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Effects of Nitro Groups on Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in Carbon Acids and Their Radical Anions

F. G. Bordwell* and Yongyu Zhao

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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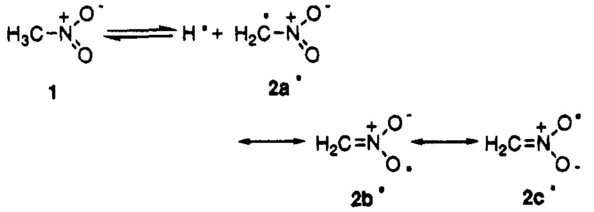
The introduction of a nitro group into methane or into the α or para positions of toluene has been found to increase the heterolytic bond dissociation energies of the C−H bonds (acidities in DMSO) by about 50, 40, and 30 kcal/mol, respectively, whereas the homolytic bond dissociation enthalpies (BDEs) are decreased by only about 7.6, 2.8, and 1.5 kcal/mol, respectively. The BDE_{HA} values for the acidic C−H bonds in 2-nitropropane, phenylnitromethane, (*m*-nitrophenyl)nitromethane, 1-phenylnitroethane, and seven *m*- and *p*-substituted 1-phenylnitroethanes have been compared with the $BDE_{HA^{\bullet-}}$ values for cleavage of the bonds in the corresponding radical anions by path c, $HA^{\bullet-} \rightarrow H^{\bullet} + A^-$, or by path d, $HA^{\bullet-} \rightarrow H^- + A^{\bullet}$.

The Hammett σ_m, σ_p, and σ^- constants for the nitro group of 0.71, 0.78, and 1.27, respectively,[1] have shown it to be the strongest of the common electron-withdrawing groups at increasing the acidities of benzoic acids or phenols by virtue of its powerful field/inductive and delocalizing effects. Meta and para nitro groups are also the strongest of the common substituents in increasing the BDE of the O−H bond in phenol,[2] and it has been suggested that attractive dipole−dipole interactions between the p-NO_2 group and the hydroxyl group in *p*-nitrophenol cause a decrease in its ground state energy that leads to an increase in the BDE of the O−H bond by 5.3 kcal/mol.[2b] (Henceforth, kcal/mol will be abbreviated as kcal.) The p-NO_2 groups in *p*-nitroaniline and *p*-nitrothiophenol likewise cause increases in the BDEs of the N−H and S−H bonds of 3.2 and 2.3 kcal, respectively.[2b] These effects are believed to conform to a general rule that we have been using as a working hypothesis for some time,[3] which states that *when a structural change causes a decrease in the ground state energy of a weak acid, the BDE of its acidic H−A bond will increase, and vice versa.* It is also possible that these BDE increases may be due, in part, to the electron-withdrawing effects of the nitro groups, since it is known that electron withdrawal destabilizes radicals.

In contrast to the increases in BDEs caused by *m*- and *p*-nitro groups in phenols, the introduction of a nitro group into methane has been found to *decrease* the BDE by 7.6 kcal, an effect that can be attributed to the stabilization of the corresponding radical by delocalization of the odd electron. This nitro-radical-stabilizing effect is 4.4 kcal, or about two-thirds that of the CH_3CO group.[4a] The effect of the NO_2 group in the $\sigma^{\bullet}_{jj}$ scale[4b] is also about two-thirds that of the CH_3CO group.



Introduction of an α-phenyl group into nitromethane causes a further decrease in the BDE of the acidic H−C bond in nitromethane because of an additional delocalizing effect.[4a]

The purpose of the present research was to examine further the effects of α-aryl groups on the BDE_{HA} values of the acidic C−H bonds in nitromethane and nitroethane and to examine the α-aryl effects on the $BDE_{HA^{\bullet-}}$ values of the acidic C−H bonds in the radical anions, $ArCH_2NO_2^{\bullet-}$ and $ArCH(Me)NO_2^{\bullet-}$, derived therefrom.

Estimates of the BDE_{HA} values for the acidic H−A bonds in several hundred weak acids have been made during the past 6 years using the thermodynamic cycle shown in Scheme 1.

The value of *C* in eq 1 is 56 kcal when $E_{ox}(A^-)$ is referenced to NHE_{aq}, which is equivalent to 73.3 kcal, when $E_{ox}(A^-)$ is referenced to the ferrocene/ferrocenium couple (Fc/Fc^+). This referencing is preferred since it allows easy comparison with data from other laboratories. The BDEs estimated using eq 1 with $C = 73.3$ kcal have been found to agree with most gas-phase BDEs (enthalpies) to within ±3 kcal.[5] Recent work from Parker's laboratory uses a value of $C = 69.6$ kcal to estimate BDEs as *free energies*, indicating a 3.7 kcal entropy term.[6]

Thermodynamic cycles can often be devised to obtain fundamental data that are difficult to obtain experimentally, including BDEs of the H−A bonds in radical cations and radical anions. Radical cations can dissociate by either path a, $HA^{\bullet+} \rightleftarrows H^+ + A^{\bullet}$, or path b, $HA^{\bullet+} \rightleftarrows H^{\bullet} + A^+$, and radical anions can dissociate by either path c or d,[7d] as shown in Scheme 2.

Griller et al. concluded that path c is generally favored,[7a] but a recent study of $BDE_{HA^{\bullet-}}$ values for a variety of

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

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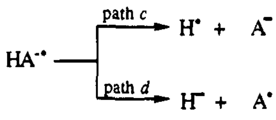
Scheme 1

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

$$\mathrm{BDE_{HA}} = 1.37\mathrm{pK_{HA}} + 23.1\mathrm{E_{ox}(A^-)} + C \tag{1}$$

Scheme 2



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

$$\mathrm{BDE_{HA^{-\bullet}}}\ (\text{path } c) = 1.37\mathrm{pK_{HA}} + 23.1\mathrm{E_{rd}(HA)} + C \tag{2}$$

$$
\begin{array}{lll}
\mathrm{HA^{-\bullet}} \rightleftharpoons \mathrm{HA + e} & & \mathrm{E_{rd}(HA)} \\
\mathrm{HA} \rightleftharpoons \mathrm{H^\bullet + A^\bullet} & & \mathrm{BDE_{HA}} \\
\mathrm{H^\bullet + e} \rightleftharpoons \mathrm{H^-} & & \mathrm{-E_{rd}(H^\bullet)} \\
\hline
\mathrm{HA^{-\bullet}} \rightleftharpoons \mathrm{H^- + A^\bullet} & & \mathrm{BDE_{HA^{-\bullet}}}\ (\text{path } d)
\end{array}
$$

$$\mathrm{BDE_{HA^{-\bullet}}}\ (\text{path } d) = \mathrm{BDE_{HA}} + 23.1\mathrm{E_{rd}(HA)} + C \tag{3}$$

hydrocarbons substituted by donor or acceptor groups indicated that either path c or path d may be preferred, depending on the type of substituent present.[7d] Direct measurements for these cleavage modes is not feasible in solution because of the high reactivity of H•, H^-, and A• species. Our studies have now been extended to nitroalkanes.

Results and Discussion

The effects of α-NO_2, *m*-NO_2, and *p*-NO_2 groups on the acidities and BDEs of a number of carbon acids are summarized in Table 1.

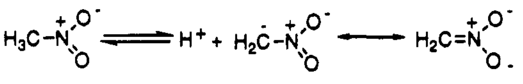
Examination of entries 1–6 in Table 1 shows that, in contrast to the effects of nitro groups on phenols, introduction of a nitro group into (a) methane, (b) the α-position of toluene, or (c) the para position of toluene causes a *decrease* in the BDE of the acidic C–H bonds of 7.6, 2.8, and 1.5 kcal, respectively. These effects are probably associated with increases in ground state energies that lead to bond-weakening effects and to the delocalizing (stabilizing) effects of the NO_2 group on the odd electron in the $NO_2CH_2^\bullet$, $C_6H_5{}^\bullet CHNO_2$, and *p*-$NO_2C_6H_4CH_2^\bullet$ radicals.[4a] These effects are small, however, compared to the increases in acidities for CH_3NO_2 (> 50 kcal), $C_6H_5CH_2NO_2$ (>40 kcal), and *p*-$NO_2C_6H_4CH_3$ (> 30 kcal), relative to CH_4 and $C_6H_5CH_3$, respectively.

Table 1. Effects of *m*-NO_2, *p*-NO_2, and α-NO_2 Groups on the Acidities and BDEs of C–H Bonds in DMSO

weak acid	pK_{HA}	$E_{ox}(A^-)^e$	BDE^g	ΔBDE
1. CH_4	~56^a		105^h	(0.0)
2. CH_3NO_2	17.2^b	0.024^b	97.4^b	−7.6
3. Me_2CHNO_2	16.8^b	-0.413^b	86.8^b	−18.2
4. $C_6H_5CH_3$	~43^a	−0.289	88^h	(0.0)
5. $C_6H_5CH_2NO_2$	12.2^b	-0.209^f	85.2^f	−2.8
6. *p*-$NO_2C_6H_4CH_3$	20.4^c	-1.644^c	86.5^c	−1.5
7. *m*-$NO_2C_6H_4CH_2NO_2$	10.0^d	−0.019	86.6	−1.4
8. $C_6H_5CH_2Me$	~45^a		85.4^h	(0.0)
9. $C_6H_5CH(Me)NO_2$	14.0	−0.276	86.1	0.7
10. *p*-$CH_3OC_6H_4CH(Me)NO_2$	14.6	−0.366	84.9	−0.5
11. *m*-$CH_3OC_6H_4CH(Me)NO_2$	14.1	−0.242	86.9	1.5
12. *p*-$CH_3C_6H_4CH(Me)NO_2$	14.3	−0.315	85.6	0.2
13. *p*-$FC_6H_4CH(Me)NO_2$	13.6	−0.252	86.1	0.7
14. *m*-$NO_2C_6H_4CH(Me)NO_2$	11.5	−0.083	86.1	1.9
15. *p*-$NO_2C_6H_4CH(Me)NO_2$	10.3	−0.020	86.9	1.5
16. 3,5-$(NO_2)C_6H_3(Me)NO_2$	9.9	−0.078	88.7	3.3

[a] Estimated. [b] Reference 4. [c] Reference 7e. [d] Reference 23. [e] In volts; irreversible oxidation potentials measured by cyclic voltammetry in DMSO and referenced to the ferrocene/ferrocenium couple. [f] The values of $E_{ox}(A^-)$ of 0.289 V and BDE = 83 kcal reported in ref 4 are incorrect. [g] Homolytic bond dissociation energies estimated by eq 1 with $C = 73.3$ kcal. [h] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

The increase in acidity for CH_3NO_2 vs CH_4 is due to the large resonance and electron-withdrawing field/inductive effects of the nitro group in stabilizing anion $\mathbf{3}^-$. In



1 **3a⁻** **3b⁻**

aqueous solution nitromethane is a stronger acid by an additional 10 kcal because of the strong H-bond donor solvent stabilizing effect on $\mathbf{3}^-$, which is absent in DMSO.

The nitro effect on homolytic cleavage of the C–H bond in nitromethane (**1**) is much smaller than for heterolytic cleavage because (a) the resonance effect in **2**• is diminished because the spin density in the radical is primarily on carbon (**2a**•)[8–10] and (b) the nitro group has a dual effect on the •CH_2NO_2 radical, stabilizing by virtue of its delocalizing ability, but strongly destabilizing by electron withdrawal.[4a] Its effect is similar in this regard to that of other acceptor groups such as a pyridinium group.[11]

Other electron-withdrawing groups exert similar effects on acidities in DMSO and on the BDEs of C–H bonds in GCH_2–H methanes for similar reasons. For example, with G = CH_3CO ($\Delta pK_{HA} \simeq 41$ kcal; $\Delta BDE \simeq 11$ kcal), with G = CN ($\Delta pK_{HA} = 34$ kcal; $\Delta BDE \simeq 11$ kcal), with G = $PhSO_2$ ($\Delta pK_{HA} = 37$ kcal; $\Delta BDE = 6$ kcal), and with G = F_3CSO_2 ($\Delta pK_{HA} \simeq 51$ kcal; $\Delta BDE = 2$ kcal).[12] On the other hand, when G is a powerful donor group, such as Me_2N, ΔpK_{HA} is much smaller due to the weak electron-withdrawing effect of Me_2N (e.g., $\sigma_I = 0.21$ for Me_2N vs $\sigma_I = 0.71$ for NO_2[1]), whereas ΔBDE is large (21 kcal[13]).

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(8) ESR studies have shown that for radicals of the type GC•, the spin density is primarily on carbon when G is RCO, RCO_2, CN, or NO_2.[9,10]

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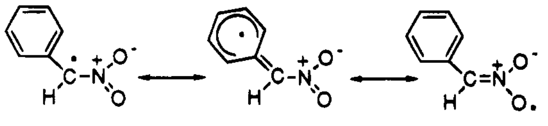
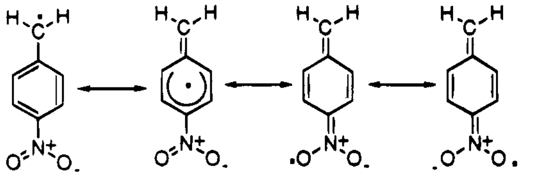
Examination of entries 1 and 4 in Table 1 shows that, contrary to the effects of substituting a nitro or other strong electron-withdrawing groups into methane, substitution of a phenyl group into methane has nearly as large an effect in decreasing the BDE as increasing the acidity ($\Delta pK_{HA} \simeq 18$ kcal; $\Delta BDE = 17$ kcal). And substitution of a phenyl group into nitromethane (entry 5 vs 2) has a *larger* effect in decreasing the BDE than increasing the acidity ($\Delta pK_{HA} = 6.8$ kcal; $\Delta BDE = 12$ kcal). Evidently, delocalization of an odd electron by a phenyl group is about as effective in stabilizing a radical as delocalization of a negative charge by a phenyl group is at stabilizing a carbanion.



4a• **4b•** **4c•**

The surprisingly large α-phenyl effect on the BDE of nitromethane and the smaller, or nearly equal, effect on acidity is similar to the α-phenyl effects observed for other carbon acids bearing strong electron-withdrawing groups, such as acetone ($\Delta pK_{HA} = 9$ kcal; $\Delta BDE = 11$ kcal) or acetonitrile ($\Delta pK_{HA} = 12.9$; $\Delta BDE = 11$ kcal). These large ΔBDE effects can be attributed to extra stabilization provided by the presence of *both* a donor (phenyl) and an acceptor ($COCH_3$ or CN) group attached to a carbon-centered radical.[13]

Turning to the effects of NO_2 groups on BDEs of C−H bonds, we note that the BDE of the acidic C−H bond in *p*-nitrotoluene (entry 6) is *decreased* by 1.5 kcal, relative to that of toluene. The effect of the *p*-NO_2 group on the BDE of the C−H bond in toluene is therefore opposite to that of a *p*-NO_2 group on the BDEs of the O−H bond in phenol, the N−H bond in aniline, or the S−H bond in thiophenol discussed earlier. Evidently, the (stabilizing) delocalizing effect of the NO_2 group in the *p*-$NO_2C_6H_4CH_2^•$ radical (e.g., **5**) overshadows (a) the relatively small attractive dipole/dipole interaction of the NO_2 group with the (weak) H−C dipole and (b) the electron-withdrawing effect of the nitro group, both of which would be bond strengthening. The α-NO_2 effect on the BDE of the acidic C−H bond in phenylnitromethane (entry 5) is also bond weakening (by 2.8 kcal relative to toluene), apparently due to delocalization of the odd electron into the α-nitro group, as occurs in the $NO_2CH_2^•$ radical (**2**). This α-nitro bond-weakening effect also prevails in *m*-$NO_2C_6H_4CH_2NO_2$ but is diminished to a 1.4 kcal bond-strengthening effect by the electron-withdrawing effect of the *m*-NO_2 group. Substitution of one of the hydrogen atoms of nitromethane by a methyl group causes a 6 kcal decrease in BDE, and a substitution of a second methyl group causes an additional 4.6 kcal decrease.[4a] These effects can be attributed to methyl stabilization of the corresponding radicals. But methyl substitution of one of the α-hydrogen atoms in phenylnitromethane causes a 0.7 kcal *increase* in BDE (entry 9). This reversal of the methyl effect is not without precedent since the congestion in tertiary radicals bearing large functions, such as a phenyl group, often makes tertiary radicals less stable than the corresponding secondary radicals by decreasing the possibility of effective orbital overlap.[14]



5a• **5b•** **5c•** **5d•**

The Effects of Remote Substituents on the Acidity and BDE_{HA} Values of ArCH(Me)NO_2 Acids. The acidities of 12 ArCH(Me)NO_2 acids have been measured previously in 50% (v/v) H_2O−MeOH.[15] In this hydroxylic solvent the total acidity range covered was only about 1 pK_{HA} unit, and the Hammett $\rho \simeq 1.5$. In DMSO, the pK_{HA} of $C_6H_5CH(Me)NO_2$ is 14.0, compared to 8.5 in 50% H_2O/MeOH, and the Hammett $\rho \simeq 3.5$ for *m*- and *p*-substituted 1-phenylnitroethanes (see the data in Table 1). These large differences in pK_{HA} and ρ arise because of the leveling by the strong donor hydrogen bonding of H_2O to $ArC(Me){=}NO_2^-$ anions in the hydrolytic solvent and its absence in DMSO.

The BDE values for the acidic C−H bonds in ArCH(Me)NO_2, omitting that for 3,5-$diNO_2C_6H_3CH(Me)NO_2$, are constant (86 ± 1 kcal; Table 1). This constancy of BDEs arises because of the small effects of the remote substituents on the BDEs of C−H acids. Near constancy of BDEs has been observed for a number of other carbon acid families where the radical-stabilizing effects of remote substituents are small, including (a) 12 *m*-substituted fluorenes (BDE = 79.5 ± 0.3 kcal),[16] (b) 17 *m*- and *p*-substituted benzyl phenyl sulfones, $GC_6H_4CH_2SO_2Ph$ (BDEs 90 ± 2 kcal),[17] (c) 14 *m*- and *p*-substituted arylacetonitriles, $GC_6H_4CH_2CN$ (BDE = 82 ± 1 kcal--omitting the point for *p*-Me_2N),[18] (d) 13 10-substituted 9-methylanthracenes (81 ± 1 kcal),[7c] and (e) 8 $GC_6H_4CH_3$ toluenes (85 ± 1 kcal).[19] Plots of $E_{ox}(A^-)$ vs pK_{HA} values in these families are linear with slopes near unity indicating that there is an intrinsic relationship between pK_{HA} and $E_{ox}(A^-)$.[3c]

$BDE_{HA}{}^{•-}$ Values for Homolytic Cleavage of the Acidic C−H Bond in Radical Anions by Paths c and d (Scheme 2). In a recent paper, estimates of homolytic bond dissociation enthalpies, $BDE_{HA}{}^{•-}$ values, for the acidic C−H bonds in the radical anions derived from (a) 18 2- or 9-substituted fluorenes, (b) 7 *m*- or *p*-substituted triphenylmethanes, (c) 10 anilines and related nitrogen acids, and (d) 17 anthracenes (seven 9-GCH_2An and 10 10-G-9-MeAn) were made using eq 3 for path c, assuming that the constant *C* has the same value (73.3 vs Fc^+/Fc) as that used to estimate homolytic bond dissociation enthalpies by eq 1. Equation 3 was used to make $BDE_{HA}{}^{•-}$ estimates for path d.[7d]

$$BDE_{HA}{}^{•-}\ (\text{path d}) = BDE_{HA} + 23.1[E_{rd}(HA) - E_{rd}(H^•)] \quad (3)$$

Our estimates of $BDE_{HA}{}^{•-}$ values for path d by eq 3 must be corrected, by −4.8 kcal, however, because the

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Table 2. Reduction Potentials and $\mathrm{BDE_{HA}}^{\bullet-}$ Values Compared to $\mathrm{BDE_{HA}}$ Values for 2-Nitropropane, *p*-Nitrotoluene, Arylnitromethanes, and 1-Arylnitroethanes

			$\mathrm{BDE_{HA}}^{\bullet-}$		
G	$E_{rd}(\mathrm{HA})^a$	$\mathrm{BDE_{HA}}^d$	path c^e	path d^f	$\Delta\mathrm{BDE}^g$
1. Me_2CHNO_2	−2.160	87	46.5	62	16
2. *p*-$NO_2C_6H_4CH_3$	−1.479^b	86.5^b	67^b	77	10
$GC_6H_4CH_2NO_2$					
3. H	−2.030	85	43	63	20
4. *m*-NO_2	−1.450	87	54	79	25
$GC_6H_4CH(Me)NO_2$					
5. *p*-CH_3O	−2.000	85	47	64	17
6. *m*-CH_3O	−1.961	87	47	67	20
7. *p*-CH_3	−1.985	85.5	47	65	18
8. H	−1.970	86	47	66	19
9. *p*-F	−1.956	86	47	66	19
10. *m*-NO_2	−1.491^c	87	55	77	22
11. *p*-NO_2	−1.451	87	54	79	25
12. 3,5-$(NO_2)_2$	−1.221^c	89	59	86	27

[a] In volts; irreversible reduction potentials were measured in DMSO solution in the manner previously described unless otherwise indicated. [b] Reference 7d. [c] Reversible reduction potentials. [d] See Table 1. [e] In kcal/mol; estimated by eq 3 with $C = 73.3$. [f] In kcal/mol; estimated by eq 4 with $C = 25.1$. [g] In kcal/mol; $\Delta\mathrm{BDE} = \mathrm{BDE_{HA}}^{\bullet-}$ (path d) − $\mathrm{BDE_{HA}}^{\bullet-}$ (path c).

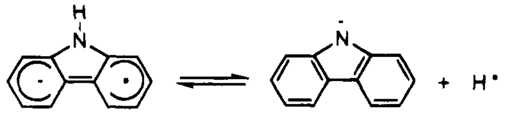
difference between $\mathrm{NHE_{aq}}$ and $\mathrm{Fc^+/Fc}$ potentials in DMSO was taken as 0.75 V, whereas Parker and his colleagues later showed the difference to be 0.54 V.[20]

Estimates of the homolytic bond dissociation *free energies* for the radical anions derived from 15 of the same anthracenes we examined earlier have recently been reported as hydride affinities of the corresponding radicals.[6,21]

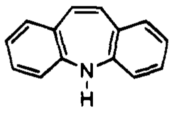
The $\mathrm{BDE_{HA}}^{\bullet-}$ values that were reported earlier for cleavage by path d averaged 7.9 ± 1 kcal higher than the $-\Delta G_{\mathrm{hydride}}(\mathrm{R}^\bullet)_s$ (kcal) values reported by Handoo et al.[6] Part of this difference (4.8 kcal) is due to the need for correcting our referencing of the $\mathrm{NHE_{aq}}$ potentials to the $\mathrm{Fc^+/Fc}$ couple. In addition, our values are made 3.7 kcal higher due to the $T\Delta S°$ entropy term. When these differences are taken into consideration the $\mathrm{BDE_{HA}}^{\bullet-}$ values differ by less than 1 kcal of one another.

In reviewing our corrected values for the anthracenes, we find that for 10-G-9-MeAn where G is Me, MeO, Ph, Cl, or PhS, path d is favored by 2.5 to 10.5 kcal. But when G is PhCO, CN, CHO, or NO_2 path c is favored by about 4, 5, 10, and 17 kcal, respectively. For 4-Ph-, 4-PhS-, and 3-CF_3-phenyldiphenylmethanes, path d is favored by 5−8 kcal, but path c becomes more favorable by 5, 6, and 4 kcal, respectively, when the 4-substituent is changed to PhCO, $PhSO_2$, and NO_2. A similar pattern of behavior is observed for fluorenes, where paths c and d are about equally favored for fluorene itself, 2-Me_2N-fluorene, and 9-Ph- or 9-Mes-fluorenes, but path c is favored by 5 or more kcal for 2-CN-, 2-$PhSO_2$-, 2-NO_2-, 9-$PhSO_2$, and 9-MeOCO-fluorenes. For 9-EtS-fluorene path d is slightly favored, and for 9-EtO- and 9-R_2N-fluorenes path d is favored by 5−10 kcal. In each of these examples, the electron added to the parent can be accommodated in the benzene ring, and the presence of a donor group in the ring can stabilize the initially formed radical anion, and also the $A^\bullet$ radical formed in cleavage by path d,[7d] but will have little or no stabilizing effect on the A^- anion formed by path c. Acceptor groups in the benzene ring will stabilize the negative charge in the radical anion and also the A^- anion formed by path c, but will tend to destabilize the $A^\bullet$ radical formed in path d.[7d] The NO_2 group is the strongest of the acceptor groups in favoring path c over path d.

The six anilines examined previously all have electron-withdrawing groups in the benzene ring. The three anilines bearing *p*- or *o*-nitro groups have $\mathrm{BDE_{HA}}^{\bullet-}$ values for path d that are 15−25 kcal less favorable than for path c. The $\mathrm{BDE_{HA}}^{\bullet-}$ values by path c for these nitro anilines are about 65% of those of the parents, and the $\mathrm{BDE_{HA}}^{\bullet-}$ values by path c for the radical anions derived from *p*-CN-, *m*-CN-, and 2,4,6-trichloroanilines are about 50% of those of the parent. The $\mathrm{BDE_{HA}}^{\bullet-}$ values by path c for the radical anions derived from three carbazoles are only about 30% of those of the parents, suggesting that odd electron and negative charge can be accommodated in the two benzene rings in a manner similar to stabilization of fluorene radical anion ($\mathbf{6}^{\bullet-}$).[7d] Path d is about equally favored to path c only for iminostilbene (**7**).

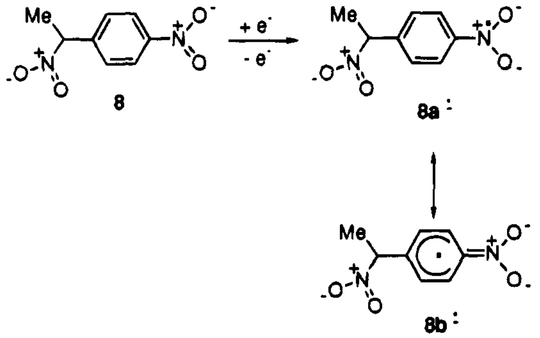


6$^{\bullet-}$ **6**$^{-}$



7

The nitro compounds in Table 2 wherein the nitro group is attached to a benzene ring have $E_{rd}(\mathrm{HA})$ potentials about 0.5 V (11 kcal) more positive than those for 2-nitropropane or phenylnitromethane, which can be rationalized in terms of delocalization of the odd electron into the benzene ring (e.g., $\mathbf{8}^{\bullet-}$). In other words, $\Delta G°$ for acceptance of an electron by a nitro group attached to an aromatic ring is about 11 kcal less positive than that for a nitro group in a nitroalkane.



8 **8a**$^{\bullet-}$ **8b**$^{\bullet-}$

Summary and Conclusions. One of the reasons that the introduction of a nitro group into methane or the α or para position of toluene has a much smaller effect on BDEs of the acidic C−H bonds (homolytic cleavage) than acidities (heterolytic cleavage) is that α-NO_2 groups exert a dual effect on carbon-centered radicals, formed in the homolytic cleavage, i.e., stabilizing by virtue of their delocalizing ability, but strongly destabilizing by virtue of their electron-withdrawing effects. The BDE data revealed that the *p*-NO_2 group in *p*-nitrotoluene weakens the acidic C−H bond, as does the α-NO_2 group in

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[20] Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493−7498.

[21] The Handoo et al. paper[6] (received by *J. Am. Chem. Soc.* 1/7/93) appeared in print while our paper[7d] (received by *J. A. Chem. Soc.* 1/21/93) was being reviewed and revised.

phenylnitromethane, whereas *p*-nitro groups in phenols, thiophenols, and anilines *strengthen* the O−H, S−H, and N−H bonds, respectively. The bond-weakening effect in *p*-$NO_2C_6H_4CH_2H$ is probably associated with an increase in ground state energy. The BDE_{HA} values of seven arylnitroethanes, ArCH(Me)NO_2, have been estimated and found to be nearly constant (86 ± 1 kcal). A review of choices of cleavage of the acidic H−A bonds in radical anions derived from fluorenes, triphenylmethanes, and anthracenes showed that the presence of donor groups favored cleavage by path d in Scheme 2, whereas acceptor groups tend to favor cleavage by path c. The $BDE_{HA^{\bullet -}}$ values of the radical anions derived from 2-nitropropane, two phenylnitromethanes, and eight 1-arylnitroethanes were estimated to favor path c over path d by 25−30 kcal. Nitro groups attached to aromatic rings have more positive E_{rd}(HA) values by about 0.5 V than those for nitroalkanes. In other words their acceptance of a single electron by an aromatic nitro group is more favorable by about 11 kcal than by an aliphatic nitro group.

Nitro groups have been shown to exert dual effects on radicals by (a) stabilizing by virtue of their delocalizing effect on the odd electron and (b) destabilizing by virtue of their electron-withdrawing effect.

Table 3. Equilibrium Acidities of *m*- and *p*-Substituted 1-Phenylnitroethanes

G	HIn(or HS)[a]	pK_a(HIn or HS)[a]	pK_a(HA)	std devn
p-CH_3O	HZF[b]	14.95	14.92	0.205
			14.63	0.053
			14.63	0.103
m-CH_3O	HZF[b]	14.95	14.47	0.345
			14.17	0.228
			14.00	0.165
p-CH3	$HZFO_2$[c]	12.95	14.27	0.103
	HZF[b]	14.95	14.63	0.331
			14.46	0.159
			14.40	0.135
p-H	$HZFO_2$[c]	12.95	14.00	0.042
			13.98	0.038
p-F	$HZFO_2$[c]	12.95	13.65	0.015
			13.66	0.008
m-NO_2	NBY300[d]	12.25[e]	11.54	0.012
			11.55	0.008
p-NO_2	NBY300[d]	12.25[e]	10.29	0.028
	$PhSO_2CH_2COPh$	11.39[e]	10.36	0.022
3,5-diNO_2	NBY300[d]	12.25[e]	10.02	0.090
	$PhSO_2CH_2COPh$	11.39[e]	9.84	0.060
			9.90	0.082

[a] HIn (indicator) or HS (standard acid). [b] HZF: 9-fluorenone phenylhydrazone. [c] $HZFO_2$: 9-fluorenone 4-chloro-phenylhydrazone. [d] NBY300: bis(phenylsulfonyl)methane. [e] pK_{HA} measured by a standard acid method; the dimsyl anion was quenched with the standard acid *p*-$CNC_6H_4CH_2SO_2Ph$.[24]

Experimental Section

All of the compounds studied were previously synthesized in our laboratory.[15] The equilibrium acidities in DMSO were determined by either the overlapping indicator method[22,24] or the standard acid method. The indicator method was used for weak acids where the corresponding anions are colorless or do not absorb in the region of visible spectrum of the indicator used. For weak acids having anions with interfering absorbances, the standard acid method was used. In this method the acid of unknown pK_{HA} is used as its own indicator by titrating it against an acid of known pK_{HA} having colorless or almost colorless anions (namely, standard acids). In addition, for weak acids that are not stable in the presence of excess of the strongly basic dimsyl anion ($CH_3SOCH_2^-$), the dimsyl was quenched with another standard acid before the titration. The results, together with the indicators or standard acids used, are summarized in Table 3. The oxidation potentials and reduction potentials were measured by cyclic voltammetry as described previously.[5,7d] The working electrode (BAS) consists of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal for the measurements of oxidation potentials of conjugate anions of weak acids. It was polished with a 0.05-μm 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 the ferrocenium/ferrocene couple. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under argon atmosphere.

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