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ACIDITIES OF RADICAL CATIONS DERIVED FROM ARYLACETONITRILES

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ABSTRACT

The equilibrium acidities of phenylacetonitrile, and 20 of its *m*- and *p*-substituted derivatives have been measured in Me_2SO solution. Their pK_a's plot linearly with those of the corresponding anilines. Combination of the pK_a's of these acids with their oxidation potentials, $E_{ox}(HA)$, and those of their conjugate bases, $E_{ox}(A^-)$, provide an estimate of the acidities of the corresponding radical cations. The p$K_{HA^{+\cdot}}$ values for $ArCH_2CN^{+\cdot}$, where Ar is Ph, 1- and 2-naphthyl, and 9-anthryl, are −32, −18·5, −17·5, and −11, respectively, compared to 21·9, 20·85, 20·65, and 19·8 for the corresponding $ArCH_2CN$ acids. Acidities of $PhCH(Me)CN^{+\cdot}$, $Ph_2CHCN^{+\cdot}$, 9-CN-FlH$^{+\cdot}$, and 9-CN-XnH$^{+\cdot}$ are −33, −35, −25, and −27, respectively, compared to 23·0, 17·5, 8·3, and 13·6 for the corresponding acids from which they were derived. The homolytic bond dissociation energies (BDEs) for the benzylic C—H bonds in these arylacetonitriles, estimated by combining pK_{HA} with $E_{ox}(A^-)$, fall in the range of 69 kcal/mol for 9-CN-XnH to 82 kcal/mol for $PhCH_2CN$. For $GC_6H_4CH_2CN^{+\cdot}$ radical cations the acidities are decreased, relative to G = H, when G is an electron donor substituent and increased when G is an acceptor. The BDEs of the benzylic C—H bonds in $GC_6H_4CH_2CN$ are weakened by up to 4 kcal/mol by *para* donors and strengthened by up to 1·2 kcal/mol by *m*- or *p*-acceptors. The significance of these changes in BDEs with regard to the use of σ' scales and the ΔAOP method for estimating substituent effects on radical stabilities is discussed.

INTRODUCTION

The cyano function is strongly electron-withdrawing and has minimal steric demands. Its introduction into any hydrocarbon acidifies the α-hydrogen atoms sufficiently to allow the pK_a of the resulting cyanocarbon to be measured in Me_2SO solution. For example, phenylacetonitrile is estimated to be about 21 pK_a units more acidic than toluene, which is much too weakly acidic to measure in Me_2SO. Our initial objective in this research, which was begun over 10 years ago, was to use $PhCH_2CN$ as a model for toluene in order to examine the effects on acidities (and on the corresponding conjugate carbanion stabilities) of: (a) introducing substituents into the benzene ring, (b) introducing substituents into the α-position, and (c) replacing the Ph group with naphthyl and other aryl substituents. More recently we have found that these acidity values, pK_{HA}, can be combined in two ways with oxidation potentials to estimate (a) the acidity of the corresponding radical cation, p$K_{HA^{+\cdot}}$, and (b) to estimate the homolytic bond dissociation energy (BDE) of the benzylic C—H bond in the

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acid. Equations (1) and (2), which are used to make these estimates, are both based on thermodynamic cycles.[1,2]

$$\mathrm{p}K_{\mathrm{HA}^{+\cdot}} = \mathrm{p}K_{\mathrm{HA}} + [E_{\mathrm{ox}}(\mathrm{A}^-) + E_{\mathrm{ox}}(\mathrm{HA})]23{\cdot}06/1{\cdot}37 \qquad (1)$$

$$\mathrm{BDE} = 1{\cdot}37\mathrm{p}K_{\mathrm{HA}} + 23{\cdot}06E_{\mathrm{ox}}(\mathrm{A}^-) + 55{\cdot}86 \qquad (2)$$

In these equations, $E_{\mathrm{ox}}(\mathrm{HA})$ is the oxidation potential of a weak acid, HA, and $E_{\mathrm{ox}}(\mathrm{A}^-)$ is the oxidation potential of its conjugate base, A^-, both measured in $\mathrm{Me_2SO}$ solution. The constant 55·86 in equation (2) represents the algebraic sum of: (a) the free energy of formation of the hydrogen atom, $\Delta G_{\mathrm{f}}{}^{\circ}(\mathrm{H}^{\cdot})_{\mathrm{g}}$, (b) the free energy of solvation of the hydrogen atom in water, $\Delta G^{\circ}{}_{\mathrm{sol}}(\mathrm{H}^{\cdot})$, (c) the free energy of the transfer of the proton from water to $\mathrm{Me_2SO}$, $\Delta G^{\circ}{}_{\mathrm{tr}}(\mathrm{H}^+)$, and (d) $T\Delta S^{\circ}$ at 25 °C.

The oxidation potentials of the arylacetonitriles for which acidity constants were available from previous work in our laboratory have now been measured in order to use equations (1) and (2) to obtain $\mathrm{p}K_{\mathrm{HA}^{+\cdot}}$ and BDE values.

There appears to be very little prior work in this area. The $\mathrm{p}K_{\mathrm{a}}$ value for $\mathrm{Ph_2CHCN}$ in $\mathrm{Me_2SO}$ measured in Shatenshtein's laboratory,[3] which agrees to within ±0·2 with that we have previously reported,[4] appears to constitute the total $\mathrm{p}K_{\mathrm{a}}$ literature. No prior literature on acidities of the radical cations derived from arylacetonitriles is available. No prior literature exists on estimates of BDE's of arylacetonitriles, but data are available for a number of the corresponding hydrocarbons. In a recent review McMillen and Golden have selected BDE values of 88, 85, and 80 kcal/mol for toluene, 1-methylnaphthalene, and 9-methylanthracene, respectively, as the best available values.[5] They also cite a 4 kcal/mol decrease in BDE for α-Ph substitution into toluene and a 3 kcal/mol decrease for α-Me substitution, as examples of substituent effects on BDEs.

There have been numerous studies of the effects of ring substituents on the rates of abstraction of benzylic hydrogen atoms in toluenes by radicals. Over 20 different radicals have been used in such rate studies, many of which give surprisingly good Hammett plots.[6] These correlations with (polar) σ constants have often been interpreted in terms of polar contributions to the transition states of the radical reactions. Dual parameter Hammett relationships, often combining $\sigma^+ \rho^+$ with $\sigma^{\cdot} \rho^{\cdot}$, have been used in attempts to factor out the polar contribution and assign $\sigma^{\cdot}$ values to substituents for use in radical reactions. The poor agreement between the various $\sigma^{\cdot}$ scales has been discussed by Dust and Arnold, who have established a $\sigma^{\cdot}{}_{\alpha}$ scale based on the effect of substituents on the hyperfine coupling constants of benzylic radicals.[7] In 1973 the observation that, for reactions of five different radicals with toluenes, the ρ values plot linearly with exothermicities prompted the suggestion that ρ is determined by the effect of the substituents on the C—H BDEs rather than by the polar nature of the transition state.[8] Because the ρ values are usually negative the assumption requires that electron-donor groups weaken and electron-withdrawing groups strengthen benzylic C—H bonds. Pryor and his coworkers have pointed out, however, that this assumption requires that ρ values for radical reactions *always* be negative, whereas they have found two cases where they are positive.[9] Nevertheless, in a study of reactions in cyclohexane wherein the benzylic hydrogen atoms in $\mathrm{ArCH_3}$ were abstracted by iodine atoms they found small differences in BDEs conforming to the Zavitsas and Pinto postulate,[8] i.e., 4-Me (85·2) < 4-*t*-Bu (85·5) < 3-Me, H (85·9) < 4-Cl (86·0) < 3-Cl, 3-Br (87·1).[9c] The conclusion has been drawn, therefore, that *both* polar factors and BDEs are important in determining the size of ρ.[9d] This is the only study of which we are aware wherein BDEs for remote substituents in toluenes have been measured. The present study provides additional information regarding the nature of the BDE-determined ρ.

RESULTS AND DISCUSSION

Effects of substituents on acidities in $GC_6H_4CH_2CN$

The results of acidity measurements in Me_2SO solution for phenylacetronitrile and 20 *meta*- and *para*-substituted phenylacetonitriles are shown in Table 1.

Table 1. Equilibrium acidities of substituted phenylacetonitrile, $GC_6H_4CH_2CN$ in Me_2SO solution at 25°

G	pK_{HA}[a]	G	pK_{HA}[a]
4-Me_2N	24·6	3-Cl	19·5
4-OCH_3	23·8	3-Br	19·4
4-CH_3	22·9	3-CF_3	19·2
4-F	22·2	3-CN	18·7
H	21·9	3-SO_2Ph	18·5
3-OCH_3	21·6	3-NO_2	18·1
4-Ph	20·8	4-COPh	16·0
4-Cl	20·5	4-CN	16·0
3-SPh	20·4	4-SO_2Ph	15·8
3-F	20·0	4-NO_2	12·3
4-SPh	19·6		

[a] J. C. Branca, Ph.D. Dissertation, Northwestern University, 1979. Most determinations were made using two or more indicators. See reference 12 and references cited therein for further details.

A Hammett plot including points for 9 *meta* substituents and hydrogen is shown in Figure 1. The σ constant for the *m*-OCH_3 point is that derived from acidities of acetophenones in Me_2SO.[10] The small deviations for 4-OCH_3, 4-CH_3, and 4-F points are in the range of the usual scatter in Hammett plots. The significant deviations for the 4-Ph, 4-PhS, 4-PhCO, 4-CN, 4-$PhSO_2$, and 4-NO_2 points are similar to those observed for Hammett plots of acidities of phenoxides and anilines in Me_2SO solution. A plot of pK_a's of anilines[11] vs. arylacetonitriles is nicely linear for all points, where the data are available, with a slope of 1·03 (R^2 = 0·95) (Figure 2). This plot reveals a remarkable similarity in the sensitivities of these nitranions and carbanions to substituent changes. The similarity of the slopes in the Hammett plots for *meta* substituents show that ρ values remain essentially constant for phenols,[12] arylacetonitriles, and anilines, even though the acidities change over progressively higher ranges (14 to 18, 18 to 22, and 27 to 31, respectively). Evidently the size of the *meta* substituent effects does not change with either the nature of the atom at the acidic site or with its basicity. The deviations of the electron-withdrawing group points from the line in Figure 1 are now believed to be caused in part by substituent solvation assisted resonance (SSAR) effects.[13] The close fit of the points

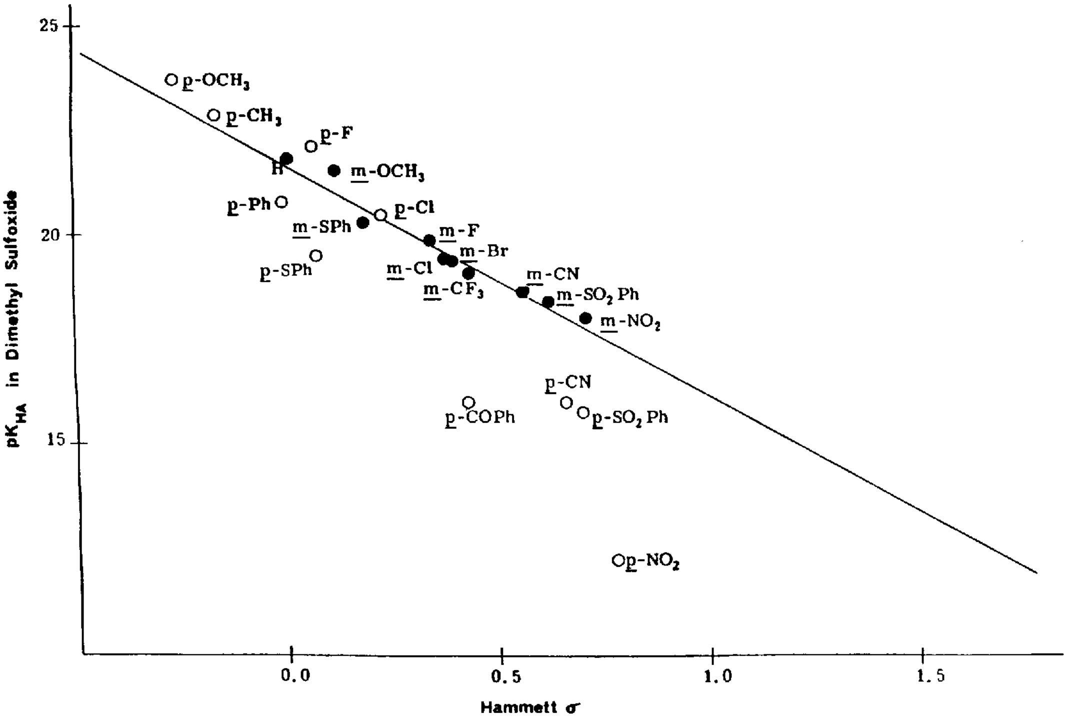


Figure 1. Hammett plot for *m*-substituted phenylacetonitriles. The deviations for the *para* electron acceptors are attributed to SSAR effects (see text). Darkened points alone were included in the correlation

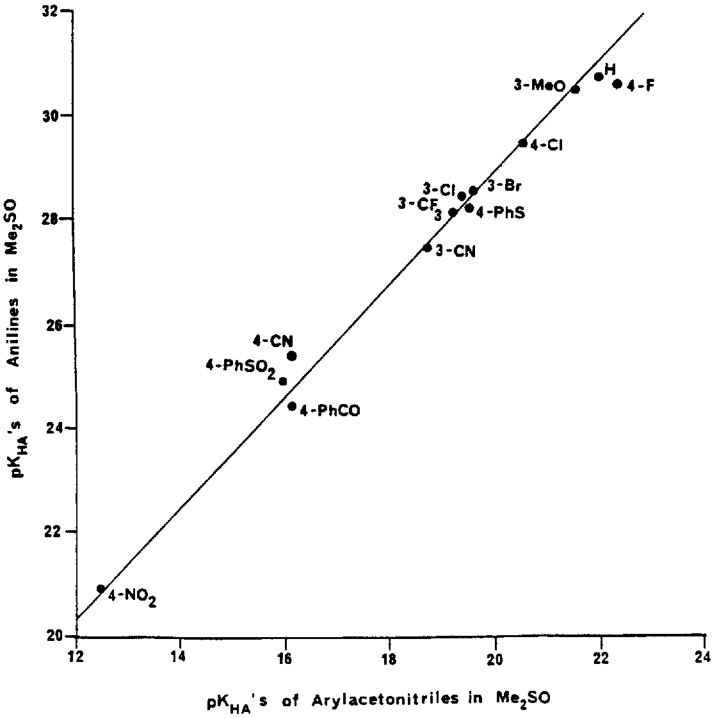


Figure 2. Plot of the equilibrium acidities of anilines vs. those for phenylacetonitriles, both in Me_2SO solution

for 4-PhSO$_2$, 4-PhCO, and 4-NO$_2$ points in Figure 2 indicate that enhanced solvation of these substituents for ArNH$^-$ nitranions and ArCHCN$^-$ carbanions are nearly the same.

Effects of aryl and alpha structural changes on radical cation acidities

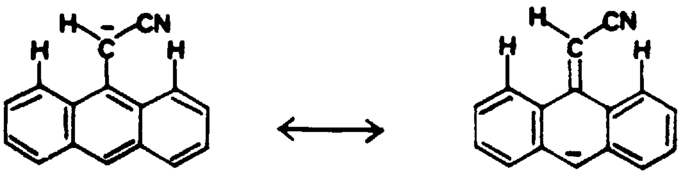
Substitution of an α-hydrogen atom of toluene by CN increases the acidity by about 21 pK_a units, equivalent to 29 kcal/mol. Structural changes along the series phenylacetonitrile, 1- and 2-naphthylacetonitriles, and 9-anthrylacetonitrile cause a further increase of only 2·9 pK_a units in acidity (Table 2), however, indicating that much of the negative charge in the PhCHCN$^-$ anion resides in the side chain and that but little additional stability of the anion accrues from

Table 2. Effects of aryl and alpha structural changes on acidities, radical cation acidities, and bond dissociation energies

Nitrile	pK_{HA}[f]	E_{ox}(HA)[g]	E_{ox}(A$^-$)[i]	p$K_{HA^{+\cdot}}$[j]	BDE[k]
PhCH$_2$CN	21·9	3·15 (140)	−0·034 (45)	−32	82·2
1-NpCH$_2$CN[a]	20·85	2·32 (75)	−0·012 (45)	−18·5	81·3
2-NpCH$_2$CN[b]	20·65	2·27 (65)	0·004 (45)	−17·5	81·4
9-AnCH$_2$CN[c]	19·8	1·89 (70)	−0·055 (50)	−13	78·8
9-AnCH$_3$	31·1	1·68 (90)	−0·614 (60)	−7·5	81·4
PhCH(Me)CN	23·0	3·12[h] (150)	−0·195 (45)	−33	80·0
PhCH(Ph)CN	17·5	3·16[h] (160)	−0·023 (45)	−35	77·5
9-CN-FlH$_2$[d]	8·3	2·41 (60)	0·451 (45)	−25	74·7
FlH$_2$	22·6	2·15 (60)	−0·194 (45)	−17	79·5
9-CN-Xn[e]	13·6	2·28 (70)	−0·118 (45)	−27	68·9
XnH$_2$	30·0	2·01 (60)	−0·810 (60)	−18	75·4

[a] 1-Naphthylacetonitrile.
[b] 2-Naphthylacetonitrile.
[c] 9-Anthrylacetonitrile.
[d] 9-Cyanofluorene.
[e] 9-Cyanoxanthene.
[f] Measured in Me$_2$SO against two or more indicators or standard acids.
[g] In MeCN vs. Ag/AgI.
[h] Shoulder attached to a wide peak.
[i] In Me$_2$SO vs. Ag/AgI.
[j] Calculated using equation (1).
[k] Calculated using equation (2).

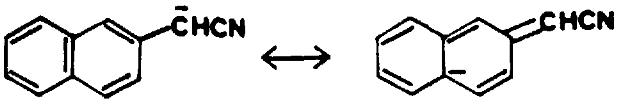
the delocalization afforded by the larger hydrocarbon skeletons. In 9-anthrylacetonitrile delocalization in the anion is inhibited by the inability of the $CHCN^-$ moiety to become coplanar with the anthracene ring because of steric interference with the peri hydrogen atoms (**1**),



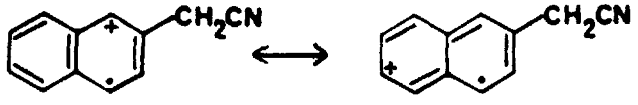
1a **1b**

Some indication of the extent of this steric inhibition of resonance is given by the observation that substitution of a hydrogen atom in 9-methylanthracene by CN causes only about a 12 pK_a unit increase in acidity compared to about a 21 pK_a unit increase for substitution into toluene.

In sharp contrast to the 2·9 pK_a unit acidity decrease along the series $PhCH_2CN$, $2\text{-}NpCH_2CN$, and $9\text{-}AnCH_2CN$, a 19 unit acidity decrease occurs for the corresponding radical cations in this series. The difference is that, in the carbanions, delocalization is accompanied by loss of aromaticity (e.g., **2**), whereas in the radical cations aromaticity has already been lost (e.g., **3**). Note also that in the carbanions the cyano function provides charge stabilization whereas in the radical cations it causes charge destabilization. As a consequence, the $PhCH_2CN^{+\cdot}$ radical cation is a stronger acid than the $PhCH_3^{+\cdot}$ radical cation by about 13 p$K_{HA^{+\cdot}}$ units in Me_2SO.

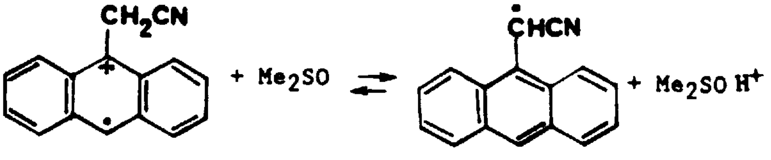


2a **2b**



3a **3b**

The position of the equilibrium in the dissociation of radical cations, e.g., equation (3), is affected both by the stabilizing effect of Ar on the radical cation (**4**) and by its stabilizing effect on the radical (**5**) formed by proton loss. The $E_{ox}(HA)$ part of equation (1) is associated primarily with the radical cation stability and the combination of $E_{ox}(A^-)$ and pK_{HA} in equation (1) is associated primarily with the radical stability. This can be illustrated by showing how the Δp$K_{HA^{+\cdot}}$ of 19 between the acidity of $PhCH_2CN^{+\cdot}$ and $9\text{-}AnCH_2CN^{+\cdot}$ (**4**) can be arrived at by considering the individual terms in equation (1).



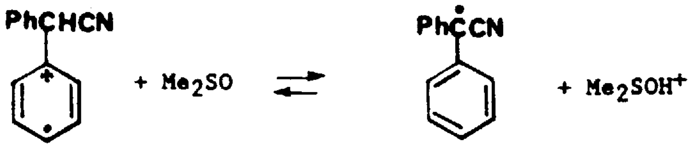
4 **5** (3)

The difference in E_{ox}(HA) values between $\mathrm{PhCH_2CN}$ and 9-$\mathrm{AnCH_2CN}$ is 1·26 V, equivalent to 29 kcal/mol. If we assume that this is a measure of the stabilization of **4**, relative to $\mathrm{PhCH_2CN^{+\cdot}}$, we would expect about a 21 $\mathrm{p}K_{\mathrm{HA}^{+\cdot}}$ unit decrease in the acidity of **4**, but this will be offset to some extent by the greater stability of radical **5**, relative to $\mathrm{PhCHCN^{\cdot}}$. The size of the latter effect can be estimated by the ΔAOP method (equation (4)).[14] From equation (4) we can estimate that radical

$$\Delta\mathrm{AOP} = 1{\cdot}37\Delta\mathrm{p}K_{\mathrm{HA}} + 23{\cdot}06\Delta E_{ox}(\mathrm{A}^-) \qquad (4)$$

5 will be stabilized by 2·4 kcal/mol, relative to the $\mathrm{PhCHCN^{\cdot}}$ radical, an effect that will be acid *strengthening* by 1·8 $\mathrm{p}K_{\mathrm{HA}^{+\cdot}}$ units. The net change is 26·6 kcal/mol equivalent to the 19 $\Delta\mathrm{p}K_{\mathrm{HA}^{+\cdot}}$ unit effect calculated by using equation (1).

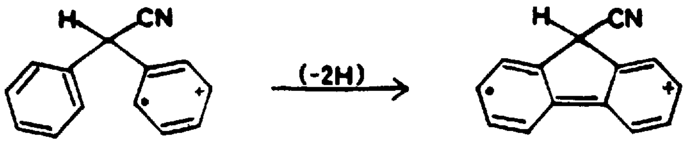
The radical cation acidities of $\mathrm{PhCH(Me)CN^{+\cdot}}$ and $\mathrm{Ph_2CHCN^{+\cdot}}$ are estimated by equation (1) to be slightly greater than that of the parent, $\mathrm{PhCH_2CN^{+\cdot}}$ ($\mathrm{p}K_{\mathrm{HA}^{+\cdot}} = -33$ and -35, respectively, vs. -32). This is reasonable since the α-Me and α-Ph groups are separated by a carbon atom from the benzene ring bearing the positive charge in the radical cations and can offer little in the way of stabilization. They can stabilize the radical (**7**) formed on deprotonation, however, which is an acid-strengthening effect (equation (5)).



(5)

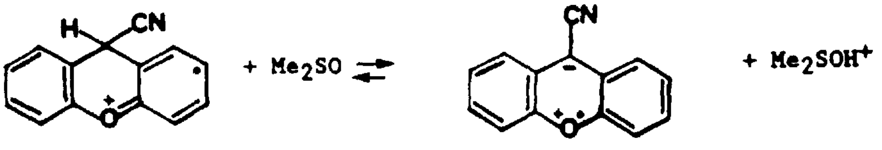
6 **7**

The effect of removing two *ortho* hydrogen atoms from $\mathrm{Ph_2CHCN}$ and joining the rings to form 9-cyanofluorene causes the acidity of the α-hydrogen to increase by 12·6 kcal/mol. This increase is associated primarily with the aromaticity of the fluorenide ion, a 14 π-electron system. A similar elision and ring closure from the radical cation, $\mathrm{Ph_2CHCN^{+\cdot}}$ (**8**→**9**) causes a 13·7 kcal/mol *decrease* in acidity. Here the ring closure establishes communication between the two rings, thereby allowing much more effective delocalization of the positive charge and odd electron in **9**, an acid-weakening effect.



8 **9**

The elision of two *ortho* hydrogen atoms from $\mathrm{Ph_2CHCN}$ and replacement with oxygen to form 9-cyanoxanthene enforces coplanarity of the rings and causes a 5·3 kcal/mol increase in carbanion stability. (No antiaromaticity effect is evident.) The radical cation (**10**) is stabilized by about 20 kcal/mol, relative to $\mathrm{Ph_2CHCN^{+\cdot}}$, as judged by differences in E_{ox}(HA) values. The acidity of **10** is, however, only about 11 kcal/mol less than that of $\mathrm{Ph_2CHCN^{+\cdot}}$ (Table 2). Here the stability of the radical (**11**), which is 7·5 kcal/mol greater than that of $\mathrm{Ph_2CCN^{\cdot}}$



(6)

10 **11**

(calculated by the ΔAOP method) plays an unusually strong role in determining the position of equilibrium in equation (6).

Effects of aryl and alpha structural changes on BDEs

Differences in BDEs are equivalent in kcal/mol to the differences in radical stabilities calculated within a family by the ΔAOP method (equation (4)). The *absolute* BDEs, calculated by equation (2) and referred to Me_2SO as the standard state, provide better perspective, however, since they can be compared with C—H bond strengths between different families. For example, we can compare the BDE of $PhCH_2CN$ with that of $PhCH_3$ and the effects of alpha structural changes on BDE's with those observed for the corresponding hydrocarbons.

The BDE of the benzylic C—H bond in $PhCH_2CN$ is estimated to be about 82 kcal/mol in Me_2SO, which places it about 6 kcal/mol below the favored value for $PhCH_3$ in the gas phase.[2,5] This 6 kcal/mol weakening by CN of the C—H bond in toluene is only one-half as large as that exerted by the CN group in methane (ΔBDE = 12 kcal/mol).[5] This is evidently a saturation effect. (Note that ΔBDE of $PhCH_3$ vs. CH_4 is 19 kcal/mol.) The effects of α-Me and α-Ph substitutions are also smaller for $PhCH_2CN$ than for toluene,[5] i.e., 2·2 vs. 3 and 5·8 vs. 8 kcal/mol, respectively. The decrease in BDEs along the series $PhCH_2CN$, $1\text{-}NpCH_2CN$, and $9\text{-}AnCH_2CN$ are 82, 81, and 79 (Table 2). They parallel those reported for the hydrocarbons, i.e., 88, 85, and 80 kcal/mol for $PhCH_3$, $1\text{-}CH_3Np$, and $9\text{-}CH_3An$, respectively.[5]

It is instructive to compare the effects of BDEs resulting from introduction of an α-CN group into the hydrocarbons 9-methylanthracene, fluorene, and xanthene with the 6 kcal/mol decrease for $PhCH_2CN$ vs. $PhCH_3$ mentioned earlier. The decreases in BDEs are 6·5, 4·8, and 2·6 kcal/mol for 9-CN-XnH, 9-CN-FlH, and $9\text{-}AnCH_2CN$, respectively, as calculated by equation (2). If we equate these differences in BDEs with the size of the stabilization of the radicals formed on deprotonation of the corresponding radical cations, as seems reasonable, we would expect the acidities of the latter to increase by about 4·7, 3·5, and 1·9 $pK_{HA^{\cdot+}}$ units, respectively. The increases calculated by equation (1) are actually 9, 8, and 4·5 units, respectively (Table 2). It would appear, therefore, that a second acid-strengthening factor is present. This is no doubt the electron-withdrawing field effect of the CN group, which will act to destabilize the radical cation. (Note, for example the proximity of the CN group to the positive charge in resonance contributor **10**.)

Remote substituent effects on radical cation acidities and BDEs

We have seen that acidities of 3-substituents in $ArCH_2CN$ plot linearly with Hammett ρ constants and that strongly electron-accepting 4-substituents give points deviating from this line (Figure 1) due in part to enhanced solvation in the anions (SSAR effects). *Para* electron donors exert much larger and opposite effects on the acidities of the corresponding radical cations, the $\Delta pK_{HA^{+\cdot}}$ order being 4-Me$_2$N > 4-PhS > 4-MeO > 4-Ph > 4-Me (Table 3). The $\Delta pK_{HA^{+\cdot}}$ values, relative to H, are -37, -19, -13, -12, and -4 units, respectively, compared to $-2{\cdot}7$, $2{\cdot}3$, $-1{\cdot}9$, $1{\cdot}1$, and -1 unit, respectively, for ΔpK_{HA}. The acid-strengthening effects of *para* electron acceptors in ArCH$_2$CN$^{+\cdot}$ and ArCH$_2$CN appear to be of more nearly equal size (e.g., 6, 4, and 0 units, respectively, for the 4-CF$_3$, 4-PhCO, and 4-CN radical cations vs. 3·8, 5·85 and 5·9 for the neutrals). The larger ΔpK_{HA} for 4-PhCO than 4-CF$_3$ is the result of enhanced acidity for 4-PhCOC$_6$H$_4$CH$_2$CN caused in part by an SSAR effect. The larger $\Delta pK_{HA^{+\cdot}}$ for 4-CF$_3$ than 4-PhCO is in line with the stronger electron-withdrawing effect of 4-CF$_3$ ($\sigma_p^{CF_3} = 0{\cdot}54$ vs. $\sigma_p^{PhCO} = 0{\cdot}44$), which accounts for the more positive E_{ox}(HA) value observed (Table 3).

Table 3. Acidity and oxidation potential data for arylacetonitriles, GC$_6$H$_4$CH$_2$CN

G	E_{ox}(HA)[a]	E_{ox}(A$^-$)[c]	$pK_{HA^{+\cdot}}$[d]	BDE[e]	ΔBDE[f]
4-Me$_2$N	1·37	−0·381	−5	77·9	−4·0
4-MeO	2·33	−0·217	−19	80·5	−1·4
3,4-diMeO	2·08	−0·196	−15	80·5	−1·4
4-Ph	2·44	−0·016	−20	81·1	−0·8
4-Me	2·88[b]	−0·126	−28	81·5	−0·4
4-PhS	2·02	+0·078	−13	81·6	−0·3
4-F		−0·070		81·8	−0·1
3-MeO		−0·034		81·8	−0·1
4-Cl		+0·034		81·8	−0·1
H	3·15	−0·048	−32	81·9	(0·0)
3-Me		−0·055		82·1	0·2
3-F		+0·083		82·2	0·3
3-Cl		+0·137		82·8	0·9
3-CF$_3$		+0·167		83·1	1·2
3-CN		+0·179		82·7	0·8
3,4-diCl		+0·173		82·5	0·6
3-PhSO$_2$		+0·200		82·9	1·1
4-CF$_3$	3·57[b]	+0·225	−38	83·0	1·0
4-PhCO	3·28	+0·294	−34	82·7	0·8
4-CN	3·47[b]	+0·337	−37	82·6	0·7

[a] Determined in MeCN solution by cyclic voltammetry.

[b] Shoulder on a broad peak.

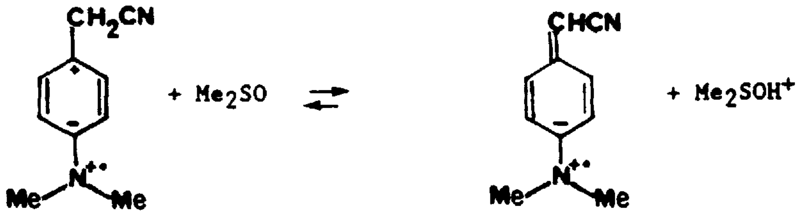
[c] Oxidation potentials of GC$_6$H$_4$CHCN$^-$ ions measured by cyclic voltammetry in Me$_2$SO solution. These values are an average of those reported earlier[14] and presently.

[d] Calculated using equation (2); estimated to be accurate to ±2 units.

[e] Estimated to be accurate to ±2 kcal/mol.

[f] Relative to that of phenylacetonitrile.

The difference in E_{ox}(HA) values between C$_6$H$_5$CH$_2$CN and 4-Me$_2$NC$_6$H$_4$CH$_2$CN is 1·78 V, equivalent to a stabilization of radical cation **12** of about 41 kcal/mol by the Me$_2$N group. This effect could be expected to cause about a 30 $pK_{HA^{+\cdot}}$ unit decrease in the acidity of **12**, relative to that of PhCH$_2$CN$^{+\cdot}$. This is offset by the stabilizing effect of the Me$_2$N group on radical **13**, which amounts to 4 kcal/mol (equivalent to 2·9 $pK_{HA^{+\cdot}}$ units) according to the ΔAOP method. The net effect is that calculated by equation (1), i.e., a 27 $pK_{HA^{+\cdot}}$ unit decrease.



12 **13** (7)

As discussed earlier, other electron donor groups weaken the acidities of the radical cations to a lesser extent, and acceptor groups increase the acidities. The $pK_{HA^{+\cdot}}$ values plot linearly with E_{ox}(HA) values (Figure 3), which shows the dominant effect of the oxidation potential of the neutral in equation (1) in controlling the acidity of the radical cation. Referring to equation (7), the dominant effect of the substituent on $pK_{HA^{+\cdot}}$ is its ability to stabilize the radical cation, the effect on the stability of the radical is relatively small.

Examination of Table 3 shows that ΔBDEs in kcal/mol for *para* electron donors are bond weakening in the order: H (0·0) < 4-Cl, 4-F, 3-MeO (−0·1) < 4-PhS (−0·3) < 4-Me (−0·4) < 4-Ph (−0·8) < 3,4-diMeO, 4-MeO (−1·4) < 4-Me_2N (−4). Points for substituents (omitting 4-Me) gave a linear Hammett plot ($\rho = -4{\cdot}0$; $R^2 = 0{\cdot}94$) with scatter (Figure 4). The wide deviations for 3-Me and 4-Me are no doubt caused by the polar nature of σ constants derived from benzoic acid acidities (−0·07 and −0·17). It is generally accepted now that σ_I (or σ_F) constants for these groups should be essentially zero,[13c] as first proposed by Ritchie and

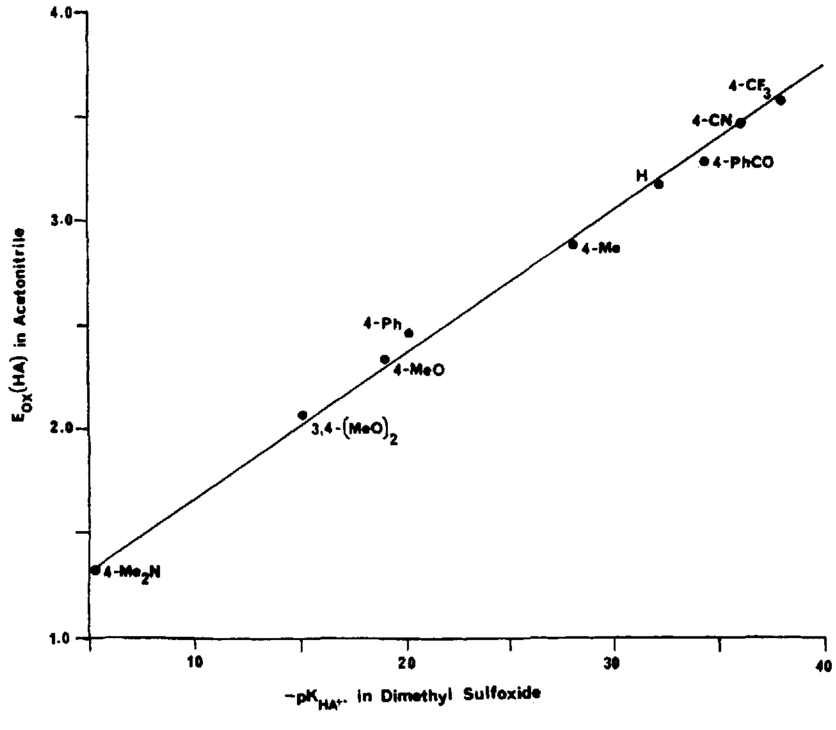


Figure 3. Plot of oxidation potentials for 4-substituted phenylacetonitriles in acetonitrile vs. acidities ($pK_{HA^{+\cdot}}$) of the corresponding radical cations in dimethyl sulfoxide

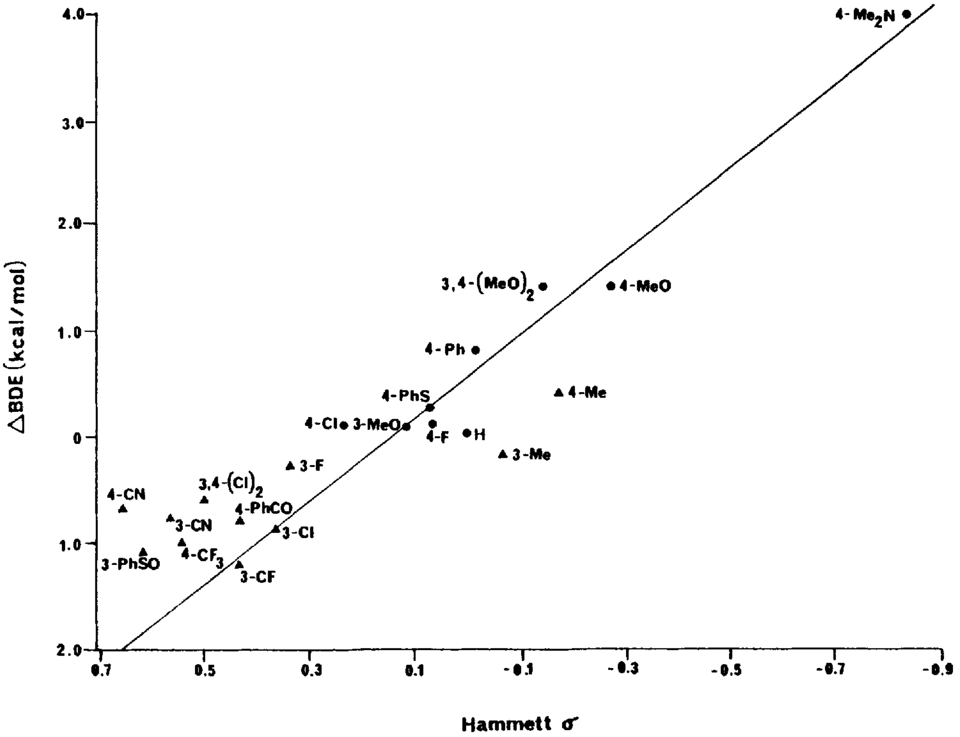


Figure 4. Hammett plot for ΔBDEs for electron donor substituents (omitting 3-Me and 4-Me). Acceptor (and 3-Me and 4-Me donor) substituents are shown as triangles; these were not used in the correlation

Sager.[15] Electron acceptors cause mild bond strengthening in the apparent order: 3-F (0·3) < 3,4-diCl (0·6) < 4-CN (0·7) < 4-PhCO, 3-CN (0·8) < 3-Cl (0·9) < 4-CF_3 (1·0) < 3-$PhSO_2$ (1·1) < 3-CF_3 (1·2). Most of the points for strong acceptors scatter above the extended donor Hammett line in a seemingly random fashion. This scatter is caused, at least in part, by the dual nature of the effects of some of the substituents. For example, the 4-CN group is both bond strengthening and radical stabilizing.

The ρ of −4 suggests that BDEs must be the controlling factor in determining the relative reactivities towards radicals of benzylic C—H bonds *para* to donor substituents, irrespective of the polar nature of the transition states. This is in accord with the Zavitsas suggestion[8] and contrary to earlier postulates.[6,9] On the other hand, the ΔBDEs are small for most *meta* or *para* acceptors, and polar factors, as well as BDEs, may be important in deciding benzylic C—H bond reactivities towards radicals in these systems, as suggested by Pryor.[9d] There is no encouragement here, however, for the belief that the Hammett equation can be used to estimate substituent effects on benzylic C—H bond reactivities toward radicals. This is consistent with the poor agreement found in σ• scales.[7]

Application of the ΔAOP method to arylacetonitriles

Our earlier application of the ΔAOP method to arylacetonitriles led to the conclusion that only 5 of the 17 substituents were radical stabilizing, the order being 4-Me_2N (−3·1) > 4-MeO

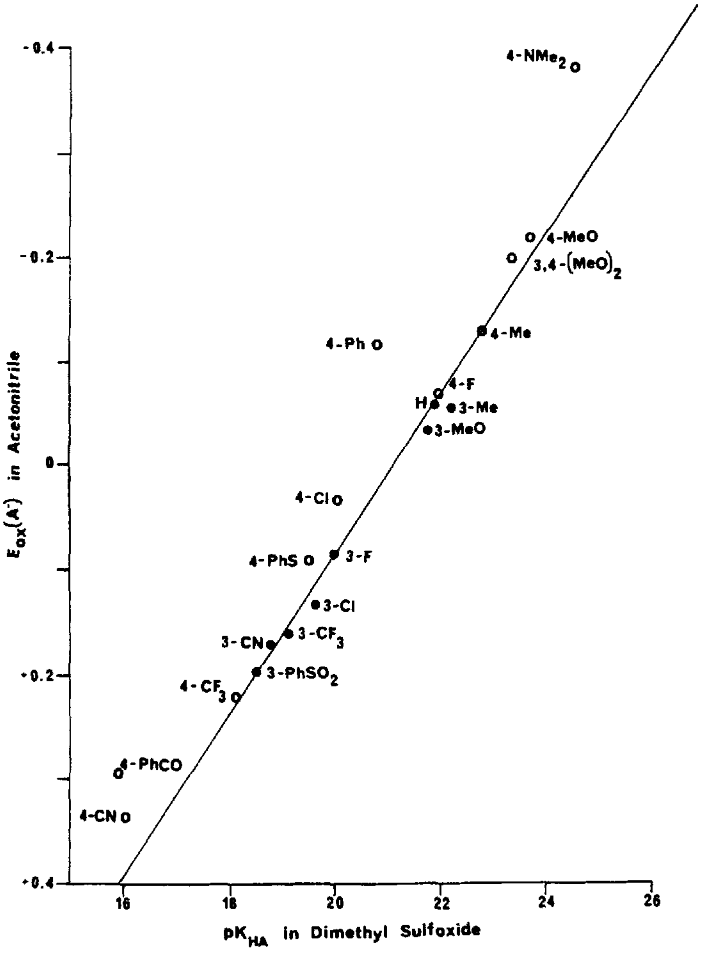


Figure 5. Plot of oxidation potentials for *m*-substituted arylacetonitrile ions vs. equilibrium acidities, both in dimethyl sulfoxide solution. Points for *p*-substituents are shown as open circles

(−1·3), 4-Ph, 4-PhS (−0·68) > 4-Me (−0·56). (The stabilizing effects calculated are given in parentheses in kcal/mol.) The plot of $E_{ox}(A^-)$ vs. pK_{HA} for *m*-substituents reported earlier[14] is reproduced in Figure 5 with points for 4-CN and 4-PhCO added. The slope of the line, when the axes are each expressed in kcal/mol, is 1·23, indicating that pK_{HA} values are about 20% less sensitive to substituent effects than are $E_{ox}(A^-)$ values. This pattern differs from that for 2- and 2,7-disubstituted fluorenes and for three other benzylic-type hydrocarbon systems (3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes,[16] 9-substituted xanthenes,[16] and 10-substituted-9-methylanthracenes[16]) where the slope of the $E_{ox}(A^-)$ vs. pK_{HA} plot is near unity. It seems likely that the cause of increased slope may lie in the partial delocalization of the negative charge to nitrogen in the ArCHCN$^-$ ion. This effect will decrease the sensitivity of the pK_{HA} values to substituent changes. In view of the disparity in these sensitivities it appears better to estimate the effects of remote substituents directly from the deviations in Figure 5 than by the ΔAOP method. The data are summarized in Table 4.

Table 4. Radical-stabilizing effects of remote substituents in arylacetonitriles, $GC_6H_4CH_2CN$

G	$\Delta E_{ox}(A^-)$[a]	G	$\Delta E_{ox}(A^-)$[a]
4-Me_2N	2·5	4-Cl	1·2
4-MeO	0·5	4-PhS	0·7
3,4-di-MeO	0·7	4-CN	1·3
4-Ph	3·2	4-PhCO	2·3

[a] Deviations from the line in Figure 4 in kcal/mol.

This analysis differs from that derived from the ΔAOP method in revealing radical-stabilizing effects for 4-Cl, 4-CN, and 4-PhCO substituents. The radical-stabilizing effects for the electron donor substituents are consistent with their weakening effect on C—H BDEs (Table 3), but the effects for the electron acceptors, CN and PhCO, are observed despite their strengthening effect on BDEs.

SUMMARY AND CONCLUSIONS

The deviations of 4-Ph, 4-PhS, 4-PhCO, 4-CN, 4-$PhSO_2$, and 4-NO_2 from the Hammett plot for equilibrium acidities of $GC_6H_4CH_2CN$ are equivalent to those observed with $GC_6H_4NH_2$ acidities. Both are attributed in part to substituent solvent assisted resonance (SSAR) effects. Increased delocalization of the positive charge (and odd electron) causes the acidity of the radical cation derived from 9-cyanomethylanthracene to be stabilized by about 26 kcal/mol, relative to that derived from 9-cyanomethylbenzene. The CN group in the 9-cyanoxanthene radical cation increases the acidity, relative to $XnH_2^{+\cdot}$, by about 6 kcal/mol by destabilizing the radical cation and by about 6·5 kcal/mol by stabilizing the $XnH^\cdot$ radical formed on deprotonation. Introduction of a 4-NMe_2 group stabilizes the $C_6H_4CH_2CN^{+\cdot}$ radical cation by about 41 kcal/mol. The *para* electron donor groups Me_2N, MeO, Ph, PhS, Me, F, Cl cause decreases in homolytic bond dissociation energies (BDEs) of C—H bonds in 4-$GC_6H_4CH_2CN$ compounds over a range of 4 to 0·1 kcal/mol. A Hammett plot of ΔBDEs for donors is linear with scatter ($\rho = -4$; $R^2 = 0{\cdot}94$). Both *meta* and *para* acceptor groups increase the BDEs over a range of 0 to 1·2 kcal/mol; these points scatter in a random fashion around an extension of the Hammett line. The conclusion is drawn that BDEs of donor substituents play a major role in determining rates of reactions of radicals with *m*- and *p*-substituted toluenes, and that estimation of $\sigma^\cdot$ values from Hammett plots using these data is a futile exercise.

EXPERIMENTAL SECTION

Materials and syntheses

Samples were purified shortly before pK_a measurements by conventional methods and stored in the refrigerator until use. Purity of samples was ascertained by vpc, thin-layer chromatography, nmr, ir, mp, bp, and elemental analysis (for new compounds). Syntheses of samples not commercially available were generally by reaction of the appropriate halide with sodium cyanide. The preparation of *3-(phenylthio)phenylacetonitrile* will serve as an example. 3-(Phenylthio)toluene was prepared by the method of Bourgeois[17] and the crude product obtained by distillation was freed from phenyl disulfide by reduction with zinc and acetic acid followed by distillation, bp 119–121 °C (0·4 mm); nmr (CCl_4) δ 2·28 (s, 3H); δ 6·95–7·4; 99·5% pure by vpc. Dropwise addition of bromine to the sample of 3-(phenylthio)toluene in CCl_4 under illumination gave a crude sample of 3-(phenylthio)benzyl bromide which, after distillation, was reacted with two equivalents of sodium cyanide in Me_2SO by stirring at 75° for 1 hr. After distillation at reduced pressure the product was chromatographed on silica gel eluting with 5% ether–hexane, and then subjected to short path distillation: nmr (CCl_4) δ 3·50 (s, 2H). δ 7·1–7·4 (m, 9H).

3-(Phenylsulfonyl)phenylacetonitrile, mp 72–75 °C (CH_3OH): nmr ($CDCl_3$) δ 3·79 (s, 2H) δ 7·45–7·65 (m, 5H) δ 7·8–8·05 (m, 4H), was obtained by oxidation of 3-(phenylthio)-phenylacetonitrile with a slight excess of *m*-chloroperoxybenzoic acid in CH_2Cl_2.

4-(Phenylthio)phenylacetonitrile was prepared from *p*-toluidine in the same manner as described for 3-(phenylthio)phenylacetonitrile: bp 109–111 °C (0·5 mm) nmr (CCl_4) δ 2·10 (s, 3H) δ 6·7–7·1 (m, 9H).

Elemental analyses for carbon and hydrogen (Microtech, Skokie, IL) were satisfactory for all three of these compounds, which appear to be new.

pK_a Measurements in Me_2SO were carried out as described in earlier publications.[18]

Cyclic voltammetry. Cyclic voltammetry was carried out in the manner previously described.[19]

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REFERENCES

1. F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.* **108**, 2473–2474 (1986).
2. F. G. Bordwell, J.-P. Cheng and J. A. Harrelson, Jr., *J. Am. Chem. Soc.* **110**, 1229–1231 (1988). The BDEs in Me_2SO estimated by equation (2) have been shown in this paper to agree reasonably well with those obtained in the gas phase for 9-methylanthracene, Ph_2CH_2, Ph_3CH, cyclopentadiene, indene, fluorene, acetone, phenol, thiopenol, and aniline.
3. M. I. Terekova, E. S. Petrov, S. P. Mesyats and A. I. Shatenshtein, *J. Gen. Chem. USSR (Eng)* **45**, 1499–1501 (1975).
4. F. G. Bordwell, *et al. J. Org. Chem.* **42**, 321–325 (1977).
5. D. I. McMillen and G. M. Golden, *Ann. Rev. Phys. Chem.* **37**, 493–533 (1982).
6. C. Walling, *Free Radicals in Solution*: Wiley, New York, 1957, pp. 132–140, 365–369, 375–376, 474–491. W. A. Pryor, *Free Radicals*: McGraw-Hill, New York, 1986, pp. 170–177.
7. J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.* **105**, 1221–1227 (1983).
8. A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.* **94**, 7390–7396 (1973).
9. (a) W. A. Pryor, W. H. Davis, Jr. and J. P. Stanley, *J. Am. Chem. Soc.* **95**, 4754–4756 (1973). (b) R. W. Henderson and R. D. Ward, Jr., *J. Am. Chem. Soc.* **96**, 7556–7557 (1974). (c) W. A. Pryor and W. H. Davis, Jr., *J. Am. Chem. Soc.* **96**, 7557–7559 (1974). (d) W. H. Davis, Jr. and W. A. Pryor, *J. Am. Chem. Soc.* **99**, 6365–6372 (1977). (e) W. A. Pryor, D. V. Church, F. Y. Tang and R. H. Tang, *Frontiers of Free Radical Reactions*, W. A. Pryor, Ed., Academic Press, 1980.

10. F. G. Bordwell and F. J. Cornforth, *J. Org. Chem.* **43**, 1763–1768 (1978).
11. F. G. Bordwell and D. J. Algrim, *J. Am. Chem. Soc.* **110**, in press (1988).
12. F. G. Bordwell, R. J. McCallum and W. N. Olmstead, *J. Am. Chem. Soc.* **49**, 1424–1427 (1984).
13. (a) M. Fujio, R. T. McIver, Jr. and R. W. Taft, *J. Am. Chem. Soc.* **103**, 4017–4029 (1981). (b) M. Mishima, *et al. J. Am. Chem. Soc.* **106**, 2717–2718 (1984). (c) R. W. Taft and R. D. Topsom, *Progress in Phys. Org. Chem.* **16**, 1–83 (1987); see the σ_F values on p. 16. (d) F. G. Bordwell, J. C. Branca and T. A. Cripe *Israel J. Chem.*, **26**, 357-366 (1985).
14. F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.* **108**, 1979–1985 (1986).
15. C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.* **2**, 323–400 (1964).
16. Unpublished work from this laboratory.
17. Ed. Bourgeois, *Chem. Ber.* **28**, 2312–2330 (1895).
18. W. N. Olmstead, Z. Margolin and F. G. Bordwell, *J. Org. Chem.* **45**, 3295–3299 (1980) and references cited therein.
19. F. G. Bordwell, J.-P. Cheng and M. J. Bausch, *J. Am. Chem. Soc.* **110**, in press (1988).