being observed at different temperatures and with different initial concentrations of electrolyte. It is seen that for water concentrations exceeding 2M, the variation of $\log k_2$ with $1/\epsilon$ is almost linear, although no such simple relation is shown at water concentrations less than this. Kacser⁷ has, however, developed a theory which takes into

TABLE I. *Rate constants (k_2 in l. mole⁻¹ sec.⁻¹) calculated from eqn. (2).*

[H ₂ O]	10 ² c	10 ³ k ₂	ϵ	[H ₂ O]	10 ² c	10 ³ k ₂	ϵ
Temp. = 19.80°							
0	1.76	1.016	19.58	0.496	1.77	0.545	20.14
0.071	1.76	0.873	19.66	0.922	1.77	0.426	20.62
0.082	1.76	0.850	19.67	1.86	1.78	0.283	21.68
Temp. = 30.35°							
0	1.69	3.28	18.64	0.483	1.67	1.69	19.16
0.015	1.68	3.22	18.66	0.928	1.67	1.29	19.63
0.061	1.69	2.84	18.70	1.86	1.67	0.842	20.63
0.096	1.64	2.65	18.74	2.98	1.68	0.638	21.80
0.246	1.67	2.15	18.90	4.96	1.70	0.434	23.88
Temp. = 40.03°							
0	1.69	8.74	17.80	0.906	1.71	3.44	18.74
0.084	1.69	7.28	17.89	1.84	1.67	2.29	19.71
0.247	1.70	5.61	18.06	2.94	1.69	1.69	20.83
0.472	1.70	4.52	18.29	4.84	1.72	1.13	22.79
0	0.802	9.59	17.80	0.481	0.789	5.25	18.30
0.091	0.789	7.56	17.89	0.945	0.797	3.89	18.78
0.254	0.792	6.51	18.06	1.82	0.811	2.64	19.70

account the angular dependence of the electrostatic energy of interaction between an ion and a dipole. This theory requires that $\log(k_2/\epsilon)$ shall be inversely proportional to the dielectric constant, but this is also unsuccessful in dealing with our rate constants.

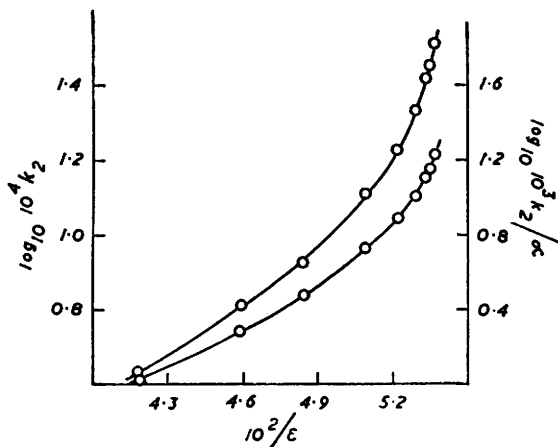


FIG. 1. *Plots of $\log 10^4 k_2$ (upper curve) and $\log 10^3 k_2 / \epsilon$ (lower curve) against the reciprocal of the dielectric constant for 30.35°.*

However, theoretical relations are usually deduced by assuming that the reacting system is infinitely dilute, so that the failure to explain our kinetic results in terms of a particular theory might result from the finite concentrations used. Now the specific rate of an ion-dipolar molecule reaction generally increases with increasing dilution^{8,9} and the increase in rate is usually explained by assuming that, at finite concentrations, the electrolyte is not completely dissociated, the undissociated molecules reacting at a rate negligible compared with that of the negative ions. Requisite conductances for the calculation of

⁷ Kacser, *J. Phys. Chem.*, 1952, **56**, 1101.

⁸ de la Mare, *J.*, 1955, 3180; Fowden, Hughes, and Ingold, *ibid.*, p. 3187; and other papers in this series.

⁹ Evans and Sugden, *J.*, 1949, 270.

the degree of dissociation α of lithium iodide in mixtures of acetone and water are not available, but calculations by Evans and Sugden⁹ for lithium bromide in dry acetone suggest that in this solvent the proportion of lithium iodide dissociated into ions is likely to be small. If the remainder of the electrolyte is in the form of ion pairs then a dissociation constant K_d for the equilibrium between free ions and ion pairs can be calculated by means of

$$-\log_{10} K_d = 13.547 - 3 \log_{10} (\epsilon T) + \log_{10} Q(b) \quad \dots \quad (3)$$

where $b = 10^4(6.02/\epsilon T)$ and $Q(b) = \int_2^b e^2 q^{-4} dq$, numerical values of which can be obtained from tables.¹⁰ Dissociation constants have been calculated at two temperatures for the range of dielectric constants covered in our experiments, and from these dissociation constants, shown in Table 2, the corresponding degrees of dissociation of the electrolyte have been obtained. Experimental rate constants corrected for the effect of ion association by dividing each of them by the appropriate value of α are also shown in Table 2. The plot $\log k_2/\alpha$ against $1/\epsilon$ (Fig. 1) is not straight, however, so that ion association is not solely responsible for the absence of the linear relation between $\log k_2$ and $1/\epsilon$ required by the theories.

TABLE 2. *Dissociation constants of lithium iodide calculated from eqn. (3), and rate constants corrected for ion-association.*

$T = 303.5^\circ \text{ K}$									
ϵ	18.64	18.70	18.74	18.90	19.16	19.63	20.63	21.80	23.88
$10^4 K_d$	8.04	8.26	8.41	9.10	10.19	12.56	18.2	26.8	48.0
$10^3 k_2/\alpha$	16.73	14.34	13.12	10.34	7.75	5.40	3.01	1.95	1.061
$T = 313.2^\circ \text{ K}$									
ϵ	17.80	17.89	18.06	18.29	18.74	19.71	20.83	22.79	
$10^4 K_d$	7.05	7.40	8.04	8.95	11.02	16.33	24.2	43.7	
$10^3 k_2/\alpha$	47.5	38.7	28.8	22.05	15.36	8.48	5.38	2.87	

Many ion-dipolar molecule reactions are subject also to a kinetic salt effect¹¹ which arises because the expressions for the activity coefficients of the reactants and for the activity coefficient of the transition state contain terms which are proportional to the ionic strength and which are not necessarily equal. In such cases $\log k_2$ may also be proportional to the ionic strength, the proportionality constant being a function of the dielectric constant of the solvent. Laidler and Landskroener⁵ consider that this proportionality constant should be inversely proportional to the dielectric constant, so that such a salt effect cannot explain the failure of the specific rate of the reaction studied to change with the dielectric constant in the way expected from theory. In any case, when rate constants, obtained with different initial electrolyte concentrations and corrected for ion association, are compared, the kinetic salt effect appears to be small.

The difficulty of accounting for the effect of small amounts of water upon the specific rate of the reaction between iodide ions and *n*-butyl bromide might be resolved by assuming water to play a more direct part in the reaction than simply increasing the dielectric constant. Suppose, for example, that an equilibrium $\text{I}^- + \text{H}_2\text{O} \rightleftharpoons (\text{I}, \text{H}_2\text{O})^-$ is rapidly established. For our purpose the nature of the interaction need not be specified, although in a medium having a dielectric constant of 20, the electrostatic energy of interaction between an iodide ion and a water molecule will be about 1500 cal. mole⁻¹. This should be sufficiently large for the entity $(\text{I}, \text{H}_2\text{O})^-$, if it exists, to persist through a number of collisions with other solvent molecules at ordinary temperatures. If, in a medium of dielectric constant ϵ_0 , the specific rates with which I^- and $(\text{I}, \text{H}_2\text{O})^-$ react with *n*-butyl bromide are k_0 and k_∞ respectively then, when the concentration of water is s , the rate

¹⁰ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co. New York, 2nd edn., p. 190.

¹¹ Ref. 6, p. 130.

concentration of water. Most of the points lie close to the same straight line in satisfactory agreement with the requirements of the equilibrium postulated above, although in view of the assumptions this agreement cannot be taken as establishing the correctness of the initial hypothesis. Deviations from linearity are, however, observed at the highest water concentrations, but these may be due to the increasing sensitivity of $(k_0 - k_s)/(k_s - k_\infty)$ to errors in k_s as the value of the latter approaches that of k_∞ .

TABLE 3. *Values of k_s calculated by means of eqn. (5).*

Temp. = 30.35°. $m = 43.5$. $10^3 k_0 = 3.28$. $10^3 k_\infty = 1.41$.									
[H ₂ O]	0	0.061	0.096	0.246	0.483	0.928	1.86	2.98	4.96
$10^3 k_s$	3.28	2.89	2.73	2.32	1.96	1.69	1.42	1.39	1.41
Temp. = 40.03°. $m = 44.5$. $10^3 k_0 = 8.74$. $10^3 k_\infty = 3.97$.									
[H ₂ O]	0	0.084	0.247	0.472	0.906	1.84	2.94	4.84	
$10^3 k_s$	8.74	7.50	6.10	5.28	4.59	4.00	3.91	3.99	

The correction for ion association has been omitted because of the uncertainties involved in the evaluation of the dissociation constants given in Table 2. Nevertheless, had this correction been applied then the result obtained would have been similar to that illustrated in Fig. 2 for the uncorrected rate constants.

The Arrhenius parameters shown in Table 4 were calculated from the experimental rate constants (Table 1) by the method of least squares. Apart from an occasional irregularity, the pre-exponential factor A_2 decreases continuously as the water concentration is increased, although it is most sensitive to changes in water concentration when the

TABLE 4. *Parameters of the equation $k_2 = A_2 \exp(-E_A/RT)$ (with A_2 in l. mole⁻¹ sec.⁻¹, and E_A in kcal. mole⁻¹).*

[H ₂ O] *	0	0.086	0.246	0.484	0.919	1.86	2.96	4.90
$\log_{10} A_2$	11.5	11.3	10.8	11.0	10.7	10.5	10.5	10.1
E_A	19.4	19.2	18.7	19.1	18.8	18.9	19.0	18.7

* Average values, calculated from water concentrations appropriate to the rate constants used in evaluating the Arrhenius parameters concerned.

solvent is most nearly dry. An increase in water concentration has, however, little effect on the energy of activation E_A , the maximum change in which is 700 cal. mole⁻¹.

EXPERIMENTAL

Lithium iodide was crystallised from water and dried by heating *in vacuo* over phosphoric oxide for 1 hr. at 60° and then at 120° until no further loss in weight occurred. *n*-Butyl bromide was washed with acid, then alkali, and finally with water. It was dried over phosphoric oxide and then fractionated through a column packed with glass helices; b. p. 101.2—101.8°/760 mm., n_D^{15} 1.4423.

"AnalaR" acetone was refluxed with solid potassium permanganate and lime for several hours, then distilled and kept over anhydrous potassium carbonate for some days. It was then fractionated through a column packed with metal-gauze rings, the fraction of b. p. 56.0—56.2° being collected. Sufficient of this acetone for a kinetic run was distilled under reduced pressure over phosphoric oxide¹⁴ to remove the last traces of water, the final concentration of which was about 0.005M (Karl Fischer). In all subsequent operations the solvent was protected from the atmosphere by guard tubes containing phosphoric oxide and silica gel.

Solutions of known concentration were prepared by distilling sufficient dried acetone into two calibrated vessels, each of which contained a weighed amount of one reactant and, where appropriate, a known weight of water. 5 ml. aliquot portions of each reactant solution were transferred with an automatic pipette into a series of glass bulbs at -80°. The bulbs were sealed off after they had been charged with both solutions and were kept at -80° until required. To carry out a kinetic run, sufficient bulbs were transferred simultaneously to a thermostat,

¹⁴ Timmermans and Gillo, *Roczniki Chem.*, 1938, 18, 812.

each bulb being shaken several times during about 2 min. to ensure that the contents had reached thermostat temperature. To provide a time zero, two bulbs were then withdrawn and cooled rapidly to -80° to stop the reaction. The concentration of iodide ion present in each was determined by Lang's iodine cyanide method by use of 0.005M-potassium iodate. Further bulbs were withdrawn after suitable intervals until equilibrium had been attained; these were treated similarly. In some cases the total halide-ion concentration was determined instead, by means of Volhard's method with 0.02N-ammonium thiocyanate.

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