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Homolytic Bond Dissociation Energies in Solution from Equilibrium Acidity and Electrochemical Data

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Abstract: A simple method of estimating homolytic bond dissociation energies (BDEs) in Me_2SO solution for H–A type substrates has been devised by combination of their equilibrium acidities, pK_{HA}, and the oxidation potentials of their conjugate bases, $E_{ox}(A^-)$, by using an equation derived from a thermodynamic cycle. For 9-methylanthracene, diphenylmethane, triphenylmethane, cyclopentadiene, indene, fluorene, acetone, thiophenol, phenol, and aniline reasonable agreement with gas-phase BDEs was obtained. The method has been extended to the benzylic C–H bonds in phenylacetonitrile, ethyl phenylacetate, and benzyl phenyl sulfone for which gas-phase BDEs do not appear to be available. The effects of CN, CO_2Et, and SO_2Ph groups on the C–H BDEs, relative to that in toluene in these three compounds, were found to correspond closely to the effects of CN, CO_2Me, and SO_2Ph groups on the 9-C–H BDEs in 9-substituted fluorenes, relative to that in fluorene.

Homolytic bond dissociation energies (BDEs) provide fundamental information about bond strengths that has proved useful in studies of reaction mechanisms and in assessing stabilities of radicals.[1] A variety of methods have been used for the determination of BDEs in the gas phase, including rates of halogenation, bond scission reactions, and thermodynamic cycles.[2] Recently, eq 5, derived from the thermodynamic cycle shown in eq 1–4, was

$$\text{H–A} \rightleftarrows \text{H}^+ + \text{A}^- \qquad pK_{HA} \tag{1}$$

$$\text{A}^- \rightleftarrows \text{e}^- + \text{A}^\bullet \qquad E_{ox}(\text{A}^-) \tag{2}$$

$$\text{H}^+ + \text{e}^- \rightleftarrows \text{H}^\bullet \qquad E_{rd}(\text{H}^+) \tag{3}$$

$$\text{H–A} \rightleftarrows \text{H}^\bullet + \text{A}^\bullet \qquad \text{BDE} \tag{4}$$

$$\Delta\text{BDE} = 1.37\Delta pK_{HA} + 23.06\Delta E_{ox}(\text{A}^-) \tag{5}$$

used to estimate BDEs in Me_2SO solution for the 9-C–H bond in 9-substituted fluorenes, relative to that in fluorene (the acidity oxidation potential or ΔAOP method).[3]

This method is useful for estimating relative BDEs (or relative radical-stabilizing abilities) within a family, such as 9-substituted or 3-substituted fluorenes,[3] but it is desirable also to be able to estimate absolute BDEs, which would allow comparisons between H–A bonds in different families. This has now been accomplished.

Results

Equation 6 is derived from the thermodynamic cycle shown in Figure 1, which is a modified form of one used by Nicholas and Arnold to estimate radical cation acidities from gas-phase BDEs.[4] By substituting eq 7, which we have used to estimate $pK_{HA^{+\bullet}}$ values

$$\text{BDE} = 1.37pK_{HA^{+\bullet}} + 23.06E_{ox}(\text{HA}) + \Delta G^\circ_{sol}(\text{H}^\bullet) + \Delta G^\circ_f(\text{H}^\bullet)_g - \Delta G^\circ_{tr}(\text{H+}) \tag{6}$$

$$pK_{HA^{+\bullet}} = pK_{HA} + [E_{ox}(\text{A}^-) - E_{ox}(\text{HA})]23.06/1.37 \tag{7}$$

$$\text{BDE} = 1.37pK_{HA} + 23.06E_{ox}(\text{A}^-) + \Delta G^\circ_f(\text{H}^\bullet)_g + \Delta G^\circ_{sol}(\text{H}^\bullet) - \Delta G^\circ_{tr}(\text{H}^+) \tag{8}$$

for a wide variety of radical cations,[5] into eq 6, one obtains eq 8. Equation 8 provides a means of estimating the BDE (ΔG° for eq 4) of an acid, H–A, in solution from the equilibrium acidity constant of the acid and the oxidation potential of its conjugate base (A^-).

The pK_{HA} values used in eq 8 are measured in dilute Me_2SO by an overlapping indicator method,[6] and the $E_{ox}(A^-)$ values are obtained from cyclic voltammetric (CV) measurements in dilute Me_2SO,[5] relative to the standard hydrogen electrode (SHE). The other terms are defined as follows: $\Delta G^\circ_f(H^\bullet)_g$ is the free energy of formation of the hydrogen atom, $\Delta G^\circ_{sol}(H^\bullet)$ is the free energy of solvation of the hydrogen atom, and $\Delta G^\circ_{tr}(H^+)$ is the free energy of transfer of the proton from water to the solvent of choice. The value for $\Delta G^\circ_f(H^\bullet)_g$ is taken as 48.6 kcal/mol[4] and that for $\Delta G^\circ_{sol}(H^\bullet)$ is estimated to be −5.7 kcal/mol by assuming that the free energy of solvation of the hydrogen atom is the same in Me_2SO as that for the hydrogen molecule.[7] Values of −4.5[8a] and −5.0[8b] kcal/mol have been reported for $\Delta G^\circ_{tr}(H^+)$, the proton transfer from water to Me_2SO, by using the tetraphenylborate assumption.[8] The average is −4.8 ± 0.4 kcal/mol, which we have used in the calculation of the BDEs. The uncertainty in the values of the other terms in eq 8 is probably of the same order of magnitude. The pK_{HA} values are believed to be accurate to 0.5 kcal/mol or less. The CV waves observed in the $E_{ox}(A^-)$ measurements are usually narrow ($Ep - Ep/2$ = 45–55 mV at 100 mV/s sweep rate) and, although irreversible, are reproducible to ±25 mV (0.6 kcal/mol). The values for $\Delta G^\circ_f(H^\bullet)$ and $\Delta G^\circ_{sol}(H^\bullet)$ are also expected to be accurate to ±1 kcal/mol or less. We believe, therefore, that our estimates of solution BDEs are reliable to ±3 kcal/mol or less. For BDEs within a family, where changes in BDEs are caused by remote substituents, greater accuracy can be expected for relative values.

Discussion

Application of the Method. One major advantage of the method is its simplicity. For estimation of the BDE of an acid, H–A, only the equilibrium acidity, pK_{HA}, and the oxidation potential of its conjugate base, $E_{ox}(A^-)$ vs the standard hydrogen electrode [obtained by cyclic voltammetry, CV)] are required (eq 9).

$$\text{BDE} = 1.37pK_{HA} + 23.06E_{ox}(\text{A}^-) + C \tag{9}$$

A second advantage is the general applicability of the method to acidic H–A bonds in large organic molecules for which BDE measurements in the gas phase are difficult. The method is

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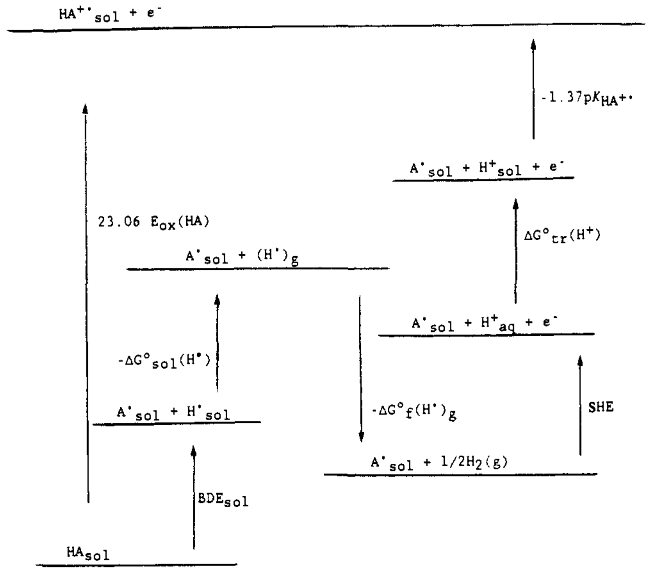


Figure 1. Schematic thermodynamic cycle showing the relationship between solution homolytic bond dissociation energies (BDEs) of an acid, HA, and the acidity of the corresponding radical cation, $HA^{\cdot+}$. The oxidation potential of hydrogen at the standard hydrogen electrode (SHE) is zero, by definition.

limited, of course, primarily to H–A bonds for which pK_{HA}'s are measurable in Me_2SO solution, i.e., compounds with acidities in the range of pK_{HA} 0–32.[6] Since acidities for over 1000 compounds have been measured in our laboratory and CV measurements on their conjugate bases are readily carried out, a large number of BDEs for H–A bonds in organic molecules with wide variations in structure are made easily accessible.

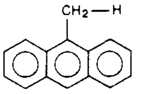
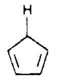
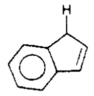
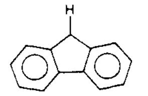
It appears reasonable to expect these solution BDEs to be comparable to gas-phase BDEs since the effect of solvent on the hydrogen atom formed in the HA $\rightleftarrows$ $H^\cdot + A^\cdot$ equilibrium has been taken into account in the $\Delta G°_{sol}(H^\cdot)$ term, and the $\Delta G°_{sol}(HA)$ and $\Delta G°_{sol}(A^\cdot)$ terms for large organic molecules should cancel. For comparison with gas-phase BDEs ($\Delta H°$ values) it is necessary to convert the $\Delta G°$ BDE values calculated by eq 8 to $\Delta H°$ values by adding $T\Delta S°$. Values of $\Delta S°$ for $PhCH_3$ (26.0 eu), PhOH (25.8 eu), and $PhNH_2$ (27.4 eu) have been calculated.[4] For other C–H and N–H acids, the assumption was made that $S°_{(RH)g} = S°_{(R\cdot)g}$, i.e.,

$$\Delta S° \simeq S°_{(H\cdot)g} \simeq 27.4 \text{ eu}$$

The size of the constant, C, varies slightly with the $\Delta S°$ term. For C–H and N–H acids, C is assigned a value of 55.86, and for O–H and S–H acids a value of C = 55.39 has been used (see the Results section).

The solution BDEs for 10 compounds are compared in Table I with gas-phase BDEs taken from the literature.

Table I. Comparison of Estimates of Homolytic Bond Dissociation Energies (BDEs) from Eq 3 with Gas-Phase (lit) BDEs at 25 °C

compound	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[c]	BDE (lit.)[d]	ref
	31.1	−0.739	81.4	81.8 ± 1.5[e]	9
Ph_2CH–H	32.25	−0.790	81.8	80.4	10
				81.4	11
				84 ± 2[e]	12
Ph_3C–H	30.6	−0.736	80.8	75	13
	18.0	+0.028	81.2	81.2 ± 1.2[f]	14
				81.7 ± 3	15
				82.9 ± 2	19
	20.1	−0.202	78.8	84 ± 3[e]	12
	22.6	−0.319	79.5	80 ± 5	16
PhS–H	10.3	+0.390	78.5	75	17
				83.3 ± 2[e]	18
PhO-H	18.0	+0.425	89.9	86.5 ± 2[e]	18
				86.5 ± 2	19
				88 ± 5	20
PhNH–H	30.6	−0.242	92.2	88 ± 2[e]	18b
				92.9 ± 3	21
CH_3COCH_3	26.5	+0.076	93.9	98.3 ± 1.8	22
				92.0 ± 1.5	23

[a] The pK_{HA} values in Me_2SO have been reported in earlier papers from this laboratory,[6] except for that of 9-methylanthracene (determined by J. E. Bares, Ph.D. Dissertation, Northwestern University, 1976). [b] The $E_{ox}(A^-)$ values were determined by the method previously described vs Ag/AgI[5a] with a ferrocene–ferrocenium ion standard and are irreversible. For use in eq 9 these values have been corrected to the standard hydrogen electrode by subtracting 0.125 V. The experiments were carried out on carefully purified commercial samples. [c] These BDEs ($\Delta H°$) were calculated from eq 9. The uncertainty is estimated to be about ±3 kcal/mol (see Results section). [d] $\Delta H°$ values in the gas phase; for the methods used, see the reference cited. [e] Chosen by McMillen and Golden[2d] as the best value.

Structural Effects on BDEs—Phenyl Effects. The solution BDE for the C–H bond in the methyl group of 9-methylanthracene, 9-MeAn, the first entry in Table I, agrees well with the single gas-phase BDE that has been reported. The BDE is 6 kcal/mol lower than that chosen by McMillen and Golden as the best value for the C–H bond in toluene, 88 ± 1,[2d] which is reasonable in light of the additional delocalization afforded by the two benzo groups in the 9-$AnCH_2^\cdot$ radical. Toluene is too weak an acid to be measured in Me_2SO, but combination of an extrapolated pK_{HA} value of 43 with a literature $E_{ox}(PhCH_2^-)$ of −1.185 (vs SHE) obtained from $E_{ox}(PhCH_2Li)$ in THF/HMPA,[24] or from E_{rd} $(PhCH_2^\cdot)$,[25] gives a BDE for toluene of 87–88 with use of eq 9. The presence of the phenyl group in toluene therefore causes a 17 kcal/mol weakening of the α-C–H bond, relative to that in methane (BDE = 105 kcal/mol[2d]). Substitution of a second Ph group causes a further decrease in solution BDE of 6–7 kcal/mol (Table I). Our solution BDE for Ph_2CH–H agrees well with the gas-phase value determined in 1984 by Rossi, McMillen, and Golden[11] and is in line with the 4.7 kcal/mol decrease in the solution BDE for the substitution of a second Ph group into $PhCH_2CN$ to give Ph_2CHCN,[5c] where steric inhibition of resonance in the corresponding radical should be larger than that for the $Ph_2CH^\cdot$ radical. It is also in line with the 5.9 kcal/mol bond-weakening effect for the 9-C–H bond in fluorene caused by

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Table II. Bond Dissociation Energies for α-Substituted Toluenes

compound	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[c]
$C_6H_5CH_2CN$	21.9	−0.159	82.2
$C_6H_5CH_2CO_2Et$	22.6	−0.129	83.9
$C_6H_5CH_2SO_2Ph$	23.4	+0.098	90.2

[a] The pK_{HA} values in Me_2SO have been reported in earlier papers from this laboratory. [b] Determined by CV, as in Table I, and referred to the standard hydrogen electrode by adding −0.125 V. [c] The uncertainty in these values is estimated to be ±3 kcal/mol.

the introduction of a 9-Ph substitutent.[3]

Substitution of a Ph group for an α-hydrogen atom in Ph_2CH_2 causes a further 1 kcal/mol decrease in the solution BDE, indicating only a small increase in stabilization of the incipient $Ph_3C^•$ radical, relative to $Ph_2CH^•$. A similar small increase in stabilization (2.2 kcal/mol) is indicated for the Ph_3C^- carbanion, relative to Ph_2CH^-, as judged by relative pK_{HA} values in Me_2SO solution. On the basis of these results the gas-phase BDE of 75 kcal/mol reported for Ph_3CH[13] appears to be too low. (We note that the BDE reported for toluene and most other compounds in this reference are 4–10 kcal/mol lower than currently accepted values.)

Cyclopentadiene, Indene, and Fluorene. The solution BDEs estimated for the sp^3 C–H bonds in these three compounds are nearly the same, 80 ± 1 kcal/mol. The gas-phase values reported are a little higher, 82.5 ± 1.5 kcal/mol. The resonance stabilization energy of the cyclopentadienyl radical of about 19 kcal/mol[2d] may be the dominating factor here, since the cyclopentadienyl moiety is present in all three substrates. One might have expected the delocalization of the odd electron in the incipient radical in the indenyl and fluorenyl systems to cause progressively lower BDEs, but no effect of this kind is evident in either the solution or gas-phase BDEs. In this respect the effects are similar to those observed on fusion of a benzene ring onto the 1,2- or 2,3-position of the fluorene ring, which produce little or no change in solution BDEs.[5c]

Thiophenol, Phenol, and Aniline. The solution BDEs increase in the order PhS–H < PhO–H < PhNH–H, as anticipated from the gas-phase results. The solution BDE for the S–H bond in thiophenol of 78 kcal/mol is about midway between the gas-phase literature values of 75 and 83. The solution BDE that we estimate for PhO–H is about 12 kcal/mol higher, which is within the experimental error of one gas-phase value but 3.5 kcal/mol above the McMillen and Golden best value.

The solution BDEs for PhOH and PhSH are in line with solution BDEs for β-naphthol and β-thionaphthol, which are 1.3 and 1.2 kcal/mol lower than those of PhOH and PhSH, respectively. The lower BDEs are expected in view of the increased delocalization of the odd election in these radicals.[5c]

Our estimate for the PhNH–H bond of 92.2 kcal/mol is close to the higher value listed in Table I but is 4 kcal/mol above the value given by McMillen and Golden.[2d] Our higher value is more in line with the solution BDE of 87.4 obtained for Ph_2N–H[5c] than is the latter value. The 4.8 kcal/mol lower value for the N–H bond in Ph_2NH compared to that for $PhNH_2$ can be reasonably ascribed to the increased delocalization of the odd electron caused by the presence of the second Ph group.

The solution BDE for acetone of 93.9 kcal/mol is 4.4 kcal/mol below the value obtained by King, Golden, and Benson[22] but is within experimental error of the recent corrected gas-phase BDE reported by Holmes, Lossing, and Terlouw.[23]

Effects of CN, CO_2Et, and $PhSO_2$ Substituents. An earlier study indicated the 9-CN and 9-CO_2Me groups weaken the 9-C–H bond in fluorene, whereas the 9-$PhSO_2$ group is bond strengthening.[3] It was of interest to check this observation since the CO_2Me and $PhSO_2$ functions are subject to steric constraints in the 9-position of fluorene. The results of BDE measurements carried out for this purpose are shown in Table II.

Examination of the data in Table II shows that introduction of a cyano or ethoxycarbonyl group into the α-position of toluene decreases the BDE of the α-C–H bond by 5.8 and 4.1 kcal/mol, respectively. On the other hand, a phenylsulfonyl group *increases* the BDE by 2.2 kcal/mol. These effects correspond well with those on the BDEs of the 9-C–H bonds in fluorene when these groups are introduced into the 9-position where the ΔBDEs are −5.3, −3.5, and +2.3 kcal/mol, respectively (calculated from the data in ref 3). It is noteworthy that, whereas the α-CN and α-$PhSO_2$ groups have closely similar effects in stabilizing carbanions, they have opposite effects on radicals, CN stabilizing, and $PhSO_2$ destabilizing.

Summary and Conclusions

Estimates of homolytic BDEs in Me_2SO solution for C–H, S–H, O–H, and N–H in several weak acids, HA, obtained from pK_{HA} and $E_{ox}(A^-)$ data, have been shown to be self consistent and to agree reasonably well with corresponding gas-phase BDEs. Measurements of solution BDEs of α-C–H bonds in $PhCH_2G$ substrates have confirmed a bond-weakening effect for G = CN and a bond-strengthening effect for G = SO_2Ph. The simplicity and broad applicability of this quasi-thermodynamic method opens the way for estimates of BDEs to be made for a host of additional H–A bonds. Subsequent papers will describe the application of the method to other substrates including fluorenes, cyclopentadienes, and arylacetonitriles.

Acknowledgment. We are grateful to the National Science Foundation for support of this work. This method evolved from the exploratory research of Mark J. Bausch, to whom we express our appreciation.

Registry No. Ph_2CH_2, 101-81-5; Ph_3CH, 519-73-3; PhSH, 108-98-5; PhOH, 108-95-2; $PhNH_2$, 62-53-3; Me_2CO, 67-64-1; $PhCH_2CN$, 140-29-4; $PhCH_2CO_2Et$, 101-97-3; $PhCH_2SO_2Ph$, 3112-88-7; 9-methylanthracene, 779-02-2; 1,3-cyclopentadiene, 542-92-7; indene, 95-13-6; fluorene, 86-73-7.