

Homolytic Bond Dissociation Energies of the Benzylic C-H Bonds in Radical Anions and Radical Cations Derived from Fluorenes, Triphenylmethanes, and Related Compounds

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Abstract: A method for estimating the homolytic bond dissociation energies of the benzylic C-H bonds in radical anions, $BDE_{HA\cdot-}$, has been devised. The method, which is potentially applicable to all weak acids, has been applied to the radical anions derived from 19 fluorenes, 15 triphenylmethanes, *p*-nitrotoluene, diphenylmethane, bis(4-nitrophenyl)methane, and three xanthenes. (In this abstract and in the text, the C-H bonds referred to are all of the benzylic type.) The $BDE_{HA\cdot-}$ values for the C-H bonds in the radical anions derived from fluorene and 18 of its 2- and 9-substituted derivatives averaged 35 kcal/mol compared to an average of 75 kcal/mol for the BDE_{HA} values of the corresponding C-H bonds in the parent fluorenes. The average $BDE_{HA\cdot-}$ values for the C-H bonds in the radical anions derived from 9-(dialkylamino)- and 9-(cycloalkylamino)fluorenes of 36 ± 3 kcal/mol were found to be close to the average value of the homolytic bond dissociation energies of the C-H bonds in the corresponding radical cations, $BDE_{HA\cdot+} = 39 \pm 4$ kcal/mol. The $BDE_{HA\cdot-}$ values for the C-H bonds in the radical anions derived from diphenylmethane and four meta- and para-substituted triphenylmethanes averaged 46 ± 3 kcal/mol compared to 81 ± 1 kcal/mol for the BDE_{HA} values of the C-H bonds in the corresponding parent molecules. The $BDE_{HA\cdot-}$ value for 4-PhCOC₆H₄CHPh₂ was 8 kcal/mol higher than the average for the triphenylmethanes, and the average $BDE_{HA\cdot-}$ value for 4-NO₂C₆H₄CH₃, (4-NO₂C₆H₄)₂CH₂, (4-NO₂C₆H₄)₃CH, and five 4-NO₂-substituted triphenylmethanes was 16 kcal/mol higher, i.e., 62 kcal/mol. (The BDE_{HA} values for the C-H bonds in these nitro compounds were, for the most part, near 81 kcal/mol). In contrast, the average $BDE_{HA\cdot+}$ value for the C-H bonds in the radical cations derived from (4-NO₂C₆H₄)₂CH₂, 4-PhCOC₆H₄CHPh₂, 4-NO₂C₆H₄CHPh₂, and (4-NO₂C₆H₄)₃CH is only 27 ± 1 kcal/mol.

Introduction

Bond breaking, one of the fundamental processes in chemistry, is known to be facilitated either by removal of one electron from a bonding orbital of a neutral molecule to form a radical cation or by addition of one electron to an antibonding orbital of a neutral molecule to form a radical anion.¹ Baird has treated three-electron bonds on the basis of simple MO theory and has concluded that their maximum strength is about one-half that of the corresponding two-electron bond.^{2a} Camaioni recently carried out extensive AM1 calculations on homolytic bond dissociation energies of the C-C bonds in various substituted ethane radical cations and found that these BDE values are dependent on the substituents that are present on the carbon atoms.^{2b} Clark has proposed a general equation to predict the homolytic bond dissociation energies of one- and three-electron bonds on the basis of theoretical calculations³ but points out that the experimental data for dissociation energies of one- and three-electron bonds are remarkably sparse. Recently, however, Arnett and his colleagues have estimated the homolytic bond dissociation energies for C-C, C-O, C-N, and C-S bonds in radical cations and radical anions derived from molecules formed by combining resonance-stabilized anions with resonance-stabilized cations.^{4,5} For example, molecules with labile C-C bonds were formed by combining various 9-substituted fluorenyl anions with tropylium, trityl, xanthylium, or 1,2,3-triphenylcyclopropenyl carbenium ions. The homolytic bond dissociation energies for the molecules formed were among the smallest ever recorded for C-C bonds, e.g., about 16 and 25 kcal/mol for the 9-trityl- and 9-tropylium-9-substituted fluorenes, respectively. The $\Delta H_{\text{cleav}}[C-X]^{\cdot-}$ values for the corresponding radical anions were about half this size, i.e., about 12 kcal/mol. The homolytic bond dissociation energies for 9-(1,2,3-triphenylcyclopropenyl)-9-substituted fluorenes were somewhat higher (~ 40 kcal/mol) and the $\Delta H_{\text{cleav}}[C-X]^{\cdot-}$ values for the corresponding radical anions were

also higher (~ 30 kcal/mol). (Henceforth kcal/mol will be abbreviated as kcal.) The $\Delta H_{\text{cleav}}[C-X]^{\cdot+}$ values for the corresponding radical cations were all exothermic and fell in the narrow range of about -20 to -27 kcal, probably reflecting the instability of the fluorenyl radical cation moiety and the relatively high stability of the resonance-stabilized carbenium leaving groups.

In 1986, Nelsen and Ippoliti used eq 1, based on a thermodynamic cycle, to estimate the homolytic bond dissociation for

$$BDE_{HA\cdot+} = BDE_{HA} + 23.1[E_{\text{ox}}(A^{\cdot}) - E_{\text{ox}}(\text{HA})] \quad (1)$$

a C-H bond energy in a radical cation ($BDE_{HA\cdot+}$).^{6a} Dinnocenzo and Banach later used this method to estimate the upper limit of $BDE_{HA\cdot+}$ value for the acidic C-H bond in the (*p*-MeOC₆H₄)₂NCH₃^{•+} radical cation to be about 47 kcal compared to about 72 kcal for the acidic C-H bond in the parent compound (*p*-MeOC₆H₄)₂NCH₂-H.^{6b} Acidities of radical cations can be estimated by a similar thermodynamic cycle.^{6c,d}

Griller, Wayner, and their colleagues have presented a general cycle that defines the thermodynamics for all the homolytic and heterolytic cleavage reactions of a hydrocarbon R-R' in solution⁷ and have given estimates for the $\Delta H_{\text{cleav}}(R-R')^{\cdot+}$ values for the C-C bonds in the radical cations derived from PhCH₂-CH₃ (38 kcal), PhCH₂-CH₂Ph (24 kcal), Ph₂CH-CH₂Ph (12 kcal), PhC(CH₃)₂-CHPh₂ (5 kcal), and (CH₃)₂NCH₂-CH₂N(CH₃)₂ (17 kcal). They also report $\Delta H_{\text{cleav}}(R-H)^{\cdot+}$ values for the radical cations derived from PhCH₂-H (50 kcal) and (CH₃)₂NCH₂-H (34 kcal). The latter values are 57 and 36%, respectively, the size of the BDE_{HA} values of their corresponding parents.

Application of eq 1 has been limited by the lack of information concerning BDE_{HA} values. The development of a simple method for estimating these values⁸ has solved this problem and allowed us to estimate $BDE_{HA\cdot+}$ values for 35 radical cations derived from various types of weak acids.⁹

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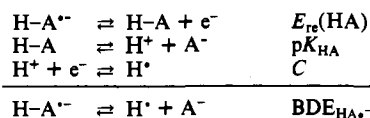
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Scheme I



Little or no quantitative information concerning the homolytic bond dissociation energies of the H-A bonds in H-A^{·-}-type radical anions appears to be available in the literature. In the present paper we present a simple method of estimating the homolytic bond dissociation energies of the C-H bonds in radical anions derived from a number of 2- and 9-substituted fluorenes, meta- and para-substituted triphenylmethanes, and related compounds. The method should be applicable to radical anions derived from most weak acids for which pK_{HA} values can be measured in DMSO (over 1500 to date).¹⁰

Results and Discussion

The homolytic bond dissociation energies of the H-A bonds in radical anions derived from weak acids, HA, can be estimated from the thermodynamic cycle shown in Scheme I.

The summation of the terms in Scheme I, expressed in kcal, gives the homolytic bond dissociation energies of the H-A bonds in H-A^{·-}-type radical anions (eq 2).

$$\text{BDE}_{\text{HA}^{\cdot-}} = 1.37pK_{\text{HA}} + 23.1E_{\text{re}}(\text{HA}) + C \quad (2)$$

The constant *C* (73.3 kcal/mol) is a semiempirical value used in an analogous equation (3), derived from a similar thermodynamic cycle, that has been applied successfully to estimate BDE_{HA} values for the H-A bonds in several hundred uncharged weak acids, HA.¹¹

$$\text{BDE}_{\text{HA}} = 1.37pK_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-) + 73.3 \quad (3)$$

Estimates of the homolytic bond dissociation energies of C-H and N-H bonds made by using eq 3 have been found to agree with the best gas-phase literature BDE values (enthalpies) to within ±2 kcal for 14 of the 16 compounds where literature values were available.⁸ For the two exceptions Ph₃C-H and PhNH-H, the gas-phase values were shown to be in error. This method can be used to estimate BDE_{HA} values for the H-A bonds in literally thousands of weak acids that would be difficult or impossible to be obtained by other methods. During the past 4 years we have published estimates of BDEs for several hundred such bonds.¹¹ Equation 2 should have a similar general applicability for estimating BDE_{HA^{·-}} values. Since the constant *C* used in eq 3 is the same as that used in eq 2, which gives values agreeing with gas-phase enthalpies, the BDE_{HA^{·-}} values obtained probably should be considered to be enthalpy values.

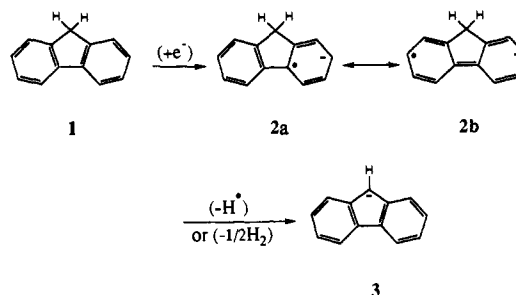
Table I. Homolytic Bond Dissociation Energies of the C-H Bonds in Fluorenes (BDE_{HA}) and in Their Corresponding Radical Anions (BDE_{HA^{·-}})

substituents	pK _{HA} ^a	E _{ox} (A ⁻) ^b	E _{re} (HA) ^c	BDE _{HA} ^d	BDE _{HA^{·-}} ^e
H	22.6	-1.069 ^c	-3.006	80	35
2-PhSO ₂	18.1	-0.792 ^c	-2.236	80	46.5
2-CN	18.2	-0.813 ^c	-2.313	80	45
2-NO ₂	17.0	-0.684 ^d	-1.418 (rev)	81	64
2-Me ₂ N	24.2	-1.123 ^e	-3.142	80	34
9-PhSO ₂	11.55	-0.309 ^c	-2.132	82	40
9-CO ₂ Me	10.35	-0.492 ^c	-2.847	76	22
2,7-Br ₂ -9-CO ₂ Me	6.5	-0.243 ^f	-2.344	76.5	28
9-Ph	17.9	-1.028 ^c	-3.032	74	28
9-(2,4,6-Me ₃ C ₆ H ₂)	18.6	-1.049 ^{c,g}	-3.080	74.5	28
9-EtO	22.0	-1.322 ^h	-2.589	73	44
9-EtS	17.5	-0.993 ^g	-2.493	74.5	40
9-Me ₂ N	22.5	-1.418 ^{e,g}	-2.868	71.5	38

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Homolytic Bond Dissociation Energies of the Benzylic C-H Bonds in Radical Anions Derived from Fluorenes. In Table I the pK_{HA} and electrochemical data are given for the C-H bonds and corresponding anions for fluorene and 12 of its 2- and 9-substituted derivatives. These data allow estimates to be made of the BDE_{HA} values of the C-H bonds in fluorenes, using eq 3, and of the BDE_{HA^{·-}} values of the corresponding radical anions, using eq 2.

Examination of Table I shows that addition of an electron to the fluorene ring (1) to form the radical anion 2 decreases the homolytic bond dissociation energy of the C-H bond by about 45 kcal. ESR spectroscopic investigations of the radical anion



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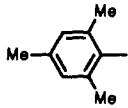




of fluorene 2 have shown that it undergoes a first-order decay, and it was concluded that the C-H bond undergoes cleavage to form a hydrogen atom and the fluorenyl radical anion (3).¹² Studies of electrochemical reductions in DMF of fluorene and its 9-methyl, 9-phenyl, and 9-benzyl derivatives have shown that fluorenyl ions and hydrogen are the products of this reaction. The hydrogen was apparently formed by dimerization of hydrogen atoms on the electrode surface.¹³ We assume that the same pathway for the cleavage of the C-H bond in fluorene radical anions will be followed in DMSO. Evidently, loss of a hydrogen atom from radical anion 2 to give the fluorenyl radical anion (3) is the lowest energy pathway available to the fluorenyl radical anion.

If we look first at the overall picture with regard to the effect of substituents, we find that the BDE_{HA^{·-}} values for the C-H bond in the radical anions derived from the 19 fluorenes listed in Tables I and II average about 35 kcal compared to an average of 75 kcal for the BDE_{HA} values of the corresponding C-H bonds in the

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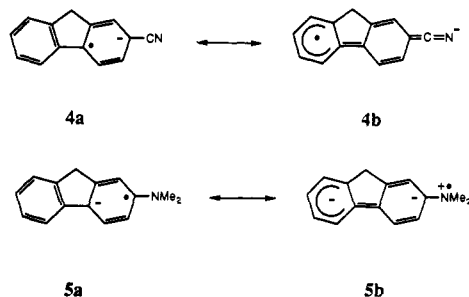
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Table II. Comparison of BDE_{HA} , $BDE_{HA\cdot-}$, and $BDE_{HA\cdot+}$ Values for the C-H Bonds in Radical Anions and Radical Cations Derived from 9-Substituted Fluorenes (9-G-FIH)

no.	substituents (G)	pK_{HA}^a	$E_{ox}(A\cdot)^b$	$E_{re}(HA)^c$	BDE_{HA}^d	$BDE_{HA\cdot-}^e$	$BDE_{HA\cdot+}^f$
1	H	22.6	-1.069	-3.006	80	35	56
2	Ph	17.9	-1.028	-3.032	75	28	46
3		18.6	-0.977	-3.080	76	28	50
4	Me_2N	22.5	-1.418	-2.868	71.5	38	37
5		22.2	-1.553	-2.894	68	37	35
6		22.5	-1.382	-2.863	72	38	39
7	$PhCH_2(Me)N$	22.0	-1.334	-2.822	72.5	38	39
8	$(i-Pr)_2N$	20.8	-1.242	-2.955	73	33.5	40
9		19.4	-1.198	-2.888	72	33	41
10		18.2	-1.166	-2.982	71	29	54.5

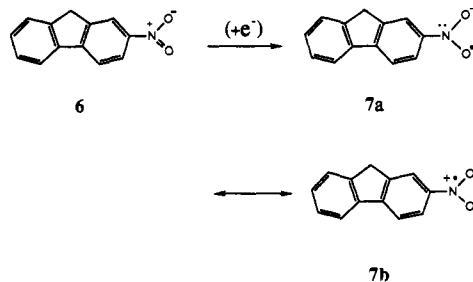
^aReferences 10, 11b, 11e, and 11g. ^bReversible oxidation potentials measured by cyclic voltammetry in DMSO and referenced to the ferrocene/ferrocenium couple in DMSO (0.875 V).^{8,9} ^cIrreversible reduction potentials measured by cyclic voltammetry in DMSO and referenced to the ferrocene/ferrocenium couple in DMSO (0.875 V).⁸ ^dCalculated using eq 3. ^eCalculated using eq 2 with $C = 73.3$. ^fReference 9.

parent fluorenes. The introduction of substituents in the 2-position of fluorene ring can stabilize the radical anion by either stabilizing the negative charge ($4a \leftrightarrow 4b$) or the odd electron ($5a \leftrightarrow 5b$).



We can anticipate that the stabilizing effects of electron-acceptor groups, such as CN, will be sizable because the effects on pK_{HA} are sizable but that the stabilizing effects of electron-donor substituents, such as Me_2N , will be small because their effects on pK_{HA} and on radical stabilities (ΔBDE_{HA}) are relatively small.^{11e,14} Examination of Table I shows that the introduction of 2- $PhSO_2$, 2-CN, and 2- NO_2 groups increases the BDE_{HA} -values of the C-H bonds by 11.5, 10, and 27.5 kcal, respectively, relative to that of the $FIH_2^{\cdot-}$ radical anion. This is the order expected on the basis of σ_R constants (0.12, 0.18, and 0.64, respectively)¹⁵ and σ_1 constants (0.59, 0.60, and 0.65, respectively).¹⁵ The stabilizing effects are exaggerated, however, compared to the effects on anion stabilities derived from the ΔpK_{HA} values in Table I (6.2, 6.0, and 7.7 kcal, respectively, relative to the HFI^- ion) because of the higher energies of the radical anions. In other words, the introduction of these electron-withdrawing groups strengthens the C-H bonds in the intermediate radical anions and overrides the effects of anion product stability, which are potentially bond weakening. (Maslak and Guthrie have postulated that the fragmentation process for radical anions is controlled by factors other than anion product stability.¹⁶) The effect of the 2- NO_2 group is clearly out of line with the effects of the other elec-

tron-withdrawing groups. This is understandable since nitro groups are excellent single electron acceptors in their own right ($7a \leftrightarrow 7b$), and for 2- NO_2FIH_2 the odd electron is presumably added directly to the NO_2 group rather than to the fluorene ring.



In terms of eq 2, the effects of the 2- $PhSO_2$, 2-CN, and 2- NO_2 groups manifest themselves by making the $E_{re}(HA)$ values more positive by 17.7, 16.0, and 36.6 kcal, respectively, relative to that of FIH_2 . We see, however, that these effects on the $BDE_{HA\cdot-}$ values are offset somewhat in eq 2 by the lowering of the pK_{HA} values. On the other hand, the powerful 2- Me_2N electron-donating group causes the $E_{re}(HA)$ to become more negative than that for FIH_2 by 3 kcal and causes the pK_{HA} to increase by 2.2 kcal, leading to about a 1 kcal decrease in the $BDE_{HA\cdot-}$ value for the C-H bond in the 2- $Me_2NFIH_2^{\cdot-}$ radical anion, relative to that in the $FIH_2^{\cdot-}$ radical anion.

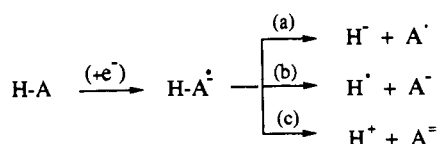
Substituents attached to the sp^3 carbon at the 9-position of fluorene are insulated from direct interaction with the charge or the odd electron in the fluorenyl ring of the radical anion. The 9- $PhSO_2$ group, nevertheless, renders the $E_{re}(HA)$ value more positive by 20 kcal through its field/inductive effect ($\sigma_1 = 0.59$). Its effect on lowering the pK_{HA} is also large (15 kcal), and the net effect (eq 2) is to increase the $BDE_{HA\cdot-}$ value for the C-H bond in the 9- $PhSO_2FIH^{\cdot-}$ radical anion by 5 kcal relative to that of the $FIH_2^{\cdot-}$ radical anion. The 9- CO_2Me group has a small field/inductive effect ($\sigma_1 = 0.24$), leading to only a 3.7 kcal more positive $E_{re}(HA)$, which is overshadowed by the 16.8 kcal decrease in pK_{HA} . The net result is a 13 kcal decrease in the $BDE_{HA\cdot-}$ value of the C-H bond in the 9- $CO_2MeFIH^{\cdot-}$ radical anion relative to that of the $FIH_2^{\cdot-}$ radical anion. The Ph group has a much smaller field/inductive effect ($\sigma_1 = 0.1$), and $\Delta E_{re}(HA)$ is negative (-1.7 kcal). When combined with the ΔpK_{HA} value of 6.4 kcal, this

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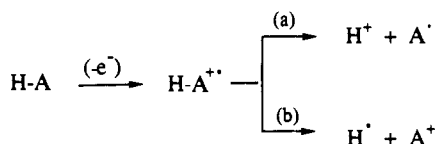
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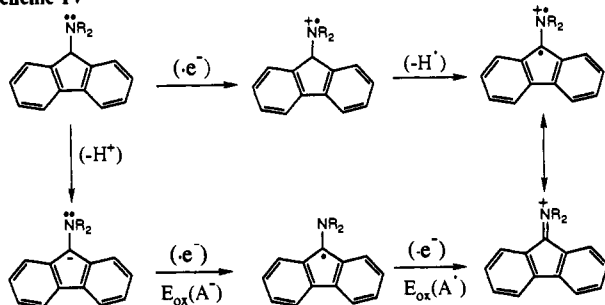
Scheme II



Scheme III



Scheme IV



leads to an 8 kcal decrease in the $BDE_{\text{HA}\cdot-}$ value for the C–H bond in 9-PhFIH $^{\cdot-}$ radical anion relative to that of the FIH $_2^{\cdot-}$ radical anion. The small σ_1 values for R $_2$ N (0.1), EtO (0.25), and EtS (0.25) and the small decreases in ΔpK_{HA} lead, for the most part, to small increases in the $BDE_{\text{HA}\cdot+}$ values relative to that of the FIH $_2^{\cdot+}$ radical cation (Tables I and II). The surprisingly low pK_{HA} values for the sterically congested 9-R $_2$ N-FIH compounds in Table II (entries 8, 9, and 10) cause small *decreases* in the $BDE_{\text{HA}\cdot-}$ values for the C–H bonds in the radical anions derived from these molecules, however. (The low pK_{HA} values are presumably due to increases in ground-state energies in these highly congested fluorenes.)

Comparisons of Homolytic Bond Dissociation Energies for the Benzylic-Type C–H Bonds in Radical Anions and Radical Cations. Estimates of the $BDE_{\text{HA}\cdot-}$ values for the C–H bonds in the radical anions derived from fluorene and nine of its 9-substituted derivatives are compared in Table II with the $BDE_{\text{HA}\cdot+}$ values of the C–H bonds in the corresponding radical cations. These appear to be the first comparisons of this kind to be made. Before discussing the results in Table II, let us look at the possible pathways for cleaving the H–A bonds in HA $^{\cdot-}$ -type radical anions and in HA $^{\cdot+}$ -type radical cations.

Three possible pathways for cleavage of the H–A bond in HA $^{\cdot-}$ -type radical anions are shown in Scheme II. Paths a and

c, which involve formation of a high-energy hydride ion and dianion, respectively, are clearly disfavored from a thermodynamic standpoint compared to path b, the path observed experimentally.^{12,13}

This behavior contrasts with the cleavage of the C–H bonds in the HA $^{\cdot+}$ -type radical cations (Scheme III), where loss of a proton (path a) is often the favored pathway in solution because of the high acidities of most radical cations.^{6d} Path b should be competitive in the gas phase, however, and perhaps in solution for less acidic radical cations.⁹

The $BDE_{\text{HA}\cdot+}$ values of 35–56 kcal listed in Table II for the C–H bonds in radical cations derived from 9-G-fluorenes contrast sharply with the –20 to –25 kcal exothermic $\Delta H_{\text{deav}}(\text{C–C})^{+\cdot}$ values reported by Arnett and his colleagues for the labile 9-G-FI-R $^{\cdot+}$ radical cations, where R is a tropyli, xanthyl, or 1,2,3-triphenylcyclopropenyl moiety.⁵ The exothermicity of Arnett's labile fluorenyl radical cations is apparently associated with the unusual stability of the product radicals and carbenium ions being ejected, augmented by steric relief of strain. Loss of a hydrogen atom and a 9-substituted fluorenyl cation from 9-G-FIH $^{\cdot+}$ radical cations is evidently much less favored thermodynamically.

In an earlier paper we suggested that the $BDE_{\text{HA}\cdot+}$ values for the radical cations derived from the 9-(dialkylamino)fluorenes listed in Table II, as calculated by eq 1, could be related to the ease with which the 9-R $_2$ N-FI $^{\cdot}$ radicals are converted to the product cations (Scheme IV).

As the 9-R $_2$ NFI $^{\cdot}$ radicals become more congested in going from entries 4 to 9 in Table II, the (reversible) $E_{\text{ox}}(\text{A}^{\cdot})$ values change from –0.980 to –0.825 and drop to –0.200 for entry 10 (an irreversible value). The energies of the product cations presumably decrease because of the increase in steric hindrance (eclipsing of the substituents at C and N) caused by formation of the short $\text{N}=\text{C}$ bond.⁹ Loss of a hydrogen atom from the 9-R $_2$ N $^{\cdot+}$ -FIH radical cation should be subject to a similar steric effect. We note that, in contrast to the behavior of the radical cations, the $BDE_{\text{HA}\cdot-}$ values for the 9-R $_2$ NFIH $^{\cdot-}$ radical anions derived from entries 8–10 in Table II are *decreased* relative to entries 4–7. Here the 4–8-kcal decrease is caused primarily by a 5-kcal decrease in pK_{HA} values. As brought out earlier, the stability of the anion product does not appear to be a factor.

The pathways for the loss of a hydrogen atom from 9-pyrrolidino fluorene (**8**) to form the 9-pyrrolidino fluorene cation (**9 $^+$**) via the radical cation intermediate **8 $^{\cdot+}$** (path b in Scheme III) and the loss of a hydrogen atom from radical anion intermediate **8 $^{\cdot-}$** to form the 9-pyrrolidino fluorene anion (**9 $^-$**) (path a in Scheme II) are outlined in Scheme V.

In Scheme V the transformation of **8** to **8 $^{\cdot+}$** involves the loss of an electron, whereas the transformation of **8** to **8 $^{\cdot-}$** requires the addition of an electron. Nevertheless, the $BDE_{\text{HA}\cdot+}$ and $BDE_{\text{HA}\cdot-}$ values are almost equal, i.e., 35 and 37 kcal, respectively, which suggests that cleavage of the C–H bonds in the radical cations by path b in Scheme III is feasible. Note that most of the other entries in Table II, including that for fluorene itself, have $BDE_{\text{HA}\cdot-}$

Scheme V

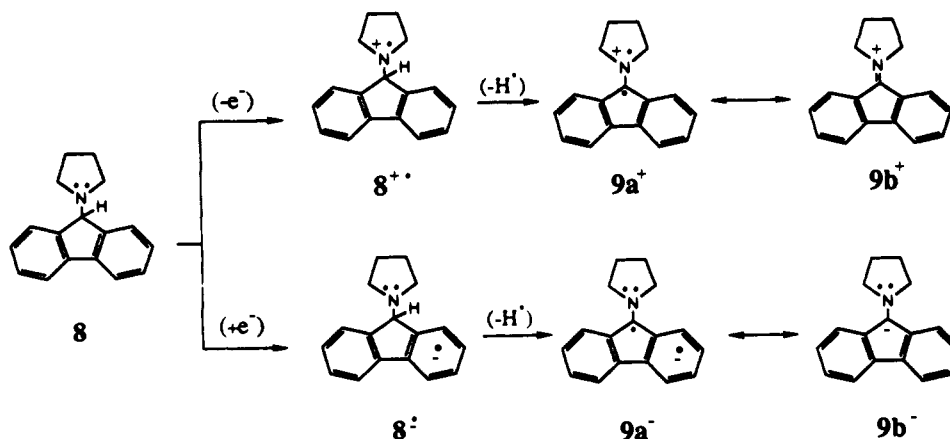


Table III. Comparison of BDE_{HA}, BDE_{HA•-}, and BDE_{HA•+} Values for the C-H Bonds for Triphenylmethanes and Related Compounds and the Radical Anions and Radical Cations Derived Therefrom

no.	parent compd	pK _{HA} ^a	E _{re} (HA) ^c	BDE _{HA} ^e	BDE _{HA•-} ^f	BDE _{HA•+} ^g
1	4-NO ₂ C ₆ H ₄ CH ₃	20.4	-1.479 (rev)	86	67	
2	Ph ₂ CH ₂	32.2	<-3.1 ^d	82	<46	36
3	(4-NO ₂ C ₆ H ₄) ₂ CH ₂	15.1	-1.495 (rev)	81	59	
4	Ph ₃ CH	30.6	<-3.1 ^d	81	<43	45
5	4-PhC ₆ H ₄ CHPh ₂	29.4	-2.889 (rev)	81	47	
6	4-PhSC ₆ H ₄ CHPh ₂	28.3	-2.807 (rev)	80.5	47	
7	3-CF ₃ C ₆ H ₄ CHPh ₂	28.4	-2.970	81	44	
8	3-NO ₂ C ₆ H ₄ CHPh ₂	26.6 ^b	-1.386 (rev)	81	77	
9	4-PhSO ₂ C ₆ H ₄ CHPh ₂	23.6	-2.457	81	49	
10	4-PhCOC ₆ H ₄ CHPh ₂	22.4	-2.147 (rev)	79	54	28
11	4-NO ₂ C ₆ H ₄ CHPh ₂	16.8	-1.495 (rev)	81	62	27
12	(4-NO ₂ C ₆ H ₄) ₃ CH	12.7	-1.404 (rev)	79	58	26 ^h
13	4-NO ₂ C ₆ H ₄ (4-MeOC ₆ H ₄) ₂ CH	18 ^b	-1.510 (rev)	80	63	
14	4-NO ₂ C ₆ H ₄ [2,4-(MeO) ₂ C ₆ H ₃] ₂ CH	18 ^b	-1.520 (rev)	81	63	
15	4-NO ₂ C ₆ H ₄ (4-MeC ₆ H ₄) ₂ CH	17 ^b	-1.510 (rev)	81	62	
16	4-NO ₂ C ₆ H ₄ (2,4-Me ₂ C ₆ H ₃) ₂ CH	17.5 ^b	-1.490 (rev)	82	63	
17	xanthene	30.0	<-3.1 ^d	75	<43	41
18	9-phenylxanthene	27.9	<-3.1 ^d	76	<40	40
19	9-cyanoxanthene	13.6	-2.843	69	26	39

^aReferences 10 and 17. ^bEstimated; a precise measurement is difficult to obtain because of the slow rate of attainment of equilibrium. ^cMeasured by cyclic voltammetry and referenced to the ferrocene/ferrocenium couple in DMSO (0.875 V). ^dThe limit of E_{re} measurable in DMSO; E_{re} is presumably close to that of benzene, i.e., ca. -4.0 V (vs Fc/Fc⁺) at -60 °C.¹⁸ ^eCalculated using eq 3; for 4-NO₂C₆H₄CH₂⁻, E_{ox}(A⁻) = -0.644 V relative to the Fc/Fc⁺ couple (0.106 V vs SHE). ^fCalculated using eq 2 with the constant C = 73.3. ^gReference 9 unless otherwise noted. ^hThis work; E_{ox}(A⁻) for the (4-NO₂C₆H₄)₃C⁻ anion is -0.492, E_{ox}(A^{•-}) for the (4-NO₂C₆H₄)₃C^{•-} radical is 0.284 V, and E_{ox}(HA) for the neutral molecule is 2.575 V.

values close to that of 9-pyrrolidinofluorene. The E_{re}(HA) values are all of similar size, which is consistent with our assumption that the addition of the electron is to the fluorene ring. Lower pK_{HA} values cause the BDE_{HA•-} values for entries 2, 3, and 10 to be slightly lower than the others.

The BDE_{HA•+} values for fluorene and its 9-phenyl and 9-mesityl derivatives are about 5–15 kcal higher than those for most of the fluorenes bearing a dialkylamino group at the 9-position. This is a consequence of the necessity of abstracting the odd electron from the fluorene π system rather than from a nitrogen lone pair; this leads to more positive E_{ox}(HA) values and higher BDE_{HA} values for the neutral acids.

Homolytic Bond Dissociation Energies of the Benzylic-Type C-H Bonds in the Radical Anions Derived from Triphenylmethanes and Related Hydrocarbons. The homolytic bond dissociation energies of the C-H bonds in the radical anions derived from meta- and para-substituted triphenylmethanes and the related hydrocarbons are summarized and compared with some of the homolytic bond dissociation energies of the C-H bonds in the corresponding radical cations in Table III.

Examination of Table III shows that triphenylmethanes with 4-Ph, 4-PhS, 3-CF₃, or 4-PhSO₂ groups in one of the phenyl rings give E_{re}(HA) values that are about 0.3–0.4 V more negative than those for 2-PhSO₂- or 2-CN-fluorene. This apparently corresponds to the higher energy needed to add an electron to a benzene ring than to a fluorene ring. (No reduction potential peaks were observed for triphenylmethane, diphenylmethane, xanthene, and 9-phenylxanthene before the solvent (DMSO) was reduced. The reduction potentials for these compounds are therefore listed as <-3.1 V.) The higher pK_{HA} values for triphenylmethanes than for fluorenes compensate for the more negative E_{re}(HA) values, and the BDE_{HA•-} values for these substituted triphenylmethanes and fluorenes are all in the 45–49 kcal range. The presence of a 4-PhCO group leads to a more positive E_{re}(HA) value, and the BDE_{HA•-} value increases by about 5 kcal. It is conceivable that the C=O group may be involved in accepting the electron from the electrode, i.e., [•]C=O + e⁻ → C=O^{•-} ↔ ⁻C=O[•]. (Note that the E_{re}(HA) value is reversible.)

The unique ability of a nitro group to stabilize an electron internally has been commented on and illustrated earlier in the

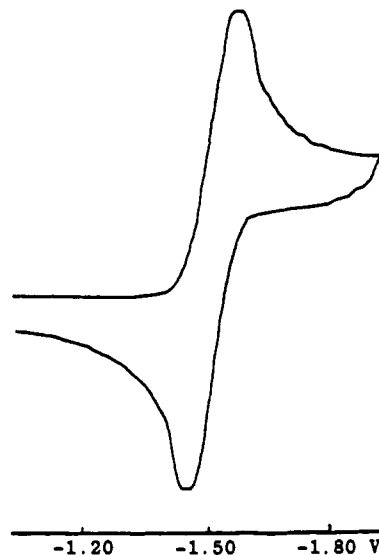
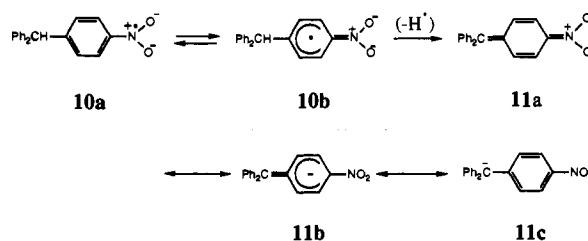


Figure 1. Reversible reduction potential of *p*-nitrotriphenylmethane in DMSO, referenced to Fc/Fc⁺ couple. The scan rate was 100 mV/s, and Et₄N⁺BF₄⁻ was the supporting electrolyte.

paper in connection with the behavior of 2-nitrofluorene. Nine additional examples are given in Table III. Note that the reduction potentials are, for the most part, in the range of 1.50 ± 0.02 V regardless of the structure of the rest of the molecule. Exceptional behavior is shown, however, for (4-NO₂C₆H₄)₃CH, E_{re}(HA) = -1.40 V, and for 3-NO₂C₆H₄CHPh₂, E_{re}(HA) = -1.386 V. The BDE_{HA•-} values for compounds containing NO₂ groups range from 58 to 77 kcal and average 63.5 kcal. The relatively small negative E_{re}(HA) value for 3-NO₂C₆H₄CHPh₂ and record high BDE_{HA•-} value of 77 kcal warrant further investigation.



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The cyclic voltammogram for the reduction potential in DMSO of (*p*-nitrophenyl)diphenylmethane shown in Figure 1 is typical of those for the hydrocarbons containing one or more nitro groups.

The $E_{r,c}(\text{HA})$ value for 9-cyanoxanthene (9-CN-Xn) is in the same region as observed for most monosubstituted triphenylmethanes (-2.843), but 9-CN-Xn has a pK_{HA} about 20 kcal lower than most $\text{GC}_6\text{H}_4\text{CHPh}_2$ compounds. As a consequence, its BDE_{HA^-} value is also about 20 kcal lower. On the other hand, its $E_{\text{ox}}(\text{A}^{\bullet})$ and BDE_{HA} are of moderate size, and the $\text{BDE}_{\text{HA}^{\bullet}}$ value is 39 kcal, i.e., 50% larger than its BDE_{HA^-} value, rather than 50% smaller, which is the rule for the other $\text{BDE}_{\text{HA}^{\bullet}}$ values in Table III.

Experimental Section

Materials. The compounds used have all been prepared previously (see the footnotes in the tables for references).

Electrochemistry. The reduction potentials of the neutral weak acids and the oxidation potentials of the corresponding conjugate anions were measured in DMSO solution by cyclic voltammetry with 0.1 M tetraethylammonium tetrafluoroborate as supporting electrolyte. The working electrode for the measurements of the reduction potentials was a glassy carbon electrode, and that for the measurements of the oxidation potentials was a Pt electrode. The auxiliary electrode was Pt, and the reference electrode was Ag/AgI. The sweep rate was 100 mV/s, and the redox potentials reported were referenced to ferrocene-ferrocenium (Fc/Fc^+) couple ($E_{1/2} = 0.875 \text{ V}$).⁸

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation.

Registry No. 1, 86-73-7; 2, 34484-03-2; 4, 143959-25-5; 5, 144017-24-3; 6, 607-57-8; 7, 90405-77-9; 8, 7596-59-0; 8⁺, 144017-27-6; 8⁺, 116997-79-6; 10, 144017-34-5; 2- $\text{PhSO}_2\text{FIH}_2$, 59014-85-6; 2- $\text{PhSO}_2\text{FIH}_2^{\bullet-}$, 143959-24-4; 2- CNFIH_2 , 2523-48-0; 2- Me_2NFIH_2 , 13261-62-6; 9- PhSO_2FIH , 22010-78-2; 9- $\text{PhSO}_2\text{FIH}^{\bullet-}$, 144017-25-4;

9- CO_2MeFIH , 3002-30-0; 9- $\text{CO}_2\text{MeFIH}^{\bullet-}$, 135256-58-5; 2,7- Br_2 -9- CO_2MeFIH , 73838-62-7; 2,7- Br_2 -9- $\text{CO}_2\text{MeFIH}^{\bullet-}$, 135356-41-1; 9-EtOFIH, 2868-70-4; 9-EtOFIH^{•-}, 143959-26-6; 9-EtSFIH, 60147-53-7; 9-EtSFIH^{•-}, 143959-27-7; FIH₂^{•+}, 34985-70-1; 9-PhFIH, 789-24-2; 9-PhFIH^{•-}, 38691-37-1; 9-PhFIH^{•+}, 113566-64-6; 9-mesityl-FIH, 18153-40-7; 9-mesityl-FIH^{•-}, 144017-26-5; 9-mesityl-FIH^{•+}, 113533-48-5; 9-Me₂NFIH, 53156-46-0; 9-Me₂NFIH^{•-}, 83936-72-5; 9-Me₂NFIH^{•+}, 117065-69-7; 9-piperidino-FIH, 3333-06-0; 9-piperidino-FIH^{•-}, 144017-28-7; 9-piperidino-FIH^{•+}, 116997-80-9; 9- $\text{PhCH}_2(\text{Me})\text{NFIH}$, 102478-64-8; 9- $\text{PhCH}_2(\text{Me})\text{NFIH}^{\bullet-}$, 144017-29-8; 9- $\text{PhCH}_2(\text{Me})\text{NFIH}^{\bullet+}$, 141320-02-7; 9-(*i*-Pr)₂NFIH, 109495-00-3; 9-(*i*-Pr)₂NFIH^{•-}, 144017-30-1; 9-(*i*-Pr)₂NFIH^{•+}, 116997-76-3; 9-(2,6-dimethylpiperidino)FIH, 116997-66-1; 9-(2,6-dimethylpiperidino)FIH^{•-}, 144017-31-2; 9-(2,6-dimethylpiperidino)FIH^{•+}, 116997-81-0; 9-(2,2,6,6-tetramethylpiperidino)FIH, 116997-84-3; 9-(2,2,6,6-tetramethylpiperidino)FIH^{•+}, 144017-32-3; 9-(2,2,6,6-tetramethylpiperidino)FIH^{•+}, 141320-04-9; 4- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_3$, 99-99-0; 4- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_3^{\bullet-}$, 34509-96-1; Ph_2CH_2 , 101-81-5; $\text{Ph}_2\text{CH}_2^{\bullet-}$, 34512-70-4; $\text{Ph}_2\text{CH}_2^{\bullet+}$, 82189-87-5; (4- $\text{NO}_2\text{C}_6\text{H}_4$)₂CH₂, 1817-74-9; (4- $\text{NO}_2\text{C}_6\text{H}_4$)₂CH₂^{•-}, 34533-75-0; Ph_3CH , 519-73-3; $\text{Ph}_3\text{CH}^{\bullet-}$, 75366-18-6; $\text{Ph}_3\text{CH}^{\bullet+}$, 88424-77-5; 4- $\text{PhCH}_2\text{CHPh}_2$, 745-36-8; 4- $\text{PhC}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 143959-28-8; 4- $\text{PhSC}_6\text{H}_4\text{CHPh}_2$, 85554-39-8; 4- $\text{PhSC}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 143959-29-9; 3- $\text{CF}_3\text{C}_6\text{H}_4\text{CHPh}_2$, 13865-59-3; 3- $\text{CF}_3\text{C}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 143959-30-2; 3- $\text{NO}_2\text{C}_6\text{H}_4\text{CHPh}_2$, 6630-83-7; 3- $\text{NO}_2\text{C}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 143959-31-3; 4- $\text{PhSO}_2\text{C}_6\text{H}_4\text{CHPh}_2$, 85554-27-4; 4- $\text{PhSO}_2\text{C}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 143959-32-4; 4- $\text{PhCOC}_6\text{H}_4\text{CHPh}_2$, 7375-38-4; 4- $\text{PhCOC}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 144017-33-4; 4- $\text{PhCOC}_6\text{H}_4\text{CHPh}_2^{\bullet+}$, 141320-07-2; 4- $\text{NO}_2\text{C}_6\text{H}_4\text{CHPh}_2$, 2945-12-2; 4- $\text{NO}_2\text{C}_6\text{H}_4\text{CHPh}_2^{\bullet-}$, 141320-08-3; (4- $\text{NO}_2\text{C}_6\text{H}_4$)₃CH, 603-49-6; (4- $\text{NO}_2\text{C}_6\text{H}_4$)₃CH^{•-}, 143959-33-5; (4- $\text{NO}_2\text{C}_6\text{H}_4$)₃CH^{•+}, 144017-36-7; 4- $\text{NO}_2\text{C}_6\text{H}_4(4\text{-MeOC}_6\text{H}_4)_2\text{CH}$, 128527-22-0; 4- $\text{NO}_2\text{C}_6\text{H}_4(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet-}$, 143959-34-6; 4- $\text{NO}_2\text{C}_6\text{H}_4[2,4(\text{MeO})_2\text{C}_6\text{H}_3]_2\text{CH}$, 143959-23-3; 4- $\text{NO}_2\text{C}_6\text{H}_4[2,4(\text{MeO})_2\text{C}_6\text{H}_3]_2\text{CH}^{\bullet-}$, 143959-35-7; 4- $\text{NO}_2\text{C}_6\text{H}_4(4\text{-MeC}_6\text{H}_4)_2\text{CH}$, 69361-51-9; 4- $\text{NO}_2\text{C}_6\text{H}_4(4\text{-MeC}_6\text{H}_4)_2\text{CH}^{\bullet-}$, 143959-36-8; 4- $\text{NO}_2\text{C}_6\text{H}_4(2,4\text{-Me}_2\text{C}_6\text{H}_3)_2\text{CH}$, 98293-92-6; 4- $\text{NO}_2\text{C}_6\text{H}_4(2,4\text{-Me}_2\text{C}_6\text{H}_3)_2\text{CH}^{\bullet-}$, 143959-37-9; Xn, 92-83-1; Xn^{•-}, 41174-13-4; Xn^{•+}, 41174-12-3; 9-PhXn, 3246-80-8; 9-PhXn^{•-}, 58378-46-4; 9-PhXn^{•+}, 141394-69-6; 9-CN₂Xn, 85554-24-1; 9-CN₂Xn^{•-}, 144017-35-6; 9-CN₂Xn^{•+}, 130920-17-1.

Dimethyl Phosphate Hydrolysis at Neutral pH

Jung Hee Kim and Jik Chin*

Contribution from the Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6. Received June 23, 1992

Abstract: [(cyclen)Co(OH₂)₂]³⁺ (1) hydrolyzes dimethyl phosphate with a second-order rate constant of $6.2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C, pD 6.3 (cyclen: 1,4,7,10-tetraazacyclododecane). In contrast, [(tetren)Co(OH₂)₂]³⁺ (2) does not hydrolyze the diester to any observable extent, even when the reaction solution is heated to 100 °C for 1 month (tetren: tetraethylenepentamine). The mechanism for 1-promoted hydrolysis of dimethyl phosphate involves joint Lewis acid activation and metal hydroxide activation.

Nature has chosen the ester linkage for lipids, the amide linkage for proteins, and the phosphate diester linkage for nucleic acids. Among the three types of linkages, phosphate diesters are by far the most stable. Under basic conditions, dimethyl phosphate¹ is about 10⁶ times more stable than *N*-methylacetamide,² which in turn is about 3×10^5 times more stable than methyl acetate³ (Table I). Perhaps not surprisingly, the linkage that is by far the most difficult to hydrolyze is the one that nature chose to preserve the genetic material. Over the years, there has been considerable interest in developing catalysts that hydrolyze unactivated phosphate diesters like DNA. Although artificial

Table I. Second-Order Rate Constant (k_{OH}) for Hydroxide-Catalyzed Hydrolysis of Substrates at 25 °C

substrate	$k_{\text{OH}} (\text{M}^{-1} \text{s}^{-1})$
$\text{NaOP}(\text{O})(\text{OCH}_3)_2$	6.8×10^{-12}
$\text{CH}_3\text{C}(\text{O})\text{NHCH}_3$	5.0×10^{-6}
$\text{CH}_3\text{C}(\text{O})\text{OCH}_3$	1.5×10^{-1}

restriction enzymes that cleave DNA oxidatively with amazing sequence specificity have been synthesized,^{4,5} those that cleave DNA hydrolytically have yet to be developed. It has recently been shown that ribozymes activated by metal ions hydrolyze DNA sequence specifically.^{6,7} However, the mechanistic role of metal

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