

# The O-H Bond Dissociation Energies of Substituted Phenols and Proton Affinities of Substituted Phenoxide Ions: A DFT Study

Asit K. Chandra<sup>1</sup> and Tadafumi Uchimaru<sup>2</sup>

<sup>1</sup> Research Institute of Innovative Technology for the Earth (RITE), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, Tsukuba 305-8565, Japan.

Email: asit-chandra@aist.go.jp Fax: 81-298-614487

<sup>2</sup> National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, Tsukuba 305-8565, Japan

Email: t-uchimaru@aist.go.jp Fax: 81-298-614487

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**Abstract:** The accurate O-H bond dissociation enthalpies for a series of *meta* and *para* substituted phenols (X-C<sub>6</sub>H<sub>4</sub>-OH, X=H, F, Cl, CH<sub>3</sub>, OCH<sub>3</sub>, OH, NH<sub>2</sub>, CF<sub>3</sub>, CN, and NO<sub>2</sub>) have been calculated by using the (RO)B3LYP procedure with 6-311G(d,p) and 6-311++G(2df,2p) basis sets. The proton affinities of the corresponding phenoxide ions (X-C<sub>6</sub>H<sub>4</sub>-O<sup>-</sup>) have also been computed at the same level of theory. The effect of change of substituent position on the energetics of substituted phenols has been analyzed. The correlations of Hammett's substituent constants with the bond dissociation enthalpies of the O-H bonds of phenols and proton affinities of phenoxide ions have been explored.

**Keywords:** Substituted Phenol, Bond Dissociation Energy, Acidity, DFT.

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## I. Introduction

Phenols are widely used as synthetic organic materials and also as antioxidants in living organisms [1]. Phenoxy radicals are known as important intermediates in many biological and industrial applications [2]. Phenols are of special interest in organic chemistry, since their acid-base equilibria have often been used as reference values in establishing linear free energy relationships [3]. Consequently, much effort has been put to understand the factors governing the O-H bond dissociation energies, BDE(O-H), and acidities of substituted phenols, both in the solution and gas phase [4-11].

There are many experimental studies [4,5,11,12] for the determination of the BDE(O-H)s of substituted phenols. These studies were generally carried out in solutions (such as water, DMSO, etc.) and subsequently gas-phase BDE(O-H) values were determined under some assumptions [11,12]. Unfortunately, the BDE(O-H) values obtained from different experimental studies vary in a wide range [6]. For example, different experimental studies suggested the BDE(O-H) for phenol from 83.3 kcal/mol to 89.6 kcal/mol [6]. These discrepancies clearly show that there remains a lot of uncertainties even in the experimentally determined BDE(O-H) values. Very recently, Santos and Simoes [6] made a comprehensive analysis of the available experimental BDE(O-H) values of substituted phenols and finally predicted the most likely BDE(O-H) values for a series of substituted phenols. However, they feel that new theoretical and experimental data may invalidate some of their selections because of large discrepancies in the experimental results [6].

Accurate estimation of BDE from theoretical calculations is also a challenging task, since high levels of calculations are necessary for taking into account the effect of both dynamical and non-dynamical parts of electron correlation. High level *ab initio* calculations are thus prohibitive for the large size of the substituted phenol molecules. Recently, Brinck et al. used MP2 and MP4 methods for calculating the BDE(O-H) of phenol and observed that both these methods significantly overestimate the absolute BDE(O-H) value [13]. On the other hand, there are a few theoretical studies on substituent effects on the BDE(O-H) of phenols using density functional theory (DFT) based methods [13-16]. Although, the calculated relative BDE values are found to be in good agreement with the experimental values, but in most of the cases the absolute values differ widely from the experimental value [13,16]. Wright et al. used the B3LYP method with a modified 6-31G(p') basis set and obtained quite accurate BDE(O-H) values for substituted phenols [15]. Very recently, it has been observed that reliable BDE values can be obtained from the (RO)B3LYP procedure [17,18]. In this procedure, restricted open shell formalism of the B3LYP (ROB3LYP) method is used for calculating the energies of the open shell radicals. During the course of this study, Wright and co-workers also reported an extensive study on the BDE(O-H) of *ortho*, *meta*, and *para* substituted phenols [19]. They obtained accurate relative BDE(O-H) values by using (RO)B3LYP/6-311+G(2d,2p)//AM1 method [19].

In the present study, we have calculated the accurate BDE(O-H) values for a series of *meta*- and *para*-substituted phenols by using the same (RO)B3LYP method with two different basis sets, namely 6-311G(d,p) and 6-311++G(2df,2p). The effect of the change in substituent position on the O-H bond strength has been discussed in the light of the stability of the phenoxy radical and the parent phenol molecules. We have also made an attempt to calculate the accurate proton affinities (PAs) of *meta* and *para* substituted phenoxide anions (X-Ph-O<sup>-</sup>) from the results of the B3LYP calculations. Haeberlein and Brinck calculated the PA values [approximated as  $\Delta E = E(\text{XC}_6\text{H}_4\text{-OH}) - E(\text{XC}_6\text{H}_4\text{O}^-)$ , where E's are the total energies of the systems] for a series of *para* substituted phenoxide ions using the BLYP/6-31+G\* basis set [20]. They observed a good correlation between  $\delta\Delta E$  ( $\delta\Delta E$  is the difference of  $\Delta E$

values between a substituted phenol and phenol molecule) and  $V_{\min}$ , where  $V_{\min}$  denotes the minimum value of the electrostatic potential near the oxygen atom of the phenoxide ion. They also observed that the PA values of phenoxide anions and acidities of the corresponding parent phenol molecules are close to each other. Thus gas-phase acidity of a phenol molecule can approximately be calculated from the PA value of the corresponding phenoxide anion. It has been observed that the gas-phase acidities of substituted phenols correlate well with the Hammett's parameters derived for the solution phase acidities. Thus there should be a good linear correlation between the gas-phase and solution phase acidities [8,20]. Elucidation of the relationship between structure and reactivity has long been a chief goal of physical organic chemistry. Attempts have been made to find out such correlation from the results of BDE(O-H) and PA calculations. Thus the present study can also be helpful to shed more light on this front.

## II. Computational Details

The geometries of the para, and meta substituted phenol molecules ( $X-C_6H_4-OH$ ,  $X=H, F, Cl, CH_3, OCH_3, OH, NH_2, CF_3, CN, \text{ and } NO_2$ ), phenoxy radicals ( $X-C_6H_4-O$ ), and phenoxide anions ( $X-C_6H_4-O^-$ ) were optimized at the B3LYP/6-311G(d,p) level. Single point energies were then calculated at the B3LYP/6-311++G(2df,2p) level. ROB3LYP method was used for calculating the energies of the open-shell phenoxy radicals at the UB3LYP/6-311G(d,p) optimized geometry. In the ROB3LYP procedure restricted open shell Hartree-Fock (ROHF) formalism was used to generate the DFT orbitals. The UB3LYP method was used for geometry optimization of phenoxy radicals because analytic energy gradients are not available for the ROB3LYP method and numerical optimization is generally very slow. We estimated the change in the ROB3LYP energies of phenoxy radical and *para* fluoro-phenoxy radical when the geometries were optimized at the UB3LYP and ROB3LYP levels. It was observed that the two energies differ by less than 0.1 kcal/mol. Thus the faster UB3LYP/6-311G(d,p) method was used for the geometry optimization of all the substituted phenoxy radicals. All the calculations were performed by using Gaussian-98 suite of programs [21].

The homolytic O-H bond dissociation energies of the substituted phenols at the 298 K, BDE(O-H), were estimated from the expression:

$$BDE(O-H) = H_f(X-C_6H_4-O) + H_f(H) - H_f(X-C_6H_4-OH) \quad (1)$$

where  $H_f$ 's are the enthalpies of different species at the 298 K. The exact energy of the hydrogen atom (-0.5 a.u.) was used for the above calculations, since DFT methods suffer from the problem of self-energy. The enthalpies were estimated from the expression:  $H_f(298K) = E_o + ZPE + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT$ .  $H_{\text{trans}}$ ,  $H_{\text{rot}}$ , and  $H_{\text{vib}}$  are the translational, rotational and vibrational contributions, respectively, to the enthalpy, where  $H_{\text{trans}} = \frac{3}{2}RT$ ,  $H_{\text{rot}} = \frac{3}{2}RT$  (RT for linear molecule) and  $H_{\text{vib}}$  can be calculated from the standard formulas [22]. The PA of  $X-C_6H_4-O^-$  was calculated from the following expression:

$$PA(X-Ph-O^-) = H_f(X-Ph-O^-) + H_f(H^+) - H_f(X-Ph-OH) \quad (2)$$

### III. Results and Discussion

The B3LYP functional have already been shown to provide accurate geometries and vibrational frequencies for the phenolic systems [15]. These aspects are, therefore, not discussed in the present article. However, it is important to check first whether the methodology used for calculating the bond dissociation energy can provide reliable BDE(O-H) values. Since our aim is to calculate the accurate absolute BDE(O-H) values for substituted phenols, the appropriate choice of the theoretical method is very important. To this end, we have calculated the BDE(O-H) values for three molecules, H<sub>2</sub>O, CH<sub>3</sub>OH and Ph-OH. The accurate BDE(O-H) values are known for the first two molecules, while reliable estimation is available for the BDE(O-H) value of PhO-H from a number of experimental studies. Table 1 presents the calculated and experimental BDE(O-H) values for these three molecules. As we mentioned earlier, the experimental BDE(O-H) value of phenol varies within a wide range. However, Santos and Simoes suggested a value of 88.7±0.5 kcal/mol for the same analyzing the available experimental results [6]. This value is close to the “best” experimental value of 87.3±1.5 kcal/mol for the BDE(O-H) of PhO-H, suggested from the experimental measurements by photoacoustic calorimetry in different solvents [15,23]. The B3LYP values, both for the 6-311G(d,p) and the 6-311++G(2df,2p), are found to be lower than the experimental values, whereas the (RO)B3LYP values with the larger basis set, 6-311++G(2df,2p), are in close agreement with the experimental values. For estimating BDE(O-H) values (RO)B3LYP method is superior to the usual B3LYP method. The (RO)B3LYP/6-311++G(2df,2p) has, therefore, subsequently been used for the BDE(O-H) calculations of all the substituted phenols (mentioned in Tables 2 and 3).

**Table 1.** The homolytic bond dissociation enthalpies (in kcal/mol and at 298 K) of the O-H bonds calculated by using the B3LYP and (RO)B3LYP procedures with two different basis sets, 6-311G(d,p) [sb] and 6-311++G(2df,2p) [lb].

System	B3LYP		(RO)B3LYP		Expt.
	sb	lb	sb	lb	
H <sub>2</sub> O	114.2	117.0	115.1	118.2	117.6±0.1 <sup>a</sup>
CH <sub>3</sub> OH	99.7	101.2	100.8	102.6	104.2±0.9 <sup>b</sup>
Ph-OH	84.1		86.4	87.5	88.7±0.5 <sup>c</sup> 87.3±1.5 <sup>d</sup> 86.5±1.9 <sup>b</sup>

<sup>a</sup>Ref.24; <sup>b</sup>Ref.25; ; <sup>c</sup>Ref.6; <sup>d</sup>Ref.15

### A. BDE(O-H) of Substituted Phenols

Table 2 presents the calculated BDE(O-H) values for a series of *para*-substituted phenols along with the available experimental results. The results obtained from the (RO)B3LYP calculations with smaller 6-311G(d,p) basis set are nearly 1 kcal/mol lower than those obtained from the larger 6-311++G(2df,2p) basis set. Direct experimental gas-phase results are not available for these molecules. Bordwell and Cheng estimated the BDE(O-H) values from the oxidation potential measurements of phenoxide ions in DMSO and the  $pK_{HA}$  values in DMSO of their conjugate acids [12]. In most of the cases these BDE(O-H) values are significantly higher than the corresponding calculated gas-phase BDE(O-H) values. Only for *para*-hydroxy and *para*-amino phenols, their estimated values are fairly close to our calculated results. Lind and co-workers [11] calculated the BDE(O-H) of substituted phenols by calculating the free-energy for the reaction:  $X-C_6H_4OH(aq) \rightarrow X-C_6H_4O(aq) + 1/2H_2(g)$  from the aqueous redox potentials and  $pK_a$  values and setting  $\Delta G_{solv}^o$  (the difference of solvation free energies between a phenol molecule and the corresponding phenoxide anion) to zero. They believed their calculated values can only be considered as an upper limit to the exact BDE(O-H) values [11]. Our calculated values are found to be significantly lower than their estimated values. But as these estimations were made from the results of solution phase data (such as DMSO and water) under some assumptions, much emphasis should not be given to the correlation between our calculated BDE(O-H) values and these experimental values. However, our calculated BDE(O-H) values can be compared to the values predicted by Santos and Simoes [6] from the extensive analysis of the available experimental results. The calculated and experimental relative BDE(O-H) values [ $\Delta BDE(O-H)$ ] are given in Table 2 for comparison. The agreement between their  $\Delta BDE(O-H)$  values and corresponding ours is found to be good. Only in the case of *para*-cyanophenol the calculated relative BDE(O-H) value (1.9 kcal/mol) is lower than the value ( $4.3 \pm 1.9$  kcal/mol) predicted by them [6]. Our calculated absolute BDE(O-H) values are quite close to those reported by Wright and coworkers using (RO)B3LYP/6-311+G(2d,2p)//AM1 method [19]. Since their method is computationally cheaper than the method used here, the former method may preferentially be applied to larger molecules. The B3LYP/6-31G(d,p) calculated  $\Delta BDE(O-H)$  values for *para* substituted phenols reported in the reference [13] are not much different from those reported here and in the reference [19]. The differences in our calculated  $\Delta BDE(O-H)$  values and those reported in reference [13] vary within a narrow range of 0.2 (*p*-NO<sub>2</sub>) to 1 kcal/mol (*p*-NH<sub>2</sub>). So, if one is interested only in  $\Delta BDE(O-H)$  values, B3LYP/6-31G(d,p) procedure can be used for getting reasonable results.

The effects of electron withdrawing and donating groups on the BDE(O-H) of the *para* substituted phenol are opposite. Electron withdrawing groups (such as CF<sub>3</sub>, CN, and NO<sub>2</sub>) at the *para* position increase the BDE(O-H) value from that in the parent phenol molecule, while *para*-donor substituents (such as CH<sub>3</sub>, OCH<sub>3</sub>, and NH<sub>2</sub>) tend to weaken the O-H bond of phenol. It is interesting to note that F

**Table 2.** The homolytic bond dissociation enthalpies at 298K [BDE(O-H) in kcal/mol] of the O-H bonds of para substituted phenols (X-C<sub>6</sub>H<sub>4</sub>-OH) calculated by using the (RO)B3LYP procedures with two different basis sets, 6-311G(d,p) [sb] and 6-311++G(2df,2p) [lb].

Substituent (X)	BDE(O-H)				Calculated $\Delta$ BDE <sup>c</sup>	Expt. <sup>d</sup> $\Delta$ BDE <sup>c</sup>
	sb	lb	Expt. <sup>a</sup>	Expt. <sup>b</sup>		
H	86.4	87.5	89.8	88.2	0.0	0.0
F	84.4	85.4		87.4	-2.1	-1.0±1
Cl	85.5	86.1	90.3	87.6	-1.4	-0.2±1
CH <sub>3</sub>	84.3	85.1	88.7	86.1	-2.4	-1.9±1
OCH <sub>3</sub>	80.5	81.3	84.6	82.6	-6.2	-5.3±1
OH	80.6	81.7	81.5	80.2	-5.8	-6.5±2.4
NH <sub>2</sub>	76.9	77.9	77.3	75.5	-9.6	-9.6±3.1
CF <sub>3</sub>	89.2	90.4	95.3		2.9	4.1±1
CN	88.6	89.4	94.2	92.9	1.9	4.3±1.9
NO <sub>2</sub>	90.5	91.7	94.7	94.2	4.2	6.0±1.9

<sup>a</sup> Ref.12; <sup>b</sup> Ref.11. <sup>c</sup>  $\Delta$ BDE = BDE(O-H)[X-C<sub>6</sub>H<sub>4</sub>-OH] – BDE(O-H) [C<sub>6</sub>H<sub>5</sub>-OH]. <sup>d</sup> Ref.6.

and Cl substitutions at the *para*-position reduce the O-H bond strength of phenol, although they are generally considered as electron-withdrawing groups. Here, F and Cl behave like an electron donating substituent. It is generally believed that electron donating substituents at *para* position decrease the BDEs of the O-H bonds of substituted phenols primarily by stabilizing the corresponding radicals and also to some extent by raising the ground-state energies [5]. On the other hand, electron withdrawing substituents at the *para* position interact with the O-H dipoles causing a lowering of ground-state energies and thereby increasing the BDE(O-H) values [5]. The BDE(O-H) value of *para*-aminophenol is 77.9 kcal/mol, which is 9.6 kcal/mol lower than that of the parent phenol molecule. Among the electron-withdrawing groups, NO<sub>2</sub> group affects the BDE(O-H) value most and the BDE(O-H) value increases by 4.2 kcal/mol.

The calculated BDE(O-H) values for the *meta*-substituted phenols are given in Table 3. The predicted  $\Delta$ BDE(O-H) values from the experimental results are also included in Table 3. These values are found to be in good agreement with our calculated values. Our calculated values are also quite close to those calculated by Wright and co-workers [19]. The effect of electron donor group at the *meta*- and *para*-position of phenol is strikingly different. Electron donor-group at the *meta* position does not have any significant effect on the bond strength of the O-H bond in comparison to the parent unsubstituted phenol molecule, whereas the same at the *para* position reduces the O-H bond strength significantly. Thus there is a substantial difference in the O-H bond strengths between the *para* and *meta*-substituted phenols for electron-donor substituents (see the values of  $\Delta$ BDE<sub>*p-m*</sub> in Table 3). For

**Table 3.** The homolytic bond dissociation enthalpies at 298 K [BDE(O-H) in kcal/mol] of the O-H bonds of *meta* substituted phenols (X-C<sub>6</sub>H<sub>4</sub>-OH) calculated by using the (RO)B3LYP procedures with two different basis sets, 6-311G(d,p) [sb] and 6-311++G(2df,2p) [lb].

Substituent (X)	BDE(O-H)		Calculated $\Delta\text{BDE}_{p-m}^a$	Calculated $\Delta\text{BDE}^b$	Expt. <sup>c</sup> $\Delta\text{BDE}^b$
	sb	lb			
H	86.4	87.5	0.0	0.0	0.0
F	87.5	88.4	-3.0	0.9	1.4±1.9
Cl	87.5	88.4	-2.3	0.9	1.2±1
CH <sub>3</sub>	86.0	86.9	-1.8	-0.6	-0.7±1
OCH <sub>3</sub>	85.2	86.1	-4.8	-1.4	0.0±1
OH	86.1	87.0	-5.3	-0.5	0.2±1
NH <sub>2</sub>	86.0	86.9	-9.0	-0.6	-1.2±1
CF <sub>3</sub>	88.3	89.5	0.9	2.0	3.1±1
CN	89.3	90.3	-0.9	2.8	3.1±1.9
NO <sub>2</sub>	89.7	90.7	1.0	3.2	4.5±1.9

<sup>a</sup>The difference between the calculated (the large basis set) BDE(O-H) values of the *para* and *meta* substituted phenol.

<sup>b</sup> $\Delta\text{BDE} = \text{BDE(O-H)[X-C}_6\text{H}_4\text{-OH]} - \text{BDE(O-H) [C}_6\text{H}_5\text{-OH]}$ .

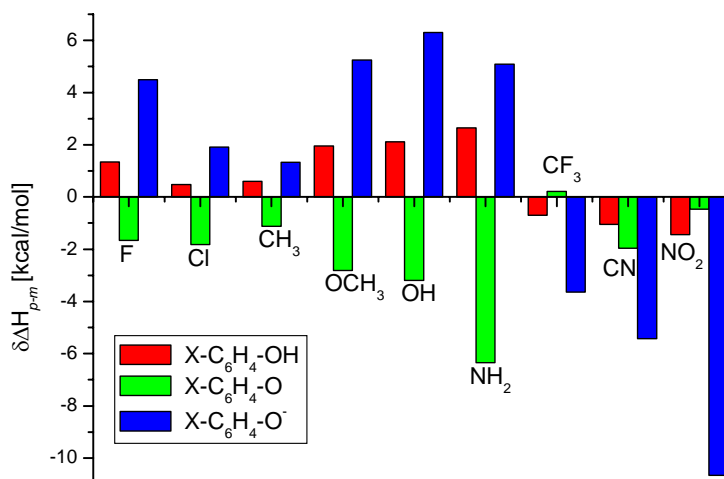
<sup>c</sup>Ref.6

example, the calculated BDE(O-H) value of *meta*-aminophenol is 9 kcal/mol higher than that of *para*-aminophenol.

In the case of electron-withdrawing groups, the difference in the BDE(O-H) values for the *meta* and *para* substituent is less significant. An electron-withdrawing group at both the *meta* and *para* positions increases the BDE(O-H) values as compared with that for the unsubstituted phenol. Interestingly, however, F and Cl substituent at the *meta* position enhance the BDE(O-H) value from that in the parent phenol molecule. Therefore, these two atoms behave like weak electron withdrawing groups at the *meta* position, which is opposite to that observed at the *para* position.

To analyze the origin of differences between the BDE(O-H) values of the *meta* and *para* substituted phenols, we have estimated the change in the enthalpy values ( $\delta\Delta\text{H}_{p-m} = \Delta\text{H}_{para} - \Delta\text{H}_{meta}$ ) while going from *para* to *meta* substituted phenol, phenoxy radical, and phenoxide anion for each of the substituents. The  $\delta\Delta\text{H}_{p-m}$  values are shown in Figure 1. The positive values of  $\delta\Delta\text{H}_{p-m}$  mean that the *meta* substituted species is more stable than the corresponding *para* substituted one.

In the case of electron-donating substituents, such as CH<sub>3</sub>, OCH<sub>3</sub>, OH, and NH<sub>2</sub>, the substitutions at the *meta*-position provide extra stability to the phenol molecule than the substitution at the *para* position (see Figure 1). The situation is opposite in the case of phenoxy radicals. Here the presence of electron donating group at the *para* position provides additional stabilization to the system in comparison to that at the *meta* position. These two opposing effects result in increase of O-H bond strength for an electron donating *meta* substituent phenols compared to the corresponding *para*



**Figure 1.** The differences between the enthalpies ( $\delta\Delta H_{p-m}$ ) of *para* and *meta* substituted phenols ( $X-C_6H_4-OH$ ), phenoxyl radicals ( $X-C_6H_4-O$ ), and phenoxide ions ( $X-C_6H_4-O^-$ ) calculated at the (RO)B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) level.

substituted counterpart. In the case of electron-withdrawing groups, such as CN, CF<sub>3</sub>, and NO<sub>2</sub>, *para*-substituted phenols are more stable than the corresponding *meta* substituted phenols. The situation is the same for the substituted phenoxyl radicals, except for the CF<sub>3</sub> group. As a result, the difference in the BDE(O-H) values between the *para* and *meta* substituted cyanophenol (nitrophenol as well) is found to be small. However, in the case of CF<sub>3</sub> group, *meta* substituted phenoxyl radical is slightly more stable than the *para* substituted one.

## B. Proton Affinities of Substituted Phenoxide Ions

The gas-phase acidities of substituted phenols are estimated from the proton affinities of the corresponding phenoxide anions ( $X-ph-O^-$ ). The lower the PA value of the phenoxide anion is the greater should be the acidity of the corresponding parent phenol molecule [20]. The PAs are calculated from the enthalpies of the substituted phenols and phenoxide anions by using equation (2). Table 4 presents the PA values for both the *para* and *meta* substituted phenols along with the available experimental values. The experimental PA values are obtained by adding the ionization potential of hydrogen IP(H) (313.6 kcal/mol) to the difference of BDE(O-H) and the electron affinity of phenoxyl radical [8]. The PA values calculated at the B3LYP/6-311G(d,p) level are almost 5-6 kcal/mol larger than those obtained from the B3LYP/6-311++G(2df,2p) results and also from the experimental values. This is primarily due to the poor representation of the electronic structure of the phenoxide anions when 6-311G(d,p) basis set is used. Because it is well known that diffuse functions in the basis set is



**Table 4.** Proton affinities [PA in kcal/mol] of the *para* and *meta* substituted phenoxide ions (X-C<sub>6</sub>H<sub>4</sub>-O<sup>-</sup>) calculated by using the B3LYP/6-311++G(2df,2p) method. The  $\Delta PA_{p-m}$  and  $q(O^-)$  represent the difference of the calculated PA values between the *para* and *meta*-substituted phenoxide ions and the net Mulliken charge on the oxygen atom at the B3LYP/6-311G(d,p) level.

Substituent (X)	PA		$\Delta PA_{p-m}$	PA		$\Delta PA_{p-m}$	$q(O^-)$		
	<i>para</i>	Expt. <sup>a</sup>		$\Delta PA_p^b$	<i>meta</i>		Expt. <sup>a</sup>	$\Delta PA_m^b$	<i>para</i>
H	347.8	346.9	0.0	347.8	346.9	0.0	0.0	-0.5188	
F	345.2	344.3	-2.6	342.0	341.1	-5.8	3.2	-0.5209	-0.5098
Cl	341.3	340.3	-6.5	339.8	339.0	-8.0	1.5	-0.5053	-0.4982
CH <sub>3</sub>	349.0	348.2	1.2	348.3	347.3	0.5	0.7	-0.5185	-0.5165
OCH <sub>3</sub>	350.2	347.6	2.4	346.9	345.4	-0.9	3.3	-0.5262	-0.5105
OH	350.1		2.3	345.9	341.8	-1.9	4.2	-0.5300	-0.5163
NH <sub>2</sub>	352.3	351.1	4.5	349.8	347.8	2.0	2.5	-0.5193	-0.5185
CF <sub>3</sub>	334.6		-13.2	337.5		-10.3	-2.9	-0.4856	-0.5000
CN	329.4	329.2	-18.4	333.7	332.6	-14.1	-4.3	-0.4733	-0.4951
NO <sub>2</sub>	323.6		-24.2	332.8	331.2	-15.0	-9.2	-0.4528	-0.4927

<sup>a</sup>Ref.8; <sup>b</sup>The  $\Delta PA_p$  ( $\Delta PA_m$ ) represents the difference in the calculated PA values of *para* (*meta*) substituted phenoxide ion and unsubstituted phenoxide ion.

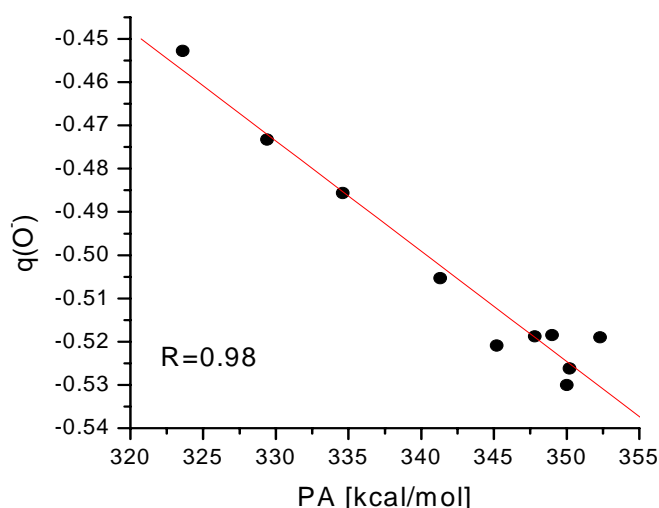
necessary for the proper calculation of electronic structure of an anionic system. Indeed, the PA values obtained from the latter method, which includes diffuse functions in the basis set, agree quite well with the experimental results. Only in the case of *para*-methoxy phenol and *meta*-hydroxy phenol, our calculated PA values are significantly larger than those obtained from the experiment.

The electron donating group (such as CH<sub>3</sub>, OCH<sub>3</sub>, etc.) at the *para*-position of phenoxide anion increases the PA value slightly from that of the parent unsubstituted phenoxide anion (see Table 4). On the other hand, the effect of the presence of electron donating group at the *meta*-position of phenoxide anion depends upon the nature of the substituent, while CH<sub>3</sub> and NH<sub>2</sub> groups tend to increase the PA value from the parent unsubstituted phenoxide anion, OCH<sub>3</sub> and OH groups work in the opposite direction. On the other hand, the electron withdrawing groups at the *meta* or *para*-position have a strong lowering effect (from 10 to 24 kcal/mol) on the PA values of the phenoxide anion. Electron withdrawing group at the *para*-position reduces the PA value much more than that caused by the same group at the *meta*-position. The difference of PA values between the *para* and *meta* substituted phenoxide anions are given in Table 4.

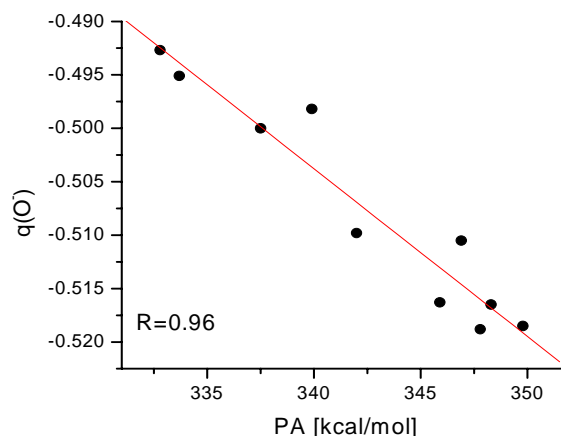
It is clear that in the case of electron donating groups, *meta* substituted phenol is more acidic than the corresponding *para* substituted phenols, whereas the opposite is true for the strong electron withdrawing groups. In the cases of F and Cl, *meta* substitution increases the acidity much more than *para* substitution does. But in both the positions, F and Cl behave similarly as the electron withdrawing groups, like CN and NO<sub>2</sub>.

To understand clearly the reason behind the variation of PA with the position of substituent, we have calculated the enthalpy differences between *meta* and *para* substituted phenols and phenoxide anions. Figure 1 displays the graphical representation of the same. As can be seen from the figure, the change in the stability order with the change in the position (*meta/para*) of the substituent remains the same for both phenol molecules and phenoxide anions. Like the substituted phenol molecules, electron donating *meta* substituent stabilizes the phenoxide anion much more than that at the *para* position, whereas the opposite is true for the electron withdrawing substituents. The F and Cl act as an electron donating substituent for this case. Of course, the difference in the enthalpy values of *meta* and *para* substituted phenoxide anions is always much more than that for the corresponding phenol molecules. As a result, there is a substantial difference in the PA values of the *meta* and *para* substituted phenoxide anions.

In search for a molecular parameter which can be correlated to the PA values of phenoxide anions, the first obvious choice is the point charge on the oxygen atom. The PA value is expected to increase (conversely, the acidity to decrease) with the increase in electronic population on the oxygen atom. Table 4 presents the net electronic charge (Mulliken population) on the oxygen atoms of the substituted phenoxide anions. As expected, generally the electron donating groups increase the net electronic charge on the oxygen atom, while the electron withdrawing groups decrease the net charge on the oxygen atom. Figures 2 and 3 display the correlation between the net Mulliken charge on the oxygen atom and the PA of the *para* and *meta* substituted phenoxide anions, respectively.



**Figure 2.** Plot of proton affinities (PA) of *para* substituted phenoxide ions (mentioned in Table 4) against the net electronic population on the oxygen atom of the phenoxide ions.



**Figure 3.** Plot of proton affinities (PA) of *meta* substituted phenoxide ions (mentioned in Table 4) against the net electronic population on the oxygen atom of the phenoxide ions.

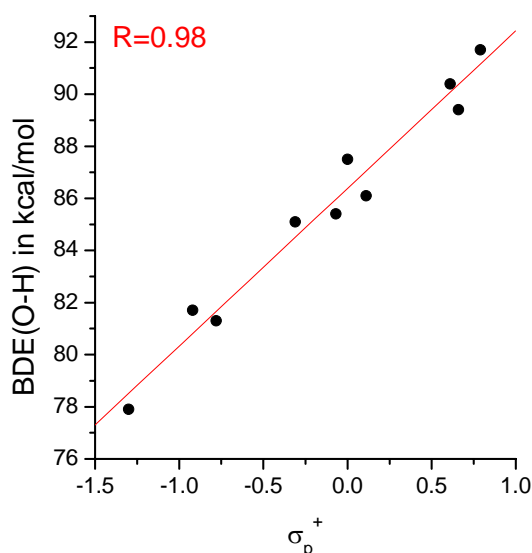
Although there are some deviations, the overall correlation is reasonably well, especially in the case of *para* substituted phenoxide anions. Such correlation can be used for the approximate estimation of PA value (hence acidity as well) from the point charge on the oxygen atom of substituted phenoxide anion.

#### IV. Substituent Constants

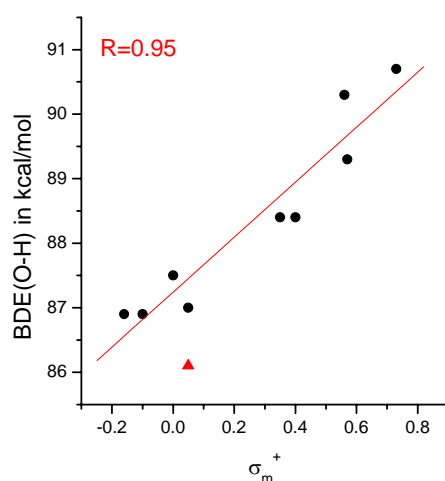
##### A. Correlation of Hammett's parameter with BDE(O-H)

Table 2 shows that the BDE(O-H) of *para* monosubstituted phenols depends strongly on the nature of substituent, which is clear from the fact that the BDE(O-H) values of *para* substituted phenols vary within a range of nearly 15 kcal/mol. The effect is much less in the case of *meta* monosubstituted phenols, where BDE(O-H) values vary within a range of almost 3 kcal/mol. This arises mainly from the large differences in the BDE(O-H) values of *meta* and *para* substituted phenols for electron donating groups (such as -OH and -NH<sub>2</sub>), as discussed before. The substituent effects on the O-H bond strength can be seen in terms of Hammett's substituent parameters ( $\sigma$ ). However, generally a modified Hammett parameter ( $\sigma^+$ ) has been used for such correlation [4,6], since it accounts for through conjugation effects, which will be important for electron-donor groups at the *para* position, such as -CH<sub>3</sub>, -OH, -OCH<sub>3</sub>, and -NH<sub>2</sub> [26]. In fact, only for these electron-donor groups the  $\sigma_p^+$  and  $\sigma_p$  values differ significantly. In the case of *meta* substituents, the  $\sigma_m^+$  and  $\sigma_m$  values are found to be virtually the same.

Figure 4 presents the correlation between the  $\sigma_p^+$  and the calculated BDE(O-H) values for the *para* substituted phenols. The  $\sigma_p^+$  values are taken from the compilations of Hammett parameters by Hansch, Leo and Taft [27]. The correlation between the two is very impressive with a correlation



**Figure 4.** The correlation between the O-H bond dissociation enthalpies [BDE(O-H)] of *para* substituted phenols and the modified Hammett parameters  $\sigma_p^+$ .



**Figure 5.** The correlation between the O-H bond dissociation enthalpies [BDE(O-H)] of *meta* substituted phenols and the modified Hammett parameters  $\sigma_m^+$ .

coefficient of 0.98. The similar correlation between the  $\sigma_m^+$  and BDE(O-H) values for the 10 *meta* substituted phenols (see Table 3) is shown in Figure 5. Here the  $\sigma_m^+$  value for the  $-\text{OCH}_3$  group (marked by red up-triangle in Figure 5) is significantly higher than that expected.

The equations obtained from such correlations of the  $\sigma^+$  values with *para* and *meta* (except the  $-\text{OCH}_3$  group) are as follows:

$$\text{BDE(O-H)} = 86.38 + 6.05\sigma_p^+ \quad (3)$$

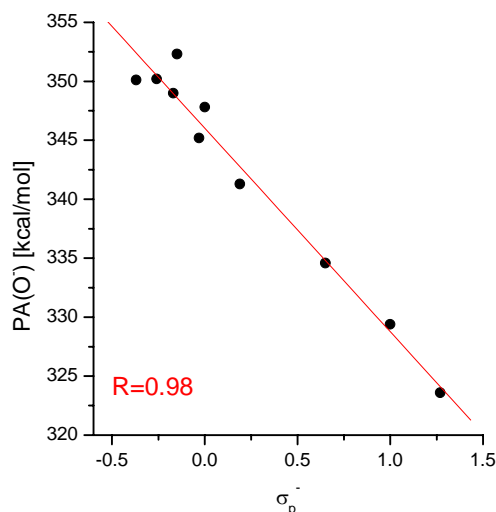
$$\text{BDE}(\text{O-H}) = 87.24 + 4.26\sigma_m^+ \quad (4)$$

These equations can be used to predict new BDE(O-H) values (in kcal/mol) for the *meta* and *para* substituted phenols from their  $\sigma^+$  values or vice versa.

### B. Correlation of Hammett's parameter with Proton Affinity [PA(O<sup>-</sup>)]

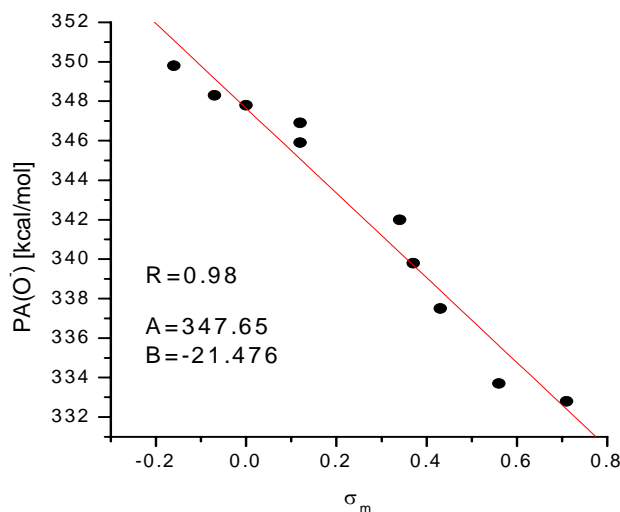
It has been demonstrated that the substituent effects in phenoxide ions in solution and gas-phase are linearly related [20]. Thus Hammett's substituent constants can be used in the correlation study with the gas-phase PA values of phenoxide ions. However, it is argued that the regular substituent constants ( $\sigma$ ) are not generally applicable to systems with a direct conjugation between the substituent and the reaction center. Thus a different set of parameters ( $\sigma_p^-$ ) has been proposed for systems where a permanent negative charge on the reaction center can be resonance stabilized by a substituent [27]. The  $\sigma_p^-$  parameters have been determined mainly from the aqueous acidities of phenols and from the aqueous basicities of anilines. We have used the PA values of the substituted phenoxide ions as the theoretical descriptors to correlate with the  $\sigma_p^-$ .

Figure 6 displays the correlation between the PA values of 10 *para* substituted phenoxide ions listed in Table 4 and  $\sigma_p^-$ . The PA values are well correlated with the  $\sigma_p^-$  constants, with a correlation coefficient of 0.98. It may be worth noting that the correlation between  $\sigma_p$  and PA values was less impressive (R=0.95) and the electron withdrawing substituents deviated most from the correlation line.



**Figure 6.** The correlation between the proton affinities (PA) of *para* substituted phenoxide ions and the modified Hammett parameters  $\sigma_p^-$ .

The similar correlation between the PA values for the *meta* substituents (see Table 5) and the  $\sigma_m$  values are shown in Figure 7. Once again, the correlation between the two is found to be rather good.



**Figure 7.** The correlation between the proton affinities (PA) of *meta* substituted phenoxide ions and the modified Hammett parameters  $\sigma_m$ .

The correlation equations obtained for the *para* [Eqn.(5)] and *meta* [Eqn.(6)] substituents are given below,

$$\text{PA}(\text{O}^-) = 346.03 - 17.26\sigma_p^- \quad (5)$$

$$\text{PA}(\text{O}^-) = 347.65 - 21.48\sigma_m \quad (4)$$

These equations can be used to derive the  $\sigma$  values from the calculated PA values (in kcal/mol) for substituents for which their  $\sigma$  values are not yet known and vice versa.

## V. Conclusions

The (RO)B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) method can be used for the calculation of accurate O-H bond dissociation energy. The method gives almost the same BDE(O-H) values for substituted phenols as obtained from the (RO)B3LYP/6-311+G(2d,2p)/AM1 method [19]. Thus the latter method may be useful for the larger systems. Strong electron withdrawing groups, both at the *para* and *meta* positions, increase the O-H bond strength from that in the unsubstituted phenol molecule. The electron donating group at the *para* position reduces the O-H bond strength of phenol, whereas the same at the *meta* position does not have any strong effect on the BDE(O-H). The F and Cl should be considered as borderline groups, because they behave as electron-donating group at the *para* position and electron withdrawing group at the *meta* position of phenol. It has been shown that accurate PA values of substituted phenoxide ions can be obtained from the B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) procedure. The electron withdrawing groups increase the acidity of the substituted phenol from that of the parent phenol molecule. On the other hand, the effect of electron donating groups depends upon the position of substitution. Good correlations have been

observed between Hammett's substituent constants and BDE(O-H) values of substituted phenols and also between Hammett's substituent constants and PA values for phenoxide anions. Similar studies on substituted benzoic acids have produced many interesting results, which will be published elsewhere.

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