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# Homolytic Bond Dissociation Energies of Acidic C–H Bonds Activated by One or Two Electron Acceptors

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Estimates of homolytic bond dissociation energies (BDEs) have been made for the acidic H–C bonds in $CH_3SO_2Ph$, $CH_3SO_2CF_3$, $CH_3CO_2Et$, $CH_3COCH_3$, $CH_3COPh$, and $CH_3NO_2$ by combining their $\mathrm{p}K_{\mathrm{HA}}$ values with the $E_{\mathrm{ox}}(\mathrm{A^-})$ values of their conjugate bases, both measured in DMSO. Similar estimates were made for the BDEs of the acidic H–C bond in 17 compounds of the type $GCH_2G$ and $GCH_2G'$ where G and G′ are both one of these functions or $SO_2CH_3$ or CN. Most of the BDEs for these methylene compounds bearing two electron acceptors fall in the range of 90–103 kcal/mol. The BDEs are generally within 3 kcal/mol of half the sum of the $GCH_2$–H and $G'CH_2$–H BDEs. The small effects caused by introduction of a second electron acceptor are rationalized in terms of the leveling effect of the first substituent and the dual nature of the effects most acceptors have on the stabilities of adjacent radicals, i.e., stabilizing by virtue of their delocalizing ability and destabilizing by virtue of their field/inductive electron-withdrawing ability. The $E_{\mathrm{ox}}(\mathrm{A^-})$ values of $PhCH_2SO_2G$ compounds, where G = Me, *t*-Bu, N(Me)Ph, $CH_2Ph$, Ph, OPh, and $CF_3$, plot linearly with $\mathrm{p}K_{\mathrm{HA}}$ and all have BDEs of 90 ± 1 kcal/mol.

Numerous studies have shown that when an electron acceptor and an electron donor are attached to a nitrogen-centered or carbon-centered radical the stabilizing effect on the radical is usually greater than that provided by either substituent individually.[1] Relatively little information is available, however, with regard to the effect on radical stability of having two acceptors or two donors attached to a radical center. Electron spin resonance (ESR) hyperfine coupling constants for benzylic radicals of the type $p\text{-MeC}_6\text{H}_4\dot{\text{C}}\text{XY}$ have been interpreted to mean that the effects are "antagonistic" when X and Y are both MeO or both CN groups.[2] Perusal of the data reveals, however, that a second CN group causes a slight decrease in the $a_{\mathrm{H}}^{\mathrm{Me}\bullet}(\mathrm{G})$ value, suggesting an additional increase in radical stability, whereas a second MeO group causes an increase in $a_{\mathrm{H}}^{\mathrm{Me}\bullet}(\mathrm{G})$,[2a] suggesting a decrease in radical stability. These effects are small, however, which is not unexpected, since these benzyl radicals are already stabilized by 17 kcal/mol, relative to the methyl radical. (Henceforth kcal/mol will be abbreviated as kcal.) Similar effects were found for MeO and CN effects on ESR-determined activation energies for rotational barriers in substituted allyl radicals. Here both a second CN and a second OMe decreased $E_a$ slightly (1–2.7 kcal) compared to the first substituent.[2b] Calculations by LeRoy suggest that a single OR or CN group when substituted for a hydrogen atom of methane lowers the BDE of the C–H bond from 105 to 93 kcal. A second OR causes a further decrease of only 3 kcal, but a second CN group decreases the BDE by 12 kcal.[3] Recent calculations by Pasto also indicate that a second CN group has essentially the same radical stabilizing effect on the methyl radical as does the first (~5.3 kcal).[4c]

**Table I. Acidities and Homolytic Bond Dissociation Energies (BDEs) of Monofunctional Acids in DMSO**

| acid | $\mathrm{p}K_{\mathrm{HA}}$[a] | $E_{\mathrm{ox}}(\mathrm{A^-})$[d] | BDE[e] | ΔBDE |
|---|---|---|---|---|
| $CH_4$ | ~56 | | 105[f] | (0.0) |
| $CH_3CN$ | 31.3 | | 93[f] | 12 |
| $CH_3SO_2CH_3$ | 31.1 | | 99[g] | 6 |
| $CH_3SO_2Ph$ | 29.0[b] | 0.145 (120) | 99 | 6 |
| $CH_3SO_2CF_3$ | 18.75 | 0.940 (140) | 103 | 2 |
| $CH_3CO_2Et$ | (29)[c] | | 95[h] | 10 |
| $CH_3COCH_3$ | 26.5 | 0.076 (100) | 94 | 11 |
| $CH_3COPh$ | 24.7 | 0.143 (60) | 93 | 12 |
| $CH_3NO_2$ | 17.2 | 0.899 (90) | 98 | 7 |

[a] Reference 7, unless otherwise noted. [b] Reference 8. [c] Estimated from a one-point titration. [d] Irreversible potentials vs SHE (wave widths in parentheses) measured under conditions previously described.[9] [e] Calculated according to eq 1, unless otherwise noted. [f] McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 483–532. [g] Assumed to be the same as for $CH_3SO_2Ph$. [h] Estimated from the BDE for $PhCH_2CO_2Et$ (84 kcal) and the assumption that ΔBDE was the same as that between $PhCH_2COPh$ and $CH_3COCH_3$

In earlier studies we have shown that equilibrium acidities of weak acids, HA, in DMSO can be combined with the oxidation potentials of the conjugate bases ($\mathrm{A^-}$) of the acids to obtain estimates of homolytic bond dissociation energies (BDEs) according to eq 1.[5] In the present

$$\mathrm{BDE\ (kcal)} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.06E_{\mathrm{ox}}(\mathrm{A^-}) + 56 \qquad (1)$$

paper we apply this method to obtain estimates of the BDEs for the acidic C–H bonds in molecules of the type $CH_3G$, $GCH_2G$, and $GCH_2G'$, where G and G′ are the electron acceptors of the type CN, $SO_2Ph$, COPh, $NO_2$, and $Me_3N^+$.

## Results and Discussion

**Effects of Single Electron Acceptors.** Equilibrium acidities in DMSO and estimates of the BDEs of the acidic bonds in the monofunctional acids $CH_3CN$, $CH_3SO_2CH_3$, $CH_3SO_2Ph$, $CH_3SO_2CF_3$, $CH_3CO_2Et$, $CH_3COCH_3$, $CH_3COPh$, and $CH_3NO_2$ are shown in Table I.

Examination of Table I shows that in the monofunctional compounds, the electron acceptors lower the BDEs of the acidic H–C bond by 2–12 kcal, relative to that of the H–C bond in methane (105 kcal), according to our estimates. These ΔBDEs can be taken as a measure of the relative radical stabilization energies (RSEs) of the cor-

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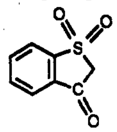
responding $GCH_2^{\bullet}$ radicals.[6] The BDEs for only two of the compounds in Table I have been reported in the gas-phase literature. A BDE of 93 ± 3 kcal for acetonitrile has been estimated from very low pressure pyrolysis measurements,[10] and the most recent estimate places the BDE of acetone at 92 ± 1.5 kcal, based on the rate of hydrogen atom abstraction and a recently corrected value for the heat of formation of the acetonyl radical.[11] A closely similar value, 92 ± 2 kcal has been estimated for the acidic H–C bond in acetaldehyde.[11] Our estimates from eq 1 place the BDEs of the acidic H–C bonds in acetone, *tert*-butyl methyl ketone, and acetophenone at 94, 94, and 93 kcal, respectively.[12] We see that the CN function and carbonyl-containing functions are strongly radical stabilizing (RSEs = 10–12 kcal), whereas sulfonyl-containing functions are weakly radical stabilizing, and $NO_2$ is intermediate in this regard. Although the $PhSO_2$ group in the $PhSO_2CH_2^{\bullet}$ radical appears to be radical stabilizing, relative to the $CH_3^{\bullet}$ radical, substitution of the $PhSO_2$ group for an acidic C–H bond in toluene, fluorene, β-methylnaphthalene, 9-methylanthracene, or xylene appears to destabilize the corresponding radicals by 2–7 kcal.[13] It would appear that the $PhSO_2$ group in some situations has a net weakening effect on adjacent C–H bonds and in other situations has a net strengthening effect. We believe that most electron acceptors have similar inherent radical-destabilizing, as well as radical-stabilizing, propensities. This idea is supported by the calculations of Pasto, which have led him to conclude that there is an "electronegative inductive (destabilizing) effect" on radicals.[4a] The dual nature of the effects of acceptors first became apparent to us in a study of ΔBDEs of the acidic C–H bonds in arylacetonitriles, $GC_6H_4CH_2CN$. The C–H bonds were weakened by G donors, such as *p*-MeO and *p*-$Me_2N$ groups, but were strengthened by G acceptors, such as *p*-CN and *p*-PhCO groups, despite the known ability of CN and PhCO groups to stabilize radicals, which should make them bond weakening.[14] Similar bond-strengthening effects were observed for *p*-CN and *p*-PhCO groups in phenols, but here, once corrections were made for the field/inductive effects, the radical stabilizing effects for these groups were brought to the fore.[15] The radical destabilization caused by field/inductive electron withdrawal is best illustrated by the $Me_3N^+$ group, which has been shown to *increase* the BDE of the acidic C–H bonds in acetophenone, acetonitrile, and ethyl acetate[16] (Table I), as well as in fluorene,[17] when substituted for one of the acidic hydrogen atoms. The calculations of Pasto also indicate that the $Me_3N^+CH_2^{\bullet}$ radical is destabilized, relative to the methyl radical.[4] Substitution of an α-pyridinium group, $C_5H_5N^+$, into acetophenone, acetonitrile, or ethyl acetate must also strengthen the acidic C–H bond by virtue of this powerful electron-withdrawing field/inductive effect, but its overall effect is *bond weakening* because of its delocalizing effect on the incipient radical (**1a** ↔ **1b**).[16]

**Table II. Acidities and Homolytic Bond Dissociation Energies (BDEs) of Difunctional Acids in DMSO**

| acid | $pK_{HA}$[a] | $E_{ox}(A^-)$[d] | BDE[g] | BDE (calcd)[h] |
|---|---|---|---|---|
| $CH_2(CN)_2$ | 11.0 | 0.813 (60)[e] | 90 | 93 |
| $CH_2(SO_2CH_3)_2$ | 15.0[b] | 1.075 (70) | 100 | 100 |
| $CH_2(SO_2Ph)_2$ | 12.2 | 1.093 (60) | 98 | 99 |
| $CH_2(SO_2CF_3)_2$ | 2.1 | 2.35 (85)[f] | 113 | 103 |
| $CH_2(CO_2Et)_2$ | 16.4 | 0.728 (70)[e] | 95 | 95 |
| $CH_2(COCH_3)_2$ | 13.3 | 0.756 (60)[e] | 92 | 94 |
| $CH_2(COPh)_2$ | 13.4 | 0.782 (102) | 92 | 93 |
| $CH_2(CN)CO_2Et$ | 13.1[c] | 0.746 (60) | 91 | 94 |
| $CH_2(CN)SO_2Ph$ | 12.0 | 1.039 (100) | 96 | 96 |
| $CH_2(CN)COPh$ | 10.2 | 0.861 (72) | 90 | 93 |
| $CH_2(COCH_3)CO_2Et$ | 14.2 | 0.755 (60)[e] | 93 | 94 |
| $CH_2(COPh)SO_2Ph$ | 11.4 | 1.029 (80) | 95 | 96 |
| $CH_2(SO_2Ph)NO_2$ | 7.1 | 1.455 (85) | 99 | 99 |
|  | 10.1 | 1.047 (60) | 94 | 96 |
| $CH_2(CN)NMe_3^+$ | 20.6 | 0.479 (65) | 95 | 99 |
| $CH_2(COPh)NMe_3^+$ | 14.6 | 0.898 (95) | 97 | 99 |
| $CH_2(CO_2Et)NMe_3^+$ | 20.0 | 0.609 (95) | 97 | 100 |

[a] Reference 7 unless otherwise noted. [b] Bordwell, F. G.; Drucker, G. D.; McCollum, G. J. *J. Org. Chem.* 1982, *47*, 2504–2509. [c] Bordwell, F. G.; Branca, J. C.; Bares, J. E.; Filler, R. *J. Org. Chem.* 1988, *53*, 750–782. [d] Irreversible potentials vs SHE (wave widths in parentheses) measured under the conditions previously described.[9] [e] The $E_{1/2}$ oxidation potential measured with a microelectrode under high-speed scans was reversible and agreed to 55 mV, or less, with this value.[18] [f] Measured in $CH_3CN$; $E_{ox}(A^-)$ for $F_3CSO_2CH_2^-$ in $CH_3CN$ is more positive by 60 mV than in DMSO. [g] Estimated by eq 1. [h] $BDE = 0.5[BDE_{A_1C-H} + BDE_{A_2C-H}]$.

**1a** **1b**

This gives strong support to the concept of a dual nature for the effects of most α-acceptors on radical stabilities, i.e., destabilizing by virtue of their field/inductive effects and stabilizing by virtue of their delocalizing effects.[4,16]

**Effects of Two Electron Acceptors.** The only previous estimates of the BDEs for the acidic H–C bonds in compounds of this type appear to be the calculations of LeRoy[3] and Pasto[4] on malononitrile. As mentioned earlier, these calculations indicate that the second CN group is appreciably more bond weakening than the 3 kcal estimate we obtained by eq 1. Our value has now been checked in two ways. First, the value of the oxidation potential for the conjugate base of malononitrile was measured using a microelectrode under high-speed scans to obtain reversibility. The $E_{1/2}$ of the reversible oxidation potential was found to be within experimental error (30 mV) of the peak potential obtained under irreversible conditions.[18] Under these conditions the $E_{1/2}$ reversible and $E_{pa}$ irreversible potentials for the anions derived from (*p*-methoxyphenyl)- and (*m*-chlorophenyl)malononitriles were also essentially identical (±5 mV). The BDEs estimated for these two compounds were 76 and 80 kcal, respectively. The BDE

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(18) Unpublished results obtained by A. V. Satish working in collaboration with Prof. Joseph T. Hupp and his students.

**Table III. Effects of Substituents on the Acidities of Compounds $PhCH_2SO_2G$, the Oxidation Potentials of Their Conjugate Bases, and Acidities of the Corresponding Radical Cations in DMSO**

| compound | $pK_{HA}$[a] | $E_{ox}(A^-)$[e] | $E_{ox}(HA)$[e] | $pK_{HA^{+\cdot}}$[f] | BDE[g] |
|---|---|---|---|---|---|
| $PhCH_2SO_2Me$ | 25.4[b] | −0.004 (60) | 2.99 (130) | −25 | 91 |
| $PhCH_2SO_2$-*t*-Bu | 24.9[c] | −0.016 (60) | 2.935 (150) | −25 | 90 |
| $PhCH_2SO_2NMePh$ | 24.1[d] | 0.031 (50) | 2.13 (100) | −11 | 90 |
| $PhCH_2SO_2CH_2Ph$ | 23.9 | 0.075 (50) | 2.95 (170) | −24 | 90 |
| $PhCH_2SO_2Ph$ | 23.4 | 0.098 (50) | 2.95 (100) | −25 | 90 |
| $PhCH_2SO_2OPh$ | 19.95 | 0.263 (60) | 3.40 (200) | −33 | 89 |
| $PhCH_2SO_2CF_3$ | 14.6 | 0.564 (45) | 3.10 (150) | −28 | 89 |

[a] Reference 7, except as noted. [b] Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* 1974, *76*, 1214–1216. [c] Bordwell, F. G.; Drucker, G. E.; McCollum, G. J. *J. Org. Chem.* 1982, *47*, 2504–2510. [d] Present study; measured against two indicators. [e] Irreversible potentials (wave widths in parentheses) measured under the conditions previously described (ref 9) and referenced to SHE. [f] Estimated by the equation $pK_{HA^{+\cdot}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]\ 23.06/1.37$ (Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* 1986, *108*, 2473–2474). [g] Calculated by eq 1.

for the latter is about 10 kcal lower than the value for malononitrile, which is consistent with the BDEs estimated for phenylacetonitrile (82 kcal)[13] and phenylacetone (83 kcal),[12] which are each 11 kcal lower than their parent acids.

The concept of a dual nature for the effect of acceptors on radical stabilities can be applied also to the effects of two acceptors in molecules of the type $CH_2(G)_2$ and $CH_2(G')G$. The most notable feature of these data (Table II) is the remarkably small effects observed on the BDE of introducing the second electron acceptor compared to that of the first acceptor.

Both the stabilizing and destabilizing effects of the second acceptor tend to be leveled by the prior effects of this kind existing in the monofunctional molecules. The groups with good odd electron delocalizing abilities (CN, $CH_3CO$, PhCO) tend to give rise to further small bond weakening effects, whereas groups with strong field/inductive (*F*) effects and little or no delocalizing ability ($SO_2Ph$, $SO_2CF_3$, $Me_3N^+$) tend to give rise to further small bond-strengthening effects. Note, for example, the 2–3 kcal decrease in BDE caused by replacing one $SO_2Ph$ group in $CH_2(SO_2Ph)_2$ by CN or COPh and the corresponding 3–6 kcal increase in BDE caused by replacing one of the COPh groups in $CH_2(COPh)_2$ or one of the CN groups in $CH_2(CN)_2$ by $SO_2Ph$ or $Me_3N^+$. (The $pK_{HA}$ of $CH_3NMe_3^+$ is too high to measure in DMSO; we assume that the BDE of the H–C bond is at least 105 kcal.) On the other hand, interchanging CN, $COCH_3$, COPh, or $CO_2Et$ groups in $GCH_2G'$ compounds has but little effect on the BDEs. These balancing and leveling effects lead to a relationship where the effects of two acceptors, $A_1$ and $A_2$, on the BDE usually lead within ±3 kcal to half the sum of their individual BDEs (column 5 in Table II).

**Leveling Effects of Sulfonyl Groups.** The postulate of a leveling effect of a $SO_2Ph$ group on BDEs was made earlier when it was observed that for 17 meta- and para-substituted benzyl phenyl sulfones, $GC_6H_4CH_2SO_2Ph$, the BDEs were estimated to be within ±1 kcal of that of the parent, G = H. Although the $pK_{HA}$ values varied over a range of 11.5 kcal, only the *p*-$NMe_2$ group evoked a significant change in BDE (lower by 5 kcal).[13] A similar leveling effect has now been observed for sulfonyl-containing compounds of the type $PhCH_2SO_2G$ when G is changed along the series Me, *t*-Bu, Ph, $CH_2Ph$, NMePh, OPh, and $CF_3$ (Table III).

The acidities in Table III cover a range of 10.8 $pK_{HA}$ units (14.8 kcal) as a consequence of increases in the *F* effects of G as we go down the table. Despite a sizable change in *F*, the BDEs remain constant, within experimental error (90 ± 1 kcal). A linear correlation is observed between $E_{ox}(A^-)$ and $pK_{HA}$ when both are expressed in kcal ($R^2 = 0.994$; slope = 0.93; Figure 1). Delocalization of the negative charge into the phenyl ring is the dominant factor, with the *F* effect falling off rapidly with distance. The effects of G on radical stability are evidently small, since there is a general tendency for $E_{ox}(A^-)$ values to increase linearly with basicity when substituent effects on radical stabilities are small.[9,14]

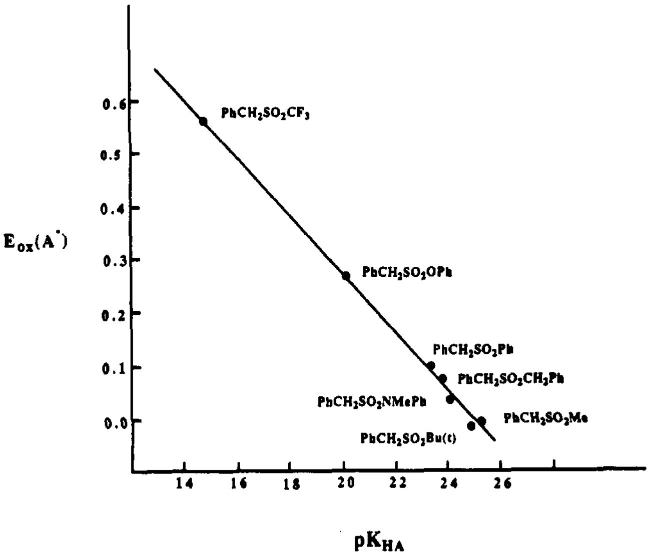

**Figure 1.** Plot of $E_{ox}(A^-)$ versus $pK_{HA}$ for sulfonyl compounds of the type $PhCH_2SO_2G$.

Note that, in the absence of a delocalization effect, an *F* effect does cause an appreciable increase in BDE for the H–C bond in $H{-}CH(SO_2CF_3)_2$, relative to that in $H{-}CH_2SO_2CF_3$.

**Contiguous Donor–Acceptor Effects.** In earlier papers we have examined the effects of combining Ph and $R_2N$ donor groups with the COPh group in carbon-centered radicals. In $R_2N\dot{C}HCOPh$ type radicals the effect of the $R_2N$ and COPh groups are more than additive, i.e., synergistic, but become less than additive in $R_2N\dot{C}(Ph)$-COPh radicals, or when the donor and acceptor are contained in a ring.[6] For the Ph donor and COPh acceptor in $PhCH_2COPh$ the acidic H–C bond BDE is decreased by 22 kcal, relative to the BDE of the H–C bond in methane.[12] The total effect is therefore greater than either of the individual effects (17 kcal for Ph and 12 kcal for COPh, both relative to methane), but is less than additive by 7 kcal. In $PhCH_2SO_2Ph$, the BDE is decreased by 15 kcal, relative to that of methane, whereas the individual effects are 17 kcal for Ph and 6 for $SO_2Ph$. Here we have an example where the combined effects are *less than that of one of the individual effects* due to the radical destabilizing effect and steric demands of the $SO_2Ph$ group.

Radical cation acidities for $PhCH_2SO_2G$ compounds are also estimated in Table III. The absence of a good donor group makes the estimated radical cation acidities all strongly negative because of the high values for $E_{ox}(HA)$. The presence of a nitrogen atom in $PhCH_2SO_2NMePh$ leads, however, to a less positive $E_{ox}(HA)$ and a less negative $pK_{HA^{+\cdot}}$ value results.

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