554. *Reaction-kinetic Investigations of the Incomplete Dissociation of Salts. Part IV.* The Neutralization of Nitroethane by Solutions of Metallic Hydroxides.*

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Kinetic measurements have been made on the reaction between nitroethane and hydroxyl ions at 25°, in the presence of sodium, calcium, barium, and thallous ions. The results are interpreted in terms of the incomplete dissociation of the species $CaOH^+$, $BaOH^+$, and TlOH, and the dissociation constants derived agree with previous estimates within the rather wide limits of uncertainty about activity coefficients.

In two earlier papers of this series[1, 2] it was shown that the ions Tl^+, Ca^{2+}, and Ba^{2+} exert a specific retarding effect on the decomposition of diacetone alcohol catalysed by hydroxyl ions, and on the reaction of hydroxyl ions with ethoxycarbonyltrimethylammonium iodide. This effect was attributed to the incomplete dissociation of these hydroxides, and dissociation constants were derived which were in fair agreement with those arrived at by other methods. On the other hand, no such effect was observable in the alkaline hydrolysis of ethyl acetate[2] and it is therefore of interest to study other types of reaction. The present paper deals with the effect of the same cations on the neutralization of nitroethane by hydroxyl ions. The kinetics of this reaction have previously been studied by Maron and La Mer,[3] Wynne-Jones,[4] and Bell and Clunie.[5] It is well established that the reaction follows second-order kinetics, and there is good agreement

* Part III, *J.*, 1951, 2357.

[1] Bell and Prue, *J.*, 1949, 362.
[2] Bell and Waind, *J.*, 1950, 1979.
[3] Maron and La Mer, *J. Amer. Chem. Soc.*, 1938, **60**, 2588.
[4] Wynne-Jones, *J. Chem. Phys.*, 1934, **2**, 381.
[5] Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16.

between the three investigations on the value of the velocity constant at 0°. At 25° the reaction is too fast for study by conventional means, and Bell and Clunie used a thermal method suitable for half-times of a few seconds. The same method has been employed in the present investigation.

EXPERIMENTAL

Nitroethane was purified by three distillations, giving a product of b. p. 114°. Its aqueous solutions were not kept for more than a few hours before use. Sodium hydroxide solution was made from washed sticks and titrated by weight against hydrochloric acid, which either had been prepared by diluting constant-boiling acid, or had been standardized against borax. Thallous hydroxide solution was prepared by adding a solution of " AnalaR " barium hydroxide to a solution of " AnalaR " thallous sulphate until the solution gave negative tests for both sulphate and barium ions. The precipitated barium sulphate (and perhaps carbonate) was filtered off and the filtrate concentrated under reduced pressure in an atmosphere of nitrogen. The resulting solution was analysed for thallous and hydroxide ions by titration with potassium iodate solution and hydrochloric acid respectively, the two estimations agreeing within 0·2%. Sodium chloride solutions were made by weight from the "AnalaR" salt, and solutions of " AnalaR " calcium chloride and barium chloride were analysed by gravimetric estimation of chloride.

The reaction velocity was measured by the thermal maximum method previously described.[5, 6] A platinum reaction vessel was used, and the temperature measured by a single chromel–constantan thermocouple in conjunction with a galvanometer amplifier. The heat of reaction between nitroethane and hydroxyl ions is about 12 kcal./mole, which is ample for the use of this method. Experiments were first carried out with solutions of sodium hydroxide, in which there are no complications due to incomplete dissociation. T_0, the temperature change under adiabatic conditions, was determined by the extrapolation procedure already described;[6] bulbs of sodium hydroxide solution were broken in 50 ml. of nitroethane solution of concentration 0·06—0·4M, the amount of sodium hydroxide being always one-tenth of that of the nitroethane. The reaction was treated as a first-order one between hydroxyl ions and a constant concentration $[EtNO_2]_0 - \frac{1}{2}[OH^-]_0$ of nitroethane. This assumption was justified by considering the exact expression for second-order reactions [equation (12), ref. 5] and expanding in powers of $1/r$, where r is the ratio of the initial concentrations. In this way it was shown that under our conditions the true value of T_m (the maximum temperature rise) differs by less than 0·5% from the value corresponding to the above assumption. There is no appreciable instantaneous temperature change for the dilution of sodium hydroxide solutions in the relevant concentration range, so that T_0 can be determined from the empirical extrapolation equations given in ref. 6 for first-order reactions. A typical set of experiments gave T_0 = 186, 187, 188 mm. deflection per millimole of sodium hydroxide, on use of the first three equations of Table 3, ref. 6.

It is possible to obtain a value for the velocity constant in sodium hydroxide solutions from the slope of the extrapolation graph, and the set of experiments quoted above gives k = 6·0, 5·9, 5·8 l. mole^{-1} sec.$^{-1}$ on the basis of the three equations used. However, it is more accurate to use the extrapolated value of T_0 in conjunction with measurements of T_m at lower concentrations, and this was done for equal concentrations of sodium hydroxide and nitroethane in the range 0·02—0·06M. The results are given in Table 1, which also gives the results of measurements with added sodium chloride. The velocity constants were calculated from the observed values of T_m by using Table 1 of ref. 6, and each value represents the mean of at least three

TABLE 1. *Reaction between equal concentrations of nitroethane and sodium hydroxide at 25°.*

k = second-order velocity constant (l. mole^{-1} sec.$^{-1}$).

10^4c	180	193	201	225	235	246	262	347	404	424	517	619
k	$5{\cdot}8_5$	$5{\cdot}7_5$	$5{\cdot}8_5$	$5{\cdot}8_5$	5·8	5·8	5·8	$6{\cdot}1_5$	5·8	$5{\cdot}7_5$	5·7	$5{\cdot}8_5$
10^4c	256	271	257	267	242	313	275	259	247	256	305	291
10^3[NaCl]	110	155	258	273	304	301	325	383	438	474	590	869
k	$5{\cdot}7_5$	$5{\cdot}6_5$	$5{\cdot}5_5$	5·5	5·5	$5{\cdot}5_5$	5·6	$5{\cdot}6_5$	$5{\cdot}5_5$	5·6	$5{\cdot}7_5$	$5{\cdot}8_5$

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[6] Bell, Gold, Hilton, and Rand, *Discuss. Faraday Soc.*, 1954, **17**, 151.

determinations. The mean value in the absence of added salt is $k = 5{\cdot}8_3$ l. mole^{-1} sec.$^{-1}$, in excellent agreement with $k = 5{\cdot}8_8$ found by Bell and Clunie.[5] The results with added sodium chloride show that as the ionic strength increases, k first falls slightly and then rises again.

Similar measurements were carried out in hydroxide solutions containing the ions Ca^{2+}, Ba^{2+}, and Tl^{+}, the initial stoicheiometric concentration of hydroxide being throughout equal to that of nitroethane. The interpretation of these experiments involves several complications which are not present in reactions with completely dissociated hydroxides. In the first place, we no longer have a strictly second-order reaction between reactants of equal concentration. If the rate equation in sodium hydroxide solution is $\mathrm{d}x/\mathrm{d}t = k_0(a - x)^2$, the corresponding equation in an incompletely dissociated solution will be $\mathrm{d}x/\mathrm{d}t = \alpha k_0(a - x)^2$, where α is the fraction of the hydroxyl ions which are unassociated, and it is assumed that only the unassociated hydroxyl ions react. The reaction will therefore behave like a second-order change with velocity constant αk_0 as long as the variation of α can be neglected. In our experimental method we are only interested in the course of the reaction up to the time corresponding to the temperature maximum, which under our conditions corresponds to not more than 50% reaction. Rough values for the dissociation constants involved being used, calculation shows that during the first half of the reaction α deviates by less than 1% from its mean value, corresponding to an uncertainty of less than 0·3% in T_m, which is considerably less than the experimental error. The deviations from simple second-order behaviour will be even less if it is supposed that the associated hydroxyl ions also react with nitroethane.

The other complications arise in determining the velocity constant from the observed value of T_m. The method of applying the corrections will be illustrated for solutions containing calcium. The reaction was started by breaking a bulb containing sodium hydroxide solution in a solution containing nitroethane and calcium chloride. This gives an instantaneous deflection $-T_i$ (per millimole of sodium hydroxide) due to the heat absorbed in the formation of $CaOH^+$ from Ca^{2+} and OH^-. As the reaction proceeds heat is evolved by the dissociation of $CaOH^+$, and in place of T_0 (as determined in sodium hydroxide solutions) we must use a value $T_0 + T_i$: further, the initial temperature change must be taken into account in the relation between T_m and k, as in equation 9 of ref. 5. Since the magnitude of T_i depends upon the amount of $CaOH^+$ formed, it is necessary to determine it by successive approximations using the value of ΔH for $Ca^{2+} + OH^- \longrightarrow CaOH^+$ given by Bell and George.[7] First, an approximate value for k is calculated from T_m, assuming $T_i = 0$. This gives an approximate value of α from $\alpha = k/k_0$, where k_0 is the rate constant in a sodium hydroxide–sodium chloride solution of the same ionic strength interpolated from Table 1. An approximate value of T_i follows from α and ΔH, and a more accurate value of k can now be calculated by using $(T_0 + T_i)$ in place of T_0, and the full expression relating T_m, T_i, and k. This in turn leads to a more accurate value of α, and the whole process can be repeated, though in practice it was found that no further approximations were necessary. The two corrections involving T_i work in opposite directions, so that the final values of α and k do not differ much from the uncorrected ones.

The results for solutions containing barium were treated in the same way. An approximate value of ΔH is given by Gimblett and Monk,[8] and was confirmed by observing the initial deflection when bulbs of sodium hydroxide solution were broken in solutions of barium chloride. The two corrections again compensate one another. This is not the case in the experiments with thallous hydroxide, where the reaction was started by breaking a bulb of concentrated thallous hydroxide solution in a solution of nitroethane: heat is therefore evolved both initially and during the reaction, and the two corrections now act in the same direction. Bell and George[7] give $\Delta H = -0{\cdot}37 \pm 0{\cdot}15$ kcal./mole for $TlOH \longrightarrow Tl^+ + OH^-$, while our own rough experiments on the heat of dilution indicate a smaller value. The values of α and k in the Table correspond to $\alpha H = -0{\cdot}22$ kcal./mole, but are less accurate than those for the other hydroxides.

The final values of α lead directly to K_c, the concentration dissociation constants for the species $CaOH^+$, $BaOH^+$, and TlOH. Because of the high ionic strengths (especially in the first two instances) the thermodynamic constants K_a differ considerably from these. The values of K_a in Table 2 are calculated from K_c by assuming $-\log f_i = 0{\cdot}50 z_i^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ for all ionic species. Within the rather large experimental error the values of K_a thus calculated show no trend with ionic strength, and there seems to be no justification for adding an empirical term linear in I to the expression for the activity coefficient.

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[7] Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

[8] Gimblett and Monk, *ibid.*, 1954, **50**, 965.

TABLE 2. *Neutralization of nitroethane in presence of various hydroxides at* 25°.

a = initial stoicheiometric concn. of NaOH or TlOH; also of nitroethane. b = initial stoicheiometric concn. of $CaCl_2$ or $BaCl_2$. k = second-order velocity constant, l. mole^{-1} sec.$^{-1}$, mean of several expts. α = fraction of hydroxyl ions unassociated. k and α have been corrected for the heat effects arising from incomplete dissociation.

10^4a	10^4b	k	α	K_c	K_a
			$Ca(OH)_2$		
262	198	4·9$_5$	0·86	0·098	0·036
301	198	4·8$_5$	0·84	0·082	0·030
250	198	4·7$_5$	0·83	0·075	0·028
280	294	4·7	0·82	0·112	0·036
206	395	4·5$_5$	0·80	0·142	0·042
224	330	4·5$_5$	0·79	0·110	0·035
231	395	4·4$_5$	0·78	0·121	0·036
204	593	4·1	0·72	0·145	0·036
					0·035 ± 0·005

10^4a	10^4b	k	α	K_c	K_a
			$Ba(OH)_2$		
220	606	5·2	0·92	0·66	0·16
233	506	5·1$_5$	0·91	0·46	0·12
218	544	5·1$_5$	0·91	0·49	0·12
228	878	5·0	0·90	0·76	0·16
249	878	5·0	0·90	0·76	0·15
324	878	5·0$_5$	0·90	0·80	0·16
519	1070	4·9	0·89	0·79	0·14
402	1331	4·9	0·88	0·97	0·16
220	794	4·9	0·87	0·53	0·11
408	1475	4·8	0·86	0·89	0·14
478	1475	4·6$_5$	0·84	0·79	0·12
					0·14 ± 0·02

10^4a	k	α	K_c	K_a
		TlOH		
211	5·3	0·91	0·18	0·14
284	5·1$_5$	0·88	0·19	0·14
286	5·2	0·89	0·22	0·16
388	5·0	0·86	0·20	0·14
431	4·9$_5$	0·85	0·21	0·14
448	4·8	0·82	0·17	0·12
476	5·0$_5$	0·86	0·26	0·18
488	4·7$_5$	0·82	0·18	0·12
507	4·6	0·79	0·15	0·10
				0·14 ± 0·03

DISCUSSION

The results in Table 2 show clearly that the presence of calcium, barium, or thallous ions reduces the rate of the reaction between hydroxyl ions and nitroethane, and the values of α and K have been calculated on the assumption that only the unassociated hydroxyl ions are capable of reaction. The dissociation constants derived from different sources are collected in Table 3. These are normally the values given by the authors themselves, but the value for $CaOH^+$ based on the conductivity measurements by Lea and Bessey[9] has been calculated by us using the procedure of Righellato and Davies.[10] This involves assumptions about the mobility of $CaOH^+$ (taken as 35·0 in our calculations) and also the use of empirical conductivity equations in what is really a mixture of 1 : 1 and 1 : 2 electrolytes, so that no

TABLE 3. *Collected thermodynamic dissociation constants at* 25°.

K_a	Method	Authors
	$CaOH^+$	
0·041	Solubility	Kilde[15]
0·031	,,	Kilde,[15] recalc. by Davies[16]
0·050	,,	Davies and Hoyle[17]
0·04	,,	Bell and George[5]
0·043	E.m.f.	Gimblett and Monk[8]
0·049	Conductivity	Lea and Bessey[9]
0·050, 0·051	Kinetic	Bell and Prue[1]
0·046, 0·056	,,	Bell and Waind[2]
0·035	,,	This paper

K_a	Method	Authors
	$BaOH^+$	
0·23	E.m.f.	Davies[18]
0·23	,,	Gimblett and Monk[8]
0·21, 0·24	Kinetic	Bell and Prue[1]
0·14	,,	This paper
	TlOH	
0·15	Solubility	Bell and George[5]
0·25	Conductivity	Ostwald[11]
0·23	Spectrophotometric	Bell and Panckhurst[19]
0·38	Kinetic	Bell and Prue[1]
0·14	,,	This paper

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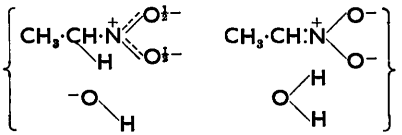
[9] Lea and Bessey, *J.*, 1937, 1612.

[10] Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592.

great reliance can be placed upon the results. For thallous hydroxide the conductivity data are simple to interpret, but the experimental position is not clear. Ostwald's results,[11] combined with recent values for the mobilities of Tl^+ and OH^- and the empirical conductivity equation of Robinson and Davies,[12] give an average value $K_a = 0{\cdot}25$ in the range 0·05—0·2M. As pointed out by Biedermann [13] the more recent conductivity measurements of Hlasko and Salitowna [14] suggest that thallous hydroxide is almost completely dissociated in this range. However, it is doubtful whether this conclusion can be accepted, since the results of these authors for other electrolytes (for example, hydrochloric acid) differ considerably from accepted values, and approximate conductivity measurements of our own give results close to those of Ostwald, though somewhat higher.

The range of values in Table 3 is disconcertingly wide, but it is doubtful whether there is any proven inconsistency between the results of the different methods. Most of the values depend upon small differences between large quantities, and many of the measurements were made at high ionic strengths, so that the values of K_a obtained are sensitive to the expressions used for ionic activity coefficients. Different authors have used different expressions, and in any case it cannot be expected that a single type of expression will describe the behaviour of different electrolyte mixtures. It is likely, therefore, that the apparent discrepancies in Table 3 are mainly due to uncertainties in the activity coefficients. The only real anomaly is the high value obtained for thallous hydroxide by Bell and Prue [1] using the kinetic method, and this rests heavily on an extrapolation from the values in the two most dilute solutions.

Our results indicate that the species $CaOH^+$, $BaOH^+$, and TlOH do not react at an appreciable rate with nitroethane, or (which comes to the same thing) that the cations Ca^{2+}, Ba^{2+}, and Tl^+ do not associate appreciably with the transition state of the reaction. It was suggested by Bell and Waind [2] that this behaviour would be found in reactions where the charge on the transition state is spread over a number of atoms. This fits in with the present example, where the transition state can be written



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