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Bond Dissociation Free Energies (BDFEs) of the Acidic H−A Bonds in $HA^{\bullet-}$ Radical Anions by Three Different Pathways

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Cleavage of radical anions, $HA^{\bullet-}$, have been considered to give either $H^{\bullet} + A^{-}$ (path a) or $H^{-} + A^{\bullet}$ (path b), and factors determining the preferred mode of cleavage have been discussed. It is conceivable that cleavage to give a proton and a radical dianion, $HA^{\bullet-} \rightleftharpoons H^{+} + A^{\bullet 2-}$ (path c), might also be feasible. A method, based on a thermodynamic cycle, to estimate the bond dissociation free energy (BDFE) by path c has been devised. Comparison of the BDFEs for cleavage of the radical anions derived from 24 nitroaromatic OH, SH, NH, and CH acids by paths a, b, c has shown that path c is favored thermodynamically.

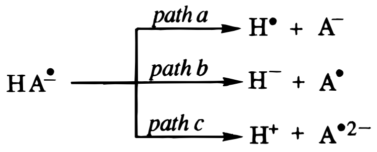
Introduction

Radical anions, formed by addition of an electron to an antibonding orbital of neutral compounds, are important and highly reactive intermediates in chemistry.[1] In the past two decades, significant contributions to kinetic and thermodynamic studies of radical anions have been made by a number of research groups.[2−7] The bonds in radical anions are greatly weakened by the extra electron, and bond breaking is facilitated thereby. The question of the modes of cleavage has been addressed,[2,5−7] and bond dissociation energies for $HA^{\bullet-}$ radical anions by path a and path b in Scheme 1 have been estimated by using equations based on thermodynamic cycles.[2,7] In solution, Griller et al. concluded that "hydride loss from radical anions is generally not as favorable as hydrogen atom loss because the solvation of H^{-} and the organic anions are similar."[2] Recent comparisons of bond dissociation energies for path a and path b show that either path is viable, the favored path depending on the nature of the substituents.[7] In this paper, a thermodynamic cycle has been devised to estimate the bond dissociation free energy for the $HA^{\bullet-}$ radical anion by path c, and comparisons with paths a and b are made.

Results and Discussion

The Thermodynamic Cycle. A general method, based on a thermodynamic cycle, for estimating the bond dissociation free energies (BDFEs) of the radical anions to give a proton and a radical dianion (path c) has been devised by combination of the equilibrium acidity, pK_{HA}, the reduction potential of the neutral compound, $E_{rd}(HA)$, and that of the conjugate base, $E_{rd}(A^{-})$, as illustrated by Scheme 2.

Scheme 1



Scheme 2

$$
\begin{array}{lcll}
HA & \rightleftharpoons & H^{+} + A^{-} & 1.37pK_{HA} \\
HA^{-\bullet} - e & \rightleftharpoons & HA & 23.06E_{rd}(HA) \\
A^{-} + e & \rightleftharpoons & A^{\bullet 2-} & -23.06E_{rd}(A^{-}) \\
\hline
HA^{-\bullet} & \rightleftharpoons & H^{+} + A^{\bullet 2-} & \Delta G_{H^{+}}(A^{\bullet 2-})
\end{array}
$$

$$\Delta G_{H^{+}}(A^{\bullet 2-}) = 1.37pK_{HA} + 23.06[E_{rd}(HA) - E_{rd}(A^{-})] \qquad (1)$$

The pK_{HA}, $E_{ox}(A^{-})$, $E_{rd}(HA)$, and $E_{rd}(A^{-})$ values for 26 nitro-substituted aromatic compounds containing acidic O−H, S−H, N−H, or C−H bonds arranged by functional groups, are listed in Table 1. The bond dissociation free energies (BDFEs) of the acidic H−A bonds in the neutral compounds and in the corresponding radical anions by paths a, b, and c are summarized in Table 2.

The Thermodynamic Choice among Three Different Cleavage Pathways of the Radical Anions. The cleavage of the radical anions by path a has been thought to be the most favorable owing to the available experimental evidence and the lower bond dissociation energies as compared to those for path b.[7b] For example, ESR spectroscopic studies have shown that the radical anion derived from fluorene undergoes a first order decay to form the conjugate base and a hydrogen atom.[8] Studies of electrochemical reductions in DMF of fluorene and its 9-methyl, 9-phenyl, and 9-benzyl derivatives have shown that fluorenide anions and molecular hydrogen are the products of the reductive cleavage reactions. The molecular hydrogen is evidently formed by the dimer-

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Table 1. Equilibrium Acidities and Electrochemical Data of the Nitro Aromatic Compounds

no.	compounds	pK_{HA}[a]	$E_{ox}(A^-)$[m]	$E_{rd}(HA)$[o]	$E_{rd}(A^-)$[s]
1	p-$\mathrm{NO_2C_6H_4OH}$	10.8[b]	0.405	−1.609	−2.215
2	m-$\mathrm{NO_2C_6H_4OH}$	14.4[b]	0.085	−1.573	−1.873
3	p-Cl-2,6-$\mathrm{(NO_2)_2C_6H_2OH}$	3.6[c]	0.837	−0.898	−1.620
4	p-$\mathrm{NO_2}$-2,6-(t-Bu)$_2$$\mathrm{C_6H_3OH}$	7.3[c]	0.141[n]	−1.572[p]	−2.372
5	2,4-dinitronaphthol	2.1[c]	0.664	−0.871[p]	−1.764
6	p-$\mathrm{NO_2C_6H_4COOH}$	9.0[c]	1.111	−1.281	−1.554
7	3,5-$\mathrm{(NO_2)_2C_6H_3COOH}$	7.3[c]	0.112	−1.135	−1.336
8	*cis*-m-$\mathrm{NO_2C_6H_4CH{=}NOH}$	17.7[d]	−0.461	−1.462[q]	−1.605
9	*trans*-m-$\mathrm{NO_2C_6H_4CH{=}NOH}$	17.6[d]	−0.459	−1.460[q]	−1.631
10	*cis*-p-$\mathrm{NO_2C_6H_4CH{=}NOH}$	17.0[d]	−0.405	−1.393[q]	−1.658
11	p-$\mathrm{NO_2C_6H_4SH}$	5.5[e]	0.040	−1.284	−1.877
12	p-$\mathrm{NO_2C_6H_4NH_2}$	20.9[f]	−0.239	−1.792	
13	p-$\mathrm{NO_2C_6H_4NHPh}$	16.9[f]	−0.260[f]	−1.658[p]	−2.209
14	p-$\mathrm{NO_2C_6H_4NHCOMe}$	17.6[g]	0.216	−1.572[q]	−1.869
15	2,4-$\mathrm{(NO_2)_2C_6H_3NH_2}$	15.9[c]	−0.027	−1.416[q]	−1.676
16	2-nitrofluorene	17.0[f]	−0.784	−1.491[q]	−1.949
17	2,7-dinitrofluorene	12.2[h]	−0.513	−1.378[p]	−1.715
18	p-$\mathrm{NO_2C_6H_4CH_3}$	20.4[c]	−0.728	−1.560	
19	p-$\mathrm{NO_2C_6H_4CH_2CN}$	12.3[c]	−0.388	−1.479[p,r]	−2.151
20	m-$\mathrm{NO_2C_6H_4CH_2CN}$	18.1[c]	−0.681	−1.445[q]	−1.792
21	m-$\mathrm{NO_2C_6H_4CH_2NO_2}$	10.0[i]	−0.019	−1.429	−1.624
22	p-$\mathrm{NO_2C_6H_4CH(Me)NO_2}$	10.3[j]	−0.020	−1.396	−1.659
23	m-$\mathrm{NO_2C_6H_4CH(Me)NO_2}$	11.5[j]	−0.083	−1.420[q]	−1.635
24	3,5-$\mathrm{(NO_2)_2C_6H_3CH(Me)NO_2}$	9.9[j]	−0.078	−1.167[q]	−1.392
25	p-$\mathrm{NO_2C_6H_4CH_2P^+Ph_3Br^-}$	11.4[k]	0.046	−1.419[p,r]	−1.883
26	p-$\mathrm{NO_2C_6H_4C(Ph){=}NCH_2CO_2Et}$	16.7[l]	−0.611	−1.397[q]	−1.784

[a] In pK_{HA} units; equilibrium acidities were measured in DMSO solution. [b] Reference 18. [c] Reference 16. [d] Reference 19. [e] Reference 20. [f] Reference 7a. [g] Reference 15. [h] Measured by Satish, A. V. [i] Reference 13. [j] Reference 7d. [k] Reference 17. [l] Measured by Zhang, X.-M. [m] In volts; irreversible oxidation potentials of the conjugate base were measured in DMSO solution unless otherwise noted and reference to ferrocenium/ferrocene couple. [n] Reversible oxidation potentials. [o] In volts; irreversible reduction potentials of the neutral compounds were measured in DMSO solution unless otherwise noted and reference to ferrocenium/ferrocene couple. [p] Partially reversible reduction potential. [q] Reversible reduction potential. [r] Sweep rate: 500 mV/s. [s] In volts; reversible reduction potentials of the conjugate base were measured.

Table 2. Bond Dissociation Free Energies[a] of the Neutral Compounds and the Corresponding Radical Anions by Three Different Pathways

no.	compounds	BDFE[b]	$\Delta G_{H^\bullet}(A^-)$[c]	$\Delta G_{H^-}(A^\bullet)$[d]	$\Delta G_{H^+}(A^{\bullet 2-})$[e]
1	p-$\mathrm{NO_2C_6H_4OH}$	93.7	47.3	81.8	28.8
2	m-$\mathrm{NO_2C_6H_4OH}$	91.3	53.1	80.2	26.6
3	p-Cl-2,6-$\mathrm{(NO_2)_2C_6H_2OH}$	93.8	53.8	98.2	21.5
4	p-NO2-2,6-(t-Bu)$_2$$\mathrm{C_6H_3OH}$	82.9	43.4	71.8	28.4
5	2,4-dinitronaphthol	92.0	52.4	92.8	23.4
6	p-$\mathrm{NO_2C_6H_4COOH}$	107.5	52.4	103.2	18.6
7	3,5-$\mathrm{(NO_2)_2C_6H_3COOH}$	82.4	53.4	81.3	14.6
8	*cis*-m-$\mathrm{NO_2C_6H_4CH{=}NOH}$	83.2	60.1	74.6	27.5
9	*trans*-m-$\mathrm{NO_2C_6H_4CH{=}NOH}$	83.1	60.0	74.6	28.1
10	*cis*-p-$\mathrm{NO_2C_6H_4CH{=}NOH}$	83.6	60.8	76.6	29.4
11	p-$\mathrm{NO_2C_6H_4SH}$	76.2	47.5	72.7	21.2
12	p-$\mathrm{NO_2C_6H_4NH_2}$	92.7	56.9	76.5	
13	p-$\mathrm{NO_2C_6H_4NHPh}$	86.7	54.5	73.6	35.9
14	p-$\mathrm{NO_2C_6H_4NHCOMe}$	98.7	57.5	87.6	31.0
15	2,4-$\mathrm{(NO_2)_2C_6H_3NH_2}$	90.8	58.7	83.2	27.8
16	2-nitrofluorene	74.8	58.5	65.6	33.9
17	2,7-dinitrofluorene	74.5	54.5	67.8	24.5
18	p-$\mathrm{NO_2C_6H_4CH_3}$	80.8	61.6	69.9	
19	p-$\mathrm{NO_2C_6H_4CH_2CN}$	77.5	52.3	68.5	32.3
20	m-$\mathrm{NO_2C_6H_4CH_2CN}$	78.7	61.0	70.4	32.8
21	m-$\mathrm{NO_2C_6H_4CH_2NO_2}$	82.7	50.3	75.0	18.2
22	p-$\mathrm{NO_2C_6H_4CH(Me)NO_2}$	83.2	51.5	76.2	20.2
23	m-$\mathrm{NO_2C_6H_4CH(Me)NO_2}$	83.4	52.6	75.8	20.7
24	3,5-$\mathrm{(NO_2)_2C_6H_3CH(Me)NO_2}$	81.4	56.3	79.6	18.8
25	p-$\mathrm{NO_2C_6H_4CH_2PPh_3Br}$	86.3	52.5	78.7	26.3
26	p-$\mathrm{NO_2C_6H_4C(Ph){=}NCH_2CO_2Et}$	78.4	60.3	71.3	31.8

[a] In kcal/mol, calculated by using data listed in Table 1. [b] Estimated by using BDFE $= 1.37pK_{HA} + 23.06E_{ox}(A^-) + 69.6$. [c] Estimated by using $\Delta G_{H^\bullet}(A^-) = 1.37pK_{HA} + 23.06E_{rd}(HA) + 69.6$. [d] Estimated by using $\Delta G_{H^-}(A^\bullet) = 1.37pK_{HA} + 23.06[E_{rd}(HA) + E_{ox}(A^-)] + 94.8$. [e] Estimated by using $\Delta G_{H^+}(A^{\bullet 2-}) = 1.37pK_{HA} + 23.06[E_{rd}(HA) - E_{rd}(A^-)]$.

ization of hydrogen atoms on the electrode surface.[9] The bond dissociation energy of the acidic C−H bond in the radical anion derived from fluorene has been estimated to be decreased by about 45 kcal/mol relative to that of the parent (80 kcal/mol).[7b] Most of the 17 2- and 9-substituted fluorenyl radical anions examined earlier were also found to have BDEs of their acidic C−H bonds in the 28−40 kcal/mol range.[7b]

An inspection of Scheme 3 and eq 2 shows that the choice between path a and path b is determined entirely by the difference between the oxidation potential of the anion, $E_{ox}(A^-)$, and the reduction potential of the hydro-

Scheme 3

$$\begin{array}{llll}
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{H}^\bullet + \mathrm{A}^- & \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) \\
\mathrm{A}^- - e & \rightleftharpoons & \mathrm{A}^\bullet & 23.06E_{\mathrm{ox}}(\mathrm{A}^-) \\
\mathrm{H}^\bullet + e & \rightleftharpoons & \mathrm{H}^- & -23.06E_{\mathrm{rd}}(\mathrm{H}^\bullet) \\
\hline
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{H}^- + \mathrm{A}^\bullet & \Delta G_{\mathrm{H}^-}(\mathrm{A}^\bullet)
\end{array}$$

$$\Delta G_{\mathrm{b-a}} = \Delta G_{\mathrm{H}^-}(\mathrm{A}^\bullet) - \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) = 23.06[E_{\mathrm{ox}}(\mathrm{A}^-) - E_{\mathrm{rd}}(\mathrm{H}^\bullet)] \quad (2)$$

Scheme 4

$$\begin{array}{llll}
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{H}^\bullet + \mathrm{A}^- & \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) \\
\mathrm{H}^\bullet - e & \rightleftharpoons & \mathrm{H}^+ & 23.06E_{\mathrm{rd}}(\mathrm{H}^+) \\
\mathrm{A}^- + e & \rightleftharpoons & \mathrm{A}^{\bullet 2-} & -23.06E_{\mathrm{rd}}(\mathrm{A}^-) \\
\hline
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{H}^+ + \mathrm{A}^{\bullet 2-} & \Delta G_{\mathrm{H}^+}(\mathrm{A}^{\bullet 2-})
\end{array}$$

$$\Delta G_{\mathrm{c-a}} = \Delta G_{\mathrm{H}^+}(\mathrm{A}^{\bullet 2-}) - \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) = 23.06[E_{\mathrm{rd}}(\mathrm{H}^+) - E_{\mathrm{rd}}(\mathrm{A}^-)] \quad (3)$$

gen atom, $E_{\mathrm{rd}}(\mathrm{H}^\bullet)$. The value of $E_{\mathrm{rd}}(\mathrm{H}^\bullet)$ in DMSO has recently been estimated to be −0.55 V when referred to $\mathrm{NHE}_{\mathrm{aq}}$, and −1.09 V when referred to $\mathrm{Fc}^+/\mathrm{Fc}$ couple.[3a]

Examination of eq 2 shows that (a) When the $E_{\mathrm{ox}}(\mathrm{A}^-)$ value is more negative than −1.09 V, i.e., $E_{\mathrm{ox}}(\mathrm{A}^-) < -1.09$ V, the difference between the bond dissociation free energies for path b and path a, $\Delta G_{\mathrm{b-a}}$, is a negative value. This means that path b requires less energy than path a, and that the radical anion will cleave preferentially by path b; (b) When the $E_{\mathrm{ox}}(\mathrm{A}^-)$ value is less negative than −1.09 V, i.e., $E_{\mathrm{ox}}(\mathrm{A}^-) > -1.09$ V, the radical anion will cleave preferentially by path a; (c) when the $E_{\mathrm{ox}}(\mathrm{A}^-)$ value is equal to −1.09 V, i.e., $E_{\mathrm{ox}}(\mathrm{A}^-) = -1.09$ V, the two pathways are equally favorable.

The NO_2 group has been shown to be the strongest of the acceptor groups studied to date in favoring path a over path b.[7d] It is not surprising then to find that in Table 1 all of the $E_{\mathrm{ox}}(\mathrm{A}^-)$ values are less negative than −1.09 V. Comparing the data in columns 4 and 5 of Table 2 shows that path a is favored over path b for all the radical anions by 7−35 kcal.

A similar thermodynamic cycle (Scheme 4) can be devised to decide the preference between path a and path c. Examination of eq 3 shows that only when the reduction potential of an anion, $E_{\mathrm{rd}}(\mathrm{A}^-)$, is more negative than that of the proton, $E_{\mathrm{rd}}(\mathrm{H}^+)$, i.e., −3.02 V vs the $\mathrm{Fc}^+/\mathrm{Fc}$ couple,[3a] will path a be more favorable than path c. But none of the $E_{\mathrm{rd}}(\mathrm{A}^-)$ data in Table 1 are more negative than −3.02 V, so the radical anions *all* favor path c over path a thermodynamically.

Comparison of the $\Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-)$, $\Delta G_{\mathrm{H}^-}(\mathrm{A}^\bullet)$, and $\Delta G_{\mathrm{H}^+}(\mathrm{A}^{\bullet 2-})$ data listed in Table 2 shows that the bond dissociation free energies of the radical anions to give a proton and radical dianion by path c provides the lowest energy pathway as compared to those of the other two pathways. The bond dissociation free energies of the radical anions to give a hydride ion and a radical by path b is the highest energy pathway, and that for radical anions to give a hydrogen atom and an anion is intermediate between the two. For example, the bond dissociation free energy of the radical anion derived from *p*-nitrophenol by path c is 28.8 kcal/mol, which is 18.5 kcal/mol lower than that by path a, and 53.0 kcal/mol lower than that by path b. For the radical anion derived from $p\text{-}\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{CH}_2\mathrm{CN}$, path c is favored over path a and path b by 20 kcal and 36 kcal, respectively. The relatively low $\Delta G_{\mathrm{H}^+}(\mathrm{A}^{\bullet 2-})$ values are no doubt due to the enormous solvation energy of the proton in DMSO solvent (the standard transition free energy of a proton from the gas phase to the DMSO solvent is −265 kcal/mol).[10]

Scheme 5

$$\begin{array}{llll}
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{H}^\bullet + \mathrm{A}^- & \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) \\
\mathrm{H}^\bullet(\mathrm{DMSO}) + e & \rightleftharpoons & 1/2\mathrm{H}_2(\mathrm{g}) & -\Delta G^\circ_{\mathrm{f}}(\mathrm{H}^\bullet)_{\mathrm{DMSO}} \\
\hline
\mathrm{HA}^{-\bullet} & \rightleftharpoons & \mathrm{A}^- + 1/2\mathrm{H}_2(\mathrm{g}) & \Delta G
\end{array}$$

$$\Delta G = \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) - \Delta G^\circ_{\mathrm{f}}(\mathrm{H}^\bullet)_{\mathrm{DMSO}} = \Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-) - 52.6\ \mathrm{kcal/mol} \quad (4)$$

The Kinetic Choice among Three Different Cleavage Pathways of the Radical Anions. Although the path c is clearly most thermodynamically favorable, this does not mean that it will be the most kinetically favorable pathway. Actually, it seems likely that path a will be the predominant path taken by most organic radical anions. This conclusion is based on electrochemical studies of a variety of nitro-substituted aromatic compounds. A number of nitro-substituted aromatic compounds have been observed to give irreversible or partially reversible reduction potentials (Table 1), which were usually followed in the CV scan by a reversible reduction potential. The later reversible potentials proved to be identical to those of the conjugate bases produced by addition of 1 equiv of dimsyl ($\mathrm{CH}_3\mathrm{SOCH}_2{}^-\mathrm{K}^+$, the conjugate base of the solvent DMSO) to the DMSO solution of the neutral compounds.[21]

The kinetic preference of path a is understandable since it can be linked with the strongly exothermic dimerization of the hydrogen atoms formed by this pathway (Scheme 5). (The standard free energy of formation for the hydrogen atom, $\Delta G^\circ_{\mathrm{f}}(\mathrm{H}^\bullet)$, has been estimated by Parker to be 52.6 kcal/mol in DMSO.[11]) It is interesting in this regard to note that in Table 2 the nitro-substituted aromatic compounds for which the $\Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-)$ values are lower or comparable to the $\Delta G^\circ_{\mathrm{f}}(\mathrm{H}^\bullet)$ value (52.6 kcal/mol) generally undergo irreversible electron transfer on the electrode to give unstable radical anions ($\Delta G < 0$ or $\Delta G = 0$), whereas those with higher $\Delta G_{\mathrm{H}^\bullet}(\mathrm{A}^-)$ values give reversible reduction potentials ($\Delta G > 0$), and relatively stable radical anions.

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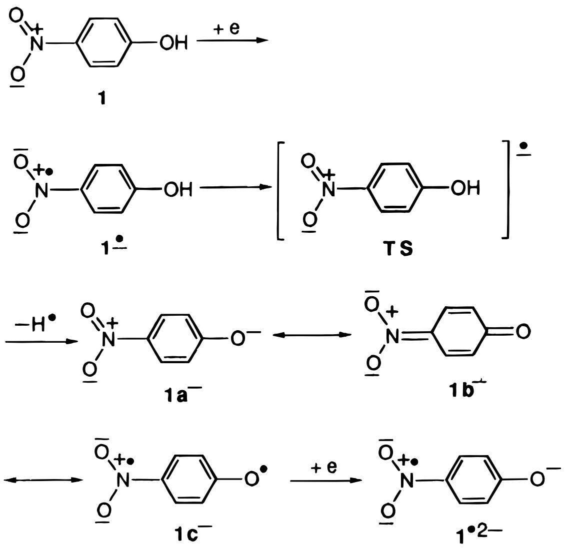
Scheme 6



It is not uncommon in chemistry and biochemistry that many reactions with a large positive value of ΔG do, in fact, occur when they are coupled to a second reaction having a large negative value of ΔG, so that $\Delta G < 0$ for the pair of reactions. When path a (with a positive ΔG value) is coupled with the dimerization of the hydrogen atom (with a negative ΔG value), the ΔG values for the coupled reaction (Scheme 5) fall in the range of −9.2 to 9.0 kcal.

A mechanism for the cleavage of radical anions and for the formation of the corresponding radical dianions is presented in Scheme 6 (taking *p*-nitrophenol as an example). First, the radical anion is formed by addition of an electron to the conjugated system including the nitro group and the benzene ring, then the electron is transfered from the π^* orbital of the nitro group through the benzene ring to the σ^* orbital of the O−H moiety in a rate-determing step via a transition state (TS). The O-H bond is weakened by the transfer of the electron, and is broken, perhaps concertedly with electron transfer, to give a hydrogen atom and the corresponding *p*-nitrophenoxide ion. The negative charge in the anion is delocalized, and another electron can be added to form the radical dianion.

An inspection of the $\Delta G_{H^\bullet}(A^-)$ values for the radical anions derived from entries 1, 12, and 18 in Table 2 shows that there seems to be some relationship between the $\Delta G_{H^\bullet}(A^-)$ values and the electronegativities of the donor atoms in the acidic H−A bond. The radical anion derived from entry 1 with the strongly electronegative oxygen atom as the donor atom gives the lowest $\Delta G_{H^\bullet}(A^-)$ value, whereas the radical anion derived from entry 18 with the weakly electronegative carbon atom as the donor atom has the highest $\Delta G_{H^\bullet}(A^-)$ value. A roughly linear plot (Figure 1; $r = 0.979$) was obtained when the $\Delta G_{H^\bullet}(A^-)$ values for the radical anions derived from entries 1, 12, and 18 were plotted versus the electronegativity differences between the donor atoms and the hydrogen atom in the acidic H−A bonds.

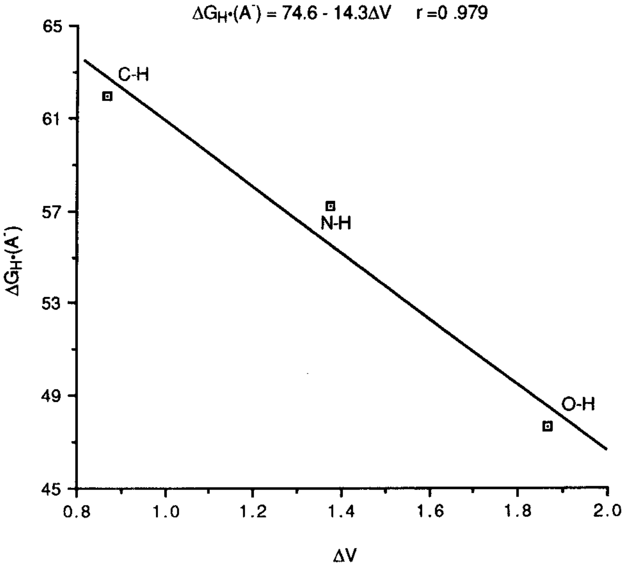


Figure 1. Plot of $\Delta G_{H^\bullet}(A^-)$ values of radical anions derived from 4-nitrotoluene, 4-nitroaniline, and 4-nitrophenol versus the differences in electronegativities of the atoms forming the bonds being cleaved (ΔV).

Experimental Section

All of the compounds studied in this paper were previously synthesized in our laboratory[21] or purchased. The oxidation and reduction potentials were measured in DMSO by cyclic voltammetry (CV). The working electrode (BAS) consists of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal. It was polished with a 0.05-mm Fischer polishing aluminum or cleaned with an ultrasonic instrument, rinsed with ethanol, and dried before each run. The counter electrode was a platinum wire (BAS). The reference electrode was Ag/AgI, and the reported potentials were referenced to ferrocenium/ferrocene (Fc^+/Fc) couple. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under argon atmosphere.

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