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

By E. A. S. Cavell and J. A. Speed.

The rate of exchange of radioactive iodine between n-butyl iodide and sodium iodide has been measured in acetone containing various small concentrations of water. By use of carrier-free sodium radio-iodide as the only source of ions, it has been possible to study the kinetics of the reaction under conditions where the effect of ion association can be neglected. Changes of reaction rate with solvent composition have been interpreted in terms of changes in dielectric constant, and of a specific interaction between iodide ions and water molecules. The effect of various concentrations of potassium iodide on the rate of the iodine exchange has also been investigated and the results obtained have been discussed in terms of the formation of ion pairs.

In solvents of low dielectric constant the kinetics of reactions between ions and dipolar molecules are often complicated by ion association, a fact which is usually neglected in the derivation of the integrated rate equations for such reactions. As a result, rate constants calculated by using these equations tend to increase in value when the initial concentration of the electrolyte used is decreased. The effect of ion association on the kinetics of the reaction of iodide ions with n-butyl bromide, and also the possibility of a kinetic salt effect in this reaction, have been discussed in Part I. It was there concluded that failure of the rate of this reaction to change with dielectric constant of the solvent in the way expected theoretically could not be attributed to either effect.[1] As far as ion association is concerned, however, the validity of this conclusion depended upon the certainty with which the dissociation constant of the electrolyte in a series of mixtures of acetone and water could be calculated theoretically. Such calculations necessarily involve a number of assumptions and approximations, so that in the present work we have tried to justify this conclusion experimentally.

Swart and le Roux [2] have pointed out that, by using the appropriate carrier-free radioactive isotope, it is possible to study the kinetics of halogen exchanges under conditions in which ionic concentrations are negligible, thus avoiding the necessity of correcting rate constants for ion association altogether. We have therefore studied the effect of small amounts of water, from 0 to 5M, on the rate in acetone of the exchange reaction $^*\mathrm{I}^- + \mathrm{Bu^nI} \rightleftharpoons \mathrm{I}^- + \mathrm{Bu^{n*}I}$, using carrier-free sodium radio-iodide as the only source of iodide ions. Rate constants k_2 obtained from these experiments are given in Table 1; they were calculated by means of the equation

Table 1. *Rate constants (k_2 in l. mole^{-1} sec.$^{-1}$) obtained with sodium radio-iodide alone and calculated by means of equation* (1).

$[\mathrm{Bu^nI}]_0$ = 0·030—0·035M. Temp. = 19·71°.

$[H_2O]$	ε	10^2k_2	$[H_2O]$	ε	10^2k_2	$[H_2O]$	ε	10^2k_2
0	19·56	4·31	0·502	20·13	2·14	2·03	21·87	0·786
0	19·56	4·38	0·756	20·42	2·04	2·48	22·38	0·611
0	19·56	4·08	0·828	20·50	1·76	3·03	23·00	0·546
0·079	19·65	3·40	1·00	20·70	1·47	4·03	24·14	0·420
0·252	19·85	2·84	1·55	21·32	1·01	4·98	25·22	0·325
0·388	20·00	2·51	2·01	21·84	0·825			

$$k_2t = -(2{\cdot}303/a)\log_{10}(1 - x/c) \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the total concentration of n-butyl iodide and x/c is the ratio of the radioactivity associated with the butyl iodide at time t to the total radioactivity. For the experiments

---

* Part I, *J.*, 1958, 4217.

[1] Cavell, *J.*, 1958, 4217.

[2] Swart and le Roux, *J.*, 1956, 2110.

considered here, equation (1) is sufficiently accurate for evaluating rate constants, because in all cases kinetic measurements were confined to a period of less than 19 hr.,[2] *i.e.*, 1/10th half-life of ^{131}I. Dielectric constants ε of acetone–water mixtures, also given in Table 1, have been interpolated from Åkerlof's data.[3]

In Fig. 1 values of log k_2 obtained for the reaction between iodide ions and n-butyl iodide with carrier-free sodium radio-iodide as the only source of iodide ions have been plotted against the reciprocal of the dielectric constant of the solvent. Essentially the same variation of log k_2 with $1/\varepsilon$ as that illustrated in Fig. 1 has also been observed (but in use of finite electrolyte concentrations) for the reaction of iodide ions with n-butyl bromide.[1] It seems, therefore, that the view expressed in Part I, concerning the latter reaction, namely, that the absence of a linear relation between log k_2 and $1/\varepsilon$ at water concentrations of less than 2M was not due to the finite concentrations of electrolyte used, was justified since a similar deviation from linearity is here observed in a closely related reaction when ionic concentrations are negligibly small.

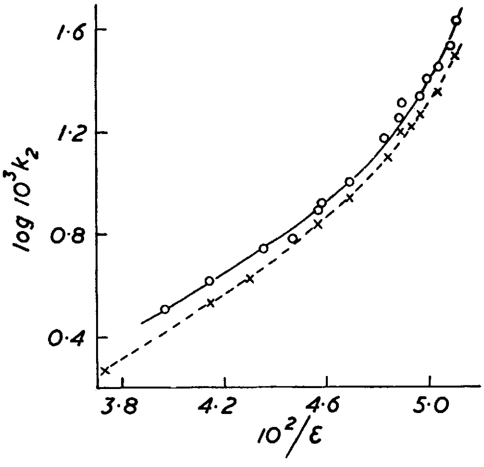

FIG. 1. *Plots of* $\log_{10} 10^3k_2$ *against reciprocal of the dielectric constant.*

○ *Rate constants obtained with carrier-free sodium radio-iodide alone.*
× *Rate constants obtained with* 0·015M-*potassium iodide present.*

Following the suggestion made in Part I, we assume that the observed departure from the linearity predicted theoretically is due to an equilibrium $I^- + H_2O \rightleftharpoons (I,H_2O)^-$. However, before experimental rate constants can be used to test the implications of this hypothesis, they must be corrected to a standard dielectric constant. This has been done for the rate constants k_2 given in Table 1 by means of the equation

$$\log k_s = \log k_2 + m(1/\varepsilon_0 - 1/\varepsilon_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where m is the slope of the linear portion of the appropriate log k_2–$1/\varepsilon$ curve (Fig. 1), ε_0 is the dielectric constant of dry acetone, and ε_s that of the solvent mixture to which k_2 refers. The assumptions and approximations involved in this method of correction have been discussed previously.[1] Values of corrected rate constants k_s for different concentrations of water are recorded in Table 2.

TABLE 2. *Values of* k_s *calculated by means of equation* (2) *from rate constants* k_2 *given in Table* 1.

$m = 56{\cdot}5$. $10^2k_0 = 4{\cdot}26$ l. mole^{-1} sec.$^{-1}$

$[H_2O]$	0	0·079	0·252	0·388	0·502	0·756	0·828	1·00
10^2k_s	4·26	3·50	3·13	2·90	2·58	2·41	2·39	2·12
$[H_2O]$	1·55	2·01	2·03	2·48	3·03	4·03	4·98	
10^2k_s	1·99	1·65	1·59	1·41	1·48	1·48	1·49	

---

[3] Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

Now, the equilibrium postulated above requires the quotient $(k_0 - k_s)/(k_s - k_\infty)$ to be directly proportional to the concentration of water, provided that this is large compared with the total iodide-ion concentration; k_0 and k_∞ are the specific rates at which I^- and $(I,H_2O)^-$ react with n-butyl iodide in a solvent of dielectric constant ε_0. However, in order to test our hypothesis we prefer a plot of $(k_0 - k_s)/[H_2O]$ against k_s, as shown in Fig. 2, to the equivalent plot of $(k_0 - k_s)/(k_s - k_\infty)$ against water concentration, because the first procedure requires one fewer parameter. Most of the points in Fig. 2 lie close to the same straight line, in satisfactory agreement with the requirements of the equilibrium postulated above. Up to water concentrations of about 1M, an error of 5% in k_s would be more than sufficient, in most cases, to account for the divergence of the points from the straight line, although above this concentration, deviations are more pronounced.

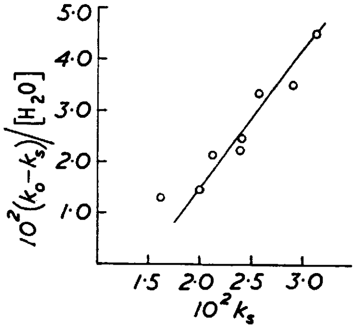

FIG. 2. *Plot of* $(k_0 - k_s)/[H_2O]$ *against* k_s *for data given in Table* 2.

The effect of small amounts of water on the rate of the reaction $*I^- + Bu^nI \rightleftharpoons I^- + Bu^n{*}I$ in acetone solution has also been investigated in the presence of various concentrations of potassium iodide. Rate constants obtained from these experiments are summarised in Table 3; they were calculated by means of the equation

$$k_2t = -[2\cdot303/(a + b)] \log_{10} [1 - (x/c)(1 + b/a)] \qquad . \quad . \quad . \quad (3)$$

where b is the concentration of potassium iodide, the other symbols having the same significance as for equation (1). The results given in Table 3 show that, for the same

TABLE 3. *Rate constants (k_2 in l. mole^{-1} sec.$^{-1}$) obtained with various concentrations of potassium iodide and calculated by means of equation* (3).

$[Bu^nI]_0$ = 0·030—0·035M. Temp. = 19·71°.

$[H_2O]$	10^2k_2	$[H_2O]$	10^2k_2	$[H_2O]$	10^2k_2	$[H_2O]$	10^2k_2
			[KI] ~1·5 × 10^{-2}M				
0	3·05	0·651	1·67	2·00	0·691	4·05	0·345
0	3·13	0·776	1·59	2·07	0·703	6·39	0·187
0·251	2·25	0·979	1·25	3·25	0·432	8·38	0·137
0·490	1·82	1·55	0·896	3·96	0·352		
			[KI] ~1·6 × 10^{-3}M				
0	3·53	0·481	2·22	1·11	1·40	3·85	0·398
0	3·61	0·610	1·84	1·98	0·815	6·00	0·229
0·200	2·72	0·801	1·72	3·20	0·472	8·31	0·151
			[KI ~3·3 × 10^{-4}M				
0	4·02						
			[KI] ~9 × 10^{-5}M				
0	4·20	0·523	2·50	1·00	1·54	3·37	0·475
0·242	2·99	0·700	2·00	2·05	0·762	4·01	0·374
0·401	2·65	0·823	1·84	2·07	0·782	5·04	0·296

solvent composition, rate constants evaluated by using equation (3) usually decrease in value as the concentration of potassium iodide is increased. However, some of the results for 9 × 10^{-5}M-potassium iodide are slightly larger than the corresponding rate constants obtained when sodium radio-iodide was used alone (Table 1), although in all such cases the difference is less than 10%, so these anomalous results may be due to experimental error.

The effect on the rate constant of a given increase in concentration of potassium iodide is most pronounced in dry acetone, as is to be expected if the effect is a result of ion association. However, these rate constants can be corrected for incomplete dissociation of the salt, because for dry acetone the requisite data are available. In this solvent, Reynolds and Kraus[4] found that at 25° the dissociation constant of potassium iodide was 8·02 × 10^{-3}, from which by means of Fuoss's equation[5] a value of 8·30 × 10^{-3} has been calculated for 19·71°, the temperature at which our kinetic measurements were made. It is from this value that degrees of dissociation α, given in Table 4 together with corrected rate constants k_2/α, have been calculated by using the method given by Evans and Sugden.[6] The values of k_2/α obtained are in fairly good agreement with the average value of the rate constant found when carrier-free sodium radio-iodide was used alone, namely, (4·26 ± 0·12) × 10^{-2} l. mole^{-1} sec.$^{-1}$. It seems probable therefore that the variation of rate constant with electrolyte concentration observed in our experiments is due principally to incomplete dissociation of the salt, a conclusion which was also reached by Evans and Sugden[6] for the reaction between lithium bromide and n-butyl bromide in dry acetone.

TABLE 4. *Degrees of dissociation of potassium iodide in dry acetone and rate constants corrected for ion association.*

[KI] (M)	1·5 × 10^{-2}	1·6 × 10^{-3}	3·3 × 10^{-4}	9 × 10^{-5}
α	0·770	0·917	0·973	0·993
$10^2k_2/\alpha$	4·01	3·89	4·13	4·23

Requisite experimental data for calculating degrees of dissociation of potassium iodide in various mixtures of acetone and water are not available. No attempt has therefore been made to correct rate constants obtained in aqueous acetone as solvent for the effect of ion association. The kinetic results given in Table 3, however, indicate that the addition of water to acetone has the effect of increasing the degree of dissociation of the salt. Part, at least, of this increased dissociation may be attributed to the increase in dielectric constant. Recent theoretical treatments of ion-pair formation[5,7] require the dissociation constant K_d of an electrolyte to be proportional to exp $(-b)$, where the function b is inversely proportional to the dielectric constant of the solvent. As the reciprocal of the dielectric constant decreases, therefore, log K_d should increase linearly, the degree of dissociation increasing accordingly. However, if the addition of water also produces a new ionic species, such as that postulated above to account for the variation of reaction rate with solvent composition, then the increase in dissociation may well be different from that expected from the change in dielectric constant alone.

In spite of concomitant changes in degree of dissociation of the salt, the form of the curve connecting dielectric constant with the rate of the iodine exchange is not appreciably affected by the concentration of potassium iodide present. For each of the three concentrations of this electrolyte examined, the variation of log k_2 with $1/\varepsilon$ is essentially the same as that illustrated in Fig. 1, the water concentration above which a linear relation between log k_2 and $1/\varepsilon$ is observed being approximately independent of the concentration of potassium iodide present. After correction to a standard dielectric constant, the kinetic data for each concentration of potassium iodide given in Table 3 have been examined

---

[4] Reynolds and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709.

[5] Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 3163.

[6] Evans and Sugden, *J.*, 1949, 270.

[7] Denison and Ramsay, *J. Amer. Chem. Soc.*, 1955, **77**, 2615; Gilkerson, *J. Chem. Phys.*, 1956, **25**, 1199.

in terms of the postulated equilibrium $I^- + H_2O \rightleftharpoons (I,H_2O)^-$ as described above, and the results obtained were similar to that shown in Fig. 2.

EXPERIMENTAL

Potassium iodide was crystallised from water and dried by heating it *in vacuo* over phosphoric oxide at 100° for 3 hr. n-Butyl iodide was purified as described by Vogel.[8] It was dried (P_2O_5) and then fractionated through a column packed with glass helices; it had b. p. 130·2—130·6°/760 mm. Purified n-butyl iodide was stored in the dark over mercury and redistilled just before use. Acetone was purified as described previously.[1]

Radioactive iodine-131 was obtained as a solution of carrier-free sodium iodide in water. This was evaporated to dryness, and the residue extracted several times with dry acetone, the combined extracts being filtered and kept as a stock solution.

To carry out a kinetic run, a solution in acetone of n-butyl iodide of known concentration and one containing a known amount of radioactivity and, where appropriate, known concentrations of potassium iodide and water, were prepared at thermostat temperature. Equal volumes of each of these solutions were then transferred to a stoppered flask, the moment of mixing being taken as the time-zero. After suitable intervals, aliquot parts were withdrawn and run into a mixture of benzene and 3% aqueous potassium sulphate solution, the presence of this salt facilitating separation of the two layers. The benzene layer was washed once with potassium sulphate solution, and its activity determined in a liquid-immersion type Geiger–Muller counter tube. In several cases the corresponding aqueous layer was evaporated to dryness, the residue extracted with potassium iodide solution, and the activity of the resulting solution measured. Values of rate constants calculated from the two sets of measurements usually agreed to within about 5%.

Measurements of total radioactivity (c) were made by using the acetone solution of the reaction mixture, whereas measurements of the activity associated with the n-butyl iodide (x) were made on benzene extracts. Values of the ratio x/c were therefore multiplied by a correction factor f, which was determined experimentally as described by le Roux and Swart.[9] In addition, all activity measurements within a given experiment were corrected to the same arbitrary time in order to allow for variations in the amount of radioactive decay undergone by individual samples.

Within a given experiment the mean deviation of individual rate constants from the mean value of the rate constant was about 5%, whilst mean values of rate constants obtained from independent experiments did not differ by more than 10%. It was shown by using the sealed-bulb technique described in Part I that no significant absorption of water by the reaction mixture occurred during the course of the reaction. Rate constants obtained by the two methods agreed within the limits of experimental error.

We thank the Chemical Society for a grant to purchase the radioactive isotope, and the University of Southampton for a research scholarship to one of us (J. A. S.).

THE UNIVERSITY, SOUTHAMPTON. [*Received, October 2nd*, 1959.]

---

[8] Vogel, *J.*, 1943, 636.
[9] le Roux and Swart, *J.*, 1955, 1475.