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- (28) F. G. Bordwell and F. D. Cornforth, *J. Org. Chem.*, **43**, 1763 (1978).
- (29) (a) J. E. Bartmess and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **99**, 4163 (1977); (b) R. W. Taft, J. A. Abboud, and J. E. Bartmess, manuscript in preparation.
- (30) Y. E. Rhoads and L. Vargas, *J. Org. Chem.*, **38**, 4077 (1973).
- (31) Kinetic evidence, based on rates of deuterium exchange for PhCH₂-i-Pr and PhCH₂-c-Pr with t-BuOK-Me₂SO-d₆,³² or relative rates of addition of i-PrLi in Et₂O to PhC(R)=CH₂,³³ suggests a somewhat greater stabilizing ability for c-Pr vs. i-Pr on an adjacent carbanion center. It is difficult to relate such kinetic results to carbanion stabilities, however,³⁴ even if we accept i-Pr as a good model for c-Pr.
- (32) M. J. Perkins and P. Ward, *Chem. Commun.*, 1134 (1971).
- (33) J. A. Landgrebe and J. D. Shoemaker, *J. Am. Chem. Soc.*, **89**, 4465 (1967).
- (34) F. G. Bordwell, W. S. Matthews, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 442 (1975).
- (35) In the next paper in this series we will see that this greater negative charge density on carbon in the anion causes the equilibrium acidities of nitroalkanes of the type GCH₂CH₂CH₂NO₂ to be much more sensitive to the nature of the substituent, G, in Me₂SO than in 50% MeOH-H₂O. These effects are related to the changes in the acidifying effect of Ph in molecules of the type PhCH₂G, where G is a strongly acidifying function. Here the relative charge density on carbon in the PhCHG⁻ anion changes with the nature of G, and the size of the phenyl-acidifying effect changes accordingly. Thus, substitution of phenyl for α-H in weak carbon acids, such as acetonitrile, causes a much larger effect than substitution for α-H in a stronger carbon acid, such as nitromethane. As one progresses from weak to strong carbon acids the progressive decrease (saturation) of the phenyl effect observed has been referred to as a resonance saturation effect.³⁶ Similarly, we can refer to the diminution of the substituent effects in the present instances in changing from Me₂SO to H₂O solvent as saturation of the substituent effects by solvation.
- (36) (a) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and S. S. Matthews, *J. Org. Chem.*, **42**, 321 (1977); (b) F. G. Bordwell and G. J. McCollum, *ibid.*, **41**, 2391 (1976).
- (37) Reference 12, pp 193-199.
- (38) I. M. Kolthoff, J. J. Lingane, and W. D. Larson, *J. Am. Chem. Soc.*, **60**, 2512 (1938).
- (39) E. M. Arnett, *Faraday Symp. Chem. Soc.*, No. 10 (1975).
- (40) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, **97**, 3226 (1975).
- (41) Additional experimental details may be found in the Ph.D. Dissertation of J. A. Hautala (June, 1971) and J. E. Bartmess (June, 1975).
- (42) W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 4557 (1955).
- (43) N. Kornblum and H. E. Ungande, *Org. Synth.*, **38**, 75 (1958).
- (44) L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 4047 (1951).
- (45) A. Hart and O. E. Curtis, *J. Am. Chem. Soc.*, **78**, 113 (1956).
- (46) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).
- (47) W. H. Perkin and T. R. Marshall, *J. Chem. Soc.*, 865 (1891).
- (48) D. E. Pearson and J. D. Burton, *J. Org. Chem.*, **19**, 957 (1954).
- (49) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Am. Chem. Soc.*, **92**, 5926 (1970).
- (50) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975).
- (51) J. E. Bartmess and R. T. McIver, Jr., private communication.
- (52) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 4050 (1973).
- (53) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969.
- (54) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943).
- (55) A. Talvik, A. Pihl, H. Timotheus, A. Osa, J. Vira, and V. Timotheus, *Org. React.*, **12**, 135 (1975).
- (56) J. E. Bares, Ph.D. Dissertation, Northwestern University, 1976.
- (57) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 652 (1971).
- (58) J. B. Cumming, T. F. Magnera, and P. Kebarle, unpublished data privately communicated. J. E. Bartmess and R. T. McIver have observed a similar order (private communication).
- (59) G. E. Drucker, Ph.D. Dissertation, Northwestern University, June, 1978.

The Taft Equation As Applied to Equilibrium Acidities of Nitroalkanes, G(CH₂)_nNO₂

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Equilibrium acidities for 25 nitroalkanes, G(CH₂)_nNO₂, with *n* = 1, 2, or 3, are reported in two different solvents. The acidities of nitroalkanes G(CH₂)₃NO₂ were found to be reasonably well correlated with Taft σ*_{CH₂CH₂G} constants in 50% (v/v) MeOH-H₂O (ρ* = 1.2) and Me₂SO (ρ* = 3.4). Reversals in acidity order from that predicted by σ* constants were observed, however, for PhSO₂ vs. CN, PhS vs. PhO, CH₃CO vs. HO, and Me vs. H, and it is concluded that substituent effects in the Taft relationship vary with the geometry of the system. The five points examined for nitroalkanes GCH₂CH₂NO₂ all deviated widely from the Taft line, which is interpreted to mean that "methylene transmission coefficients" vary with the nature of G and the nature of the system because of changes in conformations. Points for nitroalkanes GCH₂NO₂ deviated widely from the Taft line. The general conclusion is drawn that, although σ*_{CH₂G} (or σ₁) constants give an approximate measure of polar effects, their size and sometimes even their relative order change as the geometry of the system is changed.

Quantitative evaluations of substituent effects on equilibria and rates in aliphatic systems in solution are fundamental to the understanding of organic chemistry, yet progress in this area has been slow. Twenty years ago Taft made an important contribution by applying a Hammett-type linear free-energy relationship based on hydrolysis rates for esters of the type G(CH₂)_nCO₂R [or an equilibrium acidities in water of acids of the type G(CH₂)_nCO₂H] where *n* is 0, 1, or 2.¹ Stated in terms of equilibrium acidity constants the Taft relationship is given by the equation

$$\log(K/K_0) = \Delta pK = \sigma^* \rho^* \quad (1)$$

where σ* represents the polar (i.e., inductive) effect of G and ρ* represents the sensitivity of the system to structural changes.

The σ*'s for hydrogen and alkyl points (σ*_{Me} = 0) were derived from G(CH₂)_nCO₂R systems where *n* = 0. Most of the σ* constants for substituents containing heteroatoms (Cl, F, O, S, etc.) were derived from data where *n* = 1, but in some

instances (CCl₃, CO₂Me, and COCH₃, as well as Ph and CH=CHMe) σ*'s were derived from *n* = 0. In three instances (COCH₃, Ph, and CH=CHMe) these σ*_G constants were shown to be related to σ*_{CH₂G} constants by assuming a falloff factor of 2.8, which Branch and Calvin had found useful in correlations of aliphatic acids.² This falloff factor (equivalent to a methylene transmission coefficient of 0.36) was also found to be suitable for relating σ*_{CH₂G} and σ*_{CH₂CH₂G} constants when G is Ph or CF₃.

Although the Taft equation has enjoyed considerable success,³ two fundamental problems have arisen. The first relates to the question of whether or not σ*_H, σ*_R, and σ*_G constants derived from data where H, R, or G is attached to an sp² carbon atom can be applied, as Taft did originally, to systems where these substituents are attached to an sp³ carbon atom.⁴ The second relates to the applicability of σ* constants to systems of differing geometry and the use of methylene transmission coefficients to relate σ*_G, σ*_{CH₂G}, σ*_{CH₂CH₂G}, etc., constants. The first of these questions was discussed in the

Table I. Equilibrium Acidity Constants of Nitro Compounds, GCH_2NO_2

G	registry no.	σ^{*a}	pK_a (50% MeOH-H ₂ O) ^b	pK_a (Me ₂ SO) ^c
C(CH ₃) ₃	34715-98-5	-0.30	11.66 ± 0.07	18.13
CH(CH ₃) ₂	625-74-1	-0.19	10.32	17.1 ± 0.3
(CH ₂) ₂ CH ₃	627-05-4	-0.115	9.77	16.83
CH ₂ CH ₃	108-03-2	-0.10	9.93	17.01
CH ₃	79-24-3	0.0	9.58	16.72
(CH ₂) ₂ Ph	22818-69-5	0.08	9.79	16.36
c-Pr	2625-33-4	0.01 ^d	9.35	16.53
(CH ₂) ₂ OH	25182-84-7	0.20 ^e	9.65	16.26
(CH ₂) ₂ COCH ₃	22020-87-7	0.21 ^e	9.60	16.41
CH ₂ Ph	6125-24-2	0.215	9.82	16.14
(CH ₂) ₂ SPh	66291-17-6	0.24 ^e	9.43	15.66
(CH ₂) ₂ OPh	66291-15-4	0.30 ^e	9.49	15.76
CH=CH ₂	625-46-7	0.40 ^d	6.29	11.25
CHPh ₂	5582-87-6	0.405	9.63	15.79
(CH ₂) ₂ SO ₂ Ph	66291-13-2	0.46 ^e	9.28	15.33
(CH ₂) ₂ CN	58763-41-0	0.46 ^e	9.33	15.21
H	75-52-5	0.49	11.05 ± 0.04	17.20
(CH ₂) ₂ NO ₂	6125-21-9	0.50	8.93 (10.29) ^g	14.74
CH ₂ OH	625-48-9	0.555	10.34	16.30
Ph	622-42-4	0.60	7.87	12.20
COPh	614-21-1	1.7 ^f	5.59	7.7 ± 0.2
SPh	60595-16-6	1.8 ^e	7.3 ± 0.1	11.93
CO ₂ Et	626-35-7	2.0	6.79	9.25
Br	563-70-2	2.8 ^e	8.7 ± 0.2	12.5 ± 0.1
SO ₂ Ph	21272-85-5	3.7 ^e	5.69	7.2 ± 0.2

^a Reference 4. ^b At 23 ± 1 °C with nitroalkane concentrations of ~0.01 M; standard deviation ±0.02, unless otherwise stated. ^c Determined at 23 ± 1 °C by the method described in ref 7; standard deviation ±0.05, unless otherwise stated. ^d From $pK(c\text{-PrCO}_2\text{H}) = 1.49 \times 10^{-5}$ [G. Kortüm, W. Vogel, and K. Andrussov, *Pure Appl. Chem.*, 1, 190 (1960)] and $\rho^* = 1.72$. ^e Extrapolated from $\sigma^*_{CH_2G}$ using a falloff factor of 2.8. ^f Estimated from $\sigma_m(\text{COPh})$ and $\sigma^*_{COCH_3}$. ^g Second ionization.

preceding paper in this series. It was concluded that the σ^*_H constant cannot be used and that, although σ^*_R constants may represent intrinsic electron-donor properties of alkyl groups, correlations are frequently obscured by other factors. In this paper the question of the applicability of σ^*_G , $\sigma^*_{CH_2G}$, and $\sigma^*_{CH_2CH_2G}$ constants to the nitroalkane system, $G(\text{CH}_2)_n\text{NO}_2$, which differs appreciably in geometry from the $G(\text{CH}_2)_n\text{CO}_2\text{R}$ system from which these constants were derived, will be examined.

Results

The equilibrium acidity constants were determined potentiometrically in 50% (v/v) methanol-water and by an indicator method in anhydrous dimethyl sulfoxide (Me₂SO). The constants in MeOH-H₂O were corrected for both activity coefficient and true hydrogen ion activity in the mixed aqueous solvent,⁵ but not for statistical corrections. Measurements were made at ambient temperature, but since the acidities of nitroalkanes vary only slightly with temperature,⁶ this introduces relatively little error. All nitro compounds gave measurements stable with time during 0.5–12 h equilibration save BrCH₂NO₂, PhSCH₂NO₂, and PhCOCH₂NO₂. These all gave yellow solutions and drifting of pH within minutes of the addition of base. The acidities in these cases were computed from the potentiometric measurements after 1–2 min of equilibration with base. This time was found to be sufficient for equilibration of compounds of comparable acidity. For less acidic compounds, the aliquots with differing partial neutralizations gave widely varying calculated pK 's immediately upon base addition; after 0.5–2 h equilibration, the values were within 0.02 pK units.

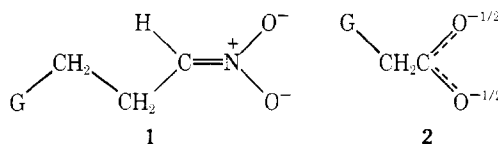
The equilibrium acidities in Me₂SO were determined by the method described previously.^{7,8} All compounds behaved well during measurements (±0.05 pK units for differing partial neutralizations) save for those listed as having larger standard deviations. For these, trends in the calculated pK 's were ob-

served; this usually indicates decomposition of the anion.

The data for equilibrium acidities in 50% (v/v) MeOH-H₂O and in Me₂SO are summarized in Table I.

Discussion

Taft Correlation. The pK 's of 3-substituted nitroalkanes, $GCH_2CH_2CH_2NO_2$, in 50% (v/v) MeOH-H₂O are plotted against $\sigma^*_{CH_2CH_2G}$ constants in Figure 1 (circles). A regression analysis of the plot shows a reasonably good relationship, $\rho^* = 1.18 \pm 0.30$ at the 95% confidence level ($r = 0.956$; $R^2 = 0.914$). The smaller size of ρ^* than that obtained for α -substituted acetic acids, GCH_2CO_2H ($\rho^* = 1.72$), may, at first sight, be surprising, since G is separated from the acidic proton by the same number of atoms in each instance. Examination of the structural formulas for the anions (1 and 2) shows,



however, that in 1 the negative charge is delocalized to oxygen, and is thereby removed two atoms further from G.

Judging from the original work of Taft,¹ and numerous apparently successful extensions,³ one might have anticipated a better correlation. By separating G from the acidic site by two methylene groups we have minimized steric effects. Also, in plotting the data we have avoided using the original Taft σ^* 's for the hydrogen and methyl points, since these were derived from situations where these groups were attached to an sp² carbon atom, rather than an sp³ carbon atom.⁴ (A value of 0.0 was assumed for $\sigma^*_{CH_2CH_2R}$ when R = H, and a value of -0.05 was assumed when R = Me.) The $\sigma^*_{CH_2CH_2G}$ constants used were extrapolated from $\sigma^*_{CH_2G}$ constants, assuming a transmission coefficient (ϵ) of 0.36,¹ but the size of ϵ chosen

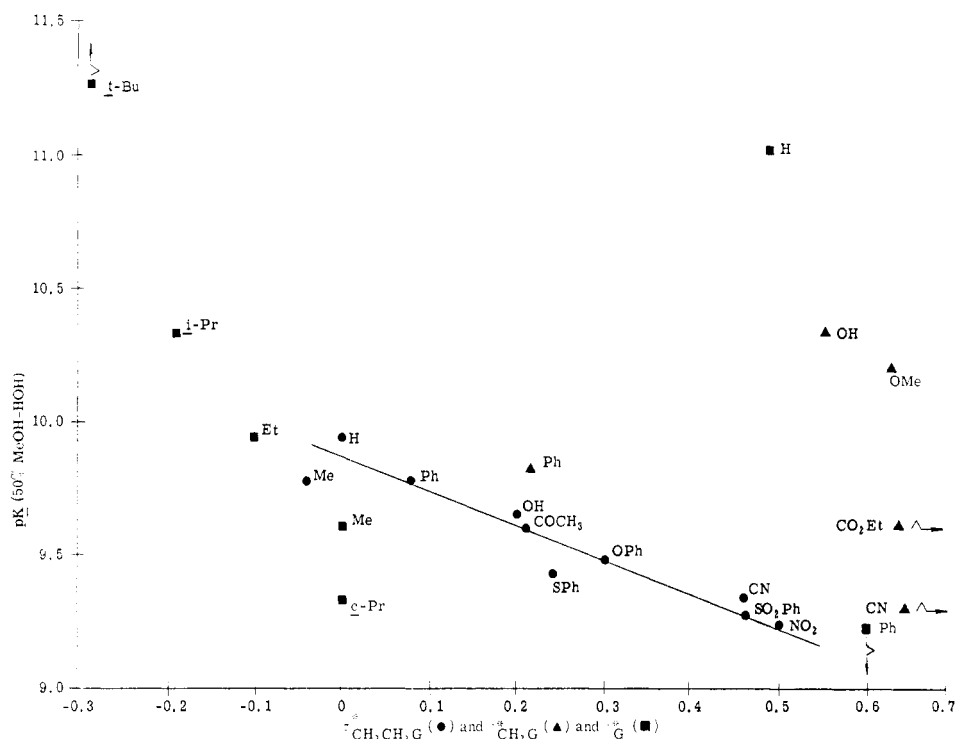


Figure 1. Taft plots of pK 's in 50% (v/v) MeOH–H₂O of $GCH_2CH_2CH_2NO_2$ vs. $\sigma^*_{CH_2CH_2G}$ (●), $GCH_2CH_2NO_2$ vs. $\sigma^*_{CH_2G}$ (▲), and GCH_2NO_2 vs. σ^*_G (■). (For $\sigma^*_{CH_2CH_2R}$ a value of 0 was assumed for $R = H$ and a value of -0.05 was assumed for $R = Me$.)

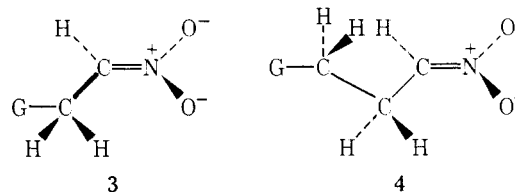
should not affect the linearity of the plot as long as it has a constant value. On the other hand, it is remarkable that the data fit the line as well as they do when one considers that the Taft equation fails to take into account the geometric relationships between G and the acidic site, which must differ for the $G(CH_2)_nNO_2$ system, relative to the $G(CH_2)_nCO_2R$ systems from which the Taft constants were derived.⁹ Inspection of anion structures **1** and **2** shows that the relative geometric relationships of G and the centroid of charge in the anion may vary greatly, depending on the conformations of **1** and **2** to be compared. Current theory indicates that these geometric relationships are of primary importance. The variation of electrostatic effects of this type with geometry appears to be best approximated by the Kirkwood–Westheimer approach using eq 2 and an elliptical cavity model.¹⁰

$$\Delta pK = (\mu \cos \theta) / r^2 D \quad (2)$$

According to eq 2 the change in acidity (ΔpK) on substitution of G for a γ -hydrogen atom in **1** will depend on: (a) the dipole moment (μ) of G ; (b) the cosine of the angle (θ) this dipole makes with the acidic site; (c) the inverse square of the distance, r , between G and the acidic site; and (d) the reciprocal of the effective dielectric constant, D . The high degree of significance in our Taft correlation, as revealed by the statistical analysis of the data, shows that the geometric relationships of varying substituents to the centroid of negative charge must vary in such a way that $\cos \theta / r^2$ is similar in **1** and **2** for each substituent, G . There are some reversals in the relative effects of groups, however. For the $G(CH_2)_2CH_2NO_2$ series we see from Table I that in Me_2SO the acidifying effects are in the order $PhSO_2 > CN$, $PhS > PhO$, $CH_3CO > HO$, and $Me > H$, whereas the reverse order for each of these pairs is observed for GCH_2CO_2H . These differences may be caused by variations in the conformations of the two systems with changes in the nature of G .

Conformational Effects. The importance of geometric relationships in determining the effect of G on acidity in nitroalkanes, $G(CH_2)_nNO_2$, is brought out by comparing substituent effects in 2- and 3-substituted nitroalkanes

($GCH_2CH_2NO_2$ vs. $GCH_2CH_2CH_2NO_2$). For the five substituents for which information is available (Ph, MeO, HO, CO_2Et , and CN) the acidities of the $G(CH_2)_3NO_2$ compounds are equal to or greater than those of the $G(CH_2)_2NO_2$ compounds despite the presence of one less methylene group in the latter (Table II). For the compounds of about equal acidity, i.e., those with G equal to Ph, CO_2Et , or CN, this means that the "methylene transmission coefficient" (ϵ) is ~ 1.0 , rather than 0.36. For the $GCH_2CH_2NO_2$ compounds with lower acidities, i.e., when G is MeO or HO, ϵ would have to be negative. These five points deviate markedly from the Taft plot, of course (triangles in Figure 1; the CN and CO_2Et points are off the scale of the plot). Evidently the geometric relationship of G to the centroid of charge in the anion $GCH_2CH=NO_2^-$ relative to the anion $GCH_2CH_2CH=NO_2^-$ is quite different from the comparable geometric relationship in the $GCH_2CO_2^-$ and $GCH_2CH_2CO_2^-$ anions.¹¹ Examination of scalar models of the former shows that conformations are available in which the orientation of the C– G dipole and the distance, r , between G and the centroid of charge do not differ greatly (**3** and **4**).



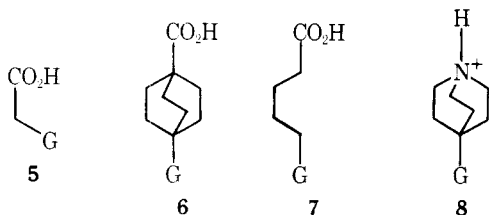
The importance of geometry in determining the size of substituent effects was considered by Taft in his original analysis of polar effects. Taft showed that there was a close correspondence between substituent effects in the acetic acids (**5**) and the 4-substituted bicyclo[2.2.2]octanecarboxylic acids (**6**), supporting his claim that σ^* constants have some generality. At the same time, this close correspondence points up the danger inherent in using "methylene transmission" coefficients. For example, the σ_1 's ($\sigma_1 = 0.45 \sigma^*_{CH_2G}$) deter-

Table II. Comparison of pK 's of β - and γ -Substituted Nitroalkanes

nitroalkane	registry no.	$pK(H_2O)$	$pK(50\% MeOH)^a$	σ^*
Ph(CH ₂) ₂ NO ₂		8.78 ^b	9.82	0.215
Ph(CH ₂) ₃ NO ₂			9.79	0.08
MeO(CH ₂) ₂ NO ₂	35461-44-0	9.26 ^c	(10.2)	0.52
MeO(CH ₂) ₃ NO ₂	42472-01-5	8.62 ^d	(9.6)	0.18
HO(CH ₂) ₂ NO ₂			10.34	0.555
HO(CH ₂) ₃ NO ₂			9.65	0.21
EtO ₂ C(CH ₂) ₂ NO ₂	3590-37-2	8.65 ^d	(9.6)	0.71
EtO ₂ C(CH ₂) ₃ NO ₂	2832-16-8		(9.6) ^e	0.25
NC(CH ₂) ₂ NO ₂	35461-45-1	8.31 ^c	(9.3)	1.3
NC(CH ₂) ₃ NO ₂			9.33	0.46

^a Values in parentheses were calculated from $pK(H_2O)$ using an equation, $pK(50\% MeOH) = (0.97 \pm 0.04)pK(H_2O) + 1.19 \pm 0.33$, which was derived for RCH_2NO_2 with $R = i\text{-Pr}, n\text{-Pr}, Et, Me, PhCH_2, H, O_2NCH_2CH_2, HOCH_2,$ and Ph ($r = 0.995$). ^b S. Hiidma, A. Pihl, and A. Talvik, *Reakts. Sposobn. Org. Soedin.*, **3**, 62 (1965). ^c A. Talvik, H. Timotheus, V. Loodmaa, V. Timotheus, T. Sarapan, A. Laht, and V. Kõõbi, *Org. React. (USSR)*, **8**, 409 (1971). ^d A. Talvik, V. Timotheus, and H. Timotheus, *ibid.*, **4**, 478 (1967). ^e Interpolated by Taft equation with $\rho^* = 1.18$.

mined for **5** and **6** are essentially identical (0.56 vs. 0.58), whereas the σ_1 calculated for **6**, or its open-chain analogue (**7**), using σ_1 for **5** and a "methylene transmission coefficient" of 0.36 is only 0.025 for **6** or **7**.



The ability of groups in **6** to exert effects comparable to groups in **5**, despite the fact that in **6** G is separated from the carboxyl group by three additional carbon atoms, is remarkable. Apparently the bulky aliphatic moiety separating G from CO_2H in **6** markedly reduces the effective dielectric constant, D , whereas in **5** (or **7**) the presence of solvent molecules in the molecular cavity leads to a much higher value for D . The favorable orientation of the $C-G$ dipole in **6** is no doubt also a contributing factor. Since these substituent effects have been shown to be primarily field, and not bond-mediated inductive effects, the number of bridges between the substituent and the acidic site should not matter.¹⁰ A similar effect has been observed in the 4-substituted quinuclidine system (**8**), where substituent effects are transmitted *more* readily than in the acetic acid system, despite the intervention of one additional σ bond between the substituent and the acidic site.¹²

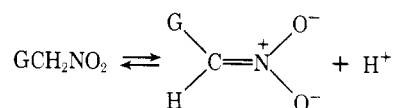
Solvent Effects. A plot of the pK 's in Me_2SO for nitroalkanes, $GCH_2CH_2CH_2NO_2$, vs. $\sigma^*_{CH_2CH_2G}$ is linear ($r = 0.96$) and shows about the same amount of scatter as was observed in 50% (v/v) $MeOH-H_2O$ ($r = 0.96$). Comparison of the plots shows only a few minor changes in the positions of the points. The phenyl group in $Ph(CH_2)_3NO_2$ is relatively more acidifying in the Me_2SO solvent, and this is true also for the phenyl group in $Ph(CH_2)_2NO_2$. The apparent "methylene transmission coefficient" is now slightly on the positive side, rather than being negative as it is in $MeOH-H_2O$; $HO(CH_2)_3NO_2$ is still more acidic than $HO(CH_2)_2NO_2$ in the Me_2SO solvent, however. Hydrogen-bond effects are absent in Me_2SO , but H bonding does not appear to make the PhO more acidifying than PhS ; the latter is *more* acidifying in both solvents.

Since the absolute acidities for most of the nitroalkanes listed in Table I are about 6.5 pK units lower in Me_2SO than in 50% (v/v) $MeOH-H_2O$, it is clear that large solvent effects are operative. The ρ^* for the $G(CH_2)_3NO_2$ series is 3.4 in Me_2SO vs. 1.2 in $MeOH-H_2O$, corresponding to a greater than three orders of magnitude sensitivity of the K_a 's in Me_2SO to

substituent effects. Both this larger ρ^* and the lower acidities in Me_2SO are due largely to the absence of H bonding between the oxygen atoms in the nitronate ion and the Me_2SO solvent. The strong H bonding of $MeOH$ and H_2O to these negatively charged oxygen atoms stabilizes the anion and decreases the negative charge density on carbon in the $CH=NO_2^-$ function. In Me_2SO the greater charge density on this carbon atom greatly increases the sensitivity of the anion toward stabilization by the substituents G . [A similar solvent effect is observed in the GCH_2NO_2 series, when $G = Ph$ or $CH_2=CH$ (see the preceding paper) and in comparing ρ 's in H_2O and in Me_2SO for meta- and para-substituted phenols.]

Perhaps the most striking feature of the data is that, despite large differences in the type and magnitude of the solvent effects of Me_2SO and $MeOH-H_2O$, the *relative effects with varying substituents are remarkably similar*. Note in particular that in each solvent the PhS substituent is slightly more acidifying than the PhO substituent, although the σ^* constants predict an appreciable difference in the opposite direction. Similarity in relative substituent effects in Me_2SO and in protic solvents appears to be the general rule.^{13,14,15}

α -Substituted Nitroalkanes. The points for α substituents deviate widely from the line defined for $G(CH_2)_3NO_2$ compounds in either 50% (v/v) $MeOH-H_2O$ (Figure 1) or in Me_2SO . This is expected since: (a) it is unlikely that Taft σ^* 's derived for substituents attached to sp^3 carbon atoms can be applied to these same substituents when attached to sp^2 carbon atoms;⁴ (b) steric effects are enhanced at the α position; and (c) delocalization of the negative charge in the anion by resonance is often possible. Deprotonation of nitroalkanes (or other carbon acids) differs from that of carboxylic acids with respect to a, b, and c, since the hybridization of carbon changes during deprotonation.



When G is $c\text{-Pr}$, Me , Et , or $i\text{-Pr}$ the nitroalkanes are appreciably more acidic than when G is $t\text{-Bu}$ or H (squares on Figure 1). These alkyl and hydrogen effects have been discussed in a previous paper, as have the effects for $G = Ph$ and $CH=CH_2$.¹³

The order of acidifying effects for the other substituents, G , are, with a single exception, in the same order as for methane carbon acids, i.e., $PhCO > PhSO_2 > EtO_2C > PhS > Ph$ (Table I). The differences in acidities in Me_2SO for the nitroalkanes, GCH_2NO_2 , are much smaller than for the methane carbon acids, GCH_3 , as is brought out by comparing

Table III. Comparison of Acidifying Effects in Me₂SO for Nitroalkanes, GCH₂NO₂, and Methane Carbon Acids, GCH₃

G	pK (GCH ₃) ^a	ΔpK (GCH ₃)	pK (GCH ₂ -NO ₂)	ΔpK (GCH ₂ NO ₂)
H	~65 ^b	(0.0)	17.2	(0.0)
Ph	~44 ^c	~21	12.2	5.0
PhS	~40 ^d	~25	11.9	5.3
CO ₂ Et	~31 ^c	~34	9.2	8.0
PhSO ₂	29.0	~36	7.2	10.0
PhCO	24.7	~40	7.7	9.5

^a Reference 7 unless otherwise noted. ^b Based on unpublished data of D. Algrim. ^c Reference 14. ^d Estimate based on data in ref 14. ^e Based on unpublished data of H. Fried.

the ΔpK's in Table III. The much smaller ΔpK's for the GCH₂NO₂ acids than the GCH₃ acids are caused by the much smaller concentration of charge on carbon in the GCH=NO₂⁻ anions (resonance saturation effect¹⁵). Steric effects will play a role in dictating the stabilizing effect in GCH=NO₂⁻ anions, and offer a possible explanation for the reversal of the PhSO₂ and PhCO effects.

Summary

It is apparent from this study that the Taft relationship can be applied in only a limited sense to systems of the type G(CH₂)_nX, where X is a reactive function or one that activates the α-C-H bond, and G is a substituent. Taft σ*_{CH₂G} (or σ_I) constants can be used only when n is kept constant; they are not applicable in instances where G is attached to an sp² carbon atom, and cannot be related quantitatively to σ*_G or σ*_{CH₂CH₂G} constants by the use of "methylene transmission coefficients". The Taft σ*_H constant is not applicable and the

small effects of alkyl groups are often strongly affected by factors other than the inductive σ*_R effect. Finally, although ρ*_{CH₂G} (or σ_I) constants give an approximate general measure of polar effects, their size and sometimes even their relative order changes as the geometry of the system is changed. This last statement is strongly supported by the work of Grob and Schlageter on the 4-substituted quinuclidine system.¹²

Experimental Section

Materials. The 50% methanol solvent was made by mixing equal volumes of methanol (Fisher Certified, acetone free) and deionized water. The 50% methanol-water lyate ion solutions were made by diluting aqueous Anachemia Acculute 0.10 M NaOH solution with an equal volume of methanol, followed by further dilution with prepared 50% MeOH-H₂O solvent. The lyate ion concentration was checked by titration against standard acid. The details of Me₂SO purification and measurement of acidity constants in that solvent have been published elsewhere.⁷ The pK_a's in 50% MeOH-H₂O were determined by the method of Bordwell, Boyle, and Yee¹⁶ save that an activity coefficient correction of -log γ[±] = 0.04⁵ and a true hydrogen ion activity correction⁵ to the pH of -0.10 have been applied to the reported data.

All of the nitro compounds reported here were purified by fractional distillation to >99% purity, unless otherwise stated. Four of the nitroalkanes were obtained as gifts from Commercial Solvents Corp.: nitromethane (99.99% pure by VPC) and nitroethane (99.92% by VPC) were used as received, while 1-nitropropane and 1-nitrobutane were distilled. Literature methods were followed for the syntheses of 5-nitro-2-pentanone,¹⁷ 2-phenyl-1-nitroethane,¹⁸ 2-nitroethanol,¹⁹ phenylnitromethane,²⁰ 3-nitropropene,²¹ bromonitromethane,²² benzoylnitromethane,²³ and ethyl nitroacetate.²⁴ Phenylnitromethane was purified by column chromatography on silica gel with CCl₄ as eluent, followed by Kugelrohr evaporative distillation [70 °C (5 mm)]. Benzoylnitromethane was twice recrystallized from hexane. 2,2-Diphenylnitroethane was a gift of C. J. M. Stirling.

3-Phenyl-1-nitropropane. Following the procedure of Kornblum,²⁵ 3-phenyl-1-bromopropane (Aldrich) was stirred in DMF for 3 h with 1.5 equiv of sodium nitrite and 1.5 equiv of urea. The mixture was poured into water and extracted with ether, followed by washings

Table IV. Physical Constants of Nitro Compounds, RCH₂NO₂

R	bp, °C (mm)	n _D ²³	bp, lit., °C (mm)	n _D ²⁰ , lit.	ref	NMR (CDCl ₃), δ
CH ₃ CH ₂	131-132	1.3996	130-131.5	1.3994	38	
CH ₃ CH ₂	50-51 (20)	1.4112	152-153	1.4024	39	0.7-2.2 (m, 7 H); 4.30 (t, 2 H)
CH ₂						
(CH ₃) ₂ CH	65 (50)	1.4070 (21 °C)	71 (65)	1.4069	40	0.95 (d, 6 H); 2.38 (m, 1 H); 4.17 (d, 2 H)
(CH ₃) ₃ C	65 (45)	1.4132 (21 °C)	150-151	1.4099 (30 °C)	41	1.05 (s, 9 H); 4.20 (s, 2 H)
c-Pr	80 (30)	1.4375 (21 °C)	71.5-73 (25)	1.4383	42	0.5 (m, 4 H); 1.4 (m, 1 H); 4.20 (d, 2 H)
Ph(CH ₂) ₂	80-81 (0.3)	1.5181	147-148 (11)		43	2.1-2.8 (m, 4 H); 4.30 (t, 2 H); 6.9-7.5 (m, 5 H)
HO(CH ₂) ₂	72-73 (0.3)	1.4450	138-140 (32)		44	2.20 (s, 1 H); 2.23 (quintet, 2 H); 3.80 (t, 2 H); 4.52 (t, 2 H)
CH ₃ C-O(CH ₂) ₂	101-102 (4.5)	1.4420	117-120 (10)	1.4445	17	2.18 (s, 3 H); 2.0-2.6 (m, 4 H); 4.48 (t, 2 H)
PhS(CH ₂) ₂	108-110 (0.1)	1.5695				2.21 (quintet, 2 H); 2.95 (t, 2 H); 4.47 (t, 2 H); 7.0-7.4 (m, 5 H)
PhO(CH ₂) ₂	98-100 (0.3)	1.5220	171-177 (17)		45	2.40 (quintet, 2 H); 4.01 (t, 2 H); 4.56 (t, 2 H); 6.7-7.4 (m, 5 H)
CN(CH ₂) ₂	73-74 (0.1)	1.4502	160 (35)		29a	2.0-2.7 (m, 4 H); 4.45 (t, 2 H)
PhS-O ₂ (CH ₂) ₂	mp 45.0-45.5					2.40 (quintet, 2 H); 3.27 (t, 2 H); 4.57 (t, 2 H); 7.4-8.0 (m, 5 H)
NO ₂ (CH ₂) ₂	87-88 (0.2)	1.4630	103 (1)	1.4638	28	2.65 (quintet, 2 H); 4.55 (t, 4 H)
PhCH ₂	85-86 (0.3)	1.5243	73-74.5 (0.15)	1.5270	18	3.20 (t, 2 H); 4.48 (t, 2 H)
HOCH ₂	84-85 (3.5)	1.4428	94 (10)		20	2.55 (s, 1 H); 3.9-4.2 (m, 2 H); 4.35-4.60 (m, 2 H)
Ph		1.5314		1.5315	46	5.36 (s, 2 H); 7.36 (s, 5 H)
CH ₂ =CH	53-54 (55)	1.4270	39-40 (20)	1.4260	21	5.0 (d, 2 H); 5.3-5.5 (m, 2 H); 6.1 (m, 1 H)
Br	68-70 (42)	1.4820	70-72 (45)		22	5.72 (s)
PhCO	mp 105-105.5		mp 105.5		23	5.95 (s, 2 H); 7.5-8.0 (m, 5 H)
PhS		1.5785				5.38 (s, 2 H); 7.1-7.5 (m, 5 H)
PhSO ₂	mp 76-77		mp 69-72		47	6.65 (s, 2 H); 7.7-8.2 (m, 5 H)
EtO ₂ C	79-80 (5)		94 (11)	1.4243	48	1.63 (t, 3 H); 4.40 (quartet, 2 H); 5.13 (s, 2 H)

with sodium bisulfite solution and with brine. Drying and removal of solvent gave a 60% yield (by NMR) of crude material. Two fractionations gave >99% pure material.

3-Phenoxy-1-nitropropane. As with the 3-phenyl compound, 3-phenoxy-1-bromopropane (Aldrich) was converted to crude nitro compound in 55% yield and fractionated twice.

3-Thiophenoxy-1-nitropropane. Sodium iodide (1.2 equiv) was refluxed in acetone for 24 h with 3-thiophenoxy-1-chloropropane. Workup identical with that for the 3-phenyl-1-nitropropane reaction gave a 75% yield of crude iodo sulfide. As with the 3-phenyl compound, this was converted to the nitro sulfide in 18% crude overall yield from the chloro sulfide. The dry sodium nitronate salt²⁶ was prepared and recrystallized from absolute ethanol containing a trace of water. Reprotonation with hydroxylamine hydrochloride,²⁷ followed by vacuum distillation, gave material >99% pure.

Anal. Calcd for C₉H₁₁NO₂S: C, 54.80; H, 5.62. Found: C, 54.95; H, 5.72.

1,3-Dinitropropane and 3-Nitro-1-propanol. As in the 3-thiophenoxy-1-nitropropane synthesis, 1-bromo-3-chloropropane was diiodinated with 2.2 equiv of sodium iodide. The crude diiodopropane was treated with silver nitrite following the method of Kispersky,²⁸ save that after removal of the silver salts, 1 equiv of methanol was added to hydrolyze the nitrite esters. Removal of solvent after 24 h and distillation at 1 mm gave crude yields of 28% 3-nitro-1-propanol (from hydrolysis of the nitronitrite compound), bp 80–85 °C, and 47% 1,3-dinitropropane, bp 100–116 °C.

4-Nitrobutyronitrile. Iodination of 4-chlorobutyronitrile with 1.2 equiv of sodium iodide, as for the 3-thiophenoxy compound, followed by reaction of the crude iodo compound with silver nitrite,²⁹ gave a 42% yield of crude product.

3-Phenylsulfonyl-1-nitropropane. The nitro sulfide (1.1 g, 5.8 mmol) and 20 mL (20 mmol) of 30% H₂O₂ were stirred for 2 h in 60 mL of glacial acetic acid at 23 °C, and for 1 h on the steam bath. It was poured into 200 mL of H₂O and extracted with ether, and the combined extracts were washed with NaHCO₃ solution and with brine solution. Drying and removal of solvent under reduced pressure, followed by two recrystallizations from ether, gave white prisms, mp 45.0–45.5 °C, in 42% yield.

Anal. Calcd for C₉H₁₁NO₄S: C, 47.15; H, 4.84. Found: C, 47.22; H, 4.78.

2-Methyl-1-nitropropane. The oxime of isobutyraldehyde (Chemical SAMPLES Co.) was prepared by the method of Pearson and Bruton,³⁰ save that a 24-h reflux was employed. The oxime was oxidized by trifluoroacetic acid²⁰ employing a 24-h reflux to obtain 42% crude yield.

2,2-Dimethyl-1-nitropropane. As for 2-methyl-1-nitropropane, pivaldehyde (Chemical Samples Co.) was converted to its oxime, and oxidized to the nitro compound in 69% yield for the oxidation step.

Cyclopropyl nitromethane. Cyclopropyl cyanide (Aldrich) was reduced to cyclopropylcarboxaldehyde with LiAlH₄.³¹ The oxime was prepared by the method of Roberts and Chambers³² and oxidized as for 2-methyl-1-nitropropane, save that refluxing was continued for only 5 h. A 6% overall crude yield was achieved.

Phenylthionitromethane. To 21 mL (0.21 mol) of benzenethiol in 100 mL of pentane at 0 °C was added dropwise with stirring 18 mL (0.24 mol) of sulfur chloride over 1 h. The red mixture was stirred 1 h more at 23 °C, then solvent and excess SO₂Cl₂ were removed under reduced pressure. Distillation gave 24 g (80% yield) of benzenesulfonyl chloride as a red liquid, bp 66 °C (4 mm) [lit.³³ 73–75 °C (9 mm)]. This was converted to phenyl benzenethiosulfinate by the addition of 1.25 equiv of sodium benzenesulfinate in small portions over 15 min to the sulfonyl chloride in CCl₄ at 0 °C, followed by 1 h at 23 °C. Filtration and removal of solvent under reduced pressure gave a viscous oil, which upon crystallization from hexane gave a 74% yield of white crystals, mp 35–37 °C [lit.³⁴ mp 44–46 °C]. Conversion to 4-(phenylthio)morpholine³⁵ was accomplished in 72% yield, mp 29–33 °C [lit.³⁵ 33–36 °C].

Following the general procedure of Mukaiyama,³⁶ in 50 mL of CH₂Cl₂ were stirred 3.9 g (38 mmol) of ethyl nitroacetate and 6.5 g (38 mmol) of 4-(phenylthio)morpholine for 3 h. Removal of solvent under reduced pressure gave a tan salt, which was heated for 45 min on the steam bath in 125 mL of 40% ethanol–water solution, 1 M in KOH. The ethanol was removed under reduced pressure, and the solution was neutralized to pH 7 with 30 mL of 10% HCl solution. To this at 0 °C was added 10 g (0.14 mol) of hydroxylamine hydrochloride in 20 mL of water over 15 min. Ether extraction afforded on workup 5 mL of yellow oil, which was 92% product and 8% diphenyl disulfide by NMR and VPC. Column chromatography on 50 g of silica gel, eluting with CCl₄, gave material >99% pure in the fourth column volume of eluent.

Anal. Calcd for C₇H₇NO₂S: C, 49.69; H, 4.17. Found: C, 49.64; H, 4.23.

All attempts at direct benzenesulfonation of nitromethane or nitroethane with Mukaiyama's reagents³⁶ were unsuccessful.

Phenylsulfonylnitromethane. Acetic acid (10 mL) containing 1.0 g (5.9 mmol) of phenylthionitromethane and 5 mL (50 mmol) of 30% H₂O₂ was refluxed 1 h. Removal of solvent under reduced pressure followed by crystallization from ethanol–water gave 0.3 g of crystals (25% yield). Recrystallization from hexane gave white needles, mp 78.0–78.5 °C.

Anal. Calcd for C₇H₇NO₄S: C, 41.79; H, 3.51. Found: C, 41.66; H, 3.49.

Truce³⁷ reports this as the product of nitration of phenyl methyl sulfone with amyl nitrate and potassium amide in ammonia: mp 150–150.5 °C. Of his two literature references for mp 151 °C, neither reports this compound, but rather *p*-tolylsulfonylnitromethane, mp 115 °C.

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Registry No.—3-Phenyl-1-bromopropane, 637-59-2; 3-phenoxy-1-bromopropane, 588-63-6; 3-thiophenoxy-1-chloropropane, 4911-65-3; 1-bromo-3-chloropropane, 109-70-6; 1,3-diiodopropane, 627-31-6; 4-chlorobutyronitrile, 628-20-6; 4-iodobutyronitrile, 6727-73-7; isobutyraldehyde oxime, 151-00-8; pivaldehyde, 630-19-3; pivaldehyde oxime, 637-91-2; cyclopropylcarboxaldehyde oxime, 66291-30-3; benzenethiol, 108-98-5; benzenesulfonyl chloride, 931-59-9; phenyl benzenethiosulfinate, 1208-20-4; 4-(phenylthio)morpholine, 4837-31-4.

References and Notes

- R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.
- G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1941.
- J. Shorter, "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, N.Y., 1972, Chapter 2 (221 references).
- See J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1975, pp 89–99, for a lucid presentation.
- R. G. Bates, M. Paako, and R. H. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).
- D. Turnbull and S. H. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943).
- W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCollum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975).
- We are indebted to Zafra Margolin and W. S. Matthews for carrying out these measurements.
- At the time the Taft relationship was derived the importance of the geometric relationship between G and the acidic site was not apparent, since the polar effect of G was thought to be transmitted mainly through the σ -bond framework. It now appears that very little of the effect is transmitted in this way.¹⁰
- See L. Stock, *J. Chem. Educ.*, **49**, 400 (1972), and references cited therein; S. Ehrenson, *J. Am. Chem. Soc.*, **98**, 7510 (1976).
- It must be kept in mind, however, that the constancy of the methylene transmission coefficient $\sigma^*_{\text{CH}_2\text{CH}_2\text{G}}/\sigma^*_{\text{CH}_2\text{G}}$ was tested by Taft for only three groups (Ph, 0.37; CH=CHMe, 0.36; COCH₃, 0.36). Using the data on acetic acids supplied by Charton, together with Taft's data,¹ suggests considerable variation (CF₃, 0.33; Cl, 0.32; Br, 0.40; I, 0.42; MeO, 0.28; CN, 0.32; CO₂Et, 0.38); M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).
- C. A. Grob and M. G. Schlageter, *Helv. Chim. Acta*, **59**, 264 (1976).
- F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, companion paper in this issue (paper 1 in this series); F. G. Bordwell and F. D. Cornforth, *J. Org. Chem.*, **43**, 1763 (1978); unpublished data from this laboratory.
- (a) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 312 (1977); (b) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *ibid.*, **42**, 326 (1977); (c) F. G. Bordwell and D. Algrim, *ibid.*, **42**, 1817 (1977).
- See ref 14a and 14b and F. G. Bordwell and G. J. McCollum, *J. Org. Chem.*, **41**, 2391 (1976), for examples and discussion of the resonance saturation effect.
- F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Am. Chem. Soc.*, **92**, 5926 (1970).
- H. Shechter, D. E. Ley, and L. Zeldiv, *J. Am. Chem. Soc.*, **76**, 3664 (1954).
- H. Shechter, D. E. Ley, and E. B. Roberson, Jr., *J. Am. Chem. Soc.*, **78**, 4984 (1956).
- A. S. Sopova, V. V. Perekalin, V. M. Lebednova, and O. A. Yurchenko, *Zh. Obshch. Khim.*, **34**, 1185 (1964).
- W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 4557 (1955).
- N. Kornblum and D. C. Iffland, unpublished work reported in *Org. React.*

- 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

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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 $\text{GCH}_2\text{CH}_2\text{NO}_2$ and GCH_2NO_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, $\text{GCH}_2\text{CH}_2\text{CH}_2\text{NO}_2$, 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 $\text{GCH}_2\text{CH}_2\text{CH}_2\text{NO}_2$ 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 $\text{p}K$'s for nitroalkanes is known to be small,⁷ and should be similar for a series such as $\text{G}(\text{CH}_2)_3\text{NO}_2$, 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. $\text{p}K$'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