The S−H Bond Dissociation Enthalpies and Acidities of Para and Meta Substituted Thiophenols: A Quantum Chemical Study

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The accurate S−H bond dissociation enthalpies [BDE(S−H)] for a series of meta and para substituted thiophenols ($X{-}C_6H_4{-}SH$, X = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN, and NO_2) have been estimated by using the (RO)B3LYP procedure with 6-311++G(2df,2p) basis set. The proton affinities [PA(S^-)] at the sulfur site of the corresponding thiophenoxide ions ($X{-}C_6H_4{-}S^-$) and adiabatic electron affinities (EA_a) of thiophenoxy radicals have also been evaluated at the same level of calculations. The BDE(S−H) of the parent thiophenol has been evaluated to be 332.6 ± 4.0 kJ/mol, which is in agreement rather with the earlier experimental value of 331.0 kJ/mol (Bordwell et al., *J. Am. Chem. Soc.* **1994**, *116*, 6605) than the more recent value of 349.4 kJ/mol (Santos et al., *J. Phys. Chem. A* **2002**, *106*, 9883). The effects of para and meta substituents on the BDE(S−H) and PA(S^-) have been critically analyzed considering the change in stabilities of the neutral molecule, radical and anions with the change in substituent, and its position. The correlations of Hammett's substituent constants with the BDE(S−H) and PA(S^-) values have also been explored.

Introduction

Sulfur-centered radicals are very important to chemistry because of their role in diverse fields such as atmospheric chemistry, biochemistry, organic synthesis, and coal and oil industry.[1] Reliable thermochemical data are indeed necessary to understand the chemistry of these compounds. This necessity has stimulated researchers to study the thermochemistry of different sulfur containing species including the heats of formation, ionization potentials, and most importantly, homolytic bond dissociation enthalpies (BDE),[2−7] because those are crucial parameters when we are dealing with radical species. Thiophenoxy radicals has gained special attention because they can help in understanding the chemistry of the related phenoxy radicals, which are well known for their antioxidant activities. BDEs are important in determining antioxidant activity not only from a kinetic but also from a thermodynamic point of view. Because BDEs can provide information about the energetic nature (exothermic or endothermic) of the inhibition reaction involved in antioxidant activity, BDEs are also useful for the understanding of a diversity of processes ranging from surface chemistry to many enzyme reactions. Theoretical methods that can be applied for accurate BDE calculations in large molecules are especially useful, because in general, experimental BDE data have large uncertainties.

The BDEs for the S−H bonds in thiophenol and substituted thiophenols are the subject of recent experimental and theoretical studies.[2,3] In 1986, Bordwell and co-workers[8] have prescribed a method to determine gas-phase BDEs of the acidic A−H bonds from the solution phase data and using a thermodynamic cycle. These authors obtained an empirical equation relating BDEs with the oxidation potentials of the conjugate anions and pK_a values. Using this empirical equation, they estimated BDE(S−H) values for thiophenol and some meta and para substituted thiophenols.[9] They obtained a BDE(S−H) value of 332.0 kJ/mol for thiophenol, which was very close to that (332.2 kJ/mol) obtained earlier by Venimadhavan et al.[10] Very recently, Santos et al.[2] have reported a value of 349.4 ± 4.5 kJ/mol for the BDE(S−H) value of thiophenol. In fact, the literature value for the BDE(S−H) of thiophenol varies within a wide range of 331.0 to 349.4 kJ/mol.[11] Moreover, BDE(S−H) values for most of the meta and para substituted thiophenols are not available. Owing to this disparity among various results and lack of data, we set out to investigate this problem by applying accurate density functional theory (DFT) procedures for estimating the BDE values.

Accurate estimation of BDE from quantum chemical calculations is always a challenging task, because it is necessary to take into account the effect of both dynamical and nondynamical part of electron correlation. This involves high levels of ab initio calculations, which is prohibitive for large-size molecules such as substituted thiophenols. Thus, DFT based methods can be very useful for this study. In fact, Fu et al.[3] have recently reported the BDE(S−H) values for some of the para substituted thiophenols at the UB3LYP/6-311++G(d,p) level of theory. However, their calculated values differ widely from the experimental values. Here, we have applied the (RO)B3LYP/6-311++G(2df,2p) procedure to estimate the BDE(S−H) values for a series of meta- and para-substituted thiophenols. The (RO)B3LYP method is known to produce very accurate BDE values for various types of bonds.[12−14] Very recently, we calculated

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the BDE(O−H) values for a series of meta and para substituted phenols by applying this procedure and obtained very good results with an error bar of ±6 kJ/mol.[15] Because many times even the experimental values have large uncertainties, theoretical results can be reliable if they give consistent results on trial molecules. We have also estimated the PA values for the substituted thiophenoxide ions. The gas-phase acidity of thiophenol molecule can be approximately calculated from the PA value of the corresponding thiophenoxide ion. Haeberlin and Brinck indeed observed that the PA values of phenoxide anions and acidities of the corresponding parent phenol molecules were close to each other.[16] Finally, elucidation of the structure−activity relationship has long been a major goal of physical organic chemistry. Attempts have, therefore, been made here to establish such correlation from the results of BDE(S−H) and PA calculations. The effect of changing the position of a substituent on the stabilities of neutral thiophenol molecules, thiophenyl radicals, and thiophenoxide anions has also been analyzed. As a byproduct, the electron affinities of the substituted thiophenoxy radicals, EA($S^\bullet$), have also been derived. As far as we are aware, experimental result of this quantity is available only for the thiophenoxy radical ($C_6H_5S^\bullet$), and the reported value amounts to 2.26 ± 0.1 eV.[17] Recently, Brinck and co-workers[18] calculated the EA values for para-substituted thiophenoxy radicals at the B3LYP/6-31+G(d) level of theory. Our results can, therefore, be compared to the EA values reported by them.

Computational Details

The structures of the para- and meta-substituted thiophenol molecules ($X-C_6H_4-SH$, X = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN, and NO_2), the corresponding thiophenoxy radicals ($X-C_6H_4-S^\bullet$), and thiophenoxide anions ($X-C_6H_4-S^-$) were first optimized at the B3LYP/6-311G(d,p) level. Single point energies were then calculated at the B3LYP/6-311++G(2df,2p) level. Earlier studies show that geometry optimization and frequency calculation at the B3LYP/6-311G(d,p) level are sufficient for getting reliable results.[12,14,15] ROB3LYP procedure was used for the open shell thiophenoxy radicals at the UB3LYP/6-311G(d,p) optimized geometry. In the ROB3LYP method, the spin restricted open shell Hartree−Fock (ROHF) formalism was used to generate the DFT orbitals. It was demonstrated before that UB3LYP and ROB3LYP produced nearly the same optimized structure for radicals.[15] We therefore used UB3LYP for geometry optimization of radicals, because this is much faster than the ROB3LYP method. All the calculations were performed using Gaussian-98 suite of programs.[19]

The gas-phase homolytic S−H bond dissociation energies of thiophenols at 298 K were obtained from the enthalpies of different species (H_f's) at 298 K and using the expression

$$\mathrm{BDE(S-H)} = H_f(X-C_6H_4-S^\bullet) + H_f(H) - H_f(X-C_6H_4-SH) \quad (1)$$

The enthalpies at 298 K were estimated by adding thermal correction to the energies at 0 K

$$H_f(298K) = E_o + ZPE + H_{trans} + H_{rot} + H_{vib} + RT$$

where H_{trans}, H_{rot}, and H_{vib} are the translational, rotational, and vibrational contributions to the enthalpy, respectively.

The exact energy of the hydrogen atom (−0.5 au) was used for the calculations, since DFT methods suffer from the problem of self-energy.[12,13] The PA at the sulfur atom of $X-C_6H_4-S^-$ and the adiabatic electron affinity of the radical ($X-C_6H_4-S^\bullet$) at 298 K were estimated from expressions (2) and (3), respectively

TABLE 1: The Calculated and Experimental S−H Bond Dissociation Enthalpies [BDE(S−H) in kJ/mol] for Para- and Meta- Substituted Thiophenols [$X-C_6H_4-SH$]

	para		meta		
X	calc	expt	calc	expt	ΔBDE_{p-m}
H	332.6	331.0[a], 332.2[b] 334.7[c], 349.4[d]	332.6		0.0
F	325.5		336.0		−10.5
Cl	326.4	331.4[a]	336.0	335.1[a]	−9.6
CH_3	324.3	327.6[a]	331.8	330.1[a]	−7.5
OCH_3	317.6	321.7[a]	330.5		−12.9
NH_2	310.0	292.0[d]	331.8		−21.8
CF_3	340.2		337.2		3.0
CN	340.6		339.3		1.3
NO_2	345.2	340.6[a]	340.6		4.6

[a] Ref 9. [b] Ref 10. [c] Ref 28. [d] Ref 2.

$$\mathrm{PA}(S^-) = H_f(X-C_6H_4-S^-) + H_f(H^+) - H_f(X-C_6H_4-SH) \quad (2)$$

$$EA_a = H_f(X-C_6H_4-S^\bullet) - H_f(X-C_6H_4-S^-) \quad (3)$$

Results and Discussion

A. Bond Dissociation Enthalpies. The B3LYP procedure is known to provide reliable geometries and frequencies for the phenolic or thiophenolic systems.[3,4,20] We therefore are not going to discuss these aspects here. However, it is important to check first whether the methodology used for calculating the BDE(S−H) values can provide reliable results. The choice of an appropriate method is very important, since one of our aims is to calculate the accurate BDE(S−H) values for thiophenols. As we mentioned earlier, we applied the (RO)B3LYP/6-311++G(2df,2p) method for calculating BDE(O−H) values of substituted phenols and obtained very good results.[15] However, to reconfirm the efficacy of the procedure, we have calculated the BDE(S−H) values for two model systems, namely H_2S and CH_3SH, for which exact experimental results are known. Our calculated BDE(S−H) values for H_2S and CH_3SH are 382.8 and 363.2 kJ/mol, respectively, which is very close to the experimental values of 381.6 ± 2.9 kJ/mol for the former and 365.7 ± 2.5 kJ/mol for the latter molecule.[21] These results give us confidence to apply the same procedure for calculating the accurate BDE(S−H) values of the thiophenol series.

The calculated BDE(S−H) values for the para- and meta-substituted thiophenols are given in Table 1. The available experimental results are also given for comparison. As mentioned before, the experimental BDE(S−H) values of thiophenol vary within a wide range of 331.0 to 349.4 kJ/mol.[11] The most recent value (349.4 kJ/mol) was determined from the time-resolved photoacoustic calorimetry (TR−PAC) experiment by Santos et al.[2] Our calculated value (332.6 kJ/mol) is lower by almost 17 kJ/mol from the TR−PAC value but quite close to those estimated by Bordwell and co-workers (331.0 kJ/mol)[9] and also by Venimadhavan et al. (332.2 kJ/mol).[10] Our calculated values for para substituted chloro, methyl, methoxy, and nitro thiophenols are also found to be very close to those estimated by Bordwell and co-workers.[9] For *para* aminothiophenol, the calculated value is much larger than that estimated from the TR−PAC results. As pointed out by Fu et al.[3] the lower TR−PAC value is due to the hydrogen bonding between the amino group and the solvent molecules. As a result,

TABLE 2: The Change in the S−H Bond Dissociation Enthalpies upon Substitution[ΔBDE(S-H) = BDE(XC_6H_4S−H) − BDE(C_6H_5S−H) in kJ/mol] for Para- and Meta-Substituted Thiophenols [X−C_6H_4−SH]

	para				meta	
X	calc[a]	expt[b]	calc[c]	ΔBDE (O−H)[d]	calc[a]	ΔBDE (O−H)[d]
H	0		0	0	0	0
F	−7.1			−8.8	3.4	3.8
Cl	−6.2	3.6 ± 2.7	−2.3	−5.9	3.4	3.8
CH_3	−8.3	−1.9 ± 2.9	−4.9	−10.0	−0.8	−2.5
OCH_3	−15.0	−8.3 ± 2.9	−13.9	−25.9	−2.1	−5.9
NH_2	−22.6			−40.2	−0.8	−2.5
CF_3	7.6	3.1 ± 2.8	7.3	12.1	4.6	8.4
CN	8.0			7.9	6.7	11.7
NO_2	12.6			17.6	8.0	13.4

[a] Present work. [b] Experimental value, ref 2. [c] Calculated value at the MPW1PW91/aug-cc-pVTZ level, ref 2. [d] Calculated values, ref 15.

the solution phase BDE(S−H) value itself is too low. We could find out experimental BDE(S−H) values for only meta chlorothiophenol and meta methyl-thiophenol, and in both the cases our calculated values are in very good agreement with the experimental results. Our calculated BDE(S−H) values are, in fact, the first reported results for most of the meta-substituted thiophenols.

It is interesting to observe how the BDE(S−H) value changes with the change in substituent at the para or meta position of thiophenols. Table 2 shows the change in BDE(S−H) values [ΔBDE(S−H) = BDE(XC_6H_4S−H) − BDE(C_6H_5S−H)] for different substituents in going from the parent thiophenol to a substituted thiophenol. Our results for para-substituted thiophenols are found to be in resonably good agreement with the available experimental results reported in the literature. The effects of electron donating and withdrawing groups on the BDE(S−H) of the para-substituted thiophenols are opposite. Strong electron donating groups, such as OCH_3 and NH_2, at the para position result in a sharp decrease for the BDE(S−H) value. For example, the BDE(S−H) value of p-aminothiophenol is more than 22 kJ/mol lower than that for thiophenol. On the other hand, the strong electron donating group at the meta position of thiophenol does not have any appreciable influence on the BDE(S−H) value. The differences of the BDE(S−H) values (ΔBDE_{p-m}) between the para and meta substituted thiophenols are given in the last column of Table 1. This clearly shows how the effect of a substituent changes with the change in substituent position. The behavior of −F and −Cl at the para and meta position is opposite. At the para position, they reduce the BDE(S−H) value from the parent molecule by more than 6 kJ/mol, whereas at the meta position, they enhance the BDE(S−H) value from that of the unsubstituted thiophenol. These two groups, therefore, do not have specific electron donation or withdrawing character. Their behavior rather depends on the site of substitution. On the other hand, electron withdrawing groups, such as CF_3, CN, and NO_2 at the para or meta position, induce an increase of the BDE(S−H) value significantly. Of course, the enhancement is more pronounced at the para position than that at the meta position. Thus electron withdrawing groups at the para and meta position of thiophenol produce a worsening effect on its antioxidant activity, while electron donating groups, especially at the para position, show an opposite effect.

To understand the reason behind the variation of BDE(S−H) value with the change in substituent position, we have estimated the change in the enthalpy values ($\Delta H_{p-m} = H_{para} - H_{meta}$) while going from para to meta substituted thiophenol and thiophenoxy radical. The ΔH_{p-m} values for all the substituents studied here are shown in Figure 1. The positive values of the ΔH_{p-m} indicate the higher stability of the meta substituted species over the corresponding para substituted one. Electron withdrawing groups, such as CN, NO_2, at the para position of thiophenol stabilize the system much more than when they are at the meta position, whereas energies of the thiophenoxy radicals do not depend much on the position (para or meta) of such groups. As a result, for electron withdrawing groups, the higher BDE(S−H) value for para substituted thiophenol over the corresponding meta substituted one is primarily due to the extra stability of the para substituted thiophenol. The situation is quite different for electron donating groups, such as CH_3, OCH_3, and NH_2, including F and Cl. Here para substituted thiophenols have lower stability than the corresponding meta substituted counterparts, and it is just the opposite for thiophenoxy radicals. Especially for OCH_3 and NH_2 substituents, the ΔH_{p-m} value is found to be quite large. These two effects add together and make the S−H bond in meta substituted thiophenols substantially stronger than the corresponding para substituted product.

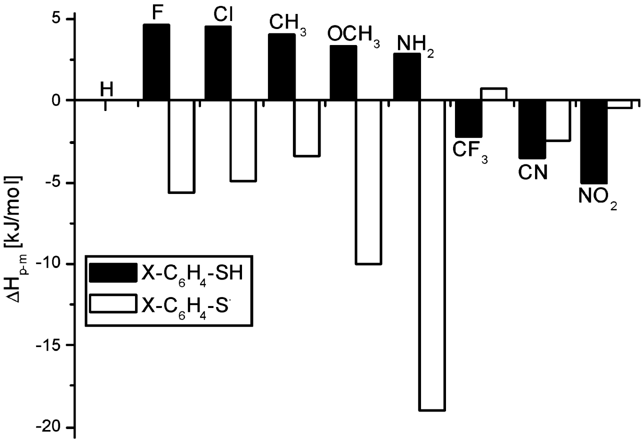

Figure 1. The difference in enthalpy values between the corresponding para and meta substituted thiophenols and thiophenoxy radicals.

The substituent effect on the strength of the O−H bond in phenol could not be explained in terms of the changes in the properties of the bond itself. It was, indeed, observed[22] that the force constant value of the O−H bond in phenol increases with increasing electron-donating power of the substituent, which is opposite to that expected from the BDE value. Even the electron density around the O−H bond was found to give a negative correlation with the BDE value.[22] It is generally believed that electron donor substituents at para position decrease the BDEs of the O−H bonds of substituted phenols primarily by stabilizing the corresponding radicals, and to some extent, by raising the ground-state energies of neutral molecules. In fact, Brinck et al. showed that the ΔBDEs for phenols with electron donor substituents were mainly determined by the stabilization of the radical due to spin delocalization.[22] On the other hand, the delocalization of the oxygen lone pair of electrons was found to be the dominating factors in determining ΔBDEs for electron withdrawing substituents.[22] Wu and Lai[23] analyzed the substituent effects on the O−H bond of phenol in terms of radical effect (RE) and ground-state effect (GE) and made almost similar observations as those mentioned before. We believe that the same phenomena are occurring even in the case of thiophenols. In fact, Fu et al.[3] pointed out that the major source of the substituent effects on BDE(S−H) of thiophenols was the stability of the thiophenol radicals. The electron-withdrawing substituent at the para position is likely to interact with the S−H dipole, causing a lowering of the ground-state energy of the neutral and thereby increasing the BDE(S−H) value from the parent molecule. We have calculated the change in enthalpies at 298 K for a substituted thiophenol and thiophenoxy radical while going from the corresponding parent molecules, and this information provides a clear idea about the substituent effect on the BDE(S−H) values. For strong electron donating groups, the substituted radical is getting more stabilized than the corresponding substituted thiophenol molecule, and as a result, the BDE(S−H) value decreases. For example, *p*-amino thiophenoxy radical gains 22 kJ/mol more substitution enthalpy than the *p*-amino thiophenol molecule while going from the corresponding parent unsubstituted molecules. Opposite effect can be observed for the electron withdrawing groups. The *p*-nitro thiophenol molecule gains nearly 13 kJ/mol more substitution enthalpy than the *p*-nitro thiophenoxy radical while going from the corresponding parent unsubstituted molecules. Thus, in the case of electron donating substituents, extra stability of the thiophenoxy radical decreases the BDE(S−H) value from the parent molecule, whereas additional stability gained by the substituted thiophenol molecule for electron withdrawing substituents results in increasing the BDE(S−H) value. This observation agrees well with that made by Clark and Wayner in the context of phenolic O−H bond.[24] They noted that the effects of meta and para-electron acceptors are best looked on as lowering the ground-state energies of the neutral phenols and thereby strengthening the O−H bond.

We report also the ΔBDE(O−H) values for substituted phenols calculated at the same level of (RO)B3LYP theory in Table 2 to compare the effect of a substituent on the BDE(S−H) value of thiophenol and BDE(O−H) value of phenol. The substituent effect is much greater for phenol than that for thiophenol, especially for strong electron donor or withdrawing groups. For example, the ΔBDE(S−H) values for *p*-amino and *p*-nitro thiophenol molecules are −22.6 and 12.6 kJ/mol, respectively, whereas the ΔBDE(O−H) values for these two related phenols are −40.2 and 17.6 kJ/mol, respectively. The effect of F^- and Cl^- on BDE(S−H) and BDE(O−H) are found to be more or less similar. It is noteworthy that the direction of the effects is not changed, i.e., electron withdrawing substituents, such as NO_2, make the S−H bond stronger, whereas electron donor substituents, such as OCH_3, weaken that bond. As pointed out by Bordwell, the smaller dipole moments of the S−H bonds in thiophenols than those for the O−H bonds in phenols lead to smaller ΔBDE(S−H) values.[9]

B. Acidities of Substituted Thiophenols. The gas-phase acidities of substituted thiophenols are determined from the proton affinities of the corresponding thiophenoxide anions ($X-C_6H_4-S^-$). The PAs are calculated from the enthalpy values of the substituted thiophenols and thiophenoxide anions at the B3LYP/6-311++G(2df,2p) level as described in eq 2. The greater the PA value of the thiophenoxide anion, the lower should be the acidity of the corresponding thiophenol molecule. The PA values for para and meta substituted phenols are given in Table 3. Experimental PA value is available only for the thiophenoxide anion ($C_6H_5-S^-$). Our calculated PA value of 1420.0 kJ/mol is in good agreement with the experimental value of 1424.0 ± 8.8 kJ/mol for thiophenol.[25] We therefore believe that the calculated PA values for the substituted thiophenols should be very close to the exact values.

The electron donating group at the para position of thiophenoxide ion increases the PA value. The effect is especially strong for the NH_2 group, where the PA value increases by almost 19 kJ/mol. It is interesting to note that, although CH_3 and NH_2 increase the PA value also at the meta position, OCH_3 works in an opposite direction at the meta position, due to a larger stabilization of the anion. On the other hand, an electron withdrawing group (such as CN, CF_3, or NO_2) at the para or meta position of thiophenoxide anion has a strong lowering effect on the PA value. Again, the effect is much more pronounced for the para position. For example, the PA value for *para* nitro thiophenoxide ion is 82.8 kJ/mol lower than the PA value for thiophenoxide anion. The −F and −Cl substituents behave like an electron withdrawing group here, and their effect does not have much position dependence. For strong electron donating and withdrawing substituents, the PA values depend strongly on the position of the substituent, which is clear from the last column of Table 3. The largest effect is observed for the NO_2 group, where PA values for the para and meta position differ by almost 30 kJ/mol. It may be interesting to compare the PA values of substituted thiophenoxide anions with those for substituted phenoxide anions. The substituent effect follows the same trend in both thiophenoxide and phenoxide anions. However, in general, the PA values of thiophenoxide anions are from 16 kJ/mol (for *para* nitrothiophenoxide anion) to 38 kJ/mol (for *para* methylthiophenoxide ion) lower than the corresponding phenoxide ions. Thiophenol is thus a stronger acid than phenol. Our calculated PA value for thiophenoxide anion (1420 kJ/mol) is lower than the PA value of phenoxide anion (1455.2 kJ/mol) by 35.2 kJ/mol, which is very close to the experimental value of 35.6 kJ/mol.[25]

TABLE 3: The Calculated Proton Affinities [PA(S^-) in kJ/mol]of Para- and Meta-Substituted Thiophenoxide Anions [$X-C_6H_4-S^-$ [a]

X	PA(S^-) (para)	PA(S^-) (meta)	ΔPA_{p-m}
H	1420.0	1420.0	0.0
F	1406.7	1400.4	6.3
Cl	1393.1	1393.9	−0.8
CH_3	1421.7	1422.6	−0.9
OCH_3	1428.2	1417.9	10.3
NH_2	1439.1	1428.2	10.9
CF_3	1375.4	1383.5	−8.1
CN	1356.7	1369.8	−13.1
NO_2	1337.2	1366.8	−29.6

[a] The last column shows the difference of PA values between thecorresponding para- and meta-substituted thiophenoxide anions.

In general, electron-withdrawing substituents significantly increase the acidity of thiophenol, whereas electron donor groups reduce the acidity. The PA values also indicate that, for electron donor groups, meta substituted thiophenol is more acidic than the corresponding para substituted counterpart. On the other hand, the opposite trend is true for electron withdrawing substituents; here, a para substituted thiophenol is more acidic than its meta product. The substituent effect is much stronger on PA than that on BDE(S−H). For the present set of substituents, the maximum change in BDE(S−H) value from the parent molecule is observed for *para* nitrothiophenol, and it amounts to 12.6 kJ/mol, for the corresponding *para* nitro thiophenoxide anion the change in PA value amounts to 82.8 kJ/mol.

C. Correlation of BDE(S−H) and PA(S^-) with Hammett's Parameter. Table 2 shows that the BDE(S−H) values of para substituted thiophenols vary within a range of nearly 23 kJ/mol. Thus BDE(S−H) values of para substituted thiophenols depend strongly on the nature of the substituent. The effect is found to be much smaller for meta substituted thiophenols, where BDE(S−H) values vary up to 8 kJ/mol. These substituent effects can be seen in terms of Hammett's substituent parameters (σ). However, a modified set of parameters (σ^+) is generally

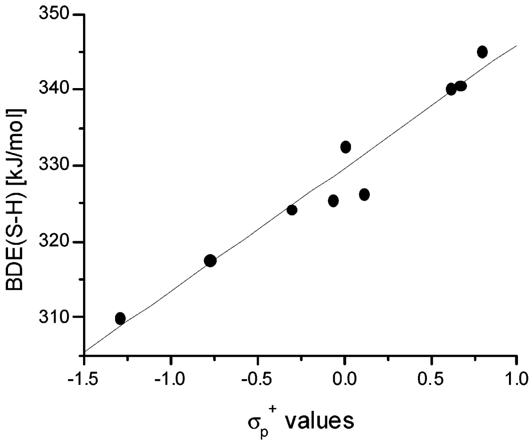

Figure 2. The Hammett plot of BDE(S−H) for para substituted thiophenols.

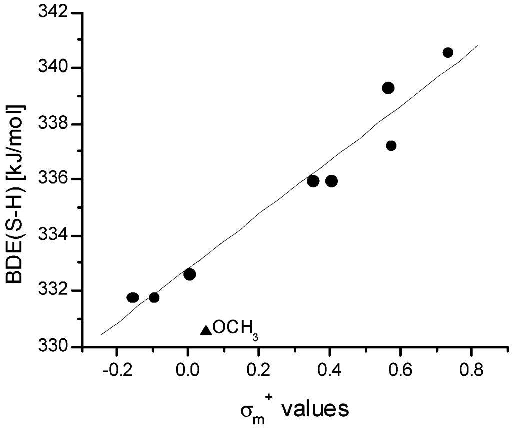

Figure 3. The Hammett plot of BDE(S−H) for meta substituted thiophenols.

used for such correlation to account for through conjugation effects. This effect is important for electron donor groups, such as $-CH3$, OCH_3, and NH_2, at the para position. The σ_m^+ and σ_m values are nearly the same for meta substituents.

A Hammett plot for the BDE(S−H) values of nine para substituted thiophenols and σ_p^+ is shown in Figure 2. The σ_p^+ values are taken from the compilations of Hammett parameters by Hansch, Leo, and Taft.[26] An impressive linear correlation ($R = 0.97$) is observed between the BDE(S−H) and σ_p^+ values. The BDE(S−H) value increases with the increasing electron withdrawing ability of the substituent (i.e., higher value for σ_p^+). Figure 3 displays the similar correlation for the meta substituted thiophenols and σ_m^+ values. Here, the OCH_3 group deviates strongly from the correlation line, and the σ_m^+ value for this group is expected to be significantly lower than the assigned value of 0.05. A similar deviation was also observed for the correlation between BDE(O−H) of phenols and σ_m^+ values.[15] In fact, from the nature of the OCH_3 group, it can be expected that the σ_m^+ value should be less than zero, like $-CH_3$ and $-NH_2$ groups. The correlation equations obtained for para and meta (except the $-OCH_3$ group) thiophenols are given in equations (3) and (4), respectively

$$\text{BDE(S-H)} = 329.7 + 16.24\,\sigma_p^{+} \tag{3}$$

$$\text{BDE(S-H)} = 332.8 + 9.73\,\sigma_m^{+} \tag{4}$$

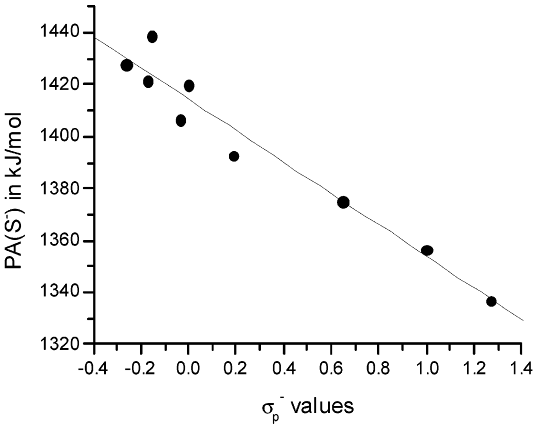

Figure 4. Plot of the proton affinities of the sulfur atom [PA(S$^-$)] for para substituted thiophenoxy radicals against the σ_p^+ values.

As mentioned before, the effect of substituents on BDE(S−H) is found to be more pronounced for para substituted thiophenols. The slopes of these correlation lines can be compared to those for the O−H bonds in phenols because they indicate the reaction constant ρ. For both para and meta substituents, the slopes are much higher for phenols. For example, in the case of para substituted thiophenols and phenols, the slopes are 16.2 and 25.3. Thus, the ρ values of linear Hammett plots for the BDEs increase with the increasing dipole moment of the breaking bond, and these correlation equations can be useful to predict BDE(S−H) value (in kJ/mol) for a new para- or meta-substituted thiophenol, for which a Hammett's parameter could be established.

Haberlein and Brinck[16] demonstrated that the gas phase PA values for phenoxide anions are strongly correlated with the Hammett's substituent constants. Such correlation stems from the observation that substituent effects in phenoxide anions in solution and gas phase are linearly related. Thus, PA values of substituted thiophenoxide anions should correlate with Hammett's substituent constants. It should be mentioned here that instead of using the regular Hammett's parameters a different set of parameters (σ^-) is generally used for systems where a direct conjugation between the reaction center and the substituent exists.[26] This is especially important for para substituents, because of the resonance stabilization of negative charge center by substituent. The σ_p^- parameters have been determined primarily from the aqueous basicities of anilines and acidities of phenols. For the meta substituents, the σ_m^- and σ_m values are the same due to the absence of direct conjugation with the charge center. The correlation between the PA values of para-substituted thiophenoxide ions and σ_p^- is given in Figure 4, whereas Figure 5 shows the similar correlation for meta substituted thiophenoxide ions. Both the correlations are also found to be very good. This indicates that Hammett's parameters can be used for determining the substituent effect on the acidities of thiopenols. The linear equations obtained from such correlations are as follows:

$$\text{PA(S}^-\text{) (kJ/mol)} = 1414.4 - 60.6\,\sigma_p^{-} \tag{5}$$

$$\text{PA(S}^-\text{) (kJ/mol)} = 1419.9 - 76.4\,\sigma_m \tag{6}$$

These equations can be used for determining the gas-phase acidities of substituted thiophenols from the Hammett's parameters or vice versa.

D. Electron Affinities of Thiophenoxy Radicals. The calculated electron affinities of the substituted thiophenoxy radicals are given in Table 4. The EA of the parent PhS$^\bullet$ radical amounting to 225.5 kJ/mol (2.34 eV) is slightly larger than that

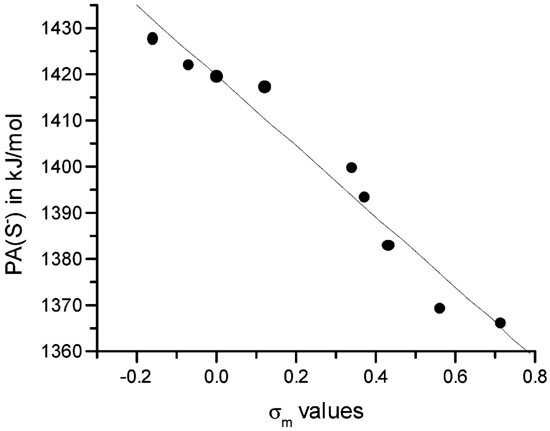

Figure 5. Plot of the proton affinities of the sulfur atom [PA(S^-)] for meta substituted thiophenoxy radicals against the σ_m values.

TABLE 4: The Electron Affinities [EA_a in kJ/mol] of Para- and Meta-Substituted Thiophenoxy Radicals [$X-C_6H_4-S^\bullet$][a]

X	EA_a (para)	EA_a (para)[b]	EA_a (meta)	ΔEA_{p-m}
H	225.5	219.0	225.5	0.0
F	231.6	228.7	248.2	6.3
Cl	246.0	241.2	254.7	−0.8
CH_3	215.4	209.4	221.9	−0.9
OCH_3	201.9	197.8	225.6	10.3
NH_2	183.6	179.5	216.4	10.9
CF_3	296.4		282.2	−13.1
CN	277.6	289.5	266.5	−8.1
NO_2	320.7	317.4	286.5	−29.6

[a] The lastcolumn shows the difference of EA values between the corresponding para- and meta-substituted thiophenoxide anions. [b] B3LYP/6-31+G(d) results from ref 18.

of 2.23 eV determined earlier for phenoxy radical ($PhO^\bullet$).[27] The calculated EA value for $PhS^\bullet$ (2.34 eV) is also somewhat larger than the experimental value of 2.26 ± 0.1 eV. The B3LYP/6-31+G(d) results reported earlier by Brinck and co-workers[18] for para substituted thiophenoxy radicals are also given in Table 4. Our calculated results with larger basis set are found to be 3−6 kJ/mol greater than their values, except in the case of *para* cyano thiophenoxy radical. It is difficult to judge at this point which results are better, because experimental result is available only for one system. However, it appears from the B3LYP results with two different basis sets that the calculated EA values do not have strong basis set dependence.

As in the cases of BDE(S−H) and PA(S^-), strong substituent effects can be observed on the EA values. As expected, the electron donor groups reduce the electron affinity and the effect is quite large when the group is at the para position. Electron withdrawing groups, like CF_3 and NO_2, have a dramatic increasing effect on EA. For example, in the case of the *para* nitro thiophenoxy radical, the EA value increases by as much as 95 kJ/mol. Here the −F and −Cl substituents increase the EA values from the parent radical and thus behave like weak electron withdrawing groups. The difference in the EA values of para and meta substituted thiophenoxy radicals (ΔEA_{p-m}) are also given in Table 4. For electron donor groups, EA is larger when the group is at the meta position, whereas in the case of electron withdrawing groups, para substituted radical has higher EA than the meta counterpart. Interestingly, now the behavior of −F and −Cl is like electron donor groups (such as CH_3, NH_2), whereas in both the positions they enhance the EA value like other electron withdrawing groups in the series. As discussed before, unlike the normal chemical conception, these two groups should not be strictly classified as either electron donor or withdrawing groups.

Summary and Conclusions

The accurate BDE(S−H) values are reported for a series of para and meta substituted thiophenols. Our calculated BDE(S−H) values are the first reported results for most of the meta substituted thiophenols. The electron donor groups at the para position of thiophenol decrease the BDE(S−H) value from the parent molecule, whereas they do not have any significant influence at the meta position. The presence of electron withdrawing groups makes the S−H bond of thiophenol much stronger, and the effect is greater when they are at the para position. These two opposite effects for electron donor and withdrawing groups are found to be due to the extra stability of radicals for electron donor groups and extra stability to the ground state of thiophenols for electron withdrawing groups. For strong electron donor groups, the large difference in BDE(S−H) values for the para and meta substituted thiophenols arises from the opposite stabilizing effects of the substituents on thiophenol and thiophenoxy radical. The electron donor group at the meta position stabilizes thiophenol more than that at the para position, whereas the reverse is true for thiophenoxy radical. The effect of substituents on the BDEs is much less pronounced in thiophenol than in phenol, but the trend is found to be similar. Linear Hammett correlation is observed for BDE(S−H) values. The slope of such correlation line is lower for thiophenols in comparison to phenols. The acidities for the same series of thiophenols are also determined from the PA values of the sulfur atom of the corresponding thiophenoxide anions. For most of the cases, the PA values are reported for the first time. The substituent effect on PA is found to be opposite to that observed for BDE(S−H). Electron withdrawing substituents, such as CN and NO_2, reduce the PA value significantly, whereas electron donor groups, like CH_3 and NH_2, enhance the PA value of thiophenols. Thiophenol is found to be more acidic than phenol. The electron affinities of thiophenoxy radicals are also evaluated. The electron-withdrawing substituent has a dramatic increasing effect on the EA value, whereas electron donor groups tend to reduce the EA value from the parent molecule.

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