413. *The Effect of Solvent on a Simple Ion–Dipole Reaction. Part I. The Order and Mechanism of the Methyl Iodide–Iodide Ion Exchange Reaction in Different Solvents.*

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The isotopic exchange of radioactive iodine between methyl iodide and sodium iodide was studied in water and ethanol over a range of ionic concentrations. A kinetic equation was derived which allows for the hydrolysis of methyl iodide in water.

It was shown that carrier-free isotopes can be used to study the reaction at extremely low ionic concentrations. A kinetic equation was found to allow for the radioactive decay in these circumstances.

The reaction was found to be of the second order only, in both solvents.

ALTHOUGH much work has been done on ion–dipole reactions in solution, a relatively small amount has been directed towards the solvent effect. The problem is complicated since it is virtually impossible to vary one property of the solvent without causing other properties to vary. Moreover, the same reaction may have different mechanisms in different solvents. This fact, as well as the incomplete dissociation of electrolytes in solvents of low dielectric constants, has frequently been neglected in such investigations.

We have chosen as simple a reaction as possible, which has the same mechanism in a series of pure solvents, namely the exchange of radioactive iodine between methyl iodide and sodium iodide: $CH_3I + {}^*I^- \rightleftharpoons CH_3{}^*I + I^-$. This reaction has the advantage that it can be followed in a wide range of solvents including water. The formation of olefins is excluded; further, the intermediate complex in its critical state is symmetrical.

The purpose of this paper is to furnish the exact rate equations for the reaction in different solvents and to show that the same mechanism is followed in all the solvents used. Part II will deal with the effect of solvent on the rate.

The above nucleophilic substitution reaction denoted by S_N can proceed according to two mechanisms S_N2 and S_N1 illustrated respectively by the schemes

$$\text{(i)}\quad RI + {}^*I^- \rightleftharpoons {}^*I \cdots\cdots R \cdots\cdots I \rightleftharpoons {}^*IR + I^-$$

giving rise to a second-order reaction and

$$\text{(ii)}\quad RI \rightleftharpoons R^+ + I^-$$

followed by

$$R^+ + {}^*I^- \rightleftharpoons R{}^*I$$

which is of the first order.

The constant rate of exchange of this reaction is given by equation (1) regardless of order or mechanism:

$$R = -[ab/t(a+b)]\ln[1 - x/c(1 + b/a)] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a and b are the total concentrations of the methyl iodide and sodium iodide, respectively, and x/c is the ratio of the radioactivity in the methyl iodide to the total radioactivity after a time t.

It follows that for a first-order reaction

$$k_1 = R/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for a second-order reaction

$$k_2 = R/ab \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In a previous paper [1] we have shown that if both mechanisms contribute to the overall exchange, the rate of the reaction is given by

$$R = k_1a + k_2ab \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or if the incomplete dissociation of the salt in the solvent is taken into account,

$$R = k_1a + k_i a\alpha b$$

whence $$R/a = k_1 + k_i\alpha b \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The contribution of each mode of exchange can then be evaluated from a plot of R/a against αb.

In general, the more protogenic the solvent used, the greater is the chance that the exchange will be of the S_N1 type. Since water is the most protogenic of the common solvents the reaction was first investigated in that solvent.

The exchange in water is, however, complicated by the fact that the methyl iodide is hydrolysed to methyl alcohol and hydrogen iodide, the relevant reactions being :

$$\begin{tikzcd}
CH_3I + {}^*I^- \arrow[r, shift left, "k_2"] \arrow[d, "k"', "H_2O"] & CH_3{}^*I + I^- \arrow[l, shift left] \arrow[d, "k"', "H_2O"] \\
CH_3{\cdot}OH + H^+ + I^- & CH_3{\cdot}OH + H^+ + {}^*I^-
\end{tikzcd}$$

It being assumed that, at a time t, x g.-ions of iodine have exchanged, and y moles of inactive and z moles of radioactive methyl iodide have been hydrolysed, the initial concentrations and those after a time t can be denoted as follows :

	CH_3I	${}^*I^-$	$CH_3{}^*I$	I^-	H^+
Initial concn.	a	b	0	0	0
Concn. at time t	$a - x - y$	$b - x + z$	$x - z$	$x + y$	$y + z$
or alternatively	$a - p$	$b - q$	q	p	$p - q$

where $p = (x + y)$ and $q = (x - z)$.

The following equation is derived on the assumption that a second-order rate law is followed for the exchange reaction. Any first-order contribution can in any case be evaluated from equation (4) or (5).

Since the hydrolysis is a pseudo-first-order reaction and practically irreversible, the rate of exchange is given by

$$\mathrm{d}q/\mathrm{d}t = k_2(a - p)(b - q) - k_2pq - kq \quad . \; . \; . \; . \; . \; . \quad (6)$$

The total rate of hydrolysis of methyl iodide is given by the rate of formation of hydrogen ions, or the rate of increase of the iodide ion concentration, and may be written as

$$\mathrm{d}(p - q)/\mathrm{d}t = k[a - (p - q)]$$

whence $$k = (1/t)\ln a/[a - (p - q)] \quad . \; . \; . \; . \; . \; . \quad (7)$$

and $$p = a(1 - \mathrm{e}^{-kt}) + q$$

Substitution of this value of p in equation (6) yields

$$dq/dt + k_2(a + b) + kq = k_2ab\mathrm{e}^{-kt}$$

which on integration gives

$$k_2 = -\,[1/t(a + b)]\ln[(1 - \mathrm{e}^{-kt})q/b(1 + b/a)] \quad . \; . \; . \; . \; . \quad (8)$$

The value of q/b is given by the ratio of the activity in the methyl iodide to the total activity. If hydrolysis is neglected, k can be equated to zero and equation (8) reduces to the simpler equation (3).

In order to determine the extent of hydrolysis, a series of reactions was carried out in

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[1] le Roux and Swart, *J.*, 1955, 1475.

water at 25° with different sodium iodide concentrations. The hydrogen-ion concentration, increase in iodide-ion concentration, and the activity ratio were measured after the reaction had proceeded for a time t, with results recorded in Table 1. These values indicate a tendency for k to decrease with decreasing iodide-ion concentration. The magnitude of

TABLE 1. *Hydrolysis of methyl iodide in water at* 25°.

		$10^4(p - q)$							$10^4(p - q)$				
10^2a	10^3b	from $[\text{I}^-]$	from $[\text{H}^+]$	Mean	t (sec.)	10^8k	10^2a	10^3b	from $[\text{I}^-]$	from $[\text{H}^+]$	Mean	t (sec.)	10^8k
2·676	9·80	1·20	—	1·20	52,500	8·3	2·676	3·94	1·05	1·15	1·10	52,860	7·8
2·806	9·80	1·10	1·20	1·15	55,200	7·6	2·806	3·94	1·00	1·15	1·08	55,440	7·1
2·806	7·85	1·15	1·05	1·10	55,260	6·9	2·676	1·95	1·05	—	1·05	59,280	6·6
2·676	3·94	1·05	1·15	1·10	52,860	7·8	2·806	1·95	—	1·00	1·00	55,560	6·6
												Mean	7·3

the hydrolysis correction, however, did not warrant a more exact analysis, the mean value of k being sufficiently accurate for calculation of k_2 from equation (8). It may be noted that the mean value of k is about the same as that found by Moelwyn-Hughes[2] for the hydrolysis of methyl iodide in pure water.

The values of k_2 calculated from the experimental results are shown in Table 2. For comparison the values calculated from equation (3), *i.e.*, with neglect of hydrolysis, are included. In order to test whether the ionization mechanism contributes to the exchange, values of R/a were calculated and are tabulated in the last column of Table 2.

The values of k_2 calculated from the second-order rate equation are constant and the plot of R/a against b gives a straight line through the origin. The reaction is therefore of the second kinetic order with no perceptible first-order contribution.

TABLE 2. *Rate constants of the exchange reaction in water at* 25°.

10^2a	10^3b	10^4k_2 from eqn. (8)	10^4k_2 from eqn. (3)	$10^6R/a$	10^2a	10^3b	10^4k_2 from eqn. (8)	10^4k_2 from eqn. (3)	$10^6R/a$
2·806	1·95	4·97	4·94	0·97	2·806	7·85	4·72	4·69	3·71
2·676	1·95	4·60	4·56	0·90	2·676	7·85	4·90	4·86	3·85
2·676	3·94	5·03	4·98	1·98	2·676	9·80	4·79	4·75	4·69
3·219	4·75	4·85	4·82	2·30	2·676	9·80	4·86	4·82	4·76
2·880	7·15	4·91	4·88	3·51					
						Mean	4·85±0·03		

The value of k_2 calculated by the method of least squares from equation (4) is $4{\cdot}84 \times 10^{-4}$ l. mole^{-1}.

For the above experiments the difference between the corrected and the uncorrected values of k_2 is about 1%, which is negligible. The hydrolysis correction is, however, proportional to an exponential function of t, thus increasing rapidly with increasing duration of the reaction. Further, the activation energy of the hydrolysis is much larger than that of the exchange, so that the effect of hydrolysis at higher temperatures may be considerable and must be taken into account for reactions at temperatures higher than 25°. Since the reaction in water does not show any evidence of the ionisation mechanism, it is reasonably safe to assume that it is purely of the second order in all less protogenic solvents.

In the other solvents used the sodium iodide is only partially ionised. It was therefore necessary to calculate the specific rate from the equation

$$k_i = k_2/\alpha = R/ab \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This necessitates the calculation of the degree of dissociation α of the sodium iodide in all those solvents. This can be done for those solvents for which conductivity data are available, as with ethanol. The assumption that the exchange is free from the ionisation mechanism in solvents less protogenic than water was therefore checked by carrying out a series of reactions in ethanol at 25°. The method used to calculate the degrees of

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[2] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295.

dissociation of sodium iodide in ethanol is similar to that previously described.[1] The conductivity data employed are those of Goldschmidt and Dahll[3] and of Thomas and Marum.[4] The value of Λ_0 was found to be 47·6 ohm^{-1} cm.^{2} at 25° and the corresponding value of the dissociation constant K was $2{\cdot}52 \times 10^{-2}$. All the values of α used in the calculation of the kinetic data at 25° were calculated from this value of K.

The kinetic data for the exchange in ethanol at 25° are summarised in Table 3, the concentration of the methyl iodide used being 0·0105N.

It is seen from Table 3 that the values of k_i calculated from equation (9) are constant. Moreover, the plot of R/a against αb gives a straight line through the origin. This proves that the reaction in ethanol is of the second kinetic order only. The calculated value of k_i is $2{\cdot}10 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

TABLE 3. *Rate constants of the exchange reaction in ethanol at 25°.*

10^3b	α	$10^3\alpha b$	10^2k_i	$10^5R/a$	10^3b	α	$10^3\alpha b$	10^2k_i	$10^5R/a$
2·00	0·957	1·914	2·27	4·34	7·85	0·907	7·120	2·09	14·9
2·00	0·957	1·914	2·28	4·32	7·85	0·907	7·120	2·16	14·6
4·02	0·932	3·746	2·05	7·61	9·615	0·899	8·644	2·07	17·9
6·00	0·917	5·503	2·16	11·9	9·615	0·899	8·644	2·14	18·5
6·00	0·917	5·503	2·13	11·7			Mean	2·15±0·02	

In order to avoid the necessity of calculating dissociation constants for sodium iodide at a series of temperatures in solvents other than water, the possibility of using extremely low ionic concentrations was investigated. When the ionic concentrations are negligible in comparison with those of the methyl iodide, it is permissible to put $\alpha = 1$ and $b = 0$ relative to a in equation (9), which may then be written as

$$k_2 = R/ab = -(1/at)\ \ln\ (1 - x/b) \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where the value of x/b is given by the ratio of the activity in the methyl iodide to the total activity at the time t.

Such conditions can be realised by using carrier-free sodium iodide. It will then be necessary to account for the decay of the radioactive iodine, which continuously reduces the concentration of the radioactive iodide, thus producing an apparent retardation in the rate of the reaction.

The second-order rate equation is derived on the assumption that after a time t the concentrations of the iodide ion and the radioactive methyl iodide are $(b - x)e^{-\lambda t}$ and $xe^{-\lambda t}$ respectively. The rate of the reaction is then given by

$$dx/dt = k_2(a - x)\ (b - x)e^{-\lambda t} - k_2x^2e^{-\lambda t}$$

By integrating this equation and neglecting b relative to a, we have for the specific rate

$$k_2 = -[(\lambda/a)(1 - e^{-\lambda t})]\ \ln\ (1 - x/b) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If λt is very small, the expression $1 - e^{-\lambda t}$ can be replaced by λt and equation (11) reduces to equation (10). In the case of ^{131}I, $\lambda = 1{\cdot}002 \times 10^{-6}$ sec.$^{-1}$; hence for all reaction periods less than 19 hr. (one-tenth of the half-life) the simpler equation (10) may be used to calculate k_2.

In order to test the applicability of equation (11) it is necessary to compare reactions carried out with carrier-free iodide, with reactions employing finite sodium iodide concentrations. At the same time a reaction must be chosen such that it does not proceed too far within 19 hr., in order that the exchange may be followed for various periods exceeding that time. A case in point is the exchange reaction in water at 0°. The experimental results, with finite concentrations, are summarised in Table 4. Hydrolysis under these conditions is negligibly small, so k_2 was calculated according to equation (3).

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[3] Goldschmidt and Dahll, *Z. phys. Chem.*, 1924, **114**, 1.
[4] Thomas and Marum, *ibid.*, 1929, *A*, **143**, 191.

The experimental results, with carrier-free iodine, are recorded in Table 5. The values of k_2 calculated by both equations (10) and (11) are given.

The values of k_2 calculated from equation (10) show a continuous decrease, but those from equation (11) give a constant value, which compares favourably with that obtained by using finite ionic concentrations. Most reactions in solvents other than water are complete in less than 19 hr., however, under which condition equation (10) is applicable.

TABLE 4. *Rate constants of the exchange reaction in water at* 0°.

$10^2 a$	3·226	3·266	2·886	
$10^3 b$	4·76	4·76	7·16	
$10^5 k_2$	3·26	3·03	3·21	Mean 3·17 ± 0·05

TABLE 5. *Rate constants of the exchange reaction in water at* 0° *with carrier-free iodide ions.*

Time (sec.)	146,100	167,300	319,680	339,300	426,600	604,440	778,200
$10^5 k_2$ (eqn. 10)	3·12	3·13	2·62	2·62	2·50	2·51	2·35
$10^5 k_2$ (eqn. 11)	3·39	3·40	3·05	3·10	3·08	3·34	3·38
						Mean 3·25±0·04	

A further check on the validity of equation (10) was therefore made by carrying out reactions at 25° with carrier-free iodide, and ethanol as solvent. The values of k_2 found for two such reactions were $2{\cdot}21 \times 10^{-2}$ and $2{\cdot}22 \times 10^{-2}$, in good agreement with the values found for finite ionic concentrations.

EXPERIMENTAL

Radioactive Iodine and Sodium Iodide.—Radioactive ^{131}I was obtained from Harwell in the form of carrier-free sodium iodide solution. After filtration and evaporation to dryness, the iodide was dissolved directly in the appropriate solvent and kept in a well-stoppered bottle as stock solution.

Inactive sodium iodide was prepared from "AnalaR" hydriodic acid and Merck's *pro analysi* grade sodium carbonate, and was purified by successive recrystallisations from ethanol.

Methyl Iodide.—This was obtained by distilling Merck's purest product over silver foil through a 20″ fractionating column with a theoretical plate factor of about 28 plates. Only the middle fraction was retained for use; n_D^{20} 1·5299.

Solvents.—The conductivity water used had a specific conductivity of 1×10^6 ohm^{-1} cm.$^{-1}$. Dry ethanol (n_D^{20} 1·3610, d_4^{20} 0·7893) was prepared by refluxing absolute alcohol over magnesium ethoxide and distilling it through the fractionating column described above.

Standard Solutions and Methods of Analyses.—All solutions were made up at 25°, which was taken as the reference temperature, and concentrations at the reaction temperatures were corrected for by using the expressions for the volume expansion of the pure solvents concerned.

The methyl iodide concentration, in aqueous solutions, was determined gravimetrically by precipitation as silver iodide. For ethanol solutions it was determined by hydrolysis, followed by titration with standard silver nitrate solution with eosin as indicator. The sodium iodide concentration was determined by titration with standard silver nitrate solution. The extent of hydrolysis of methyl iodide in water was determined by titrating the aqueous layer after the methyl iodide was extracted with benzene. The total acid was determined by titration against standard sodium hydroxide solution, bromothymol-blue being used as indicator. A blank titration was done on an equal volume of distilled water. The titrated solution was then evaporated down to a volume of 20 ml. and titrated with standard silver nitrate solution in order to determine the increase in iodide-ion concentration.

Kinetic Procedure.—The reactions were carried out on similar lines to those previously described.[1] The correction factors necessary to give the true activity ratio were found to be 0·849 for water and 1·129 for ethanol.

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