42. Effect of Solvent Composition on the Kinetics of Reactions between Ions and Dipolar Molecules. Part III.[1]

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A kinetic study of the exchange of radioactive iodine between sodium iodide and n-butyl iodide has been made in a series of mixtures of methyl cyanide and methanol as solvents, with carrier-free sodium radio-iodide providing all the iodide ions present initially. The reaction rate falls as the concentration of methanol is increased and this reduction in rate has been discussed in terms of a specific interaction between iodide ions and methanol molecules: changes in dielectric constant are small and have been neglected.

It has also been found, by the use of various phenols in place of methanol, that the capacity of a hydroxylic compound to retard the iodine exchange reaction increases with its strength as an acid. However, the integrated intensity of the infrared absorption band associated with the O–H stretching vibration appears to be a better measure than its acid strength of the capacity of a phenol to retard iodine exchange.

Spectroscopic evidence for hydrogen-bonding between anions and hydroxylic molecules is discussed briefly.

IN previous investigations into the effect of solvent composition on the kinetics of reactions between ions and dipolar molecules,[1,2] we have been concerned with the effect of water on the rate in acetone solution of reactions between iodide ions and n-butyl halides. Reductions in the rates of these reactions produced by progressively increasing the water concentration cannot be satisfactorily ascribed to changes in dielectric constant alone. We have, therefore, postulated the existence of two kinetically distinguishable ionic species, designated as I^- and $(I,H_2O)^-$, in the solution, the relative proportions of the two species being assumed to depend on the concentration of water present. Quantitative interpretation of experimental kinetic data in terms of this hypothesis was, of course, only possible after the rate constants obtained with various water concentrations had been corrected for differences in dielectric constant of the solvent. The method by which this correction was made was open to a number of objections, so that in the present investigation we have tried to avoid the need for such a correction by using mixtures of methyl cyanide ($\varepsilon = 35{\cdot}9$ at 30°) [3] and methanol ($\varepsilon = 31{\cdot}6$ at 30°) [3] as solvents in our kinetic experiments, methanol and water being expected to interact similarly with iodide ions.

Rate measurements on the isotopic exchange reaction $^*I^- + Bu^nI \rightleftharpoons I^- + Bu^{n*}I$ have been made over the entire range of solvent compositions from pure methyl cyanide to pure methanol. Carrier-free sodium radio-iodide provided all the iodide ions present

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[1] Part II, Cavell and Speed, *J.*, 1960, 1453.

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

[3] Simmonds, personal communication.

initially, so that rate constants did not require correction for ion association.[4] In most of our experiments, kinetic observations were confined to periods of less than 19 hr., *i.e.*, less than one-tenth half-life of ^{131}I. Eqn. (1), in which x is the radioactivity associated with n-butyl iodide at time t, c is the total radioactivity present, and a is the concentration of n-butyl iodide, was therefore used to obtain the rate constants k_2, which were usually evaluated graphically.

$$k_2 t = -(2{\cdot}303/a) \log_{10} (1 - x/c) \qquad . \; . \; . \; . \; . \; . \; . \quad (1)$$

In those experiments where k_2 was less than 10^{-4} l. mole^{-1} sec.$^{-1}$, measurements were necessarily made over longer periods than 19 hr. In such cases, the relevant rate constants were evaluated by means of eqn. (2), which allows for radioactive decay,[4] λ being the decay constant of ^{131}I, *viz.*, $1{\cdot}002 \times 10^{-6}$ sec.$^{-1}$. Rate constants k_2 calculated from kinetic

$$k_2(1 - e^{-\lambda t}) = -(2{\cdot}303\lambda/a) \log_{10} (1 - x/c) \qquad . \; . \; . \; . \quad (2)$$

measurements at three temperatures are summarised in Table 1.

TABLE 1. *Rate constants (k_2 in l. mole^{-1} sec.$^{-1}$) obtained with various mixtures of methanol and methyl cyanide as solvents.*

$[\mathrm{Bu^nI}]_0 = 0{\cdot}030$—$0{\cdot}035$M.

Temp. = 19·71°.

[MeOH] (M)...	0	0	0·501	1·02	2·19	5·01	10·0	22·3	24·7 *
10^3k_2	1·85	2·00	1·40	0·972	0·570	0·219	0·103	0·0414	0·0358, 0·0363

Temp. = 32·50°

[MeOH] (M)...	0	0	0	0·246	0·501	0·790	1·02	2·19
10^3k_2	7·43	7·96	7·80	6·42	5·50	4·70	4·18	2·11
[MeOH] (M)...	3·28	5·01	10·0	17·0	22·0	24·3 *	24·3	24·3
10^3k_2	1·44	0·981	0·416	0·228	0·155	0·152	0·154	0·144

Temp. = 45·00°.

[MeOH] (M)...	0	0	0·501	1·02	2·19	5·01	16·7	21·6	24·0 *
10^3k_2	23·6	24·2	16·9	12·1	7·43	3·19	0·809	0·560	0·492

* Pure MeOH.

TABLE 2. *Variation of dielectric constant (ε) of mixtures of methanol and methyl cyanide with mol.-fraction of methanol (N) at 30·0°.*

N	0	0·127	0·244	0·398	0·562	0·663	0·790	0·916	1
ε	35·93	35·58	35·25	34·90	34·46	34·04	33·27	32·44	31·64

The progressive reduction in the specific rate constant of the iodine exchange reaction produced by increasing the proportion of methanol in the solvent is illustrated in Fig. 1, where log k_2 has been plotted against concentration of methanol. The variation of rate constant observed can hardly be attributed to changes in dielectric constant, since, as indicated in Table 2, this falls in value with increasing methanol concentration.[3] Theoretically, for reactions between ions and dipolar molecules, a reduction in dielectric constant would be expected to increase the rate constant. However, in the present investigation the overall change in dielectric constant is quite small, and such effect as is caused has been neglected altogether: the observed variation of rate constant with solvent composition is attributed entirely to an equilibrium $\mathrm{I^-} + \mathrm{MeOH} \rightleftharpoons (\mathrm{I,HOMe})^-$, the ions $\mathrm{I^-}$ and $(\mathrm{I,HOMe})^-$ being assumed to react with n-butyl iodide at different specific rates, namely, k_0 and k_∞ respectively. It follows from this equilibrium that the quotient $(k_0 - k_2)/[\mathrm{MeOH}]$ should be directly proportional to the experimental rate constant k_2 appropriate to the methanol concentration chosen,[1] k_0 being the rate constant obtained with pure methyl cyanide.

In Fig. 2, $(k_0 - k_2)/[\mathrm{MeOH}]$ has been plotted against k_2 for the experimental results obtained at 32·5° given in Table 1. Points corresponding to the lower concentrations

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

of methanol lie close to the same straight line in satisfactory agreement with the requirements of the equilibrium postulated above. However, deviations from this line are observed when the methanol concentration exceeds 1M. These are probably too large to be attributed to random experimental error and are in the wrong sense to be due to the failure to correct for the variation of dielectric constant.

There is the further possibility, especially at high concentrations of methanol, that significant errors in the values of k_2 might arise from neglect of the reaction between n-butyl iodide and the solvent methanol. Errors from side reactions of this kind may be avoided, however, by the use of equation (3) to calculate the second-order rate constant k_2 of the exchange reaction,[4] k being the pseudo-first-order constant of the solvolysis, which is assumed to be irreversible; the other symbols have their previous significance.

FIG. 1. *Plot of* $(4 + \log_{10} k_2)$ *against concentration of methanol for data given in Table* 1 *for* 32·5°.

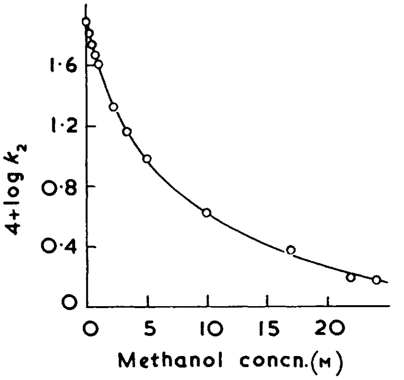
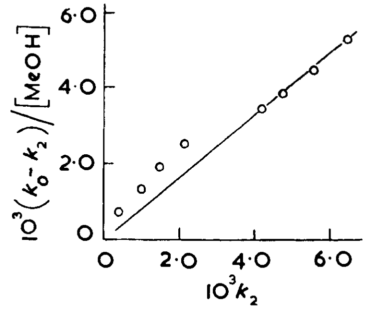


FIG. 2. *Plot of* $(k_0 - k_2)/[\text{MeOH}]$ *against* k_2 *for data given in Table* 1 *for* 32·5°.



$$k_2t = -(2{\cdot}303/a)\log_{10}(1 - e^{-kt}x/c) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From measurements at 45° in pure methanol as solvent, we have found k to be about 2×10^{-8} sec.$^{-1}$. Errors in the value of k_2 arising from methanolysis of the alkyl halide are, therefore, negligible, since the factor e^{-kt} appearing in eqn. (3) will not be significantly less than unity until t reaches a value far in excess of 19 hr. At temperatures lower than 45°, methanolysis will probably be even less important because its energy of activation is likely to be larger than that of the iodine exchange reaction.

It seems, therefore, that the divergence from the straight line of points corresponding to higher concentrations of methanol, illustrated in Fig. 2, is probably not due to errors in the experimental rate constants. However, provided that the concentration of methanol does not exceed M, the variation of rate constant with solvent composition may be adequately accounted for in terms of the proposed equilibrium between iodide ions, methanol molecules, and the ionic species (I,HOMe)$^-$. It is possible, too, that the range of methanol concentrations over which this explanation satisfactorily accounts for the kinetic results might be extended by expressing methanol concentrations as thermodynamic activities.

The Arrhenius parameters of the iodine exchange reaction are shown in Table 3. They were calculated graphically from the rate constants given in Table 1. The pre-exponential

TABLE 3. *Parameters of the equation,* $k_2 = A_2 \exp(-E_A/\mathbf{R}T)$ *(with* A_2 *in l. mole*$^{-1}$ *sec.*$^{-1}$*, and* E_A *in kcal. mole*$^{-1}$*), for rate constants given in Table* 1.

[MeOH] (M)	0	0·50	1·02	2·19	5·0	10·0	16·9	22·0	24·3
$\log_{10} A_2$	11·1	10·8	10·9	10·8	11·1	10·5	10·3	9·9	10·0
E_A	18·5	18·3	18·6	18·9	19·7	19·4	19·5	19·2	19·3

factors A_2 tend to decrease in value as the proportion of methanol in the solvent is increased, although the overall change in log A_2 is quite small. The value of the energy of activation E_A, on the other hand, increases with increasing methanol concentration, reaching a maximum of 19·7 kcal. mole^{-1} at about 5M-methanol, above which concentration it remains almost constant.

In the interpretation of the effect of methanol upon the rate of the iodine exchange reaction discussed above, no assumptions about the nature of the interaction between iodide ion and hydroxylic molecule needed to be made. However, if this interaction involves the hydrogen atom of the hydroxyl group, then we should expect that the larger the acid dissociation constant K_a of the hydroxylic compound concerned, the larger would be the value of the association constant K_s for the equilibrium $I^- + ROH \rightleftharpoons (I,HOR)^-$. Thus if methanol were replaced by phenol in our kinetic experiments, we should expect the slope of the straight line obtained by plotting $(k_0 - k_2)/[ROH]$ against k_2 to be larger in the case of phenol, because the slopes of such plots are equal to the appropriate association constants.

So we measured the rate of the isotopic exchange reaction $^*I^- + Bu^nI \rightleftharpoons I^- + Bu^{n*}I$ in methyl cyanide containing various concentrations, up to about M, either of phenol or of some *meta*- or *para*-substituted phenols covering a range of acid strengths. As in our experiments with methanol, carrier-free sodium radio-iodide provided all the iodide ions present initially, and rate constants were evaluated graphically by means of eqn. (1). These are recorded in Table 4.

TABLE 4. *Rate constants (k_2 in l. mole^{-1} sec.$^{-1}$) obtained with various phenols present in methyl cyanide as solvent.*

$[Bu^nI]_0$ = 0·030—0·035M. Temp. = 32·50°.

Phenol						
[ROH] (M)	0·251	0·382	0·499	0·501	0·797	0·997
10^3k_2	4·59	3·84	2·70	2·96	1·86	1·56
p-Methoxyphenol						
[ROH] (M)	0·249	0·384	0·498	0·501	0·788	0·998
10^3k_2	4·56	3·54	2·54	2·94	1·95	1·60
p-Chlorophenol						
[ROH] (M)	0·145	0·250	0·382	0·500		
10^3k_2	4·80	3·42	2·34	1·82		
m-Chlorophenol						
[ROH] (M)	0·154	0·250	0·401	0·505		
10^3k_2	4·20	3·14	2·20	1·75		
m-Nitrophenol						
[ROH] (M)	0·103	0·145	0·147	0·253	0·402	
10^3k_2	4·22	3·52	3·35	2·15	1·43	
p-Nitrophenol						
[ROH] (M)	0·101	0·150	0·250	0·501		
10^3k_2	3·79	3·04	2·20	1·20		
2,4,6-Tribromophenol						
[ROH] (M)	0·150	0·250	0·401			
10^3k_2	6·90	6·48	5·90			

To illustrate the effect of increasing acid strength of the hydroxylic compound on the value of the association constant, we have, in Fig. 3, plotted $(k_0 - k_2)/[ROH]$ against k_2 for methanol and for each of the phenols studied. In most of the examples considered, the slope of the best straight line drawn through the experimental points increases as the acid strength of the hydroxylic compound increases. A complete comparison between association constants, evaluated graphically from plots shown in Fig. 3, and acid dissociation constants in water [5] of the phenols concerned is given in Table 5. There is evidently

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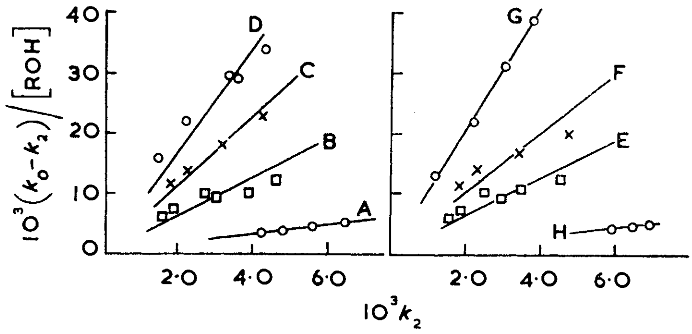
[5] Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3110; Biggs, *Trans. Faraday Soc.*, 1956, **52**, 35.

no simple quantitative relation between K_s and K_a and none would be expected. Nevertheless, it is generally true that, other things being equal, the capacity of a phenol to retard the iodine exchange reaction increases with its strength as an acid, a result which can be explained by the increasing tendency of a phenol to associate with iodide ions in the way postulated above as its acid strength increases. 2,4,6-Tribromophenol is an apparent exception. The acid dissociation constant of this phenol is not available, but it is probably not less than 10^{-7} (for 2,4,6-trichlorophenol[6] pK_a at 25° = 6·46). However, comparison of the appropriate plots in Fig. 3 shows that, despite its probable marked strength as an acid, 2,4,6-tribromophenol is only about as effective as methanol in retarding the iodine exchange. The relative ineffectiveness may arise from the presence of its large *ortho*-substituents, which prevent the close approach of an iodide ion and the hydrogen atom of the hydroxyl group.

TABLE 5. *Comparison of association constants* (K_s) *with acid dissociation constants in water* (K_a) *and integrated absorption intensities in* 3600 *cm.*$^{-1}$ *region* (A) *for various phenols* ($X \cdot C_6H_4 \cdot OH$).

Group X	H	*p*-OMe	*p*-Cl	*m*-Cl	*m*-NO$_2$	*p*-NO$_2$
K_s (32·5°)	3·2	3·2	5·0	5·8	8·6	10·3
$10^{10}K_a$ (25°)	1·12	0·62	4·19	9·48	45·1	725
10^7A	5·8	5·6	6·6	6·7	8·7	8·5

FIG. 3. *Plots of* $(k_0 - k_2)/[ROH]$ *against* k_2 *for various phenols from data given in Table* 4.



(A) *Methanol*; (B) *phenol*; (C) m-*chlorophenol*; (D) m-*nitrophenol*; (E) p-*methoxyphenol*; (F) p-*chlorophenol*; (G) p-*nitrophenol*; (H) 2,4,6-*tribromophenol*.

More suitable than acid dissociation constants, for comparison with the association constants obtained from our kinetic experiments, would be the integrated intensities (A) of the infrared absorption band associated with the stretching vibration of the O–H bond,[7,8] because these depend only on the structure of the undissociated phenol molecules concerned. Relevant values for the integrated intensities of the absorption in the 3600 cm.$^{-1}$ region obtained by Stone and Thompson[7] are given in Table 5. Fig. 4, in which these values have been plotted against log K_s, shows an approximately linear relation and it may well be, therefore, that the formation of the ionic species (I, HOR)$^-$ involves a small change in O–H bond length, which is an important factor in determining the stability of such species.

Direct spectroscopic evidence for the existence of an interaction between anions and hydroxylic molecules has been obtained by Lund,[9] who found that solutions of hydroxylic compounds containing a small amount of tetrabutylammonium bromide possess an

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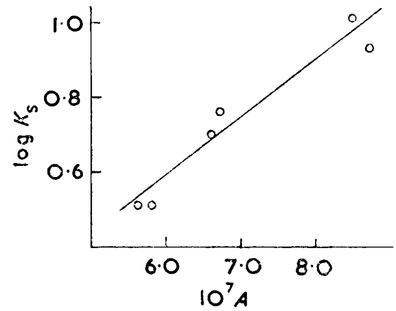
[6] Tiessens, *Rec. Trav. chim.*, 1931, **50**, 112.
[7] Stone and Thompson, *Spectrochim. Acta*, 1957, **10**, 17.
[8] Brown, *Chem. Rev.*, 1958, **58**, 581; Flett, *Spectrochim. Acta*, 1957, **10**, 21.
[9] Lund, *Acta Chem. Scand.*, 1958, **12**, 298.

absorption band in the 3 μ region, the frequency of which is lower, and the integrated intensity larger, than those of the absorption band attributed to the free stretching vibration of the O–H bond. Several authors have pointed out, however, that the frequency of the absorption band corresponding to O–H stretching is generally lower and its integrated intensity higher, when the hydroxyl group forms part of some hydrogen-bonded system.[8,10] Hydrogen bonding between anion and hydroxyl group has, therefore, been invoked by Lund to account for his spectroscopic observations, and this would also explain why the shift in frequency of absorption produced by the addition of bromide ions increases with increasing acid strength of the hydroxylic compound. The apparent integrated intensity of the absorption band attributed to the hydrogen-bonded anion complex also increases with increasing acid strength, except in the case of phenols with *ortho*-substituents. These behave anomalously in this respect, presumably for the same reason that 2,4,6-tribromophenol is relatively ineffective in retarding the iodine exchange reaction.

FIG. 4. *Plot of* $\log_{10} K_s$ *against integrated absorption intensity* (A) *for various phenols.*



EXPERIMENTAL

Reagent-grade methyl cyanide was stored over anhydrous potassium carbonate for several days. It was then fractionated through a column packed with metal gauze rings, the fraction of b. p. 81·5—81·7° being retained for use. It was finally distilled under reduced pressure over phosphoric oxide to remove the last traces of water, and then refractionated.

After a preliminary treatment with anhydrous potassium carbonate, commercial methanol was distilled, then dried by Lund and Bjerrum's method [11] and fractionated. The fraction retained had b. p. 64·4—64·6°. The final water content of both purified solvents was about 0·02% by weight (Karl Fischer).

Radioactive iodine-131 was obtained as a solution of carrier-free sodium iodide in water. This was evaporated to dryness and then extracted with the appropriate dry solvent. n-Butyl iodide was purified as described in Part II.[1]

Phenols, except *m*-chlorophenol, were crystallised from light petroleum and then dried *in vacuo* over phosphoric oxide at room temperature. *m*-Chlorophenol could not be obtained as a solid product from solution. It was, therefore, purified by distillation under reduced pressure. M. p.s of purified phenols were within 1° of published values.

Kinetic procedure was that previously described.[1] Within a given experiment mean deviation of individual rate constants from the mean value of the rate constant was about 5%. Mean values of rate constants obtained from independent experiments did not usually differ by more than 10%.

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[10] Barrow, *J. Phys. Chem.*, 1955, **59**, 1129.
[11] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.