404. *Reaction-kinetic Investigations of the Incomplete Dissociation of Salts. Part II. The Hydrolysis of Carbethoxymethyltriethylammonium Iodide and of Ethyl Acetate by Solutions of Metal Hydroxides.*

By R. P. BELL and (MRS.) G. M. WAIND.

Kinetic measurements have been made on the alkaline hydrolysis of carbethoxymethyltriethylammonium iodide at 0°. The reaction shows a large primary negative salt effect, and is specifically retarded by calcium and barium ions. This retardation can be accounted for by the formation of $CaOH^+$ and $BaOH^+$, and agrees quantitatively with the dissociation constant of $CaOH^+$ at 0°, which was determined by measuring the solubility of calcium iodate in solutions of sodium hydroxide. Measurements on the alkaline hydrolysis of ethyl acetate showed that calcium and barium ions have no detectable retarding effect in this reaction. The varying behaviour in different reactions involving hydroxyl ions is accounted for in terms of the properties of the transition state.

IN the first paper of this series (Bell and Prue, *J.*, 1949, 362) it was shown that, when diacetone alcohol decomposes in presence of hydroxyl ions, the presence in the solution of calcium, barium, or thallium ions causes a reduction in reaction velocity which can be reasonably accounted for in terms of the incomplete dissociation of the hydroxides concerned. For the hydroxides of barium and thallium the degrees of dissociation agreed with those obtained by other methods (*e.g.*, solubility measurements), but for calcium hydroxide the kinetic value was higher by an amount which probably exceeded the experimental error. It was pointed out that the apparent degrees of dissociation derived from kinetic measurements will be too high if the metallic ions concerned associate with the transition state of the reaction as well as with the hydroxyl ion. This association with the transition state is likely to be a minimum in a reaction such as

$$^{+}NEt_3{\cdot}CH_2{\cdot}CO_2Et + OH^- \longrightarrow {}^{+}NEt_3{\cdot}CH_2{\cdot}CO_2^- + EtOH$$

where the transition state has a net charge of zero, and we have therefore made measurements of the velocity of this reaction in presence of sodium, calcium, and barium ions. In order to determine the degree of dissociation of $CaOH^+$ at 0°, a study was made of the solubility of calcium iodate in solutions of sodium hydroxide at this temperature, and some kinetic experiments were made on the hydrolysis of ethyl acetate by various hydroxides.

EXPERIMENTAL.

Carbethoxymethyltriethylammonium chloride was prepared by the reaction of equivalent quantities of triethylamine and ethyl monochloroacetate in alcohol at 0°. The crude chloride was dissolved in acetone and treated with one equivalent of potassium iodide; after the potassium chloride had been filtered off, the solution was evaporated to dryness and the iodide recrystallized from acetone, giving fine white crystals, m. p. 126—127°, 99·9% pure by titration with silver nitrate.

Kinetic measurements were carried out at 0° with equal initial concentrations (0·003—0·006M.) of ester salt and sodium hydroxide free from carbonate. In most experiments the solutions also contained sodium chloride, barium chloride, or calcium chloride; the concentrations of the last two substances were determined in their stock solutions by the gravimetric estimation of chloride (as silver chloride) and barium (as barium sulphate), and the volumetric determination of calcium as oxalate.

In making kinetic measurements the solution containing sodium hydroxide and added salt was contained in a small flask, and 1 c.c. of a stock solution of ester (which was stable for at least several days) in a thin-walled glass bulb resting on the bottom of the flask. A slow stream of air freed from carbon dioxide was passed through during the whole experiment. After 20 minutes at 0° the bulb was broken and a clock started simultaneously. After a suitable reaction time (0·5—4 minutes) the reaction was stopped by adding 10 c.c. of N/100-hydrochloric acid, and the excess of acid titrated with N/100-ammonia solution (methyl-red). Six such experiments were carried out with each reaction mixture, using reaction times covering about two-thirds of the total reaction. As a check one experiment in each set was allowed to continue to completion: the observed titres agreed with those calculated, within experimental error.

Because of the short times and high dilutions involved the individual observations are not very accurate. The second-order velocity constants k were obtained by plotting $x/(a - x)$ (a = initial concentration of both reactants, $a - x$ = concentration after time t) against the time in minutes, and determining the slope of the best straight line (ak) by the method of least squares. Fig. 1 shows the lines for two typical reactions. Table I gives the observed velocities for all the solutions studied.

TABLE I.

Hydrolysis of carbethoxymethyltriethylammonium iodide by sodium hydroxide.

$10^3 a$.	Added salt.	Ionic strength (I).	k.	$10^3 a$.	Added salt.	Ionic strength (I).	k.
5·66	—	0·0057	241	5·66	0·218M-NaCl	0·224	142
5·91	—	0·0059	254	5·66	0·0726M-$CaCl_2$	0·224	104
3·30	0·0234M-NaCl	0·0267	202	4·22	0·274M-NaCl	0·278	136
5·60	0·118M-NaCl	0·124	169	4·22	0·0913M-$BaCl_2$	0·278	127
6·10	0·175M-NaCl	0·181	156	3·98	0·291M-NaCl	0·295	140
6·10	0·0582M-$CaCl_2$	0·181	119	3·98	0·145M-NaCl	—	—
5·13	0·178M-NaCl	0·184	158		+0·0484M-$CaCl_2$	0·295	115
5·13	0·0395M-$BaCl_2$	0·184	154	3·98	0·0969M-$CaCl_2$	0·295	93

The solubility of calcium iodate in colutions of sodium chloride and hydroxide at 0° was measured exactly as described by Davies (*J.*, 1938, 277), using a Dewar flask containing ice and water as a thermostat, and excluding carbon dioxide from the saturator. The values obtained are given in the first two columns of Table II. In interpreting the results it is necessary to make a small correction for the presence of the species $CaIO_3^+$ and $NaIO_3$, and for this purpose we have used the thermodynamic dissociation constants given by Davies (*loc. cit.*) for 25°, $K(CaIO_3^+) = 0{\cdot}13$, $K(NaIO_3) = 3{\cdot}0$. The thermodynamic solubility product of calcium iodate, $P[Ca(IO_3)_2]$, is obtained by extrapolating to $I = 0$ the measured solubilities in water and in dilute sodium chloride solutions. The ionic strengths are sufficiently low for the limiting law to be obeyed, and the resulting values are $s_0 = 1{\cdot}940 \times 10^{-3}$, $P = 4s_0^3 = 2{\cdot}921 \times 10^{-8}$. The concentrations of the various species present are then given by the equations

$$\left.\begin{aligned} \log_{10}[NaIO_3] &= \log_{10}[Na^+] + \log_{10}[IO_3^-] - \log_{10}K(NaIO_3) - f(I) \\ \log_{10}[CaIO_3^+] &= \log_{10}[Ca^{++}] + \log_{10}[IO_3^-] - \log_{10}K(CaIO_3^+) - 2f(I) \\ \log_{10}[Ca^{++}] &= \log_{10}P(Ca(IO_3)_2) - 2\log_{10}[IO_3^-] + 3f(I) \\ 2s &= [IO_3^-] + [NaIO_3] + [CaIO_3^+] \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

together with the condition for electrical neutrality and a knowledge of the total amount of sodium added. s is the measured solubility in moles per litre, and $f(I)$ is a function representing the dependence of the ionic activity coefficients on ionic strength. For $\mathrm{f}(I)$ we have used two alternative expressions,

$$\left.\begin{array}{ll}(a) & \mathrm{f}(I) = -\log_{10}\mathrm{f} = 0{\cdot}490\, I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \\ (b) & \mathrm{f}(I) = -\log_{10}\mathrm{f} = 0{\cdot}490\, I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2\, I\end{array}\right\} \qquad (2)$$

By use of either of these, the equations in (1) can be solved by successive approximations, and the concentrations of $CaOH^+$ and OH^- calculated by difference. An approximate value for the thermodynamic dissociation constant of $CaOH^+$ is then given by

$$\log_{10}K'_d = \log_{10}[Ca^{++}] + \log_{10}[OH^-] - \log_{10}[CaOH^+] - 2\mathrm{f}(I) \qquad (3)$$

FIG. 1.

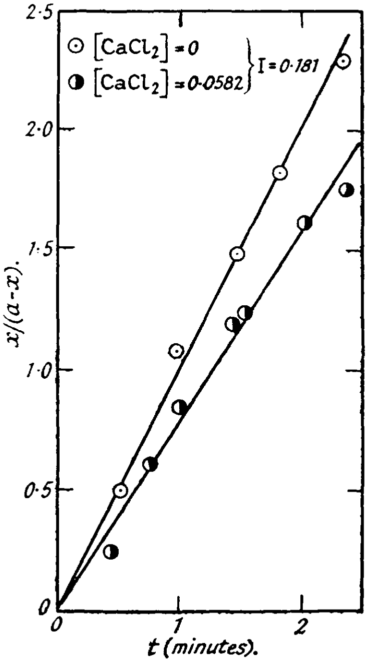
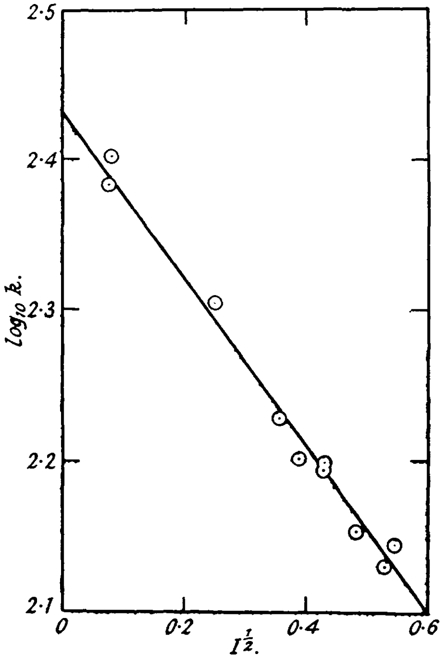


FIG. 2.



The values obtained are given in Table II. The mean values of K'_d do not differ much from the value 0·03 at 25° obtained by the same method by Davies.

TABLE II.

Solubility of calcium iodate at 0°

10^3[NaCl].*	10^3s.	$10^3[NaIO_3]$	$10^3[CaIO^+_3]$.	$10^3[CaOH^+]$.	I.	K'_d.
—	2·333	—	—	—	0·0070	—
1·000	2·371	—	—	—	0·0081	—
2·000	2·423	—	—	—	0·0093	—
3·000	2·459	—	—	—	0·0104	—
4·000	2·488	—	—	—	0·0115	—
10^3[NaOH].*						
18·16	2·836	(*a*) 0·025	(*a*) 0·054	(*a*) 0·415	(*a*) 0·0257	(*a*) 0·054
		(*b*) 0·025	(*b*) 0·054	(*b*) 0·510	(*b*) 0·0255	(*b*) 0·043
31·37	3·093	(*a*) 0·044	(*a*) 0·054	(*a*) 0·601	(*a*) 0·0397	(*a*) 0·060
		(*b*) 0·045	(*b*) 0·053	(*b*) 0·737	(*b*) 0·0394	(*b*) 0·047
45·40	3·350	(*a*) 0·065	(*a*) 0·052	(*a*) 0·897	(*a*) 0·0535	(*a*) 0·052
		(*b*) 0·067	(*b*) 0·051	(*b*) 1·063	(*b*) 0·0532	(*b*) 0·042
68·10	3·606	(*a*) 0·098	(*a*) 0·052	(*a*) 1·014	(*a*) 0·0767	(*a*) 0·063
		(*b*) 0·102	(*b*) 0·050	(*b*) 1·266	(*b*) 0·0762	(*b*) 0·046
					Mean	(*a*) 0·057 (*b*) 0·044

* Denotes stoicheiometric concentration.

The alkaline hydrolysis of ethyl acetate was studied at 25° by the usual titration method, using approximately 0·02M-concentrations of ester and sodium hydroxide. Experiments with varying quantities of added sodium chloride up to 0·5M. gave the following values (in order of increasing ionic strength) for the second-order velocity constant k (minutes, moles/l.) : k = 5·92, 5·97, 5·90, 6·04, 6·05, 5·95, 5·99, 5·93, 6·01. There is thus no detectable salt effect under these conditions. Experiments were also done with varying additions of barium chloride and calcium chloride, and in each group of these experiments the ionic strength was made up to a constant value by the addition of sodium chloride. The results are given in Table III. It will be seen that the effect of barium chloride is to increase the velocity slightly, whereas calcium chloride had no detectable effect. In neither case is there any decrease which could be related to the incomplete dissociation of barium or calcium hydroxide.

TABLE III.

Hydrolysis of ethyl acetate at 25°.

[Ester.]	[NaOH.]	Added salt.	k.	
0·0111	0·0207	Nil	5·90	$I = 0{\cdot}198$
		0·0099M-$BaCl_2$	5·92	
		0·0197M-$BaCl_2$	6·21	
		0·0394M-$BaCl_2$	6·31	
		0·0592M-$BaCl_2$	6·50	
0·0219	0·0219	Nil	5·92	$I = 0{\cdot}153$
		0·0437M-$BaCl_2$	6·38	
0·0159	0·0159	Nil	5·99	$I = 0{\cdot}442$
		0·0711M-$CaCl_2$	5·78	
		0·1421M-$CaCl_2$	5·63	
0·0117	0·0117	Nil	6·01	$I = 0{\cdot}489$
		0·0995M-$CaCl_2$	6·03	
		0·1592M-$CaCl_2$	5·97	

DISCUSSION.

As would be expected for a reaction between oppositely charged ions, the reaction between the ester cation and hydroxyl ions shows a large negative salt effect. When the added salt is sodium chloride the magnitude of this effect agrees approximately with theoretical predictions. This is shown in Fig. 2, where $\log_{10}k$ is plotted against $I^{\frac{1}{2}}$: the straight line drawn has a slope of 0·6, while the theoretical slope (from the Debye–Hückel limiting law) is 0·98. The limiting law would not be expected to hold at the high ionic strengths which we have used, and our results are consistent with those of Nielsen (*J. Amer. Chem. Soc.*, 1936, **58**, 206), who found for the same reaction that the limiting law is obeyed for $I < 0{\cdot}1$, with deviations towards a smaller slope in more concentrated solutions.

If a comparison is made between the effect of adding sodium chloride and that of adding calcium chloride to the same ionic strength (cf. Table I), it is clear that the presence of calcium ions has a specific effect in reducing the reaction velocity still further. Since it is unlikely that there will be considerable interaction between calcium ions and the uncharged transition state, the simplest explanation of the reduced velocity is the removal of some hydroxyl ions as the species $CaOH^+$ In our experiments the concentration of Ca^{++} was considerably greater than that of OH^-, and under these conditions it is easily seen that the replacement of Na^+ by Ca^{++} at constant ionic strength will reduce the velocity by a factor $1 + [Ca^{++}]/K_c$, where $K_c = [Ca^{++}][OH^-]/[CaOH^+]$. The values of K_c can thus be obtained directly from the observed reaction velocities, and are given in the fifth column of Table IV. They can be converted into approximate thermodynamic dissociation constants K'_d by the use of equation (3), and the resulting values [obtained with the alternative expressions 2(a) and 2 b) for f(I)] are given in the last column of Table IV.

TABLE IV.

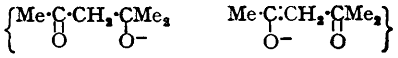
Hydrolysis of carbethoxymethyltriethylammonium iodide by sodium hydroxide.

				K'_d.	
I.	[$CaCl_2$.]	k.	K_c.	(a).	(b).
0·181	0	156	—	—	—
	0·0582	119	0·19	0·049	0·058
0·224	0	142	—	—	—
	0·0726	104	0·20	0·047	0·058
0·295	0	140	—	—	—
	0·0484	115	0·23	0·047	0·061
	0·0969	93	0·20	0·041	0·057
			Mean	0·046	0·056

The values obtained for K'_d are close to those derived from the solubility measurements at the same temperature (cf. Table II), though the order of the constants from assumptions (a) and (*b*) is reversed. The discrepancy is not greater than would be expected in extrapolating from the high ionic strengths used in the kinetic measurements.

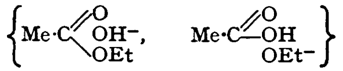
The results with added barium salts (cf. Table I) show a small retarding effect, but the accuracy of measurements in this very fast reaction is not sufficient to justify a quantitative treatment. The results are consistent with $K_c \sim 0{\cdot}4$ for $BaOH^+$ obtained previously (Bell and Prue, and Davies, *locc. cit.*).

It remains to consider why calcium and barium ions have no detectable retarding effect in the alkaline hydrolysis of ethyl acetate, in contrast with their effect in the decomposition of diacetone alcohol (cf. introduction to this paper). The difference probably lies in the transition states of the two reactions. In the diacetone alcohol decomposition the transition state can be written



$$\left\{\mathrm{Me{\cdot}\underset{O}{\underset{\|}{C}}{\cdot}CH_2{\cdot}\underset{O^-}{\underset{|}{C}}Me_2} \qquad \mathrm{Me{\cdot}\underset{O^-}{\underset{|}{C}}{:}CH_2{\cdot}\underset{O}{\underset{\|}{C}}Me_2}\right\}$$

where the negative charge is shared between two distant oxygen atoms, and the tendency to associate with cations will be small. In the hydrolysis of ethyl acetate, on the other hand, the transition state will be



where the negative charge is much more concentrated, and the association with cations may well resemble that of the hydroxyl ion. It is probable that some reactions will exhibit behaviour intermediate between these two extremes.

Our thanks are tendered to the Department of Scientific and Industrial Research for a grant to one of us (G. M. W.).

Physical Chemistry Laboratory, Oxford.

[*Received, April 5th,* 1950.]