661. *Base Catalysis in Solvent Mixtures. Part I. The Neutralisation of Nitroethane*

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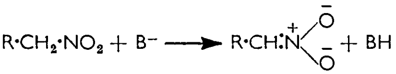
The rate of neutralisation of nitroethane by lyate ions at 25° has been measured by the thermal-maximum method in the solvents water–deuterium oxide, water–methanol, and water–ethanol. The extents to which changes in position of the lyate-ion equilibria determine the variations of the rate constant with solvent composition are discussed.

THE mechanism proposed by Pedersen [1] for the neutralisation of nitroparaffins by bases has been generally accepted.[2,3] The reaction velocity is determined by the rate of transfer of a proton from the α-carbon atom of the nitroparaffin to the base. The product is the anion of the aci-form,



$$R{\cdot}CH_2{\cdot}NO_2 + B^- \longrightarrow R{\cdot}CH{:}\overset{+}{N}\begin{smallmatrix} \diagup \overset{-}{O} \\ - \\ \diagdown O \end{smallmatrix} + BH$$

(1)

The proton transfer is relatively slow because of the extensive electron redistribution involved.[4] The mechanism is consistent with the observation of general base-catalysis in these reactions. Bell and Clunie [5] have shown that the thermal-maximum method is suitable for following the rate of neutralisation of nitroethane at 25° in aqueous solution, and their method has been used in the present work.

In this Paper, measurements of the rate of neutralisation of nitroethane by lyate ions at 25° in the solvent mixtures water–deuterium oxide, water–ethanol, and water–methanol are reported. Our purpose was to measure the variation of the rate of a base-catalysed process of known and simple mechanism as the solvent composition was progressively changed, and to examine in particular the extent to which the observed changes in rate reflect the accompanying changes in position of the lyate-ion equilibria.

EXPERIMENTAL

Water and deuterium oxide (Norsk Hydro 99·8 wt. % D_2O) were distilled from alkaline permanganate and then from dilute phosphoric acid. Alcohols for solvent mixtures were distilled; the pure solvents were prepared by the method of Lund and Bjerrum.[6] Carbonate-free sodium hydroxide volumetric solution (B.D.H.) was used. In the preparation of solutions of sodium deuteroxide, ethoxide, and methoxide, sodium was melted under xylene, drawn up into glass capillaries and then dissolved from the capillary in the appropriate solvent.

B.D.H. nitroethane was distilled under reduced pressure, and then set aside over anhydrous sodium carbonate. Before use, the material was again distilled under reduced pressure and the middle fraction retained.

The technique differed in some details from that described by Bell and Clunie.[5] The reaction was started by injecting reactant from a hypodermic syringe. A thermistor was used for temperature measurement. For experiments with alcohol–water mixtures a calorimeter of 100 ml. capacity was used, but a smaller (25 ml. capacity) calorimeter was used for the water–deuterium oxide solvent. In these experiments, the measured T_m (notation of Bell and Clunie [5]) required correction for heat loss to the internally mounted components of the calorimeter. The corrections were obtained by direct measurement. In the 100 ml.-apparatus, the correction was about 5%, but on the 25 ml.-apparatus the correction was larger (~12%).

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[1] K. J. Pedersen, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1932, **12**, 1.
[2] R. Junell, *Arkiv Kemi*, 1934, **11***B*, 34.
[3] W. F. K. Wynne-Jones, *J. Chem. Phys.*, 1934, **2**, 381.
[4] R. P. Bell, " The Proton in Chemistry," Methuen, 1959, p. 15.
[5] R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.*, 1952, A, **212**, 16.
[6] H. Lund and N. Bjerrum, *Ber.*, 1931, **64**, 210.

The rate constants obtained for neutralisation of nitroethane in aqueous solution at 25° compared well with the value reported by Bell and Clunie.[5]

		k_{obs} (l. mole^{-1} min.$^{-1}$)	
		k	
	Bell and Clunie	353 ± 1·8%	
This work	100 ml.-calorimeter	347 ± 2·6%	(mean of 8 measurements)
	25 ml.-calorimeter	355 ± 2·5%	(mean of 10 measurements)

RESULTS AND DISCUSSION

The results are given in the Table. In all the experiments, the initial concentrations of reactant were equal. The rate constants reported are the means of at least eight measurements for experiments in alcohol–water mixtures, and at least five measurements for experiments in water–deuterium oxide. The initial reactant concentrations were varied in the range 0·002—0·01M, and the rate constants were independent of reactant concentration within the experimental error. The cation used throughout was the sodium ion.

Rate constants (l. mole^{-1} min.$^{-1}$) for the neutralisation of nitroethane at 25°

H_2O–D_2O								
Atom % D	0	18·7	38·6	58·0	78·6	98·3		
k_{obs}	355	363	381	410	456	492		
H_2O–MeOH								
Mole % MeOH	0	5·8	15·4	27·2	40·2	55·2	76·7	100
k_{obs}	347	423	613	873	952	968	1023	984
H_2O–EtOH								
Mole % EtOH	4·2	11·7	20·4	31·7	47·5	60·5	76·4	109
k_{obs}	544	962	1465	1977	3069	3586	4710	5290

The relative concentrations of the lyate ions in the mixed hydroxylic solvents studied are governed by equilibria of the type

$$\mathrm{L_1^- + HL_2 \overset{K_{12}}{\rightleftharpoons} L_2^- + HL_1}$$

i.e., by the relative acidities of the solvent components. The total lyate ion concentration $[L_0^-] = [L_1^-] + [L_2^-]$ and the overall rate constant for the neutralisation of nitroethane in these solvents is related to the contributions of the individual lyate ions by

$$k_{\mathrm{obs}} = k_1[L_1^-] + k_2\,[L_2^-]$$

In the following discussion $[L_2^-] = [OH^-]$.

The variation of k_{obs} with solvent composition depends upon the position of the lyate-ion equilibrium and upon the extents to which k_1 and k_2 are themselves functions of solvent composition. The variations of k_1 and k_2 cannot be measured directly, and it is necessary to assume that they are independent of solvent composition, or to use some indirect argument to assess their variation. Both procedures are discussed below.

In the present work, an overall increase in rate constant of about 40% was found when the solvent was changed from water to deuterium oxide. This is similar to the change reported by Wynne-Jones,[3] and by Maron and La Mer,[7] from conductivity measurements at 0 and 5°, respectively. In analysing the variation of k_{obs} with solvent composition, we first assumed that k_1 and k_2 are independent of solvent composition.

This type of assumption has commonly been made for reactions in mixtures of water and deuterium oxide. In this case, it is possible to assess its correctness by reference to the work of Reitz,[8] who found that the rate constant for the catalysis by acetate ion of the bromination of nitroethane decreased by 12% when the solvent was changed from water to deuterium oxide.

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[7] S. H. Maron and V. K. La Mer, *J. Amer. Chem. Soc.*, 1938, **60**, 2588.

[8] O. Reitz, *Z. phys. Chem.*, 1936, **176**, 363.

Theoretical curves were calculated by using values of 3·205 (Swain *et al.*[9]) and 3·88 (Purlee [10]) for the equilibrium constant for

$$2OH^- + H_2O \overset{K_{12}}{\rightleftharpoons} 2OH^- + D_2O$$

It is also necessary to allow for the solvent equilibrium

$$H_2O + D_2O \overset{K_S}{\rightleftharpoons} 2HDO$$

and for K_S, values of 3·96 (Urey [11]) and 4·00 (ideal) have been used. The various combinations yield calculated rate constants differing by less than 1·5% and in Figure 1 the experimental results are compared with a curve calculated by using $K_{12} = 3{\cdot}88$; $K_S = 4{\cdot}00$. The fit is within the experimental error, showing that the change in k_{obs} is essentially a response to the lyate-ion equilibrium but, with the exception of the value at 80%D, the mean observed rate constants lie below the theoretical line. It is of interest that a nearly perfect fit may be obtained by assuming that k_1 and k_2 decrease linearly with increasing deuterium content of the solvent to an extent similar to that observed by Reitz for the catalysis by the acetate ion of the bromination of nitroethane.

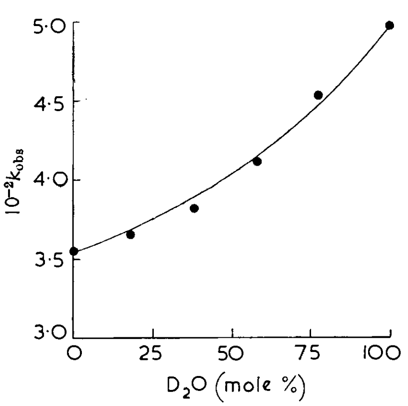

FIGURE 1. Variation of k_{obs} with solvent composition in H_2O–D_2O mixtures at 25°

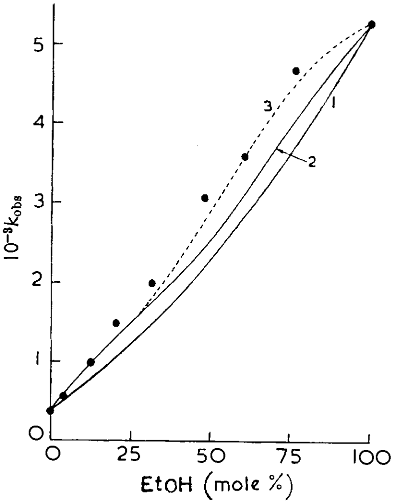

FIGURE 2. Variation of k_{obs} with solvent composition in H_2O–EtOH mixtures at 25°

A number of investigations of the relative acidities of ethanol and water have been reported, and the literature has recently been reviewed by Murto.[12] The most comprehensive investigation for ethanol–water mixtures is that due to Caldin and Long,[13] who derive values for a constant, dependent upon solvent composition,

$$K_{12}' = [OH^-]a_a/[OEt^-]a_w$$

where a_w and a_a are the activities (referred to the pure solvent in each case) of water and ethanol in the mixed solvent. Log K_{12}' was found to vary linearly with the reciprocal dielectric constant of the medium and the limiting values were K_{12}' (water) = 4·5, K_{12}' (ethanol) = 0·5. Although their calculations contain assumptions, the extreme values

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[9] C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, 1960, **10**, 200.

[10] E. L. Purlee, *J. Amer. Chem. Soc.*, 1959, **81**, 263.

[11] H. C. Urey, *J.*, 1947, 569.

[12] J. Murto, *Ann. Acad. Sci. Fennicae.*, 1962, *Series A.II Chemica*, 117.

[13] E. F. Caldin and G. Long, *J.*, 1954, 3737.

compare well with other investigations.[13,14] Murto[12] has pointed out that Caldin and Long's data suggest that a constant defined by

$$K_{12}'' = [OH^-]X_a/[OEt^-]X_w$$

(where X_a and X_w are the mole fractions of alcohol and water, respectively, in the mixed solvent), is substantially independent of solvent composition.

For alcohol–water mixtures, there is less justification for assuming that k_1 and k_2 are independent of solvent composition, although Murto[12] has concluded that, for a large number of alkaline solvolytic reactions in ethanol–water mixtures, the total change in reaction velocity with solvent composition is very largely accounted for by the changing position of the lyate-ion equilibrium. If one makes this assumption, curves 1 and 2 of Figure 2 are obtained by using K_{12}'' and K_{12}', respectively.

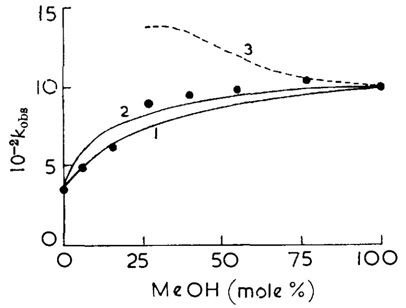

FIGURE 3. Variation of k_{obs} with solvent composition in H_2O–MeOH mixtures at 25°

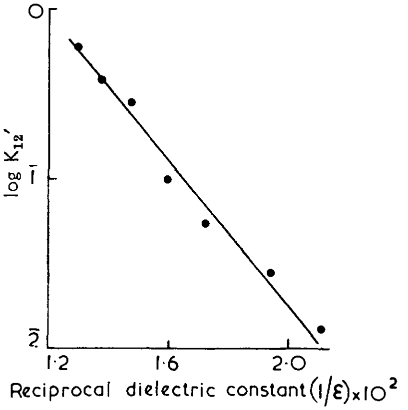

FIGURE 4. Variation of log K_{12}' calculated from kinetic data, in H_2O–MeOH mixtures with the reciprocal dielectric constant of the solvent

Refinement of the treatment requires a procedure for estimating k_1 and k_2. One possibility is to use the Brönsted relationship to calculate the catalytic constants for ethoxide ion and hydroxide ion in water and ethanol, respectively. The separate rate constants could then be interpolated in mixed solvents by using the electrostatic model for ion–dipole reactions.[15] Unfortunately, the validity of the Brönsted relationship does not extend to the hydroxide ion[16] but, if the ethoxide ion behaves as a " normal " base, the relationship suggests that the rate constant for ethoxide ion in water (k_1^w) is more than 10^2 times greater than that for hydroxide ion (k_2^w). This in turn implies that k_1^w is greater than k_1^a, a result which is consistent with the convex-upwards shape of the experimental curve in Figure 2, but contrary to the predictions of the electrostatic model for the variation of the rate constant with the dielectric constant of the solvent.

Murto[12] has suggested an alternative approach to this type of problem by making use of reference reactions. The thiophenoxide and naphthoxide ions are powerful nucleophiles but very weak bases, so that the variations of the rate constants for reactions of these ions with alkyl halides should be independent of the lyate-ion equilibrium. Although a numerical correlation could hardly be expected, it is of interest to examine the result derived from the assumption that the electrostatically similar reaction of ethoxide ion with nitroethane varies in a similar manner. The correction can be made for $X_a > 0{\cdot}4$. The result is that k_1 passes through a maximum, increasing from its value in pure ethanol by

[14] F. A. Long and P. Ballinger, " Electrolytes," ed. Pesce, Pergamon, 1962, p. 152.
[15] A. A. Frost and R. G. Pearson, " Kinetics and Mechanism," 2nd edn., Wiley, 1961, p. 149.
[16] S. H. Maron and V. K. La Mer, *J. Amer. Chem. Soc.*, 1939, **61**, 2018.

about 40%. The resultant curve obtained by using Caldin and Long's equilibrium data is curve 3 in Figure 2. It is of interest that this approach also suggests that k_1 is greater in mixtures than in pure ethanol, which is in contrast with the electrostatic prediction.

For methanol–water mixtures, the overall change of reaction velocity is about threefold. Here we first assume that k_1 and k_2 are independent of solvent composition and use the equilibrium data of Bender and Glasson [17] to obtain curve 1, Figure 3. The fit at higher values of X_a is improved by the use of Koskikallio's data,[18] as recalculated by Murto [12] (curve 2, Figure 3) but only at the expense of a poorer fit at low values for X_a. The gross effect is clearly consistent with a lyate-ion equilibrium that distinctly favours the methoxide ion. The existence of a rate maximum in the experimental curve implies that k_1 increases as water is added to methanol. An effect of this type is again suggested by Murto's approach but, in this case, the correction is numerically much too large (curve 3 Figure 3). It seems probable that in this case the variations in rate constant are small, and that the change in rate is essentially a response to the lyate-ion equilibrium. In this situation, it is possible to calculate values of the lyate-ion equilibrium from the kinetic data. In Figure 4, values of K_{12}' obtained in this way are plotted against the reciprocal dielectric constant of the solvent, and show a similar linear variation to that found by Caldin and Long [13] for ethanol–water mixtures.

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[17] M. L. Bender and W. A. Glasson, *J. Amer. Chem. Soc.*, 1959, **81**, 1590.

[18] J. Koskikallio, *Suomen Kem.*, 1951, **30***B*, 111.