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A Density Functional Study of Substituent Effects on the O−H and O−CH_3 Bond Dissociation Energies in Phenol and Anisole

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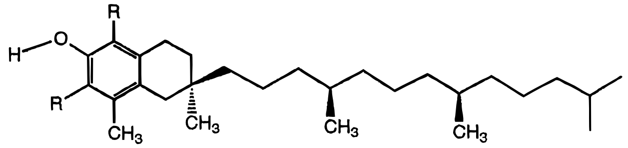
The substituent effects on O−H and O−CH_3 bond dissociation energies for a series of 18 para-substituted phenols (p-XC_6H_4OH) and 11 para-substituted anisoles have been studied using the density functional method in order to understand the origin of these effects. The calculated substituent effects agree well with experimental measurements for phenols but are substantially larger than the reported values for anisoles. Both ground-state effect and radical effect contribute significantly to the overall substituent effect. An electron-donating group causes a destabilization in phenols or anisoles (ground-state effect) but a stabilization in the phenoxy radicals (radical effect), resulting in reduced O−R bond dissociation energy. An electron-withdrawing group has the opposite effect. In most cases, the radical effect is more important than the ground-state effect. There is a good correlation between the calculated radical effects and calculated variations in charge and spin density on the phenoxy oxygen. This supports the concept that both polar and spin delocalization effects influence the stability of the phenoxy radical. While almost every para-substituent causes a stabilization of the phenoxy radical by spin delocalization, electron-donating groups stabilize and electron-withdrawing groups destabilize the phenoxy radical by the polar effect.

Introduction

Phenols are widely used as antioxidants in living organisms and synthetic organic materials.[1−3] For example, vitamin E (**1**) is a chain-breaking antioxidant that interferes with one or more of the propagation steps in autooxidation by atmospheric oxygen.[3,4] It functions by trapping the chain-carrying peroxyl radicals, as shown in eq 1. The O−H bond energy is significantly reduced by the two m-alkyl groups (−R) and the para oxygen. Recently, Ingold showed that the good antioxidant activity of vitamin E is due to the stabilization of the phenoxy radical by the conjugative electron delocalization contributed mainly from the lone pair of the para OR group.[4−5]



1. Vitamin E and derivatives

$$ROO^{\bullet} + ArO\text{-}H \longrightarrow ROO\text{-}H + ArO^{\bullet} \quad (1)$$

The substituent effect on the O−H bond dissociation energy (BDE) has been studied by many research teams.[6−13] Remote substituent effects in phenoxy systems are much larger than in benzyl systems, allowing more accurate measurements. For para-substituted phenols, electron-donating groups such as NR_2, OR, and SR significantly reduce the O−H BDE, while electron-withdrawing groups such as NO_2, CN, COR, and SO_2R have the opposite effect. The substituent effect can be correlated reasonably well with Hammett-type σ^+ parameters. Therefore, it is often assumed that the polar effect is responsible for the remote substituent effect on the O−H BDE of phenols.

This situation contrasts with the substituent effect on benzylic systems, however. For example, both electron-donating and electron-withdrawing groups reduce the BDE of a benzylic C−H bond.[14] This substituent effect cannot be correlated with Hammett-type polar parameters.[15] It has been suggested that a radical spin delocalization effect in the benzyl radical is largely responsible for the reduced benzylic C−H bond energy.[15−17] Thus, several different sets of $\sigma^{\bullet}$ parameters have been

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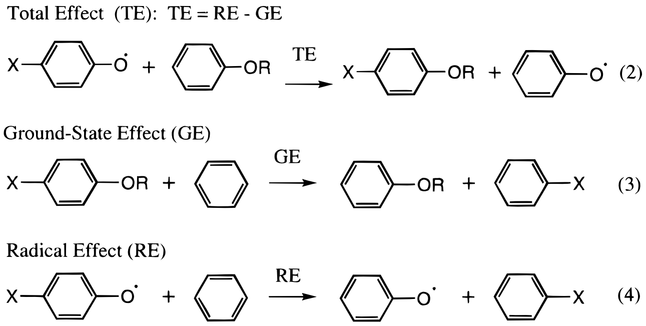
Scheme 1



developed. One intriguing question is whether the radical spin delocalization effect is also involved in the stability of the phenoxy radicals.

Suryan *et al.* used a very-low-pressure pyrolysis technique to study the substituent effect on the rate of anisole $O-CH_3$ homolysis.[18] The BDE of the unsubstituted anisole was determined to be 63.5 kcal/mol,[19] which is much smaller than that of phenol (≈84−88 kcal/mol).[8] The reported substituent effects on the $O-CH_3$ BDE in the para-substituted anisoles (−1.1 to +4.0 kcal/mol, see Table 2)[18] are much smaller than those of substituted phenols (−6.0 to 15.8 kcal/mol, see Table 1).[8] It is not immediately clear why the substituent effects on $O-CH_3$ BDE should be much smaller than those on the O−H BDE.

The substituent effect on the O−R (R = H and CH_3) BDEs can be conveniently calculated by an isodesmic reaction (Scheme 1, eq 2),[20] which gives the relative BDE of a substituted phenol or anisole with respect to the unsubstituted parent species. This substituent effect, which is referred to as the total effect (TE), is comprised of contributions from both a ground-state effect and a radical effect. The ground-state effect (GE), eq 3, effectively gives the interaction between the substituent and the OR group. The radical effect (RE), eq 4, indicates the effect of the substituent on the stability of the phenoxy radical.

The substituent effects on the BDE are often discussed on the basis of the stabilities of radicals (radical effect).[21] Recent evidence suggests that the ground-state effect cannot be ignored.[22,23] Early *ab initio* calculations by Hehre *et al.* suggest that the ground-state effect is within 1.5 kcal/mol for typical electron donors (NH_2, OH, destabilization) or typical electron acceptors (CN, NO_2, stabilization).[20] Recently, Bordwell *et al.* suggested that meta- and para-electron-acceptors increase the O−H BDE of phenol and analogs primarily by stabilizing the ground-state energies.[24] On the other hand, para-donors decrease the BDE of the acidic H−A bond primarily by stabilizing the corresponding radicals and also, to some extent, by raising the ground-state energies in the Ar−OH.

In this paper, we report a density functional study of a series of 18 para-substituted phenols and 11 para-substituted anisoles and quantitatively evaluate the magnitudes of substituent effects on the stabilities of phenol, anisole, and the phenoxy radical. We correlate the calculated substituent effect on the stability of the phenoxy radical with calculated variations in charge and spin density of the phenoxyl oxygen, and evaluate the relative importance of the polar effect and the radical spin delocalization effect.[25,26] In addition, our calculations indicate that the substituent effects on the O−H and $O-CH_3$ BDEs are nearly identical for phenol and anisole.

Method of Calculation

In the first step, calculations were carried out with the DMol program.[27] The local density approximation[28] (LDA) of Janak, Moruzzi, and Williams (JMW)[29] was used. Geometries were optimized with the double numerical (DN) basis set. This method is referred to as JMW/DN. The para-substituted phenols were further optimized by Pople's Gaussian 92/DFT program.[30] We employed the BLYP method, which uses Becke's 88 nonlocal exchange functional[31] and Lee−Yang−Parr nonlocal correlation functional.[32] These calculations were carried out with the standard 6-31G* basis set. The BLYP/6-31G* method has been shown to give satisfactory results for many systems.[33] For the substituents HCO, COMe, and NO_2, a planar geometry was assumed on the basis of recent calculations by Head−Gordon *et al.*[34] A planar structure was also adapted for OH, OMe, SH, and SMe to assure conjugation.

Results and Discussion

The O−H and $O-CH_3$ BDEs. The calculated total energies of monosubstituted benzenes, phenols, phenoxy radicals, and anisoles are given in Table 1. The BDEs of the unsubstituted phenolic O−R bonds (R = H, CH_3) were evaluated with zero-point energy (ZPE) correction. The ZPE for phenol, anisole, phenoxy radical, and methyl

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Table 1. Calculated Total Energies (au) of Monosubstituted Benzenes (H), Para-Substituted Phenols (OH), Phenoxy Radicals (Orad), and Anisoles (OCH_3)[a]

X	JMW/DN				BLYP/6-31G*		
	H	OH	Orad	OCH_3	H	OH	O rad
H	−230.192 42	−304.911 22	−304.270 88	−343.857 96	−232.132 39	−307.342 35	−306.714 79
Me	−269.157 89	−343.875 89	−343.240 19	−382.822 58	−271.422 71	−346.631 94	−346.007 40
F	−328.852 52	−403.569 17	−402.931 45	−442.516 40	−331.366 14	−406.574 00	−405.950 17
Cl	−688.329 41	−763.046 68	−762.408 82	−801.994 19	−691.718 12	−766.927 17	−766.301 22
Br	−2800.181 87	−2874.899 51	−2874.261 65	−2913.847 04			
OH	−304.911 22	−379.627 27	−378.997 09	−418.574 04	−307.342 35	−382.548 78	−381.931 23
OMe	−343.857 96	−418.574 04	−417.944 99	−457.520 88	−346.622 34	−421.829 55	−421.211 54
SH	−627.014 75	−701.732 08	−701.100 94		−630.301 89	−705.510 53	−704.889 96
SMe	−665.976 49	−740.693 52	−740.064 13		−669.589 77	−744.798 24	−744.179 47
NH_2	−285.135 10	−359.849 30	−359.228 26	−398.796 79	−287.466 83	−362.675 62	−362.062 53
NMe_2	−363.037 58	−437.750 50	−437.132 53		−366.028 00	−441.234 84	−440.623 62
O^-	−304.368 09	−379.082 82	−378.498 13		−306.764 85	−381.968 90	−381.393 89
CHO	−342.679 26	−417.398 45	−416.753 69		−345.441 23	−420.653 86	−420.022 44
COMe	−381.649 04	−456.370 04	−455.727 01	−495.317 45	−384.735 32	−459.947 60	−459.317 05
SO_2Me	−815.250 06	−889.969 34	−889.322 39		−819.967 08	−895.178 45	−894.545 40
CN	−321.686 97	−396.407 18	−395.763 62	−435.354 63	−324.365 67	−399.577 31	−398.946 68
NO_2	−433.286 40	−508.007 83	−507.364 08	−546.955 44	−436.633 15	−511.845 49	−511.211 41
CF_3	−565.141 44	−639.861 70	−639.214 70		−569.140 12	−644.350 94	−643.719 62

[a] The total energies corresponding to H, OH, and Orad calculated by the JMW/DND for substituent H are −230.237 62, −304.987 98, and −304.345 73, respectively, and for substituent OH are −304.987 98, −379.735 15, and −379.704 16, respectively.

radical are 63.7, 81.2, 55.9, and 18.3 kcal/mol with the BLYP/6-31G* method, respectively. The BDE of phenol was calculated to be 87.8 and 89.4 kcal/mol at the JMW/DN and the JMW/DND[35] levels, respectively. The reported gas phase values range from 85.1 to 88.3 kcal/mol.[6,13] The latest recommendation by Wayner *et al.* is 87.0 kcal/mol.[6a] However, the BLYP/6-31G* calculations gave a BDE of 75.1 kcal/mol for phenol, which is much lower than the experimental values. To assess the accuracy of the BDE calculated by the BLYP/6-31G* method, we calculated the O−H BDE of methanol to be 92.0 kcal/mol and the $O-CH_3$ BDE of methyl ether to be 76.7 kcal/mol with the BLYP/6-31G* method. The experimental values are 104.4 and 83.3 kcal/mol, respectively, for the two molecules.[36] The BDE of the O−H bond of H_2O calculated by the BLYP/6-31G* method is also about 10 kcal/mol smaller than the experimental value.[33] Thus, the BLYP/6-31G* calculations systematically underestimate O−R BDEs.

The BDE of anisole under the same treatment by the JMW/DN method is 72.1 kcal/mol, which is somewhat higher than the experimental values reported by Suryan *et al.* (64.7 kcal/mol),[18] Mackie *et al.* (64.0 kcal/mol),[11] and Back (61.0 kcal/mol)[12] based on the activation enthalpy of $O-CH_3$ bond dissociation. As will be discussed later, the BDE is likely to be higher than the activation enthalpy. Once again, the BLYP/6-31G* method gives a lower BDE of 57.1 kcal/mol.

Geometry. Recently, Feller *et al.* calculated the geometry of phenol with the MP2/6-31G* method.[37] The DFT calculations gave a very similar geometry.[38] There is little bond-length alternation in the benzene ring.[39] The C-O bond is 1.382 Å with JMW/DN and 1.384 Å with BLYP/6-31G* compared to 1.396 Å with MP2/6-31G*. On the other hand, there is considerable C−C bond length alternation in the phenoxy radical.[40] The C-O bond of the phenoxy radical has a considerable double-bond character, as indicated by the short bond length.

In general, substituents cause only small geometric variations, as exemplified by NMe_2 and SO_2Me groups (Figure 1). The NMe_2 group is slightly pyramidal. The SO_2Me prefers a conformation with the methyl perpendicular to the ring.[41]

Substituent Effect on BDE. Vibrational frequency calculations were not carried out for the para-substituted systems. Since substituents cause only minor geometrical changes, we assume that the ZPE contributions to the O−H and $O-CH_3$ BDEs are similar to those to phenol and anisole, respectively.[25] Thus, the relative BDEs were calculated according to eq 2, based on calculated total energies. The calculated TE, GE, and RE of para-substituents on phenol O−H BDE are shown in Table 2.

The calculated energetics with the JMW/DN and BLYP/6-31G* methods are similar, with the former giving somewhat larger TE for most of the substituents. The substituents are divided into two groups. The electron-donating substituents, Me, F, Cl, Br, OH, OMe, SH, SMe, NH_2, and NMe_2, cause a reduction in the O−H BDE. These substituents destabilize the ground-state (negative GE) but stabilize the radical (positive RE). Both strong σ-withdrawing (CF_3) and π-withdrawing substituents stabilize the ground-state but destabilize the phenoxy radical, resulting in an increase in the O−H BDE. This is qualitatively shown in Scheme 2. Our results support the argument by Bordwell *et al.* that the ground-state effects of electron-withdrawing groups play an important role in the overall substituent effects. However, the calculations also clearly indicate that these substituents cause substantial destabilization to the phenoxy radical. This is especially true for SO_2Me, NO_2, and CF_3 groups.

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(41) For SO_2Me, the fully optimized structure is shown in Figure 3. We found that the potential energy surface for SO_2Me group rotation is quite flat, and the true minimum needs to be determined by thermal energy and entropy corrections. We also found that the ΔS is very dependent upon the SO_2Me conformation. For example, the conformation with S−Me eclipsed coplanar with the benzene ring results in a spin delocalization of 0.04 units.

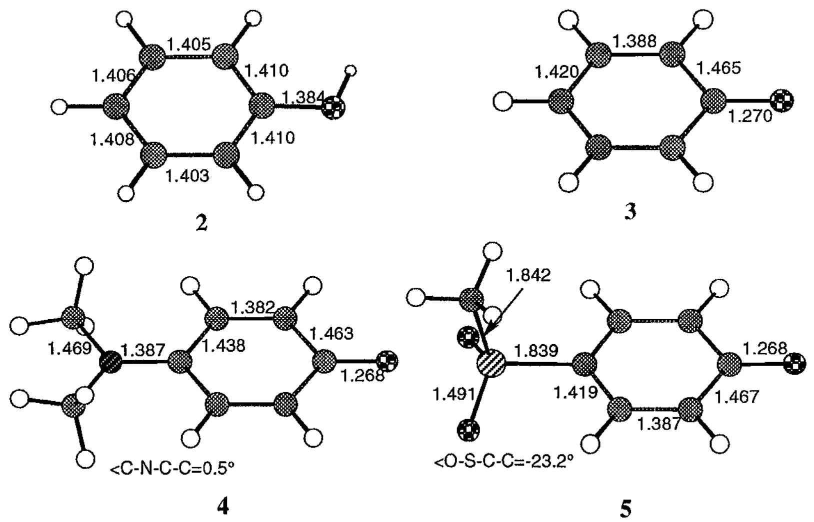


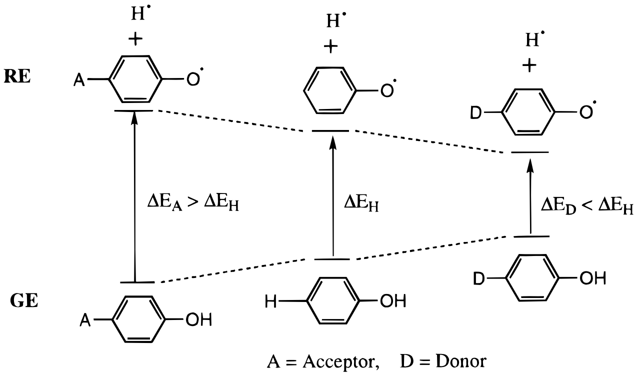
Figure 1. Calculated geometries of phenol (**2**), phenoxy radical (**3**), *p*-(dimethylamino)phenoxy radical (**4**), and *p*-(methylsulfonyl)-phenoxy radical (**5**) by the BLYP/6-31G* method.

Table 2. Calculated Radical Effect (RE), ground-state Effect (GE), and Total Effect (TE) of Para-Substituents on Bond Dissociation Energy of the Phenoxy O−H Bond (Reported Experimental Substituent Effects Are Listed for Comparison)

	JMW/DN			BLYP/6-31G*			expt TE		
	RE	GE	TE	RE	GE	TE	ref 8a	ref 7	ref 10
H	0.00	0.00	0.00	0.00	0.00	0.00	0	0	0
Me	2.41	−0.50	2.91	1.44	−0.46	1.90	1.1	2.1	2.2
F	0.30	−1.35	1.65	1.02	−1.32	2.34			0.9
Cl	0.60	−0.96	1.56	0.44	−0.57	1.01	−0.42	0.6	0.6
Br	0.83	−0.72	1.55				−0.86		0.2
OH	4.65[a]	−1.72[a]	6.37[a]	4.07	−2.22	6.28	8.3	8.0	
OMe	5.38	−1.70	7.08	4.27	−1.73	5.99	5.3	5.6	5.3
SH	4.85	−0.92	5.77	3.56	−0.83	4.39			
SMe	5.76	−1.11	6.87	4.58	−0.93	5.52			
NH_2	9.23	−2.88	12.11	8.35	−0.73	9.08	12.6	12.7	
NMe_2	10.36	−3.68	14.04	8.30	−1.96	10.25	9.6	14.1	
O^-	32.37	−2.55	34.92	29.27	−3.71	32.98	17.0	15.8	22.7[b]
CHO	−2.52	0.25	−2.77	−0.75	1.68	−2.42			
COMe	−0.30	1.38	−1.68	−0.42	1.46	−1.88	−2.9	−2.1	−2.1
SO_2Me	−3.84	0.31	−4.15	−2.56	0.88	−3.45	−5.2		
CN	−1.14	0.88	−2.02	−0.87	1.05	−1.93	−4.4	−4.7	−4.7
NO_2	−0.48	1.65	−2.13	−2.60	1.49	−4.09	−4.8	−6.0	−5.9
CF_3	−3.26	0.92	−4.18	−1.82	0.54	−2.36	−5.5		

[a] RE, GE, and TE of substituent OH by using DND//DN are 5.18, −1.74, and 6.92 kcal/mol, respectively; the values are 5.07, −2.00, and 7.07 kcal/mol, respectively, with DND geometry optimizations. [b] Reference 42.

Scheme 2



The calculated ground-state effects are similar to the STO-3G results reported earlier.[20,23] The hydroxyl group of phenol is stabilized by the benzene ring through π-delocalization, and an electron-donating group causes destabilization through a repulsive π-saturation effect.[20] On the other hand, an electron-withdrawing group causes stabilization because it promotes further π-delocalization from the hydroxy group.

Bordwell *et al.* reported that OH and NH_2 groups cause about 3 kcal/mol larger reductions in the O−H BDE than OMe and NMe_2 groups, respectively.[8] Our calculated results are the opposite. As shown in Table 2, OMe, SMe, and NMe_2 groups have somewhat larger RE and TE than OH, SH, and NH_2 groups, respectively. This reflects the electron-donating nature of the methyl group. Thus, OMe, SMe, and NMe_2 groups are somewhat better donors than OH, SH, and NH_2 groups. The larger substituent effects for OH over OMe and NH_2 over NMe_2 observed experimentally might be due to possible hydrogen bonding involving OH and NH_2 groups in solution. The hydrogen bonding allows more negative charge on the oxygen or nitrogen atom, resulting in larger stabilization of the phenoxy radical.

The calculated TE for the O^- substituent is almost 33 kcal/mol, largely due to the RE (29 kcal/mol). The experimental values range from 16 to 23 kcal/mol.[7−8,10,42] The large discrepency is expected since our result corresponds to the gas-phase situation. The O^- is unstable

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(42) Parker, V. D.; Cheng, J.-P.; Handoo, K. L. *Acta Chem. Scand.* **1993**, *47*, 1144.

Table 3. Calculated Radical Effect (RE), Ground-State Effect (GE), and Total Effect (TE) of Para-Substituents on Bond Dissociation Energy of Anisole OCH_3 Bond by JMW/DN (Reported Experimental Substituent Effects Are Listed for Comparison)

	JMW/DN				
	RE	GE	TE	lit. 1[a] (expt)	lit. 1 (calcd)
H	0.0	0.0	0.0	0	0.0
Me	2.4	−0.5	2.9	1.9	1.4
F	0.3	−1.0	1.3	1.1	2.4
Cl	0.6	−0.5	1.1		−0.5
Br	0.8	−0.2	1.1		−0.9
OH	4.7	−1.7	6.4	2.5	4.0
OMe	5.4	−1.6	7.0	3.9	4.1
NH_2	9.2	−2.4	11.6	2.9	7.2
COMe	−0.3	1.8	−2.1	−0.6	−1.9
CN	−1.1	1.3	−2.5	−0.3	−1.8
NO_2	−0.5	2.2	−2.7	−1.2	−4.3

[a] Lit 1: Suryan, M. M.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 4594.

Table 4. Calculated Relative Atomic Charges and Spin Densities on the Oxygen Atom of Substituted Phenoxy Radicals with Respect to the Phenoxy Radical[a]

	JMW/DN		BLYP/6-31G*	
	ΔC	ΔS	ΔC	ΔS
H	0.000	0.000	0.000	0.000
Me	−0.010	−0.023	−0.010	−0.016
F	0.005	−0.011	−0.007	−0.013
Cl	0.002	−0.027	−0.003	−0.022
Br	−0.000	−0.033		
OH	−0.017	−0.044	−0.026	−0.036
OMe	−0.021	−0.050	−0.029	−0.039
SH	−0.017	−0.067	−0.023	−0.053
SMe	−0.024	−0.079	−0.031	−0.062
NH_2	−0.038	−0.080	−0.046	−0.062
NMe_2	−0.047	−0.094	−0.055	−0.073
O−	−0.157	−0.157	−0.172	−0.137
CHO	0.025	−0.043	0.014	−0.039
COMe	0.018	−0.039	0.009	−0.034
SO_2^{Me}	0.027	0.005	0.019	0.000
CN	0.021	−0.037	0.013	−0.037
NO_2	0.022	−0.017	0.027	−0.021
CF_3	0.028	0.001	0.014	−0.002

[a] The calculated charge (*C*) and spin density (*S*) on the phenoxy oxygen are as follows. JMW/DN: −0.281, 0.437. BLYP/6-31G*: −0.466, 0.402.

in the gas phase and is a very good electron donor. While in solution, the negative charge is stabilized by solvation, resulting in a reduced effect.

The calculated substituent effects on the anisole $O-CH_3$ BDE are given in Table 3, along with reported experimental values and earlier AM1 calculations.[18] Our results are nearly identical to those for the phenol system. This is because they have the same radical effect and similar ground-state effects. However, the calculated substituent effects are much larger in magnitude than the reported experimental values. Since the latter are actually the substituent effects on the activation enthalpy of $O-CH_3$ bond dissociation, we suggest that in the transition state the $O-CH_3$ is only partially broken so that no full phenoxy radical character is developed. Thus, the $O-CH_3$ BDE and the substituent effects on the $O-CH_3$ BDE determined by pyrolysis are smaller than the real values. In the case of vitamin E derivatives, a similar descrepancy between the O−H BDEs and antioxidant activities has been reported and explained using the same reason as given.[5]

Charge and Spin Density Variation. Table 4 shows the calculated relative atomic charge and spin density on the oxygen atom of substituted phenoxy radicals with respect to the phenoxy radical. In general, electron-donating groups increase the negative charge on the oxygen atom but electron-withdrawing groups decrease the negative charge on the oxygen atom. This is consistent with the polar effects of these groups. On the other hand, both electron-donating groups and electron-withdrawing groups decrease the spin density on the oxygen atom, except for the SO_2Me and CF_3 groups, which have little effect on the spin density.[41] More detailed information on calculated atomic charges and spin densities is exemplified in Figure 2. There is considerable spin density delocalization from the oxygen to the benzene ring. Overall, the oxygen behaves as an electron-withdrawing group. Both charge and spin density alternate. Our calculated spin densities on the ring atoms are qualitatively in agreement with α-hyperfine splitting patterns reported in the literature.[43] The summation of the spin densities at the ortho- and meta-positions is nearly a constant for most of the substituents, in agreement with experimental observations.[44]

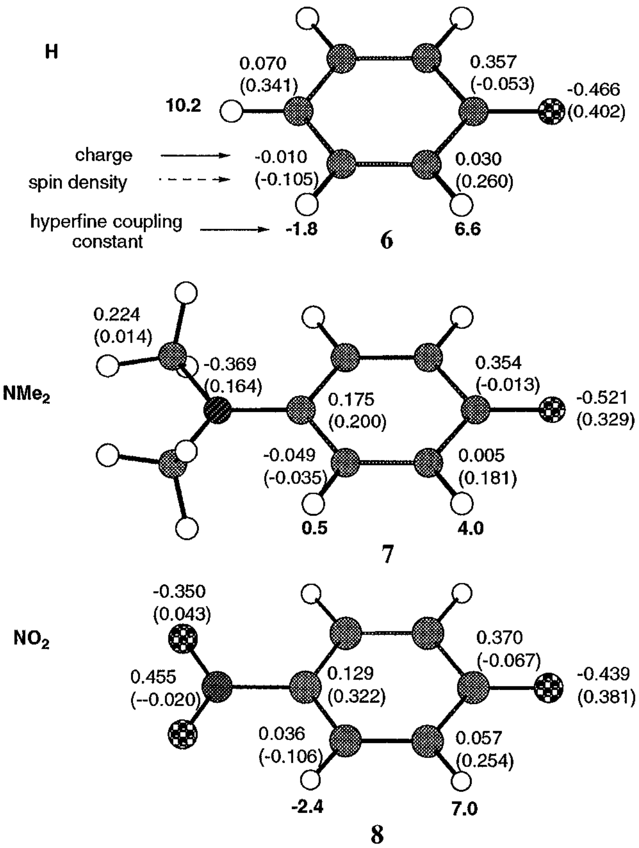

Figure 2. Calculated natural atomic charges (with H atom summed in) and spin densities (in parentheses) of phenoxy radical (**6**), *p*-(dimethylamino)phenoxy radical (**7**), and *p*-nitrophenoxy radical (**8**) by BLYP/6-31G* calculation. Reported hyperfine coupling constants are also shown for comparison.

Figure 3 shows the correlation plots of calculated (BLYP/6-31G*) variations in charge (ΔC) and spin density (ΔS) on phenoxy radical oxygen against σ^+, $\sigma^{\bullet}_{\alpha}$, and $\sigma^{\bullet}_{jj}$ in the literature. The calculated ΔC correlates very well with σ^+ ($r = 0.987$), indicating that the polar effect of substituents can be well represented by the calculated

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(43) (a) Dixon, W. T.; Moghim, M.; Murphy, D. *J. Chem. Soc.* **1974**, 1913. (b) Qin, Y.; Wheeler, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 6083.

(44) The SO_2Me substituent is excluded in Figure 2c.

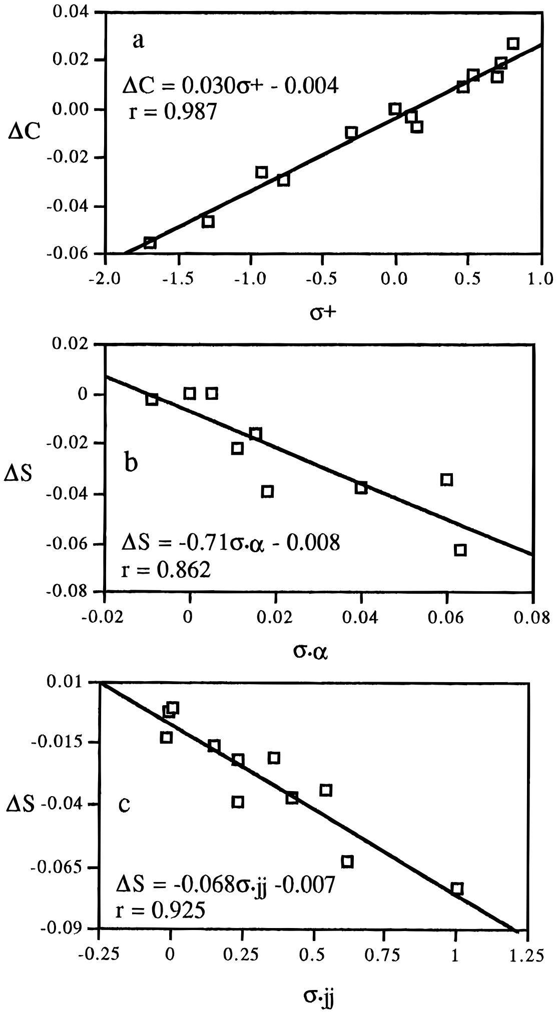

Figure 3. Correlation plots of calculated Δ*C* and Δ*S* (BLYP/6-31G*) with σ^+, $\sigma^{\bullet}_{\alpha}$ (Arnold), and $\sigma^{\bullet}_{jj}$ (Jiang-Ji).

Δ**C**. The correlation between the calculated Δ*S* and $\sigma^{\bullet}_{\alpha}$ derived by Arnold and $\sigma^{\bullet}_{jj}$ by Jiang and Ji[44] is not as good. It should be noted that $\sigma^{\bullet}_{\alpha}$ and $\sigma^{\bullet}_{jj}$ are derived based on benzyl radicals, and the spin delocalization effects on the phenoxy radical and the benzyl radical may be somewhat different.

The Origin of the Substituent Effect on Radical Stability (RE). Panels a and c of Figure 4 show the calculated RE plotted against the variation in Mulliken charge (Δ*C*) (JMW/DN) and natural population charge[45] (BLYP/6-31G*) on the phenoxy radical (without O^- substituent) oxygen atom, respectively. The correlations are very good, with $r = 0.977$ and 0.988, respectively. If substituent O^- is also included, the correlation is even better. This is in accord with the good correlation between the experimentally observed substituent effect on O−H BDE and σ^+ reported by Bordwell *et al.*[8,24] The good correlation indicates that the stability of the phenoxy radical is largely influenced by the polar effect of a para-substituent. On the other hand, the correlation between the calculated RE and the calculated spin density variation (Δ*S*) is not as good ($r = 0.803$, BLYP/6-31G*) and the plot is not shown.

Despite the good correlation between the calculated RE and Δ*C*, we note that the parent system (X = H) does not fall on the lines in Figure 4a,c. This indicates that some other factors also influence the stability of the phenoxy radical. In the case of benzyl radicals, it has been clearly shown that spin delocalization is the dominant effect on the relative stability.[15−16,25] Panels b and d of Figure 4 give the correlation plots of the calculated RE's with both Δ*C* and Δ*S*. For both the JMW/DN and BLYP/6-31G* methods, the dual parameters give improved correlation and the parent phenoxy radical falls exactly on the line. The negative coefficient for Δ*S* indicates that the spin delocalization stabilizes the phenoxy radical.

Table 5. Contributions (kcal/mol) of Polar Effect (Δ*C*) and Spin Delocalization Effect (Δ*S*) to the Stability of Phenoxy Radical According to Equations RE = −131.0Δ*C* − 43.7Δ*S* by JMW/DN and RE = −126.6Δ*C* − 20.7Δ*S* by BLYP/6-31G*

	JMW/DN		BLYP/6-31G*	
X	*E*(Δ*C*)	*E*(Δ*S*)	*E*(Δ*C*)	*E*(Δ*S*)
H	0.0	0.0	0.0	0.0
Me	1.3	1.0	1.3	0.3
F	−0.7	0.5	0.9	0.3
Cl	−0.3	1.2	0.4	0.5
Br	0.0	1.4		
OH	2.2	1.9	3.3	0.7
OMe	2.8	2.2	3.7	0.8
SH	2.2	2.9	2.9	1.1
SMe	3.1	3.4	3.9	1.3
NH_2	5.0	3.5	5.8	1.3
NMe_2	6.2	4.1	7.0	1.5
CHO	−3.3	1.9	−1.8	0.8
COMe	−2.4	1.7	−1.1	0.7
SO_2Me	−3.5	−0.2	−2.4	0.0
CN	−2.8	1.6	−1.6	0.8
NO_2	−2.9	0.7	−3.4	0.4
CF_3	−3.7	0.0	−1.8	0.0

Table 5 gives the contribution of polar effect *E*(Δ*C*) and spin delocalization effect *E*(Δ*S*) to the RE based on dual-parameter correlations. Overall, both methods indicate that the polar effect is more important than the spin delocalization effect. This is especially true for the BLYP/6-31G* method. For electron-donating substituents, both the polar effect and spin delocalization effect stabilize the phenoxy radical. Thus, powerful electron-donating groups strongly stabilize the phenoxy radical. On the other hand, electron-withdrawing groups considerably destabilize the phenoxy radical by the polar effect; although the spin delocalization effect stabilizes the phenoxy radical, the destabilizing polar effect is dominant.

The above radical effect (RE) is just opposite to the ground-state effect (GE). This is because the OH of phenol is a strong π-donor but the oxygen atom of phenoxy radical is a strong π-acceptor. It is also significant that the RE for the phenoxy radical contrasts the RE for the benzyl radical where both electron-donating and electron-withdrawing para-substituents cause a stabilization.[25] While both phenoxy and benzyl radicals are stabilized to similar extents by the spin delocalization effect of a para-substituent, they have quite different responses to the polar effect. Since the oxygen atom of the phenoxy radical is a strong π-acceptor, the phenoxy radical is significantly stabilized by an electron-donating group and significantly destabilized by an electron-withdrawing group. The methylene group of the benzyl radical is a poor electron-withdrawing group, and the stability of the benzyl radical is insensitive to the polar effect of a substituent.

Summary. We have shown that (1) the density functional method gives satisfactory substituent effects

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[45] NBO Version 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weihold, F. University of Wisconsin, Madison.

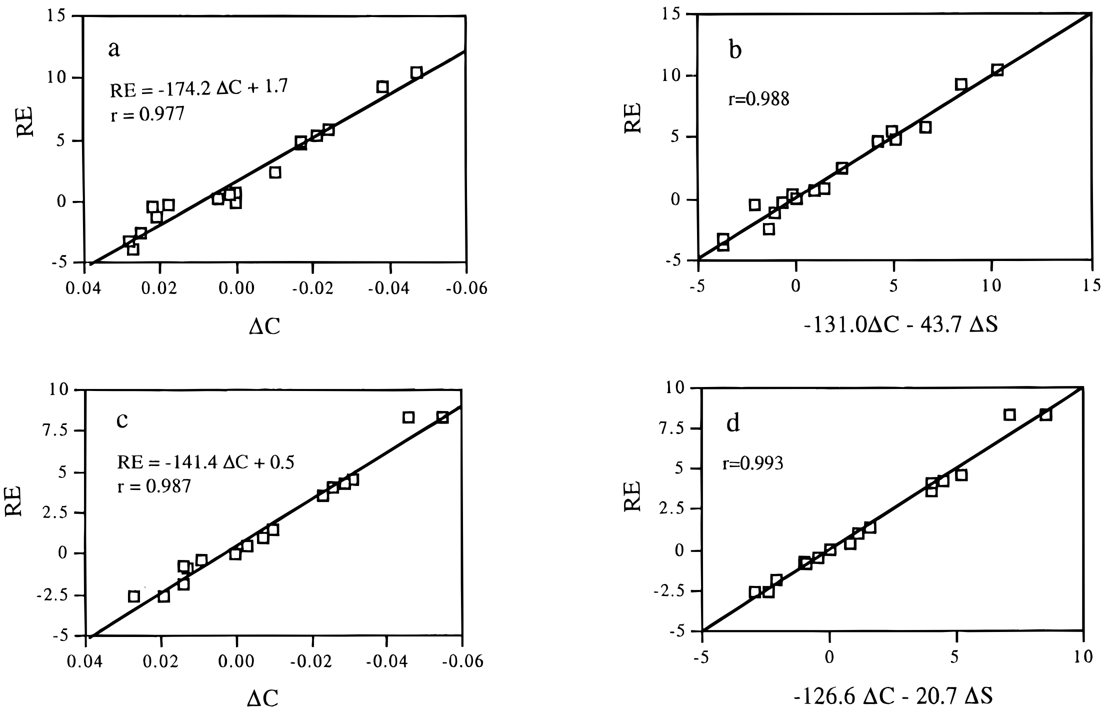

Figure 4. Correlation plots of the calculated radical effect (RE) with (a) Δ*C* and (b) Δ*C* and Δ*S* by the JMW/DN method and (c) Δ*C* and (d) Δ*C* and Δ*S* by the BLYP/6-31G* method.

on the phenol O—H and anisole O—CH_3 BDEs; (2) both the ground-state effect and the radical effect of para-substituents contribute to the overall substituent effect, and the latter is dominant for electron-donating substituents; (3) a para-electron-donating substituent destabilizes phenol or anisole but stabilizes the phenoxy radical, resulting in reduced H-O or O—CH_3 BDE; a para-electron-withdrawing group stabilizes phenol or anisole and destabilizes the phenoxy radical, resulting in increased O—H or O—CH_3 BDE; (4) the calculated charge variation and spin density variation of phenoxy radical oxygen correlate well with experimental σ^+ and $\sigma^\bullet$ parameters, respectively; (5) the radical effect is comprised of contributions from both polar and spin delocalization effects of substituents; and (6) the substituent effects on anisole O—CH_3 BDE and phenol O—H BDE are nearly identical. This suggests that the O—CH_3 bond in the transition state of pyrolysis of anisole is only partially broken, which results in the smaller substituent effects observed experimentally.

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Supporting Information Available: Cartesian Coordinates (in CHEM3D format) of all calculated structures of the phenol system (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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