

Ionisation Rates of β -Substituted Nitroethanes

By Peter F. Cann and Charles J. M. Stirling,* School of Physical and Molecular Sciences, University College of North Wales, Bangor

Ionisation rates of a series of aliphatic nitro-compounds, $\text{YCH}_2\cdot\text{CH}_2\cdot\text{NO}_2$, have been measured in aqueous sodium hydroxide and in ethanolic sodium ethoxide. Rectilinear $\sigma^*\rho^*$ plots for substituents Me, H, Ph, OH, and EtO with $\rho^*_{\text{H}_2\text{O}} = 2.07$ and $\rho^*_{\text{EtOH}} = 1.88$ have been obtained; the β -diphenyl compound, $\text{Ph}_2\text{CH}\cdot\text{CH}_2\cdot\text{NO}_2$ ionises more slowly than the monophenyl compound notwithstanding the expected rate-accelerative effect of the second phenyl group.

Solvent and salt effects are discussed in connection with transition states for ionisation.

IONISATION rates and acid-base equilibria involving organic nitro-compounds have been the subject of much recent discussion.¹⁻¹⁵ Ionisation of nitro-compounds is particularly interesting because of their anomalously low rates of ionisation compared with other carbon acids of similar acidities (Table 1) and because of the

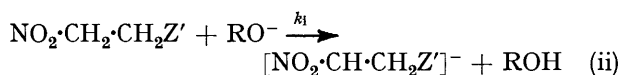
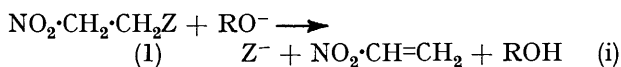
TABLE 1

Acid	pK _a	k _{rel}	Ref.
$\text{CH}_2(\text{SO}_2\text{Me})_2$	12.5	6.0×10^4	13
$\text{CH}_2(\text{CN})_2$	11.2	3.5×10^5	14
$\text{CH}_2(\text{COMe})_2$	9.0	4.0×10^5	14
MeNO_2	10.2	1	15

† Water at 25°.

abnormal Brønsted coefficients associated with their ionisation.^{8,10,11}

In connection with our studies of β -elimination reactions of aliphatic nitro-compounds (1) [equation (i); Z = PhO or PhS], we wished to predict rates of ionisation of compounds which eliminate Z⁻ in basic media.¹⁶



¹ C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2154.

² E. S. Lewis and J. D. Allen, *J. Amer. Chem. Soc.*, 1964, **86**, 2022.

³ J. A. Feather and V. Gold, *J. Chem. Soc.*, 1965, 1752.

⁴ P. Jones, J. L. Longridge, and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 1965, 3606.

⁵ R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, *A*, **294**, 273.

⁶ M. Fukuyama, P. W. K. Flanagan, F. T. Williams, jun., L. Frainier, S. A. Miller, and H. Shechter, *J. Amer. Chem. Soc.*, 1970, **92**, 4689.

⁷ F. G. Bordwell, W. J. Boyle, jun., and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

⁸ F. G. Bordwell and W. J. Boyle, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 511, 512.

⁹ F. G. Bordwell, K. C. Yee, and A. C. Knipe, *J. Amer. Chem. Soc.*, 1970, **92**, 5945.

RESULTS AND DISCUSSION

Reactions of the substrates (1a—e) with lyate ion in water and ethanol ($\mu = 0.1\text{M}$) were followed at 25.0° by u.v. stopped-flow spectrophotometry. Results are summarised in Table 2. Most rate constants are the average

TABLE 2

Rates of base-catalysed ionisation of $\text{ZCH}_2\cdot\text{CH}_2\cdot\text{NO}_2$ ^a					
Z	σ^*	$10^2 k_1(\text{EtOH})$ ^{b/} 1 mol ⁻¹ s ⁻¹	$k_1(\text{H}_2\text{O})$ ^{b/} 1 mol ⁻¹ s ⁻¹	$\frac{k_1(\text{EtOH})}{k_1(\text{H}_2\text{O})}$	
Me	-0.10	1.03 (2.7)	4.69 (4.0)	22	
H	0.00	1.44 (0.7)	5.36 (2.3)	27	
Ph	0.22	4.12 (2.1)	24.6 (4.3)	21	
HO	0.55	14.7 (1.2)	81.8 (4.1)	17	
EtO	0.66	28.8 (2.4)	168.0 (2.8)	21	
$\text{ZCH}_2 = \text{Ph}_2\text{CH}$	0.44	3.72 (2.8)			

^a All solutions brought to 0.1M ionic strength by the addition of NaClO₄; rates measured at 25.0°. ^b Figures in parentheses are standard deviations expressed as a percentage of k_1 .

of at least six independently determined values at two or more base concentrations.

Rates of base-catalysed ionisation of simple nitroalkanes have been studied by variety of methods.^{4,5,12,17-20} Comparison of our results with those of others (Table 3) shows general agreement except for data obtained by the megacycle conductivity method. This discrepancy has previously been discussed.⁵

¹⁰ F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.

¹¹ A. J. Kresge, *J. Amer. Chem. Soc.*, 1970, **92**, 3210.

¹² R. P. Bell and B. G. Cox, *J. Chem. Soc. (B)*, 1971, 783.

¹³ J. Hine, J. C. Phillips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943.

¹⁴ D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 10.

¹⁵ R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

¹⁶ P. F. Cann and C. J. M. Stirling, following paper.

¹⁷ R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16.

¹⁸ R. G. Pearson and L. H. Piette, *J. Amer. Chem. Soc.*, 1954, **76**, 3081.

¹⁹ R. P. Bell and M. H. Pankhurst, *J. Chem. Soc.*, 1956, 2836.

²⁰ P. J. Elving and J. Lakritz, *J. Amer. Chem. Soc.*, 1955, **77**, 3217.

The data were correlated with Taft's σ^* values and the plots gave slopes (ρ^*) of 1.88 ($r = 0.999$) and 2.07 ($r = 0.993$) in ethanol and in water, respectively.

TABLE 3

Values of k_1 for nitroethane in OH^- - H_2O at 25° obtained by various methods

Ionic strength (M)	$k_1/\text{l mol}^{-1} \text{s}^{-1}$	Ref.
0.0	5.88 ± 0.11^a	17
0.1 (KCl)	5.92 ± 0.55^b	18
0.0	3.93 ± 0.13^c	20
0.0	5.83^a	19
0.1 (NaCl)	5.75^a	19
0.0	5.83 ± 0.15^a	4
0.0 or 0.2 (KCl)	5.19 ± 0.13^b	5
0.0	5.2^e	12
0.1 (NaClO ₄)	5.36 ± 0.12^f	This work

Methods: ^a Thermal maximum. ^b Steady state formation/destruction of OH^- . ^c Megacycle conductivity. ^d pH-Stat. ^e U.v. of EtNO_2 (λ_{max} , 185 nm). ^f U.v. of $\text{MeCH}_2\text{NO}_2^-$ (λ_{max} , 235 nm).

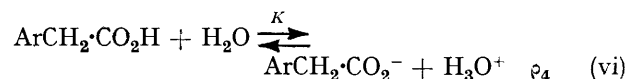
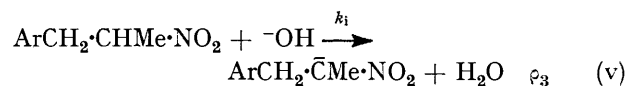
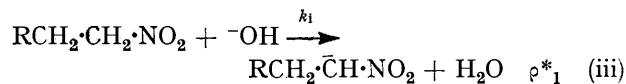
We find that rates of ionisation increase by factors of 17–27 (Table 2) on changing from solvent water ($\mu = 0.1\text{M}$) to ethanol ($\mu = 0.1\text{M}$). These results are in accord with earlier work⁴ in which k_1 for nitroethane was found to be fifteen times greater in ethanol ($\mu = 0.0\text{M}$) than in water ($\mu = 0.0\text{M}$). More rapid ionisation in ethanol is probably due to the greater basicity of the solvent-base system.²¹ In other work,⁸ however, ionisation rates of nitroalkanes were found to decrease on transfer from 50% water-methanol to pure methanol. The differential basicity of the media is less and dielectric effects perhaps become over-riding.

Ionisation rate changes little with increasing ionic strength in water. Bell and Pankhurst¹⁹ found that k_1 falls slightly and then rises again as μ is increased with NaCl as electrolyte. Comparison of our results for ethanol ($\mu = 0.1\text{M}$) with those of earlier work⁴ for ethanol ($\mu = 0.0\text{M}$) shows a positive salt effect of 1.64. This we attribute to stabilisation of the partial negative charge on the nitro-group in the transition state by association with sodium ions.

The slightly larger ρ^* value for the hydroxide-water system compared to that for reaction in ethoxide-ethanol is opposite to the trend observed by Bordwell⁸ in methanol-water. This is readily explained by the greater difference in base strength in the present system. With the weaker base, hydroxide, more inductive demand is made on the substitution in the transition state, which is likely to resemble the product more in water than in ethanol since, in the former solvent, the reaction is less exothermic:²² $[\text{p}K_a(\text{H}_2\text{O}) - \text{p}K_a(\text{RNO}_2 \text{ in } \text{H}_2\text{O})] < [\text{p}K_a(\text{EtOH}) - \text{p}K_a(\text{RNO}_2 \text{ in } \text{EtOH})]$.

While estimation, from the ρ^* value, of the position of the transition state on the reaction co-ordinate in an absolute sense has been shown to be meaningless for

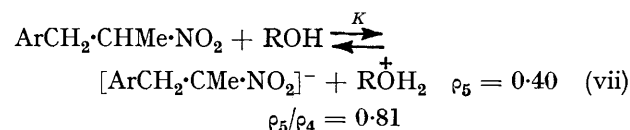
nitro-compounds,⁸ relative ρ^* values should indicate positions of transition states in related reactions. Thus for the four reactions in equations (iii)–(vi), ρ^*_1/ρ^*_2



should equal ρ_3/ρ_4 if the transition states for the two ionisation reactions are at the same distance along the reaction co-ordinate. Literature values²³ and an estimate of ρ^*_3 in water obtained by extrapolation of Bordwell's values⁸ in methanol and 50:50 methanol-water using $\rho \propto 1/D$ (D is the dielectric constant of the medium) and literature D values²⁴ give:

$$\begin{aligned} \rho^*_1 &= 2.07 \\ \rho^*_2 &= 1.72 & \rho^*_1/\rho^*_2 &= 1.20 \\ \rho^*_3 &= 0.60 & \rho_3/\rho_4 &= 1.23 \\ \rho^*_4 &= 0.49 \end{aligned}$$

The close agreement between these ratios suggests that transition states for two ionisations are indeed similar, and that the inductive demand is about 20% greater than for the equilibria. This larger demand, despite only a partial negative charge in the transition state, is compatible with the site of charge creation being on carbon and hence nearer to the substituent in reactions (iii) and (v) than in reactions (iv) and (vi). For the equilibrium acidities of the nitro-compounds [equation (vii)], on the other hand, the charge is located mainly on oxygen and thus further from the substituent than in the equilibria (iv) and (vi). ρ Values consequently are lower.⁸



Talvik and his collaborators^{25,26} have obtained linear free-energy plots for iodination rates of aliphatic nitro-compounds in which ionisation of the substrate is rate-determining, and similarly to the present work, ρ^* values were found²⁶ to be lower in methanol than in water.

²¹ R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959, ch. 4.

²² See ref. 8 for a brief summary.

²³ J. Hine, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1962, pp. 99, 102.

²⁴ P. S. Albright and L. J. Gosting, *J. Amer. Chem. Soc.*, 1946, **68**, 1061.

²⁵ A. Pimli, V. Timotheus, and A. Talvik, *Reacts. spos. org. Soedinenii*, 1966, **3**, 7 (*Chem. Abs.*, 1968, **68**, 77,377).

²⁶ T. Tenno and A. Talvik, *Reacts. spos. org. Soedinenii*, 1969, **6**, 743 (*Chem. Abs.*, 1970, **72**, 99,775).

An outstanding anomaly in the present results is the ionisation rate of 2-nitro-1,1-diphenylethane. In spite of the additional inductive effect of the second phenyl group, this compound ionises *more slowly* than the monophenyl analogue. We attribute this effect to steric interaction between the base and the substrate and the result is discussed further in the following paper in connection with β -steric interaction in elimination. It has recently been shown²⁷ that ionisation rates of sulphones bearing β -trialkylammonium substituents are depressed by the insertion of phenyl groups.

EXPERIMENTAL

Ethanol was purified by the magnesium-iodide method.²⁸ Solutions of sodium ethoxide were prepared by addition of clean sodium to dry ethanol under nitrogen. Aqueous sodium hydroxide solutions were made up from B.D.H. concentrated volumetric solutions. All base solutions were standardised by titration with standard hydrochloric acid (phenolphthalein as indicator). Sodium perchlorate (A.R.) was used without further purification for water solutions; for ethanol solutions it was dehydrated at 150° for 24 h and cooled in a desiccator. Nitroethane and 1-nitropropane were twice distilled. ¹H N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 60 MHz.

Kinetics.—Reactions were followed at 25.0° using a Durrum-Gibson stopped-flow spectrophotometer. The change in intensity of the 235 nm maximum of the nitronate anion was monitored. Substrate concentrations were about 5×10^{-5} M and base concentrations ranged from 2×10^{-3} to 10^{-2} M. Reactions were followed for at least three half-lives, and pseudo-first-order rate constants were obtained from the transmittance *vs.* time output [lines with correlation coefficient (*r*) < 0.999 were neglected] or directly by attaching a log-log amplifier²⁹ to the output of the photomultiplier. Both methods gave results agreeing within the experimental error.

2-Nitroethylbenzene.— β -Nitrostyrene (14.9 g, 0.1 mol) in ether (25 ml) was added to a stirred suspension of lithium aluminium hydride (1.7 g, 0.05 mol) in ether (80 ml) and tetrahydrofuran (25 ml) at -40° during 2 h. The mixture was stirred at -40° for a further 3 h and acidified below 0° during 0.75 h with a solution of urea (13.2 g) and acetic acid (13.2 g) in water (33 ml). The aqueous layer was saturated with sodium chloride and the organic layer was separated. The aqueous portion was extracted with ether (2 \times 25 ml) and the organic layers were combined, dried (Na₂SO₄), and evaporated. Distillation of the residue afforded the product (7.2 g, 48%), b.p. 130–138° at

15 mmHg, n_D^{20} 1.5350 (lit.³⁰ b.p. 130–135° at 14 mmHg, n_D^{25} 1.5270), τ (CDCl₃) 2.62 (5H, s), 5.51 (2H, t, *J* 7 Hz), and 6.80 (2H, t, *J* 7 Hz).

2-Nitroethanol.—This was prepared³¹ from nitromethane and formaldehyde and thrice distilled; b.p. 106° at 14 mmHg, n_D^{20} 1.4490, τ (CDCl₃) 5.40 (2H, t, *J* 6 Hz), 5.90 (2H, t, *J* 6 Hz), and 6.11 (1H, s).

2-Nitroethyl Ethyl Ether.—2-Nitroethyl acetate, prepared³² from 2-nitroethanol, had b.p. 62–64° at 1.3 mmHg, n_D^{20} 1.4302. The acetate (13.3 g, 0.1 mol) in ethanol (10 ml) was added during 2 h to ethanolic 0.5M-sodium ethoxide (150 ml). Polymerised nitroethylene (6 g) was filtered off and the filtrate, after acidification with acetic acid, was evaporated below 40° to 15 ml. The residue was poured into saturated brine (50 ml) and extracted with dichloromethane (3 \times 25 ml). The combined extracts were dried (Na₂SO₄) and evaporated. To the residue was added diphenyl ether (8 g) and the mixture was distilled at 0.1 mmHg. The distillation was stopped while some diphenyl ether remained in the pot. The distillate (6 g of *ca.* 2:1 mixture of diphenyl ether and product) was fractionated at 15 mmHg to give the *nitro-ether* (1.90 g, 16%), b.p. 65–70° at 15 mmHg, n_D^{16} 1.4192 (Found: C, 40.8; H, 7.8; N, 12.0. C₄H₉NO₃ requires C, 40.4; H, 7.6; N, 11.8%), τ (CDCl₃) 5.68 (2H, t, *J* 5 Hz), 6.21 (2H, t, *J* 5 Hz), 6.58 (2H, q, *J* 7 Hz), and 8.86 (3H, t, *J* 7 Hz).

Caution. Addition of diphenyl ether to the residue before distillation is essential to prevent the pot residue exploding violently *after* the apparatus has cooled to room temperature.

2-Nitro-1,1-diphenylethane.—Bromobenzene (10.4 g, 0.067 mol) in tetrahydrofuran (15 ml) was slowly added to magnesium (1.60 g, 0.067 mol) stirred under tetrahydrofuran. The solution was then heated under reflux for 0.5 h. Cadmium chloride (12.2 g, 0.067 mol) was then added in portions and the mixture was stirred for 0.5 h. 2-Nitrostyrene (7.45 g, 0.05 mol) in tetrahydrofuran (10 ml) was then slowly added and the mixture was heated under reflux for 0.5 h. The cooled mixture was poured into cold aqueous sulphuric acid (3N) and extracted with dichloromethane (2 \times 25 ml). The extracts were washed with water, dried (Na₂SO₄), and evaporated to give an oil (9.8 g), which on distillation gave the product (5.6 g, 49%), b.p. 198–205° at 15 mmHg, m.p. 70° [from light petroleum (b.p. 60–80°)] (lit.³³ b.p. 195° at 15 mmHg, m.p. 70°).

We thank the S.R.C. for provision of equipment and a post-doctoral fellowship (to P. F. C.), and Mrs. Beryl Davies for technical assistance.

[3/2373 Received, 19th November, 1973]

²⁷ K. N. Barlow, D. R. Marshall, and C. J. M. Stirling, *J.C.S. Chem. Comm.*, 1973, 175.

²⁸ A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 167.

²⁹ D. McLean and R. L. Tranter, *J. Phys. (E)*, 1971, 4, 455.

³⁰ O. R. Gottlieb and M. T. Magalhaes, *Bol. Inst. Quím. agric. (Brazil)*, 1960, 60, 7 (*Chem. Abs.*, 1962, 56, 13,027g).

³¹ W. E. Noland, *Org. Synth.*, 1961, 41, 67.

³² H. L. Cates, Ph.D. Dissertation, Ohio State University, 1951 (quoted in R. B. Kaplan and H. Shechter, *J. Org. Chem.*, 1961, 26, 982).