

- 12, 131 (1962).
- (22) H. R. Slagh, U.S. Patent 2 632 776; *Chem. Abstr.*, **48**, 1412 (1954).
- (23) M. M. Holleman, *Recl. Trav. Chim. Pays-Bas*, **23**, 299 (1904).
- (24) V. M. Rodionov, I. M. Machinskaya, and V. M. Belikov, *Zh. Obshch. Khim.*, **18**, 917 (1948); *Chem. Abstr.*, **43**, 127 (1949).
- (25) N. Kornblum, H. O. Larsen, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).
- (26) A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **30**, 1687 (1965).
- (27) N. Kornblum and G. E. Graham, *J. Am. Chem. Soc.*, **73**, 4041 (1951).
- (28) J. P. Kispersky, H. B. Hass, and D. E. Holcomb, *J. Am. Chem. Soc.*, **71**, 516 (1949).
- (29) (a) L. Henry, *Bull. Acad. R. Belg.*, **36**, 149 (1898); *J. Chem. Soc., Abstr.*, 251 (1899); (b) N. Kornblum and H. E. Ungnade, *Org. Synth.*, **38**, 75 (1958).
- (30) D. E. Pearson and J. D. Bruton, *J. Org. Chem.*, **19**, 957 (1954).
- (31) L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 4047 (1951).
- (32) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).
- (33) H. Lecher and F. Holschneider, *Ber. Dtsch. Chem. Ges.*, **57**, 755 (1924).
- (34) F. Klivenyi, *Magy. Kem. Folyoirat*, **64**, 121 (1958); *Chem. Abstr.*, **54**, 16416e (1959).
- (35) J. E. Dunbar and J. H. Rodgers, *J. Org. Chem.*, **31**, 2842 (1966).
- (36) T. Mukaiyama, *Tetrahedron Lett.*, 5115 (1970).
- (37) W. E. Truce, T. C. Klinger, J. E. Parr, H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).
- (38) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2876 (1949).
- (39) J. G. Miller and H. S. Angel, *J. Am. Chem. Soc.*, **68**, 2358 (1946).
- (40) N. Kornblum, B. Taub, and H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954).
- (41) A. P. Howe and H. B. Hass, *Ind. Eng. Chem.*, **38**, 251 (1946).
- (42) F. T. Williams, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1958, p 65.
- (43) J. V. Braun and O. Kruber, *Ber. Dtsch. Chem. Ges.*, **45**, 395 (1912).
- (44) L. Henry, *Rec. Trav. Chim. Pays-Bas*, **16**, 193 (1897).
- (45) J. V. Braun, H. Deutsch, and A. Schmatlock, *Ber. Dtsch. Chem. Ges.*, **45**, 1252 (1912).
- (46) N. Kornblum and W. M. Weaver, *J. Am. Chem. Soc.*, **80**, 4333 (1958).
- (47) J. Tröger and E. Nolte, *J. Prakt. Chem.*, [2], **101**, 136 (1920).
- (48) K. v. Auwers and L. Harres, *Ber. Dtsch. Chem. Ges.*, **62**, 2287 (1929).

Kinetic and Equilibrium Acidities for Nitroalkanes

F. G. Bordwell,* John E. Bartmess, and Judith A. Hautala¹

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received March 14, 1977

Rates of deprotonation for 20 nitroalkanes, $G(\text{CH}_2)_n\text{NO}_2$, where n is 1, 2, or 3, catalyzed by lyate ion or by pyridine were measured in 50% (v/v) MeOH–H₂O. The rates were correlated reasonably well by the Taft relationship, but this is believed to be fortuitous for $n = 1$ or 2. A Brønsted plot for lyate rates vs. equilibrium acidities for $n = 3$ gave a slope of 1.67 and for pyridine rates gave a slope of 1.89. Rates of deprotonation by lyate ion of seven secondary nitroalkanes, $\text{RR}'\text{CHNO}_2$, with R or R' = Me, Et, Pr, *i*-Pr, or *c*-Pr, were measured in 50% (v/v) MeOH–H₂O. Changes in R (or R') caused larger effects in kinetic acidities than in equilibrium acidities; these effects were frequently in inverse directions. A three-step mechanism involving a singly H-bonded anion intermediate or a virtual intermediate is postulated to account for the large $k_{\text{H}}/k_{\text{D}}$ isotope effects and "anomalous" Brønsted coefficients observed for the deprotonation of nitroalkanes in protic solvents. Six examples are given from kinetic and equilibrium acidity data where the order of polar effects is PhS > PhO, which is opposite to the order of Taft σ_1 constants.

Although there is a wealth of information concerning rates of deprotonation of simple nitroalkanes with varied bases (HO⁻, AcO⁻, pyridine, etc.),²⁻⁴ relatively little information concerning the effect of introducing heteroatom substituents into the alkyl groups is available. We now present data for rates of deprotonation of nitroalkanes, $G(\text{CH}_2)_n\text{NO}_2$, where G is a heteroatom substituent and where $n = 1, 2, \text{ or } 3$, with lyate ion in 50% (v/v) MeOH–H₂O and with pyridine in 50% (v/v) MeOH–H₂O. These results, together with those on the effect of alkyl substitution into nitromethane, are then compared with the equilibrium acidity data⁵ for these compounds in the same solvent.

Results

Rates of deprotonation by lyate ion in 50% (v/v) methanol–water at 15 °C of 20 nitroalkanes of the type $G(\text{CH}_2)_n\text{NO}_2$, where n is 1, 2, or 3 and G is hydrogen, methyl, or a functional group, were measured by observance under pseudo-first-order conditions of the appearance of nitronate ion absorbance at 225–240 nm. Excellent kinetics were obtained in most instances with correlation coefficients of >0.999 for each run (Table I). The behavior of 3-chloro-1-nitropropane was exceptional in that the infinity absorbance slowly decreased with time, probably due to cyclization to form isoxazoline oxide. Lyate rates were also measured for a number of secondary nitroalkanes, $\text{RR}'\text{CHNO}_2$. The data are summarized in Table III.

A Taft plot (Figure 1) constructed from the lyate rates for 3-substituted-1-nitropropanes, $G(\text{CH}_2)_3\text{NO}_2$, vs. $\sigma^*\text{CH}_2\text{CH}_2\text{G}$, with G = H, Ph, OH, SPh, COCH₃, OPh, Cl, SO₂Ph, and CN, gave $\rho^* = 2.09 \pm 0.17$ ($r = 0.975$; $R^2 = 0.950$; $\text{SD} = \pm 0.39$ at

95% confidence level). Points for $G\text{CH}_2\text{CH}_2\text{NO}_2$ and $G\text{CH}_2\text{NO}_2$ compounds vs. $\sigma^*\text{CH}_2\text{G}$ and $\sigma^*\text{G}$, respectively, are also included in Figure 1, but were not used in the least-squares plot to determine ρ^* .

The rates of deprotonation of the $G(\text{CH}_2)_n\text{NO}_2$ compounds with pyridine base in 50% MeOH–H₂O were determined by a buffer dilution method, using triiodide ion as a scavenger for the nitronate ion^{6a} (Table I). The zero-order disappearance of triiodide is the actual kinetic variable. Iodination of the nitroalkanes does not go to completion,^{6b} but is extensive enough to allow successful measurement of rate constants. For 3-substituted-1-nitropropanes, $G\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$, with G = H, Ph, OH, OPh, SO₂Ph, and CN, a Taft plot gave $\rho^* = 2.27 \pm 0.26$ ($r = 0.957$; $R^2 = 0.916$; $\text{SD} = \pm 0.62$ at 92% confidence level). Points for 1,3-dinitropropane and 5-nitro-2-pentanone were not included because of complications due to side reactions. The distribution of the other points (Table I) along the line was similar to that shown in Figure 1.

A Brønsted plot (Figure 2) for lyate ion deprotonation in 50% MeOH–H₂O (at 15 °C) vs. equilibrium acidities in 50% MeOH–H₂O (at 25 °C) for $G\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$ compounds, with G = H, Ph, OH, COCH₃, OPh, SPh, SO₂Ph, and CN, gave $\alpha = 1.67 \pm 0.19$ ($r = 0.957$). Since the temperature dependence for pK 's for nitroalkanes is known to be small,⁷ and should be similar for a series such as $G(\text{CH}_2)_3\text{NO}_2$, the fact that the kinetic and equilibrium measurements were made at temperatures 10 °C apart should not affect α appreciably. The Brønsted α for a plot of pyridine deprotonation rates in 50% MeOH–H₂O (at 25 °C) vs. pK 's in 50% MeOH–H₂O (at 25 °C) was 1.89 ± 0.19 ($r = 0.965$).

The correlations of the (calculated) rates of protonation of

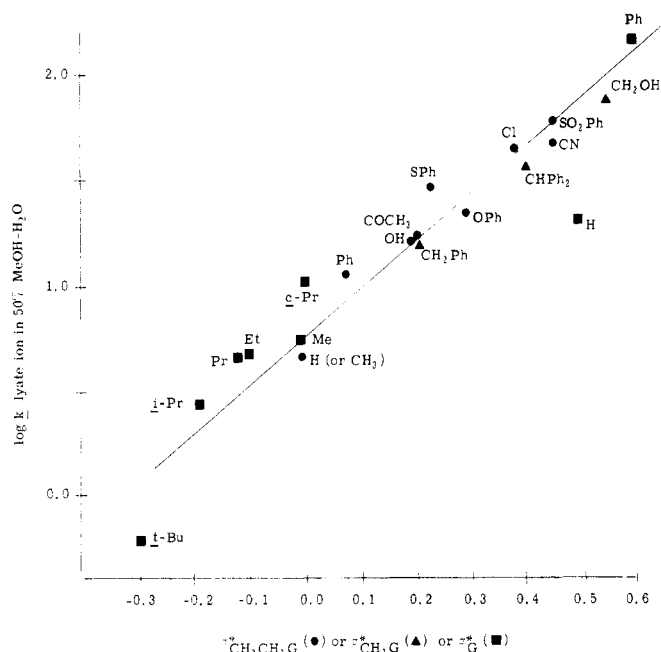


Figure 1. Plot of the logarithm of the rates of deprotonation by lyate ion in 50% MeOH-H₂O at 15 °C for 3-substituted 1-nitropropanes, GCH₂CH₂CH₂NO₂, vs. σ^* CH₂CH₂G (●). Points for GCH₂CH₂NO₂ vs. σ^* CH₂G (▲) and GCH₂NO₂ vs. σ^* G (■) are also shown, but were not used to determine ρ^* .

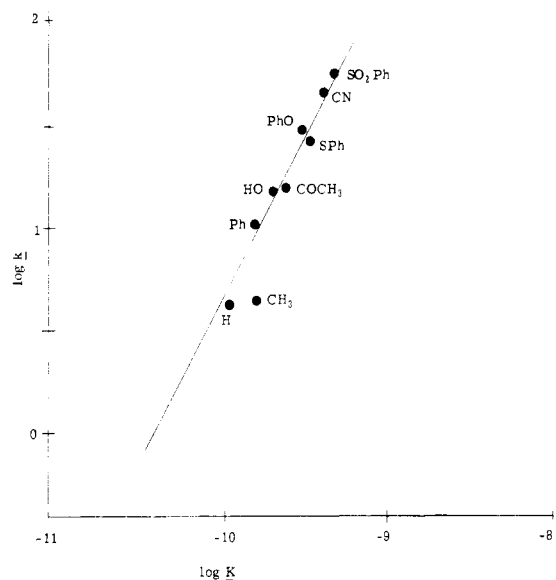


Figure 2. Brønsted plot of the rates of deprotonation by lyate ion vs. pK's for 3-substituted nitroalkanes, GCH₂CH₂CH₂NO₂, in 50% (v/v) MeOH-H₂O.

GCH₂CH₂CH=NO₂⁻ on carbon by solvent are less satisfactory than those in the opposite direction. Examination of Table II shows that for protonations of ArCH=NO₂⁻ on carbon there is a general trend for electron-withdrawing groups to accelerate the rate, in agreement with the calculated ρ of 0.45, but that the acceleration is irregular and generally smaller than expected. In particular, we note that the protonation of *m*-ClC₆H₄CH=NO₂⁻ is as rapid as that of *m*-NO₂C₆H₄CH=NO₂⁻, despite a sizable difference in the electron-withdrawing power of these two groups. Also, *m*-CF₃C₆H₄CH=NO₂⁻ is protonated at almost the same rate as C₆H₅CH=NO₂⁻, despite the moderately strong electron-withdrawing properties of the CF₃ group. Similar discon-

Table I. Deprotonation Rates of Nitroalkanes, GCH₂NO₂, by Lyate Ion and Pyridine in 50% (v/v) Methanol-Water

G	registry no.	k , M ⁻¹ s ^{-1a}	$10^5 k$, M ⁻¹ s ^{-1b}
<i>t</i> -Bu	34715-98-5	0.63	0.182
<i>i</i> -Pr	625-74-1	3.3	1.35
<i>n</i> -Pr	627-05-4	4.6	2.68
Et	108-03-2	4.7	2.17
Me	79-24-3	5.5	2.83
(CH ₂) ₂ Ph	22818-69-5	10.9	4.08
<i>c</i> -Pr	2625-33-4	10.6	3.95
(CH ₂) ₂ OH	25182-84-7	15.4	6.25
(CH ₂) ₂ COCH ₃	22020-87-7	16.4	
CH ₂ Ph	6125-24-2	16.3	6.05
(CH ₂) ₂ SPh	66291-17-6	27.8	12.2
(CH ₂) ₂ OPh	66291-15-4	21.3	9.61
CHPh ₂	5582-87-6	36.6	
(CH ₂) ₂ Cl	16694-52-3	43.8	
(CH ₂) ₂ SO ₂ Ph	66291-13-2	58.5	24.6
(CH ₂) ₂ CN	58763-41-0	45.2	21.6
H	75-52-5	30 ^c	8.04
(CH ₂) ₂ NO ₂	6125-21-9		68
CH ₂ OH	625-48-9	79.3	11.4
Ph	622-42-4	144	147

^a At 15 °C, with lyate ion as the base; reproducible to $\pm 5\%$. ^b At 25 °C, with pyridine as the base; reproducible to $\pm 5\%$. ^c Extrapolated from the rate with hydroxide in water.

tinuities of this type have been observed in protonation of ArCH=NO₂⁻ by the conjugate acids of amine bases.⁸ In protonations of GCH₂CH₂CH=NO₂⁻ on carbon we note that, despite the calculated ρ^* of 0.81, there is little or no change in rate for G = Ph, OH, CH₃CO, or PhO for a change in Taft constants of over 0.2 unit. We do not propose to interpret these results except to note that they are consistent with a complex mechanism for the forward and reverse reactions, involving solvent reorganization, such as presented herein.

Discussion

Taft and Brønsted Correlations for G(CH₂)₃NO₂ Nitroalkanes. Let us look first at the data for G(CH₂)₃NO₂ nitroalkanes, a system where steric effects appear to be relatively constant, judging from the success of the Taft and Brønsted correlations (Figures 1 and 2). The pyridine rates correlate well with the lyate rates for these compounds (slope = 0.950 \pm 0.053 for ten points; $r = 0.991$). It is noteworthy that the pyridine rates have about the same sensitivity to the effect of the substituent, G, as do the lyate rates, despite the fact that the pyridine rates are over five powers of ten slower. This result is similar to that observed in the deprotonation of ArCH₂NO₂ and ArCH(Me)CH₂NO₂ systems, where the Hammett ρ values were slightly larger for deprotonation by hydroxide ion in water than by amine bases in water.⁸ These results can be rationalized, since with amine bases the negative charge developing on carbon in the transition state is offset by the positive charge developing on the nitrogen of the amine base. Furthermore, if H-C bond breaking is greater in the transition state for deprotonation by the amine base, as seems likely (Hammond postulate), more of the negative charge in this transition state (see 2) may be delocalized to the nitro group, making the reaction less sensitive to changes in the nature of G or to substituent effects in Ar.

The Brønsted α for ArCH₂NO₂ and GCH₂CH₂CH₂NO₂ nitroalkane systems can be expressed in terms of Hammett ρ and Taft ρ^* values,

$$\alpha = \rho_{k_B} / \rho_{K_a} \text{ and } \alpha^* = \rho^*_{k_B} / \rho^*_{K_a}$$

where ρ_{k_B} and $\rho^*_{k_B}$ refer to the sensitivity of the rates of deprotonation in the series of nitroalkanes by a given base, B,

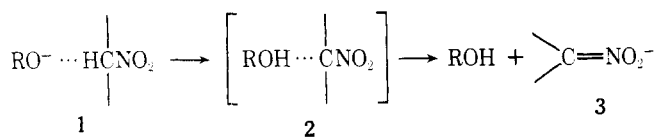
Table II. Relative Rates of Protonation on Carbon of $\text{GC}_6\text{H}_4\text{CH}=\text{NO}_2^-$ by Solvent Water and of $\text{GCH}_2\text{CH}_2\text{CH}=\text{NO}_2^-$ by Solvent 50% MeOH-HOH

$\text{GC}_6\text{H}_4\text{CH}=\text{NO}_2^-$				$\text{GCH}_2\text{CH}_2\text{CH}=\text{NO}_2^-$			
G	registry no.	σ	$(k/k^\circ)^a$	G	registry no.	$\sigma^*_{\text{CH}_2\text{CH}_2\text{G}}$	$(k/k^\circ)^b$
<i>m</i> -CH ₃	66291-11-0	-0.07	1.01	CH ₃	34430-24-5	-0.04	0.66
H	12413-18-2	(0.0)	(1.0)	H	25590-60-7	(0.0)	(1.0)
<i>m</i> -F	66322-97-2	0.34	1.01 ₄	Ph	66291-18-7	0.080	1.69
<i>m</i> -Cl	66291-22-3	0.37	1.25	HO	66291-16-5	0.20	1.73
<i>m</i> -CF ₃	66291-21-2	0.43	1.03 ₅	CH ₃ CO	66291-14-3	0.21 ₆	1.64
<i>m</i> -NO ₂	66291-20-1	0.71	1.26	PhO	66291-12-1	0.30 ₆	1.66
<i>p</i> -NO ₂	66291-19-8	0.78	1.20 ₅	CN	66291-10-9	0.46 ₈	2.40
				PhSO ₂	66291-09-6	0.47 ₅	2.80

^a Calculated from data in ref 8. ^b Calculated from data in the present paper.

to substituent effects, and ρ_{K_a} and $\rho^*_{K_a}$ refer to the sensitivity of the equilibrium acidities in the same nitroalkane series to changes in substituent effects. The same pattern of response is observed in each series, the kinetic acidities being more sensitive to changes in remote substituent effects than are the equilibrium acidities, causing α and α^* to be >1.

For deprotonation by lyate ion $\alpha^* = 2.09/1.25 = 1.67$. For deprotonation by pyridine $\alpha^* = 2.27/1.25 = 1.8$. A simulated reaction coordinate diagram comparing the rates of deprotonation of a nitroalkane, $\text{GCH}_2\text{CH}_2\text{CH}_2\text{NO}_2$, and a more acidic nitroalkane, $\text{G}'\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$, by lyate ion is shown in Figure 3. It is assumed in Figure 3 that substitution of substituent, G, by a more powerful electron-withdrawing substituent, G', will have essentially no effect on the ground-state energy of the nitroalkane (reactant), but will lower the energy of the transition state and the ground-state energy of the nitronate ion (product). A noteworthy feature of Figure 3 is that the effect of the substitution is *greater* in lowering the transition-state energy than in lowering the energy of the products. The assumption of a greater substituent effect on the transition-state than on the ground-state energies, which presumably correspond to the ground-state energies in the equilibrium, is necessary to explain the greater sensitivity of the kinetic acidity ($\rho^*_{k_1}$) than the equilibrium acidity ($\rho^*_{K_2}$) to substituent changes. The greater sensitivity of rates to substituent changes is understandable in terms of transition state 2 for lyate ion (RO^- ; R = H or Me) depro-



tonation, since in 2 the negative charge is developing primarily on carbon, whereas in the reactant ground state (1) the negative charge is primarily on the lyate ion base (RO^-), and in the product ground state (3) it is primarily on the oxygen atoms of the nitronate ion, two atoms further removed.

In the reverse reaction, protonation of 3 on carbon by solvent, the greater lowering of transition-state energy than product ground-state energy by substitution of a more powerful electron-withdrawing substituent, G', requires that electron withdrawal in nitronate ion 3 *accelerate* the rate. (A similar situation arises for protonation of $\text{ArCH}=\text{NO}_2^-$ by solvent.⁴) This too is understandable in terms of the formulas 3 and 2, since protonation on carbon requires that in the transition state negative charge be concentrated on carbon. Electron withdrawal from oxygen in 3 by the substituent will assist this operation.

The most important feature of this analysis is that it is contrary to the assumption of Leffler and Grunwald that in the generalized rate-equilibrium equation

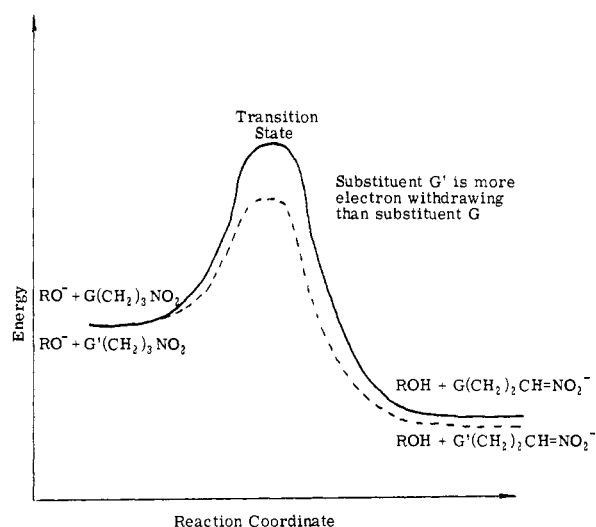


Figure 3. Simulated effect of a substituent, G (solid line), and a more electron-withdrawing substituent, G' (dashed line), on the rate of deprotonation of a nitroalkane by lyate ion (RO^-). (The assignment of the same ground-state energies for the reactants is arbitrary.)

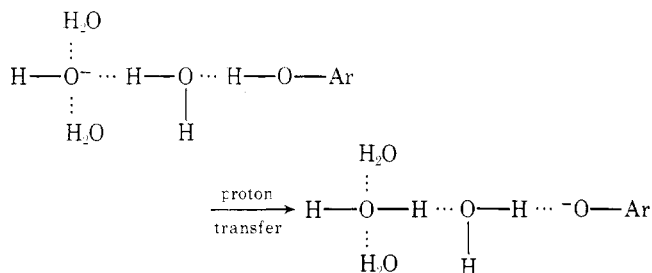
$$\delta\Delta G^\ddagger = \alpha\delta\Delta G^\circ \quad (1)$$

the effect of a substituent change, δ , on the transition-state energy will be *intermediate* to the effect of the substituent change on the energies of the reactant and product.⁹ As Kresge has pointed out,¹⁰ it is this assumption that constrains the value of the coefficient α to the limits of 0 and 1.0. It seems clear that this assumption is not correct for deprotonations of nitroalkanes. It follows that, at least for nitroalkanes, the size of α does *not* provide an index of the extent of proton transfer to the base in the transition state for deprotonation. Replacement of a substituent, G, by G' in other carbon acids of the type $\text{G}(\text{CH}_2)_n\text{A}$ and $\text{GC}_6\text{H}_4(\text{CH}_2)_n\text{A}$, where A is an acidifying function such as COR, SO_2R , CN, Ph, and the like, should lead to effects on deprotonation rates similar to those depicted in Figure 3. In deprotonation of systems of the type $\text{GC}_6\text{H}_4\text{CH}_2\text{A}$ one might expect, as a first approximation, that the size of α will decrease with the ability of A to delocalize the negative charge in the anion, i.e., $\text{NO}_2 > \text{COR} > \text{CO}_2\text{R} > \text{CN}$, SO_2R , etc. It may turn out, then, that in most systems of this type α will be less than 1.0. This does not mean, however, that such α 's provide a good index of the extent of proton transfer in the transition state.

The presentations of proton transfers in Figure 3 or by reaction $1 \rightarrow 3$ are oversimplified in that they ignore the role of the solvent. It now seems likely that such deprotonation reactions may involve an intermediate or virtual intermediate, rather than a single transition state.^{4,11,12} We will show in the next section that such mechanisms can accommodate

"anomalous" Brønsted coefficients and the surprisingly large k_H/k_D isotope effects for exoenergetic nitroalkane deprotonations.

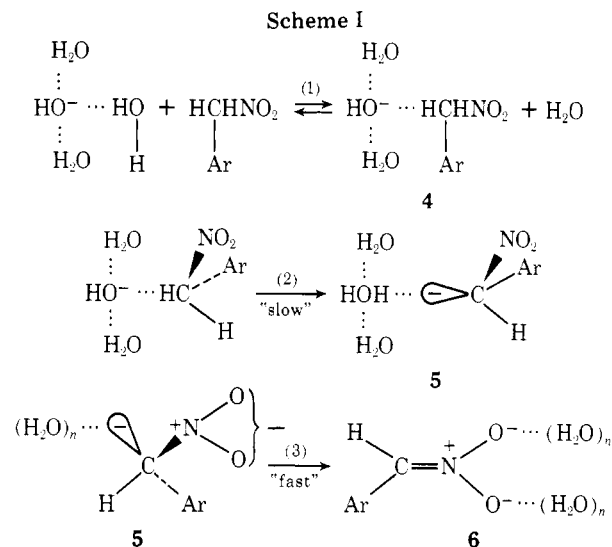
Mechanisms of Proton-Transfer Reactions. The Eigen mechanism for proton transfer with oxygen and nitrogen acids ("normal acids") visualizes a three-step mechanism:¹³ (1) formation of an "encounter complex"; (2) proton transfer; and (3) separation of the new "encounter complex" generated in the proton transfer. All three steps in this mechanism are very rapid. Proton transfer, for example deprotonation of phenol by hydroxide ion, can occur through one or more solvent molecules.¹⁴ In the representation shown the hydroxide ion is pictured as being solvated by three ("inner solvation sphere") water molecules, one of which is hydrogen bonded



to a phenol molecule. The activation energy for this (exoenergetic) proton transfer is low and the transition state is expected to be reactant-like (Hammond postulate). Substituent changes that increase the acidity of the phenol are expected to result in a small Brønsted coefficient (approaching zero),¹⁰ and the k_H/k_D isotope effect is expected to be small and to decrease as ArOH becomes more acidic.¹⁵ In the reverse (endoenergetic) proton transfer the transition state is expected to be product-like, resulting in a Brønsted coefficient approaching one and a small k_H/k_D isotope effect increasing as the basicity of ArO^- decreases.

This "normal" behavior, wherein the activation energies for proton transfers are low and the Brønsted coefficient changes abruptly from zero to one with a relatively small change in ΔG° , differs sharply from the proton transfer to hydroxide ion from a carbon acid of acidity comparable to that of a phenol, e.g., a nitroalkane such as $\text{GCH}_2\text{CH}_2\text{CH}_2\text{NO}_2$ or ArCH_2NO_2 . Here the activation energy is relatively high, and the Brønsted coefficient and k_H/k_D isotope effects are large. There is good reason to believe that the high activation energies for such proton transfers are associated to a considerable degree with desolvation of the hydroxide ion. It was pointed out many years ago that the reaction of an anion with an alkyl halide requires essentially replacing one solvent molecule of the anion with an alkyl halide molecule,¹⁶ and that the entire activation energy for the reaction of hydroxide ion with methyl iodide in water could be attributed to partial desolvation of the hydroxide ion.¹⁷ The essential correctness of this view as applied to proton transfers is supported by the much lower activation barriers and faster rates observed in dipolar aprotic solvents wherein the anions are not hydrogen bonded to the solvent. For example, deprotonation of triphenylmethane by alkoxide ions is roughly 10^6 faster in dipolar aprotic (dimethyl sulfoxide) solutions than in protic solutions.¹⁸ This large rate acceleration can be attributed to the absence of hydrogen-bonding protic solvent molecules surrounding the ethoxide ions.¹⁷ Evidently carbon acids, which form very weak hydrogen bonds, if any, are unable to utilize the Eigen mechanism for proton transfer.

The Eigen mechanism has been modified in a number of ways to take account of the appreciable solvent reorganization that occurs when a carbon acid is deprotonated by a base. Kreevoy has introduced an additional step in the mechanism to accommodate proper orientation and solvent reorganiza-



tion.¹² Albery has discussed the mechanism in terms of the Marcus equation by dividing the Marcus work term, ω^\ddagger ,¹⁹ into two parts, one of which represents solvent reorganization.¹¹ According to the Albery mechanism, rate-determining proton transfer from a nitroalkane to a base gives a relatively strongly basic pyramidal anion with much of the charge concentrated on carbon. Solvent reorganization then helps to transform this anion to the planar nitronate ion, in which the charge is concentrated on oxygen. This mechanism is comparable to one that evolved in our laboratory at about the same time.⁴ An elaboration of this mechanism, which takes specific account of the need to desolvate the attacking base, is presented in Scheme I. (The mechanism is illustrated using ArCH_2NO_2 , but would, of course, apply equally well to other nitroalkanes or other carbon acids.)

In step 1 of this mechanism one of the three solvent molecules surrounding the hydroxide ion is replaced by a nitroalkane molecule,²⁰ and complex 4 is formed. The proton transfer in step 2 is visualized as being comparable to that in the Eigen mechanism, but the activation barrier is larger because the hydrogen bond in the encounter complex (4) is very weak, and because some structural and solvent reorganization accompanies the proton transfer to form the "essentially pyramidal", "singly-solvated" carbanion 5. Carbanion 5 must be partially rehybridized, but, for reasons to be presented shortly, the major part of the rehybridization (and solvent reorganization) of 5 is believed to occur in step 3. The mechanism presented in Scheme I has been devised to account for: (a) the slow proton transfers observed for nitroalkanes in protic solvents; (b) the high k_H/k_D isotope effects observed for nitroalkane deprotonations; and (c) the "anomalous" Brønsted coefficients observed for nitroalkanes.

The rapid proton transfers to hydroxide ion from oxygen acids, such as phenols, have been explained by Eigen as being due to the ability of ArOH to fit into the hydrogen-bonded network surrounding the hydroxide ion.¹³ Carbon acids of comparable acidity, such as nitroalkanes, form only very weak hydrogen bonds, if any. They cannot fit into this network, and require a much larger activation barrier for proton transfer. Scheme I pictures this high barrier as consisting of a separate, reversible step (1) with a sizable barrier needed to desolvate the hydroxide ion, and a second step (2) with a second barrier for the actual proton transfer. If proton transfer is viewed as occurring without intervention of an intermediate, as in Figure 3, complex 4 would be converted in one step to the rehybridized nitronate ion 6. This reaction would be highly exoenergetic, however, and is not consistent with the large k_H/k_D isotope effect observed for nitroalkane deprotonations. On the other hand, intermediate (or virtual intermediate²²) 5 has

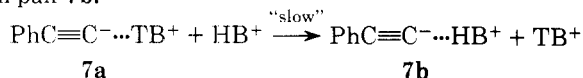
Table III. Equilibrium and Kinetic Acidities for Nitroalkanes, RR'CHNO₂, in 50% MeOH-H₂O

R	R'	registry no.	pK	ΔpK ^a	k ^b	log(k _H /k _D) ^c
H	H		11.11		30 ^d	
H	Me		9.63	(0.00)	5.6	(0.00)
Me	Me	79-46-9	8.85	-1.08	0.26	1.24
H	Et		9.99	(0.00)	4.7	(0.00)
Et	Et	551-88-2	10.17	-0.12	0.039	1.78
H	Pr		9.77	(0.00)	4.6	(0.00)
Pr	Pr	2625-37-8	9.85	-0.52	0.034	1.83
H	<i>i</i> -Pr		10.38	(0.00)	3.3	(0.00)
<i>i</i> -Pr	<i>i</i> -Pr	66291-08-5	11.0	0.32	0.00061	3.35
H	<i>c</i> -Pr		9.41	(0.00)	10.6	(0.00)
<i>c</i> -Pr	<i>c</i> -Pr	2625-39-0	10.65	0.94	0.079	1.84
H	<i>t</i> -Bu		11.4		0.63	
Me	<i>i</i> -Pr	595-42-6	9.73		0.095	
Me	<i>c</i> -Pr	2625-38-9	8.73		0.22	

^a ΔpK = pK - pK₀ (statistically corrected). ^b Lyate rates. ^c Statistically corrected. ^d Estimated from the hydroxide rate in water.

a much higher energy than does product **6**, and step 2 should have a transition state nearer to the point along the reaction coordinate at which the proton is half transferred. A large k_H/k_D isotope effect is therefore reasonable according to this mechanism.

Intermediate **5** would appear as a saddle point in the curve in Figure 3 if it is an actual intermediate, or as a discontinuity in the curve if it is a virtual intermediate; see the three-dimensional representation given by Albery in ref 12. Kurz and Kurz conclude from a detailed analysis of solvent effects that all proton transfers in which solute-solvent coupling is relatively weak, as would be expected here, should occur by an uncoupled mechanism in which virtual intermediates *must* be present.²³ Kresge has obtained evidence for an intermediate (**7a**) similar in structure to **5** in the detritiation of phenylacetylene by an amine base, B. In this reaction detritiation occurs to form an ion-pair intermediate (**7a**) and the "slow" step is exchange of the cation partner of this ion pair to form ion pair **7b**.²⁴

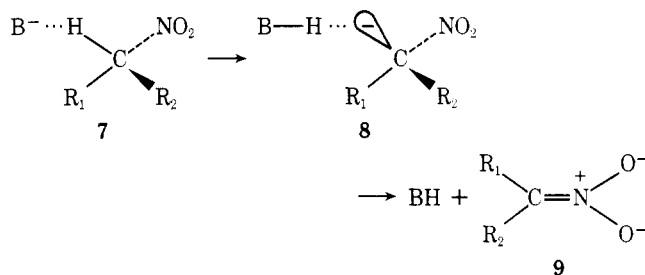


These results indicate that a localized carbanion can indeed form a strong hydrogen bond, as we have postulated in formulating intermediate **5**.

The Brønsted coefficient larger than 1.0 observed for deprotonation of ArCH₂NO₂ (or GCH₂CH₂CH₂NO₂) systems is accounted for according to Scheme I by the fact that the substituent effects on rates and equilibria change in a different manner.¹⁰ Referring to Figure 3 we see that in the deprotonation step the electron-withdrawing group, G', lowers both the transition-state energy and energy of the nitronate ion appreciably. (G' is assumed to have no effect on the ground-state energy of the nitroalkane.) The lowering of the transition-state energy is *greater* than the lowering of the ground-state energy of the nitronate ion, causing the Brønsted α to be larger than 1.0. In the reverse reaction, protonation of the nitronate on carbon, the electron-withdrawing group, G', *lowers* the transition-state energy appreciably but *increases* the difference in ground-state energies between the nitronate ion and the nitroalkane, causing the Brønsted α to be negative.

α-Alkyl Effect. Anomalous Brønsted Coefficients. Substitution of R for H in HCH₂NO₂ generally increases the equilibrium acidity in either aqueous or Me₂SO solvents due to the stabilizing influence of R in the RCH=NO₂⁻ anion.^{5a} A similar effect is observed in 50% MeOH-H₂O for substitution of H by R in RCH₂NO₂ when R is Me, Et, or Pr (Table III). On the other hand, these substitutions cause retardation of the rates of deprotonation in 50% MeOH-H₂O (Table III).

Analysis of these data in terms of the simplest representation, 1 → 2 → 3, requires that the stabilizing influence of R on the product (**3**) be overshadowed in the transition state (**2**) by a destabilizing influence. The abrupt rate decrease of over three powers of ten from *i*-PrCH₂NO₂ to *i*-Pr₂CHNO₂ (Table III) suggests that this is a steric effect of some kind, presumably steric hindrance to solvation. These inverse effects of alkyl substitution on rates and equilibria provide further examples wherein the effect of a substituent change, δ, on the transition-state energy is not intermediate to the effect of the substituent change on the energies of the reactant and product, as is required if α in eq 1 is to be confined to the limits of 0-1.0. The lack of correspondence in substituent effects on rates and equilibria may be explained in terms of a reactant-like transition state,^{4a} or by assuming that the substituent interactions develop at different rates as the system moves along the reaction coordinate.¹⁰ It is difficult to explain the large k_H/k_D isotope ratios in this way, however, since they show that H-C bond breaking is *extensive* in the transition state. Alternatively, one can postulate the formation of an intermediate^{4b,4c} or a virtual intermediate.^{11,12} If a more detailed mechanistic representation such as that shown in Scheme I is adopted, intermediates **7** and **8** can be assumed to be formed along the reaction pathway (Figure 4).



The advantage of assuming the presence of intermediate **8** is that we do not expect changes in the stabilities of the planar nitronate ion product **9** caused by substituent changes to influence the rates. Instead, the rate of deprotonation will be determined only by the height of the barrier leading to the singly H-bonded, essentially tetrahedral intermediate, **8** (**8a** or **8b** in Figure 4). For example, the substituent change from H₂CHNO₂ to *i*-Pr₂CHNO₂, which leads to a 5 × 10⁴ decrease in rate of deprotonation by lyate ion in 50% MeOH-H₂O with essentially no change in equilibrium acidity (Table III), can be rationalized in terms of Figure 4 by assuming that a higher barrier must be surmounted to produce intermediate **8b** (R₁ = R₂ = *i*-Pr) than to produce intermediate **8a** (R₁ = R₂ = H). There need be little or no change in the equilibrium acidity,

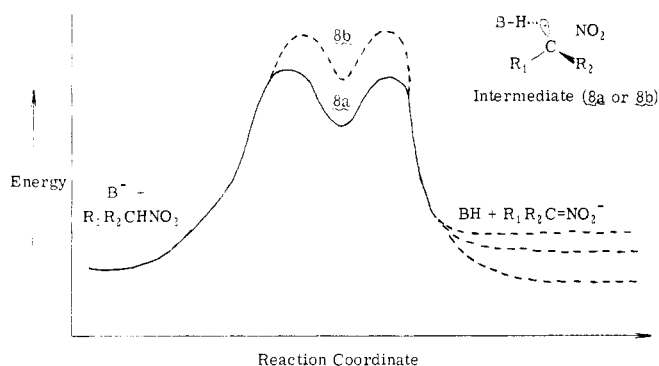


Figure 4. Simulated effect of one or two alkyl substituents (R_1 and R_2) on the rate of deprotonation of a nitroalkane by a base (B^-). (The substitution of R_1 and/or R_2 for H generally decreases the rate and increases the stability of the product, see text.)

however, because there need be little or no change in the relative ground-state energies of nitroalkane and nitronate ion product. Furthermore, a large k_H/k_D ratio is reasonable for this mechanism, since formation of either **8a** or **8b** is endoenergetic.

Substitution of Me for α -H generally produces acid-strengthening effects on the equilibrium acidities of simple nitroalkanes and ketones, but acid-weakening effects for simple nitriles and sulfones.^{5a} The difference appears to arise from the degree of delocalization of charge made possible by the two types of functions. On the other hand, substitution of Me for α -H decreases the kinetic acidities of all four types of carbon acids. We can anticipate, then, that in protic solvents, ketones, like nitroalkanes, will give "anomalous" Brønsted coefficients, whereas nitriles and sulfones will not. (Unfortunately, this prediction is not easily tested, since equilibrium acidities of simple ketones, nitriles, and sulfones can be determined only in dipolar aprotic solvents.) The observation of "normal" Brønsted coefficients for the latter does not necessarily mean, however, that the transition-state structure is "intermediate" between that of reactants and products.⁹ It could just as well mean that there happens to be a correspondence in substituent effects on the transition state and the product. We conclude that the size of such Brønsted coefficients is a poor guide to transition-state structures of deprotonation reactions.

Limitations of the Taft Equation. In the preceding paper we concluded that the Taft relationship can be applied in only a limited sense to systems such as $G(CH_2)_nNO_2$, where $n = 1, 2, \text{ or } 3$, because: (a) σ^*_G constants ($n = 1$) cannot be mixed with $\sigma^*_{CH_2G}$ constants ($n = 2$): (b) "methylene transmission coefficients", which relate $\sigma^*_{CH_2G}$ to $\sigma^*_{CH_2CH_2G}$, vary with geometry; and (c) σ^* constants in general give only a rough measure of polar effects because they are dependent on geometry.^{5b} The Taft plot in Figure 1 for the kinetic acidities of $G(CH_2)_nNO_2$ appears to contradict these first two conclusions, however, since many of the σ^*_G points (squares) and $\sigma^*_{CH_2G}$ points (triangles) fit the line almost as well as do the points for $\sigma^*_{CH_2CH_2G}$ constants, which were used to define the line (circles). In contrast, the σ^*_G and $\sigma^*_{CH_2G}$ points deviate widely from the Taft plot for equilibrium acidities.^{5b} (This represents another example of the lack of correspondence between kinetic and equilibrium acidities that have been discussed in earlier sections of this paper.) We believe that the apparent fit in Figure 1 is fortuitous, however, and that it is a consequence of the approximate nature of the Taft relationship. Note that there is appreciable scatter of the $\sigma^*_{CH_2CH_2G}$ points in Figure 1, and that the PhO and PhS points fit poorly. The deviations of these two points offer a good illustration of the dependence of the Taft relationship

on geometry. The relative order of polar effects PhO > PhS appears to be firmly established by ester hydrolysis data, which indicate a substantial difference in $\sigma^*_{CH_2G}$ constants (0.85 for PhO²⁶ and 0.66 for PhS²⁷). This order is confirmed by using the pK 's of carboxylic acids, GCH_2CO_2H , as an alternative source of σ^* constants (0.92 and 0.71, respectively).²⁸ Hammett σ_m constants also indicate PhO > PhS to be the correct polar order ($\sigma_m^{PhO} = 0.25$; $\sigma_m^{PhS} = 0.18$ ²⁹). On the other hand, all of the data on the $G(CH_2)_3NO_2$ system point to an *opposite* order for the relative polar effects of PhO and PhS. Equilibrium acidities in both Me₂SO and MeOH-H₂O give the order PhS > PhO, as do kinetic acidities using either lyate ion or pyridine in MeOH-H₂O (Table I). The deviations are substantial as may be judged by the fact that $\sigma^*_{CH_2G}$ constants give a calculated rate ratio, k^{PhO}/k^{PhS} , for lyate ion deprotonation in 50% MeOH-H₂O of 426, whereas the observed ratio is 0.77. The equilibrium acidities PhO(CH₂)₃SO₂Ph and PhS(CH₂)₂SO₂Ph are also in an order opposite to that predicted by Taft $\sigma^*_{CH_2G}$ constants.³⁰ One might have expected the order for equilibrium acidities of the carboxamides PhOCH₂CONH₂ and PhSCH₂CONH₂ to follow the Taft order, since carboxamides are closely related in structure to the carboxylic esters, GCH_2CO_2Et , from which the Taft $\sigma^*_{CH_2G}$ constants were derived. Here too, however, a reverse order is observed.³¹ It would appear that the polar effects of PhO and PhS substituents are strongly dependent on the geometry of the system used for the measurements. These results are reminiscent of those of Grob, who finds that the halogen order for the equilibrium acidities of 4-haloquinuclidinium ions in water is Br > F > Cl > I instead of the "inductive order" F > Cl > Br > I.³²

Experimental Section

Materials. The substituted nitroalkanes were prepared as previously reported,⁵ save for 3-chloro-1-nitropropane. This was synthesized by the procedure of Lampman, Horne, and Hager,³³ giving a 28% yield of crude product, along with 45% starting material and 14% 3-nitroisoxazoline as a high-boiling byproduct. Refractionation of the product gave material >99% by VPC: bp 66–67 °C (4 mm) [lit.³³ bp 98–110 °C (22 mm)]; n_D^{25} 1.453; NMR (CDCl₃) δ 2.47 (quintet, 2 H), 3.70 (triplet, 2 H), 4.58 (triplet, 2 H).

Kinetic Measurements. The procedure followed by lyate rates was that of Bordwell, Boyle, and Yee³⁴ save that data were collected with a Beckman Kintrac VII UV-visible spectrophotometer providing digital output through a Beckman 3108 Intercoupler attached to a Teletype Corp. Teletypewriter. The cell block was thermostated at 15.0 ± 0.1 °C.

The pyridine rates were determined essentially by the method of Barnes and Bell⁶ as modified in this Laboratory by Dr. R. J. Scriven. In a typical run, a solution consisting of 2 mL of weak buffer base solution (0.03–0.0002 M), 1 mL of nitroalkane solution (0.02–0.0004 M), and 0.1 M KCl were allowed to equilibrate in the Kintrac cell block. Measurement was initiated by addition of 20 μ L of triiodide solution (0.01–0.001 equiv, relative to nitroalkane) to the cell with an Eppendorf Microliter Pipette, and the change in absorbance at 353 nm was followed as a function of time. The observed pseudo-order rate constants, k_{obsd} , were evaluated on the CDC 6400 computer at Northwestern's Vogelback Computing Center, using a least-squares program written by Dr. A. C. Knipe, which discards the worst 10% of the data. The first-order rate constants, k_1 , were calculated with the equation

$$k_1 = k_{obsd}/n[\text{nitroalkane}] \epsilon$$

where $\epsilon = 33\,150$, the extinction coefficient of triiodide in 50% MeOH-H₂O at 353 nm, and n is the number of equivalents of iodide taken up by the nitroalkane. Attempts to determine n by isolation of product proved unsuccessful, and a value $n = 1$ was assumed, as has been done previously.⁶

Any values of k_{obsd} with $r < 0.999$ were rejected. All buffer dilution plots consisted of at least three runs, each with at least three different base strengths. The background reaction of the weak base buffer with the triiodide solution was negligible at all concentrations. Rates were reproducible to within $\pm 5\%$.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this research. Comments of a referee and of Professor A. J. Kresge were helpful in preparing a revised version of this manuscript.

References and Notes

- (1) National Institutes of Health Fellow, 1967–1970.
- (2) R. P. Bell and D. M. Goodall, *Proc. R. Soc. London, Ser. A*, **294**, 273 (1966); D. J. Barnes and R. P. Bell, *ibid.*, **318**, 421 (1970); R. P. Bell and B. J. Cox, *J. Chem. Soc. B*, 194 (1970).
- (3) V. M. Belikov, A. Talvik, and C. B. Korchemnaya, *Org. React. (USSR)*, **2** (1), 10 (1965); A. Talvik et al., *ibid.*, **3** (2), 179 (1966); **3** (4), 7 (1966); **4**, 494, 822 (1967); **6**, 468, 743, 882 (1969); **7**, 1194, 1206 (1970).
- (4) (a) F. G. Bordwell and W. J. Boyle, *J. Am. Chem. Soc.*, **93**, 512 (1971); (b) F. G. Bordwell and W. J. Boyle, *ibid.*, **97**, 3447 (1975), and references cited therein; (c) F. G. Bordwell, *Faraday Symp. Chem. Soc.*, **No. 10**, 100 (1975).
- (5) (a) F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, companion paper in this issue; (b) F. G. Bordwell and J. E. Bartmess, *ibid.*, companion paper in this issue. (These are papers 1 and 2 in this series.)
- (6) (a) D. J. Barnes and R. P. Bell, *Proc. Ry. Soc. London, Ser. A*, **318**, 421 (1970); (b) R. P. Bell and E. Gelles, *ibid.*, **210**, 310 (1952).
- (7) D. Turnbull and S. H. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943).
- (8) F. G. Bordwell and W. J. Boyle, *J. Am. Chem. Soc.*, **94**, 3907 (1972).
- (9) J. E. Leffler, *Science*, **117**, 340 (1953); J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions", Wiley, New York, N.Y., 1963, p 153.
- (10) A. J. Kresge, "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, Chapter 7.
- (11) W. J. Albery, A. N. Campbell-Crawford, and J. S. Curran, *J. Chem. Soc., Perkin Trans. 2*, 2206 (1972).
- (12) A. I. Hassid, M. M. Kreevoy, and T-M. Laing, *Faraday Symp. Chem. Soc.*, **No. 10**, 69 (1975).
- (13) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
- (14) E. Grunwald and D. Eustace, ref 10, Chapter 4, have shown that usually one or two water molecules separate the reactants in proton transfers of this type.
- (15) R. A. More O'Ferrall, ref 10, Chapter 8.
- (16) R. A. Ogg and M. Polyani, *Trans. Faraday Soc.*, **31**, 604 (1935).
- (17) E. A. Moelwyn-Hughes and D. Glen, *Proc. R. Soc. London, Ser. A.*, **212**, 260 (1952).
- (18) C. D. Ritchie, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, N.Y., 1969, Chapter 4, pp 266–268.
- (19) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
- (20) Hydroxide (or alkoxide) ions are believed to be solvated by three tightly bound (inner sphere) water molecules. [The additional (outer sphere) water molecules that are also present are not shown.] Judging from the energy liberated on solvation of a gas-phase chloride ion by one or two protic solvent molecules,²¹ we can expect removal of one solvent molecule from HO⁻(H₂O)₃ to require a minimum energy of about 5 kcal/mol.
- (21) P. Kebarle, "Ions and Ion Pairs in Organic Reactions", Vol. 1., M. Szwarc, Ed., Wiley, New York, N.Y., Chapter 2, p 75.
- (22) As a virtual intermediate **5** would appear as a discontinuity on the potential energy curve, rather than as a potential energy minimum.^{11,12}
- (23) J. L. Kurz and L. C. Kurz, *J. Am. Chem. Soc.*, **94**, 4451 (1972).
- (24) A. J. Kresge, *Acc. Chem. Res.*, **8**, 354 (1975).
- (25) F. G. Bordwell, W. J. Boyle, J. A. Hautala, and K. C. Yee, *J. Am. Chem. Soc.*, **91**, 4002 (1969).
- (26) R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 619.
- (27) A. Chambers and C. J. M. Stirling, *J. Chem. Soc. B*, 4558 (1965).
- (28) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).
- (29) C. Y. Meyers, *Gazz. Chim. Ital.*, **93**, 1206 (1963) (based on acidities of phenols).
- (30) N. R. Vanier, Ph.D. Dissertation, Northwestern University, 1977.
- (31) H. E. Fried, unpublished results.
- (32) C. A. Grob and M. G. Schlageter, *Helv. Chim. Acta*, **59**, 264 (1976).
- (33) G. D. Lampman, D. A. Horne, and G. D. Hager, *J. Chem. Eng. Data*, **14**, 396 (1969).
- (34) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Am. Chem. Soc.*, **92**, 5926 (1970).

Kinetic and Equilibrium Acidities of Nitrocycloalkanes

F. G. Bordwell,* John E. Bartmess, and Judith A. Hautala¹

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received March 14, 1977

Rates of deprotonation by lyate ion in 50% (v/v) MeOH–H₂O were determined for C₃–C₈ and C₁₂ nitrocycloalkanes. Equilibrium acidities in this solvent were also determined for C₄–C₈ and C₁₂ nitrocycloalkanes and were determined in Me₂SO for C₃–C₇ nitrocycloalkanes. Equilibrium acidities in the two solvents showed a remarkable similarity in their variation with ring size, despite a (constant) difference of 7.75 pK units in the acidity constants. The equilibrium acidity of nitrocyclopropane was found to be over 10⁸ times smaller than that for nitrocyclobutane, and its kinetic acidity in water was found to be over 10³ times smaller. The correspondence in the relative order of equilibrium and kinetic acidities between the C₈ and the C₄ nitrocycloalkanes is contrasted with the lack of correspondence between the equilibrium and kinetic acidities of the C₄ and the C₈ nitrocycloalkanes. This is explained by assuming a different mechanism for deprotonation of nitrocyclopropane as compared to other nitroalkanes.

In the preceding paper we discussed the "anomalous" Brønsted coefficients observed for the deprotonation of acyclic nitroalkanes in protic solvents. A lack of the "expected" correlation between kinetic and equilibrium acidities of certain nitrocycloalkanes has also been apparent for some time.^{2,3} The relative rates of deprotonation for nitrocycloalkanes by hydroxide ion in water and by lyate ion in a variety of other protic solvents has been found to vary with ring size in the order: 4 > 5 > 7 > 8 > 6 >> 3.³ (Nitrocyclopropane failed to react.) In contrast, the order of equilibrium acidities in 33% (w/w) MeOH–H₂O for nitrocycloalkanes was found to vary with ring size in the order: 8 > 7 > 5 > 6 > 4 >> 3.³ (The acidity constant for nitrocyclopropane was too small to measure.) Studies of kinetic and equilibrium acidities of nitrocycloalkanes in 50% (v/v) MeOH–H₂O were in progress at the time these data were published. The work was continued, since it seemed worthwhile to obtain kinetic and equilibrium measurements in the same solvent.⁴ The equilibrium acidity studies have now been extended to dimethyl sulfoxide

(Me₂SO) solution, and rate and equilibrium data for nitrocyclopropane have been obtained.

Results

Equilibrium Acidities for Nitrocycloalkanes. The relative values for the equilibrium acidities obtained potentiometrically in 50% (v/v) MeOH–H₂O (Table I) agreed reasonably well with those determined conductometrically in 33% (w/w) MeOH–H₂O,³ except for nitrocyclohexane, for which a higher relative value was found. Repetition of this measurement in 33% (w/w) MeOH–H₂O gave, in our hands, a pK of 9.58, instead of the value reported (8.92). (On the other hand, we were able to check the values reported for nitrocyclopentane and nitrocycloheptane in 33% MeOH–H₂O to within 0.1 pK unit.) The value of 9.58 appears to be correct, since it places the pK of nitrocyclohexane within a few tenths of a unit of that reported for nitrocyclobutane (pK = 9.53),³ and we have observed a close correspondence between the pK's for these two nitrocycloalkanes in: (a) water (8.56 and