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Assessment of the Importance of Changes in Ground-State Energies on the Bond Dissociation Enthalpies of the O–H Bonds in Phenols and the S–H Bonds in Thiophenols

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Abstract: The homolytic bond dissociation enthalpies (BDEs) for the S–H bonds in 13 thiophenols, 2-naphthiol, and phenylmethanethiol have been estimated by combination of the values of their equilibrium acidities (pK_{HA}s in DMSO) with the oxidation potentials of their conjugate anions, $E_{ox}(A^-)$. An estimate of the average BDE for the S–H bond in seven thiophenols bearing meta- or para-electron acceptor substituents gave 79.8 ± 1.6 kcal/mol; *p*-MeO and *p*-NH_2 points deviate from this average by 2.9 and 10 kcal/mol, respectively. A Hammett plot of the BDE values for the S–H bonds in *m*- and *p*-GC_6H_4SH thiophenols (excluding the *p*-NH_2 point) was linear with a slope of $\rho = 3.2$ ($r = 0.95$). Similar plots for $GC_6H_4NH_2$ anilines and GC_6H_4OH phenols gave $\rho = 5.5$ ($r = 0.92$) and $\rho = 7.3$ ($r = 0.95$), respectively. From an analysis of these and related Hammett plots, and a comparison with similar plots for the $GC_6H_4CH_2CN$ family, the following conclusions were drawn: (a) meta- and para-electron-withdrawing substituents interacting with the S–H, N–H, and O–H dipoles cause lowering of ground-state energies leading to increases in BDEs in the order S–H < N–H < O–H, and (b) para-donor substituents exert effects to decrease BDEs of the acidic H–A bonds primarily by stabilizing the corresponding radicals but also to some extent by raising the ground-state energies in the ArOH, ArSH, and $ArNH_2$ families. A plot of ρ_{ArX-Y} values for Hammett BDE correlations versus the differences in the electronegativities of the atoms forming the bonds being cleaved ($\Delta\nu$) is surprisingly linear for ArO–H, ArNH–H, ArS–H, ArO–CH_3, ArCH(CN)–H, $ArCH_2$–H, $ArCH_2$–Br, and Ar–Cl bonds. Not unexpectedly, a plot of the oxidation potentials, $E_{ox}(HA)$, for 12 ortho-, meta-, or para-substituted thiophenols versus their $pK_{HA^{\bullet+}}$ values is linear.

Introduction

During the past eight years we have developed a simple method of estimating homolytic bond dissociation enthalpies (BDE_{HA}s) of the acidic H–A bonds in weak organic acids by using eq 1and

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

have applied it successfully to estimate the BDEs of the acidic H–A bonds in several hundred weak acids. Even though the oxidation potentials of the conjugate anions are usually irreversible and the constant *C* is empirical, the BDE_{HA} values estimated by using eq 1 with $C = 73.3$ kcal/mol have been shown to be in good agreement with the best available gas-phase (enthalpy) values to ±2 kcal/mol or better when the oxidation potentials in DMSO are referenced to the ferrocenium/ferrocene couple.[1] (Henceforth kcal/mol will be abbreviated as kcal.)

Since the BDEs we are studying are all of the following type, $H\text{–}A \rightleftharpoons H^\bullet + A^\bullet$, the generally accepted assumption that changes in BDEs caused by remote structural changes in HA can be related to the relative stabilities of the $A^\bullet$ radicals being formed was adopted.[2] This assumption is similar to that used to interpret the effects of remote structural changes on the equilibrium, $HA \rightleftharpoons H^+ + A^-$, in solution in terms of the relative stabilities of the A^- anions being formed. The latter assumption is usually successful because the position of each equilibrium is largely determined by solvation effects on the anions, which are much larger than those on the undissociated acids. The solvation factor is essentially absent in the homolytic dissociation of HA, however, since solvation energies HA and $A^\bullet$ do not differ appreciably, and changes in ground-state energies of HA can assume greater relative importance. This point has been emphasized by recent evidence indicating that stereoelectronic effects are much greater for radical reactions than for anion reactions because the latter are leveled by solvent effects.[3] In other words, it is not surprising to find that sometimes the effects of substituents on the stabilities of HA and the stabilities of $A^\bullet$ *both* play an important role.[3c] We note in this regard that in the $HA^{\bullet+} \rightleftharpoons H^+ + A^\bullet$ equilibrium substituent effects on the stability of the initial radical cation ($HA^{\bullet+}$) usually play the *dominant* role,[4] as will be further illustrated later with $ArSH^{\bullet+}$ radical cations. The importance of ground-state effects on the intact molecule in rationalizing structural changes on BDEs has long been recognized,[5] but these effects are difficult to observe and evaluate. Recently, however, evidence has been presented to show that the effects of changes in ground-state energies on BDEs are important even for remote substituents within a family.[6] The four para-acceptor substituents (F, Br, CF_3, and CN) in benzyl bromides were found to weaken

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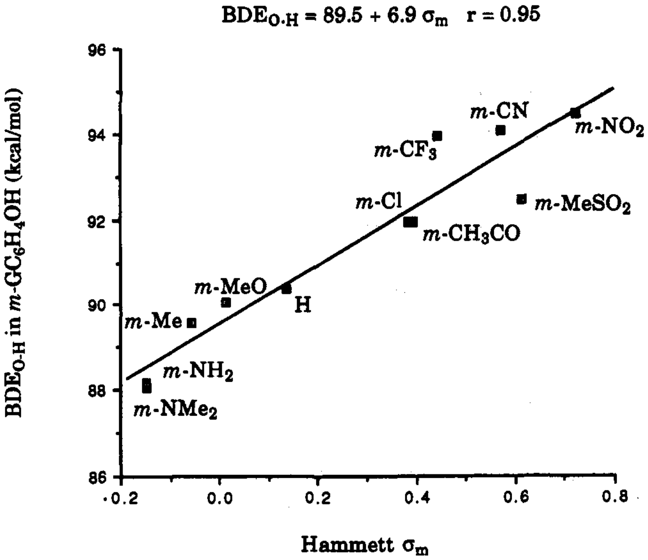


Figure 1. Plot of the BDEs of the O–H bonds in meta-substituted phenols versus Hammett σ_m values.

the C–Br bonds, relative to that of the parent, by averages of 0.52, 1.8, 2.8, and 5.0 kcal, respectively, whereas a 4-Me substituent raised the BDE by 0.25 kcal and the effect of 4-*t*-Bu was uncertain (–0.34 and 0.40 kcal in two runs).[6] The bond-weakening effects of 4-Br and 4-CN are expected in terms of the stabilities of the corresponding radicals since the Wayner-Arnold $\sigma_\alpha{}^\bullet$ scale indicates that these substituents stabilize benzyl radicals. The bond-weakening effects of 4-F and 4-CF_3 are not expected, however, since these substituents destabilize benzyl radicals according to the $\sigma_\alpha{}^\bullet$ scale.[7] The authors have interpreted the results in terms of the interaction of dipole–dipole repulsive forces between the acceptor substituents and the C–Br bond that increase the ground-state energies of the intact molecules and thereby weaken the C–Br bond with no reference to the effects of the substituents on the corresponding radicals. They support this interpretation by the observation that the slope of a plot of the BDEs of the C–Br bonds for these benzyl bromides versus Hammett σ_p values, together with the slopes for similar plots of BDEs for phenols and anisoles versus Brown σ^+ values, fit a common line when plotted against the differences in electronegativities of the atoms making up the bonds. Our interpretation of the effects on BDEs of remote substituents on the O–H bonds in a family of 39 phenols, which were made solely in terms of their effects on the stabilities of the corresponding phenoxyl radicals,[8] neglecting ground-state effects, was specifically brought into question in this paper.[6] In the present paper we will, therefore, first present an analysis of the effects of remote substituents on the BDEs of the O–H bonds of phenols, using the Hammett equation, and then apply a similar analysis to data for the BDEs of the acidic H–A bonds in carbon acids, thiophenols, and anilines.

Results and Discussion

Analysis of the BDEs of the H–O Bonds in Phenols with Use of the Hammett Equation. A Hammett plot of BDEs for the H–O bonds in nine meta-substituted phenols is linear ($r = 0.95$) with a slope of 6.9 kcal (Figure 1). The BDEs increase with the increasing electron withdrawal abilities of the substituents, as postulated in 1972 by Zavitas[9] for toluenes and confirmed by the measurements of Pryor.[10] In other words, the O–H bond is weakened by increasing the electron density within the bond and strengthened by decreasing the electron density within the bond.

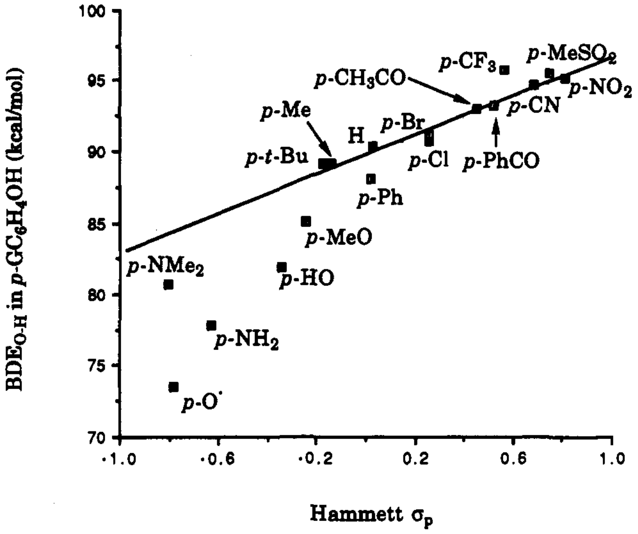
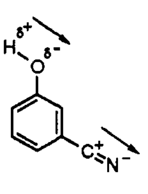


Figure 2. The Hammett meta line (Figure 1) with points for para points added.

These effects can be visualized as occurring through dipole–dipole interactions of the type shown in **1**, **2**, and **3**.[6] A meta electron-withdrawing effect is illustrated in **1**.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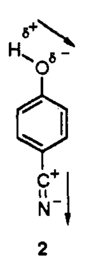
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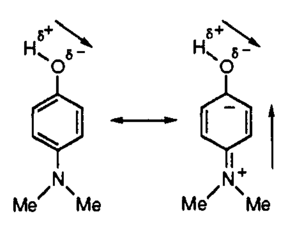
3a **3b**

A similar effect is illustrated in **2** for a para electron-withdrawing group since the points for these groups fit close to the meta line (Figure 2). The close fit for these para-acceptor points shows that it is field/inductive effects that are operative here, and that resonance effects are of minor importance. (Field/inductive effects for electron-withdrawing substituents in meta and para positions do not differ greatly.[11]) We agree with Clark and Wayner that the effects for meta- and para-electron acceptors are best looked on as lowering the ground-state energies and thereby strengthening the O–H bond.[6] For example, the ground-state effects for 3-CN and 4-CN groups in substituted phenols are estimated to be 4.1 and 4.4 kcal, respectively;[8] those for 3-CF_3, 4-CF_4, 3-$MeSO_2$, 4-$MeSO_2$, 4-MeCO, 3-NO_2, and 4-NO_2 fall in the range of 2.0–5.2 kcal, all relative to the PhOH parent.[8]

Points for electron donors deviate markedly from the meta line, however, and tend to define a line of their own with a much steeper slope (Figures 2 and 3). As illustrated for **3**, these effects can be rationalized in terms of dipole–dipole repulsive interactions that raise the ground-state energies and thereby weaken the O–H bond.[6] We believe, however, that the effects of p-O^- (12) > p-NH_2 (7) > *p*-HO (5) > *p*-MeO (3) > *p*-Ph (2) groups are best accounted for in terms of their ability to stabilize the corresponding radicals by delocalization of the odd electron. The size of these radical stabilization energies (RSEs), as estimated from the ΔBDE for these points, relative to the meta (ground state) line is given in parentheses (in kcal) after the symbols. The conclusion that the deviations of the points for the para donors from the meta phenol line represent RSEs is supported by a similar analysis of Hammett plots for the effects on the BDEs of the acidic C–H

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(7) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164.

(8) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1746.

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(10) Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.

(11) For example, the σ values for m-Me_3N^+ and p-Me_3N^+ groups are 0.88 and 0.82, respectively.[12]

(12) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

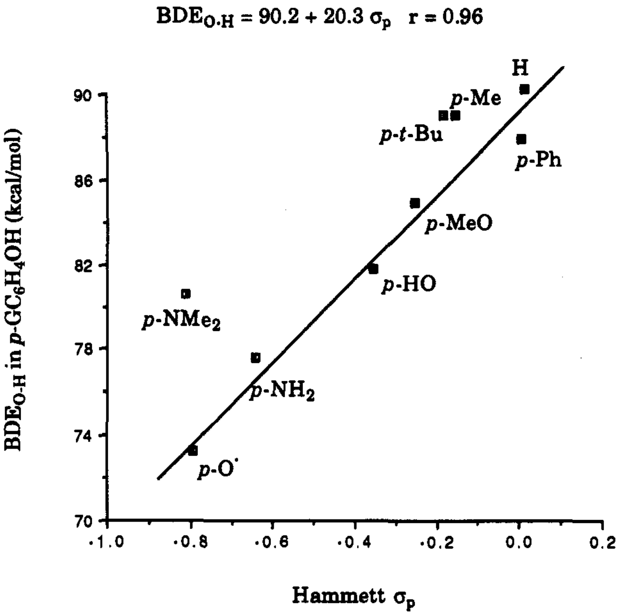


Figure 3. Plot of the BDEs of the O–H bonds in para-electron-donor-substituted phenols versus σ_p. (The point of p-NMe_2 is not included in the correlation.)

bonds in the arylacetonitrile family, $GC_6H_4CH_2CN$, where the small C–H dipole minimizes ground-state effects.

The Hammett plots for arylacetonitriles are of poorer quality than those for phenols because the BDE_{C-H} range is only 5 kcal and there are fewer points. Nevertheless, this family can provide a model where, because the acidic C–H dipole is small, remote substituents can be expected to exert their effects primarily on the corresponding radicals. Para substituents can stabilize the radicals by delocalization, and both meta and para substituents can destabilize the radicals by electron withdrawal. A Hammett plot for BDEs of the acidic C–H bonds in m-$GC_6H_4CH_2CN$ with G = H, Me, MeO, F, Cl, CF_3, CN, and $PhSO_2$ showed that the BDEs increase with increasing electron withdrawal, as for the corresponding phenol plot (Figure 2), indicating the presence of a small $^{\delta+}H\text{-}^{\delta-}C$ dipole, but the points are badly scattered (r = 0.82; ρ_m = 1.6). The p-Cl, p-PhCO, and p-CN points fit close to the meta line, however, as for phenols, but the donor points, p-NMe_2, p-MeO, p-Ph, p-PhS, and p-Me, tend to form a line of their own with a much steeper slope (Figure 4).

The ratio of the slopes of the para-donor/meta lines for phenols is 2.9 compared to 2.7 for arylacetonitriles, which supports the conclusion that decreases in BDEs caused by para donors for phenols, as well as those for arylacetonitriles, are caused *primarily* by their ability to stabilize the corresponding radicals by delocalizing the odd electron rather than their ability to increase the ground-state energies of the parent molecules.

The effects of remote substituents, with the exception of R_2N, on BDEs of the acidic C–H bonds are small. As a result, BDEs of the acidic H–A bonds are often constant to ±2 kcal, or less, in carbon acid families. For example, (a) the BDEs of the acidic C–H bonds in 12 meta-substituted fluorenes (2-G or 2,7-diG substituents) are estimated to be 79.5 ± 0.3 kcal,[13a] the BDEs for the benzylic C–H bonds in 17 $GC_6H_4CH_2SO_2Ph$ sulfones are estimated to be 90 ± 2,[4c] (c) the BDEs for the benzylic C–H bonds in 14 $GC_6H_4CH_2CN$ arylacetonitriles (omitting 4-Me_2N) are estimated to be 82 ± 1 kcal,[4a] and (d) the BDEs for the acidic C–H bonds in 10-substituted-9-methylanthracenes are 81 ± 1 kcal.[4d] Also, for the acidic C–H bond in substituted toluenes the BDEs have been estimated to be 85 ± 1 kcal.[10]

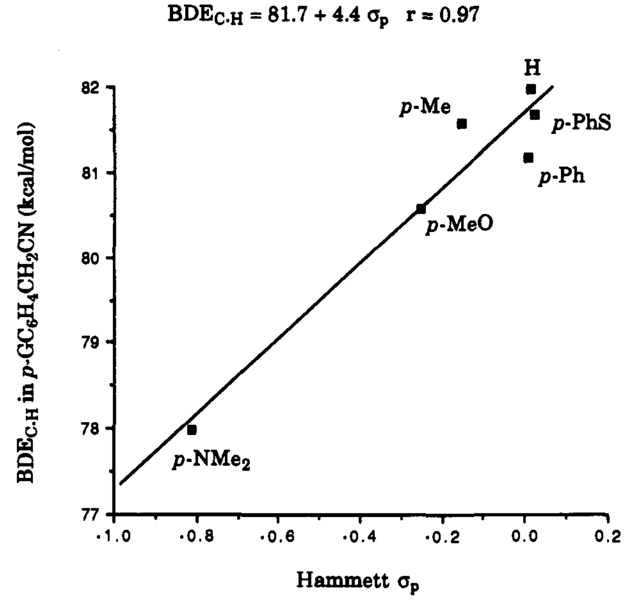
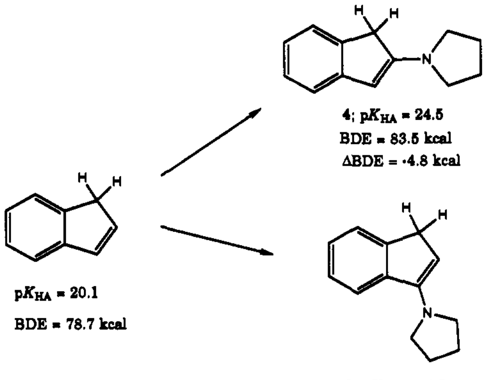


Figure 4. Plot of the BDEs of the acidic C–H bonds in para-electron-donor-substituted phenylacetonitriles versus Hammett σ_p values.

Examination of the effects of R_2N substituents in the 2- and 3-position of indene on BDEs has provided a unique way to compare substituent effects on BDEs caused by changes in ground-state energies with the substituent effects on BDEs caused by radical stabilization.[13b] The presence of a pyrrolidinyl, c-C_4H_8N, group at either the 2- or 3-position of indene causes a 6.0-kcal decrease in the acidity, relative to the parent. This acidity decrease is apparently due primarily to lowering of the ground-state energy by interaction of the C=C bond with the c-C_4H_8N substituent, which can occur from either the 2- or 3-position. This result is consistent with Hine's estimate of the size of the double bond stabilization parameter to be 8.2 kcal for an amino group.[14] Comparison shows that the 2-c-C_4H_8N group in **4** causes a 4.8-kcal increase in the BDE of the acidic C–H bond, relative to that of indene (78.7 kcal), whereas the 3-c-C_4H_8N group in **5** causes an 8.4-kcal *decrease*, relative to that of indene.



4; pK_{HA} = 24.5
BDE = 83.5 kcal
ΔBDE = -4.8 kcal

pK_{HA} = 20.1
BDE = 78.7 kcal

5; pK_{HA} = 24.5
BDE = 70.3 kcal
ΔBDE = 8.4 kcal

The 6-kcal lowering of the ground-state energy has therefore resulted in a 4.8-kcal bond-strengthening effect of the acidic C–H bond by the 2-c-C_4H_8N group, but the powerful delocalizing effect of the 3-c-C_4H_8N group completely overshadows this ground-state effect. The total bond-weakening effect (RSE) of the 3-c-C_4H_8N substituent on the acidic C–H bond in indene is estimated to be 6 + 8.4 = 14.4 kcal, which is consistent with the

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(13) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985. (b) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1992**, *114*, 10173–10176.

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Table 1. Equilibrium Acidities and Homolytic Bond Dissociation Energies of S–H Bonds in Substituted Thiophenols and Related Substrates and Equilibrium Acidities of the Corresponding Radical Cations

acids	pK_{HA}[a]	$E_{ox}(A^-)$[b]	$E_{ox}(HA)$[c]	$pK_{HA^{\cdot+}}$[d]	BDE_{HA}[e]
4-$H_2NC_6H_4SH$	12.5	−0.895	0.455	−2.6	69.8
4-$MeOC_6H_4SH$	11.2	−0.508	0.665	−8.6	76.9
4-MeC_6H_4SH	10.8	−0.425	0.835	−10.4	78.3
2-MeC_6H_4SH	10.7	−0.395	0.905	−11.2	78.8
3-MeC_6H_4SH	10.56	−0.385	0.865	−10.5	78.9
thiophenol (PhSH)	10.3	−0.360	0.945	−11.7	79.1
4-ClC_6H_4SH	9.3	−0.295	1.325	−18.0	79.2
4-BrC_6H_4SH	9.0	−0.275	1.305	−17.6	79.3
3-ClC_6H_4SH	8.6	−0.215	1.355	−17.9	80.1
2-ClC_6H_4SH	8.55	−0.215	1.355	−17.9	80.0
3-$F_3CC_6H_4SH$	8.1	−0.155	1.435	−18.7	80.8
2-$MeO_2CC_6H_4SH$	7.75	−0.224			78.7
4-$NO_2C_6H_4SH$	5.5	0.025	1.535	−20.0	81.4
2-naphthiol	9.5	−0.365	0.845	−10.9	77.9
$C_6H_5CH_2SH$	15.4	−0.324	0.449	2.4	86.9

[a] Equilbrium acidities measured in DMSO solution by the overlapping indicator method by two indicators.[17] [b] In volts; irreversible oxidation potentials of the conjugate anions in DMSO by cyclic voltammetry and referenced to the ferrocenium/ferrocene couple. [c] In volts; irreversible oxidation potentials of neutral weak acids measured in CH_3CN by cyclic voltammetry and referenced to the ferrocenium/ferrocene couple.[1] [d] Equilibrium acidities of radical cations estimated by using eq 4. [e] In kcal/mol; homolytic bond dissociation enthalpies of the acidic H–S bonds estimated by using eq 1 with $C = 73.3$.

11-kcal bond-weakening effect on the acidic C–H bonds in 9-*c*-C_4H_8N-fluorene,[15] the 16-kcal bond-weakening effect of Me_2N on the BDE of $Me_2NCH(CN)_2$,[16] and the 21-kcal bond-weakening effect of Me_2N on the BDE of Me_2NCH_2COPh.[16]

The smaller dipole moments of the S–H bonds in thiophenols than those of the O–H bonds in phenols lead to smaller differences in BDEs. For the 3-Me, H, 4-Cl, 4-Br, 3-Cl, 3-CF_3, and 4-NO_2 substituents in thiophenols in Table 1, the average BDE is 79.8 ± 1.3 kcal compared to 91.5 ± 3.2 kcal for the corresponding phenols. The BDEs for 4-Me, 4-MeO, and 4-NH_2 thiophenols deviate from this average by 1.5, 2.9, and 10 kcal, respectively, compared to 2.8, 6.9, and 14 kcal deviations, respectively, for the corresponding phenols. Since we have concluded earlier that the BDEs for 4-MeO and 4-NH_2 phenols are dictated by the stabilizing effects of the substituents on the corresponding radicals, rather than to changes in ground-state energies, it follows that this must be true also for the BDE of the S–H bond in *p*-aminothiophenol.

Acidities of the S–H Bonds in Thiophenols and in the Radical Cations Derived from Thiophenols. Acidities of thiophenols in DMSO have been reported earlier.[17] A Hammett plot of the equilibrium acidities for 5 meta-substituted thiophenols gave $\rho_m = 4.8$ ($r = 0.99$). A similar plot for 11 meta-substituted phenols gave $\rho_m = 5.6$ ($r = 0.98$).[8] Thiophenol is a stronger acid in DMSO than phenol by 7.7 pK_{HA} units (10.5 kcal); it does not exhibit homo-hydrogen bonding in DMSO, whereas log K_{hb} = 3.4 for $PhO^-\cdots H{-}OPh$.[8]

Direct measurements of radical cation acidities are difficult because short-lived radicals are present on each side of the acid–base equilibrium, eq 2.

$$H{-}A^{\cdot+} \rightleftharpoons H^+ + A^\cdot \qquad (2)$$

But estimates of the radical cation acidities can be made by using eq 3.[18]

$$pK_{HA^{\cdot+}} = pK_{HA} + 16.8[E_{ox}(A^-) - E_{ox}(HA)] \qquad (3)$$

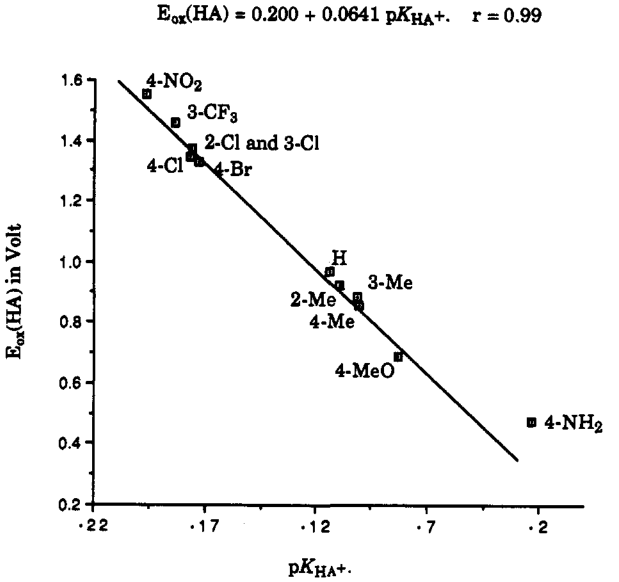
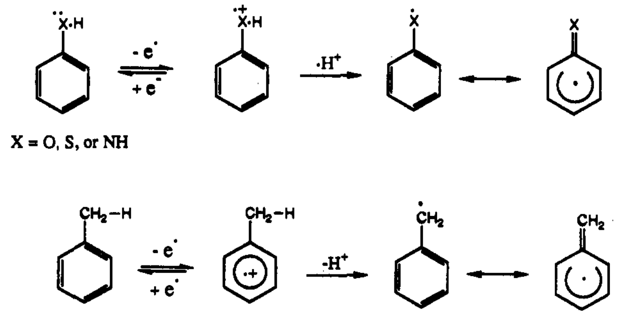


Figure 5. Plot of the oxidation potentials [E_{ox}(HA)] for substituted thiophenols versus their $pK_{HA^{\cdot+}}$ values in DMSO.

Scheme 1



Estimates for the acidities $pK_{HA^{\cdot+}}$ of the S–H bonds of the radical cations derived from 13 thiophenols are given in Table 1, along with the pK_{HA}s and BDEs of the thiophenols.

The equilibrium acidity of $PhSH^{\cdot+}$ is −11.7 in DMSO, indicating that removal of one electron from thiophenol increases the acidity by about 22 pK_{HA} units. Similar increases in acidities were also observed for removal of an electron from phenol or aniline to form the corresponding radical cations, i.e., about 24 and 26 pK_{HA} units, respectively.[8,19] The effect of removing an electron from toluene is about 63 pK_{HA} units, however.[19a] The much larger acidifying effect for toluene is probably caused by removal of the electron from the aromatic π system rather than from a lone pair (Scheme 1).

In earlier studies[4] we have shown that substituent effects on equilibrium acidities of radical cations are exerted primarily by stabilizing or destabilizing the ground-state energies of the undissociated radical cations, as judged by E_{ox}(HA) values. Electron donors stabilize the radical cations and decrease the acidities. The position of equilibrium in eq 2 is affected also by the substituent effects on the stabilities of the product radicals, but these effects are usually small. As a consequence, E_{ox}(HA) values are usually correlated linearly with the corresponding $pK_{HA^{\cdot+}}$ values.[4,8] This is true also for the radical cations derived from ortho-, meta-, and para-substituted thiophenols (Figure 5).

Examination of Figure 5 shows that the point for the radical cation derived from 4-aminothiophenol deviates appreciably from

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the line. The deviation may be caused by a difference in the source of the electron being removed, that from 4-$NH_2C_6H_4SH$ coming from the lone pair on nitrogen rather than from the lone pair on sulfur. This conclusion is supported by the near identity of the oxidation potential of 4-$NH_2C_6H_4SH$ with that of aniline in DMSO solution.[19]

Homolytic Bond Dissociation Enthalpies (BDEs) of the S–H Bonds in Thiophenols and Related Thiols. The BDEs of the S–H bonds in thiophenols and related thiols estimated by using eq 1 are summarized in Table 1. The BDE of 79.1 kcal estimated for the S–H bond in thiophenol by use of eq 1 is in good agreement with the best gas-phase value of 80.1 kcal selected by McMillen and Golden,[2d] and with the value of 78.5 kcal estimated from eq 1 using the data on thiophenol determined in sulfolane.[20] Our value is also essentially identical with that of 79 kcal obtained by photoacoustic calorimetry.[21] This value is 12 kcal lower than the value of 91 kcal for H_2S, which is consistent with, but smaller than, the effects of phenyl substitution into methane (ΔBDE = 17 kcal) or ammonia (ΔBDE = 15 kcal).[2d] The 1.2 kcal lower BDE for 2-naphthiol than thiophenol (Table 1) is consistent with the 1.8 kcal lower BDE of 2-naphthol than phenol.[8] The BDE of 87 kcal for phenylmethanethiol (Table 1) is identical with that reported for the S–H bond in CH_3SH[22] or 1-octanethiol.[21]

Comparisons of Remote Substituent Effects on BDEs of the Acidic H–A Bonds in Thiophenols, Anilines, and Phenols. A Hammett plot for the BDEs of the S–H bonds in meta- and para-substituted thiophenols (Table 1, but excluding the p-NH_2 point) has a slope of $\rho = 3.2$ ($r = 0.95$). Similar Hammett plots of BDEs for the N–H bonds in meta- and para-substituted anilines[19c] and the O–H bonds in meta- and para-substituted phenols[8] gave $\rho = 5.5$ ($r = 0.92$) and $\rho = 7.3$ ($r = 0.95$), respectively. A plot of these slope ρ values together with the ρ values for similar plots for the C–O bonds in anisoles,[23] the acidic C–H bonds in toluenes[9,10] and arylacetonitriles,[4c] the C–Br bonds in benzyl bromides,[6] and the C–Cl bonds in chlorobenzenes[24] versus modified Pauling electronegativity differences, $\Delta\nu$,[25] between the atoms in the bond being cleaved gave a remarkably good linear plot (Figure 6).

The linearity of the plot in Figure 6 provides support for the importance of dipole–dipole interactions in accounting for remote substituent effects on BDEs.[6]

We reported earlier that $E_{ox}(A^-)$ values in DMSO for 14 4-substituted phenoxide ions plotted linearly with Brown's σ^+ values with a slope of $\rho^+ = 10$ ($r = 0.999$).[8] Similarly, the reduction potentials for 14 4-$GC_6H_4O^\bullet$ radicals in aqueous solution plotted linearly against σ^+ values gave $\rho^+ = 7.0$ ($r = 0.895$).[26] Also, the BDEs for 5 4-GC_6H_4O-H phenols versus σ^+ gave a linear plot, $\rho^+ = 7.3$ ($r = 0.98$).[27] Finally, a linear plot of BDEs of the O–H bonds for 14 4-GC_6H_4OH phenols versus σ^+ gave $\rho^+ = 7.1$ (Figure 7).

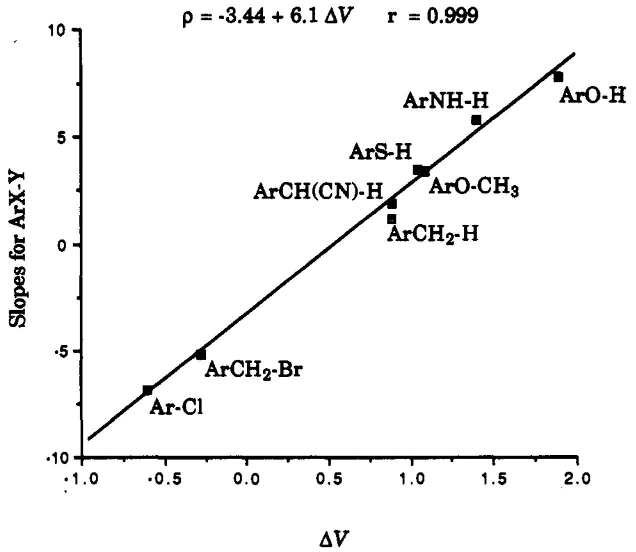

Figure 6. Plot of $\rho_{ArX\text{-}Y}$ values for Hammett BDE correlations versus the differences in electronegativities of the atoms forming the bond being cleaved (ΔV).

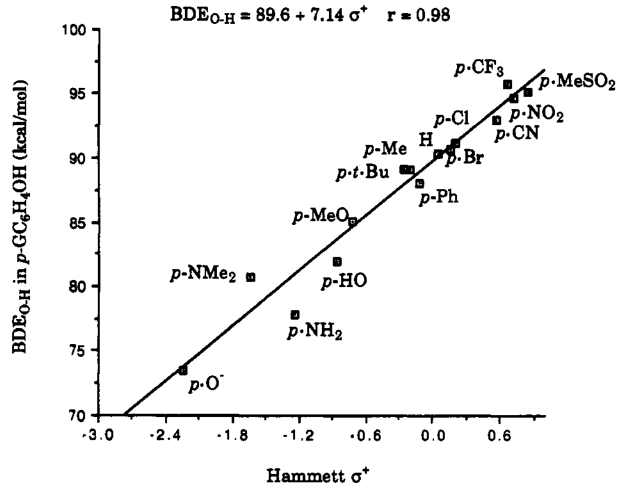

Figure 7. Plot of the BDEs of the O–H bonds in para-substituted phenols versus σ^+.

The maximal ρ^+ of 10 for the plot of $E_{ox}(A^-)$ values vs σ^+ is understandable in terms of the ease of removal of an electron at an electrode from an anion compared to the loss of an electron from carbon to chlorine during the heterolysis of the C–Cl bond in the solvolysis of cumyl chlorides ($\rho^+ = -4.54$).[28] The large ρ^+ values of 7.3 and 7.1 observed for (thermal) homolysis of the O–H bonds in solution is reasonable since the electron density in the O–H bond resides primarily on oxygen. The slopes of these lines are defined largely by the powerful electron release from donor substituents, which destabilize the undissociated phenol and stabilize the odd electron in the corresponding radical.

Summary and Conclusions. Acidities of radical cations derived from thiophenols were found, once again,[4] to be dictated by the effects of substituents on the initial radical cation stabilities rather than on the stabilities of the product radicals. The ρ values for linear Hammett plots for the BDEs of the S–H bonds in thiophenols, the N–H bonds in anilines, and the O–H bonds in phenols (excluding p-O^-, p-NH_2, and p-Me_2N points) were found to increase in the order of increasing dipole moments from 3.2 to 5.5 to 7.3. The effects of substituents on BDEs also increase in this order. This is consistent with the suggestion of Clark and Wayner[6] that dipole–dipole interactions between meta and para acceptor substituents and the acidic bonds decrease the ground-state energies leading to increase in the BDE values. The observation that points for para-acceptor substituents fit close to a meta-substituted phenol Hammett BDE line ($\rho = 6.9$) is also consistent with this idea (Figure 3). Para-donor points show a different behavior, however. They do not fit the meta-substituted phenol line, but instead form a line of their own with a much steeper slope ($\rho = 20$). Similar behavior was also observed for the arylacetonitrile family where the Hammett meta BDE line for cleavage of the acidic C–H bonds has a slope of only about

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1.6 and the points for the para-donor group form a separate line with a slope nearly 3 times as large. We conclude that the effects of para-donor groups in decreasing the BDEs of either C–H, O–H, or S–H bonds are caused primarily by their ability to stabilize the product radicals by delocalizing the odd electron. It seems likely, therefore, that, in general, remote substituents exert their effects on BDEs *both* by changing ground-state energies of HA and by stabilizing or destabilizing the corresponding radical, A$^\bullet$. Estimates of radical stabilization energies free of ground-state effects are given for para donors in the phenol series.

Experimental Section

Materials. The thiophenols and related compounds were commercial samples. The purity (and identity) of each sample was confirmed by spectral analysis. Their equilibrium acidities were determined previously.[17] The oxidation potentials of thiophenols and their conjugate anions were measured by conventional cyclic voltammetry.[1] The working electrode (BAS) consists of a 1.5 mm diameter platinum disk embedded in a cobalt glass seal. It was polished with 0.05 μm Fisher polishing aluminum or cleaned with an ultrasonic instrument and rinsed with ethanol and dried before each run. The counter electrode (BAS) was platinum wire (BAS). The reference electrode was Ag/AgI, and the reported oxidation potentials were referenced to the ferrocenium/ferrocene couple ($E_{1/2}$ = 0.875 vs the Ag/AgI couple). Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte.[1] All electrochemical experiments were carried out under argon.

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