

152. *Reaction Velocities at Low Temperatures. Part IV. The Ionisation of Nitroethane at Temperatures between -32° and $+20^{\circ}$.*

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The kinetics of the reaction of nitroethane with sodium hydroxide in aqueous methyl alcohol have been studied at six temperatures between -32° and $+20^{\circ}$. No deviations from the simple Arrhenius equation outside the experimental error have been observed. The rate of the reaction is smaller than that predicted by the simple collision theory by a factor of about 10^3 .

NITRO-PARAFFINS react with hydroxyl ions at a measurable rate according to the equation $\text{CHR}_1\text{R}_2\cdot\text{NO}_2 + \text{OH}^- = \text{CR}_1\text{R}_2\cdot\text{NO}_2^- + \text{H}_2\text{O}$. This reaction has been studied in some detail at the ordinary temperature by a number of workers (Junell, *Arkiv Kemi, Min. Geol.*, 1934, **11**, B, no. 34; *Svensk Kem. Tidskr.*, 1934, **46**, 125; Wynne-Jones, *J. Chem. Physics*, 1934, **2**, 381; Maron and LaMer, *J. Amer. Chem. Soc.*, 1938, **60**, 2588) both in water and in deuterium oxide. The present work was undertaken over a considerable range of low temperatures with the object of detecting possible deviations from the Arrhenius equation. A solvent containing about 20% of water and 80% of methyl alcohol was found to give convenient velocities.

EXPERIMENTAL.

Materials.—Methyl alcohol was fractionated and then redistilled in a current of air free from carbon dioxide. Carbon dioxide-free water was then added, and the composition determined by weight. Throughout these experiments the solvent contained 22.77% of water. Stock sodium hydroxide solutions were prepared by dissolving clean metallic sodium in the solvent, and their concentration obtained by titration against potassium quadroxalate. Nitroethane was prepared by two methods, the two products giving concordant results. (1) α -Bromopropionic acid was neutralised with sodium carbonate, treated with an equivalent amount of sodium nitrite in aqueous solution, and the mixture distilled; the insoluble nitroethane was separated from the distillate, dried over calcium chloride, and distilled. (2) Ethyl iodide was treated with silver nitrite at -20° for 24 hours, and the nitroethane distilled off. In each case the product was fractionated, the fraction of b. p. $113-116^{\circ}$ being used.

Measurement of Reaction Velocity.—The reaction was followed by the change in electrical conductivity. The cell had a capacity of about 20 c.c., and in the solvent used $M/100$ -sodium hydroxide had a conductivity of about 4×10^{-3} rec. ohm. The low-temperature thermostat has already been described (Bell and Thomas, *J.*, 1939, 1573; Bell and Norris, this vol., p. 118).

Measurements at 0° were made in ice, and at 20° in an ordinary thermostat. The sodium hydroxide was in the cell initially, and the nitroethane was introduced in a thin glass tube, sealed at the bottom, which was allowed to acquire the temperature of the solution and then broken against the bottom of the cell to start the reaction.

Calculation of Velocity Constants.—All the concentrations needed for these calculations were obtained from the observations of conductivity. The cell was calibrated at each temperature against known concentrations of sodium hydroxide and the sodium salt of nitroethane. The initial concentration of sodium hydroxide could then be readily calculated from the initial conductivity. In those reactions where the initial concentration of alkali was greater than that of nitroethane, an excess of nitroethane was added after the conclusion of the reaction. If the initial conductivity is A , the conductivity at the end of the reaction B , and that after addition of excess of nitroethane C , then the initial concentration of nitroethane is $[\text{NaOH}](A - B)/(A - C)$. Similarly, if at any stage of the reaction the observed conductivity is X , then the concentration of nitroethane ion formed is $[\text{NaOH}](A - X)/(A - C)$.

In reactions where the initial concentration of nitroethane was greater than that of alkali the following procedure was adopted. When the reaction was at an end, an excess of alkali was added, and finally an excess of nitroethane, the conductivity being measured after each addition. Let the values of the conductivity at the beginning and the end of the reaction be A and B as above, the value after adding excess of alkali D , and that when excess of nitroethane has been added E . Then if λ_a and λ_b are respectively the equivalent conductivities of sodium hydroxide and the sodium salt of nitroethane, we have :

Final concentration of nitroethane ion = $E/\lambda_b = F$ (say); this will also be the total concentration which the alkali would have had if no reaction had occurred.

After addition of excess alkali, let G be the concentration of the nitroethane ion (and hence also the initial concentration of nitroethane). The conductivity C is thus given by $C = G\lambda_b + (F - G)\lambda_a$.

The values of C and F are known, and also the two equivalent conductivities: hence the initial nitroethane concentration can be calculated. The concentrations at any stage of the reaction can then be determined as before. In making these calculations it was assumed that the equivalent conductivity of a salt in a mixed solution was the same as in a pure solution of the same ionic strength. The volume changes caused by the additions were so small that they could be neglected.

Having obtained a and b , the initial concentrations of alkali and nitroethane respectively, and x , the concentration of nitroethane ion formed after time t , we plotted $\log \{b(a - x)/a(b - x)\}$ against t . The plots thus obtained were effectively straight lines, though at the lower temperatures the first few points fell off the line, probably owing to incomplete mixing. The slope of the straight line was taken as $k(a - b)$, where k is the ordinary bimolecular velocity constant. These constants were converted to the usual units of moles per 1000 c.c. of solution by using the figures given in International Critical Tables for the densities of methyl alcohol-water mixtures, interpolating for the composition used, and extrapolating for the lower temperatures.

Results.—The following table gives the velocity constants obtained at six temperatures, expressed in moles/1000 c.c. and minutes; d is the density of the solution. The errors given represent the average deviation from the mean of the individual velocity constants.

Temp. = 19.96°; $k = 526 \pm 26$; $d = 0.8536$.					Temp. = 9.90°; $k = 300 \pm 8$; $d = 0.8618$.						
1000 a	0.645	2.206	4.78		0.928	1.518	1.622	3.46			
1000 b	0.577	0.648	3.28		0.372	2.320	1.114	2.94			
k	564	502	510		316	289	310	302			
Temp. = 0.00°; $k = 137 \pm 2$; $d = 0.8699$.					Temp. = -10.88°; $k = 63.3 \pm 6$; $d = 0.8787$.						
1000 a	1.018	1.443	1.859	2.130	2.161	2.54	2.68	2.96	3.81	3.81	4.68
1000 b	0.759	2.698	3.542	1.436	0.965	1.42	3.88	1.84	1.77	2.36	4.96
k	138	139	136	141	133	63.0	70.8	71.8	55.6	63.5	55.1
Temp. = -20.08°; $k = 27.6 \pm 4$; $d = 0.8863$.											
1000 a		2.08	3.01	3.51	3.86	4.46	6.48	7.54	8.35		
1000 b		5.62	3.74	4.19	3.86	1.78	4.68	5.70	3.28		
k		31.7	22.9	24.4	27.6	26.5	22.9	23.4	32.3		
Temp. = -31.80°; $k = 11.1 \pm 0.7$; $d = 0.8958$.											
1000 a		6.54	6.77	7.14	13.26	17.37					
1000 b		4.67	6.81	3.96	9.77	7.25					
k		11.3	9.7	11.4	12.3	10.9					

DISCUSSION.

The mean values of k at the six temperatures are expressed within the limits of the rather large experimental error by the simple Arrhenius equation. By applying the method of least squares we obtain the expression $k = 5.41 \times 10^{10} e^{-10,800/RT}$. The observed and the calculated values are given in the following table. The value of the first constant in the Arrhenius equation is less than that predicted by the simple collision theory by a factor of about 10^3 .

Temp.	19.96°	9.90°	0.00°	-10.88°	-20.08°	-31.8°
k (obs.)	526	300	137	63.3	27.6	11.1
k (calc.)	544	283	142	62.4	28.5	10.5

The data obtained thus resemble those previously given in showing no indication of the " tunnel effect " which might have been anticipated at low temperatures in reactions which involve a proton transfer (Bell, *Trans. Faraday Soc.*, 1938, **34**, 229). It should be possible to obtain more accurate data for this reaction, and it is hoped to do so in the future. There can be no doubt that the rate-determining step in this case really is a proton transfer, and the reaction should thus provide a crucial test of the " tunnel effect " if it can be studied at a low enough temperature and with sufficient accuracy. This effect might fail to appear if a large proportion of the activation energy were used in overcoming forces of repulsion, but recent theoretical calculations (Bell, *ibid.*, 1941, **37**, 493) indicate that repulsion energy is probably of minor importance in this type of reaction.

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