

Substituent Effects on the Acidity of Weak Acids. 3. Phenols and Benzyl Alcohols

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The gas-phase acidities of meta- and para-substituted phenols have been calculated at the B3LYP/6-311+G*, MP2/6-311+G**, MP2/6-311++G**, and MP2/6-311+G(2df,2pd) theoretical levels. The larger basis sets give the more satisfactory ΔH_{acid} values that are correlated with the observed acidities with a slope close to unity. They are systematically about 2 kcal/mol too small. The acidities of most substituted phenols are linearly related to those of the corresponding substituted benzoic acids and benzyl alcohols. Here, the substituent effect is a Coulombic interaction (field effect) of the distributed charge in the benzene ring with the negative charge of the anionic center. The exceptions are strong para-substituted π -acceptors such as NO_2 and CHO , and to a smaller extent, CN and CF_3 . Here there is direct charge transfer from the phenoxide oxygen to the substituent.

Introduction

We have previously reported investigations of the origin of substituent effects on the gas-phase acidities of bicyclo[2.2.2]octane-1-carboxylic acids¹ and benzoic acids.² The effects in the former case are entirely due to a field effect between the C–X bond dipoles and the carboxylate ion as shown by the good correlation between the acidities and the bond dipoles, as well as the lack of effect of substituents on the atomic charge at the carbon bearing the carboxylate group. With benzoic acids, there is an important π -electron component as shown by the difference between the dipole moments of 1-substituted bicyclooctanes and the corresponding benzene derivatives, by the effect of rotating amino, hydroxy, formyl and nitro groups on the calculated acidities, and by the effect of substituents on the calculated atomic charges in the benzene rings. The very good correlation between the acidities of substituted benzoic and phenylacetic acids shows that the substituent effect on these acids is a field effect involving the electrostatic interaction between the distributed charge of the substituted benzene ring and the CO_2^- or CH_2CO_2^- groups. A direct “resonance” effect is not possible with the phenylacetic acids, and in view of the above correlation, it is also not important with the benzoic acids.

In a continuation of a study of substituents effects on weak acids, we have now examined substituted phenols.³ Here, the substituent effects on the observed gas-phase ΔH_{acid} are somewhat larger than those for the benzoic acids (Figure 1). Most substituents, both meta and para, fall close to a correlation line, which has a slope of 1.28. This is smaller than the effect observed in aqueous

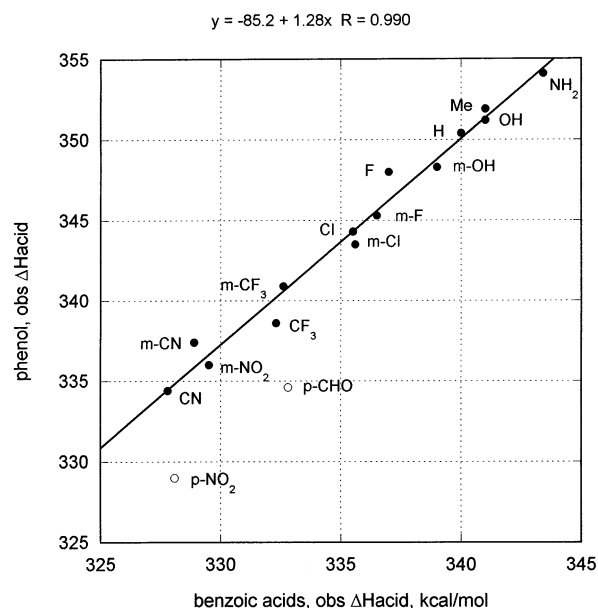


FIGURE 1. Comparison of the observed ΔH_{acid} of phenols with those of benzoic acids. The correlation line refers to the closed circles.

solution where $\rho = 2.11$.⁴ Two substituents, $p\text{-NO}_2$ and $p\text{-CHO}$, fall far from the correlation line.

The difference in substituents effects between the benzoic acid and the phenol series can result from several factors: (1) the decreased distance between the negative charge and the substituents in the phenoxide ions as compared to benzoates, resulting in a larger field effect; (2) the increased negative charge in the ring of the phenoxides that results from π -donation from the anionic site; and (3) the possibility of a direct π -electron interac-

(1) Wiberg, K. B. *J. Org. Chem.* **2002**, *67*, 1613.

(2) Wiberg, K. B. *J. Org. Chem.* **2002**, *67*, 4787.

(3) For previous studies of substituent effects on phenols, see: Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

(4) Jaffè, H. H. *Chem. Rev.* **1953**, *53*, 191.

tion between the phenoxide ion and the substituents. This type of interaction is not present in the benzoate ions.

The direct π -electron interaction is clearly important with the two substituents *p*-NO₂ and *p*-CHO that fall well off the correlation line in Figure 1. It is interesting that *p*-cyanophenol falls near the correlation line.

To gain further information, the acidities of a series of substituted phenols have been calculated. These calculations also allow the π -interactions to be "turned off" by rotating some substituents such as NH₂, OH, CHO, and NO₂ as well as allowing an examination of the effect of substituents on the charge distribution.

Calculations

The acidities of a series of substituted phenols were initially calculated⁵ at the B3LYP/6-311+G* level to resolve conformational questions. The vibrational frequencies were calculated at this level so that corrections could be made for differences in zero-point energies⁶ and for the changes in enthalpy on going from 0 to 298 K. The conformations and energies are available as Supporting Information.

Although there is a good linear relationship between the calculated and observed ΔH_{acid} , the calculated values are about 5 kcal/mol too small. In a related investigation,¹ it was found that added diffuse functions and polarization functions at hydrogen markedly improved agreement, and MP2 gave somewhat better agreement with experiments than B3LYP. MP2/6-311+G* optimizations were carried out for the lower energy conformers identified in the B3LYP calculations. The use of MP2/6-311++G** with MP2/6-311+G* optimized structures leads to markedly improved calculated energies, and whereas the larger basis set, MP2/6-311++G(2df,2pd), leads to significant changes in calculated total energies of the phenols and phenolates, it has little additional effect on the calculated acidities.

The distribution of atomic charges is of interest for the acids and their anions. This is especially the case with the phenoxide ions where the O⁻ is expected to donate significant π -electron density to the benzene ring. How will this affect the substituents and their interaction with the benzene π -electron system? There are many ways in which the charges can be calculated.⁷ For the reasons noted previously,^{1,2} we have chosen to use the Hirshfeld charges⁸ which should be ideal for calculating the changes caused by remote substituents. Here, a 3D grid is placed about the molecule in question, and the electron density is calculated at each point from the molecular wave function. A *promolecule* is constructed by placing *proatoms* (spherically symmetrical neutral atoms) at each of the nuclear positions for the real molecule. At each point on the grid, the contribution to the electron density from each of the

proatoms is calculated, and the density of the real molecule is partitioned among its atoms in proportion to the contributions from the *proatoms*. Integration of the densities for a given atom gives the number of electrons associated with the atom. The π -components of the atomic charge may be obtained in the same fashion by including only the π -MO's in the calculation.

Conformational Issues

With the para-substituted phenols and phenoxide ions, where X = F, Cl, NH₂, CF₃, NO₂, and CN, there is only one ground state conformer. With CHO, OH, and SH as the substituents, the hydrogen may be on the same side as the OH of the phenol, or on the opposite side. Not surprisingly, the difference in energy is less than 0.1 kcal/mol in all cases.⁷ The corresponding phenoxide ions do not have conformational problems. The substituents NH₂, NO₂, CHO, and OH may also adopt rotated conformations in which there is a minimal π -electron interaction with the benzene ring, and these acids and anions also were studied giving the rotational barriers.

The *p*-SH substituent is interesting. With *p*-mercaptophenoxide ion, the lowest energy conformer has the SH group approximately perpendicular to the aromatic ring, with the planar conformer being a transition state. *p*-Mercaptophenol also is nonplanar at most theoretical levels, but becomes planar at the highest level studied. The Ar-SH rotational barrier for the phenol is very small (~0.1 kcal/mol), and that for the phenoxide ion is significantly larger (3.1 kcal/mol).

Planar *p*-hydroxyphenoxide ion was found to be a transition state, and the ground state had a C-C-O-H torsional angle of 19.8° (B3LYP) or 32.5° (MP2).

The meta-substituted phenols present additional conformational possibilities since the substituents may be directed either toward or away from the phenolic oxygen, and the phenolic hydrogen may be directed either toward or away from the substituent.⁹ The differences in energy were generally small, with OH, SiH₃, Cl, CHO, CN, CF₃, and NO₂ preferring to be toward the phenolic hydrogen, and Me, NH₂, F, and SH preferring the other orientation.

The hydroxy substituent preferred to have the H pointing away from the phenol group, the thiol substituent had its hydrogen pointing toward the phenol group, and the formyl group had the C=O pointing away from the phenol group. The removal of the phenolic hydrogen eliminated most of the conformational possibilities.⁹

In contrast to *p*-mercaptophenol, *m*-mercaptophenol is found to be planar at all theoretical levels. However, the planar *m*-mercaptophenoxide is a transition state, and in the ground state there is a 43° C-C-S-H torsional angle (58° in the MP2 calculation).

Phenol Acidities

The calculated acidities (ΔH_{acid}) are summarized in Table 1, and the calculated total energies are available as Supporting Information. The ΔH_{acid} is defined by the reaction HA → A⁻ + H⁺. The calculated energies of HA and A⁻ were corrected for their zero-point energies and the changes in enthalpy on going to 298 K using the B3LYP calculated vibrational frequencies. The proton has

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Baboul, A. G.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 99*, development version (rev. B); Gaussian, Inc.: Pittsburgh, PA 1998.

(6) B3LYP calculations are known to give good calculated vibrational frequencies: Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2001.

(7) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

(8) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129. Cf. Paul Rablen, Ph.D. Thesis, Yale University, 1994.

(9) The structures and energies are shown in Table S1 of the Supporting Information.

TABLE 1. Calculated Gas-Phase Acidities (ΔH_{acid}) of Phenols.

X	B3LYP ^a	MP2 (sm) ^b	MP2 (med) ^c	MP2 (large) ^d	obsd ΔH	obsd ΔG
a. para-substituted						
H	342.7	340.6	348.4	348.2	350.4	343.3
Me	343.8	341.6	349.3	349.5	351.9	344.4
NH ₂	346.5	344.1	351.8	352.0	348.1	346.6
OH	344.5	341.9	349.5	350.2	351.6	341.1
F	339.3	337.4	345.5	345.8	348.0	340.9
SiH ₃	335.2	333.8	341.6	341.3		
SH	335.2	334.1	342.1	341.6		
Cl	335.9	334.6	342.7	342.2	344.3	337.2
CF ₃	328.4	327.1	335.2	335.9	340.6	331.1
CHO	324.6	324.7	332.7	332.3	334.6	327.1
CN	324.0	323.7	331.7	331.3	333.4	326.3
NO ₂	317.7	319.5	327.7	327.4	329.0	321.9
NH ₂ , rot	343.7	341.1	348.8	348.8		
OH, rot	342.0	339.7	347.6	348.0		
CHO, rot	334.5	332.8	340.8	341.0		
NO ₂ , rot	327.8	326.5	334.6	334.9		
b. meta-substituted						
H	342.7	340.6	348.4	348.2	350.4	343.3
Me	343.3	341.1	348.7	348.9	351.2	343.7
NH ₂	344.6	342.0	349.6	349.8	352.2	344.7
OH	340.5	338.4	346.1	346.2	348.3	340.8
F	336.4	334.5	342.5	342.8	345.3	337.8
SiH ₃	337.9	336.3	344.1	342.4		
SH	337.3	334.2	341.9	342.9		
Cl	334.4	333.1	341.0	340.7	343.5	336.0
CF ₃	331.8	339.6	337.5	338.0	340.9	333.4
CHO	332.8	333.1	339.0	338.6	342.1	334.6
CN	328.6	326.5	334.5	334.1	337.4	329.9
NO ₂	327.1	325.3	333.2	333.0	336.0	328.5
NH ₂ , rot	341.6	337.4	345.1	344.6		
HO, rot	340.3	338.2	345.9	346.2		
CHO, rot	334.3	332.7	340.5	340.4		
NO ₂ , rot	327.2	325.5	333.4	333.6		

^a B3LYP/6-311+G* optimized geometries. ^b MP2/6-311+G* optimized geometries. ^c MP2/6-311++G**//MP2/6-311+G*. ^d MP2/6-311++G(2df,2pd)//MP2/6-311+G*.

an electronic energy of zero, but at 298 K it has translation enthalpy and a $\Delta(pV)$ term which sum to 1.5 kcal/mol. When several conformers of a given substituted phenol and phenoxide ion are possible, the acidity derived from the lowest energy conformers is reported in the table.

An experimental value for ΔH_{acid} for phenol has been derived from the ionization potential of phenoxide ion¹⁰ and a reevaluation of the bond dissociation energy of phenol,¹¹ giving 350.4 ± 0.7 kcal/mol. Using 7.1 kcal/mol as the $T\Delta S$ for ionization (see below), ΔG_{acid} becomes 343.3 ± 0.7 kcal/mol. This is larger than the proton affinity of phenoxide ion reported in the NIST Chemistry Webbook¹² by 1.0 kcal/mol, and all of the values in this source have been corrected accordingly and are given in Table 1.

Table 1 compares the gas-phase acidities calculated at several theoretical levels with the observed acidities. The observed ΔG_{acid} values were converted to ΔH_{acid} by using a $T\Delta S$ value of 7.1 kcal/mol for the phenoxides with a 2-fold axis of symmetry and 7.5 kcal/mol for the other phenoxides.¹³ The observed acidities have an estimated relative uncertainty of about ± 0.5 kcal/mol.¹⁴ The average deviation between the calculated and observed ΔH_{acid}

is 2.4 ± 0.4 kcal/mol. The large basis set calculated acidities and the observed acidities for the para-substituted phenols are linearly related (Figure S1, Supporting Information) as

$$\Delta H_{\text{acid}}(\text{calcd}) = 0.993 \Delta H_{\text{acid}}(\text{obsd}) + 0.4 R = 0.998$$

A corresponding relationship for the meta-substituted compounds (Figure S2) is given by

$$\Delta H_{\text{acid}}(\text{calcd}) = 1.067 \Delta H_{\text{acid}}(\text{obsd}) - 25.9 R = 0.999$$

In both cases there is a very good linear relationship with a slope close to unity.

(13) The $T\Delta S$ terms were calculated using the free energy terms obtained in the vibrational frequency calculation. This assumes that the rotational modes may be treated as librations. Errors introduced in this fashion should approximately cancel between a given phenol and phenoxide ion. With X = H, F, Cl, CN, and NO₂ where the phenoxide ion has a symmetry number of 2, the value was 7.1 ± 0.1 kcal/mol. With the exception of X = Me and SiH₃ where very low calculated frequencies were found, leading to unreliable free energy terms, the other para substituents and all of the meta-substituents gave $T\Delta S = 7.5 \pm 0.1$ kcal/mol. A more detailed calculation would require additional information on the rotational potential energy terms for the C–O and C–X bonds, and calculations of the rotational energy levels. In view of the uncertainty in the experimental data, the additional effort did not appear to be warranted.

(14) The estimated uncertainty between pairs of acids that are directly compared is ± 0.2 kcal/mol (ref 3). For acidities derived from a ladder of comparisons, the uncertainty will be larger and ± 0.5 kcal/mol would appear to be a reasonable estimate.

(10) Gunion, R. F.; Gilles, M. K.; Polak, M. J.; Lineberger, W. C. *Int. J. Mass Spectrosc. Ion Proc.* **1992**, *117*, 601.

(11) dos Santos, R. M. B.; Simões, J. A. M. *J. Chem. Phys. Ref. Data* **1998**, *27*, 707. They reported $D(\text{PhO}-\text{H}) = 371.3 \pm 2.3$ kJ/mol (2 σ), but this is incorrect and it should be 371.3 ± 2.8 kJ/mol (1 σ).

(12) NIST Chemistry Webbook (www.nist.gov). The proton affinity data were compiled by E. P. Hunter and S. G. Lias, and the negative ion energetics data were compiled by J. H. Bartmess.

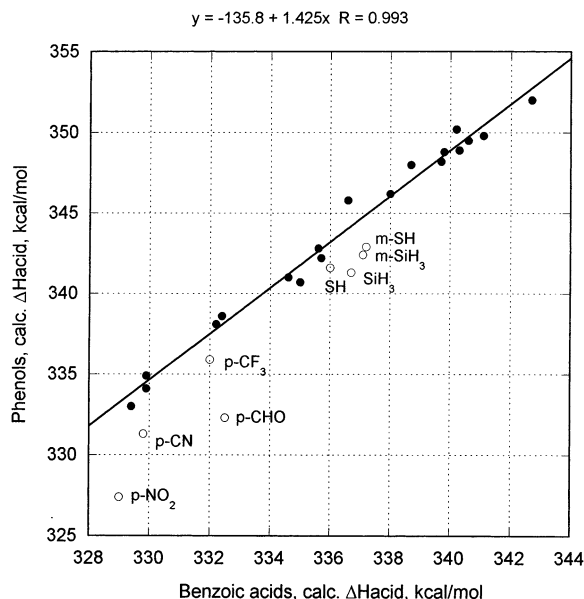


FIGURE 2. Comparison of calculated ΔH_{acid} of phenols with those of benzoic acids. The correlation line refers to the closed circles.

A comparison of the calculated phenol acidities with those for the corresponding benzoic acids also was of interest (Figure 2). Here, the line was defined by all of the groups that were studied including meta- and para-substituted, and Ar-X rotated para-substituted, but with the exception of *p*-NO₂, *p*-CN, *p*-CHO, *p*-CF₃, *m*- and *p*-SH, and SiH₃. There was a good linear relationship for the 17 phenols, with a slope of 1.45. The substituents that fall below the line are those that give enhanced acidity for phenol, and except for SH they are also the substituents that have a positively charged atom attached to the aromatic ring.

Despite the good linear relationships with respect to the observed acidities, there is a systematic difference between the calculated and observed values, with the former being somewhat smaller than the latter. To obtain a better calculated acidity for phenol, CCSD(T) calculations were carried out using the MP2/6-311+G* geometries. Short of full CI, which is impractical for the compounds in this report, CCSD appears to be one of the most satisfactory methods for correcting for electron correlation,¹⁵ and it is further improved by including the correction for triple excitations (CCSD(T)). The calculated energies using several basis sets are summarized in Table 2. Here, $\Delta G(298\text{ K})$ of the proton is -6.3 kcal/mol .¹⁶

The energy difference between phenol and phenoxide ion must be corrected for the zero-point energy change and for the change in energy on going to 298 K. The B3LYP/6-311+G* vibrational frequencies were used. The largest component of the change in zero-point energy on going from phenol to the anion is the loss of the O-H stretching mode. It is calculated to be at 3788 cm^{-1} , and

(15) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382. Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700.

(16) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

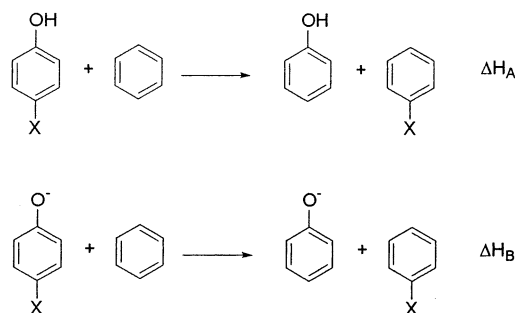
an experimental gas-phase observation places it at 3652 cm^{-1} .¹⁷ The experimental value was used in obtaining the enthalpy and free energy corrections given in the table. In calculating the free energy difference, the change in symmetry number on going from phenol to phenoxide ion was taken into account.

Several basis sets were used to be sure that the energy difference had converged with respect to basis set size. The two larger basis sets give acidities that are in good agreement. The calculated and observed ΔH_{acid} values are compared with the experimental values in Table 2, and the calculated acidity is 0.9 kcal/mol larger than the observed value. Calculations have also been reported at the G3(MP2) level giving $\Delta H_{\text{acid}} = 349.5\text{ kcal/mol}$, which is 0.8 kcal/mol smaller than the experimental value.¹⁸ The two higher level calculations bracket the observed value.

Analysis of Substituent Effects

The analysis will follow that previously used for benzoic acid.² Isodesmic reactions will be used to separate the substituent and the carboxyl group onto different benzene rings. Rotational barriers will be calculated and compared with the barriers for the corresponding Ar-X compounds. Charge distributions will be examined. The acidity of phenols will be compared with those of the corresponding benzyl alcohol derivatives where direct π -electron interactions should be minimized.

1. Isodesmic Reactions. It is possible to separate the substituent effect into components for the phenols vs their anions by the use of the following isodesmic reactions:



Here, the HO or O⁻ groups are separated from the substituents and placed on different rings, eliminating the interaction between them. The values of ΔH_A and ΔH_B are given in Table 2. As might be expected, the substituent effects are small for the phenols, and much larger for the phenoxide anions.

The ΔH_A terms are essentially zero for the meta-substituted phenols indicating that the substituents have essentially no effect on these phenols. The values are somewhat larger, but still small, for the para-substituted phenols. The electron-withdrawing substituents stabilize the para-substituted phenols by a small amount, whereas π -electron-releasing substituents generally give small destabilization,

The ΔH_B terms for the phenoxide ions become quite large with para- π -electron withdrawing substituents that

(17) Huang, P. V.; Lascombe, J.; Josien, M. L. *J. Chim. Phys.* **1961**, *58*, 694.

(18) Prof. John Bartmess, private communication.

TABLE 2. CCSD(T) Calculations

	6-311+G*	6-311++G**	6-311++G(2df,2pd)	Hcorr ^a	Gcorr ^b
		a. energies (H)			
phenol	-306.69408	-306.74690	-306.92771	0.11030	0.07476
phenoxide	-306.13457	-306.17504	-306.35616	0.09617	0.06168
		b. acidities (kcal/mol)			
ΔH_{acid}	343.7	351.5	351.3		
ΔG_{acid}	336.6	344.3	344.2		
obsd ΔG_{acid} = 342.3 kcal/mol					

^a Correction for the zero-point energy and the change in enthalpy on going to 298 K. ^b Correction for the zero-point energy and the change in free energy on going to 298 K.

TABLE 3. Isodesmic Reaction Energies

X	para		meta	
	phenol (ΔH_A)	phenoxide (ΔH_B)	phenol (ΔH_A)	phenoxide (ΔH_B)
H	0.0	0.0	0.0	0.0
Me	-0.4	-1.8	0.0	-0.7
NH ₂	-1.7	-5.5	0.0	-1.6
OH	-1.6	-3.7	-0.1	1.9
F	-1.4	1.0	-0.2	5.2
SiH ₃	0.4	7.2	0.2	5.6
SH	-0.4	6.2	0.2	5.6
Cl	-0.6	5.2	-0.2	7.4
CF ₃	0.2	12.4	0.1	10.2
CHO	2.1	17.9	2.0	11.6
CN	0.3	17.2	0.1	14.2
NO ₂	0.3	21.1	0.5	15.7
NH ₂ , rot	-0.4	-1.1	-0.2	0.9
HO, rot	-0.9	-0.7	-0.2	1.7
CHO, rot	-0.2	7.0	-0.1	7.7
NO ₂ , rot	-0.5	12.8	-0.1	14.5

TABLE 4. MP2/6-311++G(2df,2pd) Rotational Barriers

X	Ar-X	phenol	change ^a	phenoxide	change ^b
<i>p</i> -NH ₂	4.2	2.9	-1.3	-0.2	-4.4
<i>p</i> -OH	2.7	2.0	-0.7	-0.2	-2.9
<i>p</i> -CHO	7.1	8.1	1.0	16.7	9.6
<i>p</i> -NO ₂	3.8	4.6	0.8	12.1	8.3
<i>m</i> -NH ₂	4.2	4.4	0.2	1.8	-2.4
<i>m</i> -OH	2.7	2.9	0.2	2.9	-0.2
<i>m</i> -CHO	7.1	7.9	0.8	9.8	2.7
<i>m</i> -NO ₂	3.8	4.4	0.6	5.0	1.2

^a Change in barrier between Ar-X and the corresponding substituted phenol. ^b Change in barrier between Ar-X and the corresponding substituted phenoxide ion.

can help stabilize the negative charge at the oxygen. The meta-substituents also give fairly large effects, although somewhat smaller than for the para-substituents. This is similar to our observations for substituent effects on the benzoic acids.

When the NO₂ and CHO groups are rotated by 90° to minimize π -electron interactions, the ΔH_B terms decrease somewhat, and now the para and meta values become essentially equal. The large effects of these groups cannot be due to just a direct π -electron interaction since most of the effect remains when the group is rotated or placed in the meta-position.

2. Rotational Barriers. The transition state structures of Ar-X rotated phenols and phenoxide ions substituted by NH₂, OH, CHO, and NO₂ were calculated giving the data shown in Table 4. All of the MP2 theoretical levels gave essentially the same barriers, and therefore only the higher level values are given. The table also includes the Ar-X barriers calculated at the same

level, and the differences between the phenol or phenoxide barriers and those for ArX. An increased barrier indicates a greater π -electron stabilization, and a decreased barrier (minus sign) indicates a reduced π -electron stabilization.

The changes in barrier for the phenols are relatively small, and only *p*-NH₂ and *p*-OH destabilize the phenols. The largest effect is found with CHO and NO₂, and the meta effects are only slightly smaller than those for the para position. Much larger changes in barriers are found with the phenoxide ions. Here *p*-NH₂ gives the largest destabilization, and the *m*-NH₂ effect is about half as large. *p*-CHO and *p*-NO₂ give quite large stabilization of the phenoxides, and the meta effects are about one-fourth as large. It is clear that there are large π -electron effects for these substituents, and that the para effect is considerably larger than that for meta, although the latter are far from negligible.

The calculated acidities of the phenols with rotated substituents are given in Table 1. With the benzoic acids, there was a good linear relationship between the acidities of the meta- and para-substituted compounds. A plot of this type is shown in Figure 3. Here, the line is defined by the solid circles, and for X = NO₂, CHO, SH, OH, and NH₂, they correspond to the acids with rotated substituents. The corresponding ground-state acidities are indicated by open circles. There is a good linear relationship between the acids with the above substituents, as well as Cl, F, H, and Me. The substituents that fall to the left of the line are more acidic when para-substituted than would be expected from the meta-substituted acids.

In the cases of NO₂, CN, and CHO, this is clearly due to a direct π -electron interaction between the phenoxide ion and the substituent. The rotational barriers suggest that the *p*-NO₂ effect has a 64% field effect component and a 36% direct π -electron component, and that *p*-CHO has a 45% field effect and 55% direct π -electron component. The plot suggests that there is also such an interaction for CF₃, SH, and SiH₃ as substituents. This interaction should result in a change in the atomic charges associated with the substituent. The calculated charges are shown in Table 5.

3. Atomic Charges. The charges (Table 5) ortho to the phenol oxygen would be expected to become more negative on ionization as a result of π -donation from the phenoxide oxygen. They might not be expected to be effected by substituents since it is meta to the latter. This is true for the first row substituents where the change in charge is -0.096 ± 0.01 . However, it is reduced by SiH₃ and the common electron-withdrawing substituents. Rotation of CHO and NO₂ restores the change in charge,

TABLE 5. Changes in Atomic Charges on Ionization for Para-substituted Phenols

X	ortho ^a	meta ^a	para	ipso	O	H	X ^b
H	-0.097	-0.091	-0.081	-0.029	-0.298	-0.168	-0.048
Me	-0.094	-0.080	-0.067	-0.030	-0.304	-0.158	-0.093 (-0.017)
NH ₂	-0.094	-0.072	-0.066	-0.026	-0.309	-0.156	-0.109 (-0.054)
NH ₂ , rot	-0.095	-0.084	-0.064	-0.028	-0.299	-0.168	-0.082 (-0.027)
OH	-0.096	-0.079	-0.063	-0.026	-0.305	-0.167	-0.088 (-0.056)
OH, rot	-0.096	-0.084	-0.064	-0.028	-0.301	-0.168	-0.077 (-0.044)
F	-0.098	-0.085	-0.067	-0.029	-0.302	-0.170	-0.066 (-0.066)
SiH ₃	-0.085	-0.068	-0.058	-0.023	-0.277	-0.170	-0.165 (-0.076)
SH	-0.092	-0.074	-0.056	-0.025	-0.293	-0.169	-0.127 (-0.105)
Cl	-0.097	-0.074	-0.060	-0.024	-0.292	-0.171	-0.109 (-0.109)
CF ₃	-0.087	-0.086	-0.073	-0.033	-0.291	-0.174	-0.084 (-0.007)
CN	-0.086	-0.077	-0.064	-0.024	-0.268	-0.176	-0.142 (-0.031)
CHO	-0.079	-0.069	-0.049	-0.020	-0.256	-0.176	-0.204 (-0.060)
CHO, rot	-0.091	-0.080	-0.063	-0.028	-0.287	-0.172	-0.108 (-0.019)
NO ₂	-0.075	-0.065	-0.041	-0.017	-0.245	-0.178	-0.238 (-0.042)
NO ₂ , rot	-0.093	-0.081	-0.061	-0.028	-0.284	-0.175	-0.103 (-0.008)

^a The average change at each of the two positions. ^b The value in parentheses is the change for the atom attached to the benzene ring.

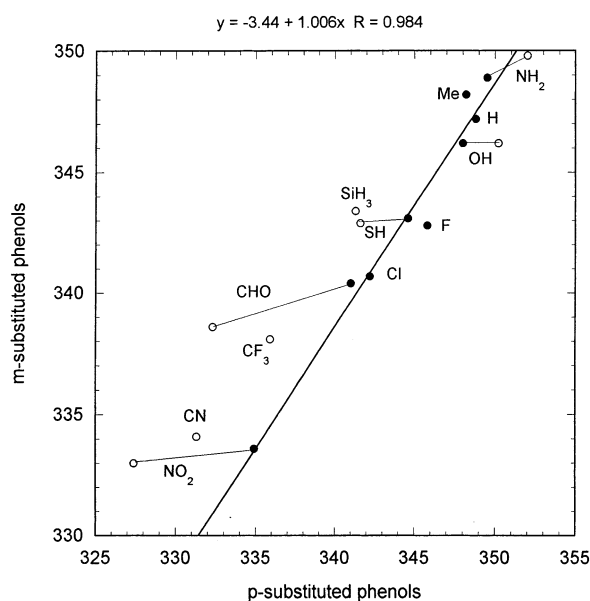


FIGURE 3. Comparison of meta- and para-substituted phenols. For some substituents, the open circles give the ground-state acidities, and the corresponding closed circles give the acidities of the phenols with rotated substituents. The correlation line refers to the closed circles.

indicating that the decreased effect for these substituents is a π -electron effect.

The changes in charge at the meta-positions (ortho to the substituent) are considerably larger as expected, but there does not appear to be a simple pattern. Except for NH₂ and Me, the change in charge for the proton that is lost on ionization gives a fairly good linear correlation with ΔH_{acid} . The change in charge at the phenolic oxygen also is roughly related to ΔH_{acid} .

More information may be obtained by separating the charges into σ and π components. This is readily done for molecules that have the benzene rings in a plane of symmetry where the σ and π MO's are completely separate. The π -components for most of the substituents are given in Table 6.¹⁹

The π -electron population at the ortho position is increased by 0.04 e on conversion of the phenol to the phenoxide ion when X = H, Me, HO, F, or Cl. A smaller

TABLE 6. Changes in π -Components on Ionization of the Phenols^a

X	ortho ^b	meta ^b	para	ipso	O ^c	X
H	0.041	0.060	0.103	-0.056	-0.272	0.020
Me	0.040	0.054	0.097	-0.059	-0.271	0.047
HO	0.041	0.051	0.087	-0.061	-0.262	0.052
F	0.044	0.056	0.091	-0.056	-0.266	0.052
SiH ₃	0.030	0.048	0.099	-0.060	-0.294	0.096
Cl	0.041	0.055	0.102	-0.057	-0.277	0.044
CF ₃	0.033	0.051	0.099	-0.058	-0.297	0.086
CN	0.030	0.050	0.085	-0.060	-0.304	0.118
CHO	0.022	0.042	0.071	-0.065	-0.319	0.183
NO ₂	0.016	0.039	0.061	-0.068	-0.334	0.229
NO ₂ , rot	0.039	0.057	0.101	-0.054	-0.286	0.042

^a A positive sign indicates an increase in π -population on ionization. ^b Average of the two positions. ^c The π -population at the phenolic hydrogen is included in the oxygen population for the HO group.

increase is found with the other substituents. It is interesting to note that it returns to the above value when the NO₂ group is rotated by 90°. The changes at the meta-positions are smaller and roughly parallel those at the ortho-positions.

Relatively large changes in π -electron populations are found at oxygen when OH is converted to O⁻. Here, the oxygen loses ~ 0.3 e. Smaller changes are found with the substituents that do not affect the ortho-positions, including rotated NO₂. The SiH₃, CF₃, CN, CHO, and NO₂ groups have a significant increase in π -electron population on ionization, and these are the groups that fall off the correlation lines in Figures 2 and 3.

4. Comparison with Benzyl Alcohol. In the study of substituent effects on benzoic acids, a particularly useful comparison was between benzoic acids and the corresponding phenylacetic acids. Here, a very good linear relationship is found. Since the CH₂ group in the latter prevents a direct π -electron interaction, the relationship showed that in both series the substituents effects have a common origin and result from a Coulombic

(19) The amino group is nonplanar and was not included. The SH group leads to unusual conformations and was not included. With the CH₃, SiH₃, and CF₃ groups, the conformation used in the calculations had a plane of symmetry containing the benzene ring. This is in some cases not the preferred conformation, but since they have a 6-fold rotational barrier, the differences in energy are negligible.

TABLE 7. Calculated Gas-Phase Acidities (ΔH_{acid}) of Benzyl Alcohols

X	B3LYP ^a	MP2 (small) ^b	MP2 (med) ^c	MP2 (large) ^d	obsd
a. para-substituted					
H	361.3	361.4	369.1	367.6	370
Me	362.7	362.6	370.2	369.1	
NH ₂	364.5	363.7	371.3	370.3	
OH	361.4	361.3	369.1	367.7	
F	358.0	358.2	366.0	364.8	
SiH ₃	357.7	358.2	365.3	364.4	
SH	357.5	357.8	365.5	364.3	
Cl	356.5	357.0	364.9	363.1	
CF ₃	352.9	353.7	361.4	360.4	
CHO	351.9	353.8	361.6	360.4	
CN	350.2	351.5	359.2	357.5	
NO ₂	347.4	350.7	358.5	356.6	
NH ₂ , rot	361.2	361.1	368.8	367.4	
HO, rot	360.4	360.2	367.8	366.8	
CHO, rot	355.9	356.3	363.9	362.7	
NO ₂ , rot	351.1	351.8	359.5	358.3	
b. meta-substituted benzyl alcohols					
H	361.3	361.4	369.1	367.6	370
NH ₂	362.4	361.8	369.3	368.4	
F	357.2	357.4	365.1	363.7	
Cl	356.0	356.8	364.5	362.8	
CN	349.8	350.6	358.3	356.7	
NO ₂	348.7	350.8	358.5	357.2	

^a B3LYP/6-311+G* optimized geometries. ^b MP2/6-311+G* optimized geometries. ^c MP2/6-311++G**//MP2/6-311+G*. ^d MP2/6-311++G(2df,2pd)//MP2/6-311+G*.

TABLE 8. Field Effect and Direct π -Electron Effects

X	field ^a	π -electron ^b	% field	% π -electron
<i>p</i> -NO ₂	15.3	5.5	74	26
<i>p</i> -CN	14.0	2.9	83	17
<i>p</i> -CHO	10.6	5.3	67	33
<i>p</i> -CF ₃	10.0	2.3	81	19
<i>p</i> -SH	4.3	2.3	65	35
<i>p</i> -SiH ₃	4.2	2.7	61	39

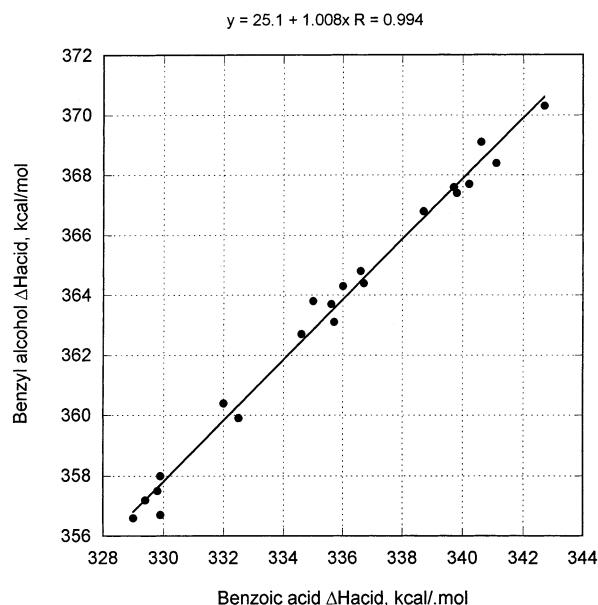
^a Change in acidity with respect to X = H, less the π -electron term, kcal/mol. ^b Difference between calculated acidity for the phenol and that predicted by the correlation line in Figure 5, kcal/mol.

field effect interaction of the carboxylate group with the charge distribution in the aromatic ring that was caused by the substituents.

A corresponding comparison would be between the phenols and the corresponding benzyl alcohols. The latter were studied in the same fashion as for the phenols, and the calculated ΔH_{acid} values are given in Table 7. One might be concerned about the ability of the CH₂ group in benzyloxide ion to act as a π -insulator. In gas-phase alkoxide ions, the negatively charged oxygen polarizes the C–H bonds, placing considerable negative charge at the hydrogens, and a positive charge at carbon. The carbon has an attractive Coulombic interaction with the negatively charged oxygen, leading to a short C–O bond.²⁰

A comparison of the calculated acidities of benzyl alcohols and phenylacetic acids is shown in Figure 4. There is a very good linear relationship indicating that the CH₂ group of the benzyl alcohol does act as an effective π -insulator. A comparison of the phenols with the benzyl alcohols is shown in Figure 5.

The data shown in Figure 5 provide another opportunity to separate π -electron and field effects on the

**FIGURE 4.** Comparison of calculated ΔH_{acid} of benzyl alcohols with those of phenylacetic acids.

acidity of the phenols. In Table 8, the π -electron effect is taken as the difference in acidity between that of a given phenol and the value predicted from the acidity of the corresponding benzyl alcohol. The field effect is taken as the increase in acidity relative to H as the substituent, less the π -electron term. The percent π -electron and field effects are derived from these changes in acidity.

As might be expected, *p*-CHO gives one of the larger percent π -electron terms. Surprisingly, *p*-SH and *p*-SiH₃ give similarly large terms, although the net effect is much smaller than that for *p*-CHO. The high polarizability of SH and SiH₃ is at probably at least in part responsible for their large percent π -electron terms.

(20) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 8765.

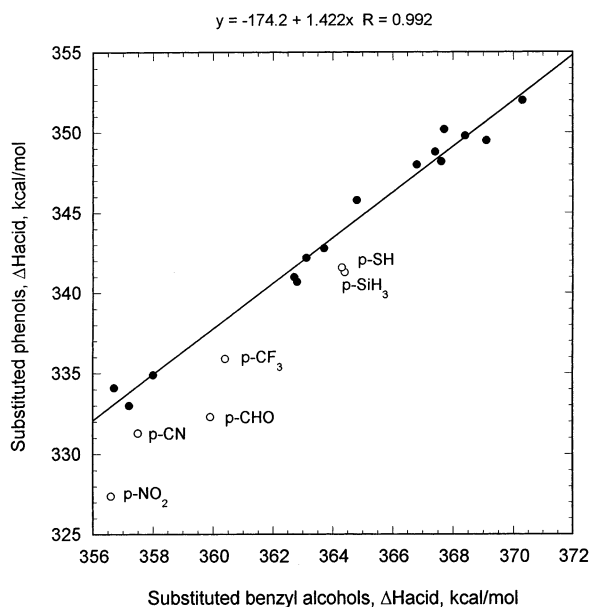


FIGURE 5. Comparison of calculated ΔH_{acid} of phenols with those of benzyl alcohols. The correlation line refers to the closed circles.

Summary

The B3LYP and MP2 calculated acidities for a variety of phenols are linearly related to the observed acidities, but there is a small systematic difference between the large basis set MP2 calculations and the observed values. The acidity of phenol at 298 K was also calculated at the CCSD(T)/6-311++G(2df,2pd) level giving $\Delta H_{acid} = 351.3$ kcal/mol and $\Delta G_{acid} = 344.2$ kcal/mol. The observed acidity is $\Delta G_{acid} = 343.3$ kcal/mol. A G3(MP2) calculation gave $\Delta G_{acid} = 342.2$ kcal/mol.¹⁸

There is a good linear relationship between the calculated acidities of the phenols and the corresponding benzyl alcohols, with the exception of $p\text{-NO}_2$, $p\text{-CHO}$, $p\text{-CN}$, $p\text{-CF}_3$, and $p\text{-SiH}_3$. For the groups that define the line in Figure 5, the substituent effect must have the same character as found for the phenylacetic and benzoic acids, i.e., it results from a Coulombic interaction (field effect) between the distributed charge in the benzene ring caused by the substituent and the negative charge in the anions.

With the other substituents noted above, there is a direct π -interaction between the phenoxide oxygen and the substituent. This interaction may in some cases be "turned off" by rotating the substituent by 90°. Then, the substituent effect still remains fairly large.

The calculations allow the separation of some of the substituent effects into σ - and π -contributions. The changes in electron population on ionization, both total and π -electron, have been calculated by using the Hirshfeld method.

Calculations

The ab initio calculations were carried out using Gaussian-99.⁵ The Hirshfeld charges were calculated by using a program written by P. Rablen.⁸

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Supporting Information Available: Structures and energies calculated at the B3LYP/6-311+G* and MP2 theoretical levels; tables of Hirshfeld charges; correlation between observed and calculated acidities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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