

From Equilibrium Acidities to Radical Stabilization Energies

FREDERICK G. BORDWELL* AND XIAN-MAN ZHANG

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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Introduction

The DMSO Acidity Scale. In the present account, we will show how our research has evolved over the past two decades from the development of a general acidity scale for organic compounds in dimethyl sulfoxide (DMSO) to the estimation of the relative stabilization energies of radicals. In the 1970's, we established an acidity scale in DMSO covering the pK_{HA} range from 2 to 32 using different families of about 30 overlapping indicators including fluorenes, indenes, arylacetoneitriles, phenols, and anilines, and a like number of standard acids.¹ Our interest in establishing this scale was (a) to obtain equilibrium constants for weak acids (pK_{HA} values) that would be useful in understanding reaction mechanisms and (b) to examine the effects of structural changes on acidities and basicities of various classes of organic compounds. In the 1980's, studies were initiated on rates of reactions in DMSO between individual electrophiles with families of bases for which the pK_{HA} values provide quantitative basicities. These studies led to the development of linear correlations of rates of reactions with pK_{HA} values (Brønsted relationships) and eventually to the combination of pK_{HA} values with electrochemical data in order to obtain estimates of relative radical stabilization energies.

The Brønsted Equation. The term *nucleophilicity* refers to the relative rate of reaction of an electron donor with a given electrophile, as distinct from basicity, which refers to the relative affinity of an electron donor for a proton in an acid-base equilibrium. A quantitative relationship between rate and equilibrium constants was discovered by Brønsted and Pedersen in 1924.² They found that the rate constants for the catalytic decomposition of nitramide by a family of bases, such as carboxylate ions ($GCH_2CO_2^-$), could be linearly correlated with the acidities of their conjugate acids, pK_{HA} . This observation led to the discovery of general base catalysis and to the first linear free-energy relationship, which later became known as the

Brønsted equation:

$$\log k_{A^-} = \beta pK_{HA} + C$$

Hammett recognized the general nature of the Brønsted relationship in 1935 and showed that it could be applied to several reactions other than proton transfer, including methyl transfers from CH_3I to a series of $ArN(CH_3)_2$ bases.³ But, with few exceptions, the equation has been applied exclusively to correlate rates of H_T^+ to a series of bases in aqueous solutions. Our studies in DMSO showed the Brønsted relationship to be the most precise of all the linear free-energy relationships.⁴ This was not the prevailing view in the 1980's, as may be judged by the following comment made by C. D. Johnson at the Conference on Correlation Analysis held at the University of Hull, England, in 1982. "No self-respecting user of the Hammett equation would stand for the scatter present in Brønsted plots." At the time, it was common practice to use bases from different families, e.g., oxygen bases, nitrogen bases, and carbon bases with different steric and stereoelectronic properties to construct Brønsted plots. This did indeed lead to much scatter and to the conclusion, predicted by the reactivity-selectivity principle, that Brønsted plots should be curved.⁵ On the other hand, our work showed that, when bases belonging to a single family such as remotely substituted fluorenone ions were used in the rate studies in DMSO over substantial ranges, along with the pK_{HA} values in DMSO of the bases in that family, precise linear plots were obtained, thus negating the supposed curvature in plots over smaller ranges, such as those of Eigen,^{5c,d} which had been used as evidence supporting the reactivity-selectivity principle.⁶

Our research demonstrated that the Brønsted equation is applicable to *all* combinations of nucleophiles and electrophiles. For example, for 20 combinations of anions, including carbanions, nitranions, oxanions, and thianions, reacting with electrophiles in DMSO by S_N2 , S_N2' , $E2$, S_NAr , H_T^+ , or e_T^- mechanisms, the relative rate constants depend on only two factors: (a) the

Frederick G. Bordwell is Professor Emeritus and Research Fellow at Northwestern University. (For a biography summarizing his earlier work, see *Acc. Chem. Res.* 1988, 21, 456.) During the past five years, his research has been concerned principally with the combination of pK_{HA} and redox values measured in DMSO according to equations based on thermodynamic cycles to estimate: (a) radical cation acidities, (b) homolytic bond dissociation energies (BDEs) of weak organic acids, HA, and (c) BDEs of the H-A bonds in radical cations, $HA^{+\bullet}$, and radical anions, $HA^{\bullet-}$. The BDE_{HA} values have provided new insights into the relative stabilization energies of radicals.

Xian-Man Zhang was born on May 19, 1964, in a small mountain village in Zhejiang province, People's Republic of China. He earned his B.Sc. degree from the Chemistry Department of Lanzhou University, China, in 1984, and received both his M.Sc. degree (1987) and Ph.D. degree (1989) with Professor You-Cheng Liu and Professor Di-Lun Yang in the same university. He joined Professor F. G. Bordwell's group in 1989 as a postdoctoral research fellow. His research interests include single electron-transfer reaction mechanisms and the kinetic and thermodynamic stabilities of radicals and radical ions.

(1) Bordwell, F. G. *Acc. Chem. Res.* 1988, 21, 456-463. References are given in this paper to acidity scales in other media, to the effects of ion pairing and homohydrogen bonding on pK_{HA} values, and to solvation effects on pK_{HA} values.

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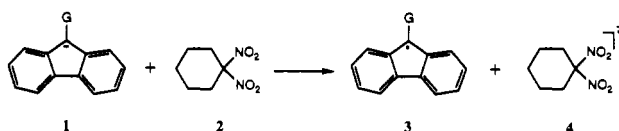
(3) Hammett, L. P. *Chem. Rev.* 1935, 17, 125-136.

(4) Bordwell, F. G.; Cripe, T. A.; Hughes, D. L. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series 215; American Chemical Society: Washington, DC 1985; pp 137-153.

(5) (a) Leffler, J. E.; Grunwald, E. *Rates and Equilibria in Organic Reactions*; Wiley: New York, 1964; pp 156-168. (b) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1959; Chapter X. (c) Ahrens, M. L.; Eigen, M.; Kruse, W.; Maas, G. *Ber. Bunsen-Ges. Phys. Chem.* 1980, 74, 380-385. (d) Jones, J. R. *The Ionization of Carbon Acids*; Academic Press: New York, 1973; Chapter 8.

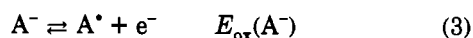
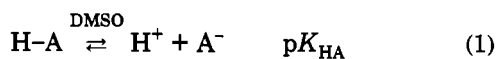
(6) Bordwell, F. G.; Branca, J. C.; Cripe, T. A. *Isr. J. Chem.* 1985, 26, 357-366.

basicity of the anion, as defined by the acidity of its conjugate acid, pK_{HA} , and (b) the sensitivity of the rate constant to changes in basicity, as measured by the slope of the line, the Brønsted β coefficient.⁴ These results showed the Brønsted equation to be not only the most precise but the *most general* of all the free-energy relationships. (The Hammett equation, as applied to reaction rates, is actually a less precise version of the Brønsted equation in which *m*- and *p*-substituted benzoate ions are arbitrarily used as bases instead of using the bases actually initiating the reaction.⁴) The Brønsted β coefficients, which measure the sensitivity of the reactions to changes in basicity, increase progressively in the above series of reactions from about 0.3 for S_N2 reactions to near unity for e_T^- reactions. For example, a plot of the rates of the e_T^- reaction ($\log k$) of 9-arylfuorenyl anions (1) with 1,1-dinitrocyclo-



hexane (2) versus the pK_{HA} values of the anions was linear with a slope near unity, and radical products (e.g., the dimer of 3) were formed.⁷ It seemed reasonable to expect that an electrode could be used in place of 2 as a single electron acceptor. A plot of $\log k$ for the reaction 1 with 2 versus the oxidation potentials, $E_{ox}(A^-)$, of the anions (1) did indeed prove to be linear with a slope near unity;⁷ it followed that a plot $E_{ox}(A^-)$ versus pK_{HA} must be linear.

Estimates of Relative Radical Stabilization Energies. Comparisons of pK_{HA} values of weak organic acids in DMSO (eq 1) usually provide reasonable



estimates of relative anion stabilities, but the comparable equilibria for radicals (eq 2) can seldom be measured because of their high reactivities. Comparisons of the oxidation potentials of anions, $E_{ox}(A^-)$ (eq 3), can provide information concerning estimates of relative radical stabilization energies (RSEs), however. For example, a plot of $E_{ox}(A^-)$ vs pK_{HA} for 2- and 2,7-substituted (meta) fluorenyl anions has been shown to be linear with a slope near unity over a range of about 13 kcal/mol (Figure 1).⁸ (Henceforth kcal/mol will be abbreviated as kcal.) This means that for every 1 kcal (~ 0.7 pK_{HA} unit) increase in fluorenyl anion basicity there is an $E_{ox}(A^-)$ shift of 1 kcal (~ 40 mV) to a more negative potential. In other words, these meta substituents affect oxidation potentials only by increasing or decreasing anion basicity. On the other hand,

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(8) (a) Bausch, M. J. Ph.D. Dissertation, Northwestern University, June 1984. (b) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979-1985. The ΔAOP values given in this table are equivalent to ΔBDE or RSE values in the present paper.

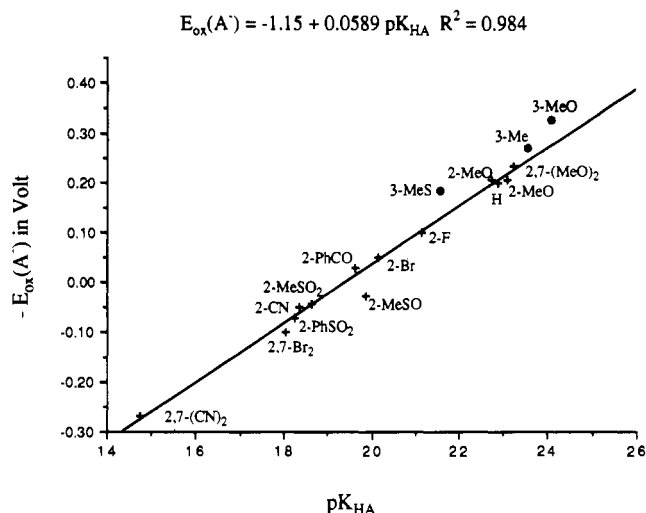
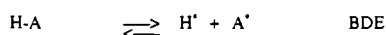
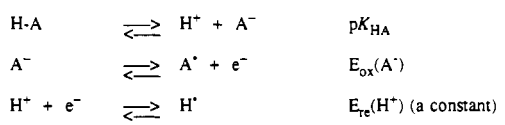


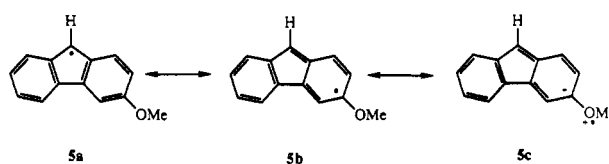
Figure 1. Plot of oxidation potentials [$E_{ox}(A^-)$] vs pK_{HA} values in DMSO solution for 2-substituted fluorenyl anions and 3-substituted fluorenyl anions.

Scheme I



$$\Delta \text{BDE} = 1.37 \Delta pK_{HA} + 23.1 \Delta E_{ox}(A^-) = \text{RSE}$$

examination of Figure 1 shows that points for 3-Me, 3-MeO, and 3-MeS groups (para electron donors) deviate from the line defined for the meta donors because their oxidation potentials are more negative than expected from their basicities. The rationale for these deviations in terms of relative RSEs is that the more negative $E_{ox}(A^-)$ values indicate that the radicals are stabilized by delocalization of the odd electron in the fluorenyl radical (e.g., 5a-c).



Gas-phase homolytic bond dissociation energies (BDEs) relative to that of a standard, such as the BDE of the C-H bond in methane (105 kcal), have long been considered to provide the best measures of RSEs.⁹ Brauman used a thermodynamic cycle similar to that shown in Scheme I to obtain gas-phase pK_{HA} values and to evaluate gas-phase homolytic bond dissociation energies.¹⁰ and Friedrich demonstrated that this cycle can also be used to estimate BDEs in solution.¹¹ In our laboratory, Bausch adapted the cycle to obtain RSEs for fluorenyl and a variety of other radicals.⁸

(9) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532. (b) Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 731-732. (c) O'Neal, H. E.; Bensen, S. W. In *Free Radicals*; Koshi, J. K., Ed.; Wiley: New York, 1973; Vol. II.

(10) (a) Janousek, B. K.; Reed, K. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125-3129. (b) Janousek, B. K.; Brauman, J. I. In *Gas-Phase Ion Chemistry*; Bowers, W. A., Ed.; Academic Press: New York, 1979; p 53.

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Table I. Equilibrium Acidities in DMSO for 3- and 9-Substituted Fluorenes, Oxidation Potentials of Their Conjugate Bases, and Δ BDE (RSE) Values for 3-G-FIH \cdot and 9-G-FI \cdot Radicals

G	pK _{HA} ^a	Δ pK _{HA} ^b	$E_{ox}(A^-)$ ^a (V)	$\Delta E_{ox}(A^-)$ ^b (V)	Δ BDE = RSE ^c (kcal)
H	22.6	(0.0)	-1.069	(0.0)	(0.0)
3-Me	23.4	-1.1	-1.134	1.5	0.4
3-MeO	23.95	-1.84	-1.191	2.8	1.0
3-MeS	21.45	+1.57	-1.047	-0.51	1.1
9-Me	22.3	0.82	-1.230	3.72	4.5
9-MeO	22.1	1.1	-1.324	5.89	7.0
9-Me ₂ N	22.5	0.55	-1.535	10.2	10.7
9-MeS	18.0	6.7	-1.001	-1.3	5.4
9-PhS	15.4	10.3	-0.849	-5.1	5.2
9-Ph	17.9	6.85	-1.028	-0.94	5.9
9-Me ₃ N ⁺	17.8 ^d	7.0	-0.563 ^d	-11.7	-4.7
9-PyN ⁺	11.8 ^d	15.2	-0.370 ^d	-16.2	-1.0
9-H ₂ NCO	11.9	15.1	-0.512	-12.8	2.3
9-MeOCO	10.35	17.0	-0.492	-13.3	3.9
9-MeCO	10.8	16.2	-0.478	-13.7	2.5
9-CN	8.3	20.0	-0.448	-14.3	5.7
9-PhSO ₂	11.5	15.6	-0.309	-17.5	-2.1

^a Reference 8b, unless otherwise indicated. The oxidation potentials in this table were referenced to the ferrocenium/ferrocene couple by substitution of 0.875 V.^{17c} ^b In kcal/mol, statistically corrected for Δ pK_{HA}. ^c Estimated by using eq 4. ^d Zhang, X.-M.; Bordwell, F. G.; Van Der Puy, M.; Fried, H. E. *J. Org. Chem.* 1993, 58, 3060-3066.

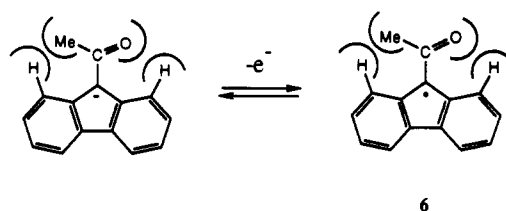
Application of eq 4 to estimate RSEs of some 3- and 9-substituted fluorenyl radicals, 3-G-FIH \cdot and 9-G-FI \cdot , relative to the RSE of the fluorenyl radical (G = H) are shown in Table I.^{8b}

$$\Delta\text{BDE} = 1.37\Delta\text{p}K_{\text{HA}} + 23.1\Delta E_{\text{ox}}(A^-) = \text{RSE} \quad (4)$$

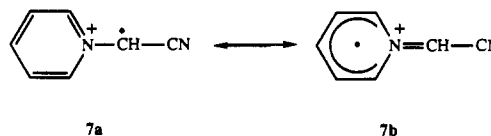
An examination of eq 4 shows that the RSEs of the 3-G-FIH \cdot and 9-G-FI \cdot radicals are determined by the sum of Δ pK_{HA} and $\Delta E_{\text{ox}}(A^-)$, each expressed in kcal. Figure 1 and other plots of this type¹² show that there is an intrinsic relationship between carbanion oxidation potentials and their basicities. In comparing substituent effects on RSEs, this means that the Δ pK_{HA} values can provide an evaluation of the effects of changing the anion basicity on oxidation potentials and RSEs. These values (in kcal) are then added to the $\Delta E_{\text{ox}}(A^-)$ values, which provide an estimate of electronic and steric factors on the RSEs. It will be instructive, therefore, to see how different kinds of substituents affect the Δ pK_{HA} and $\Delta E_{\text{ox}}(A^-)$ values.

From Table I we see that the 3-Me and 3-MeO groups increase the basicity of the fluorenyl anion by 1.10 and 1.84 kcal, respectively, which tends to increase the BDEs and to decrease the Δ BDEs (RSEs) of the corresponding radicals by these amounts. These effects are overshadowed, however, by the shifts in $E_{\text{ox}}(A^-)$ values to more negative potentials, which tend to decrease the BDEs and increase the RSEs by 1.5 and 2.8 kcal, respectively. The net effect is an increase in the RSEs for 3-Me-FIH \cdot and 3-MeO-FIH \cdot radicals by 0.4 and 1.0 kcal, respectively. On the other hand, the 1.1-kcal increase in RSE caused by the 3-MeS group is due entirely to a decrease of 1.57 kcal in the basicity of the

3-MeS-FIH \cdot anion. The $E_{\text{ox}}(A^-)$ of this anion is actually shifted to a more positive potential by 0.51 kcal, leading to a net increase in RSE of 1.1 kcal. The effects of these donor groups when placed in the 9 position of fluorene are much greater because they are attached to the site of highest electron density. For 9-Me \cdot and 9-MeO-FI \cdot ions, the negative shifts in $E_{\text{ox}}(A^-)$ cause increases of 3.7 and 5.9 kcal in BDE, respectively, and the Δ pK_{HA} values are small positive values rather than the small negative values observed for the 3 substituents. This leads to RSEs of 4.5 and 7.0, respectively. The Δ pK_{HA} for 9-MeS is positive and large (6.7 kcal), leading to a 5.4-kcal increase in RSE. The 9-Me₂N group causes the largest increase in RSE (10.2 kcal) due almost entirely to its effect on $\Delta E_{\text{ox}}(A^-)$, and the 9-Me₃N⁺ group causes the largest decrease in RSE (-4.7 kcal), caused primarily by its effect on $\Delta E_{\text{ox}}(A^-)$. The 9-Me₃N⁺, 9-pyridinium (9-PyN⁺), and 9-PhSO₂ groups destabilize fluorenyl radicals as a consequence of their powerful electron-withdrawing effects. (Radicals are electron deficient and are therefore destabilized by electron withdrawal.) The 9-Ph group exerts its radical stabilizing effect almost entirely by its ability to lower the basicity of the fluorenyl anion, and this is also the primary mode of action of the 9-PhS group. The strong electron-withdrawing groups 9-H₂NCO, 9-MeOCO, and 9-MeCO increase the acidity by 15-17 kcal, which tends to increase the RSEs, but these effects are largely offset by positive shifts in $\Delta E_{\text{ox}}(A^-)$ of 12.8-13.7 kcal. The delocalizing effects of 9-MeCO and related groups are attenuated by steric interference with the peri hydrogen atoms at the C-1 and C-8 positions of the fluorene ring which prevents optimum orbital overlap (e.g., 6). The RSE of the 9-CN-FI \cdot radical is larger (5.7 kcal vs 2.3-3.9 kcal) because the linear nature of the C \equiv N group causes minimal steric inhibition of resonance.



Most substituents play a dual role in affecting radical stability, stabilizing by virtue of their delocalizing ability but destabilizing by virtue of their electron-withdrawing ability. The PyN⁺ group serves as a prototype in this regard in that the nature of the two effects becomes obvious in comparing the effects of PyN⁺ and Me₃N⁺ groups in, for example, PyN⁺C \cdot H-CN and Me₃N⁺C \cdot H-CN radicals. The latter radical, where only the electron-withdrawing effect is operative, is destabilized by 2.3 kcal, whereas in the PyN⁺C \cdot H-CN radical, the delocalizing effect (7a-b)



(12) The existence of a linear relationship between $E_{\text{ox}}(A^-)$ and pK_{HA} with a slope near unity has been supported by the discovery of several plots of this kind for other carbanion families where substituent effects on radical stabilities are small.

(13) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* 1989, 111, 7558-7562.

overshadows the electron-withdrawing effect and leads

to a net stabilizing effect of 5.4 kcal.¹⁴ Note, however, that in the 9-PyN⁺-Fl[•] radical steric hindrance to resonance leads to a net 1-kcal destabilizing effect (Table I).

The large destabilizing effect of steric inhibition of resonance illustrated in 6 is brought out further by observing the effects of increasing the bulk of the R and R' groups in 9-RR'N-Fl[•] radicals. The changes in RSEs relative to the fluorenyl radical (in kcal) are as follows: H₂N, 15; MeHN, 13.5; Me₂N, 7.7; *i*-Pr₂N, 5.3.¹³ Since the BDE of the 9-C-H bond in fluorene is decreased by 25 kcal, relative to the C-H bond in methane, this places the BDE of the 9-C-H bond in 9-H₂N-FlH at 40 kcal below that in methane.

Comparison of BDEs in DMSO with Gas-Phase BDEs. It was desirable to cast eq 4 in terms of ΔH° , instead of ΔG° , in order to allow comparison with gas-phase BDEs. Equation 5 was devised for this purpose.¹⁵

$$\text{BDE} = 1.37pK_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-) + C \quad (5)$$

In order to evaluate the constant *C*, the $E_{\text{ox}}(\text{A}^-)$ values in DMSO were first related to the standard hydrogen electrode (SHE) in aqueous solution. An equation devised by Nicholas and Arnold¹⁶ was then used to estimate *C* from the sum of $\Delta G^\circ_{\text{f}}(\text{H}^\bullet)$, $\Delta G^\circ_{\text{sol}}(\text{H}^\bullet)$, and $\Delta G^\circ_{\text{tr}}(\text{H}^\bullet)$ from H₂O to DMSO, together with an estimate of the size of $T\Delta S^\circ$. In this way, a value of *C* of 56 kcal was arrived at, but this value was subject to considerable uncertainty, since the $\Delta G^\circ_{\text{sol}}(\text{H}^\bullet)$ and $\Delta G^\circ_{\text{tr}}(\text{H}^\bullet)$ terms were not well defined and it seemed likely that the $T\Delta S^\circ$ term would vary with the nature of A⁻. When it became apparent later that there is no precise thermodynamic way of relating $E_{\text{ox}}(\text{A}^-)$ values in DMSO to SHE values in H₂O, we concluded that *C* must be considered to be empirical.¹⁷ Nevertheless, for the 18 weak acids where literature gas-phase BDE values for the acidic H-A bonds were available (Table II), agreement to within ± 2 kcal was observed for all but three (Ph₃CH, PhNH₂, and PhOH).^{17c} For Ph₃CH and PhNH₂, the literature values were shown to be wrong or suspect. In all, the BDEs for the acidic H-A bonds in 32 acids have been established to ± 2 kcal in this one study. The $E_{\text{ox}}(\text{A}^-)$ value of the ferrocene/ferrocenium (Fc/Fc⁺) couple (875 mV on our instrument) was adopted as a reference standard in order to make comparisons easier with data from other laboratories. This necessitated changing *C* in eq 5 from 56 to 73.3.^{17c} When the best gas-phase BDE values for the 15 weak acids (Table II) were plotted against the sum, $1.37pK_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-)$, taken from our estimate of these BDEs using eq 5, a linear plot was obtained with an intercept (constant *C*) of 56 kcal when the oxidation potentials, $E_{\text{ox}}(\text{A}^-)$, were referred to SHE and with an intercept (constant *C*) of 73.3 kcal when the oxidation potentials were referred to the Fc/Fc⁺ couple. While the exact agreement is fortuitous, it is clear that the

Table II. Comparison of BDEs of the Acidic H-A Bonds in DMSO with Their Gas-Phase BDEs^a

weak acids	pK _{HA}	BDE ^a (kcal)	BDE (lit.) ^b (kcal)
diphenylmethane	32.2	82 ± 1	81.4 ± 1
9-methylanthracene	31.1	81.5	81.8 ± 1.5
aniline	30.6	92 ± 1	88 ± 2
9,10-dihydroanthracene	30.1	78	78
xanthene	30.0	75.5	74
<i>N</i> -methylaniline	29.5	89	87.5 ± 2
2-benzylpyridine	28.7	82	82.3
4-benzylpyridine	26.7	83	82.3
acetone	26.5	94	92 ± 2
diphenylamine	24.95	87.5 ± 1	87.3
pyrrole	23.05	97	99 ± 6
2,3-benzofluorene	23.1	78.4	78.8
fluorene	22.6	80 ± 1	80.1
1,3-cyclopentadiene	18.0	81	81.2
thiophenol	10.3	79 ± 1	78.5
hydrazoic acid	7.9	94	92 ± 2

^a Estimated by using eq 5. ^b For detailed literature sources, see ref 17c.

empirical value of 56 (or 73.3) for *C* is valid for estimating BDEs by eq 5. The good agreement between BDEs in DMSO and the gas phase even extends to aqueous solution.¹⁸ The rationale here is that the solvation energies of the neutral acid, HA, and the radicals in the equilibrium, $\text{HA} \rightleftharpoons \text{H}^\bullet + \text{A}^\bullet$, evidently cancel one another. The good agreement between the BDEs in DMSO and the gas phase allows us to relate the RSEs of the 9-G-Fl[•] radicals to that of the CH₃[•] radical. For example, the ΔBDE (RSE) for H-FlH vs H₃C-H (BDE = 105 kcal) is 105 - 80 = 25 kcal.

α -Substituent Effects on Methyl Radicals. The effects of substituents when attached directly to a carbon-centered radical have been examined by theoretical calculations^{19,20} and by a number of experimental approaches, including the thermolysis of azo compounds²¹ and a variety of gas-phase methods.⁹ Maximum effects are expected for substituted methyl radicals, GCH₂[•], and a scale of radical stabilization energies (RSEs) based primarily on gas-phase ΔBDEs , relative to that of the C-H bond in methane (105 kcal), is shown in Table III.⁹

Examination of Table III shows that the experimental RSE values in columns 3 and 7 are usually about twice as large as the calculated RSE values (columns 4 and 8), presumably because of the difficulty in the calculations of taking into account electron correlations.²⁹ The calculated RSE values agree fairly well in order with the RSE values in columns 3 and 7 and agree reasonably well in size with the RSE values for 9-G-Fl[•] radicals, relative to that of the 9-H-Fl[•] radical (Table I). The latter are *expected* to be smaller than the RSEs for G-CH₂[•] radicals, however, because the 9-G-Fl[•] radicals are often subject to sizable steric inhibition of resonance. Also, the H-Fl[•] radical is about 25 kcal more stable than the CH₃[•] radical, so 9-G-Fl[•] radicals should be less sensitive than GCH₂[•] radicals to substituent

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Table III. Estimates of the Relative Radical Stabilization Energies (RSEs) of Substituted Methyl Radicals, GCH_2^{\cdot}

no.	G	RSE		no.	G	RSE ^a (kcal)	RSE (calcd) ^b (kcal)
		RSE ^a (kcal)	(calcd) ^b (kcal)				
0	H	(0.0)	(0.0)	0	H	(0.0)	(0.0)
1	F	3	1.6	11	H ₂ N	22 ^c	
2	Cl	4	2.6	12	MeNH	18 ^c	
3	Me	7	3.3	13	Me ₂ N	21 ^c	
4	PhSe	7 ^c		14	F ₃ CSO ₂	2	
5	MeO	12	5.3	15	PhSO ₂	6 ^c	-0.8 (HSO ₂)
6	HO	11	5.7	16	NO ₂	7 ^c	1.7
7	RS	12 ^c	5.7 (SH)	17	CN	12 (10) ^c	5.3
8	PhS	12 ^c		18	MeOCO	10	5.7 (CO ₂ H)
9	Ph	17		19	MeCO	11	
10	CH ₂ =CH	19 ^c		20	PhCO	12 ^b	5.7 (HCO)

^a Reference 9 unless otherwise noted. ^b References 19 and 20. ^c See ref 30.

effects because they are subject to "saturation" or "leveling" effects.

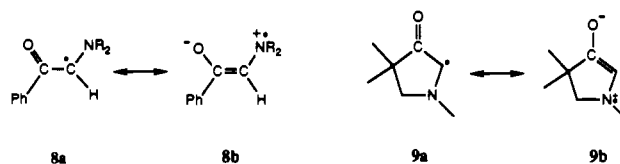
The donor effects in Table III increase in the same order, Me < MeO < Me₂N, as was observed in Table I, but are about twice as large. Acceptor effects increase in the order PhSO₂ < NO₂ < MeOCO, CN < RCO. The Ph, MeOCO, and RCO (but not CN) effects in Table I are much smaller primarily because of steric inhibition of resonance. The effects of RS and PhS are about the same size as that of MeO.

RSEs of Secondary and Tertiary Carbon-Centered Radicals. Dewar first pointed out that extended delocalization of the odd electron was possible in some secondary radicals.²² Qualitative evidence for unusual stability of radicals of this kind was first provided by Balaban,²³ who called it push-pull resonance, and later by Katritzky,²⁴ who called it merostabilization. In the period 1979-1986, Viehe and his colleagues provided many additional qualitative examples, gave it a new name, "the captodative effect", and predicted from qualitative theory that the effects of attachment of donor and acceptor groups to a radical center would always be more than additive.²⁵ In their recent review of the "captodative effect", Sustmann and Korth have (a) questioned the use of Δ BDEs in this context because ground-state effects have not been taken into account, (b) questioned the use of theory because of insufficient electron correlations, and (c) concluded that their ESR data on tertiary PhC[•]XY radicals constitute the only unambiguous case for synergism between the donors and acceptors in carbon-centered radicals.²⁶

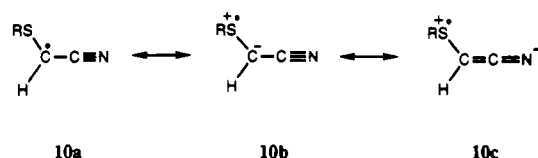
It will be of interest to see whether various combinations of the Me₂N, PhCO, and Ph groups, which provide the strongest stabilization of methyl radicals, will give secondary radicals where their effects are additive, less than additive, or more than additive. The radical stabilizing energy of the α -PhCO group in the PhCOCH₂[•] radical is 12 kcal (Table III), and the presence of an additional Ph group, as in the PhCOC[•]-HPh radical, increases the radical stability by another

10 kcal,^{27a,b} but the combined effects of these groups is only 22 kcal, whereas the sum of the individual effects (Table III) on the methyl radical is 12 + 17 = 29 kcal. The odd electron in the PhCOC[•]HCOPh radical can be delocalized to both carbonyl groups, but our Δ BDE data indicate that the presence of the second PhCO group provides *no* additional stabilization.²⁷ Analysis of the effects on ΔpK_{HA} and $\Delta E_{ox}(A^{\cdot-})$ by the method used to analyze the data in Table I suggests that these two effects cancel one another.²⁷

On the other hand, our Δ BDE measurements indicate that the presence of the strong Me₂N donor in the PhCOC[•]HNMe₂ radical increases the stability by 21 kcal over that of the PhCOCH₂[•] radical, an effect equal to the stabilization of the methyl radical by the Me₂N group!^{13,28} The donor groups MeO, PhS, and RS also have as large stabilizing effects on PhCOC[•]HG radicals as they have on methyl radicals.³⁰ There is evidence to indicate that the stabilizing effects in these instances may be augmented by an electrostatic effect between the negatively charged oxygen atom and the positively charged nitrogen in the *Z* conformation **8b**.^{28,30} In the



analogous cyclic structure (**9b**), an *E* conformation is enforced, and the Δ BDE decreases from 21 to about 11 kcal.²⁸ Pasto has calculated that the electrostatic effect in **8b** will stabilize the radical by about 5 kcal in the gas phase.²⁹ These results show that in special cases the effects in donor-C[•]H-acceptor type carbon-centered radicals may equal the sum of those in the corresponding methyl radicals. On the other hand, in radicals of the type 10, where the electrostatic effect is minimal, the



Δ BDE is about 19 kcal,³⁰ compared to about 23 kcal for the sum of the individual effects. Introducing a second α -CN group into the CNCH₂[•] radical to give N \equiv C-C[•]-HC \equiv N appears to stabilize the radical by an additional 4 kcal. Another special case has been found when the effects of MeO and CN groups on the BDE interact through the π system of the central ring of anthracene where the combined effect has been shown to be greater than the sum of the individual effects.³¹

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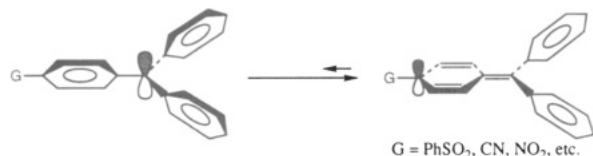
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The analysis of the effects of substituents on the stabilities of tertiary radicals is usually complicated by steric inhibition of resonance and/or cross conjugative effects. The GCH(CN)₂ substrate provides one of the simplest systems of this type for study because the two CN groups have minimal steric demands and the C(CN)₂ moiety can be considered to act as a strong acceptor unit. The Me₂NC*(CN)₂ radical has been cited as being remarkably persistent by virtue of the presence of a captodative effect.^{25b} The BDE of the H-C bond in H-CH(CN)₂ is estimated by eq 5 to be 90 kcal. Substitution of a Me₂N group for one of the hydrogen atoms gives Me₂NCH(CN)₂, which is estimated by eq 5 to have a BDE of 74 kcal.¹³ The BDE is therefore 31 kcal smaller than that of CH₃-H but 5 kcal less than the sum of the individual Me₂NCH₂-H and H-CH(CN)₂ ΔBDEs (21 + 15 = 36 kcal). The presence of two donor groups with larger steric demands in a tertiary radical, as for the changes from (a) PhSC*HPh to PhSC*Ph₂, (b) PhSC*HCOPh to (PhS)₂C*COPh, or (c) (c-C₅H₁₀N)C*HCOPh to (c-C₅H₁₀N)₂C*COPh, increase the RSEs by only 1.5, 1, and 0 kcal, respectively. Evidently the stabilizing effect of the third group in these radicals is almost completely damped out by steric and saturation effects.³⁰

In the highly congested *p*-GC₆H₄C*Ph₂ radicals, we find that the substituents have negligible effects on RSEs because the phenyl groups that bear a para substituent are twisted with respect to the p orbital on the carbon atom bearing the odd electron.³² In contrast, electron-withdrawing groups such as *p*-NO₂, *p*-PhCO, or *p*-PhSO₂ in the corresponding carbanions, *p*-GC₆H₄C-Ph₂, cause increases in acidity that are larger than those in the noncongested arylacetonitrile family.³² The large effects are a consequence of strong solvation of these para substituents, as well as the carbanion center, which causes the benzene ring to adopt a conformation where maximum overlap between the carbanion p orbital and the substituent orbitals can be achieved because of substituent solvation assisted resonance (SSAR) effects.³³



Plots of $E_{ox}(A^-)$ vs pK_{HA} for congested substrates such as triphenylmethanes, *p*-GC₆H₄CHPh₂,³² or meta and para α -*N*-morpholinylarylacetonitriles, *c*-(OC₄H₈N)-CH(CN)C₆H₄G,³⁴ are linear with a slope near unity as in Figure 1, indicating that the effects of most substituents on the RSEs in these radicals are small.

Stereoelectronic Factors in Stabilizing or Destabilizing Anions and Radicals. The rate of removal of either a proton or a hydrogen atom from a C-H bond adjacent to a nitrogen or oxygen atom has been shown to be subject to stereoelectronic control

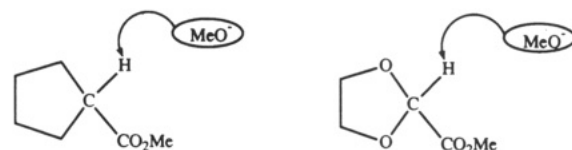
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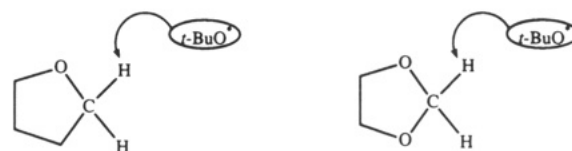
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Scheme II

Stereolectronic Kinetic Effects



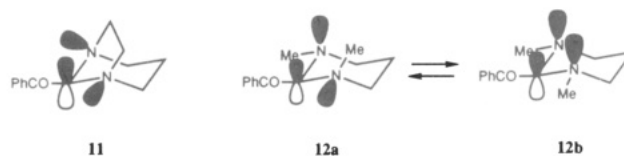
Two oxygens cause a ~5 fold rate retardation.³⁵



The second oxygen atom causes ~9 fold rate acceleration.^{37b}

because of interactions of the lone pairs on these atoms with the carbanion or carbon-centered radical being formed. The size of the destabilizing effect in carbanion formation will depend in the dihedral angle between the p (or sp³) orbital of the carbanion and the lone-pair orbital on nitrogen or oxygen, being maximal when the angle is 0° and minimal when it is 90°. In radical formation, these interactions are stabilizing because of the formation of a three-electron bond.³⁶ The stereoelectronic theory has been supported by the observation of rate retardations in the removal of a proton and rate accelerations in the removal of a hydrogen atom,^{35,37} but these effects are small, as is brought out in Scheme II.

A comparison of the differences in ΔpK_{HA} and ΔBDE values for compounds 11 and 12 has provided striking evidence concerning stereoelectronic effects on anion and radical stabilities.³⁹ In the anion of 12, the darkened



orbitals contain two electrons, and four electron repulsions involving the filled p orbital of the carbanion exist in both conformations 12a,b. In 11, the ethano bridge forces the two orbitals bearing the nitrogen lone pairs to be essentially orthogonal to the p orbital of the carbanion. As a consequence, the conjugate acid of 11

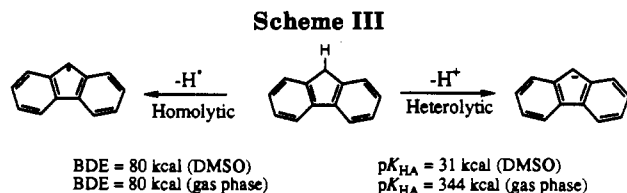
(35) Hine and Dalsin (Hine, J.; Dalsin, P. D. *J. Am. Chem. Soc.* **1972**, *94*, 6998-7002) observed a 5-fold rate retardation for α -deprotonation by the MeO⁻ ion in MeOH of methyl 1,3-dioxolane-2-carboxylate relative to methyl cyclopentane-2-carboxylate.

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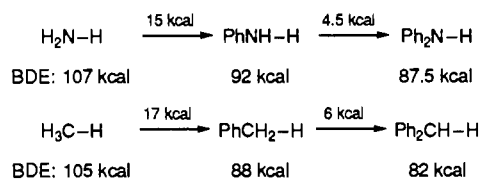
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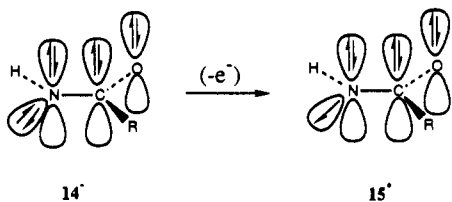
is stronger than the conjugate acid of **12** by 2.7 kcal. In the radical, the carbon p orbital contains only one electron, and the overlap with the lone pair orbitals on nitrogen in **12a,b** gives a three-electron bond that is stabilizing, whereas the orthogonal orientation of the orbitals in **11** is less stabilizing by 16 kcal! These are the only comparisons of the type of which we are aware, but it seems likely that *stereoelectronic effects of radicals will generally be much larger than those of analogous anions because the latter will be greatly attenuated by solvent effects.*

The domination of solvation forces on anions as opposed to radicals can be illustrated by the comparison of the heterolytic and homolytic bond dissociation energies of the acidic C–H bond in fluorene in the gas phase and in DMSO solution, as shown in Scheme III.

Donor and Acceptor Effects on Nitrogen-Centered Radicals. Phenyl substituent effects on the BDEs of ammonia and aniline have been shown to be similar to those observed on the BDEs of methane and toluene,^{17c} as shown below:



We expected, therefore, that nitrogen-centered radicals would also be stabilized by acceptor groups such as α -PhCO. But an estimate of the BDE of the N–H bond in the carboxamide, PhCONH–H, gave a value within experimental error of that in $\text{H}_2\text{N}-\text{H}$ (107 kcal), and this was true also of the BDE of the N–H bond in acetamide. On the other hand, our estimates indicate that the CN moiety in $\text{H}-\text{NHC}\equiv\text{N}$ weakens the H–N bond by 8 kcal,⁴⁰ which is within experimental error of the ΔBDE for the H–C bond in $\text{H}-\text{CH}_2\text{C}\equiv\text{N}$. A possible rationale is that strong conjugation in the carboxamide anion ($\text{HN}=\text{C}=\text{O} \leftrightarrow \text{HN}=\text{C}-\text{O}^-$) requires the generation of the odd electron from the nitrogen lone-pair orbital orthogonal to the p orbital of the carbonyl group ($14^- \rightarrow 15^*$).^{17b}



In the $\text{HN}=\text{C}\equiv\text{N}$ anion, however, *both* lone-pair orbitals on nitrogen are conjugated with the $\text{C}\equiv\text{N}$ moiety, and the odd electron in the corresponding radical can conjugate with the $\text{C}\equiv\text{N}$ moiety ($\text{HN}^*-\text{C}\equiv\text{N} \leftrightarrow \text{HN}=\text{C}=\text{N}^*$). This postulate is consistent with

(40) Harrelson, J. A., Jr. Unpublished result.

observations indicating that an electron is abstracted from pyrrolide⁴¹ and carbazolide⁴² anions to give the corresponding σ radicals so as not to break up the $4n + 2\pi$ electron resonance in these aromatic anions. It is not consistent, however, with the conclusion derived from ESR spectroscopy that amidyl radicals [$\text{RN}^*\text{C}(=\text{O})\text{R}'$] are π , rather than σ , radicals.⁴³

The substitution of an OH or NH_2 group for one of the hydrogen atoms on nitrogen in benzamide leads to marked changes in the acidity and the BDE of the remaining N–H bond. For example, the N–H bond in benzohydroxamic acid, PhCONHOH, is 13 kcal more acidic (heterocyclic cleavage) in DMSO than the N–H bond in benzamide and is 19 kcal weaker toward homolytic cleavage. Similarly, the α -N–H bond in benzohydrazide, PhCONHNH₂, is 6.1 kcal weaker than the N–H bond in benzamide toward heterolytic cleavage and 26 kcal weaker toward homolytic cleavage.^{17b} These large effects on $\text{p}K_{\text{HA}}$ s and BDEs are believed to be due in part to a large increase in ground-state energy caused by four electron repulsions between the lone-pair electrons on the N–O or N–N moieties. Intramolecular hydrogen bonding in the benzohydroxamate anion probably accounts for the larger effect on acidity for PhCONHOH vs PhCONHNH₂, and the much greater ability of NH_2 than OH to stabilize an adjacent radical accounts for the greater weakening of the N–H bond in benzohydrazide than in benzohydroxamic acid.

Summary and Conclusions

1. The Brønsted equation, $\log k_{\text{A}^-} = \beta\text{p}K_{\text{HA}} + C$, where A^- is a nucleophile and $\text{p}K_{\text{HA}}$ is the equilibrium acidity constant of HA, is the first, the most general, and the most precise of all the linear free energy relationships. The Hammett equation can be considered to be a derivative of the Brønsted equation.

2. Linear plots of $E_{\text{ox}}(\text{A}^-)$ vs $\text{p}K_{\text{HA}}$ with slopes near unity (e.g., Figure 1) establish the presence of an intrinsic relationship between oxidation potentials of carbanions and their equilibrium acidities in DMSO.

3. A simple equation, based on a thermodynamic cycle, $\Delta\text{BDE} = 1.37\Delta\text{p}K_{\text{HA}} + 23.1\Delta E_{\text{ox}}(\text{A}^-)$, has been used to estimate relative homolytic bond dissociation energies of the acidic H–A bonds in families of weak acids, HA, relative to that of the family parent. The ΔBDE s are assumed to be equal to RSEs of the corresponding A^* radicals.

4. An equation, $\text{BDE} = 1.37 \text{p}K_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-) + C$, has given BDEs that agree with the best gas-phase BDEs within ± 2 kcal with few exceptions and allows BDEs between families of weak acids to be compared. This method can be used to estimate BDEs of the H–A bonds and RSEs of A^* radicals that would be difficult or impossible to obtain by other methods.

5. In solution, radicals are subject to much larger thermodynamic stereoelectronic effects than are analogous anions because the latter are subject to large solvent leveling effects.

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6. Substituent solvation assisted resonance (SSAR) effects can cause changes in conformations of anions, but not of analogous radicals.

7. The presence of both donor (D) and acceptor (A) groups on a carbon-centered radical (D-C[•]-A) generally causes stabilizing effects that are larger than either of the individual effects on methyl radicals. The combined stabilizing effects are usually less, but rarely more than additive.

8. Nitrogen-centered radicals fail to be stabilized by α -C=O groups, as in the PhCONH[•] radical, relative to the NH₂[•] radical, whereas the HN[•]C≡N radical is stabilized by 8 kcal and the PhCOCH₂[•] radical is stabilized by 12 kcal, relative to the CH₃[•] radical.

9. The CH₃CONH[•] radical is stabilized by 17 and 25 kcal by substitution of the hydrogen atom on nitrogen

by MeO or NH₂ groups, respectively. These effects are about 5 kcal greater than the stabilizing effects of these groups on the CH₃COCH₂[•] radical.

10. The pyridinium group, *c*-C₆H₅N⁺, is a prototype for the dual effects displayed by most substituents on radical stabilities, i.e. destabilizing by virtue of their electron-withdrawing effects but stabilizing by virtue of their delocalizing effects.

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