THE JOURNAL OF Organic Chemistry®

VOLUME 43, NUMBER 16
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AUGUST 4, 1978

# Alkyl Effects on Equilibrium Acidities of Carbon Acids in Protic and Dipolar Aprotic Media and in the Gas Phase

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*Received February 22, 1977*

The effects on acidity of substitution of methyl for hydrogen at carbon in 28 weak acids are divided into four types: (a) acid-weakening hyperconjugative and polar methyl effects; (b) acid-strengthening hyperconjugative methyl effects (on ketones, nitroalkanes, and 9-methylfluorene); (c) acid-weakening polar methyl effects (on sulfones and nitriles); and (d) acid-weakening steric methyl effects. Similar methyl effects are observed within groups a–c in the gas phase, in $Me_2SO$ solution, and in $H_2O$ solution. $\sigma^*_H$ is found to be inadequate as a measure of the polar effect of hydrogen. Decreasing acidities of mononitroalkanes, $RCH_2NO_2$, in the series R = Me, Et, *i*-Pr, *t*-Bu, were observed to be remarkably alike in 50% aqueous MeOH and $Me_2SO$. These alkyl effects are believed to be the result of a complex blend of hyperconjugative, polar, polarizability, and steric effects. Ph and $CH_2{=}CH$ groups exhibit substantial conjugative effects which are larger in $Me_2SO$ than in aqueous MeOH. The cyclopropyl group exhibits no observable conjugative effect in the c-$PrCH{=}NO_2^-$ anion. Substitution of R for H in $RCH_2NO_2$ produces, for the most part, the same relative effects as observed for substitution of R for H in $HCH_2NO_2$. However, substitution of c-Pr for H in $HCH_2NO_2$ and $MeCH_2NO_2$ is acid strengthening, whereas substitution of c-Pr for H in c-$PrCH_2NO_2$ is (unexpectedly) acid weakening.

Alkyl groups are omnipresent in organic molecules and often are the determining factor in controlling relative rates or equilibrium positions in organic reactions. Detailed analysis of alkyl effects has proved difficult, however, because they often vary in nature and magnitude depending on the type of atom to which they are attached, the reaction, and the reaction conditions. Investigations of alkyl effects on equilibria involving carbon acids have been limited by the relatively low acidities of such compounds. Nitroalkanes are the only monofunctional carbon acids that are acidic enough to permit equilibrium acidity measurements to be made in aqueous (or other protic) media. As a consequence our knowledge of the effect of alkyl effects on the equilibrium acidities of carbon acids has previously come primarily from measurements made on nitroalkanes. Scientists in the Soviet Union have been particularly active in this area.[2,4,6,8] The data have been correlated over the years with various types of linear free-energy relationships. Data for mononitroalkanes, $R_1R_2CHNO_2$, were originally correlated using Taft $\sigma^*$ constants to represent the polar effects of alkyl and other substituents, with additional parameters added to take into account hyperconjugative and steric effects.[2] In the past few years this treatment has been modified in that all alkyl groups have been assigned $\sigma^*_R = 0$, following the suggestion of Ritchie,[3] and the data have been correlated with (a) $\sigma^*$'s (for alkyl groups containing hetero atoms), (b) two separate steric factors, $E'_s$ (steric hindrance to resonance) and $E^0_s$ (intramolecular steric interactions between remote atoms), and (c) a $\varphi$ constant, to account for the change from $sp^3$ to $sp^2$ hybridization during anion formation.[4] Hyperconjugation was assumed to be absent (or to be included in the $\varphi$ constant). Another recent analysis, made by selecting data from ten nitroalkanes, $RCH_2NO_2$ and $R_1R_2CHNO_2$, including points for seven simple alkyl groups, together with points for $CH_2CH_2Ph$, $CH_2CH_2CN$, and $CH_2CH_2CH_2NO_2$ groups, employed the original Taft $\sigma^*$ constants ($\Sigma\sigma^*$) and either a parameter representing the degree of hyperconjugation or one representing the change in hybridization.[5] It was concluded that hyperconjugation rather than changes in C–H and C–C bond energies due to hybridization changes offered the better interpretation of the data.

A correlation of substituent effects on equilibrium acidities in water for 14 alkyl-1,1-dinitroalkanes, $RCH(NO_2)_2$, with Taft $\sigma^*$ values ($\rho^* = 1.74$) was reported some time ago,[6] but when alkyl groups with heteroatom substituents were added to the list a $\rho^*$ of 3.60 was obtained (28 compounds).[7] The p$K$'s of 70 aliphatic 1,1-dinitroalkanes have been reported recently.[8] For 44 of these, in which the substituent is insulated from the reaction center by a single methylene group, a $\rho^*$ of 3.29 ($r = 0.992$) was obtained.[8] The data for 20 aliphatic 1,1-dinitroalkanes, including examples where the substituent has not been insulated from the acidic site, have also been correlated with the $E^0_s$, $E'_s$, $\varphi$, and $\sigma^*$ constants mentioned above.[4]

The variety of parameters used to correlate the acidity data for nitroalkanes and the variety of ways in which these parameters have been combined has led to a complex and confusing picture, to say the least.

## Introduction to the Series of Papers

Investigations in our laboratory during the past five years have been concerned not only with alkyl effects on equilibrium acidities of nitroalkanes, but also alkyl effects on equilibrium

0022-3263/78/1943-3095$01.00/0

**Table I. Effects of Substitution of Methyl for Hydrogen on Equilibrium Acidities in the Gas Phase and in Solution (Protic and Dipolar "Aprotic" Solvents)**

| acid | registry no. | p$K$ | solvent | (p$K_H$ − p$K_{Me}$)[a] | ref |
|---|---|---|---|---|---|
| (a) Acid-Weakening Hyperconjugative and Polar Methyl Effects | | | | | |
| 1. $HCO\mathbf{CH_3}$ | | | none | (0.0) | *c* |
| $MeCO\mathbf{CH_3}$ | | | none | −2.14[b] | *c* |
| 2. $HCO_2\mathbf{H}$ | | | none | (0.0) | *d* |
| $MeCO_2\mathbf{H}$ | | | none | −1.6[b] | *d* |
| 3. $HCO_2\mathbf{H}$ | | 3.75 | $H_2O$ | (0.0) | *e* |
| $MeCO_2\mathbf{H}$ | | 4.75 | $H_2O$ | −1.0 | *e* |
| 4. $HCON\mathbf{H}_2$ | | 23.5 | $Me_2SO$ | (0.0) | *f* |
| $MeCON\mathbf{H}_2$ | | 25.5 | $Me_2SO$ | −2.0 | *f* |
| 5. $H_2C{=}NO_2\mathbf{H}$ | | 3.25 | $H_2O$ | (0.0) | *e* |
| $MeCH{=}NO_2\mathbf{H}$ | | 4.41 | $H_2O$ | −1.16 | *e* |
| $Me_2C{=}NO_2\mathbf{H}$ | | 5.11 | $H_2O$ | −1.86 | *e* |
| 6. $HC({=}O\mathbf{H})NH_2^+$ | | −2.0 | $H_2O$–$H_2SO_4$ | (0.0) | *g* |
| $MeC({=}O\mathbf{H})NH_2^+$ | | −0.9 | $H_2O$–$H_2SO_4$ | −1.1 | *g* |
| 17. $H_2C{=}CH\mathbf{CH_2}NO_2$ | 625-46-7 | 5.22 | $H_2O$ | (0.0) | *h* |
| $MeCH{=}CHCH_2NO_2$ | 1809-69-4 | 5.44 | $H_2O$ | −0.22 | *h* |
| $Me_2C{=}CHCH_2NO_2$ | 1809-65-0 | 5.55 | $H_2O$ | −0.33 | *h* |
| 8. fluorene | | 22.6 | $Me_2SO$ | (0.0) | *i* |
| 2-methylfluorene | | 23.1 | $Me_2SO$ | −0.5 | *i* |
| (b) Acid-Strengthening Hyperconjugative and Polar Methyl Effects | | | | | |
| 1. $\mathbf{CH_3}NO_2$ | | | none | (0.0) | *c* |
| $Me\mathbf{CH_2}NO_2$ | | | none | 0.5[b] | *c* |
| $Me_2\mathbf{CH}NO_2$ | | | none | 1.2[b] | *c* |
| 2. $\mathbf{CH_3}NO_2$ | 75-52-5 | 17.20 | $Me_2SO$ | (0.0) | *h* |
| $Me\mathbf{CH_2}NO_2$ | 79-24-3 | 16.72 | $Me_2SO$ | 0.68 | *h* |
| $(CH_3)_2\mathbf{CH}NO_2$ | 79-46-9 | 16.88 | $Me_2SO$ | 0.795 | *h* |
| $(CD_3)_2\mathbf{CH}NO_2$ | 52809-86-6 | 17.03 | $Me_2SO$ | 0.645 | *h* |
| 3. $\mathbf{CH_3}NO_2$ | | 10.22 | $H_2O$ | (0.0) | *j* |
| $Me\mathbf{CH_2}NO_2$ | | 8.60 | $H_2O$ | 1.8 | *j* |
| $Me_2\mathbf{CH}NO_2$ | | 7.74 | $H_2O$ | 2.96 | *j* |
| $(CH_3)_2\mathbf{CH}NO_2$ | | 7.475 | $H_2O$ | | *k* |
| $(CD_3)_2\mathbf{CH}NO_2$ | | 7.566 | $H_2O$ | | *k* |
| 4. $\mathbf{CH_3}NO_2$ | | 11.11 | MeOH–$H_2O$ | (0.0) | *h* |
| $Me\mathbf{CH_2}NO_2$ | | 9.63 | MeOH–$H_2O$ | 1.7 | *h* |
| $Me_2\mathbf{CH}NO_2$ | | 8.85 | MeOH–$H_2O$ | 2.7 | *h* |
| 5. $CH_3CO\mathbf{CH_3}$ | | | none | (0.0) | *c* |
| $CH_3CO\mathbf{CH_2}Me$ | | | none | 1.3[b] | *c* |
| 6. $PhCO\mathbf{CH_3}$ | | | none | (0.0) | *c* |
| $PhCO\mathbf{CH_2}Me$ | | | none | 1.2[b] | *c* |
| 7. $PhCO\mathbf{CH_3}$ | 98-86-2 | 24.7 | $Me_2SO$ | (0.0) | *h* |
| $PhCO\mathbf{CH_2}Me$ | 93-55-0 | 24.4 | $Me_2SO$ | 0.5 | *h* |
| 8. fluorene | | 22.6 | $Me_2SO$ | (0.0) | *l* |
| 9-methylfluorene | | 22.3 | $Me_2SO$ | 0.60 | *l* |
| (c) Acid-Weakening Polar Methyl Effects | | | | | |
| 1. $PhSO_2\mathbf{CH_3}$ | | | none | (0.0) | *c* |
| $PhSO_2\mathbf{CH_2}Me$ | | | none | −1.1 | *c* |
| 2. $PhSO_2\mathbf{CH_3}$ | 3112-85-4 | 29.0 | $Me_2SO$ | (0.0) | *h* |
| $PhSO_2\mathbf{CH_2}Me$ | 599-70-2 | 31.0 | $Me_2SO$ | −1.8 | *h* |
| 3. $F_3CSO_2\mathbf{CH_3}$ | | 18.8 | $Me_2SO$ | (0.0) | *m* |
| $F_3CSO_2\mathbf{CH_2}Me$ | | 20.4 | $Me_2SO$ | −1.4 | *m* |
| 4. $CN\mathbf{CH_3}$ | | | none | (0.0) | *n* |
| $CN\mathbf{CH_2}Me$ | | | none | −1.2[b] | *n* |
| 5. $(CN)_2\mathbf{CH_2}$ | | 11.4 | $H_2O$ | (0.0) | *o* |
| $(CN)_2\mathbf{CH}Me$ | | 12.8 | $H_2O$ | −1.1 | *o* |
| 6. $(CN)_2\mathbf{CH_2}$ | 109-77-3 | 11.1 | $Me_2SO$ | (0.0) | *h* |
| $(CN)_2\mathbf{CH}Me$ | 3696-36-4 | 12.4 | $Me_2SO$ | −1.0 | *h* |
| 7. $CN(Ph)\mathbf{CH_2}$ | | 21.9 | $Me_2SO$ | (0.0) | *p* |
| $CN(Ph)\mathbf{CH}Me$ | | 23.0 | $Me_2SO$ | −0.8 | *p* |
| 8. $(EtSO_2)_2\mathbf{CH_2}$ | | 12.2 | $H_2O$ | (0.0) | *q* |
| $(EtSO_2)_2\mathbf{CH}Me$ | | 14.6 | $H_2O$ | −2.1 | *q* |
| 9. $(EtSO_2)_2\mathbf{CH_2}$ | | 14.4 | $Me_2SO$ | (0.0) | *r* |
| $(EtSO_2)_2\mathbf{CH}Me$ | | 16.7 | $Me_2SO$ | −2.6 | *r* |
| (d) Acid-Weakening Steric Methyl Effects | | | | | |
| 1. $CH_3CH{=}CH\mathbf{CH_2}NO_2$ | | 5.44 | $H_2O$ | (0.0) | *h* |
| $CH_3CH{=}CH\mathbf{CH}(Me)NO_2$ | 1806-28-6 | 5.35 | $H_2O$ | 0.39 | *h* |
| 2. $H_2C{=}C(CH_3)\mathbf{CH_2}NO_2$ | 1606-31-1 | 7.27 | $H_2O$ | (0.0) | *h* |
| $H_2C{=}C(CH_3)\mathbf{CH}(Me)NO_2$ | 19031-81-3 | 7.85 | $H_2O$ | −0.28 | *h* |

**Table I** (*continued*)

| acid | registry no. | p*K* | solvent | $(pK_H - pK_{Me})^a$ | ref |
|---|---|---|---|---|---|
| 3. $H_2C{=}CHCH_2NO_2$ | | 5.22 | $H_2O$ | (0.0) | *h* |
| $H_2C{=}CMeCH_2NO_2$ | | 7.27 | $H_2O$ | −2.1 | *h* |
| 4. $PhCOCH_2CH_3$ | | 24.4 | $Me_2SO$ | (0.0) | *h* |
| $PhCOCH(Me)CH_3$ | 611-70-1 | 26.3 | $Me_2SO$ | −1.6 | *h* |

[a] Corrected statistically for the number of hydrogen atoms at the acidic site. [b] (DH − EA)/1.37. [c] References 27, 51, 58. [d] Reference 52. [e] Reference 53. [f] Reference 9d. [g] Reference 12. [h] Present work. [i] Reference 36b. [j] Reference 54. [k] Reference 5. [l] Reference 50. [m] Reference 17. [n] Reference 51. [o] Reference 55. [p] Reference 56. [q] Reference 57. [r] Reference 59.

acidities of a variety of other weak acids. In this, the first paper in a series, we present equilibrium data for various types of weak acids in protic media and $Me_2SO$ solution, and compare these data with recent data obtained from gas-phase studies. In the second paper in the series the Taft equation is examined in light of data obtained for substituent effects on equilibrium acidities of the nitroalkane system $G(CH_2)_nNO_2$, where G is a heteroatom substituent and *n* is 1, 2, or 3. Then, in the third paper, the relationship between substituent effects on equilibrium and on kinetic acidities for acyclic saturated nitroalkanes is examined. This examination of Brønsted relationships is continued in the fourth and fifth papers in the series, which are concerned with nitrocycloalkanes and $\beta,\gamma$-unsaturated nitroalkanes, respectively.

## Results and Discussion

**Effects on Acidity of Methyl vs. Hydrogen.** As is apparent from the introduction, the substituent effects of hydrogen and alkyl groups on equilibria (and rates) have been the subject of much discussion and controversy occasioned by their diverse nature and (frequently) small magnitude.[3,9] Traditionally, following Ingold, the major effect of Me (vs. H) has been considered to be electron release to an $sp^3$ carbon atom by a polar (inductive) and polarizability effect. It is now clear that these effects are enhanced when Me is attached to a (more electronegative) $sp^2$ carbon atom, and that they are then augmented by hyperconjugation.

Much confusion has arisen from the original assignment by Taft of $\sigma^*_{Me}$ and $\sigma^*_H$ "polar" substituent constants of 0.0 and 0.49, respectively, based on ester hydrolysis data of $MeCO_2R$ and $HCO_2R$.[10] The $\sigma^*_H$, $\sigma^*_{Me}$, and other $\sigma^*_R$ constants derived in this way have been used successfully to correlate rate data for many reactions in which R (or H) is attached to a carbon atom that is becoming more electronegative in the transition state by changing hybridization from $sp^3$ to $sp^2$ and/or developing a positive charge (e.g., solvolysis reactions).[11] On the other hand, the correlation of rate or equilibrium data for other types of reactions are at least as successful when all $\sigma^*_R$ constants and $\sigma^*_H$ are taken as zero.[3,12] (The hydrogen point usually deviates widely in a Taft $\sigma^*$ plot for such reactions.) Furthermore, derivations of polar constants from $RCH_2CO_2H$ acidities[12] or $RCONH_2$ acidities[9d] lead to small or negligible electron-releasing effects for alkyl, relative to hydrogen. The extent of the confusion with regard to Me and H effects is indicated by the fact that $\sigma^*_{Me}$ and $\sigma^*_H$ constants continue to be presented in many recent textbooks on physical organic chemistry without critical comment,[13] despite the fact that there now appears to be general agreement that the difference in polar effects of Me and H are much smaller than is suggested by these constants ($\sigma_I^{Me} = -0.04$; $\sigma_I^H = 0.0$).[14] A recent analysis of alkyl effects on gas-phase acidities appears to have been successful in separating intrinsic inductive effects from polarizability effects.[15] A substantial electron release in the original Taft order, Me < Et < *n*-Pr < *i*-Pr < *t*-Bu, was observed. It now appears that the variable nature of alkyl effects observed in solution[3,9d,12] arise because a variety of other substantial effects are present which can modify and sometimes override the intrinsic inductive effects.

Alkyl effects on acid–base reactions are complicated further by the necessity of considering the alkyl effect on both the undissociated acid and on its conjugate base, and by the frequent presence of steric effects. The position of such equilibria depend on a blend of hyperconjugative, polar, polarizability, steric, and medium effects, which may operate to varying degrees on the undissociated acid and its conjugate base. In Table I we have attempted to group the acids into four classes depending on whether hyperconjugation, polar electron release, or steric effects are *dominant*. In groups a and b hyperconjugative effects of Me are believed to produce dominant acid-weakening and acid-strengthening effects, respectively, augmented or modified by electron-releasing polar effects. In group c an acid-weakening polar effect is believed to be dominant, and in group d acid-weakening steric effects are believed to be dominant. For acids in groups a–c comparable effects are observed in the gas phase, in dipolar aprotic solvents, and in protic solvents, indicating that the effects are independent of medium. (Gas-phase data are not yet available for group d acids.)

**Acid-Weakening Hyperconjugative and Polar Methyl Effects.** In most of the compounds in group a the Me group is attached to the positive end of the dipole of an $sp^2$-hybridized carbon atom, i.e., $Me{-}C^+{-}O^- \leftrightarrow Me{-}C{=}O$, or the like. Hyperconjugative and polar stabilization by Me is greater in the undissociated form of the acid than in the anion, causing equilibria such as that shown in eq 1 to be shifted to the left (acid weakening Me effect).

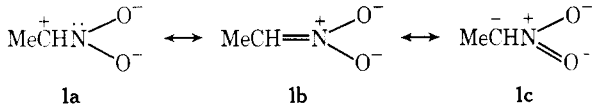
$$MeCO_2H + HCO_2^- \rightleftarrows MeCO_2^- + HCO_2H \qquad (1)$$

Examination of Table I shows that this effect is independent of medium (gas phase, $H_2O$, or $Me_2SO$) and is found in carbon and nitrogen acids, as well as in oxygen acids. Most of the effects are of the order of 1–2 p*K* units, but the effect is much smaller in $H_2C{=}CHCH_2NO_2$ vs. $MeCH{=}CHCH_2NO_2$ or fluorene vs. 2-methylfluorene, where the charge density of the carbon atom at which Me substitution is made changes but little on removal of the proton.

**Acid-Strengthening Hyperconjugative and Polar Methyl Effects.** The compounds in group b differ from those in group a in that stabilizing hyperconjugative and polar methyl effects are important in the anion, where Me is attached to an $sp^2$ carbon atom, but not in the undissociated acid, where Me is attached to an $sp^3$ carbon atom. As a consequence, the equilibria, such as eq 2, are shifted to the right (acid-strengthening Me effect).

$$MeCH_2NO_2 + H_2C{=}NO_2^- \rightleftarrows MeCH{=}NO_2^- + H_3CNO_2 \qquad (2)$$

The postulate of an important hyperconjugative and polar Me stabilizing interaction in the anions for group b compounds is based on the assumption that the negative charge density on the carbon atom to which Me is attached is relatively low. (We will see shortly that an *opposite* Me effect is believed to result when the negative charge density is high.) In valence-bond terminology this requires **1a** to be an important resonance contributor in nitronate anions.[16] (Form **1b** is, of course, the major contributor.)



**1a** **1b** **1c**

The larger Me effect observed in $H_2O$ than $Me_2SO$ or in the gas phase for the $HCH_2NO_2$, $MeCH_2NO_2$, $Me_2CHNO_2$ series may be rationalized by the strong H bonding to oxygen in water, which increases the positive charge density on carbon, and by the high dielectric constant of water, which helps to stabilize charge separation, as in **1a**. It is noteworthy that the acidifying effects of Me are smaller for both nitroalkanes and ketones in $Me_2SO$ than in the gas phase. Perhaps the greater importance of polarizability in the gas phase is the reason.

**Acid-Weakening Polar Methyl Effects.** The effect of $\alpha$-Me substitution for nitriles and sulfones (group c in Table I) is the inverse of that for nitroalkanes and ketones (group b in Table I) despite the structural similarities of carbon acids. The acid-weakening $\alpha$-Me effects are observed in the gas phase and in $Me_2SO$ solution, as well as in water. The effect seems to be independent of the acidity of the parent acid, since it is observed for weak carbon acids ($PhSO_2CH_3$), moderately weak carbon acids ($F_3CSO_2CH_3$ and $PhCH_2CN$), and moderately strong carbon acids ($CNCH_2CN$ and $EtSO_2CH_2SO_2Et$).

The origin of this effect is puzzling. At first we attributed it to steric inhibition of solvation by $\alpha$-Me in these carbanions where the negative charge is concentrated on carbon to a much greater extent than is true for nitronate or enolate anions. However, the fact that $\alpha$-Me effects on the gas phase acidities for nitriles and sulfones are also the inverse of those for nitroalkanes and ketones (Table I) rules out this explanation. A steric explanation seems unlikely also because the same $\alpha$-Me effect is observed for sulfone functions, where the steric effect is high, as for the cyano function where steric demands are negligible. There is evidence that $\alpha$-sulfonyl carbanions, as well as $\alpha$-cyano carbanions, are planar,[17] which rules out a difference in hybridization between these carbanions and $\alpha$-nitro or $\alpha$-keto carbanions as a cause for the reversal of Me effects. We are left with polar electron release from Me, relative to H, to the $sp^2$ carbon atom in the anion as the most likely acid-weakening effect. The available evidence points to a small polar effect of this kind in solution when Me is attached to an $sp^3$ carbon atom[14] and an appreciable effect in the gas phase.[15] These effects would be expected to be enhanced when Me is attached to an $sp^2$ carbon atom, as in $\alpha$-Me sulfonyl and $\alpha$-Me cyano carbanions. This destabilizing effect may be offset to some degree by a stabilizing hyperconjugative effect, since there is evidence for such an effect in $MeX^-$ anions (X = O, S, or NH) in the gas phase.[18] Also, the polarizability effect of R in $RO^-$ appears to stabilize in the gas phase,[19] and lesser, but still important polarizability effects appear to be stabilizing in solution, at least toward cations.[20] Polarizability is a short-range force, falling off as $1/r^4$,[19] and therefore should provide the greatest acid-strengthening Me effect for the most localized carbanions (group c). The observed effect is, however, exactly the opposite to that predicted by anionic hyperconjugation[18] or by polarizability.[19] We conclude that the destabilizing effect observed has its origin in electrostatic repulsion between Me and the anionic site.[15]

**Analysis on the Basis of Thermochemical Data.** These acidities may also be analyzed in terms of the thermochemistry for the corresponding gas-phase acidities.[19] For the carbon acid $GCH_3$, its gas-phase enthalpy of heterolytic cleavage, eq 7, can be determined from the C–H bond energy DH°, the electron affinity EA of $GCH_2\cdot$, and the ionization potential of the hydrogen atom, IP, by means of eq 3–7.[19]

$$GCH_2\text{–}H \rightarrow GCH_2\cdot + H\cdot \qquad DH^\circ \tag{3}$$

$$GCH_2\cdot + e^- \rightarrow GCH_2^- \qquad -EA \tag{4}$$

$$H\cdot \rightarrow e^- + H^+ \qquad IP \tag{5}$$

$$GCH_2\text{–}H \rightarrow H^+ + GCH_2^- \tag{6}$$

$$\Delta H^\circ_{\text{acid}} = DH^\circ - EA + IP \tag{7}$$

Since IP = 313.6 kcal/mol is common to all $GCH_3$ systems, the factors determining relative acidity are DH° and EA. In general, $\alpha$-Me substitution results in a decrease in DH° for the C–H bond both for systems giving localized radicals, such as the alkanes,[21] and for radicals delocalized to phenyl[21,22] or carbonyl.[23] The weakening of the bond is 3–6 kcal/mol in both cases. Since approximately the same effect is seen in such widely differing structures, we assume that this decrease is general to all carbon acids discussed here. The mechanism for this lowering of DH° appears to be radical stabilization by delocalization onto the methyl group, as shown by ESR.[24] This is roughly equivalent to the hyperconjugative interaction noted above. They are not strictly equivalent, since the thermochemical argument ignores any hyperconjugative stabilization in the anion.[18]

Methyl substitution decreases EA for aldehydes and ketones by 2–4 kcal/mol.[25] This can be attributed to methyl stabilization of the radical, as just mentioned.[24,26] For the compounds in group b this acid-weakening effect is overshadowed by a decrease in DH°, but for compounds in group c EA is decreased further by the (larger) destabilizing polar effect of Me on the anion, and the acid-weakening effect wins out. For group a acids Me substitution *increases* DH°, judging from data for $MeCOCH_3$ vs. $HCOCH_3$ ($\Delta DH^\circ$ = 2 kcal/mol).[27] The EA also increases (by ~1 kcal/mol for $MeCOCH_2\cdot$ vs. $HCOCH_2\cdot$) but, since the DH° increase is numerically larger, the net Me effect is acid weakening.

**Acid-Weakening Steric Methyl Effects.** Acid-weakening steric effects are no doubt present in some of the anions derived from compounds in groups a–c, but these effects are believed to be minor. For compounds in group d they become an important or dominant factor. In example 1 in group d we see that the strongly acidifying $\alpha$-Me effect observed for $MeCH_2NO_2$ vs. $HCH_2NO_2$ is almost negated for $CH_2{=}CHCHMeNO_2$ vs. $CH_2{=}CHCH_2NO_2$ by a steric effect in the anion. In examples 2 and 3 Me substitution introduces progressively larger steric effects in the anions, and the Me effect becomes acid weakening. (These steric effects are discussed in greater detail in the final paper in this series.) In the series $CH_3NO_2$, $MeCH_2NO_2$, $Me_2CHNO_2$ (group b) we saw that the $\alpha$-Me acidifying effect becomes progressively smaller in water, and that in dimethyl sulfoxide $Me_2CHNO_2$ is only a slightly stronger acid than $MeCH_2NO_2$. We attribute this trend to the increasing importance of an acid-weakening steric effect and/or a diminution of hyperconjugation. In the ketone series, $CH_3COPh$, $MeCH_2COPh$, $Me_2CHCOPh$, the first methyl substitution is mildly acid strengthening (group b), but the second is strongly acid weakening (group d). In the latter instance the steric effect is apparently overshadowing the hyperconjugative and polar acidifying Me effects.

**Alkyl Effects for $RCH_2NO_2$ in the Series Me, Et, *i*-Pr, *t*-Bu.** The order of acidities for mononitroalkanes, $RCH_2NO_2$, is Me > Pr > Et > *i*-Pr > H > *t*-Bu (Table II). Remarkably similar effects are observed for this series in 50% (v/v) $MeOH\text{–}H_2O$ and in $Me_2SO$, despite differences in absolute

**Table II. Equilibrium Acidities of Nitroalkanes, $RCH_2NO_2$, in 50% (v/v) MeOH-HOH and in Dimethyl Sulfoxide**

| R | registry no. | p$K$ | solvent | p$K_R$ − p$K_{Me}$ |
|---|---|---|---|---|
| H | | 11.11 | 50% MeOH-$H_2O$ | 1.47 |
| Me | | 9.63 | 50% MeOH-$H_2O$ | (0.0) |
| Et | 108-03-2 | 9.99 | 50% MeOH-$H_2O$ | 0.35 |
| Pr | 627-05-4 | 9.77 | 50% MeOH-$H_2O$ | 0.19 |
| *i*-Pr | | 10.38 | 50% MeOH-$H_2O$ | 0.74 |
| *t*-Bu | 34715-98-5 | 11.40 | 50% MeOH-$H_2O$ | 2.08 |
| c-Pr | 2625-33-4 | 9.41 | 50% MeOH-$H_2O$ | −0.23 |
| Ph | 622-42-4 | 7.85 | 50% MeOH-$H_2O$ | −1.73 |
| $CH_2$=CH | | 6.29 | 50% MeOH-$H_2O$ | −3.29 |
| H | | 17.20 | $Me_2SO$ | 0.48 |
| Me | | 16.72 | $Me_2SO$ | (0.0) |
| Et | | 17.01 | $Me_2SO$ | 0.29 |
| Pr | | 16.83 | $Me_2SO$ | 0.11 |
| *i*-Pr | | 17.1 ± 0.3 | $Me_2SO$ | 0.38 |
| *t*-Bu | | 18.13 | $Me_2SO$ | 1.41 |
| c-Pr | | 16.53 | $Me_2SO$ | −0.19 |
| Ph | | 12.20 | $Me_2SO$ | −4.52 |
| $CH_2$=CH | | 11.25 | $Me_2SO$ | −5.47 |

acidities in the two media of about seven powers of ten. The nature of the solvent effects in the two media are markedly different (H bonding only in $H_2O$ and stronger dipole interactions in $Me_2SO$), but the *relative* effects with substituent changes in R near the acidic site are similar. This appears to be a general characteristic for these two solvents, since it holds true also for substituent effects operating across benzene rings.[28] We can analyze these effects in terms of eq 8.

$$RCH{=}NO_2^- + MeCH_2NO_2 \rightleftarrows RCH_2NO_2 + MeCH{=}NO_2^- \quad (8)$$

Assuming that the stabilizing (or destabilizing) effect will be larger in the anion than in the undissociated acid, we see that Me produces a larger stabilizing effect than other alkyl groups, and a much larger effect than does hydrogen. The Me > H effect is consistent with hyperconjugative stabilization by Me. The larger R groups contribute lesser stabilizing hyperconjugative and/or polar effects. Polarizability evidently plays little role, since it would produce an order opposite to that observed. This is not surprising. Note that acidities in the gas phase for alcohols and thiols increase with increasing alkyl size because of stabilizing polarizability effects on $RO^-$ and $RS^-$ ions,[19,29] but in solution polarizability effects on these anions are overshadowed by other effects and the acidities decrease with increasing alkyl size.

Examination of Table II shows that cyclopropyl, phenyl, and vinyl groups cause acidifying effects, relative to Me, of 0.2, 1.7, and 3.3 p$K$ units, repsectively, in water, and 0.2, 4.5, and 5.5 p$K$ units, respectively, in $Me_2SO$. The small acidifying effect of c-Pr is consistent with its established small electron-withdrawing polar effect,[30] and points to little or no conjugative effect.[31-34] On the other hand, appreciable conjugative effects for phenyl and vinyl groups are indicated by the data. The conjugative effects are greater in $Me_2SO$ than in $H_2O$ by 2.2–2.8 p$K$ units (3.3–3.8 kcal/mol). In water the strong H bonding to the oxygen atoms in the $PhCH{=}NO_2^-$ and $CH_2{=}CHCH{=}NO_2^-$ nitronate ions shifts the negative charge density toward oxygen and away from carbon. As a consequence, the negative charge density on the $\alpha$-carbon atom in the anion is greater in $Me_2SO$ than in $H_2O$, and the conjugative interaction with phenyl or vinyl groups is much greater.[35,36]

**Enthalpy and Entropy Data.** Thermodynamic data for the ionization of some of the nitroalkanes in various media are collected in Table III. In aqueous solution, methyl substitution decreases both enthalpy and entropy of ionization, with the enthalpic term winning out in determining free-energy trends. The decrease in $\Delta S°$ on methyl substitution is similar to that observed for the carboxylic acid series ($HCO_2H$, $\Delta S° = -17.2$; $MeCO_2H$, $\Delta S° = -22.1$).[37] This can be attributed to steric disruption of the solvation shell about the acids upon methyl substitution. The solvent effect on the neutral acid is more important than that on the anion.[37,38] The stabilization of negative charge in the nitronate on oxygen due to solvent hydrogen bonding reduces the charge on the carbon. This should reduce the polar destabilization of the carbanion by methyl, increasing EA and $\delta\Delta H°$ thereby, as observed. In $Me_2SO$, the lack of hydrogen-bond donation by solvent should increase charge on carbon, resulting in more balance between polar and hyperconjugative effects, and reduce $\delta\Delta H°$ with $\alpha$-Me substitution. The non-monotonic trends in $\Delta H°$ and $\Delta S°$ can be ascribed to varying solvation effects on acid and nitronate. The first Me, as in $H_2O$, decreases $\Delta S°$ by the reason given above; the second Me may reverse the trend by increasing the interaction with solvent to the point where it now affects the less sensitive anion.[37,38] The higher entropy values observed in $Me_2SO$ than in water are consistent with less solvent orientation, but the values are much lower than with most other carbon acids, which have entropies of ionization near zero in $Me_2SO$.[39]

**Table III. Enthalpy and Entropy of Ionization of Some Nitroalkanes**[a]

| nitroalkane | $\Delta H°$ ($H_2O$)[b] | $\Delta S°$ ($H_2O$)[b] | $\Delta H_i$ ($Me_2SO$)[c] | $\Delta S_i$ ($Me_2SO$)[d] |
|---|---|---|---|---|
| $CH_3NO_2$ | 5.9 ± 1 | −27 ± 2 | 20.15 | −11 |
| $MeCH_2NO_2$ | 2.4 ± 1 | −31 ± 2 | 18.3 | −15 |
| $Me_2CHNO_2$ | 0.1 ± 1 | −35 ± 2 | 19.9 | −11 |

[a] $\Delta H$ in kcal/mol; $\Delta S$ in eu. [b] T. Matsui and L. G. Hepler, *Can. J. Chem.*, **51**, 1941, 3789 (1973). [c] E. M. Arnett, unpublished results privately communicated. [d] From $\Delta S_i = (\Delta H_i - 2.3RT\,pK)/T$.

**Alkyl Effects in Disubstituted Nitroalkanes, $R_1R_2CHNO_2$.** In the series $CH_3NO_2$, $MeCH_2NO_2$, $Me_2CHNO_2$ the second Me effect is acidifying, but less so than the first. The lesser effect may be due to a saturation of the hyperconjugative effect,[36] or to steric hindrance to solvation. (Examination of a scalar molecular model of $Me_2C{=}NO_2^-$ indicates slight steric inhibition of rotation of Me.) From the results in Table II we can expect hyperconjugative and/or steric hindrance to solvation effects of R on the anion to de-

**Table IV. Effect of Alkyl Substitution into Alkylnitromethanes, $RCH_2NO_2$, in 50% $MeOH-H_2O$**

| nitroalkane | registry no. | p*K* | Δp*K*[a] |
|---|---|---|---|
| $MeCH_2NO_2$ | | 9.63 | (0.0) |
| $Me_2CHNO_2$ | | 8.85 | 1.08 |
| $MeCH_2NO_2$ | | 9.63 | (0.0) |
| (Me)(c-Pr)$CHNO_2$ | 2625-38-9 | 8.73 | 1.20 |
| (Me)(*i*-Pr)$CHNO_2$ | 2625-35-6 | 9.73 | 0.20 |
| $EtCH_2NO_2$ | | 9.99 | (0.0) |
| $Et_2CHNO_2$ | 551-88-2 | 10.17 | 0.12 |
| $PrCH_2NO_2$ | | 9.77 | (0.0) |
| $Pr_2CHNO_2$ | 2625-37-8 | 9.85 | 0.22 |
| *i*-$PrCH_2NO_2$ | 625-74-1 | 10.38 | (0.0) |
| *i*-$Pr_2CHNO_2$ | 66291-08-5 | 11.0 | −0.32 |
| c-$PrCH_2NO_2$ | | 9.41 | (0.0) |
| c-$Pr_2CHNO_2$ | 2625-39-0 | 10.67 | −0.96 |

[a] p*K*($RCH_2NO_2$) − p*K*($RR'CHNO_2$) statistically corrected for the number of acidic hydrogen atoms.

crease with increasing size when a second R group is substituted for a hydrogen atom in $RCH_2NO_2$. The effect of *i*-Pr vs. Me should be acid weakening by 0.75 p*K* units on this basis. Examination of Table IV shows that substitution of Me for H in $MeCH_2NO_2$ increases the acidity by 0.88 p*K* units more than does substitution of *i*-Pr for H, in close agreement with the effect anticipated. Substitutions of Et for H in $EtCH_2NO_2$ or Pr for H in $PrCH_2NO_2$ are also slightly acid strengthening when statistical factors are taken into account (Table IV). On the other hand, substitution of *i*-Pr for H in *i*-$PrCH_2NO_2$ causes a slight acid-weakening effect. This is surprising, since examination of a model of *i*-$Pr_2C{=}NO_2^-$ does not indicate much interaction between the *i*-Pr groups, whereas there is severe crowding in *i*-$Pr_2CHNO_2$, which is relieved by formation of the anion. On this basis we might have expected the steric effect to be acid strengthening. Increased steric hindrance to solvation in the anion appears to be the most likely cause for the acid-weakening effect observed. The 1 p*K* unit lower acidity of c-$Pr_2CHNO_2$ vs. c-$PrCH_2NO_2$ is also surprising in view of the 1.3 p*K* unit *higher* acidity of (Me)(c-Pr)$CHNO_2$ vs. $MeCH_2NO_2$. Apparently there is some kind of a destabilizing interaction between the c-Pr groups in the c-$Pr_2C{=}NO_2^-$ anion. Presumably this destabilizing effect has an electronic origin, since models indicate that c-Pr is smaller than *i*-Pr sterically.

## Experimental Section[41]

**Materials.** Except for some of the nitroalkanes, the compounds listed in Tables I–IV upon which measurements were made are commercially available. They were carefully purified (99+%) prior to measurements.

Nitroalkanes not available commercially were prepared from the corresponding oximes by oxidation with peroxytrifluoroacetic acid according to the method of Emmons and Pagano.[42]

Reaction times of 1.5–5 h were employed except for 2-methyl-1-nitropropane, 2,2-dimethyl-1-nitropropane, 3-methyl-2-nitrobutane, and 2,4-dimethyl-3-nitropentane, which required 24-h reaction times to obtain satisfactory yields. The nitroalkenes were prepared from the corresponding bromides or chlorides by the method of Kornblum and Ungande.[43] The purity of all compounds synthesized was at least 99% as evidenced by vapor-phase chromatography.

**Aldehydes and Ketones.** Cyclopropanecarboxaldehyde was prepared from reagent grade cyclopropyl cyanide by the method of Smith and Rogier.[44] Dicyclopropyl ketone was prepared from butyrolactone by the method of Hart and Curtis.[45] All other ketones and aldehydes were commercially available.

**Oximes.** The oxime of cyclopropanecarboxaldehyde was prepared by the method of Roberts and Chambers,[46] that of dicyclopropyl ketone by the method of Hart and Curtis,[45] and that of cyclopropyl methyl ketone by the method of Perkin and Marshall.[47] All other oximes were prepared by the method of Pearson and Burton.[48] Since the oximes of 2-methylpropanal, 2,2-dimethylpropanal, 3-methyl-2-butanone, 3-pentanone, 4-heptanone, and 2,4-dimethyl-3-pentanone are liquids, the following isolation procedure was employed for these oximes. A large portion of the ethanol was removed from the reaction mixture by distillation, and the residue was extracted with three 50-mL portions of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated. The residue was distilled to yield the desired oxime.

**p*K* Determinations.** The p*K*'s in 50% (v/v) $MeOH-H_2O$ were determined at 23 ± 1 °C by the potentiometric partial neutralization technique described previously.[49] The pH measurements were performed on either a Sargent Model D recording titrator equipped with a Corning triple purpose glass electrode and a Corning calomel reference electrode, or on a Sargent Model DR digital readout pH meter equipped with a Corning semimicro combination electrode. A period of 1–12 h was necessary for attainment of equilibrium. The p*K*'s in $Me_2SO$ were determined by the indicator method described previously.[50]

**Acknowledgment.** We are grateful to the National Science Foundation and the National Institute of Health for support of this work. We are indebted to Walter S. Matthews and Zafra Margolin for most of the acidity measurements in $Me_2SO$ solvent. We are also indebted to Professor Robert W. Taft for a number of helpful comments.

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# The Taft Equation As Applied to Equilibrium Acidities of Nitroalkanes, $G(CH_2)_nNO_2$

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*Received February 22, 1977*

Equilibrium acidities for 25 nitroalkanes, $G(CH_2)_nNO_2$, with $n = 1, 2$, or 3, are reported in two different solvents. The acidities of nitroalkanes $G(CH_2)_3NO_2$ were found to be reasonably well correlated with Taft $\sigma^*_{CH_2CH_2G}$ constants in 50% (v/v) $MeOH$–$H_2O$ ($\rho^* = 1.2$) and $Me_2SO$ ($\rho^* = 3.4$). Reversals in acidity order from that predicted by $\sigma^*$ constants were observed, however, for $PhSO_2$ vs. CN, PhS vs. PhO, $CH_3CO$ 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 $GCH_2CH_2NO_2$ 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 $GCH_2NO_2$ deviated widely from the Taft line. The general conclusion is drawn that, although $\sigma^*_{CH_2G}$ (or $\sigma_I$) 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 $G(CH_2)_nCO_2R$ [or an equilibrium acidities in water of acids of the type $G(CH_2)_nCO_2H$] where $n$ is 0, 1, or 2.[1] Stated in terms of equilibrium acidity constants the Taft relationship is given by the equation

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

where $\sigma^*$ represents the polar (i.e., inductive) effect of G and $\rho^*$ represents the sensitivity of the system to structural changes.

The $\sigma^*$'s for hydrogen and alkyl points ($\sigma^*_{Me} = 0$) were derived from $G(CH_2)_nCO_2R$ systems where $n = 0$. Most of the $\sigma^*$ constants for substituents containing heteroatoms (Cl, F, O, S, etc.) were derived from data where $n = 1$, but in some instances ($CCl_3$, $CO_2Me$, and $COCH_3$, as well as Ph and $CH{=}CHMe$) $\sigma^*$'s were derived from $n = 0$. In three instances ($COCH_3$, Ph, and $CH{=}CHMe$) these $\sigma^*_G$ constants were shown to be related to $\sigma^*_{CH_2G}$ 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 $\sigma^*_{CH_2G}$ and $\sigma^*_{CH_2CH_2G}$ constants when G is Ph or $CF_3$.

Although the Taft equation has enjoyed considerable success,[3] two fundamental problems have arisen. The first relates to the question of whether or not $\sigma^*_H$, $\sigma^*_R$, and $\sigma^*_G$ constants derived from data where H, R, or G is attached to an $sp^2$ carbon atom can be applied, as Taft did originally, to systems where these substituents are attached to an $sp^3$ carbon atom.[4] The second relates to the applicability of $\sigma^*$ constants to systems of differing geometry and the use of methylene transmission coefficients to relate $\sigma^*_G$, $\sigma^*_{CH_2G}$, $\sigma^*_{CH_2CH_2G}$, etc., constants. The first of these questions was discussed in the

0022-3263/78/1943-3101$01.00/0