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Bond Dissociation Energies of the Acidic H–A Bonds in $HA^{\bullet+}$ Radical Cations and in $HA^{\bullet-}$ Radical Anions in DMSO Solution

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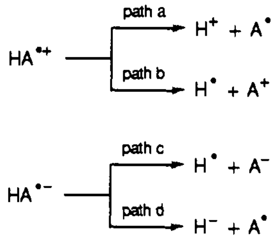
Abstract: An equation based on a thermodynamic cycle has been used for estimating the bond dissociation energies for the cleavage of the acidic H–A bonds in radical anions to form hydride ions and radicals, i.e., $HA^{\bullet-} \rightarrow H^- + A^\bullet$ (path *d* in Scheme 1). Estimates of these $BDE_{HA^{\bullet-}}$ values have been made for (a) eighteen 2- and 9-substituted fluorenes, (b) six $4\text{-}GC_6H_4CHPh_2$ triphenylmethanes, and related compounds, (c) eight $9\text{-}G\text{-}CH_2$-substituted anthracenes, (d) nine 10-substituted 9-methylanthracenes, and (e) five substituted anilines and related N–H acids. Comparisons of these path *d* $BDE_{HA^{\bullet-}}$ values are made with previously obtained $BDE_{HA^{\bullet-}}$ values for cleavage of the acidic H–A bonds in these radical anions to form hydrogen atoms ($H^\bullet$) and A^- anions, i.e., $HA^{\bullet-} \rightarrow H^\bullet + A^-$ (path *c* in Scheme 1). Analysis of the results indicates that substituents affect the $BDE_{HA^{\bullet-}}$ values so as to (a) increase the $BDE_{HA^{\bullet-}}$ values by both paths *c* and *d* by stabilizing the initial radical anions, and/or (b) decrease the $BDE_{HA^{\bullet-}}$ values for reaction by path *c* and *d* by stabilizing the initial radical anions, and/or (b) decrease the $BDE_{HA^{\bullet-}}$ values for reaction by path *d* by stabilizing the radical products. The results indicate that reactions by either path *c* or path *d* may be viable, the favored pathway depending on the nature of the substituents.

The radical cations, $HA^{\bullet+}$, and radical anions, $HA^{\bullet-}$, formed from weak acids, HA, by loss or addition of one electron are both important and highly reactive intermediates in chemistry.[1] Thermodynamic cycles have been devised for estimating the bond dissociation energies for their cleavage,[2] but only a limited number of BDEs derived from these cycles were reported. The question of modes of cleavage has also been addressed.[2a] Two modes of cleavage of $HA^{\bullet+}$ and of $HA^{\bullet-}$ radical ions are conceivable, as illustrated in Scheme 1.

Scheme 1



In the gas phase loss of a hydrogen atom from a radical cation with the formation of a cation, A^+ (path *b*), is the rule for hydrocarbon radical cations. For example, the $CH_4^{\bullet+}$ radical cation formed in a mass spectrometer by bombardment of CH_4 with high-energy electrons loses a hydrogen atom to form a CH_3^+ cation as the major pathway,[3a] and under similar conditions the $C_6H_5\text{–}CH_3^{\bullet+}$ radical cation loses a hydrogen atom to give the $C_7H_7^+$ cation as the exclusive pathway.[3b] On the other hand, in aqueous or dimethyl sulfoxide (DMSO) solution the enormous solvation energy of the proton [$\Delta G_t(H^+)_g$ to $(H^+)_{aq}$ is -260.5 kcal/mol,[4] and $\Delta G^\circ_t(H^+)_g$ to $(H^+)_{DMSO}$ is -265 kcal/mol[5]] is much greater than the solvation energy for any organic cation, and strongly favors path *a* over path *b*. (Henceforth, kcal/mol will be abbreviated as kcal.) Cleavage of the acidic H–A bonds in radical cations by path *a* has been observed experimentally in solution in a number of instances.[6–9] Furthermore, radical cations derived from a number of hydrocarbon acids have been shown to have highly negative $pK_{HA^{\bullet+}}$ values,[6b] which means that the acidic H–A bonds will dissociate spontaneously to form proton (H^+) and radical ($A^\bullet$) in H_2O, DMSO, and like solvents.

On the other hand, estimates for cleavage of the acidic H–A bonds in radical cations $HA^{\bullet+}$ in DMSO by path *b* have shown these BDEs to be endothermic, and for seventeen 9-(dialkylamino)fluorenyl radical cations $(9\text{-}R_2NFlH)^{\bullet+}$ containing carbon-centered radicals stabilized by adjacent dialkylamino groups, the $BDE_{HA^{\bullet+}}$ values were estimated to be 30–50 kcal smaller than the BDE_{HA} values for the corresponding parent $9\text{-}R_2NFlH$ acids.[10a] The relatively small $BDE_{HA^{\bullet+}}$ values for these radical cations (22–40 kcal) were correlated with the stabilization of the A^+

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cations formed by the α-dialkylamino groups. The $\mathrm{BDE}_{\mathrm{HA}^{\bullet+}}$ values for 15 substituted aromatic hydrocarbons, such as those derived from fluorene (H_2Fl) or toluene ($PhCH_3$), were found, however, to be correlated primarily with the stabilities of the initial radical cations, $H_2Fl^{\bullet+}$ or $PhCH_3^{\bullet+}$, rather than the stabilities of the product cations, HFl^+ or $PhCH_2^+$. These $\mathrm{BDE}_{\mathrm{HA}^{\bullet+}}$ values were in the 30–50-kcal range.[10a] The $\mathrm{BDE}_{\mathrm{HA}^{\bullet+}}$ values in DMSO for these 32 radical cations for proton loss (path *a*) are estimated to be smaller than those for hydrogen atom loss (path *b*) by about 35–75 kcal.[10a] Similarly, the loss of a proton from neutral weak acids (HA) has also been shown to be much more favorable than the loss of a hydrogen atom in DMSO solution.[10b]

The choice between cleavage of the acidic H–A bonds in radical anions by paths *c* and *d* is not so clear-cut. In the gas phase path *c* (loss of $H^\bullet$ and A^-) is favored. For example, fragmentation of the $NH_3^{\bullet-}$ radical anion in the gas phase gives $H^\bullet$ and NH_2^-,[11a] and fragmentation of the 1,3-dithiane radical anion gives $H^\bullet$ together with fragmentation products derived from the 1,3-dithiane-2-carbanion.[11b] 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."[2a] Their calculations of ΔG° values indicated that hydride ion and $A^\bullet$ radical loss in acetonitrile ($\Delta G^\circ{}_{16}$)[12] for toluene, fluorene, and 1-methylnaphthalene radical anions were more endothermic (32.7, 27.3, and 46.8 kcal, respectively) than for A^- and $H^\bullet$ loss (7.6, 18.0, and 25.8 kcal, respectively). Also, preference for hydrogen atom and A^- loss in solution has been observed by ESR[13] and by electrochemical studies.[14] In the latter study, the radical anions derived from fluorene and 9-methyl-, 9-phenyl-, and 9-benzylfluorenes, as well as from *p*-cyanoaniline, have been shown to undergo a first-order decay in *N,N*-dimethylformamide to form anions and molecular hydrogen. (Molecular hydrogen is evidently formed by dimerization of hydrogen atoms on the electrode surface.) In earlier papers we have used eq 1with $C = 73.3$ [the reduction potential $E_{re}(HA)$

$$\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } c) = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{re}}(\mathrm{HA}) + C \qquad (1)$$

is referenced to the ferrocene/ferrocenium couple] to estimate homolytic bond dissociation energies of the acidic H–A bonds cleaved by path *c* in $HA^{\bullet-}$ radical anions derived from 19 fluorenes,[15a] 15 triphenylmethanes,[15a] 3 xanthenes,[15a] *p*-nitrotoluene,[15a] diphenylmethane,[15a] bis(4-nitrophenyl)methane,[15a] eight α-substituted 9-methylanthracenes,[15b] and nine 10-substituted 9-methylanthracenes.[15b] We now present a method of estimating $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ vlaues for the acidic H–A bonds in $HA^{\bullet-}$ radical anions undergoing cleavage by loss of a hydride ion and an $A^\bullet$ radical (path *d*) and apply it to radical anions derived from all of these compounds. These estimates suggest that in DMSO solution cleavage by path *d* will be competitive with that of path *c* for the acidic H–A bonds in some radical anions.

Results and Discussion

By using eq 2, which is based on the thermodynamic cycle shown in Scheme 2,[2b,2d,15a] we can now estimate $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for the acidic H–A bonds in $HA^{\bullet-}$ radical anions undergoing cleavage of the acidic H–A bonds to form hydride ions and $A^\bullet$ radicals by path *d*.

Scheme 2

$$\begin{array}{lll}
\mathrm{HA}^{\bullet-} & \rightleftarrows \mathrm{HA} + e^- & E_{\mathrm{re}}(\mathrm{HA}) \\
\mathrm{HA} & \rightleftarrows \mathrm{H}^\bullet + \mathrm{A}^\bullet & \mathrm{BDE}_{\mathrm{HA}} \\
\mathrm{H}^\bullet + e^- \rightleftarrows \mathrm{H}^- & & -E_{\mathrm{re}}(\mathrm{H}^\bullet) \\
\mathrm{HA}^{\bullet-} & \rightleftarrows \mathrm{H}^- + \mathrm{A}^\bullet & \mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } d)
\end{array}$$

$$\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } d) = \mathrm{BDE}_{\mathrm{HA}} + 23.1[E_{\mathrm{re}}(\mathrm{HA}) - E_{\mathrm{re}}(\mathrm{H}^\bullet)] \qquad (2)$$

Equation 2 can be applied to a large variety of substrates because (a) $\mathrm{BDE}_{\mathrm{HA}}$ values for the acidic H–A bonds in several hundred neutral weak acids have been estimated by eq 3 in our laboratory during the past six years[16] and because (b) their reduction potentials [$E_{\mathrm{re}}(\mathrm{HA})$] can usually be determined by cyclic voltammetry.[15] Finally, the reduction potential of the hydrogen atom, $E_{\mathrm{re}}(\mathrm{H}^\bullet)$, has recently been estimated to be –0.55 V vs the $\mathrm{NHE}_{\mathrm{aq}}$. Subtraction of 0.75 V to reference to the ferrocene/ferrocenium couple F_c/F_c^+ gives –1.30 V, which was used in reference $E_{\mathrm{re}}(\mathrm{H}^\bullet)$ in eq 2.

$$\mathrm{BDE}_{\mathrm{HA}} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3 \qquad (3)$$

Estimates of $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ Values for the Cleavage of the Acidic H–A Bonds in Fluorenyl Radical Anions. Estimates of $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for the cleavage of the acidic H–A bonds in radical anions derived from fluorene, four 2-substituted fluorenes, and thirteen 9-substituted fluorenes by paths *c* and *d* are summarized in Table 1. The $\mathrm{BDE}_{\mathrm{HA}^{\bullet+}}$ values for a number of radical cations are given for comparison.

Examination of Table 1 shows that $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for cleavage of the acidic H–A bonds in fluorenyl radical anions by either path *c* or *d* are decreased by an average of 35 kcal, relative to the $\mathrm{BDE}_{\mathrm{HA}}$ values for the corresponding neutral parents to which the extra electron was added. One can visualize three ways that substituents can affect $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values. They can (a) increase the $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for both reactions by paths *c* and *d* to the same degree by stabilizing the initial radical anion by delocalizing the negative charge and/or odd electron, (b) decrease the $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for reaction by path *d* by stabilizing the fluorenyl radical product; and (c) decrease the $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for reaction by path *d* by stabilizing the fluorenyl radical product. Introduction of the 2-CN, 2-$PhSO_2$, or 2-NO_2 groups (entries 3–5 in Table 1) increases the $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for H–A cleavage by either path *c* or path *d* by stabilizing the initial radical anions, i.e., decreases the reduction potentials. The smaller effect on path *c* than path *d*, which leads to ΔBDE increases of 11–14 kcal (ΔBDE = path *d* $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ – path *c* $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$) (column 9 in Table 1), is the result of stabilization of the fluorenide ion products, but not fluorenyl radicals. Introduction of the 9-$PhSO_2$ and 9-MeOCO groups (entries 8 and 9 in Table 1) has a similar effect. On the other hand, introduction of the powerful 9-RR′N electron donors (entries 12–18 in Table 1) tends to decrease the $\mathrm{BDE}_{\mathrm{HA}^{\bullet-}}$ values for path *d* selectively by their ability to stabilize the fluorenyl radical products, giving rise to ΔBDE values that are close to zero or even negative. The negative ΔBDE means that the loss of a hydride ion (path *d*) is the favorable pathway. These effects are illustrated in Scheme 3.

Note that in radical anion **1** and in the fluorenide ion product **2** the 2-CN group can stabilize the negative charge and lower the energies, whereas in radical anion **3** the 9-Me_2N group can exert little or no stabilizing effect on the radical anion but can interact

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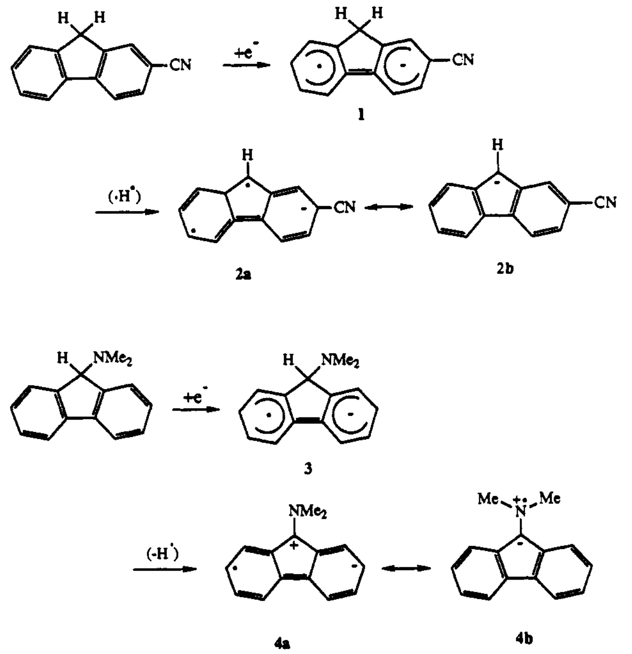
Table 1. Bond Dissociation Energies of the Acidic C–H Bonds in Fluorenes and Their Corresponding Radical Anions and Cations

						BDE$_{HA^{\cdot-}}$			
no.	substrates	pK_{HA}[a]	$E_{ox}(A^-)$[b]	$E_{re}(HA)$[d]	BDE$_{HA}$[f]	path *c*[g]	path d[h]	ΔBDE[i]	BDE$_{HA^{\cdot+}}$[j] (path *b*)
1	fluorene	22.6	−1.069	−3.006	79.5	35	40	5	56
2	2-Me_2N	24.2	−1.123	3.142	80.5	34	38	4	
3	2-CN	18.2	−0.813	−2.313	79.5	45	56	11	
4	2-$PhSO_2$	18.1	−0.792	−2.236	80	46.5	58	11.5	
5	2-NO_2	17.0	−0.684	−1.418[e]	81	64	78	14	
6	9-Ph	17.9	−1.028	−3.032	74	28	34	6	46
7	9-mesityl	18.6	−1.049[c]	−3.080	74.5	27.5	33.5	6	50
8	9-$PhSO_2$	11.55	−0.309	−2.132	82	40	63	23	
9	9-MeOCO	10.35	−0.492	−2.847	76	22	40.5	18.5	
10	9-EtS	17.5	−0.993	−2.493	74.5	40	47	7	
11	9-EtO	22.0	−1.322	−2.589	73	44	43	−1	
12	9-Me_2N	22.5	−1.418[c]	−2.868	71.5	38	35	−3	37
13	9-*c*-C_4H_8N	22.2	−1.553[c]	−2.894	68	37	31	−6	35
14	9-*c*-$C_5H_{10}N$	22.5	−1.382[c]	−2.863	72	38	36	−2	39
15	9-PhCH(Me)N	22.0	−1.334[c]	−2.822	72.5	38	37.5	−0.5	39
16	9-(*i*-Pr)$_2$N	20.8	−1.242[c]	−2.955	73	33.5	35	1.5	40
17	9-C(Me)(H)$(CH_2)_3$C(Me)(H)N	19.4	−1.198[c]	−2.888	72	33	35.5	2.5	41
18	9-C$(Me)_2(CH_2)_3$C$(Me)_2$N	18.2	−1.166	−2.982	71	29	32.5	3.5	54.5

[a] In pK_{HA} units; equilibrium acidities were measured in DMSO solution. [b] In volts; the irreversible oxidation potentials of the conjugate bases were measured in DMSO solution unless otherwise indicated. [c] Reversible oxidation potentials. [d] In volts; irreversible reduction potentials were measured in DMSO solution unless otherwise indicated. [e] Reversible reduction potentials. [f] In kcal/mol; homolytic bond dissociation energies of the acidic C–H bonds in weak acids; estimated by using $BDE_{HA} = 1.37\,pK_{HA} + 23.1E_{ox}(A^-) + 73.3$. [g] In kcal/mol; homolytic bond dissociation energies of the acidic C–H bonds in radical anions cleaved by path *c*, estimated by eq 1. [h] In kcal/mol; bond dissociation energies of the acidic C–H bonds in radical anions cleaved by path *d*, estimated by eq 2. [i] $\Delta BDE = BDE_{HA^{\cdot-}}$(path *d*) − $BDE_{HA^{\cdot-}}$(path *c*). [j] In kcal/mol; homolytic bond dissociation energies of the acidic C–H bonds in radical cations cleaved by path *b*; estimated by using $BDE_{HA^{\cdot+}} = BDE_{HA} + 23.1[E_{ox}(A^{\cdot}) - E_{ox}(HA)]$.[10a]

Scheme 3



directly with the radical (**4a** ↔ **4b**). The stabilizing effect of the 2-CN group on anion **2** causes the acidity of the conjugate acid to increase by 6 kcal but has no stabilizing effect on the fluorenyl radical (the BDE$_{HA}$ value remains constant). The stabilizing effect of the 9-Me_2N group on radical **4** is estimated to be 8 kcal (compare the BDE$_{HA}$ values of entries 1 and 12 in Table 1), but the 9-Me_2N group has no stabilizing effect on the fluorenide anion. The other substituents in Table 1 tend to have intermediate effects. For example, the 9-Ph group decreases the BDE$_{HA^{\cdot-}}$ value for reaction by path *c* by 7 kcal by virtue of its stabilizing effect on the fluorenide ion product, but it also decreases the BDE$_{HA^{\cdot-}}$ value for reaction by path *d* by its 6 kcal stabilizing effect on the fluorenyl radical.

The results in Table 1 indicate that reactions by either path *c* or path *d* are viable pathways for substituted fluorenyl radical anions, the favored pathway depending on the nature of the substituents.

When eq 2 is written in an expanded form, with eq 3 used in place of BDE$_{HA}$, and eq 1 is subtracted therefrom, the result is that $\Delta BDE = \Delta E_{ox}(A^-)$. In other words, the choice between path *d* and path *c* is determined entirely by the relative oxidation potentials of the two anions. For example, the $E_{ox}(A^-)$ value for the 2-CNFl$^-$ ion is −0.813 V and that for the 9-Me_2NFl^- ion is −1.418 V (Table 1). The difference is 0.605 V or 14 kcal (compare with the ΔBDE in Table 1). This means that we can identify the path (*c* or *d*) that will be favored for cleavage of radical anions derived from families of weak acids by merely measuring the oxidation potentials of their conjugate bases—the more negative the oxidation potential the more likely that path *c* will be followed. The primary factors controlling the oxidation potentials of anions are (a) their basicities (there is an intrinsic linear relationship between an organic anion's basicity and its oxidation potential[15b]) and (b) the stability of the corresponding radical formed on oxidation. The anions in Table 1 have pK_{HA} values falling in the range of about 10–25. Only those fluorenide anions with pK_{HA} values near the top of this range and those that bear R_2N groups at the 9-position (entries 11–15) have oxidation potentials negative enough [$E_{ox}(A^-) < -1.30$ V] to allow path *d* to be favored.

Comparison of the BDEs for the cleavage of HA$^{\cdot-}$ radical anions derived from fluorenes with the BDEs of the radical cations derived from the same fluorene shows a close similarity in values for entries 12–16. This is not surprising since the R_2N substituents stabilize radicals, and we have seen that the size of both BDE$_{HA^{\cdot+}}$ values[10] and BDE$_{HA^{\cdot-}}$ values is correlated with radical product stabilities [$E_{ox}(A^{\cdot})$ and $E_{ox}(A^-)$, respectively].

The presence of electron-withdrawing groups (entries 3–5 and 8–10) stabilizes the anion products formed by cleavage of radical anions thus favoring path *c*. These substituents are expected to destabilize the corresponding radical cations and raise the BDE$_{HA^{\cdot+}}$ values. The presence of 9-Ph and 9-methyl groups also raise the BDE$_{HA^{\cdot+}}$ values compared to R_2N groups because steric constraints lower their donor properties.

Examination of Table 2 shows that only three of the substituted triphenylmethanes (entries 1–3) have oxidation potentials negative enough [$E_{ox}(A^-) < 1.30$ V] (due to the high basicities of their anions) to make path *d* (slightly) favored over path *c*. The presence

Table 2. Bond Dissociation Energies of the Acidic C–H bonds in *p*-Nitrotoluene, Triphenylmethanes, and 9-Methylanthracenes (9-MeAn) and in Their Corresponding Radical Anions and Radical Cations

						BDE$_{\mathrm{HA}^{\bullet-}}$			
no.	substrates	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	$E_{\mathrm{re}}(\mathrm{HA})$[d]	BDE$_{\mathrm{HA}}$[f]	path *c*[g]	path *d*[h]	ΔBDE[i]	BDE$_{\mathrm{HA}^{\bullet+}}$[j] (path *b*)
1	4-$PhC_6H_4CHPh_2$	29.4	−1.430	−2.889[e]	80.5	47	44	−3	
2	4-$PhSC_6H_4CHPh_2$	28.3	−1.352[c]	−2.807[e]	81	47	46	−1	
3	3-$CF_3C_6H_4CHPh_2$	28.4	−1.337[c]	−2.970	81	44	43	−1	
4	4-$PhSO_2C_6H_4CHPh_2$	23.6	−1.078[c]	−2.457	80.5	49	54	5	
5	4-$PhCOC_6H_4CHPh_2$	22.4	−1.067[c]	−2.147[e]	79.5	54	60	6	28
6	4-$NO_2C_6H_4CHPh_2$	16.8	−0.682[c]	−1.495[e]	80.5	62	76	14	27
7	4-$NO_2C_6H_4CH_3$	20.4	−0.644	−1.479[e]	86.5	67	82	15	
8	(4-$NO_2C_6H_4)_3CH$	12.7	−0.492[c]	−1.404[e]	79.5	58	77	19	26
9	9-MeAn	31.1	−1.489	−2.417[e]	81.5	60	55.5	−4.5	
10	9-$MeOCH_2An$	30.6	−1.635	−2.295[e]	77.5	62	54.5	−7.5	
11	9-$PhOCH_2An$	30.2	−1.513	−2.153[e]	80	65	60	−5	
12	9-$PhSCH_2An$	28.6	−1.362	−2.089	81	64	63	−1	
13	9-$PhSO_2CH_2An$	21.6	−0.786	−1.929	84.5	58	70	12	
14	9-$CNCH_2An$	19.8	−0.930	−2.203[e]	79	49.5	58	8.5	
15	9-$PhCOCH_2An$	18.86	−0.645	−2.271[e]	84	46.5	62	15.5	
16	9-NO_2CH_2An	12.8	−0.205	−1.870	86	47.5	73	25.5	
17	10-Me-9-MeAn	31.8	−1.515	−2.465[e]	82	60	55	−5	
18	10-MeO-9-MeAn	31.8	−1.537	−2.389[e]	81.5	61.5	56	−5.5	
19	10-Ph-9-MeAn	30.75	−1.456	−2.340[e]	82	61.5	58	−3.5	
20	10-Cl-9-MeAn	28.2	−1.347	−2.207[e]	81	61	60	−1	
21	10-PhS-9-MeAn	25.5	−1.188	−2.102[e]	81	60	62.5	2.5	
22	10-PhCO-9-MeAn	22.2	−0.928	−2.071[e]	82	56	64.5	8.5	
23	10-CHO-9-MeAn	16.6	−0.675	−1.740[e]	80.5	56	70.5	14.5	
24	10-CN-9-MeAn	20.0	−0.895	−1.877[e]	80	57	66.5	9.5	
25	10-NO_2-9-MeAn	13.2	−0.379	−1.475[e]	82.5	57	78.5	21.5	

[a] In pK_{HA} units; equilibrium acidities were measured in DMSO solution. [b] In volts; the irreversible oxidation potentials of the conjugate bases were measured in DMSO solution unless otherwise indicated. [c] Reversible oxidation potentials. [d] In volts; irreversible reduction potentials were measured in DMSO solution unless otherwise indicated. [e] Reversible reduction potentials. [f] In kcal/mol; homolytic bond dissociation energies of the acidic C–H bonds in weak acids; estimated by using $\mathrm{BDE_{HA}} = 1.37\,\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3$. [g] In kcal/mol; bond dissociation energies of the acidic C–H bonds in radical anions cleaved by path *c*, estimated by eq 1. [h] In kcal/mol; bond dissociation energies of the acidic C–H bonds in radical anions cleaved by path *d*, estimated by eq 2. [i] $\Delta\mathrm{BDE} = \mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } d) - \mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } c)$. [j] In kcal/mol; bond dissociation energies of the acidic C–H bonds in radical cations cleaved by path *b*; estimated by using $\mathrm{BDE}_{\mathrm{HA}^{\bullet+}} = \mathrm{BDE_{HA}} + 23.1[E_{\mathrm{ox}}(\mathrm{A}^\bullet) - E_{\mathrm{ox}}(\mathrm{HA})]$.[10a]

Table 3. Bond Dissociation Energies of the Acidic N–H Bonds in Anilines and in Their Corresponding Radical Anions

no.	substrates	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	$E_{\mathrm{re}}(\mathrm{HA})$[c]	BDE$_{\mathrm{HA}}$[e]	BDE$_{\mathrm{HA}^{\bullet-}}$[f] (path *c*)	BDE$_{\mathrm{HA}^{\bullet-}}$[g] (path *d*)	ΔBDE[h]
1	*p*-$CNC_6H_4NH_2$	25.26	−0.550	−3.113	95	36	53.5	17.5
2	*m*-$CNC_6H_4NH_2$	27.5	−0.735	−2.855	94	45	58	13
3	2,4,6-$Cl_3C_6H_2NH_2$	23.5	−0.433	−2.637	95.5	44.5	64.5	20
4	*o*-NO_2-*p*-$ClC_6H_3NH_2$	18.9	−0.068	−1.436[d]	97.5	66	94.5	28.5
5	*p*-$NO_2C_6H_4NH_2$	20.9	−0.227	−1.684[d]	96.5	63	88	25
6	iminostilbene	26.1	−1.057	−2.501	84.5	51	57	6
7	*p*-$NO_2C_6H_4NHPh$	16.85	−0.260	−1.525[d]	90.5	61	85	24
8	carbazole	19.9	−0.336	−3.075	93	29.5	52	22.5
9	1,3*H*-dibenzo[*a*,*i*]carbazole	17.7	−0.207	−2.906	93	30.5	55.5	25
10	3,6-dibromocarbazole	17.15	−0.140	−2.572	93.5	37.5	64	26.5

[a] In pK_{HA} units; equilibrium acidities were measured in DMSO solution. [b] In volts; the irreversible oxidation potentials of the conjugate bases were measured in DMSO solution unless otherwise indicated. [c] In volts; irreversible reduction potentials were measured in DMSO solution unless otherwise indicated. [d] Reversible reduction potentials. [e] In kcal/mol; homolytic bond dissociation energies of the acidic N–H bonds in weak acids; estimated by $\mathrm{BDE_{HA}} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3$. [f] In kcal/mol; bond dissociation energies of the acidic N–H bonds in radical anions cleaved by path *c*, estimated by eq 1. [g] In kcal/mol; bond dissociation energies of the acidic N–H bonds in radical anions cleaved by path *d*, estimated by eq 2. [h] $\Delta\mathrm{BDE} = \mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } d) - \mathrm{BDE}_{\mathrm{HA}^{\bullet-}}(\text{path } c)$.

of strong electron-withdrawing groups, as in entries 5, 6, and 8 of Table 2, leads to relatively low pK_{HA} and relatively positive $E_{\mathrm{ox}}(\mathrm{A}^-)$ values. This combination leads, in turn, to relatively low BDE$_{\mathrm{HA}^{\bullet+}}$ values and relatively high BDE$_{\mathrm{HA}^{\bullet-}}$ values. The same factors are no doubt operative in the anthracenes listed in Table 2. The presence of the donor Me, MeO, PhO, PhS, Ph, or Cl groups in the anthracenes (entries 9, 10, 11, 12, 17, 18, 19, and 20) causes the $E_{\mathrm{ox}}(\mathrm{A}^-)$ value to become more negative than −1.30 V, however, making path *d* favored for BDE$_{\mathrm{HA}^{\bullet-}}$ values.

Handoo et al.[2d] have used a sum of comparable pK_{HA} and electrochemical data for these anthracenes to obtain the free energies of hydride affinities. These values agree reasonably well with our BDE$_{\mathrm{HA}^{\bullet-}}$(enthalpy) values when one considers that about 5 kcal needs to be added to their values to take the entropy into account.

Turning to the nitrogen acids in Table 3 we see that the anion conjugate bases all have oxidation potentials more positive than −1.30 V, which indicates that path *c* will always be favored for cleavage of their HA$^{\bullet-}$ radical anions.

Summary. General cycles have been defined for the thermodynamics of homolytic bond cleavages in solution,[2a] but application of these cycles to obtain BDEs for the acidic C–H bonds in HA$^{\bullet+}$ and HA$^{\bullet-}$ radical ions requires a knowledge of the homolytic bond dissociation energies (BDEs) of the parent HA acids, which hitherto have not been generally available. A simple method of obtaining these BDE$_{\mathrm{HA}}$ values from pK_{HA} and electrochemical data has been devised, however,[16] and BDEs for the acidic C–H bonds in 35 HA$^{\bullet+}$ radical cations[10] and 45 HA$^{\bullet-}$ radical anions[15] have been estimated. The latter were estimated for cleavage of the acidic H–A bond to form a hydrogen atom and an anion, $\mathrm{HA}^{\bullet-} \rightarrow \mathrm{H}^\bullet + \mathrm{A}^-$ (path *c*). Cleavage could conceivably also occur to form a hydride ion and a radical, $\mathrm{HA}^{\bullet-} \rightarrow \mathrm{H}^- + \mathrm{A}^\bullet$ (path *d*), but this pathway has been considered to be less likely.[2a] A recent estimate of the reduction potential of the hydrogen atom[17] has allowed us to estimate BDEs for the cleavage of $HA^{\bullet-}$ radical anions by path *d* for comparison with the BDEs for cleavage by path *c*. The presence of electron-withdrawing groups in $HA^{\bullet-}$, such as CN, promotes cleavage by path *c* since they stabilize the product anion, A^-, whereas the presence of donor groups, such as Me_2N, promotes cleavage by path *d*, since they stabilize the product radicals.[19] Since ΔBDE, the difference in BDEs between path *d* and path *c*, can be shown to be equal to $\Delta E_{ox}(A^-)$ for the conjugate bases of any two acids in any family,[21] it is possible to designate an oxidation potential (−1.30 V) where the two pathways are equally favorable. The $E_{ox}(A^-)$ values for 5 fluorenide ions, 3 triphenyl methide ions, and 6 anthracenide ions have been found to be more negative than −1.30 V (Tables 1 and 2). The corresponding radical anions will therefore cleave preferentially by path *d*. On the other hand, none of the oxidation potentials of the conjugate bases of the nitrogen acids shown in Table 3 are more negative than −1.30 V. The corresponding radical anions for these will cleave preferentially by path *c*.

Experimental Section

The equilibrium acidities of the weak acids were measured by the overlapping indicator titration.[10,15,16,20] The reduction potentials of the neutral weak acids and the oxidation potentials of the conjugate anions were determined by cyclic voltammetry as described previously.[10,15,16,20]

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(17) (a) The $E_{re}(H^\bullet)$ of −0.55 V is referenced to NHE_{aq}. We added −0.75 V algebraically to this value in order to reference it to the ferrocene/ferrocenium couple.[16] The difference of 0.75 V between F_c/F_c^+ and NHE_{aq} was based on the work of Breslow.[18] Parker has recently estimated this difference to be 0.54 V rather than 0.75 V. If the smaller difference is accepted the ΔBDE values in Tables 1–3 will be decreased by about 5 kcal. In other words, path *d* will be more favorable by 5 kcal. (b) Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655–2660.

(18) Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(19) Aniline and its derivatives with electron-donation groups or weak electron-accepting groups cannot be reduced in DMSO or acetonitrile solution due to the appreciable reduction of the solvents.[20]

(20) Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410–6416.

(21) We thank a referee for pointing out this relationship.