373. *The Kinetics of Certain Reactions of the Alkyl Halides in Hydroxylic Solvents.*

By E. A. Moelwyn-Hughes.

On account of their simple structure, the alkyl halides are very suitable for the study of chemical reactivity, a measure of which is reflected by their relative velocity coefficients, and by the manner in which these coefficients vary with temperature. The present work records some observations on the interaction of ethyl iodide and the thiosulphate ion in water. Taken in conjunction with other comparable measurements, the results form the basis of a brief discussion of the mechanism whereby dissolved alkyl halides in general become activated.

Preliminary Experiments on the Reaction between Ethyl Iodide and Sodium Thiosulphate.—Slator (J., **1904**, **85**, 1286) states that 1 equiv. of an alkyl halide reacts almost quantitatively with either 1 or 2 equivs. of thiosulphate ($RX + S_2O_3'' \longrightarrow X' + RS_2O_3'$ or $2RX + S_2O_3'' \longrightarrow 2X' + R_2S_2O_3$) and that the reaction follows the simple bimolecular law. The present work confirms neither of these statements. There exists a fractional stoicheiometric ratio between the experimental equivalents of the two reactants. Although there is no doubt that the reaction is truly bimolecular, the constants calculated in the usual way fall during any experiment, owing to a side reaction wherein some of the halide reacts with the solvent.

In order to avoid loss by evaporation, sealed glass capsules containing a weighed amount of carefully fractionated, dry ethyl iodide were broken in a sealed vessel containing water; 10-c.c. samples of a 0·0176N-solution thus prepared were sealed in tubes containing excess of sodium thiosulphate. At the end of the reaction (1,000—5,000 minutes) titrations (T_∞) with 0·01N-iodine (Table I) showed that for every g.-equiv. of halide which had disappeared only 0·605 g.-equiv. of thiosulphate was consumed. A repetition using 0·2446 g. of ethyl iodide in a large volume of solution gave a ratio of 0·615.

This fractional result is not due to establishment of an equilibrium or to reactions producing 83% of the diethyl ester; it was traced to a side reaction between ethyl iodide and water, which was examined in some detail.

TABLE I.

0·01*N*-Iodine, c.c.

Temp.	T_0.	T_∞.	$T_0 - T_\infty$.	Temp.	T_0.	T_∞.	$T_0 - T_\infty$.	Temp.	T_0.	T_∞.	$T_0 - T_\infty$.
25°	40	29·35	10·65	51·4°	40	29·64	10·36	100°	40	20·19	9·81
	40	29·35	10·65		40	29·40	10·60		20	9·74	10·26
					20	9·60	10·40		20	9·72	10·28

Experiments on the Reaction between Ethyl Iodide and Water.—The sealed-tube method was again employed, and the iodide ion was estimated by titration against silver nitrate by Volhard's method. (This method could not be used in the thiosulphate experiments owing to oxidation of the thiosulphate by the indicator.) At 100°, 10-c.c. samples of a 0·02*N*-solution of ethyl iodide gave concordant infinity titrations of 14·45 c.c. of 0·01*N*-silver nitrate instead of the 20 c.c. expected. Slightly different values were found with other initial concentrations, and with solutions containing potassium iodide. The various values did not accord with any mass-action equation such as that corresponding to $C_2H_5I + H_2O \rightleftharpoons C_2H_5OH + HI$ or to other plausible final states. Experiments conducted with aqueous solutions of pure "conductivity" ethyl alcohol and hydriodic acid (prepared by the action of hydrogen sulphide on an aqueous suspension of iodine) showed no detectable reaction during a fortnight at 60°. With the same concentration (0·05*N*) at 100°, a fraction not exceeding 1% of the total hydrogen iodide disappeared after 5,000 minutes, but was quantitatively accounted for by atmospheric oxidation. Lest this slight reaction should play an important part in the hydrolysis of ethyl iodide, all the foregoing experiments were repeated in oxygen-free solutions, with results which were substantially the same. Finally, it was thought possible that some of the ethyl iodide might condense, during the reaction, in the cold capillary tip of the sealed tube, which usually stood out of the thermostat liquid; but in smaller tubes, totally immersed, similar results were obtained.

The more obvious errors of analysis and manipulation will consequently not explain the fact that some 28—32% of ethyl iodide is converted during hydrolysis into a form which is not titratable as iodide. The formation of ethyl ether will not explain the loss. It is therefore concluded that a portion of the ethyl iodide is converted into a complex soluble organic compound (*e.g.*, an iodo-ether) in which the iodine resists the usual titration reactions. The phenomenon seems to be general for alkyl halides.

The kinetics of the hydrolysis of ethyl iodide in water appear to be, at the initial stages, quite simple. Here the complications due to secondary disturbances are absent, for the initial rate is independent of the concentration of the reactant, yielding at any given temperature a readily reproducible unimolecular constant under all conditions. The experimental values are summarised below, along with those calculated from the relation $\log_e k_1 = 21{\cdot}11 - 21{,}180/RT$.

Temp.	60·2°	77·0°	100·0°
$k_1 \times 10^5$ (sec.$^{-1}$), obs.	1·67	7·96	51·3
,, ,, calc.	1·69	7·88	50·9

Experiments on the Reaction between Ethyl Iodide and Sodium Thiosulphate.—The kinetics of the reaction between ethyl iodide and sodium thiosulphate in water are expressible by the equation

$$-d[\mathrm{EtI}]/dt = k_1[\mathrm{EtI}] + k_2[\mathrm{EtI}][\mathrm{S_2O_3}'']$$

In order to evaluate k_2 from the constant found by integration, it is necessary to know the instantaneous concentration of ethyl iodide, which, in view of the complicated hydrolytic reaction, is not possible. Since the hydrolysis is initially unimolecular, it is clear that the ratio of 0·6 for $[S_2O_3'']/[C_2H_5I]$ holds only at the completion of the reaction. The difficulty is, however, not serious, because the value of k_1 is very small compared with that of k_2. We should therefore expect that, if the ordinary bimolecular equation is employed, the values of k will fall slightly, the extrapolated value corresponding to $t = 0$ giving a true indication of the velocity. The following data for 20-c.c. samples of an equivalent solution (0·01535*N*) at 25° typify the results generally obtained. The effect of altering the initial concentration leaves no

t (mins.)	0	30	371	635	1490	3420	4740
0·009605*N*-$Na_2S_2O_3$, c.c.	21·94	21·26	17·10	14·85	10·69	8·36	7·92
$k \times 10^3$	—	1·29	1·17	1·16	1·10	0·93	0·58

doubt that the reaction is bimolecular, and the reason for the inapplicability of the simple expression is clear. Incidentally, the empirical values of k, calculated from the observed end-point, are fairly constant during the course of any experiment, but are, of course, without physical significance. Duplicate experiments performed at various temperatures gave concordant values of k_2, determined by extrapolation; the variation of k_2 with temperature is expressed by the equation $\log_e k_2 = 29{\cdot}70 - 21{,}430/RT$, as shown below :

Temp.	25·00°	36·26°	44·50°	51·65°	55·65°
$k \times 10^3$ (l./g.-mol./sec.), obs.	1·29	4·25	12·1	25·5	35·9
,, ,, calc.	1·30	4·31	12·1	25·4	37·6

The Molecular Statistics of Certain Reactions undergone by Ethyl Iodide in Hydroxylic Solvents.

If we now compare the number of molecules of ethyl iodide or of thiosulphate ions which react per c.c. per second with the number of activating collisions as given by the expression

$$n_1 n_2 \sigma_{1,2}^2 \{8\pi RT(1/M_1 + 1/M_2)\}^{\frac{1}{2}} \, . \, e^{-E/RT}$$

it is found that the experimental velocity exceeds the calculated value by a factor of about 28. The disparity may be due to error in the determination of E; the fact that second substitution of an ethyl group can take place must not be overlooked. On the other hand, the factor may be genuine, indicating that one internal degree of freedom contributes to the energy of activation. According to Hinshelwood's theory, the above expression would then have to be multiplied by the term E/RT. This brings the observed and the calculated rate very near together, their ratio being 1·2 : 1·0. It is clear that we are here dealing with a chemical reaction possessing a velocity lying within a reasonable range of the values predicted by the theory of simple collisional activation.

Data for other reactions belonging to the same category are in Table II (for details and references, see Moelwyn-Hughes, " The Kinetics of Reactions in Solution," Oxford, 1933). According to the criteria which can at present be applied, it may be concluded that each of these reactions takes place between an ion and a neutral molecule. The most significant fact concerning them is that, even to detailed parallelisms between E and $\log k$, the observed rates are consistent with the view that a very simple type of activation is sufficient guarantee for chemical change to take place. Now the variation in E, though real, is so small as to suggest the existence of a common mechanism, if not a common reaction, for them all. If we restrict attention to those reactions occurring in alcoholic solution, the second suggestion becomes plausible, for equilibria of the type $C_6H_5O' + C_2H_5{\cdot}OH \rightleftharpoons C_6H_5{\cdot}OH + C_2H_5O'$ can give rise to a common ion in each case. Purely chemical evidence, however, rules out this possibility, except as a concurrent process. As far as can be judged from the not very varied results at present available, it seems that a critical increment of 21,300 (± 700) cals. holds for the reactions occurring between ethyl iodide and different anions originating from strong electrolytes in hydroxylic solvents. The inference is that the energy of activation is concerned chiefly, though not quite completely, with one of the reacting species.

TABLE II.

Reaction of EtI with	Solvent.	$k_{25^\circ} \times 10^5$.	E (cals.).	Reaction of EtI with	Solvent.	$k_{25^\circ} \times 10^5$.	E (cals.).
KOH	EtOH	16·5	20,670	$CH_2Ph{\cdot}ONa$	EtOH	1·28	21,860
EtONa	,,	9·40	20,650	$Na_2S_2O_3$	H_2O	129	*ca.* 21,430
PhONa	,,	0·58	22,000				

Hinshelwood ("The Kinetics of Chemical Change in Gaseous Systems," 3rd edtn., Oxford, 1933) has pointed out that the expression $e^{-E/RT}$ gives the fraction of activating collisions whether E is regarded as translational energy of the colliding molecules or as the sum of separate energies of activation, E_1 and E_2, each capable of independent variation within certain limits. The expression must be valid in the special case where $E_2 = 0$, *i.e.*, when only one of the reacting species requires activation. It would appear that this is the condition to which the reactions here discussed approximate.

It is rather surprising that E for the hydrolysis of ethyl iodide (21,200 cals.) should be nearly equal to that for the reaction with thiosulphate (21,430). The result is consistent with the idea of independent activation of the halide, with a low chemical efficiency (about 1 in 25) of activating collisions with water molecules. Alternatively, the observed value of E may not be the true energy of activation (compare J., 1932, 92). The identity of the E values for the ionic and the hydrolytic reaction would scarcely deserve mention apart from the existence of a close and reputable analogue. The critical increment for the reaction $CH_2Cl{\cdot}COO' + OH' \longrightarrow CH_2(OH){\cdot}COO' + Cl'$ is 25,850 cals., and for the corresponding hydrolysis is 26,310 (van 't Hoff, " Studies in Chemical Dynamics," 1896). The latter reaction is composite (Dawson and Dyson, this vol., p. 49), but there is as yet no evidence as to the critical increments of the separate reactions.

If the theory of independent activation—which, it must be emphasised, is here discussed as a possibility rather than accepted as a final solution—is correct, the mechanism of activation demands that ionic separation of the ions $C_2H_5^{\cdot}$ and I' must take place within the halide molecule prior to, or simultaneously with, the reaction proper. How closely this corresponds to electrical dissociation can only be judged when the variation with temperature of the electrical conductivity of the halide is known. All that may be asserted at present is that the observed energy of activation of several reactions occurring between ethyl iodide and negative ions lies between two limits which may reasonably be imposed. They are the heat of dissociation of aliphatic alcohols (*ca.* 12,000 cals.) on the one hand, and the dissociation energy (*ca.* 43,000) of the non-electrical separation $C_2H_5I \rightleftarrows C_2H_5 + I$ on the other.

Ethyl iodide reacts with nitrogenous bases in hydroxylic solvents by a mechanism which is different from that discussed above. The available data (Table III; calculated from Hirniak's figures, " Tables Annuelles," 1911, **2**, 508) are not so precise, and there is no clear indication as to the ionic type of the reactions; but there remains no doubt as to the reality of the variation of the critical increments, and to the failure of the simple collision theory to account for the velocities by accepting the observed values of E as true. The observed range of velocities is 20, compared with the hypothetical range of 10^6. The problem thus presented has recently been reviewed at some length (*Chemical Rev.*, 1932, **10**, 240; Moelwyn-Hughes and Hinshelwood, J., 1932, 230; Moelwyn-Hughes and Rolfe, *ibid.*, p. 241; Polissar, *J. Amer. Chem. Soc.*, 1932, **54**, 3105; Roberts and Soper, *Proc. Roy. Soc.*, 1933, *A*, **140**, 71; Thompson and Blandon, this vol., p. 1237), and need not be reconsidered here. The position at present is simply that the assumption of simple activation of the halide accounts for the rates of those reactions mentioned in Table II, but not for those in Table III.

TABLE III.

Reactions between Ethyl Iodide and Nitrogenous Bases in Methyl-alcoholic Solution.

Base.	$k_{60^\circ} \times 10^4$ (l./g.-mol./min.; $\log_{10}$).	E, cals.	Base.	$k_{60^\circ} \times 10^4$ (l./g.-mol./min.; $\log_{10}$).	E, cals.
Dimethyl-*p*-toluidine	13·6	17,700	Quinoline	5·45	24,400
*iso*Quinoline....................	3·17	19,000	α-Naphthaquinoline ...	1·46	25,000
Pyridine	4·66	20,200	Collidine	1·30	25,800
α-Picoline......................	1·12	23,200	β-Naphthaquinoline ...	0·61	26,700

SUMMARY.

The number of molecules of ethyl iodide which react per second with thiosulphate ion in aqueous solution corresponds with the number calculated by assuming a very simple type of activation to be necessary. The energy of activation is taken to be equal to the critical increment, which is 21,430 calories.

There occurs a complicated side reaction between ethyl iodide and water, which begins with a unimolecular velocity given by the relation $k = 1{\cdot}5 \times 10^9 \times e^{-21{,}180/RT}$ sec.$^{-1}$.

The similarity in the value of E found for various reactions between ethyl iodide and anions in hydroxylic solvents suggests that the process of activation relates chiefly to the alkyl–halide link.

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FRANKFURT-AM-MAIN.

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