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Element Effects on the Homolytic Bond Dissociation Enthalpies of the Acidic H–A Bonds in $HA^{\bullet+}$ Radical Cations and Their Neutral Precursors

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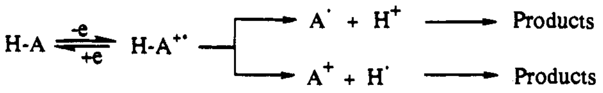
Abstract: Estimates of the homolytic bond dissociation enthalpies for reactions of the type $HA^{\bullet+} \rightarrow H^{\bullet} + A^{+}$ ($BDE_{HA^{\bullet+}}$ values) have been made by using eq 1, which has been derived from a thermodynamic cycle (Scheme 2). The $BDE_{HA^{\bullet+}}$ values for the radical cations derived by loss of an electron from three N–H and four O–H weak acids, where N–H or O–H bonds are cleaved, have been found to be smaller than the BDE_{HA} values for cleavage of those bonds in their parents by only 3–12 kcal/mol. In contrast, the $BDE_{HA^{\bullet+}}$ values for radical cations where an acidic C–H bond is cleaved have been shown to be typically 30–50 kcal/mol smaller than the BDE_{HA} values for cleavage of the corresponding acidic C–H bonds in their parents. An analysis in terms of eq 1 has shown that the difference in energies for N–H or O–H vs C–H cleavage in $HA^{\bullet+}$ radical cations lies in the relatively small energies required to remove an electron from the lone pairs on the nitrogen and oxygen heteroatoms and in the relatively low stabilities of the hypovalent divalent nitrogen and the monovalent oxygen cation products formed on N–H or O–H cleavage compared to those of the trivalent carbon cation products formed on C–H cleavage.

Introduction

Radical cations formed by loss of an electron from neutral molecules are common intermediates in numerous oxidative degradations of organic molecules.[1] The radical cations $HA^{\bullet+}$ formed from weak acids HA can react further either by losing a proton (heterolytic cleavage) to form H^+ and a radical or by losing a hydrogen atom (homolytic cleavage) to form $H^{\bullet}$ and a cation, as shown in Scheme 1.

Heterolytic cleavage is usually favored in solution because of the enormous solvation energy of the proton [$\Delta G^{\circ}_{t}(H^+)$ gas phase to $H_2O = -260.5$ kcal/mol,[2] and $\Delta G^{\circ}_{t}(H^+)$ gas phase to DMSO $= -265.0$ kcal/mol[3]] and the acidic nature of radical cations. (For example, the $pK_{HA^{\bullet+}}$ values for $PhNH_2^{\bullet+}$, $PhOH^{\bullet+}$, $PhSH^{\bullet+}$, and $PhCH_3^{\bullet+}$ are 6.5, −8, −12, and −20, respectively, in DMSO, and the same relative order is observed in the gas phase.[4]) On the other hand, homolytic cleavage is probably the preferred pathway in the gas phase because in this medium the A^+ cations are more stable than the proton, since the positive charge can be stabilized by delocalization and/or polarizability effects. Homolytic cleavage may also be favored sometimes in weakly hydrogen bond accepting solvents such as acetonitrile, benzene, or tetrahydrofuran in view of recent evidence for substantial weakening of acidic C–H bonds in radical cations toward homolytic cleavage, relative to their parents. For example, Nelsen and Ippoliti estimated the $BDE_{HA^{\bullet+}}$ value of the C–H bond in the radical cation derived from 9-(2-adamantyl)-9-azabicyclo[3.3.1]-nonane to be 18 kcal/mol;[5,6] i.e., the removal of one electron weakens the C–H bond by about 60 kcal/mol. Dinnocenzo and Banach estimated the $BDE_{HA^{\bullet+}}$ value for the C–H bond in the radical cation $(4\text{-}MeOC_6H_4)_2NCH_2\text{–}H^{\bullet+}$ to be 47 kcal/mol, as an upper limit.[7] Griller et al. estimated the $BDE_{HA^{\bullet+}}$ value for the C–H bond in the radical cation $(CH_3)_2NCH_2\text{–}H^{\bullet+}$ to be 34 kcal/mol,[8] and in our laboratory we have estimated $BDE_{HA^{\bullet+}}$ values for the acidic C–H bonds in 35 radical cations by eq 1 to fall in the range of 20–50 kcal/mol, which means that removal of one electron from the neutral acids weakens the acidic C–H bonds by 30–50 kcal/mol.[9a] Equation 1 was derived from the thermodynamic cycle shown in Scheme 2.

Scheme 1



Scheme 2

$$\begin{array}{lll}
H\text{-}A^{+\bullet} + e \rightleftharpoons H\text{-}A & & -E_{ox}(HA) \\
H\text{-}A \rightleftharpoons H^{+} + A^{-} & & pK_{HA} \\
A^{-} \rightleftharpoons A^{\bullet} + e & & E_{ox}(A^{-}) \\
A^{\bullet} \rightleftharpoons A^{+} + e & & E_{ox}(A^{\bullet}) \\
H^{+} + e \rightleftharpoons H^{\bullet} & & C \\
\hline
H\text{-}A^{+\bullet} \rightleftharpoons H^{\bullet} + A^{+} & & BDE_{HA^{\bullet+}}
\end{array}$$

$$BDE_{HA^{\bullet+}} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 + 23.1[E_{ox}(A^{\bullet}) - E_{ox}(HA)] \quad (1)$$

The first three terms in eq 1 are equal to the homolytic bond dissociation enthalpy of the acidic H–A bond in neutral weak

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193–6299.

(2) Gordon, J. C. *The Organic Chemistry of Electrolyte Solutions*; Wiley: New York, 1975; p 192.

(3) Cox, B. G. *Annu. Rep. Prog. Chem., Sect. A: Phys. Inorg. Chem.* **1973**, *70*, 249–274.

(4) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792–1795.

(5) Nelsen, S. F.; Ippoliti, T. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879–4881.

(6) This value is believed to be too low, however, because the $pK_{HA^{\bullet+}}$ value estimated is too high.[7]

(7) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8648–8653.

(8) Griller, D.; Simoes, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872–7876.

(9) (a) Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163–4168. (b) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790–9795 and references cited therein.

(10) The irreversible oxidation peaks measured by the conventional CV can sometimes be made reversible by increasing the scan rate.[11]

(11) (a) Bausch, M. J.; Gostowski, R. *J. Org. Chem.* **1991**, *56*, 6260–6262. (b) Bordwell, F. G.; Satish, A. V. Unpublished results.

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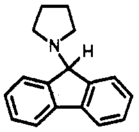
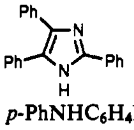
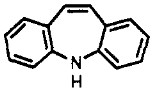
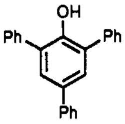
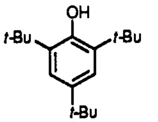
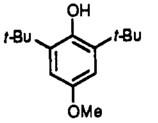
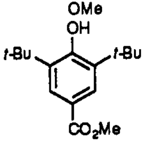
Table 1. Equilibrium Acidities, Oxidation Potentials (in V), and Homolytic Bond Dissociation Enthalpies of Iminostilbene, 2,3,5-Triphenylimidazole, *p*-(Phenylene)diphenylamine, 2,4,6-Triphenylphenol, and 4-G-2,6-Di-*tert*-butylphenols (G = *tert*-butyl, OMe, and COOMe) (The data in parentheses are in kcal/mol)

compounds	pK_{HA}[a]	$E_{ox}(HA)$[g]	$E_{ox}(A^-)$[j]	$E_{ox}(A^\bullet)$[m]	net[p]	BDE_{HA}[q]	$BDE_{HA^{\bullet+}}$[r]	ΔBDE[s]
$PhCH_3$	~43[b] (+59)	1.955[c,h] (−45.2)	−1.935[k] (−44.7)	0.220[n] (+5.1)	−26	87.5	47.5	40
	22.2[c] (+30.4)	0.455[c] (−10.5)	−1.553[c] (−35.9)	−0.980[c] (−22.6)	−36	68	35	33
	15.5[d] (+21.1)	0.667[i] (−15.4)	−0.217 (−5.0)	0.380 (+8.8)	+9.6	89.5	82.9	6.6
p-$PhNHC_6H_4NHPh$	25.6[e] (+35.1)	0.044[i] (−1.0)	−1.234 (−28.5)	−0.092 (−2.12)	+3.4	79.9	76.7	3.2
	26.1[d] (+35.7)	0.268[i] (−6.2)	−1.057[l] (−24.4)	0.130[o] (+3.0)	+8.5	85.3	81.4	3.2
	14.4[f] (+19.7)	0.569 (−13.1)	−0.334 (−7.7)	0.432 (+10.0)	+8.9	85.3	82.1	3.2
	17.8[d] (+24.4)	0.959[h] (−22.1)	−0.650 (−15.0)	0.428 (+9.9)	−2.3	82.6	70.3	12.2
	18.2[f] (+24.9)	0.464 (−10.7)	−0.806 (−18.6)	0.148 (+3.4)	−1.0	79.7	72.4	7.3
	11.90[f] (+16.3)	1.506[h] (−34.8)	−0.229 (−5.3)	0.898 (20.7)	−3.1	84.3	70.3	14

[a] In pK_{HA} units; equilibrium acidities measured in DMSO solution against two indicators by the overlapping indicator method. [b] Estimated, see: Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2964–2967. [c] Data taken from: Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163–4168. [d] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. [e] Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410–6416 [f] This work; also see Table 2. [g] Irreversible oxidation potentials of the neutral weak acids measured in DMSO by cyclic voltammetry and referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple, unless otherwise indicated. [h] Measured in acetonitrile. The oxidation potential differences measured in DMSO and acetonitrile have been found to be small, usually smaller than 50 mV; see: Cheng, J.-P. Ph. Dissertation. Northwestern University, Evanston, 1987. [i] The oxidation potentials of the neutral weak acids are reversible. [j] Reversible oxidation potentials of the conjugate anions measured in DMSO and referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple; the $E_{1/2}$ is reported. [k] Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748. [l] Irreversible oxidation potential. Ep is reported. A $E_{1/2}$ value of −1.030 V (referenced to the Fc/Fc^+ couple) for this anion has been determined by fast-scan CV.[11a] [m] Irreversible oxidation potentials of the radicals measured in DMSO unless otherwise indicated. Ep is reported. [n] Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132–137. [o] Reversible oxidation potential by a fast-scan CV.[11a] [p] The sum of the terms in columns 2–5 in kcal/mol. [q] In kcal/mol; estimated by the equation $BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3$. [r] In kcal/mol; estimated by eq 1. [s] $\Delta BDE = BDE_{HA} - BDE_{HA^{\bullet+}}$.

acids, as described by eq 2. The homolytic bond dissociation

$$BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \qquad (2)$$

enthalpies of the acidic H–A bonds estimated by eq 2, which is derived from a thermodynamic cycle, have been shown to be in good agreement with the best available gas-phase enthalpy values to ±2 kcal/mol.[9b] Ready access to these BDE_{HA} values allows eq 1 to be simplified to eq 3, which shows that the bond weakening caused by addition of one electron to HA is equal to the difference in the oxidation potential of the radical $A^\bullet$ and that of the neutral weak acid (HA).

$$BDE_{HA^{\bullet+}} = BDE_{HA} + 23.1[E_{ox}(A^\bullet) - E_{ox}(HA)] \qquad (3)$$

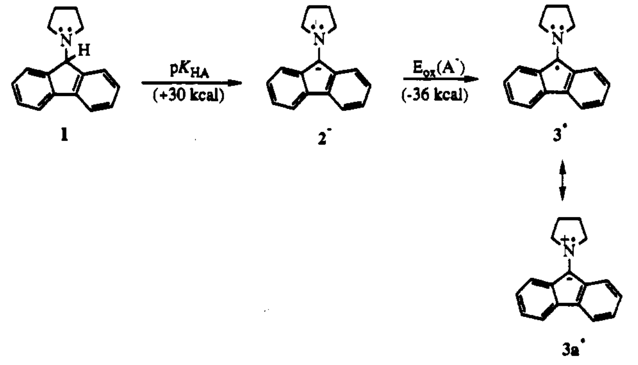
Results and Discussion

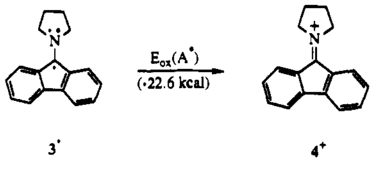
The results of the application of eq 1 to estimate the $BDE_{HA^{\bullet+}}$ values for the acidic N–H bonds in the radical cations derived from 2,3,5-triphenylimidazole, *p*-phenylenediphenylamine, and 5*H*-dibenz[*bf*]azepine (iminostilbene) and for the acidic O–H bonds in 2,4,6-triphenylphenol and three 4-G-2,6-di-*tert*-butylphenols (G = *t*-Bu, OMe, CO_2Me) are summarized in Table 1. Data for toluene and 9-pyrrolidinylfluorene are included as bench marks. To the best of our knowledge no $BDE_{HA^{\bullet+}}$ values for the acidic H–N or H–O bonds in radical cations have been reported in the literature hitherto.

Columns 2–5 in Table 1 give the experimental valuess for pK_{HA} (in pK_{HA} units) and for the E_{ox} values for HA, A^-, and $A^\bullet$ (in V) needed for the application of eq 1. The corresponding values in kcal/mol are given in parentheses below the pK_{HA} and E_{ox} values. The effects on $BDE_{HA^{\bullet+}}$ values that are bond strengthening are labeled as plus, and those that are bond weakening are labeled as minus. For weak acids, such as these, the effect of the pK_{HA} term in eq 1 on the $BDE_{HA^{\bullet+}}$ value must always be plus, By contrast, since $E_{ox}(HA)$ values provide a measure of the energy required to remove an electron from the neutral acid, an event that weakens the H–A bond, the effect of the $E_{ox}(HA)$ term in eq 1 on $BDE_{HA^{\bullet+}}$ must always be minus because this is an endothermic process. The $E_{ox}(A^-)$ values in Table 1 are all minus and become more negative as the basicity of the anion and/or the stability of the corresponding radical increases. The $E_{ox}(A^\bullet)$ term in eq 1 provides a measure of the ease of removing an electron from the radical to form the cation product. Its effect on the $BDE_{HA^{\bullet+}}$ values may be either plus or minus. This term becomes more negative as the stabilities of the cation products increase and vice versa.

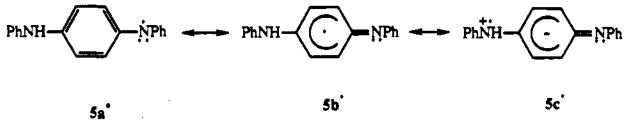
Effects of the Summation of the Terms in Eq 1 on $BDE_{HA^{\bullet+}}$ Values. The sizes of the $BDE_{HA^{\bullet+}}$ values in Table 1 are determined by the summation of the terms pK_{HA}, $E_{ox}(A^-)$, $E_{ox}(A^\bullet)$, and $E_{ox}(HA)$ in eq 1, i.e., by the "net" effects, which are subtracted from the constant 73.3 kcal/mol to obtain the $BDE_{HA^{\bullet+}}$ values. It will be instructive to analyze the relative effects of these terms on the $BDE_{HA^{\bullet+}}$ values for the radical cations derived from toluene and 9-pyrrolidinylfluorene, which are representative of the $BDE_{HA^{\bullet+}}$ values estimated for the cleavage of the acidic C–H bonds in the 35 radical cations previously studied.[9a] For toluene, we see from Table 1 that the $E_{ox}(HA)$ and $E_{ox}(A^-)$ terms each introduce bond-weakening effects of about 45 kcal. The minus $E_{ox}(A^-)$ term is countered, however, by the +59 kcal/mol pK_{HA} term. The net effect is −26 kcal/mol, which leads to a $BDE_{HA^{\bullet+}}$ value of 47 kcal/mol when subtracted from the 73.3 kcal/mol constant. This $BDE_{HA^{\bullet+}}$ value is 40 kcal/mol less than that for the $PhCH_2$–H parent.

For the 9-*c*-C_4H_8NFlH, we see from Table 1 that the $E_{ox}(A^-)$ term is relatively large because of the relatively high stability of the 9-*c*-$C_4H_8NFl^\bullet$ radical (**3**•).[12] This radical (**3a**•) has an aromaticity akin to that of the 14 π electron fluorenide ion. The (minus) $E_{ox}(A^-)$ term is in this instance largely countered, however, by the +30 kcal/mol pK_{HA} term, and it is the −0.980 V (−23 kcal/mol) $E_{ox}(A^\bullet)$ term that is primarily responsible for the strong bond weakening effect on the radical cation derived from **1**. In other words it is primarily the unusual stability of cation **4**⁺, wherein the positive charge is placed on a tetravalent nitrogen atom, that is the cause of the powerful C–H bond weakening effect in the 9-*c*-$C_4H_8NFlH^{\bullet+}$ radical cation. Cation **4**⁺ should be stable enough to be isolated in salt form.

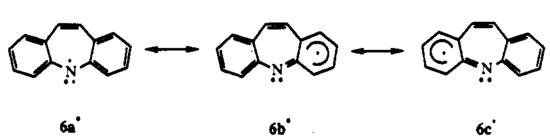


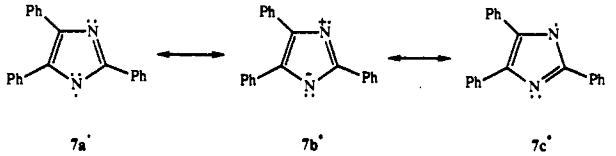


Radicals **5**• and **6**• derived from *p*-phenylenediphenylamine and iminostilbene, respectively, also have appreciable stability, as indicated by their sizable reversible negative $E_{ox}(A^-)$ values. But these bond-weakening effects on $BDE_{HA^{\bullet+}}$ are more than compensated by the relatively high pK_{HA} values of their parents.

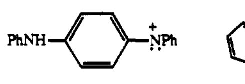


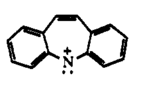
Radical **7**•, derived from the 2,3,5-triphenylimidazoylide ion, is less stable than radical **5**• or **6**•, presumably because the electron is removed from a σ orbital in the anion in order to avoid disrupting the aromaticity of the ring.[13] It is persistent and $E_{ox}(A^-)$ is reversible, however, because of the steric effects of the phenyl rings. Although the pK_{HA} term for 2,3,5-triphenylimidazole is about 15 kcal lower than that for *p*-phenylenediphenylamine or iminostilbene, it is 20 kcal/mol more bond strengthening than the $E_{ox}(A^-)$ term is bond weakening.

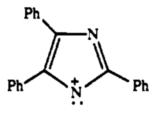




The major factor leading to less bond weakening for these three nitrogen radical cations, relative to the 9-*c*-$C_4H_8NFlH^{\bullet+}$ radical cation, is the $E_{ox}(A^\bullet)$ term, which is less bond weakening by 20–31 kcal/mol. This difference can be traced to the lesser stabilities of the divalent nitrogen cations **5**⁺, **6**⁺, and **7**⁺.


5⁺


6⁺


7⁺

The overall result is to narrow the gap between the BDE_{HA} and $BDE_{HA^{\bullet+}}$ values for the N–H bonds in the radical cations and their parents (ΔBDE in Table 1) to a range of 3.2–6.6 kcal/mol.

An analysis of the structural changes on the $BDE_{HA^{\bullet+}}$ values for the radical cations derived from the four phenols in Table 1 leads to similar conclusions. The $E_{ox}(HA)$ terms are, like those in the nitrogen acids, only mildly bond weakening because the electrons are removed from lone pair orbitals on oxygen. The largest $E_{ox}(HA)$ term, that for 4-CO_2Me-2,6-di-*t*-BuC_6H_2OH, is due to the electron-withdrawing effect of the methoxycarbonyl group. The $E_{ox}(A^-)$ terms are less bond weakening than those for the **5**⁻ or **6**⁻ nitranions, suggesting that the phenoxyl radicals have smaller radical stabilization energies. The $E_{ox}(A^\bullet)$ values for all of the phenoxyl radicals are positive, pointing to relatively low stabilities for monovalent oxygen cations such as **8**⁺. Replacement of the 4-*t*-Bu group in **8**⁺ by the donor MeO group stabilizes the cation **9**⁺ by about 6.5 kcal/mol, whereas replacement of the 4-*t*-Bu group by the acceptor CO_2Me group destabilizes the cation **10**⁺ by about 11 kcal/mol.

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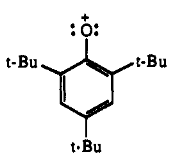
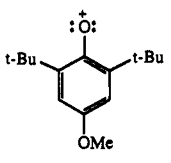
(12) Bordwell, F. G.; Cheng, J.-P.; Seyedrezai, S. E.; Wilson, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 8178–8183.

(13) There is evidence to indicate that oxidation of pyrrolide, indolide, or carbazolide anions also involves removal of a σ electron.[14]

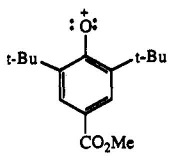
(14) (a) Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 1160–1162. (b) Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1991**, *56*, 3216–3219.



8$^+$



9$^+$



10$^+$

Although the radicals derived from 2,4,6-triphenylphenol and 2,4,6-tri-*tert*-butylphenols are both persistent, the $\mathrm{BDE_{HA^{\bullet+}}}$ value of the latter is 12 kcal/mol lower due to a greater increase in the initial state energy of the radical cation [more positive E_{ox}(HA) value] and greater radical stabilization energy [more negative E_{ox}(A^-) value].

Summary and Conclusions

Estimates of the homolytic bond dissociation enthalpies ($\mathrm{BDE_{HA^{\bullet+}}}$ values) of $HA^{\bullet+}$ radical cations, $HA^{\bullet+} \rightarrow H^\bullet + A^+$, has revealed that when the atom A is oxygen or nitrogen, the $\mathrm{BDE_{HA^{\bullet+}}}$ values are only slightly lower than those of the parent HA nitrogen or oxygen acids, whereas when the atom is carbon, the $\mathrm{BDE_{HA^{\bullet+}}}$ values are 30–50 kcal lower than those of their parents. Analysis of the data indicates that the primary factor responsible for the larger $\mathrm{BDE_{HA^{\bullet+}}}$ values in the N–H or O–H acids is the lower stabilities of the cation products. The cation products from the nitrogen and oxygen acids in Table 1, e.g., those derived from *p*-phenylenediphenylamine (**5**$^+$) or 2,4,6-tri-*tert*-butylphenol (**8**$^+$), are hypovalent compared to that derived from 9-pyrrolidinylfluorene (**4**$^+$). Carbocations are also hypovalent, but in divalent nitrogen cations and monovalent oxygen cations this property is exacerbated by the greater nuclear charge present in the more electronegative nitrogen and oxygen atoms.

Experimental Section

Materials. All of the compounds studied in this paper are commercially available. The purity and identity of each sample were confirmed by spectral analyses and melting points.

The equilibrium acidities in DMSO solution of 2,4,6-triphenylphenol, 4-methoxy-2,6-di-*tert*-butylphenol, and 4-carbomethoxy-2,6-di-*tert*-butylphenol were determined by the overlapping indicator method, as described previously.[15] The results are summarized in Table 2.

Table 2. Equilibrium Acidities for Phenols Determined in DMSO Solution

phenol	pK_{HA}(In)	pK_{HA}	pK_{HA}-(selected)
2,4,6-triphenylphenol	14.95^a	14.4 ± 0.04	14.4
	14.15^b	14.5 ± 0.05	
4-MeO-2,6-di-*t*-Bu-phenol	17.9^c	18.1 ± 0.01	18.2
	18.1^d	18.25 ± 0.01	
4-MeOCO-2,6-di-*t*-Bu-phenol	12.95^e	11.90 ± 0.01	11.9
	11.98^f	11.89 ± 0.01	

[a] 9-Fluorenone phenylhydrazone. [b] 9-Fluorenone (4-chlorophenyl)hydrazone. [c] 9-Phenylfluorene. [d] 2-(Phenylsulfonyl)fluorene. [e] 9-Fluorenone (2-chlorophenyl)hydrazone. [f] 9-Fluorenone (2,4-dichlorophenyl)hydrazone.

The oxidation potentials of the neutral weak acids and the corresponding anions and radicals were measured by cyclic voltammetry, as described previously.[9] The working electrode (Biological Analytical Systems, West Lafayette, IN) (BAS) consisted of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal. It was published with a 0.05-μm Fisher polishing aluminum and rinsed with ethanol before each run. The counter electrode (BAS) was a platinum wire. The reference electrode was Ag/AgI, and the reported oxidation potentials were referenced to the ferrocenium/ferrocene couple ($E_{1/2}$ = 0.875 versus the Ag/AgI couple).

The compounds were carefully selected so as to include only those wherein the oxidations of the conjugate anions (A^-) on the electrode were completely reversible. As a consequence, the radicals ($A^\bullet$) derived from the oxidation of the conjugate anions (A^-) are stable enough to be oxidized further to the corresponding cations (A^+). Unfortunately, most of the oxidations of the radicals to the corresponding cations were found to be irreversible. Nevertheless, there is good reason to believe that the disparity in ΔBDE values for C–H bonds vs N–H or O–H bonds is real. Thus, the potential for the oxidation of the iminostilbene radical in Table 1 is *reversible*,[10,11] and the difference in $\mathrm{BDE_{HA^{\bullet+}}}$ for this radical cation from the $\mathrm{BDE_{HA}}$ of the neutral acid is 3.2 kcal/mol; i.e., it is identical with the ΔBDEs found for *p*-phenylenediphenylamine and 2,4,6-triphenylphenol. Also, the potential for the oxidation of the radical derived from 9-pyrrolidinofluorene in Table 1 is reversible, as are those of the radicals for the 12 other 9-(dialkylamino)fluorenyl radicals reported earlier.[9a] Finally, the persistent 2,4,6-tri-*tert*-butylphenoxyl radical has been generated by controlled potential electrolysis in acetonitrile and its irreversible oxidation potential measured.[16] The oxidation potential of this radical in acetonitrile measured by CV in our laboratory is within 50 mV of this value. Our value in DMSO (Table 1) is, however, 270 mV more negative, probably because of the much better solvation for cations by DMSO. (The difference in the $E_{1/2}$ values for oxidation potentials of the 2,4,6-tri-*tert*-butylphenoxide anion in DMSO and CH_3CN is only 9 mV. Differences in oxidation potentials of HA molecules and A^- anions in DMSO and CH_3CN are usually within 100 mV of one another.) Using the acetonitrile value would increase $\mathrm{BDE_{HA^{\bullet+}}}$ by 6 kcal/mol and decrease ΔBDE to 6 kcal/mol, an even smaller difference than we report in Table 1.

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(15) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 450 and references cited therein.

(16) Richards, J. A.; Whitson, P. E.; Evans, D. H. *J. Electroanal. Chem.* **1975**, *63*, 311.