A Computational Analysis of Substituent Effects on the O−H Bond Dissociation Energy in Phenols: Polar Versus Radical Effects

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Abstract: O−H bond dissociation energies (BDEs) of phenol, *p*-aminophenol, and *p*-nitrophenol have been computed using ab initio and density functional theory (DFT) methods. The MP2 and MP4 methods consistently overestimate the absolute BDEs but provide reasonable relative BDEs. Spin projected MP2 and MP4 energies are not able to reproduce the substituent effects on the BDE. The BLYP and B3LYP DFT methods provide more reliable and economical approaches for prediction of phenol BDEs. B3LYP/6-31G** computed ΔBDEs for 10 substituted phenols have been compared with values determined by different experimental approaches. The computed values are in most cases within the uncertainty of the measurements. It is shown that the substituent effects on the BDEs can be interpreted in terms of polar and radical stabilization. The polar stabilization is found to be related to the ability of the substituent to delocalize the lone pair on the phenol oxygen. The radical stabilization is dependent on the degree of spin delocalization. A method for estimating relative polar and radical stabilization energies based on computed electrostatic potentials and spin densities is presented.

Introduction

Phenoxyl radicals are important intermediates in many biological and industrial processes and have therefore been studied extensively.[1] In particular, their importance in relation to the antioxidant activity of phenols has led to an increased interest in these systems in recent years. Some recent studies have dealt with substituent effects on the kinetics of electron-transfer reactions of phenoxyl radicals[2,3] and solvent effects on the kinetics of hydrogen abstraction reactions from phenols.[4] The reactive nature of the phenoxyl radicals has precluded direct structure determinations by experimental methods. However, considerable information about these species has been gained from numerous electron paramagnetic resonance[5−7] (EPR) and vibrational spectroscopy studies.[8−10] The phenoxyl radical has also been studied by high level ab initio[11,12] and density functional theory[13] (DFT) methods. These studies have provided detailed information about the structure, bonding, vibrational force field, and spin density distribution of this radical.

High level ab initio methods have also been used to investigate substituent effects on the structure and vibrational spectra.[11]

$$PhOH \rightarrow PhO^{\bullet} + H^{\bullet} \qquad (1)$$

The energetics for the homolytic O−H bond dissociation in phenol (reaction 1) has been studied experimentally both in the gas phase and in different solvents.[14] A number of studies have investigated the substituent effects on the O−H bond dissociation energy (BDE).[15−19] These studies have all been conducted in solution, and the relative gas phase BDEs have been estimated based on the assumption that the difference in the solvation free energy between the phenol and its radical is independent of substitution. To our knowledge, no high level ab initio or DFT study of absolute or relative BDEs has been presented so far.

It has been suggested that substituent effects on BDEs in aromatic systems can be divided into polar and radical contributions.[18,20−25] The polar effect is the substituent stabilization of mainly the parent molecule and includes both inductive and resonance stabilization. It is expected to be linear

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(1) Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Biology and Medicine*, 2nd ed.; Oxford University Press: Oxford, Great Britain, 1989.

(2) Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E.; Merényi, G. *J. Phys. Chem.* **1993**, *97*, 8229.

(3) Jin, F.; Leitich, J.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1583.

(4) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966.

(5) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 213.

(6) Dixon, W. T.; Moghimi, M.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1713.

(7) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(8) Beck, S. M.; Brus, L. E. *J. Chem. Phys.* **1982**, *76*, 4700.

(9) Johnson, C. R.; Ludwig, M.; Asher, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 905.

(10) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1988**, *92*, 5129.

(11) Liu, R.; Zhou, X. *J. Phys. Chem.* **1993**, *97*, 9613.

(12) Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *100*, 5023.

(13) Quin, Y.; Wheeler, R. A. *J. Chem. Phys.* **1994**, *102*, 1689.

(14) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737 and references therein.

(15) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 4722.

(16) Mulder, P.; Saastadt, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090.

(17) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

(18) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

(19) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1567.

(20) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.

(21) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221 and references therein.

(22) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363.

(23) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.

(24) Nau, W. M.; Harrer, H. M.; Adam, W. *J. Am. Chem. Soc.* **1994**, *116*, 10972.

(25) Wu, Y.-D.; Wong, C.-L.; Chan, K. W. K. *J. Org. Chem.* **1996**, *61*, 746.

with the regular Hammett constant (σ), σ^0, σ^+, or σ^-, depending upon the nature of the parent molecule. The radical effect is considered to be the stabilization of the radical due to spin delocalization of the unpaired electron. A number of substituent scales have also been devised for quantification of this latter effect.[21] However, the scales differ considerably depending upon the type of system used for defining them, indicating that substituent effects on radical stability are not generally transferable between different systems.[21,26] Bordwell and co-workers have interpreted the relative BDEs (ΔBDEs) of phenols in terms of polar and radical stabilization effects.[18,23] In their article of 1991,[18] they suggest that the polar effect is the stabilization of the phenol due to delocalization of the lone pair on the oxygen. Electron-withdrawing substituents in the para position are good at delocalizing the lone pair, which explains their bond strengthening effects. In their 1994 article, Bordwell et al.[23] give a different interpretation of the polar effect: Electron withdrawing substituents are considered to withdraw electron density from the O−H bond and thereby increasing its strength. Electron donating substituents have the opposite effect.

Bordwell et al.[23] estimate the relative polar and radical stabilization energies from correlations between BDE and σ_m and σ_p. A linear correlation between BDE and σ_m is interpreted as a zero radical stabilization for meta substituents. When they plot BDE versus σ_p for para-substituted phenols, they find that the electron-withdrawing substituents follow the same line as the BDE−σ_m correlation, while phenols with resonance donating substituents, e.g., OH and NH₂, have lower BDEs than predicted by the meta line, indicating that these latter substituents are stabilizing the radical. The differences between the actual BDEs and the BDEs predicted from the meta line are interpreted as the relative radical stabilization energies. It should be noted that the Bordwell et al.[23] conclusions that the substituent effects of para acceptors mainly are of polar character while para donors show strong radical stabilizing effects are not in conflict with the linear relationships between BDE and σ_p^+ that have been reported.[16,17,19] Since the polar stabilization of the phenol is expected to be linear with σ_p or even more likely σ_p^- (because of the direct conjugation between the substituent and the oxygen lone pair), the fact that σ_p^+ give the best correlation with BDE can be interpreted as large radical stabilizing effects of the donor substituents.

We have had two objectives with the current study: The first has been to investigate the performance of some standard electronic structure methods, both ab initio and density functional theory (DFT), for prediction of absolute and relative BDEs of phenols. Our second objective has been to investigate how the substituents affect the electronic structures of the phenol and the radical and how the electronic effects correlate with the BDEs.

Methods

Optimized geometries and energies have been computed at the HF/6-31G* and at the MP2/6-31G* levels of theory. The spin unrestricted approaches, UHF and UMP2, were used for the radicals. Previous calculations on the phenoxyl radical have shown that the MP2/6-31G* level provides accurate geometries.[13] Additional energies have been computed at the MP2/6-311G(2d,p) and MP4/6-31G* levels using the MP2/6-31G* geometries. The frozen core approximation was used in all Møller−Plesset (MP) calculations. To investigate the influence of spin contamination on the UMP2 and UMP4 energies, an approximate spin projector formalism was used for annihilation of up to the first

four spin contaminants to the doublet wave function.[27,28] The resulting energies are labeled PMP2(n) and PMP4(n), respectively. n refers to the number of spin contaminants that have been annihilated. PMP2-(1) and PMP4(1) are in the literature commonly referred to as PMP2 and PMP4, respectively. For comparison, the energies of phenol and the phenoxyl radical were also calculated at the CCSD(T)/6-31G*// MP2/6-31G* level of theory. The unrestricted coupled cluster approach has been shown to be much less affected by spin contamination than the perturbational (MP) methods.[29]

Optimized geometries and energies have also been computed using density functional theory within the Kohn−Sham formalism. Two different exchange-correlation functional combinations were used, BLYP and B3LYP. BLYP is a combination of Becke's gradient corrected exchange functional of 1988[30] with the gradient corrected correlation functional of Lee, Yang, and Parr.[31] B3LYP,[32] which is a modification of Becke's three-parameter exchange-correlation functional,[33] does in addition include a part of the Hartree−Fock exchange energy. The basis sets used for the geometry optimizations with BLYP and B3LYP were 6-311G** and 6-31G**, respectively. B3LYP/6-311G(2d,p) energies were calculated at the B3LYP/6-31G** geometries. Vibrational frequencies within the harmonic approximation have also been calculated at the B3LYP/6-31G** level of theory. The BLYP and B3LYP functionals have been shown to provide accurate geometries, vibrational frequencies, and spin densities for the phenoxyl radical.[13]

The Gaussian 94[34] suite of programs was used for all ab initio and DFT computations. A locally developed code was used to compute electrostatic potentials, electron densities, and spin densities from the B3LYP/6-31G** Kohn−Sham orbitals.

Results and Discussion

Computations of BDEs. The absolute BDE of phenol and the ΔBDEs of *p*-aminophenol and *p*-nitrophenol calculated at different levels of theory are listed in Table 1 together with experimental values. The computed BDEs refer to the differences in electronic energies, D_e, without addition of the zero-point vibrational energy. The experimental BDE for phenol (87.0 kcal/mol) has in Table 1 been corrected to 0 K, and the zero-point energy has been subtracted to facilitate comparison with the theoretical results. The temperature correction and the zero-point energy correction were computed from the B3LYP/6-31G** frequencies. Vibrational corrections on ΔBDEs were found to be small, i.e., in all cases below 0.35 kcal/mol, and have therefore been omitted in Tables 1 and 2. As expected from the neglect of electron correlation, the UHF method gives absolute BDEs that are too low compared to experiment. The estimate of the ΔBDE for *p*-nitrophenol is in good agreement with experiment, while the value for *p*-aminophenol is much to low. Before discussing the MP2 and MP4 computations, it should be noted that the UHF wave functions of the phenoxyl radicals are highly spin contaminated, i.e., the values of the spin operator $\langle S^2 \rangle$ are significantly higher than 0.75, the expected value of a pure doublet wave function. At the UHF/6-31G* level the $\langle S^2 \rangle$ values are 1.34, 1.30, and 1.18 for the *p*-nitrophenoxyl, phenoxyl, and *p*-aminophenoxyl radicals, re-

(26) Hansch, C.; Leo, A.; Hoekman, D. *Exploring QSAR: Hydrophobic, Electronic, and Steric Constants*; American Chemical Society: Washington, DC, 1995.

(27) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.
(28) Schlegel, H. B. *J. Phys. Chem.* **1988**, *92*, 3075.
(29) Chen, W.; Schlegel, H. B. *J. Chem. Phys.* **1994**, *101*, 5957.
(30) Becke, A. D. *J. Chem. Phys.* **1988**, *96*, 2155.
(31) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *33*, 3098.
(32) Stephens, P. J.; Devlin, F. J.; Chablovski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Gonzalez, C.; Stewart, J. J. P.; Head-Gordon, M.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

Table 1. Absolute and Relative O−H Bond Dissociation Energies[a] (D_e) Calculated at Different Levels of Theory

	BDE phenol	ΔBDE[b]	
		p-NO$_2$	*p*-NH$_2$
HF/6-31G*//HF/6-31G*	53.2	-4.5	2.8
MP2/6-31G*//MP2/6-31G*	106.4	-5.2	8.8
PMP2(4)/6-31G*//MP2/6-31G*	87.5	-4.2	5.4
MP2/6-311G(2d,p)//MP2/6-31G*	115.9	−4.8	9.6
PMP2(1)/6-311G(2d,p)//MP2/6-31G*	92.1	−2.9	4.2
MP4/6-31G*//MP2/6-31G*	97.6	−4.8	7.3
PMP4(4)/6-31G*//MP2/6-31G*	87.0	−4.0	4.3
CCSD(T)/6-31G*//MP2/6-31G*	84.1		
B3LYP/6-31G**//B3LYP/6-31G**	89.5	−4.4	8.6
B3LYP/6-311G(2d,p)//B3LYP/6-31G**	89.7	−4.2	8.8
BLYP/6-311G**//BLYP/6-311G**	86.3	−3.9	9.6
exp	94.5 (87)[c]	−6.4,[d] −4.4[e]	12.7,[d] 12.6[e]

[a] All values are in kcal/mol. [b] ΔBDE = BDE(C$_6$H$_5$OH) − BDE(X-C$_6$H$_4$OH). [c] The experimental bond dissociation energy, which is the recommended gas phase value of ref 14, has been corrected for zero-point vibrational energy and to 0 K. The vibrational correction was computed from the B3LYP/6-31G** frequencies. The uncorrected value is given in parentheses. [d] Calculated from the one-electron reduction potential of the phenoxyl radical measured by pulse radiolysis and the pK_a of the phenol in aqueous solution using Hess's law.[17] [e] Calculated from the one-electron reduction potential of the phenoxyl radical measured by cyclic voltammetry and the pK_a of the phenol in DMSO using Hess's law.[18]

Table 2. Comparison of B3LYP/6-31G** Computed ΔBDEs for Phenols with Experimental Values (in kcal/mol)

phenol	B3LYP 6-31G**	exp			
		a	*b*	*c*	*d*
p-NMe$_2$	9.5	9.6	14.1		
p-NH$_2$	8.6	12.6	12.7		
p-OH	5.4	8.3	8.0		
p-MeO	5.5	5.3	5.6	5.9	4.3
p-Me	1.8	1.1	2.1		1.8
p-Cl	0.7	−0.4	0.6	−0.4	
H	0	0	0	0	0
m-Cl	−1.2	−2.0			
p-CF$_3$	−2.6	−5.5		−3.2	
p-CN	−2.3	−4.4	−4.7	> −5.0[e]	
p-NO$_2$	−4.4	−4.5	−6.0		

[a] Calculated from the one-electron reduction potential of the phenoxyl radical measured by cyclic voltammetry and the pK_a of the phenol in DMSO using Hess's law.[18] [b] Calculated from the one-electron reduction potential of the phenoxyl radical measured by pulse radiolysis and the pK_a of the phenol in aqueous solution using Hess's law.[17] [c] Photoacoustic calorimetric measurements in benzene.[16] [d] From rate constants for reactions of phenols with hydroperoxides in chlorobenzene.[15] [e] Reference 60.

spectively. The corresponding values after annihilation of the quartet contribution to the wave function are 1.07, 1.02, and 0.91. It is necessary to annihilate also the sextet contribution to get a $\langle S^2 \rangle$ value that is close to 0.75, the value for a pure doublet state. The high spin contamination is also reflected in the computed energies. The BDEs computed from the projected MP2 and MP4 energies are consistently lower than the experimental phenol BDEs, while the corresponding unprojected values are consistently higher. The MP4/6-31G* value, 97.6 kcal/mol, and the PMP2(4)/6-311G(2d,p) value, 92.1 kcal/mol, are both close to the experimental value, 94.5 kcal/mol. However, the good agreement at the MP4/6-31G* level is most likely due to a cancellation of the effects due to a limited basis set and spin contamination. Since basis set effects have been shown to be transferable between correlated methods, and particularly between MP2 and MP4,[35] it is expected that going from MP4/6-31G* to MP4/6-311G(2d,p) would raise the computed BDE by about as much as going from MP2/6-31G* to MP2/6-311G(2d,p). This would give a MP4/6-311G(2d,p) value of 107.1 kcal/mol, which is almost 13 kcal/mol higher than experiment. The CCSD(T)/6-31G* value is 84.1 kcal/mol, and by adding the MP2/6-311G(2d,p) basis set correction from

above we end up with 93.6 kcal/mol, in good agreement with experiment. If we look at the calculated ΔBDEs of *p*-aminophenol and *p*-nitrophenol, we see that the values from the PMP2(*n*) and PMP4(*n*) calculations are of lower magnitude than the corresponding unprojected energies and lower than the experimental energies. We found the commonly used approach to annihilate only the first spin contaminant [PMP2(1) and PMP4(1)] to be particularly bad for prediction of ΔBDEs. The unprojected MP2 and MP4 estimates of the ΔBDE of *p*-nitrophenol are all within 0.4 kcal/mol and in good agreement with the experimental values. For *p*-aminophenol, there are slightly larger differences between the different methods, and the computed values are all lower than the experimental values. However, it should be noted that the two experimental values are both determined from measurements in solution and can be affected with some errors. Table 1 clearly shows that the predicted ΔBDE for *p*-aminophenol varies much more with the computational method than does the value for *p*-nitrophenol. Since substituent effects on closed shell aromatic molecules have been shown to be well predicted already at the RHF level,[36] while radicals require highly correlated methods,[11] we expect that this behavior most likely is an effect of the fact that the electronic structures of the *p*-nitrophenoxyl radical and the phenoxyl radical are more similar than the electronic structures of the *p*-aminophenoxyl radical and the phenoxyl radical. We further conclude that the unprojected MP2 and MP4 methods overestimate the absolute BDEs but seem capable of predicting reasonable ΔBDEs. The projected methods on the other hand are not able to reflect the substituent effects on the BDEs in these systems. Accurate ab initio predictions of absolute BDEs would therefore require going beyond the perturbational methods and using methods like CCSD(T) with large basis sets.

Rigorous determination of spin contamination is considerably more difficult for DFT methods than for the UHF method.[37] In the Gaussian 94 program,[34] the value of $\langle S^2 \rangle$ is computed from a Slater determinant constructed from the Kohn−Sham orbitals. The obtained $\langle S^2 \rangle$ value is not that of the real system but rather that of a system of non-interacting electrons with the same ground state density.[37] However, it has been shown that this approach provides reasonable estimates of spin contamination.[13,37−39] The $\langle S^2 \rangle$ values for our B3LYP/6-31G** and BLYP/6-311G** calculations on the phenoxyl radicals were all found to be below 0.80, which is in good agreement with the

(35) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(36) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.
(37) Wang, J.; Becke, A. D.; Smith, V. H. *J. Chem. Phys.* **1995**, *102*, 3477.

value of a pure doublet state, 0.75. Earlier studies have also shown that the spin contamination in DFT calculations generally is low even when the methods are applied to aromatic radicals or other systems with a large degree of spin delocalization.[13,38–42] The B3LYP/6-31G** calculated phenol BDE is only 5.0 kcal/mol below the experimental value. The BLYP/6-311G** value deviates slightly more, 8.2 kcal/mol. For the ΔBDEs, the DFT methods are in good agreement with the unprojected MP2 and MP4 calculations and in the case of the ΔBDE of *p*-nitrophenol also with experiment. The basis set effects on computed BDEs are much smaller for the B3LYP method than for the MP2 method. Comparison of the B3LYP results with the 6-31G** and the 6-311G(2d,p) basis sets indicates that the basis set effects on phenol BDEs are almost converged already for the 6-31G** basis set. These results show that the B3LYP/6-31G** approach may provide an accurate and economical method for predicting BDEs of phenols. We therefore decided to further investigate the performance of this method.

Table 2 lists B3LYP/6-31G** calculated ΔBDEs and experimental ΔBDEs, determined by four different methods, for 10 substituted phenols. There is a good overall agreement between computed and experimental ΔBDEs. The differences are in most cases within the uncertainty of the measurements (1–2 kcal/mol). However, there seems to be a tendency for the computations to underestimate the substituent effects of strong electron-donating substituents, e.g., OH and NH_2. In the case of NMe_2, it is remarkable that the two experimental values differ by as much as 4.5 kcal/mol. The lower value, determined by Bordwell and Cheng,[18] is in good agreement with our computed value. However, based on the results for OH and NH_2, it seems more likely that the value of Lind et al.[17] is correct.

Substituent Effects on the O−H Bond. A commonly used concept in chemistry is that the bond dissociation energy can be correlated to properties of the bond itself.[43,44] For example, for a given type of bond in different environments, the bond strength generally increases with increasing values of its force constant, k, and decreasing values of the bond length, R.[44] A bond order equation by Politzer,[45]

$$\text{bond order} = \text{constant } (k/R)^{1/2} \qquad (2)$$

has been shown to predict the right trend in bond strengths also in cases where k increases with R.[46] Our computed O−H force constants and O−H bond lengths for the phenols show very small variations. The bond length varies less than 0.002 Å and the force constant less than 1%. Although the variations in the force constant are small, there is a definite trend that it increases with increasing electron-donating power of the substituents. Based on these variations, we would therefore predict an opposite trend in the BDE than the observed.

Another property that has been related to the bond strength is the electron density in the bonding region. As mentioned in the introduction, Bordwell and co-workers have also suggested

that the increased O−H BDEs of the phenols with electron-withdrawing substituents is a consequence of their ability to decrease the electron density in the O-H bond.[23] However, this does not seem like a plausible explanation to us, since theoretical studies show that the bond strength increases with increasing electron density in the bonding region rather than the opposite.[47–49] Bader has defined a bond order index in terms of the electron density minimum (ρ_b) along the bond path.[48] The bond order for a given type of bond in different chemical environments increases linearly with ρ_b. Politzer and co-workers have shown that there exists a general linear relationship between the bond dissociation energy and the square of ρ_b.[49] We computed ρ_b for the OH bonds in the substituted phenols. As expected, ρ_b increase with increasing electron donating ability of the substituents. However, the variations in ρ_b are very small: less than 0.6% when going from the strongest electron acceptor (NO_2) to the best donor (NMe_2). Based on Politzer's relationship[49] we would, for example, predict the BDE of *p*-aminophenol to be 0.6 kcal/mol larger than the BDE of *p*-nitrophenol, which clearly is in contradiction with both the computational and experimental values of Table 2. We conclude that we have found no indications that the observed trends in the BDEs of the phenols can be linked to changes in the properties of the bond itself.

Delocalization of the Oxygen Lone Pair. Another explanation, proposed by Bordwell and Cheng,[18] for the polar effect on the BDEs of the phenols is that it is due to delocalization of the oxygen lone pair on the phenol. To investigate how the delocalization varies with the substituent, we decided to calculate the spatial minima in the electrostatic potential associated with the oxygen for the substituted phenols. The electrostatic potential was computed according to its rigorous definition:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|R_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') \, d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (3)$$

where Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electronic density function of the molecule. $V(\mathbf{r})$ is a real physical property, which can be determined both by experimental and theoretical methods.[50] It has been shown that spatial minima in $V(\mathbf{r})$ (V_{min}) associated with heteroatoms can be used to characterize the strengths and positions of lone pairs.[51,52] We have shown that V_{min} is especially suited for monitoring polar substituent effects in aromatic systems.[53,54] For example, the oxygen V_{min} of both para-substituted phenols and phenoxide anions have been shown to correlate with the σ_p^- substituent scale (which has been derived from phenol solution acidities) and with phenol gas phase acidities.[54] In Figure 1 we have plotted the B3LYP/6-31G** computed oxygen V_{min} for the phenols versus their computed ΔBDEs. There is a linear correlation between V_{min} and ΔBDE for the phenols with

(38) Baker, J.; Scheiner, A.; Andzelm, J. *Chem. Phys. Lett.* **1993**, *216*, 380.

(39) Laming, G. J.; Handy, N. C.; Amos, R. D. *Mol. Phys.* **1993**, *80*, 1121.

(40) Adamo, C.; Barone, V.; Fortunelli, A. *J. Chem. Phys.* **1995**, *102*, 384.

(41) Fox, T.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 2950.

(42) Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261.

(43) Pauling, L. *The Nature of the Chemical Bond*, 3rd. ed.; Cornell University Press: Ithaca, NY, 1960.

(44) Cotrell, T. L. *The Strengths of Chemical Bonds*, 2nd ed.; Butterworth Scientific Publications: London, Great Britain, 1958.

(45) Politzer, P. *J. Chem. Phys.* **1969**, *50*, 2780.

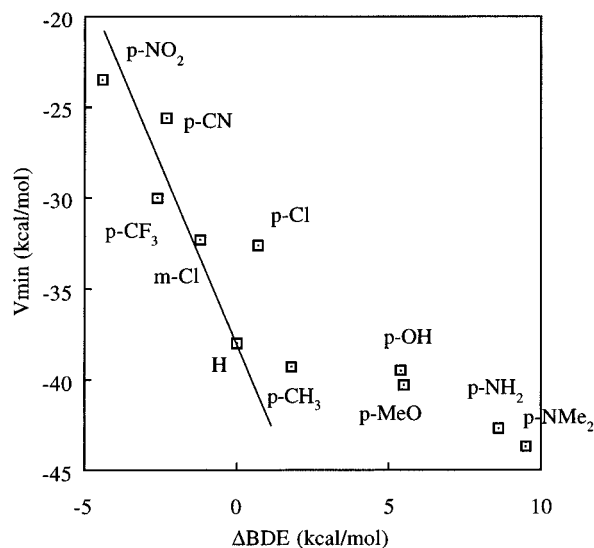(46) Politzer, P.; Habibollahzadeh, D. *J. Chem. Phys.* **1993**, *98*, 7659.

(47) Levine, I. A. *Quantum Chemistry*, 4th ed.; Prentice Hall, Inc.: Englewoods Cliffs, NJ, 1991; p 452 and references therein.

(48) Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, 1990.

(49) Wiener, J. J. M.; Murray, J. S.; Grice, M. E.; Politzer, P. *Mol. Phys.* **1997**, *90*, 425.

(50) *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981.

(51) Murray, J. S.; Brinck, T.; Grice, M. E.; Politzer, P. *J. Mol. Struct. (Theochem)* **1992**, *256*, 29.

(52) Politzer, P.; Murray, J. S. In *Chemistry of the Functional Groups, Supplement E: The Chemistry of Hydroxyl, Ether and Peroxide Groups*; Patai, S., Ed.; Wiley: Chichester, 1993; Vol. 2.

(53) Haeberlein, M.; Murray, J. S.; Brinck, T.; Politzer, P. *Can. J. Chem.* **1992**, *70*, 2209.

(54) Haeberlein, M.; Brinck, T. *J. Phys. Chem.* **1996**, *100*, 10116.

Figure 1. Plot of oxygen V_{min} versus computed ΔBDE for phenols.

Figure 2. Plot of oxygen ρ^S_{max} for phenoxyl radicals versus computed ΔBDE for phenols.

Figure 3. Predicted ΔBDE versus computed ΔBDE for phenols. The correlation equation used for predicting ΔBDE is given by ΔBDE $= -0.294\Delta V_{min} - 0.102\rho^S_{max}$.

electron-accepting substituents. However, for the electron-donating substituents, V_{min} changes more slowly, which does not reflect the large changes in the ΔBDE. This indicates that the oxygen lone pair stabilization is important for determining the ΔBDEs of phenols with electron-accepting substituents, while other effects dominate for electron-donating substituents. Our results are in qualitative agreement with Bordwell et al.[23] in that they also proposed that the ΔBDE of phenols with electron-accepting substituents are dominated by polar effects.

   Radical Stabilization. To investigate the importance of the radical effect, i.e., the stabilization of the radical due to spin delocalization of the unpaired electron, on the ΔBDE, we have computed the surface maxima in the spin density associated with the oxygen of the phenols. The spin density, $\rho^S(\mathbf{r})$, is defined as

$$\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \tag{4}$$

where $\rho^\alpha(\mathbf{r})$ and $\rho^\beta(\mathbf{r})$ are the densities of the electrons with α spin and β spin, respectively. We computed $\rho^S(\mathbf{r})$ on molecular surfaces defined in accordance with Bader et al.[55] by a constant contour of the total electron density of 0.002 au. By calculating the spin density on a surface that is significantly removed from the nuclei the spin density will emphasize the spin delocalization of the valence electrons, which is expected to be most important in relation to chemical reactivity. The more common approach of computing $\rho^S(\mathbf{r})$ at the positions of the nuclei has the disadvantage of not reflecting the spin polarization of the π-electrons, since these generally have zero densities at the nuclei.

   In Figure 2 we have plotted the B3LYP/6-31G** computed oxygen ρ^S_{max} for the phenoxyl radicals versus their computed ΔBDEs. ρ^S_{max} refer in all cases to the largest local maximum in $\rho^S(\mathbf{r})$ which is associated with the oxygen from which the hydrogen has been abstracted. There is a linear correlation between ρ^S_{max} and the ΔBDE for the phenols with electron-donating substituents. This shows that the ΔBDEs of these compounds mainly are determined by the stabilization of the radical due to the delocalization of the unpaired electron. For the phenols with electron-accepting substituents, there are smaller variations in ρ^S_{max}, and there is no correlation between ρ^S_{max} and ΔBDE.
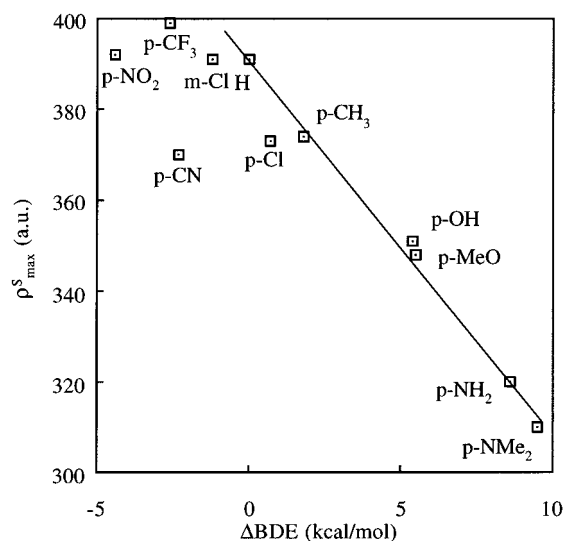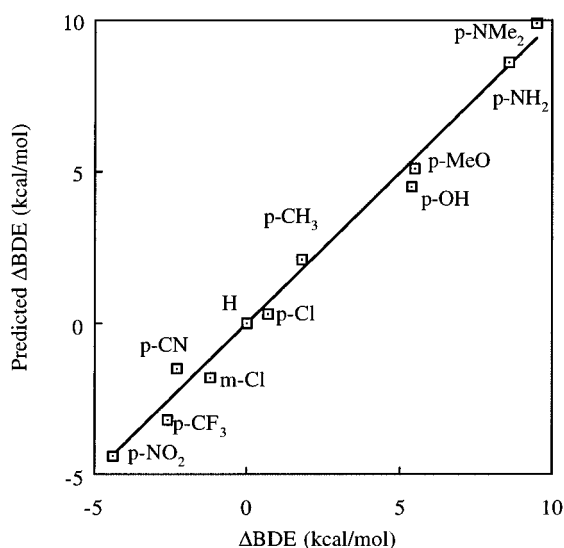
   (55) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968.

   Relative Polar and Radical Stabilization Energies. The linear correlations between V_{min} and ΔBDE for electron-accepting substituents and ρ^S_{max} and ΔBDE for electron-donating substituents prompted us to investigate if an equation of the following type could correlate the ΔBDEs of all phenols:

$$\Delta BDE = a\Delta V_{min} + b\Delta\rho^S_{max} \tag{5}$$

where $\Delta V_{min} = V_{min}(X\text{-}C_6H_4OH) - V_{min}(C_6H_5OH)$ and $\Delta\rho^S_{max} = \rho^S_{max}(X\text{-}C_6H_4O^\bullet) - \rho^S_{max}(C_6H_5O^\bullet)$. We found a very good relationship with a correlation coefficient of 0.993 (see Figure 3). $-a\Delta V_{min}$ can be interpreted as the relative stabilization energy of the phenol and $b\Delta\rho^S_{max}$ as the relative stabilization energy of the radical. We will call these two quantities ΔPSE (the relative polar stabilization energy) and ΔRSE (the relative radical stabilization energy), respectively.

   In Table 3 we have listed our calculated ΔPSE and ΔRSE for the 10 substituted phenols. The ΔBDEs of the phenols with electron-withdrawing substituents are mainly determined by the polar stabilization of the parent molecules. The polar effect is generally of smaller magnitude for the electron-donating substituents, but it is in all cases found to destabilize the phenol.

Table 3. B3LYP/6-31G** Computed Molecular Properties, Stabilization Energies, and Bond Dissociation Energies

phenol	ΔV_{min} (kcal/mol)	$\Delta\rho^S_{max}$ (au)	ΔPSE^a (kcal/mol)	ΔRSE^b (kcal/mol)	$\Delta BDE(pred)^c$ (kcal/mol)	ΔBDE (kcal/mol)
p-NMe$_2$	−5.7	−81	−1.7	8.2	9.9	9.5
p-NH$_2$	−4.7	−71	−1.4	7.2	8.6	8.6
p-MeO	−2.3	−43	−0.7	4.4	5.1	5.5
p-OH	−1.5	−40	−0.4	4.1	4.5	5.4
p-Me	−1.3	−17	−0.4	1.7	2.1	1.8
p-Cl	5.4	−18	1.6	1.8	0.2	0.7
H	0	0	0	0	0	0
m-Cl	5.7	0	1.7	0.0	−1.7	−1.2
p-CN	12.4	−21	3.6	2.1	−1.5	−2.3
p-CF$_3$	8.0	8	2.4	−0.8	−3.2	−2.6
p-NO$_2$	14.5	1	4.3	−0.1	−4.4	−4.4

^{a} $\Delta PSE = 0.294\Delta V_{min}$. ^{b} $\Delta RSE = -0.102\Delta\rho^S_{max}$. ^{c} $\Delta BDE = -\Delta PSE + \Delta RSE$.

For these substituents, it is instead the spin delocalization effect that dominates and leads to radical stabilization. The radical effect is much smaller for the electron-withdrawing substituents. CF$_3$ is the only substituent that has a significant radical destabilizing effect. This substituent has also been shown to be destabilizing in other radical systems.[56,57] NO$_2$ has an essentially zero radical effect which is in great contrast to carbon-centered radicals where most radical scales show it to be stabilizing in the para position.[21] This discrepancy can be rationalized in terms of the greater electronegativity of oxygen compared to carbon. The difference in BDE between *m*-chlorophenol and *p*-chlorophenol is due to the larger stabilization of the *p*-chlorophenoxyl radical compared to the *m*-chlorophenoxyl radical. This was confirmed by a comparison of the computed absolute electronic energies; the meta-substituted radical has a higher energy than the para-substituted radical, while the parent molecule energies are very similar.

As was discussed in the introduction, experimentally determined ΔBDEs for substituted phenols have been found to correlate linearly with the σ^+ substituent constant.[16,17,19] A similar relationship does also exist between our computed ΔBDEs from Table 2 and Brown's σ^+ constant;[58] the linear correlation coefficient is 0.992. This relationship is not in contradiction with our conclusions regarding the relative stabilizations of the parent molecules and the radicals. Because of the direct conjugation between an electron donating reaction center, the OH group, and the substituent, the stabilization of the parent molecule is expected to follow a linear relationship with σ^-. Our computed parent molecule stabilization energies (ΔPSE) follow such a relationship; the correlation coefficient for the ΔPSE vs σ^{-59} relationship is 0.984. Since the σ^- and the σ^+ scales differ in that σ^+ predicts relatively larger substituent effects for resonance donors (e.g., OCH$_3$, OH and NH$_2$) and relatively smaller substituent effects for resonance attractors (e.g., CN and NO$_2$), the overall relationship between ΔBDE and σ^+ can be explained by an extra stabilization of the radical by electron donating substituents.

Summary and Conclusions

We have found that the MP2 and MP4 methods overestimate the absolute BDEs of phenols but provide reasonable ΔBDEs.

The overestimation seems to be an effect of the high degrees of spin contamination in the reference UHF wave functions. The use of spin projection to annihilate the spin contaminants decreases the predicted BDEs. However, the projected MP2 and MP4 methods are not able to reproduce the substituent effects on the BDEs. The DFT computations are much less affected by spin contamination. Particularly, the B3LYP/6-31G** level of theory constitutes a promising approach for prediction of phenol BDEs. Computed ΔBDEs for 10 different substituted phenols have been compared with values determined by different experimental approaches. The computed values are in most cases within the uncertainty of the measurements. However, there seems to be a tendency for the B3LYP/6-31G** approach to underestimate the ΔBDEs of phenols with strong electron-donating substituents.

We have not found any indications that the substituent effects on the BDEs can be related to changes in the properties of the O−H bond. The stabilizing effects of the substituents on the parent molecule appear rather to be connected to their ability to delocalize the oxygen lone pair. We have used computed minima in the electrostatic potential, V_{min}, in the vicinity of the oxygen to quantify the degree of delocalization. The delocalization effect is most pronounced for phenols with electron-withdrawing substituents and is shown to be the dominating factor in determining their ΔBDEs. The ΔBDEs for phenols with electron-donating substituents are found to mainly be determined by the stabilization of the radical due to spin delocalization. We have found the surface spin density maxima (ρ^S_{max}) on the oxygen to be an effective tool for quantification of this effect. A dual parameter relationship, with ΔV_{min} and $\Delta\rho^S_{max}$ as the parameters, correlates the ΔBDEs of all phenols. This relationship has been used to estimate relative polar stabilization energies (ΔPSE) and relative radical stabilization energies (ΔRSE). We have shown that all the investigated electron-donating substituents destabilize the phenol and stabilize the radical although the latter effect is more pronounced. While the electron-withdrawing substituents consistently are stabilizing the phenol, their radical effects are more irregular. The methodology employed in this work could probably be used to differentiate between polar and radical substituent effects in other systems as well. We are currently investigating the substituent effects on the S−H BDE in thiophenols.

(56) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164.
(57) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct. (Theochem)* **1991**, *234*, 303.
(58) Brown, H. C.; Yamamoto, Y. *J. Org. Chem.* **1958**, *80*, 4979.
(59) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.
(60) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430.