

Acidities, Brønsted Coefficients, and Transition State Structures for 1-Arylnitroalkanes^{1a}

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Abstract: The pK_a 's for a series of meta- and para-substituted 1-arylnitroethanes and arylnitromethanes have been measured in water. Rates of deprotonation for many of these compounds have been determined with hydroxide ion, piperidine, diethylamine, piperazine, morpholine, and 2,4-lutidine bases. The ρ values for the equilibrium acidities of these carbon acids in water (1.03 and 0.83) are much smaller than for comparable oxygen or nitrogen acids. Brønsted α values for ArCH_2NO_2 reacting with hydroxide ion, morpholine, and 2,4-lutidine are 1.54, 1.29, and 1.30, respectively. A kinetic interpretation of α accounts for the large value in terms of $\alpha = \rho_{k_1}/\rho_{K_a}$ and $\rho_{K_a} = \rho_{k_1} - \rho_{k_{-1}}$. Brønsted β values for ArCHMeNO_2 reacting with a series of amine bases averaged 0.55. For a series of nitroalkanes and ketones reacting with bases, β shows little variation and no consistent trend over almost 20 ΔpK units. A kinetic interpretation of β is given, and it is concluded that neither α nor β can serve as more than a rough qualitative guide to transition state structures for carbon acids. Deprotonations by amine bases were found to have essentially constant ρ values; these were smaller than for hydroxide deprotonations.

The Brønsted linear free energy relationship

$$\log k = \alpha \log K_a + \text{constant}$$

allows a comparison between the sensitivity to structural changes of kinetic acidities (k) and the sensitivity to structural changes of equilibrium acidities (K_a). According to a commonly accepted interpretation,² the size of α (or β) provides a measure of the degree of resemblance of the transition state to reactants or products: for reactant-like transition states α should be close to zero, and for product-like transition states α should be close to one. Some experimental support for this view comes from observations of Eigen and his coworkers³ on the acidities of oxygen and nitrogen acids. As an example, let us consider a plot of $\log k$ vs. ΔpK for deprotonation of YNH_3^+ acids by acetate ion (Figure 1).

For the "uphill" reactions (positive ΔpK) of acetate ion with the relatively weak acids NH_2NH_3^+ and ImH^+ (imidazolium ion), we see that α approaches one. For such endoenergetic reactions current postulates predict a product-like transition state.⁴ As a rule the proton will be closer to the weaker base in the transition state,⁴ which in this instance is the acetate ion. As stronger YNH_3^+ acids are used (negative ΔpK) α approaches zero. Now the proton is presumably closer in the transition state to the $p\text{-ClC}_6\text{H}_4\text{NH}_2$ molecule. In other words, for these "downhill" (exoenergetic) reactions, which approach the diffusion-controlled limit in rate, the transition state will be reactant like.⁴

Less information is available concerning the much slower proton transfers involving carbon acids or their

conjugate bases. A similar trend has been observed, however, for deprotonations of a variety of acids by the conjugate base of the carbon acid, acetylacetone. Here the change in α from near one to near zero was qualitatively the same as in Figure 1, but occurred over a much broader ΔpK region (10 to -10).³ In sharp contrast to these results, deprotonation of a series of carbon acids, ArCHMeNO_2 , by hydroxide ion (exoenergetic reactions with ΔpK varying from -10 to -8.5), instead of giving an α near zero, gave an α greater than one.⁵ On the other hand, for the (exoenergetic) reactions of hydroxide ion with the series of nitroalkanes, CH_3NO_2 , MeCH_2NO_2 , and Me_2CHNO_2 , α is negative.⁵ In order to explore this unprecedented behavior further we have now carried out additional measurements of the kinetic and equilibrium acidities of the 1-arylnitroethane series and have extended the study to arylnitromethanes, ArCH_2NO_2 .

Results

The pK_a 's of the meta- and some of the para-substituted 1-arylnitroethanes, which had been determined previously in 50% (v/v) methanol-water,^{5b} were redetermined in pure water. Rates for hydroxide-initiated deprotonation of these compounds were measured spectrophotometrically at 15 and 25° (Table I). Activation parameters for 1-(*m*-tolyl)nitroethane and for 1-phenylnitroethane were also obtained from rates at three temperatures (12.5, 25, and 40°). For the parent compound $\Delta H^\ddagger = 13.1$ kcal/mol and $\Delta S^\ddagger = -11$ eu; for the *m*-Me derivative $\Delta H^\ddagger = 12.9$ kcal/mol and $\Delta S^\ddagger = -12$ eu. The correlation coefficients for the Arrhenius plots were 0.9994 and 0.9992, respectively. Judging from these two results it appears that the ΔH^\ddagger values in Table I may be low by ca. 1.5 kcal/mol and that the ΔS^\ddagger values may be too low by ca. 5 eu.

Similar data were obtained for four meta- and para-substituted arylnitromethanes. Here the rates were considerably faster necessitating use of a stopped-flow method (Table II).

(5) (a) F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *ibid.*, **91**, 4002 (1969); (b) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *ibid.*, **92**, 5926 (1970).

(1) (a) For a preliminary account of this work see F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 511 (1971); (b) National Institutes of Health Predoctoral Fellow, 1967-1970.

(2) (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 238-241; (b) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966, pp 32-35; (c) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 106; (d) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1967, Chapter 3.

(3) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

(4) (a) J. E. Leffler, *Science*, **117**, 340 (1953); (b) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955); (c) C. G. Swain and E. R. Thornton, *ibid.*, **84**, 817 (1962).

Table I. pK_a 's and Rates with Hydroxide Ion of Meta- and Para-Substituted 1-Arylnitroethanes in Water at 25°

Substituent	$k_2,^a M^{-1} sec^{-1}$	$\Delta H^\ddagger,^b$	ΔS^\ddagger	$pK_a,^{d,e}$
<i>p</i> -CH ₃ O	4.89 ± 0.05	12.1	-15	
<i>p</i> -CH ₃	4.81 ± 0.15	11.8	-16	
<i>m</i> -CH ₃	5.42 ± 0.02	11.4	-17	7.49 ± 0.01
H	6.47 ± 0.06	11.5	-16	7.39 ± 0.01
<i>m</i> -CH ₃ O	8.46 ± 0.04	10.4	-19	
<i>p</i> -F	8.50 ± 0.15	11.6	-15	
<i>p</i> -Cl	12.1 ± 0.1	10.6	-18	
<i>m</i> -F	14.2 ± 0.4	10.5	-18	7.05 ± 0.01
<i>m</i> -Cl	17.5 ± 0.1	12.0	-13	7.05 ± 0.01
<i>m</i> -CF ₃	18.0 ± 0.2	10.7	-17	6.96 ± 0.01
<i>p</i> -CF ₃	21.6 ± 3.0	10.5	-17	
<i>m</i> -NO ₂	42.7 ± 0.2	10.3	-17	6.67 ± 0.01
<i>p</i> -NO ₂	57.9 ± 1.5	9.6	-18	6.51 ± 0.01
<i>m,m'</i> -(NO ₂) ₂	302 ± 10 ^c			(5.95) ^f

^a Average of three or more spectrophotometric runs, unless otherwise noted. ^b Calculated from the present data together with runs made at 15°. ^c Determined by a stopped-flow method. ^d Average of two or more determinations at 25°; $\mu = 0.10$. ^e $\rho = 1.03 \pm 0.03$, $r = 0.999$ (meta points only), $\sigma_{p-NO_2} = 0.854$. ^f Estimated from a Hammett plot assuming $\sigma = 1.42$.

Table II. pK_a 's and Rates with Hydroxide Ion for Substituted Arylnitromethanes in Water

Substituent	$k_2,^a M^{-1} sec^{-1}$	$pK_a,^{b,c}$	$pK_a,^{d,e}$
<i>o</i> -CH ₃	9.81 ± 0.30 × 10 ¹	7.60 ± 0.01	8.70 ± 0.01
<i>m</i> -CH ₃	1.24 ± 0.04 × 10 ²	6.97 ± 0.01	8.00 ± 0.01
H	1.59 ± 0.03 × 10 ²	6.88 ± 0.01	7.93 ± 0.01
<i>m</i> -Cl	4.78 ± 0.05 × 10 ²	6.63 ± 0.02	7.48 ± 0.01
<i>m</i> -NO ₂	1.25 ± 0.06 × 10 ³	6.30 ± 0.05	7.05 ± 0.01
<i>p</i> -NO ₂	2.32 ± 0.03 × 10 ³	5.89 ± 0.02	6.49 ± 0.01

^a Average from data on three photographs each comprising three superimposed runs on a Durrum-Gibson stopped-flow apparatus at 26°. ^b Average of two or more determinations in water at 25.0°, $\mu = 0.05$. ^c $\rho = 0.83 \pm 0.05$, $r = 0.996$ (meta points only), $\sigma_{p-NO_2} = 1.20$. ^d Average of two determinations in 50% (v/v) MeOH-H₂O at 25.0°, $\mu = 0.01$. ^e $\rho = 1.22 \pm 0.02$, $r = 0.9998$ (meta points only); $\sigma_{p-NO_2} = 1.18$.

The study was extended to amine bases by using a buffer dilution method.⁶ The rates of appearance of the nitronate ions were determined spectrophotometrically in the presence of a large excess of R₂NH-R₂NH₂⁺ buffer. By varying the concentration of amine present while keeping the [R₂NH]/[R₂NH₂⁺] buffer ratio constant, the pH constant, and the ionic strength constant, the rate constant for the amine deprotonation reaction (k_2^B) can be obtained from the slope of a plot of k_{obsd} vs. [R₂NH].

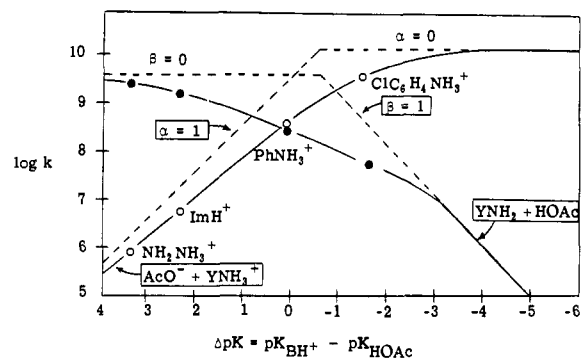
$$k_{obsd} = k_2^B[R_2NH] + k_2^{HO^-}[HO^-] + k^{H_2O}$$

Rate constants determined in this way at two or more pH's agreed well ($\pm 5\%$) for the reactions (Tables III-VIII) where diethylamine, morpholine, piperazine, and 2,4-lutidine were used as bases. With piperidine the scatter approached $\pm 10\%$.

Values of pK_{BH^+} for these amines have been reported in the literature,⁷ but the variation is such as to make it difficult to make a selection. Consequently, the pK_{BH^+} 's used (as K_a') in calculating the $k_{-2}^{BH^+}$ values given in Tables III-VIII were those calculated from the pH's of the kinetic solutions used in this study, measured

(6) M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, 89, 2327 (1967); J. E. Dixon and T. C. Bruice, *ibid.*, 92, 905 (1970).

(7) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965.

**Figure 1.** Variation of Brønsted α and β with ΔpK (adapted from ref 3).

at 25° and $\mu = 0.10$. The values calculated from the partially neutralized solutions at several pH's gave good internal agreement.

Table III. Rate Constants for the Reaction of 1-Arylnitroethanes, YC₆H₄CH(Me)NO₂, with Piperidine in Water at 25°, $\mu = 0.10$

Y	10 ¹ $k_2^B, M^{-1} sec^{-1}$	10 ⁶ $k_{-2}^{BH^+}, M^{-1} sec^{-1}$ ^a
<i>m</i> -CH ₃	4.57 ± 0.29	6.76
H	5.21 ± 0.15	6.12
<i>m</i> -CH ₃ O	6.24 ± 0.05	
<i>m</i> -Cl	11.4 ± 1.3	6.12
<i>m</i> -NO ₂	23.8 ± 1.9	5.33
<i>p</i> -NO ₂	36.9 ± 0.3	5.72
<i>m,m'</i> -(NO ₂) ₂	148 ± 26	

^a Calculated from $k_{-2}^{BH^+} = k_2^B K_a' / K_a^*$; $pK_a' = 11.21$ at 25.0°, $\mu = 0.10$; $K_a^* = K_a$ (apparent) at $\mu = 0.10$ and 25°.

Table IV. Rate Constants for the Reaction of 1-Arylnitroethanes, YC₆H₄CH(Me)NO₂, with Diethylamine in Water at 25.0°, $\mu = 0.10$

Y	10 ¹ $k_2^B, M^{-1} sec^{-1}$	10 ⁶ $k_{-2}^{BH^+}, M^{-1} sec^{-1}$ ^a
<i>m</i> -CH ₃	1.87 ± 0.03	3.56
H	2.20 ± 0.13	3.33
<i>m</i> -CH ₃ O	2.74 ± 0.18	
<i>m</i> -Cl	5.18 ± 0.41	3.58
<i>m</i> -NO ₂	11.6 ± 1.0	3.35
<i>p</i> -NO ₂	18.4 ± 1.0	3.67
<i>m,m'</i> -(NO ₂) ₂	54.7 ± 4.4	

^a Calculated from $k_{-2}^{BH^+} = k_2^B K_a' / K_a^*$; $pK_a' = 11.10$ at 25.0°, $\mu = 0.10$; $K_a^* = K_a$ (apparent) at $\mu = 0.10$ and 25°.

Table V. Rate Constants for Reactions of 1-Arylnitroethanes, YC₆H₄CH(Me)NO₂, with Piperazine in Water at 25.0°, $\mu = 0.10$

Y	10 ¹ $k_2^B, M^{-1} sec^{-1}$	10 ⁴ $k_{-2}^{BH^+}, M^{-1} sec^{-1}$ ^a
<i>m</i> -CH ₃	1.35 ± 0.01	3.80
H	1.54 ± 0.01	3.45
<i>m</i> -CH ₃ O	1.81 ± 0.02	
<i>m</i> -Cl	3.33 ± 0.04	3.41
<i>m</i> -NO ₂	6.98 ± 0.07	2.98
<i>p</i> -NO ₂	11.6 ± 0.3	3.42

^a Calculated from $k_{-2}^{BH^+} = k_2^B K_a' / K_a^*$; $pK_a' = 9.93$ at 25.0°, $\mu = 0.10$; $K_a^* = K_a$ (apparent) at $\mu = 0.10$ and 25°.

Hammett ρ values for the reactions of bases with 1-arylnitroethanes are summarized in Table IX, together with Brønsted α values calculated from $\alpha = \rho k_1 / \rho K_a$ (both k_1 and K_a measurements are in the same solvent).

Table VI. Rate Constants for Reactions of 1-Arylnitroethanes, $\text{YC}_6\text{H}_4\text{CHMeNO}_2$, with Morpholine in Water at 25.0° , $\mu = 0.10$

Y	$10^2 k_2^{\text{B}}$, $M^{-1} \text{sec}^{-1}$	$10^4 k_{-2}^{\text{BH}^+}$, $M^{-1} \text{sec}^{-1}$ ^a
<i>o</i> -CH ₃	1.77 ± 0.03	1.54
<i>m</i> -CH ₃	1.82 ± 0.03	9.12
H	2.09 ± 0.06	8.32
<i>m</i> -CH ₃ O	2.42 ± 0.03	
<i>m</i> -Cl	4.51 ± 0.05	8.21
<i>m</i> -NO ₂	9.36 ± 0.10	7.10
<i>p</i> -NO ₂	17.3 ± 0.2	9.08
<i>m,m'</i> -(NO ₂) ₂	46.8 ± 1.6	

^a Calculated from $k_{-2}^{\text{BH}^+} = k_2^{\text{B}} K_a' / K_a^*$; $pK_a' = 8.68$ at 25.0° , $\mu = 0.10$; $K_a^* = K_a$ (apparent) at $\mu = 0.10$ and 25° .

Table VII. Rate Constants for Reactions of 1-Arylnitroethanes, $\text{YC}_6\text{H}_4\text{CH}_2\text{NO}_2$, with Morpholine in Water at 25.0° , $\mu = 0.10$

Y	$10^1 k_2^{\text{B}}$, $M^{-1} \text{sec}^{-1}$	$10^2 k_{-2}^{\text{BH}^+}$, $M^{-1} \text{sec}^{-1}$ ^a
<i>o</i> -CH ₃	2.82 ± 0.01	1.82
<i>m</i> -CH ₃	8.88 ± 0.02	1.34
H	9.83 ± 0.01	1.21
<i>m</i> -Cl	27.5 ± 1.2	1.90
<i>m</i> -NO ₂	57.8 ± 1.1	1.87
<i>p</i> -NO ₂	177 ± 4	2.23

^a Calculated from $k_{-2}^{\text{BH}^+} = k_2^{\text{B}} K_a' / K_a^*$; $pK_a' = 8.68$ at 25.0° , $\mu = 0.10$; $K_a^* = K_a$ (apparent) at $\mu = 0.10$ and 25° .

Table VIII. Rate Constants for Reactions of Arylnitromethanes, $\text{YC}_6\text{H}_4\text{CH}_2\text{NO}_2$, with 2,4-Lutidine in Water at 25.0° , $\mu = 0.10$

Y	$10^2 k_2^{\text{B}}$, $M^{-1} \text{sec}^{-1}$	$10^1 k_{-2}^{\text{BH}^+}$, $M^{-1} \text{sec}^{-1}$ ^a
<i>o</i> -CH ₃	2.81 ± 0.06	2.62
<i>m</i> -CH ₃	8.89 ± 0.28	1.94
H	9.95 ± 0.01	1.77
<i>m</i> -Cl	28.0 ± 0.3	2.80
<i>m</i> -NO ₂	59.4 ± 0.5	2.78
<i>p</i> -NO ₂	181 ± 6	3.29

^a Calculated from $k_{-2}^{\text{BH}^+} = k_2^{\text{B}} K_a' / K_a$; $pK_a' = 6.63$ at 25.0° , $\mu < 0.015$.

Table IX. Hammett ρ and Brønsted α Values for Reactions of Bases with 1-Arylnitroethanes

Base-solvent ^a	ρ	r	$\sigma_{p\text{-NO}_2}$	α
NaOR-50% MeOH-H ₂ O ^b	1.58 ± 0.05	0.9970	0.856	1.40
NaOH-H ₂ O ^b	1.17 ± 0.03	0.9995	0.865	1.14
NaOH-H ₂ O	1.18 ± 0.02	0.9990	0.823	1.15 ^d
Piperidine ^c	1.02 ± 0.03	0.9985	0.852	0.99
Diethylamine ^c	0.99 ± 0.01	0.9997	0.933	0.96
Piperazine ^c	0.93 ± 0.03	0.9984	0.956	0.91
Morpholine ^c	0.96 ± 0.02	0.9994	0.978	0.94

^a In water at 25° unless otherwise noted. ^b At 15° . ^c In water, $\mu = 0.10$. ^d M. Fukuyama, P. W. K. Flanagan, F. T. Williams, Jr., L. Frainier, S. A. Miller, and H. Shechter, *J. Amer. Chem. Soc.*, **92**, 4689 (1970), have reported Brønsted α 's at 1.17-1.20 for sodium hydroxide in 50% (v/v) dioxane-water.

Only meta points were used in the Hammett plots because these gave better correlations, as would be expected.^{bb} (Nevertheless, the correlation coefficients using all points were near 0.99 or better.) Similar data are given in Table X for the reactions of bases with aryl-nitromethanes.

Brønsted β coefficients were determined for the reactions of 1-arylnitroethanes with piperidine, piperazine, and morpholine (Table XI).

Table X. Hammett ρ and Brønsted α Values for Reactions of Bases with Arylnitromethanes

Base ^a	ρ	r	$\sigma_{p\text{-NO}_2}$	α
NaOH	1.28 ± 0.02	0.9998	0.916	1.54
Morpholine	1.07 ± 0.05	0.9985	1.15	1.29
2,4-Lutidine	1.08 ± 0.04	0.9986	1.15	1.30

^a In H₂O at 25° , except for NaOH at 26° .

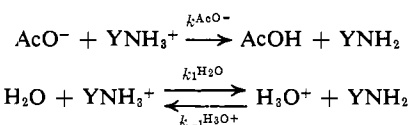
Table XI. Brønsted Coefficients for the Reaction of 1-Arylnitroethanes with Piperidine, Piperazine, and Morpholine

Substituent	pK_a^a	β	r
<i>m</i> -CH ₃	7.49	0.55 ± 0.06	0.995
H	7.39	0.55 ± 0.06	0.995
<i>m</i> -CH ₃ O		0.56 ± 0.06	0.995
<i>m</i> -Cl	7.05	0.55 ± 0.06	0.995
<i>m</i> -NO ₂	6.67	0.55 ± 0.06	0.995
<i>p</i> -NO ₂	6.51	0.52 ± 0.05	0.993

^a In water at 25° .

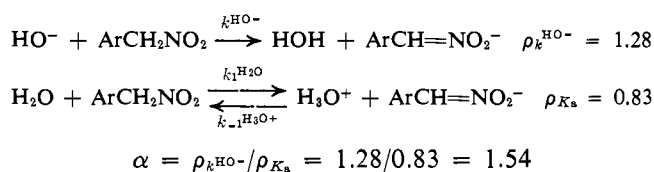
Discussion

Kinetic Interpretation of Brønsted α Values. The α values determined for the deprotonation of YNH_3^+ type acids by acetate ion (Figure 1) are essentially a measure of the sensitivity of the rates k^{AcO^-} to changes in Y as compared to the sensitivity of $k^{\text{H}_2\text{O}}$ to changes in Y.



The basis for this statement is the assumption that changes in the equilibrium acidities of YNH_3^+ , as measured by $K_a = k_1^{\text{H}_2\text{O}} / k_{-1}^{\text{H}_3\text{O}^+}$, will be determined principally by changes in $k_1^{\text{H}_2\text{O}}$. This seems reasonable, since the rates of the reverse reactions ($k_{-1}^{\text{H}_3\text{O}^+}$) approach the diffusion-controlled limit and will be relatively insensitive to changes in Y. For similar reasons α will approach zero when YNH_3^+ is a relatively strong acid (e.g., *p*-ClC₆H₄NH₃⁺) because the reaction with acetate ion is so rapid as to be insensitive to changes in Y. For weaker YNH_3^+ (e.g., NH₂NH₃⁺ and ImH⁺), acetate ion is almost as discriminatory as is water, and α approaches one. Perhaps this increased discrimination can be correlated *qualitatively* with a change to a product-like transition state, as has been commonly supposed,² but in view of the differences in charge types of the attacking bases, this conclusion appears risky even for these oxygen and nitrogen acids.

For the carbon acids ArCHMeNO_2 and ArCH_2NO_2 reacting with hydroxide ion (Tables I and II) α is 1.15 and 1.54, respectively (Tables IX and X). The ΔpK region covered (-10 to -8.5) is one where α would be zero for hydroxide deprotonations of YNH_3^+ acids (Figure 1). The reason for this striking difference in behavior between these carbon and nitrogen acids can be made understandable by extending the kinetic interpretation for YNH_3^+ acids given above to the carbon acids.



Here it is convenient to express α in terms of ρ values, as indicated. If the behavior of the carbon acid had followed that of the nitrogen acid, α would have been determined by the relative sensitivities of the k^{HO^-} and $k_{1^{\text{H}_2\text{O}}}$ rates; *i.e.*, $\alpha = \rho_{k^{\text{HO}^-}}/\rho_{k_{1^{\text{H}_2\text{O}}}}$. Since the water deprotonation reaction would be expected to be much more sensitive to substituent effects than the hydroxide ion deprotonation reaction (it is slower by a factor of *ca.* 10^8), one would expect a low value of α . The opposite result observed indicates that $k_{-1^{\text{H}_3\text{O}^+}}$ is decisive in determining the size of α . For the carbon acid this reaction is relatively slow (*ca.* 10^1 to $10^2 M^{-1} \text{sec}^{-1}$ at 25°) and is sensitive to substituent effects. This contrasts sharply with the situation with YNH_3^+ (or oxygen) acids where the $k_{-1^{\text{H}_3\text{O}^+}}$ reaction approaches the diffusion-controlled limit and is insensitive to substituent effects, and therein lies the reason for the marked discrepancy in α values for the two types of acids.

We may analyze the situation further by defining the equilibrium for the carbon acid in terms of ρ values.

$$\rho_{\text{K}_a} = \rho_{k_{1^{\text{H}_2\text{O}}}} - \rho_{k_{-1^{\text{H}_3\text{O}^+}}} = 0.83$$

If our expectation that $\rho_{k_{1^{\text{H}_2\text{O}}}} > \rho_{k^{\text{HO}^-}}$ is correct,⁸ this requires that $\rho_{k_{-1^{\text{H}_3\text{O}^+}}}$ be positive. In other words, electron-withdrawing groups *accelerate* the protonation of $\text{ArCH}=\text{NO}_2^-$ by hydronium ion. Although it is unusual for electron-withdrawing groups to *increase* the *basicity* of anions, this is not unprecedented.⁵ Indeed, it can be shown that for equilibrium established between ArCH_2NO_2 and hydroxide ion

$$\rho_{k_{1^{\text{HO}^-}}} - \rho_{k_{-1^{\text{H}_2\text{O}}}} = \rho_{\text{K}_a}; \rho_{k_{-1^{\text{H}_2\text{O}}}} = +0.45$$

Thus, ρ for protonation of $\text{ArCH}=\text{NO}_2^-$ by water molecules is positive. A similar result was observed previously for protonation of $\text{ArCMe}=\text{NO}_2^-$ by solvent.⁵

Extension of this treatment provides an explanation for the negative α value observed for hydroxide reacting with the series of nitroalkanes CH_3NO_2 , MeCH_2NO_2 , and Me_2CHNO_2 . Here the equilibrium acidity is dominated by the effect of methyl substitution, which stabilizes the nitronate ion and retards protonation by hydronium ion in the reverse reaction.⁵ As a consequence the equilibrium acidities are increased by methyl substitution. The opposite trend in kinetic acidities leads to a negative α . Since the kinetic acidities are not controlled by relative nitronate ion stabilities, the transition state for hydroxide deprotonation cannot be product like.

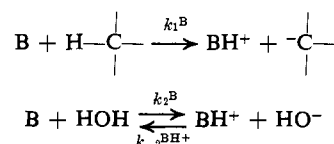
From the above interpretation we see that the size (and sign) of α is dictated largely by the influence of substituents on the rate of the reverse reaction of the equilibrium and that there is no basis for correlating α with the position of the proton in the transition state of the reaction which determines the kinetic acidities of these carbon acids.⁹

Kinetic Interpretation of Brønsted β Values. Using a kinetic analysis similar to that presented above leads to the conclusion that, for deprotonation of a nitroalkane, ketone, or other carbon acid by a series of bases, β

(8) This prediction is not so clear-cut as the approximately 10^8 -fold difference in rates might suggest. Note that for 2,4-lutidine, which effects deprotonation of $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$ at a rate 160 times slower than does hydroxide ion, the ρ value is *smaller*, *i.e.*, 1.08 *vs.* 1.28 (Table X). The size of $\rho_{k_{1^{\text{H}_2\text{O}}}}$ is under investigation by John E. Bartmess, Jr.

(9) For another interpretation of "deviant" Brønsted relationships, see A. J. Kresge, *J. Amer. Chem. Soc.*, **92**, 3210 (1970).

relates the sensitivity of deprotonation rates for the carbon acid (k_1^{B}) with changing base strength to the sensitivity of the deprotonation rates of water (k_2^{B}) with changing base strength. (Once again this analysis depends on the reasonable assumption that $k_{-2}^{\text{BH}^+}$ will be insensitive to substituent changes in BH^+ because the rate is near the diffusion-controlled limit.)



One might have expected the rates of the (slower) deprotonations of carbon acids to be more sensitive to structural changes in the base, B, than the rates of the (faster) deprotonations of the oxygen acid (water). In this event β would be larger than one, which is clearly not the case (Table XII). On the other hand, there is

Table XII. Brønsted β Values for Deprotonation of Carbon Acids

Carbon acid	ΔpK range	β	Ref and bases
1-Arylnitroethanes	-4.7 to -2.2	0.52 to 0.55	Table XI
Phenylnitromethane	-7.7 to +1.7	0.65	<i>a</i>
Nitroethane	-2.5 to +4.5	0.50 to 0.55	<i>b</i>
3-Nitropropene	-1.1 to +0.3	0.59	<i>c</i>
Nitroethane	+2.0 to +3.4	0.65	<i>d</i>
Menthone	-1.0 to +5.3	0.48	<i>e</i>
Ethyl nitroacetate	0.0 to +7.6	0.65	<i>f</i>
Acetone	+13.4 to +14.8	0.64 to 0.72	<i>g</i>

^a Calculated from the data of V. M. Belikov, Ts. B. Korehemnaya, and N. G. Faleev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1383 (1969); a variety of base types was used. ^b M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 2327 (1967); J. E. Dixon and T. C. Bruice, *ibid.*, **92**, 905 (1970); a variety of amine bases was used. ^c J. A. Hautala, Ph.D. Dissertation, Northwestern University, 1970; pyridine bases. ^d R. G. Pearson and F. V. Williams, *J. Amer. Chem. Soc.*, **76**, 258 (1954); pyridine bases. ^e R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970); HO^- in $\text{DMSO}-\text{H}_2\text{O}$. ^f D. J. Barnes and R. P. Bell, *Proc. Roy. Soc., Ser. A*, **318**, 421 (1970); a variety of base types was used. ^g J. A. Feather and V. Gold, *J. Chem. Soc.*, 1752 (1965); pyridine bases.

reason to believe that deprotonations of carbon acids and oxygen acids occur by fundamentally different mechanisms. For oxygen acids (but not for carbon acids) formation of a hydrogen-bonded complex precedes proton transfer,³ and the stability of this complex will strongly affect the variation in rates with variation in base strength. The greater sensitivity of the water deprotonation rates relative to carbon acid deprotonation rates must be a consequence of this mechanistic difference. It follows that a direct comparison of these sensitivities is meaningless, and that the *absolute* size of β for carbon acids can provide, therefore, little or no information concerning the nature of the transition state of the deprotonation.¹⁰ One would expect, however, that the sensitivities to substituent changes in base strength for the deprotonations of relatively strong carbon acids, such as nitroalkanes, would be substantially less than for the (slower) deprotonations of weaker carbon acids, such as ketones.⁴ In other words, one

(10) R. A. Marcus, *ibid.*, **91**, 7224 (1969), has presented a theoretical explanation for α values beyond the limits of 0 to 1.0. His equations show that, in contrast to α , β for nitroalkanes will be near 0.5.

would expect the transition state to change from reactant like to product like as ΔpK changes from negative to positive; this change should be manifested in an increase in the size of β . Indeed, a qualitative change of this type has been found by Bell and his students for ketonic substances of varying acidities reacting with RCO_2^- bases, where β increases from 0.42 to 0.88 for a ΔpK change of 11.7 units.¹¹ We see from Table XII, however, that for a range of almost 20 ΔpK units there is but little variation in β and no consistent trend when a series of nitroalkanes and ketones is compared. It is remarkable to find, for example, that β is essentially the same for a series of pyridines reacting with acetone as for the same series of pyridines reacting with 3-nitropropene, which is a stronger acid by about 15 powers of ten. Either the transition states for these reactions do not vary much (in contradiction to the Leffler-Hammond postulate) or variation does occur, but β is insensitive to the change. There is other evidence to indicate that β is usually relatively insensitive to changes in ΔpK . Indeed, the general success of the Brønsted correlation depends on such insensitivity. For example, Barnes and Bell found an excellent Brønsted correlation (*i.e.*, "constant" β) for ethyl nitroacetate reacting with a variety of base types covering a ΔpK range of 11.6 units.¹² We conclude that β is an insensitive guide, at best, to changes in transition state structures.

Variation of ρ with Base Strength. The size of ρ for the series ArCHMeNO_2 or ArCH_2NO_2 is a measure of the size of the negative charge developing on the α -carbon atom in the transition state. It is not unreasonable to expect, therefore, that ρ might be useful as a measure of the extent of H-C bond breaking in the transition state. If the transition state becomes more product like as ΔpK become more positive the ex-

tent of H-C bond breaking should increase and ρ might be expected to become more positive. Examination of Tables IX and X shows that this expectation is *not* realized. In changing ΔpK by *ca.* 9 units from hydroxide ion to amine bases there is actually a *decrease* in ρ for both the ArCHMeNO_2 and ArCH_2NO_2 systems. This must mean that the charge density on the α -carbon atom in the transition state is smaller with the weaker bases. If the change to the weaker (amine) bases has resulted in greater H-C bond breaking in the transition state, the potential increase in the negative charge developing on carbon must have been more than offset by other factors. One such factor is the electrostatic effect of the positive charge developing on the amine nitrogen. Greater delocalization of the negative charge resulting from a change of hybridization of the α -carbon atom (increased sp^2 character) may also be a contributing factor. It may be significant in this regard that there appears to be a definite increase in $\sigma_{p-\text{NO}_2}$ calculated for the amine reactions as compared to that with hydroxide ion (Tables IX and X).

Only a limited amount of data are available thus far wherein the charge type on the base is kept constant. Comparison of ρ for different amine bases (Tables IX and X) shows that for a change of *ca.* 3.5 pK units ρ remains essentially constant. It would appear from these data that, if the transition state changes as ΔpK becomes more positive, the change must be a gradual one. There are other indications that changes in transition state structures for changes in ΔpK must be gradual for proton transfer reactions of carbon acids. For example, the stereochemistry for protonation (on carbon) of the 2-phenylcyclohexanenitronate ion changes but little for rather marked changes in the acidity of the proton donor.¹³

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(11) See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 172.

(12) D. J. Barnes and R. P. Bell, *Proc. Roy. Soc., Ser. A*, **318**, 421 (1970).

(13) F. G. Bordwell and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5939 (1970).