71. *The Kinetics of Reactions in Solution. The Interaction of Potassium Hydroxide and the Alkyl Halides in Ethyl Alcohol.*

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SOME reactions in solution take place at a rate given approximately by the expression *number of collisions between reacting species* $\times e^{-E/RT}$. Others are many powers of ten slower (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35). The difference in mechanism between the two classes is not fully understood. The slowness of the second class is not due to solvent deactivation, as was originally supposed, but depends in some way on the nature of the reacting molecules themselves (Moelwyn-Hughes and Hinshelwood, J., 1932, 230). More information about the molecular statistics of bimolecular reactions in solution is thus needed. In particular, very careful determinations of the temperature coefficients are necessary so that the heats of activation can be found with greater accuracy than some of the older measurements allow.

In examining a list of reactions (cf. Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241) which take place roughly at the rate given by the simple equation, we were impressed by the fact that in almost all of them one of the reacting species was an ion. On the other hand, reactions such as the combination of tertiary amines and alkyl halides, or the interaction of acetic anhydride and alcohol, which belong to the " slow " group, are changes which appear *prima facie* to involve neutral molecules. The hydrolysis of esters by hydroxyl seems to be " slow " also, but looks as though it may be exceptional. The available examples are not really varied enough to justify any conclusion, but suggest that still further types of reaction should be investigated in order that the range of validity of the following hypothesis may be discovered: that reactions between an organic compound and an ion in solution tend to take place at approximately the rate given by the simple kinetic equation, while interactions of neutral molecules are frequently several powers of ten slower under comparable conditions.

The present paper deals with the simplest type of reaction between an organic compound and an ion, *viz.*, the interaction of potassium hydroxide and the ethyl halides in alcoholic solution. This, as shown by the results below, appears to belong to the class in which the collisions are " efficient."

The conventional equation gives ethylene as the product of the reactions, but Brussoff (*Z. physikal. Chem.*, 1900, **34**, 129) found, and we have confirmed, that a relatively small proportion is formed, most of the halide in dilute solution being presumably converted into alcohol. Formation of ether is only likely when there is a considerable concentration of ethoxyl ions, and that these do not play an important part in the reaction is suggested by the fact that the influence of water additions is small. As the proposed experimental method was to measure the rate of disappearance of hydroxyl ion, the question had to be considered whether the different products were formed in independent reactions, each with its individual heat of activation. The kinetic relationships would then be complex. But it is quite possible that the measured rate is determined by a single primary reaction between hydroxyl and the halide, and that the proportions of alcohol and ethylene depend upon processes subsequent to the initial act; *e.g.*, activated alcohol molecules may be formed, a certain proportion of which decompose into ethylene and water. Whether this simple view of the process was admissible could only be judged by the results. If the hydroxyl disappears in a complex reaction, the velocity constants for various temperatures would hardly be expected to conform to a simple Arrhenius equation, giving a constant heat of activation. If, by some compensation of errors, such a constant value were to be found, its introduction into any theoretical equation for the absolute rate of reaction would give completely wrong results, and the error should be very different for the three halides. The fact that for all three the Arrhenius equation is accurately satisfied, and, moreover, that the same relation between the heat of activation and the absolute rate of each is found, shows that the simple hypothesis gives a coherent interpretation of the results.

The exptl. method was simply to prepare solutions of KOH and of the carefully redistilled halides in EtOH, mix suitable quantities in a tube, which was then sealed and placed in a thermostat, and after a known time to titrate the residual alkali with acid and phenolphthalein. A standardised procedure was adopted in diluting the alc. solutions for titration, indicator errors being thereby avoided. For the time taken by the tubes to attain the temp. of the thermostat no correction was necessary except at the highest temps., where an empirically determined allowance was made.

The most detailed investigation was made with EtBr, the results for which are typical of all three halides.

Table I shows the influence of solvent purity on the rate of reaction with 0·05*N*-reactants; A, B, and C refer to various specimens of the purified substances.

TABLE I.

Alcohol.	C_2H_5Br.	KOH.	$k \times 10^3$ at 59·75°.	Alcohol.	C_2H_5Br.	KOH.	$k \times 10^3$ at 59·75°.
Crude	A	A	2·73	Specially pure for conductivity ...	B	A	3·16
Lime-distilled ...	B	A	3·21	,, ,,	B	B	2·96
,, ,, ...	B	C	3·31	,, ,,	B	B	2·99
Containing 10% H_2O	B	B	3·24				

The course of the reaction is fairly closely bimolecular, although the value of *k* tends to fall during the early stages. The fall is much more pronounced with EtI than with EtCl or EtBr. In Table II, *t* is the time in min., *x* the titre of the solution expressed as c.c. of *N*/10-acid, and *k* the bimolecular velocity const. expressed in g.-mols./l./sec.

TABLE II.

(*a*) Temp. 59·75°.
[KOH] = [EtBr] = *N*/10.

t.	*x*.	$10^3 k$.*	*t*.	*x*.	$10^3 k$.*
0	20·0	—	66	9·35	2·88
12	16·48	2·97	97	7·42	2·91
21	14·71	2·85	134	6·16	2·80
32	13·17	2·68	164	5·17	2·92
46	11·14	2·88	210	4·31	2·89

(*b*) Temp. 59·75°.
[KOH] = *N*/80, [EtBr] = *N*/20.

t.	*x*.	$10^3 k$.*	*t*.	*x*.	$10^3 k$.*
0	10·0	—	108	2·90	4·28
12	8·59	4·39	131	2·25	4·33
24	7·33	4·48	148	1·93	4·27
41	6·04	4·33	171	1·45	4·39
63	4·71	4·32	218	0·96	4·28
84	3·74	4·29			

(*c*) Temp. 50·02°.
[KOH] = [EtI] = *N*/20.

t.	*x*.	$10^3 k$.	*t*.	*x*.	$10^3 k$.
8	9·19	3·67	192	4·02	2·59
15	8·71	3·29	240	3·46	2·63
32	7·73	3·06	291	3·07	2·59
48	7·11	2·82	390	2·42	2·68
60	6·65	2·80	509	1·96	2·69
90	5·74	2·75	696	1·54	2·64
134	4·88	2·61			

(*d*) Temp. 50·02°.
[KOH] = [EtI] = *N*/20.
(Soltn. satd. with KI.)

t.	*x*.	$10^3 k$.	*t*.	*x*.	$10^3 k$.
8	9·22	3·53	144	4·82	2·50
15	8·74	3·21	192	4·12	2·48
30	7·92	2·92	291	3·13	2·51
50	7·22	2·56	386	2·61	2·44
60	6·81	2·60	503	2·18	2·38
90	5·84	2·64	647	1·70	2·52

* In these two expts. the initial fall in the const. has occurred before the first recorded reading.

The results for the chloride are almost exactly similar in form to those for the bromide, any fall in the const. occurring only in the very earliest stages of the reaction.

The series of expts. recorded in Table II (*d*) show that the initial fall in the const. for the iodide is not due to the increasing concn. of KI, since there is an almost exact correspondence between (*c*) and (*d*). This also shows that the $K^{\cdot}$ ion is not directly concerned in controlling the speed of the reaction. The drift in the const. is not due to the formation of H_2O, since the initial addition of 5% of H_2O to some very pure dry EtOH neither eliminated the drift nor changed the mean value of the const. by more than 10%.

The bimolecular velocity const. is unaffected by variation of the initial concn. of the halide, but increases as the initial concn. of the KOH falls (see Table III in which [KOH] and [EtBr] refer to initial concns.). The increase is probably due to the greater ionisation of the KOH.

A similar effect was found with EtI, and presumably exists also with EtCl; *e.g.*, by decreasing the concn. of the KOH from 0·10 to 0·025 (at 40·29°) the const. for the iodide was changed from

$9{\cdot}2 \times 10^{-3}$ to $12{\cdot}4 \times 10^{-3}$, the ratio being the same as for the bromide reaction over the same range.

TABLE III.

Temp. 59·75°.

[KOH].	[EtBr].	$10^3 k$.	[KOH].	[EtBr].	$10^3 k$.	[KOH].	[EtBr].	$10^3 k$.	[KOH].	[EtBr].	$10^3 k$.
0·1	0·1	2·89	0·05	0·1	3·33	0·025	0·1	3·65	0·0125	0·1	4·15
	0·05	2·93		0·05	3·31		0·05	3·70		0·05	4·33
	0·025	2·68		0·025	3·36		0·025	3·76		0·025	4·42
	0·0125	2·58		0·0125	3·13		0·0125	3·70		0·0125	4·56

TABLE IV.

Ethyl chloride.

Temp.	$10^3 k$ (obs.).	$10^3 k$ (calc.).	Temp.	$10^3 k$ (obs.).	$10^3 k$ (calc.).
40·35°	0·0111	0·0112	80·00°	0·773	0·766
59·75	0·0996	0·100	90·61	1·89	2·02
70·63	0·306	0·308			
	Ethyl bromide.			*Ethyl iodide.*	
15·83	0·0237	0·0245	15·83	0·0503	0·052
24·74	0·0763	0·075	24·74	0·153	0·162
32·02	0·182	0·178	32·02	0·368	0·373
40·29	0·466	0·45	40·29	0·958	0·95
50·12	1·35	1·26	50·12	2·70	2·65
59·75	3·31	3·37	59·75	6·71	6·9
70·63	10·2	9·3	70·63	19·9	19·5
80·00	22·6	21·2	80·00	46·0	45·5
90·61	52·8	52	90·61	119	110

In Table IV are recorded the mean velocity consts. at various temps. for the three reactions, and the corresponding values calculated from the equations given below. For the iodide reaction, the consts. are averaged over the second half, to eliminate any influence of the initial fall. All values of k refer to initial concns. of $N/20$ for each reacting substance.

The bimolecular course of the change, the small increase in the constant with increasing dilution of the potash but not of the halide, and the absence of any marked influence of potassium iodide on the ethyl iodide reaction, all go to show that the rate-controlling process is an interaction between the halide molecule and the hydroxyl ion. The initial drift of the constants and the dilution effect show that an exact expression of k in terms of concentration is a complex problem, the solution of which would demand detailed knowledge of the electrochemistry of potassium hydroxide in alcohol. But the principal purpose of the investigation is to find the relation between the energy of activation of the reactions and their absolute rates. The rate being an exponential function of the energy of activation, very small changes in the latter make large changes in the former. Such changes in k as are produced, *e.g.*, by dilution, are relatively unimportant, since we can only hope to correlate the exact value of E with the order of magnitude of k. The E values may be taken as correct, since the Arrhenius equation is satisfied so well.

Within a factor of about 2, the equations summarising the experimental results at different temperatures agree with those expressing the condition that the number of molecules reacting is equal to (the number of collisions between hydroxyl ions and halide molecules) $\times e^{-E/RT}$. In Table V the second column gives the equations which were used in calculating the k (calc.) values of Table IV, *i.e.*, in summarising empirically the observed results. The third column gives the equations based upon the assumption: number of molecules reacting $= Z \, . \, e^{-E/RT}$, where Z is calculated from the formula

$$Z = N_1 N_2 \sigma_{12}^2 \{8\pi RT(1/m_1 + 1/m_2)\}^{\frac{1}{2}} ;$$

m_1 and m_2 are the two molecular weights. σ_{12}, the mean of the diameters of the colliding particles, was taken as 4×10^{-8} cm. throughout. N_1 and N_2 are the numbers of molecules of the two reacting species in 1 c.c.; when they are so chosen that they correspond to 1 g.-mol. per litre, then the actual number of g.-mols. per litre reacting is numerically equal to k.

TABLE V.

Velocity constants for the interaction of ethyl halides and potassium hydroxide.

	Empirical.	Required by the collision formula.
Chloride	$k = 0{\cdot}793 \times 10^{10}\sqrt{T} \,.\, e^{-23{,}000/RT}$	$k = 1{\cdot}21 \times 10^{10}\sqrt{T} \,.\, e^{-23{,}000/RT}$
Bromide	$k = 1{\cdot}28 \times 10^{10}\sqrt{T} \,.\, e^{-21{,}000/RT}$	$k = 1{\cdot}15 \times 10^{10}\sqrt{T} \,.\, e^{-21{,}000/RT}$
Iodide	$k = 2{\cdot}70 \times 10^{10}\sqrt{T} \,.\, e^{-21{,}000/RT}$	$k = 1{\cdot}13 \times 10^{10}\sqrt{T} \,.\, e^{-21{,}000/RT}$

It is worth pointing out that the much smaller rate of reaction of the chloride is accounted for by the larger heat of activation.

SUMMARY.

Some reactions of organic substances in solution take place at a rate given by the equation: number of molecules reacting = number colliding $\times\, e^{-E/RT}$. Others are several powers of ten slower. The desirability of investigating how far the former class is confined to reactions between an ion and a molecule, and the latter to interactions of neutral molecules, is suggested. The reactions between potassium hydroxide and the ethyl halides in alcoholic solution have been measured and found to belong to the former class.

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