73. *The Effect of Solvent on a Simple Ion–Dipole Reaction. Part II.* The Rate of the Methyl Iodide–Iodide Ion Exchange in Five Different Solvents.*

By E. R. Swart and L. J. le Roux.

The isotopic exchange of radioactive iodine between methyl iodide and sodium iodide has been investigated in five pure solvents. The activation energies and collision diameters have been calculated. The difference in the rates in the different solvents is almost entirely due to a change in the activation energy. The variation in the dielectric constant appears to be the predominant factor in determining the rate of reaction. The specific rate constant for the series of solvents is given by the general equation

$$\log k_2 \text{ (l. mole}^{-1}\text{ sec.}^{-1}) = 5\cdot 68 + (3/2) \log T - E/4\cdot 574T$$

The influence of the solvent on the rate of ion–dipole reactions is commonly investigated by considering the effect of solvents of different dielectric constant. A theoretical treatment generally leads to a linear relation between the log of the rate constant and the reciprocal of the dielectric constant. This linearity has been confirmed, mainly for mixed solvents, by several investigators,[1] but it has been found to break down in solvent mixtures of low dielectric constant,[2] probably as a result of preferential adsorption of the solvent of higher dielectric constant from such a mixture.[3]

An alternative approach is to consider the influence of the solvent in terms of the more general concept of polarity, which is in effect an attempt to assess the solvating power of a given solvent. Ingold[4] has shown that the polarity of a solvent increases with an increase in the molecular dipole moment and decreases with an increased thickness of shielding of the dipole charges. The latter factor may become important in deciding the solvent polarity, often outweighing the effect of dipole moment. This is especially true where the thinly shielded proton of the hydroxyl group is concerned.

On the basis of the solvating power of a solvent a correct prediction, of a qualitative nature, can generally be made of the variation of the rate of a given reaction in different solvents.[4] In the present case, namely, the reaction between a negative ion and a neutral dipole, the activated complex in the transition state is less polar than the initial state of the reactants, because of an increased dispersal of the charge. An increase in the polarity of the solvent will therefore cause a decrease in the rate of reaction. In certain cases, however, it might not be possible to decide which of two solvents is to be considered as the more polar. The actual information that is required, namely, a quantitative measure of the polarity of a given solvent, is not forthcoming at the present state of our knowledge of the shielding of the dipole charges in a molecule.

A useful approach to an understanding of the influence of solvent on an ion–dipole reaction is found in a theoretical discussion by Kacser.[5] By considering the activation energy as a function of the direction of approach of the ion towards the dipole, he showed that the rate equation may be written in the form

$$k_2 = (Z/2)\int_0^{\pi} \exp\left[\left(E' + \frac{N\mu ze}{\varepsilon' d^2}\cos\theta\right)/\boldsymbol{R}T\right] . \sin\theta d\theta \quad . \quad . \quad . \quad (1)$$

where E' is an energy term resulting from supposedly non-electrostatic forces, ε' is the effective dielectric constant of the solvent, d the distance between the centres of the ion

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* Part I, *J.*, 1956, 2110.

[1] Fontein, *Rec. Trav. chim.*, 1928, **47**, 635; Minnik and Kilpatrick, *J. Phys. Chem.*, 1939, **43**, 259.

[2] Harned and Embree, *J. Amer. Chem. Soc.*, 1935, **57**, 1699; Harned and Kazanjian, *ibid.*, 1936, **58**, 1912.

[3] Laidler and Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303.

[4] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, p. 345.

[5] Kacser, *J. Phys. Chem.*, 1952, **56**, 1101.

and the dipole, and θ the angle which the line of approach makes with the axis of the dipole, while the other symbols have their usual significance.

On integration, equation (1) becomes

$$k_2 = \frac{Z\left[1 - \exp(-2E_e/\boldsymbol{R}T)\right]}{2E_e/\boldsymbol{R}T}\exp\left[-(E' - E_e)/\boldsymbol{R}T\right] \quad . \quad . \quad . \quad (2)$$

where $E_e = \boldsymbol{N}\mu ze/\varepsilon' d^2$

Provided that $2E_e$ is appreciably greater than $\boldsymbol{R}T$, equation (2) reduces to

$$k_2 = Z\frac{\boldsymbol{R}T}{2E_e}\exp\left[-(E' - E_e)/\boldsymbol{R}T\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As a first approximation d may be taken as equal to the collision diameter r.[5] If it is assumed that the majority of ions approach the dipoles from the most favourable direction ($\theta = \pi$), a closer approximation is given by $d = r + \Delta r$ where Δr is the distance from the centre of the dipole to the seat of the reaction. If it is further assumed that the centre of the methyl iodide dipole lies at the edge of the carbon atom,[6] Δr may be taken as the radius of the carbon atom which is 0·77 Å.

The value of ε' is difficult to assess accurately. If it is taken as equal to the dielectric constant ε of the bulk solvent, it leads to impossible values of r and it is generally recognised that such an assumption is invalid. Kacser,[5] following Frank,[7] has taken ε' as equal to $3\varepsilon/(\varepsilon + 2)$ which leads to reasonable values of r. These values are, however, not strictly correct since they are calculated indirectly from the Arrhenius parameters, ignoring both the variation of delectric constant with temperature and the difference between d and r, instead of directly from the kinetic results by means of equation (3). Alternatively, ε' may be taken as unity for a reacting collision, as has been done by Ogg and Polanyi.[6] Taking logarithms and substituting for the numerical constants then converts equation (3) into the simple form

$$\log_{10} k_2 - \tfrac{3}{2}\log_{10} T = \log_{10}\left[2{\cdot}985 \times 10^{35} r^2 (r + \Delta r)^2\right] - E/4{\cdot}574T \quad . \quad (4)$$

Both r and $E = (E' - E_e)$ may thus be calculated directly from kinetic data and the Arrhenius activation energy $E_a = (3/2)\boldsymbol{R}T + E$ may also be determined at any desired temperature.

In order to test the validity of equation (4) the methyl iodide–iodide ion exchange was investigated in five pure solvents. With the exception of work in aqueous solutions, and one set of experiments in ethanol, the reactions were carried out with carrier-free sodium iodide as described in Part 1.[8] The rate constants were calculated by means of the equations previously derived.[8]

In aqueous solutions it was necessary to measure hydrolysis at 50°. A mean value for the hydrolysis rate constant was found to be $2{\cdot}8 \times 10^{-6}$ sec.$^{-1}$. This value was taken into account in calculating the exchange rate constant. Although side reactions are known to occur between methyl iodide and the other solvents, such as ether formation in methyl alcohol, the relative extent of such reactions was found to be negligible. This was demonstrated by the fact that only very slight discrepancies were found from the theoretical equilibrium exchange, for reactions that were allowed to proceed for more than six times the half-time of exchange.

The experimental results are summarised in Tables 1—5. The parameters in the equations below the Tables were calculated from equation (4) by the method of least squares.

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[6] Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

[7] Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 174.

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

TABLE 1. *Water as solvent.*

T (K)	10^2a	10^3b	10^5k_2 (exp.)	10^5k_2 (calc.)
273·2°	3·23	4·76	3·13	2·94
273·2	3·23	4·76	2·90	
273·2	2·89	3·16	3·05	
273·2	2·89	7·16	2·80	
323·2	3·08	4·71	495	509
323·2	2·75	7·09	536	
323·2	2·75	7·09	528	

T (K)	10^2a	10^3b	10^5k_2 (exp.)	10^5k_2 (calc.)
298·2°	2·81	1·95	49·7	48·5
298·2	2·68	1·95	46·0	
298·2	2·68	3·94	50·3	
298·2	3·22	4·75	48·5	
298·2	2·89	7·15	49·1	
298·2	2·81	7·85	47·2	
298·2	2·68	7·85	49·0	
298·2	2·68	9·80	47·9	
298·2	2·68	9·80	48·6	

$$\log k_2 = 5{\cdot}56 + \tfrac{3}{2}\log T - (17{,}200 \pm 200)/4{\cdot}574T.$$

TABLE 2. *Ethylene glycol as solvent.*

T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)	T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)	T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)
273·2°	3·25	6·17	6·19	298·2°	3·20	82·8	82·8	323·2°	3·15	687	739
273·2	3·25	5·82		298·2	3·20	85·8		323·2	3·15	729	
273·2	3·25	5·58		298·2	3·20	90·4		323·2	3·15	679	

$$\log k_2 = 5{\cdot}85 + \tfrac{3}{2}\log T - (15{,}400 \pm 300)/4{\cdot}574T.$$

TABLE 3. *Methanol as solvent.*

T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)	T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)	T (K)	10^2a	10^4k_2 (exp.)	10^4k_2 (calc.)
273·2°	1·16	6·61	6·54	298·2°	1·13	77·5	77·3	323·2°	1·09	620	632
273·2	1·16	5·83		298·2	1·13	81·8		323·2	1·09	617	
273·2	1·16	6·70		298·2	1·13	82·1		323·2	1·09	630	

$$\log k_2 = 5{\cdot}28 + \tfrac{3}{2}\log T - (15{,}100 \pm 300)/4{\cdot}574T.$$

TABLE 4. *Ethanol as solvent.*

T (K)	10^3a	10^3b	d	10^3k_2 (exp.)	10^3k_2 (calc.)
273·2°	9·75	—	—	1·80	1·91
273·2	9·75	—	—	1·83	
323·2°	9·22	—	—	169	162
323·2	9·22	—	—	166	
323·2	9·72	—	—	170	
323·2	9·72	—	—	170	

T (K)	10^3a	10^3b	d	10^3k_2 (exp.)	10^3k_2 (calc.)
298·2°	9·50	—	—	22·1	21·1
298·2	9·50	—	—	22·2	
298·2	10·50	2·00	0·957	22·7	
298·2	10·50	2·00	0·957	22·6	
298·2	10·50	4·02	0·932	20·5	
298·2	10·50	6·00	0·917	21·6	
298·2	10·50	6·00	0·917	21·3	
298·2	10·50	7·85	0·907	20·9	
298·2	10·50	7·85	0·907	21·6	
298·2	10·50	9·62	0·899	20·7	
298·2	10·50	9·62	0·899	21·4	

$$\log k_2 = 5{\cdot}38 + \tfrac{3}{2}\log T - (14{,}700 \pm 300)/4{\cdot}574T.$$

TABLE 5. *Acetone as solvent.*

T (K)	10^2a	$10k_2$ (exp.)	$10k_2$ (calc.)	T (K)	10^2a	$10k_2$ (exp.)	$10k_2$ (calc.)	T (K)	10^2a	$10k_2$ (exp.)	$10k_2$ (calc.)
273·2°	1·50	7·32	7·91	283·2°	1·48	19·3	18·9	298·2°	1·45	57·8	63
273·2	1·50	7·36		283·2	1·48	18·3		298·2	1·45	61·7	
273·2	1·50	7·90		283·2	1·48	19·4		298·2	1·45	60·2	
				283·2	1·48	19·3					

$$\log k_2 = 6{\cdot}33 + \tfrac{3}{2}\log T - (12{,}600 \pm 500)/4{\cdot}574T.$$

TABLE 6. *Derived parameters for the methyl iodide–iodide ion exchange at* 25°.

Solvent	Water	Ethylene glycol	Methanol	Ethanol	Acetone
r (10^{-8} cm.)	3·16	3·55	2·46	2·76	4·73
$10^{-11}Z$	0·58	0·73	0·35	0·44	1·3
10^2P	4·1	4·9	2·8	3·3	8·0
E' (kcal. mole^{-1})	24·4	21·9	25·9	23·2	16·3
E_e (kcal. mole^{-1})	7·2	6·0	10·7	9·0	3·7
E (kcal. mole^{-1})	17·2	15·9	15·1	14·7	12·6
E_a (kcal. mole^{-1})	18·1	16·8	16·0	15·6	13·5

The values of the derived parameters r, Z, $P = \boldsymbol{R}T/2E_e$, E', E_e, and E_a at 25° are shown in Table 6. An inspection of the E_e values shows that the condition $1 - \exp(-2E_e/\boldsymbol{R}T) \simeq 1$ is valid for all five solvents. The large contribution of E_e to the total activation energy supports the assumption made in equation (4), namely, that the reaction takes place mainly in the direction represented by $\theta = \pi$.

If it is reasonably assumed that only directions of approach within the cone bounded by the three C–H bonds lead to inversion, it is possible to estimate quantitatively the fraction of successful collisions leading to inversion. By analogy with other methyl halides it may be assumed that the angle of the H–C–I bonds does not differ appreciably from the symmetrical value of 109° 28′. The corresponding angle which an approaching ion makes with the centre of the dipole is roughly 135°. Integration of equation (1) between the limits $3\pi/4$ to π, therefore, gives directly the number of successful collisions leading to inversion, namely,

$$k_{\text{invers.}} = \frac{Z\left[1 - \exp(-E_e/2\boldsymbol{R}T)\right]}{2E_e/\boldsymbol{R}T} \exp\left[-(E - E_e)/\boldsymbol{R}T\right] \quad . \quad . \quad (5)$$

By comparing this result with equation (2) it is obvious that the fraction of the successful collisions leading to inversion is given by $[1 - \exp(-1/4P)]/[1 - \exp(-1/P)]$. In all the solvents investigated this fraction was found to be greater than 0·99 which shows that, for the type of reaction considered, substitution is accompanied by almost complete inversion, irrespective of the assumptions made as to the nature of the transition state.

The order of increasing rate corresponds with the normally accepted order of decreasing polarity, though it is difficult to decide which of the two solvents, methanol or ethylene glycol, is to be regarded as the more polar.

As pointed out by Moelwyn-Hughes [9] the change in rate brought about by using different solvents is almost entirely due to a change in activation energy. In fact the rate depends so little on the value of PZ that the experimental rate constants, in the solvents investigated, may be reproduced, with a mean deviation of only 3%, by the general equation

$$\log_{10} k_2 = 5{\cdot}68 + \tfrac{3}{2}\log_{10} T - E/4{\cdot}574T \quad . \quad . \quad . \quad . \quad (6)$$

in which E has slightly different values from those recorded in Table 6.

The value of r for the above reaction may be calculated theoretically on lines similar to those by which Ogg and Polanyi [6] calculated the activation energy of the same reaction. When $2{\cdot}12 \times 10^{-8}$ cm. is used as the intranuclear separation of carbon and iodine in methyl iodide, the value obtained is $r = 2{\cdot}37 \times 10^{-8}$ cm. This value is virtually independent of the solvent and should therefore be equal to the value determined experimentally. With the possible exception of acetone the discrepancy is in no case excessive.

The value of the total activation energy in the various solvents depends on a large number of factors and no simple relation between the dielectric constant and the rate of reaction can be expected. Nevertheless the graph of $\log k_2$ against $1/\varepsilon$ at 25° yields approximately a straight line and it permits the estimation of k_2 to within a factor of about 3, which is not large considering that the total range in the rate, from water to acetone, varies by a factor of 10^5. This is of course only true provided the mechanism remains constant, degrees of dissociation are allowed for, and the relation between dielectric constant and polarity is not disturbed by preferential adsorption from a mixed solvent. It seems, therefore, that, provided the above conditions are fulfilled, the dielectric constant of a solvent is the predominating factor in determining the rate of ion–dipole reactions, and probably to a smaller extent of dipole-dipole reactions as well. If one or more of the above conditions is not fulfilled, however, other factors may take precedence over the

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[9] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1949, **45**, 167.

dielectric constant. This probably accounts for many, if not all, of the anomalous results reported in the literature.[10]

EXPERIMENTAL

Solvents.—Dry methanol (n_D^{15} 1·3312, d_4^{15} 0·7958) was prepared by refluxing absolute methanol over magnesium methoxide and distilling it through a fractionating column with a theoretical plate factor of about 36 plates.

Ethylene glycol (n_D^{20} 1·4274) was purified by fractional distillation through the same column.

Acetone, ethanol, and water were prepared as previously described.[8, 11]

Procedure.—The reactions were carried out, and concentrations at reaction temperatures were corrected for, as previously described.[11] Carbon tetrachloride proved to be a better extraction medium than benzene when reactions were carried out in ethylene glycol, although benzene was used for all the other solvents. The correction factors necessary to give the true activity ratio were found to be 1·402 for ethylene glycol, 1·136 for methanol, and 1·194 for acetone.

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[10] Norris and Prentiss, *J. Amer. Chem. Soc.*, 1928, **50**, 3042; Farinacci and Hammett, *ibid.*, 1937, **59**, 2536; Swain, *ibid.*, 1948, **70**, 1119.

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