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Effects on the Acidities of Phenols from Specific Substituent–Solvent Interactions. Inherent Substituent Parameters from Gas-Phase Acidities[1]

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Abstract: The gas-phase acitities relative to phenol have been obtained by the ion cyclotron resonance (ICR) equilibrium constant method for 38 meta- and para-substituted phenols. The substituent effects obtained are compared with recent theoretical calculations at the STO-3G level of approximation and limited satisfactory accord is found, as discussed. Comparison has also been made with the corresponding gas-phase substituent effects on the acidities of pyridinium ions. While field/inductive effects are shown to be quite large but linear between these two gas-phase acidity series, resonance effects are distinctly nonlinear, confirming the expectations of resonance effect theory. The gas-phase phenol acidities are found to give a limited Hammett linear free-energy relationship, allowing the calculation of inherent $\sigma^-_p(g)$ substituent parameters. Para +R oxyanionic substituents (e.g., NO_2) are shown to give significant specific substituent solvation assisted (electronwithdrawing) resonance (SSSAR) effects in aqueous phenol acidities. Previously accepted ideas regarding the scales of enhanced internal π-electron-delocalization effects are shown to be wrong. Instead, external stabilization by substituent hydrogen-bond-accepting interactions with water is found to be a major and variable contributor to the previously defined $\sigma^-_p(aq)$ values and to the solution reaction rates and equilibria which have been well correlated by these parameters. A generalized scheme for understanding of medium effects on proton-transfer equilibria is presented. Applications of the Hammett equation with the use of the inherent $\sigma^-_p(g)$ values for +R para substituents to appropriate proton-transfer equilibria (and other processes) in solution are demonstrated. The method of Taft and Lewis to separate field/inductive and resonance effects of substituents is shown to be applicable to the gas-phase phenol acidities and to provide additional insights into substituent effect behavior. Thus, for example, acid strengthening resonance effects are indicated to range from 2.9 kcal/mol for the *p*-CF_3 substituent to 9.2 kcal/mol for the *p*-CHO substituent, with *p*-CO_2CH_3, *p*-CH_3CO, and *p*-NO_2 having about 8.3 kcal/mol acid strengthening resonance effects. Although these are the largest resonance effects that have ever been reported for +R para substituents, field/inductive (*F*) effects are quite generally even larger. For example, for the *p*-NO_2 substituent, the *F* effect accounts for about 13 kcal/mol of the observed acid strengthening effect of ~21 kcal/mol. By contrast, the aqueous acidity of *p*-nitrophenol is increased over that of phenol by nearly equal resonance and field/inductive effects (~1.9 kcal/mol each). However, 0.7 kcal/mol of this aqueous *p*-NO_2 resonance effect is due to external stabilization (SSSAR effect). The acid-weakening resonance effects for π electron-donor (–R) substituents in the gas-phase phenol acidities are shown to be strongly leveled by π-electron saturation but are enhanced by π-electron-repulsion effects. Except for substituents with a high hydrocarbon content, charge-induced dipole polarizability effects for meta and para substituents on gas-phase phenol acidities are found to be small or negligible.

Introduction

Previous investigations[2,3] of the gas-phase acidities of phenols have established the large magnitudes by which an aqueous medium reduces the inherent effects of substituents on acidity. Aqueous solvent attenuation factors of five- to sevenfold for the effects on the standard free energies of ionization of meta- and para-substituted phenols have been found.[2,3] Factors of this magnitude also apply for benzoic acid acidities,[3] but for pyridinium ion acidities a smaller factor of 2–3 applies.[4] The much greater aqueous medium effects on acidity for the former have been shown to result from the correspondingly greater effects of the substituents on the energies of aquation of the oxyanions[3,5] compared to those of the pyridinium ions.[4c,6] Evidence has been presented[7–9] that the formation of specific hydrogen-bonded ion–molecule complexes, involving only a few water (or other solvent) molecules, contributes importantly (if not dominantly) to the oxyanion aqueous (or other) medium effects.

We have in the present investigation greatly extended the range of structures of meta and para substituents used to obtain gas-phase acidities of phenols. This has been done with the objective of answering a very important remaining question. Does specific hydrogen bonding of aqueous medium to the substituent itself play any significant and variable role in the observed aqueous medium effects on the phenol acidities? An affirmative answer would mean, for example, that the Hammett σ^-_p values,[10] which are based upon the effects of π-electron-acceptor (+R) substituents on phenol acidity in water, do not provide an inherent measure of electron-withdrawing effects, but instead give a scale which is in part determined by the hydrogen-bonding solvation propensities of the substituents. The latter possibility seems quite real in view of recent evidence. Thus, for example, the NO_2 substituent which is a very weak hydrogen-bond acceptor in molecules like nitrobenzene[11,12] and has a $\sigma_R{}^0$ value in hydrocarbon solvents essentially identical with that of the CO_2CH_3 substituent.[12] However, in

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hydroxylic solvents the NO_2 substituent becomes a strong hydrogen-bond acceptor in electron-rich ions[7,9a,13] or molecules[14] in line with the greater σ^-_R value[15] given for NO_2 (0.46) than for CO_2CH_3 (0.34). In order to investigate this matter we have used meta and para substituents which have been classified[11] as "chemically inert" in hydroxylic solvents (CH_3, CF_3, and halogens) as well as meta and para substituents which involve a substantial range in hydrogen-bond-acceptor propensities.[11,16]

Further objectives of this study are to provide the data required to critically define inherent substituent parameters and to test several quantitative predictions made from ab initio MO theory calculations in recent substituent effect analysis.[4d,17,18] Thus, it has been indicated that in the absence of solvation substituted phenoxide ions should serve as excellent models for the basicities of correspondingly substituted anilide ions and benzyl carbanions. We have also clarified a few discrepancies between the previously reported[2,3] gas-phase acidities of phenols.

Experimental Section

The gas-phase acidity measurements reported in this paper are performed with a pulsed ion cyclotron resonance (ICR) mass spectrometer which was constructed in our laboratory at the University of California at Irvine. The pulsed ICR technique utilizes the cyclotron resonance principle for mass analysis of gaseous ions stored in a one-region trapped ICR cell.[19,20] At a typical operating pressure of 1×10^{-6} torr, ions are stored for several seconds by a uniform magnetic field of 14 000 G and a weak electric field (0.5 V/cm). A pulsed mode of operation is used for ion formation, trapping, double-resonance irradiation, and mass analysis. Most of the experimental techniques utilized for this study are the same as those used previously for construction of the gas-phase acidity scale[20] and the proton-affinity scale.[21] Only changes or additional procedures will be described here.

The following scheme describes the sequence of reactions which occur in a typical experiment:

$$CH_3ONO + e^- \rightarrow CH_3O^- + NO \quad (1)$$

$$CH_3O^- + AH \rightarrow A^- + CH_3OH \quad (2)$$

$$CH_3O^- + BH \rightarrow B^- + CH_3OH \quad (3)$$

$$A^- + BH = B^- + AH \quad (4)$$

$$A^- + M \rightarrow \text{ion loss} \quad (5)$$

$$B^- + M \rightarrow \text{ion mass} \quad (6)$$

An experiment is initiated by a 10-ms pulse of a low-energy electron beam (0.5 eV) through the ICR cell. The electrons are captured by methyl nitrite at a partial pressure of about 1×10^{-7} torr and CH_3O^- is produced. The acids AH and BH react rapidly with CH_3O^- to yield exclusively M − 1 negative ions of the phenols. The partial pressures of the phenols were maintained lower than 2.5×10^{-7} torr to suppress the formation of proton-bound dimer negative ions. Reversible proton transfer, reaction 4, was allowed to cycle 50 to 100 times to insure that the ions were thermalized at the temperature of the neutral gas in the system. The equilibrium constant for reaction 4 was evaluated by using the expression

$$K = [B^-][AH]/[A^-][BH] \quad (7)$$

The equilibrium abundance of A^- and B^- was measured with a capacitance bridge detector[23] which accelerates the ions at their cyclotron frequency, and a Bayard-Alpert ionization gauge was used to measure the pressures of the neutral reactants with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of the various compounds.[23] Equilibrium constants measured in this way can be used to calculate $\delta\Delta G^\circ_{acid}$ (eq 8), the relative

$$\delta\Delta G^\circ_{acid} = -RT \ln K \quad (8)$$

gas-phase acidity of AH and BH at the particular temperature T of the ICR experiment. Proton-transfer reactions involving the phenylacetonitriles were noticeably slower than some involving the phenols, and it was necessary to take care to avoid artifacts caused by ion loss, reactions 5 and 6. This problem was minimized by working at constant magnetic field strength to insure that the rates of ion loss were comparable.

Most of the compounds investigated in this study are high-boiling liquids or solids. Phenols having a higher melting point than 50 °C were admitted to the spectrometer via a specially designed inlet system. The inlet system is constructed with 304 stainless steel tubing, all metal, bellows-sealed valves (Hoke Model 4213Q6Y) and variable leak valves (Varian type 951-5106). Samples were placed in individual stainless steel cups which were connected to the inlet system with the use of Cajon 6-VCR flanges. While the experiments were being run, the inlet system and the ICR analyzer were warmed to 90–100 °C with resistance heating tapes. Temperatures were measured with copper-constantan thermocouples attached to the ICR cell and to the wall of the analyzer. Normally there was a temperature gradient of only a few degrees if the cell filament current was kept below 2 A, and for the purposes of calculating free-energy changes the average of the two temperatures was taken. The analyzer system was baked at 150 °C overnight and pumped by an 8 L/s ion pump to achieve base pressures in the low 10^{-8} torr range. Positive ion mass scans were taken regularly to check for the purity of each compound and to avoid contamination, particularly, by air, water, and solvents used in recrystallization (benzene, chloroform, and ethanol).

Chemicals. Purified samples of most of the phenols and cresols were obtained as described in previous work of Dr. M. Fujio.[24] Commercial samples of the following were (a) recrystallized [*o*-cyanophenol (from benzene-petroleum ether, mp 96–96.6 °C); *p*-isopropylphenol (from petroleum ether, mp 60.5–61.5 °C); 3,4,5-trichlorophenol (from benzene-petroleum ether, mp 101.5–102 °C)], (b) sublimed [*o*-hydroquinone, 104.5–105 °C], and (c) subjected to fractional distillation [*o*-*tert*-butylphenol, bp 84.5 °C (7 mmHg); *m*-isopropropylphenol, bp 96 °C (7 mmHg); malononitrile, 77 °C (3.6 mmHg); difluoroacetic acid, bp 68 °C (4 mmHg); trifluoroacetylacetone, bp 108 °C. We are indebted to Professor F. G. Bordwell for purified samples of the following phenylacetonitriles: *m*- and *p*-CN; *p*-Cl; and *p*-NO_2. Gaseous hydrogen chloride (Matheson, 99% purity) was purified by vacuum transfer and the inlet system was conditioned by several cycles of adding the charge of HCl and then evacuating it. Methyl nitrite was synthesized under reduced pressure by adding 0.1 M H_2SO_4 dropwise to a methanol solution of sodium nitrite.

Results

Relative Acidity Scale. Our experimental data for the relative gas-phase acidities of 47 substituted phenols and various phenylacetonitriles and carboxylic acids are presented in Figure 1. The scale covers a 24.3 kcal/mol range from *p*-aminophenol to dichloroacetic acid. The most acidic compounds are at the bottom of the scale ($\delta\Delta G^\circ$ is negative). Multiple overlaps were performed to insure internal consistency of the data. For example, in separate experiments *p*-fluorophenol was found to be 1.3 kcal/mol more acidic than *m*-methoxyphenol, and *m*-methoxyphenol was found to be 1.1 kcal/mol more acidic than phenol. Then a direct measurement between *p*-fluorophenol and phenol gave 2.3 kcal/mol, in good agreement with 2.4 kcal/mol which is the sum of the other two determinations. The internal consistency of the overlaps is better than ±0.2 kcal/mol in most cases.

The experiments were run at various temperatures from 361 to 385 K, depending on the volatility of the particular compounds

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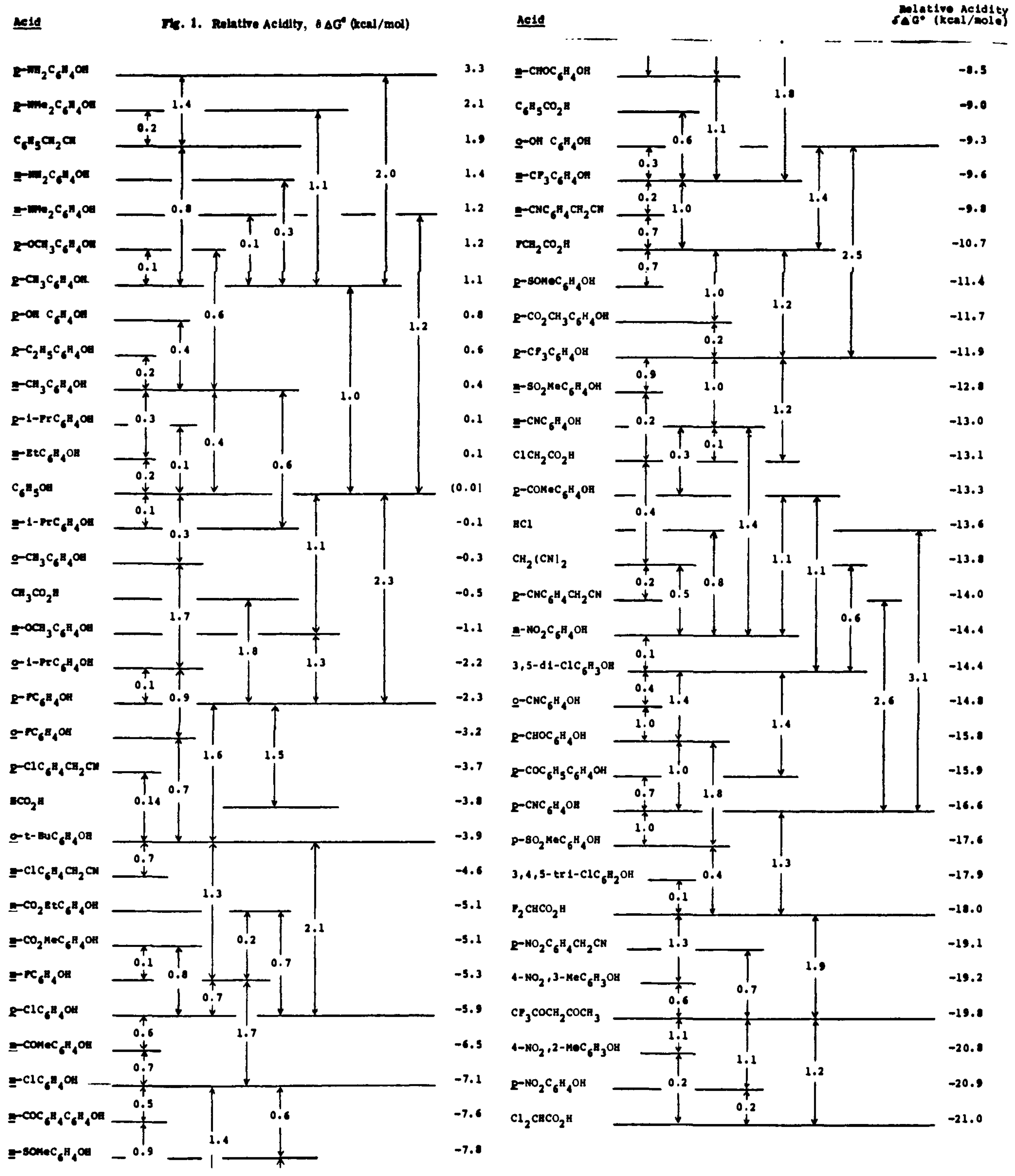

Figure 1. Multiple overlap sequence used to obtain gas-phase acidities relative to phenol, $\delta\Delta G^\circ_{380}$. Individual equilibrum constant determinations are indicated by arrows.

being studied. However, all the data shown in Figure 1 have been corrected to 380 K by using entropies estimated from rotational symmetry numbers.[20] This is a small correction and is seldom more than 0.1 kcal/mol.

Figure 2 shows a comparison between our pulsed ICR $\delta\Delta G^\circ$ values at 380 K which are common to $\delta\Delta G^\circ$ values previously obtained by Kebarle et al. at 600 K, using a pulsed electron beam high-pressure mass spectrometer (HPMS).[3] The line of unit slope which is drawn through the points emphasizes that the two sets of data are in remarkably good agreement. This implies that the relative acidities $\delta\Delta G^\circ$ are nearly temperature independent between 380 K and 600 K and that differences in entropies of deprotonation are small (generally less than 3 cal/deg). Since the equilibrium constant K does change with temperature, the correct temperature of the experiment must be known, of course, in order to calculate a correct free-energy change from the expression $\delta\Delta G^\circ = -RT \ln K$.

Unfortunately, the pulsed ICR and HPMS data are in greatest disagreement in the important region around phenol itself. This is illustrated by the fact that acidities given relative to phenol[3] tend to be 0.5 to 1.2 kcal/mol greater for the HPMS measurements compared to the corresponding ICR results (Table I).

Table I. Relative Acidities of Meta- and Para-Substituted Phenols in the Gas and Aqueous Phases, $\delta\Delta G^\circ$ in kcal/mol at 298 K

	$\delta\Delta G^\circ{}_{(g)}{}^{p}$	$\delta\Delta G^\circ{}_{(g)}{}^{m}$	$\delta\Delta G^\circ{}_{(g)}{}^{p} - \delta\Delta G^\circ{}_{(g)}{}^{m}$	$\delta\Delta G^\circ{}_{(aq)}{}^{p}$	$\delta\Delta G^\circ{}_{(aq)}{}^{m}$	$\delta\Delta G^\circ{}_{(aq)}{}^{p} - \delta\Delta G^\circ{}_{(aq)}{}^{m}$
$N(CH_3)_2$	2.1 (3.1)[a]	1.2 (1.7)[a]	0.9	0.30	−0.20	0.50
NH_2	3.3	1.4	1.9	0.44	−0.15	0.59
OH	1.2[c,d]	−2.4	3.6	0.22[c]	−0.74[c]	0.96
OCH_3	1.2	−1.1	2.3	0.29	−0.48	0.77
CH_3	1.1	0.4	0.7	0.35	0.12	0.23
C_2H_5	0.6	0.1	0.5			
i-C_3H_7	0.1	−0.1	0.2			
t-C_4H_9	−0.6[b]	−0.5[b]	−0.1			
F	−2.3	−5.3	3.0	−0.12	−1.08	0.96
Cl	−5.9	−7.1	1.2	−0.79	−1.19	0.40
H	0.0	0.0	0.0	0.00	0.00	0.00
CO_2CH_3	−11.7	−5.1	−6.6	−2.05	−1.08	−0.97
$SOCH_3$	−11.4	−7.8	−3.6	−2.39	−1.75	−0.64
CF_3	−11.9	−9.6	−2.3	−1.81	−1.43	−0.38
CN	−16.6	−13.0	−3.6	−2.76	−1.88	−0.88
SO_2CH_3	−17.6	−12.8	−4.8	−3.01	−2.16	−0.85
CH_3CO	−13.3	−6.5	−6.8	−2.66	−1.10	−1.56
C_6H_5CO	−15.9	−7.6	−8.3			
CHO	−15.8	−8.5	−7.3	−3.27		
NO_2	−20.9	−14.4	−6.5	−3.89	−2.21	−1.68

[a] With polarizability effect correction–cf. text. [b] Reference 2. [c] With statistical correction applied. [d] From C. A. Bishop and L. K. J. Tong, *J. Am. Chem. Soc.*, 87, 501 (1965).

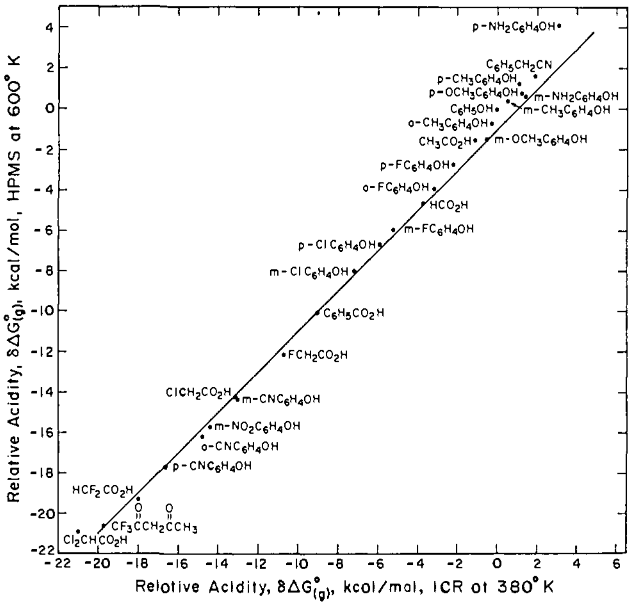

Figure 2. Gas-phase acidities relative to phenol obtained by the HPMS method at 600 K ($\delta\Delta G^\circ{}_{600}$(HPMS)) vs. corresponding values obtained by the ICR method at 380 K ($\delta\Delta G^\circ{}_{380}$(ICR)). The line of unit slope is shown.

However, the differences in acidity between corresponding para- and meta-substituted phenols obtained by the two methods agree within 0.3 kcal/mol except for the NH_2 substituent. Some of the discrepancies in acidities relative to phenol may be due to restricted rotations. Thus, for example, phenol is planar with a barrier of 3.6 kcal/mol for rotation of the OH group.[25,26] This barrier is decreased by π-electron-donor substituents and vice versa.[26] Thus, at 600 K (compared to 380 K) the entropies of phenol and phenols substituted with π-electron-donor substituents may be significantly increased (by freer, less hindered OH rotation) compared to the substituted phenols with π-electron-acceptor substituents. This is consistent with the trend in Figure 2 for the former phenols to be less acidic at 600 K.

Because of the good agreement of the overlaps in Figure 1 for the entire range of phenol acidities, the greater data base in the present study, the lower temperature, and the generally good accord shown in Figure 2, our analysis of substituent effects in this paper is based upon the gas-phase acidities of substituted phenols relative to phenol shown in Figure 1 and the assumption that $\delta\Delta G^\circ{}_{380} = \delta\Delta G^0{}_{298}$ within the experimental error of ± 0.2 kcal/mol. Table I presents a summary of the effects of meta and para substituents on phenol acidity in the gas phase and in aqueous solution at 298 K. The latter values are critically selected values from the literature.[27]

Absolute Acidity Scale. The absolute gas-phase acidity, $\Delta G^\circ{}_{acid}$(AH), is defined as the standard Gibbs' free-energy change for the reaction:

$$AH = A^- + H^+ \tag{9}$$

Absolute acidities can be calculated from the enthalpy, $\Delta H^\circ{}_{acid}$, and the entropy, $\Delta S^\circ{}_{acid}$, changes for reaction 9. The most useful method for calculating $\Delta H^\circ{}_{acid}$ involves the thermochemical cycle shown below:

$$AH = A\cdot + H\cdot;\ \Delta H^\circ{}_{298} = DH^\circ(A - H) \tag{10}$$

$$A + H = A^- + H^+;\ \Delta H^\circ{}_{298} \simeq \Delta H^\circ{}_0 = IP(H) - EA(A) \tag{11}$$

$$AH = A^- + H^+;\ \Delta H^\circ{}_{298} \simeq \Delta H_0{}^\circ \tag{12}$$

$$\Delta H^\circ{}_{acid} \simeq DH^\circ(A - H) + IP(H) = EA(A) \tag{13}$$

Since the ionization potential of hydrogen, IP(H), is a constant of 313.6 kcal/mol, the variable enthalpy change $\Delta H^\circ{}_{acid}$ is determined by the difference between the bond strength, DH°(A − H), and the electron affinity of the radical, EA(A).

Estimation of $\Delta S^\circ{}_{acid}$ can be done by using a statistical mechanistic method.[28] For reaction 9 the entropy change is

$$\Delta S^\circ{}_{acid} = S(A^-) + S^\circ(H^+) - S^\circ(AH) \tag{14}$$

The entropy of the proton is 26.012 eu, and the quantity $S^\circ(A^-) - S^\circ(AH)$ can be estimated by considering the rotational symmetry numbers of the anion and the neutral acid.[9]

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Table II. Comparison of Experimental with Theoretical Calculations of the Relative Gas-Phase Acidities of Meta- and Para-Substituted Phenols (kcal/mol)

	para		meta	
	$\delta\Delta G^\circ{}_{(g)}$[a]	$\delta\Delta E^\circ{}_{(calcd)}$[b]	$\delta\Delta G^\circ{}_{(g)}$[a]	$\delta\Delta E^\circ{}_{(calcd)}$[b]
NH_2	3.3	4.9	1.4	0.1
OH	1.2	2.9		−3.0
OCH_3	1.2	3.0	−1.1	−2.1
F	−2.3	−1.6	−5.3	−5.4
CH_3	1.1	1.0	0.4	0.4
H	0.0	0.0	0.0	0.0
CF_3	−11.9	−11.5	−9.6	−8.4
CN	−16.6	−21.4	−13.0	−14.5
CHO	−15.8	−13.8	−8.5	−5.9
NO_2	−20.9	−29.2	−14.4	−18.1

[a] $\delta\Delta G^\circ$ is for the reaction: $XC_6H_4OH + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OH$. Estimated experimental error is ±0.2 kcal/mol. Negative sign denotes greater acidity. [b] Calculated by ab initio molecular orbital theory at the STO-3G level of approximation, cf. ref 18a.

By using various "anchor points" for which $\Delta G^\circ{}_{acid}(AH)$ can be calculated, the relative acidity scale can be converted to an absolute scale. Two of the most accurate anchlor points are HF and HCl. The standard free-energy change for the gas-phase reaction

$$HF = H^+ + F^- \tag{15}$$

is 365.5 ± 0.7 kcal/mol at 298 K, and for HCl the comparable figure is 327.9 ± 0.5 kcal/mol.[20] Therefore, the calculated standard free-energy change for the reaction

$$F^- + HCl = Cl^- + HF \tag{16}$$

is −37.6 ± 0.9 kcal/mol. This value compares satisfactorily with the experimental one that we have obtained from the multiple overlap method. Previously the gap between HF and phenol was reported as −21.2 kcal/mol.[20] According to the present study (Figure 1) the gap between phenol and HCl is −13.6 kcal/mol at 380 K. Correcting for the small entropy effect, the value at 298 K is −14.0 kcal/mol. Therefore our experimental value for reaction 16 is $\Delta G^\circ = -35.2$ kcal/mol, with an estimated experimental error of ±5%. Using HF and HCl as anchor points gives an absolute acidity for phenol of 343 ± 2 kcal/mol.

Discussion

Comparison with Theoretical Calculations. Table II compares the STO-3G calculations[18a] of meta- and para-substituent effects on phenol acidities with our experimental results. For many substituents, agreement is to 1.5 kcal/mol or less for effects covering a range of ca. 15 kcal/mol. However, for *m*- and *p*-CHO, CN, and NO_2 agreement is considerably poorer (up to 8.4 kcal greater calculated than observed acidity for *p*-NO_2). The poor agreement here is not a question of the use of standard geometries in the calculations. A complete geometric optimized calculation[18b] for *p*-nitrophenol and phenol has been carried out, and this further raises $-\delta\Delta E^\circ{}_{calcd}$ to +31.6 kcal/mol for the *p*-NO_2 substituent. Clearly the proton-transfer reaction between phenol and the highly charge delocalized *p*-nitrophenoxide ion is not an isodesmic process.

As noted previously,[4d] there is evidence that a substantial part of the discrepancy between calculated and observed values belongs with the substituent itself (for example, CN and particularly NO_2 substituent effects are regularly overestimated, independent of the kind of parent acid involved). Some additional systematic characteristics of the deviations for phenols and anilines[17] are: the acidifying effects for *m*- and *p*-CF_3 and CHO substituents are underestimated; the acid weakening effects for *p*-NH_2, OH, and OCH_3 are overestimated, whereas for the corresponding meta substituents the calculations deviate from experimental values in the reverse direction. It has been noted previously[4d,29] that the π-donor effects of these substituents do not appear to be correctly distributed by the calculations between the meta and para positions. However, the calculations can be used to avoid such errors, at least in substantial part, by comparing the results for the "theoretical substituent" in one series with the corresponding "theoretical substituent" in another.[4d,17]

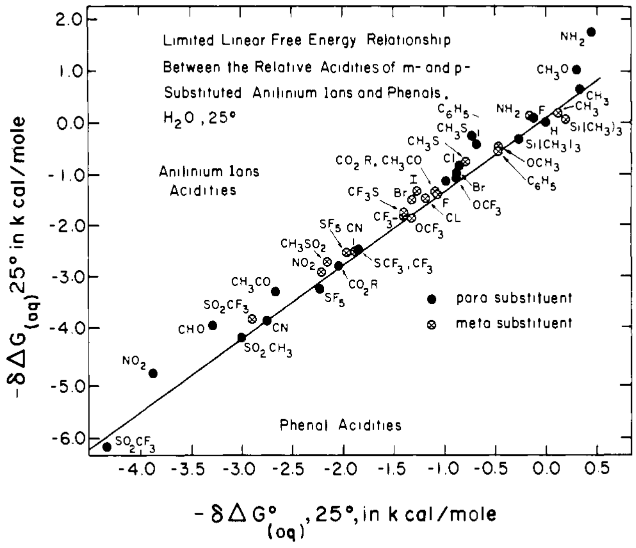

Figure 3. Limited linear free-energy relationship between the relative acidities of meta- and para-substituted anilinium ions and corresponding phenols [H_2O (25 °C)]: ordinate, $-\delta\Delta G^\circ{}_{(aq)}$, anilinium ions (kcal/mol); abscissa, $-\delta\Delta G^\circ{}_{(aq)}$, phenols (kcal/mol).

Theoretical ab initio calculations (STO-3G level) of the effects of meta and para substituents on the acidities of anilinium ions also have been recently reported.[4d] The results were found to be in general satisfactory accord with the (relatively few) available experimental values. Comparison of the more complete sets of theoretical calculations for the meta- and para-substituted phenols and the corresponding anilinium ions led to the prediction that a satisfactory linear free-energy relationship will not be observed between the gas-phase acidities for these two series.[4d] The linear free-energy relationship between the corresponding acidities in aqueous solution has served as the basis for the definition of the $\sigma^-{}_p$ scale of substituent parameters.[10] It was suggested[4d] that this long-standing LFE relationship is the somewhat accidental result of solvent and variable hybridization effects on the substituent effects which leads to less discrimination between reaction types.

Linear Free-Energy Relationships. The present results provide the needed gas-phase phenol acidity data for testing the above prediction. However, there are at present insufficient data on gas-phase anilinium-ion acidities.[4d] In the absence of these data, it is useful to critically reexamine the LFE for aqueous acidities. Since this relationship was originally observed, numerous added reliable substituent effects have been reported,[27] which now permit certain discriminations to be made. In Figure 3 are plotted effects of meta and para substituents on the free energies of ionization of anilinium ions[30] [H_2O (25 °C)], vs. the corresponding effects for phenols [H_2O (25 °C)]. Indeed, Figure 3 does fall into the category of a "limited linear free-energy relationship".[31] That is, a generally precise LFE is observed for most meta-substituent effects, and for some para-substituent effects: $\delta\Delta G^\circ{}_{(ArNH_3^+)} = (1.46)\delta\Delta G^\circ{}_{(ArOH)} + 0.23$, $n = 30$, $r = 0.988$—excluding *m*-NH_2, *m*-SCH_3, *m*-Br, *m*-I, and *m*-$Si(CH_3)_3$, but including the para substituents *p*-CH_3, *p*-F, *p*-Cl, *p*-Br, *p*-I, *p*-$Si(CH_3)_3$, *p*-OCF_3,

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(29) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 159 (1976).

(30) The data for anilinium ion acidities are selected values taken from the following sources: A. V. Willi, *Z. Phys. Chem.* (*Wiesbaden*), 233 (1961); A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961); R. A. Robinson and A. I. Biggs, *Aust. J. Chem.*, **10**, 128 (1957); W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3072 (1962); F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952); A. Bryson, *ibid.*, **82**, 4858 (1960); J. Vandenbelt, C. Hendrick, and S. Vandenberg, *Anal. Chem.*, **25**, 726 (1954); P. d. Bolton and F. M. Hall, *J. Chem. Soc. B*, 259 (1969); Y. Tsuno, private communication.

(31) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

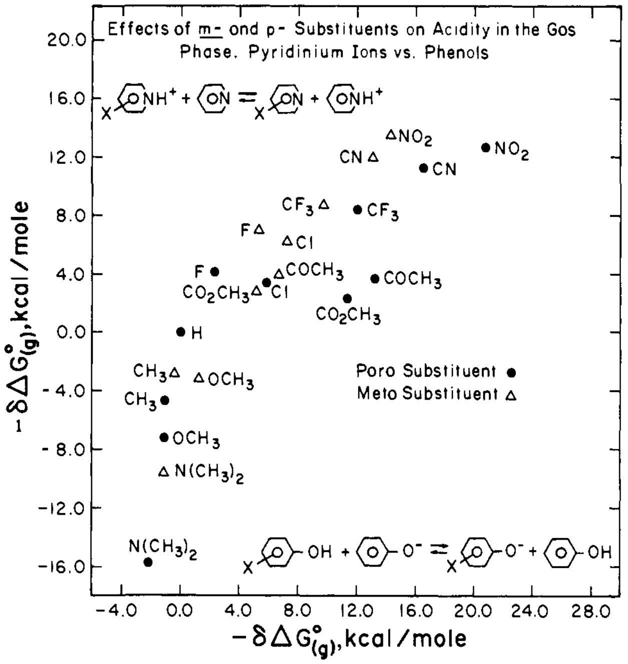

Figure 4. Effects of meta and para substituents on acidity in the gas phase. Pyridinium ions vs. phenols: ordinate, $-\delta\Delta G°_{(g)}$, pyridinium ions (kcal/mol); abscissa, $-\delta\Delta G°_{(g)}$, phenols (kcal/mol).

p-SCF$_3$, p-CF$_3$, p-SF$_5$, p-CO$_2$R, p-CN, p-SO$_2$CH$_3$, and p-SO$_2$CF$_3$. For other para substituents, deviations are chemically and statistically significant (0.5 to 2.0 kcal/mol deviation) for p-NH$_2$, p-OCH$_3$, p-C$_6$H$_5$, p-SCH$_3$, p-CH$_3$CO, p-CHO, and p-NO$_2$ substituents. We will see subsequently that the gas-phase acidities from this investigation permit an understanding of much of this behavior.

Our present results on phenol acidities may be compared with corresponding gas-phase acidities of substituted pyridinium ions.[4d] There are sufficient common substituents available between these two series to make a significant comparison, which is of interest because of the opposite conjugative types of these two reactions. That is, resonance (π-electron delocalization) effects of para substituents are expected to be enhanced for π-donor (−R) substituents for the pyridinium ion acidities,[4d] but for phenol acidities enhanced substituent effects are expected for +R substituents.[18a] In Figure 4 the effects of meta and para substituents on the gas-phase acidities ($\delta\Delta G°_{(g)}$) of pyridinium ions are plotted vs. corresponding gas-phase acidities for meta- and para-substituted phenols. Figure 4 reveals the expected unsatisfactory LFE relationship for para substituents and shows a similar result applies even for meta substituents. The nature of the scatter shown in Figure 4 is consistent with and indicates the applicability of the Taft and Lewis method[32] for separation of field/inductive from resonance effects of these gas-phase substituent effects on acidity. In a subsequent section we will consider the results of the application of this method.

Application of the Hammett Equation. The previous more-limited studies of the gas-phase acidities of phenols[2,3] could not be considered in detail from the standpoint of the Hammett $\sigma\rho$ relationship. Since a single-substituent-parameter analysis offers a good starting point, we proceed first with this consideration. Using the selected σ^n_m and σ^-_p values given by Wepster,[33] Figure 5 shows a plot of the relative gas-phase acidities of meta- and para-substituted phenols, $\delta\Delta G°_m$(g) and $\Delta\delta G°_p$(g), respectively, vs. σ. While there is a clear trend with σ values, the gas-phase acidities in general are not correlated with high precision: $\Delta\delta G°_{(g)} = -0.6 - (16.4)\sigma$; $n = 27$, SD = ±1.1 kcal/mol. The use of select meta substituents only in the correlation, however, does give a limited linear free-energy relationship[22] of much higher precision:

$$\delta\Delta G°_m = -20.0\sigma^n_m \qquad (17)$$

for m-CH$_3$, F, Cl, CF$_3$, CN, and NO$_2$ substituents. For these substituents, the average deviation is ±0.6 kcal/mol (2 to 3 times the estimated experimental error) over a range of 15 kcal/mol. If m-F is omitted (cf. subsequent discussion) the average deviation is reduced to ±0.4 kcal/mol. In Table III are given the inherent values calculated by this relationship which give an average deviation from the Wepster σ^n_m values of only ± 0.03. The average deviation of all other substituents from eq 17 is ± 2.0 kcal/mol (±2.4 for all para substituents covering a range of 24 kcal/mol). Even though precision of this magnitude is of questionable utility, the point of greater importance is that these large deviations (as we show in the following sections) are systematic and readily understandable, including important effects on σ values of hydrogen bonding of aqueous solution to hydrogen bond acceptor (HBA) substituents. However, before proceeding, it is useful to consider a generalized scheme of solvent effects on proton-transfer equilibria.

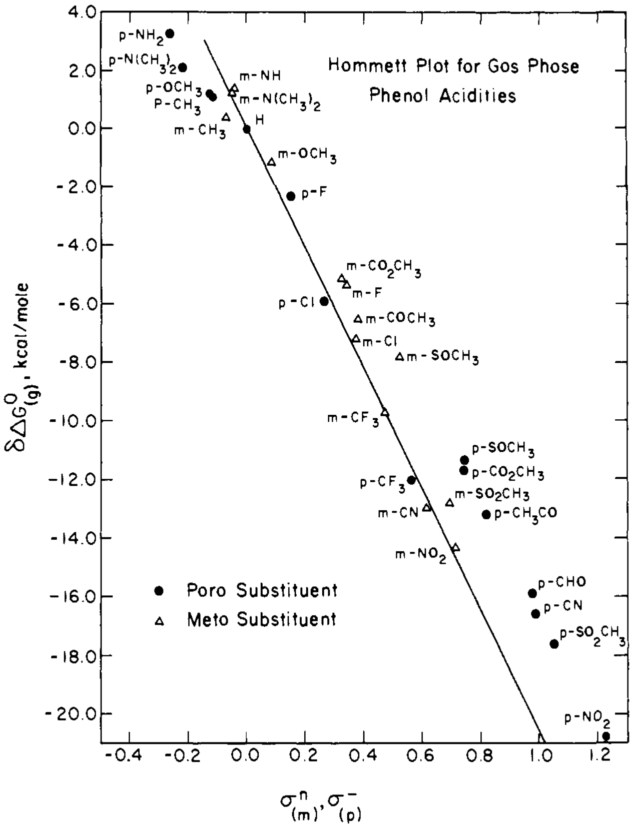

Figure 5. Hammett plot for gas-phase phenol acidities: ordinate, $\Delta\delta G°_{(g)}$ (kcal/mol); abscissa, σ^n_m, σ^-_p (from Weptser).

Table III. Agreement between Inherent $\sigma_{m(g)}$ Values from Equation 17 and σ^n_m for Select Meta Substituents

	$\sigma_{m(g)}$	σ^n_m
CH$_3$	−0.02	−0.07
H	0.00	0.00
F	0.27	0.34
Cl	0.36	0.37
CF$_3$	0.48	0.47
CN	0.65	0.61
NO$_2$	0.71	0.72

A Consideration of Solvent Effects on Proton-Transfer Equilibria. The effects of the solvent can be considered to be of two types: (a) specific solvation involving the formation of discrete solvent–solute complexes and (b) nonspecific electrostatic solvation. Specific ion–molecule complex formation can lead to very large

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[32] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); **81**, 5343 (1960).

[33] A. J. Hoefnagel and B. M. Wepster, *J. Am. Chem. Soc.*, **95**, 5357 (1973).

effects.[7-9] A simplified but powerful generalized scheme for consideration of the effect of specific solvation on the substituent effects for given series of acid–base equilibria can be represented as follows.[34] Solvation can be usefully viewed as a series of acid–base-type equilibria which are competing with the principal proton-transfer equilibria in such a manner as to obtain a maximum in stabilization (more specifically, minimum standard free energy) of both internal electronic energy and molecular motions and external solvation. The proton-transfer reactions in the gas phase which give the substituent effects of a series of X substituents are represented by eq 18, where X is a substituent for H in a rigid

$$\mathrm{X{-}G{-}BH^{\nu} + H{-}G{-}B{:}^{\nu-1} \rightleftarrows X{-}G{-}B{:}^{\nu-1} + H{-}G{-}BH} \qquad (18)$$

molecular cavity G to which is also a fixed basic center B. The charge is given by ν, which in practice is either 0 or +1. As applied to the gas-phase acidities of phenols, for example, G = C_6H_4, B = $-\ddot{\underset{..}{O}}{:}$, and $\nu = 0$.

The corresponding reactions in solution may be represented by the binding of solvent molecules (α–β) in unspecified number to the principal solvation sites in the above ions and molecules, e.g.,

$$\beta{-}\alpha\cdots\mathrm{X{-}G{-}B{-}H^{\nu}}\cdots\beta{-}\alpha + \mathrm{H{-}G{-}B^{\nu-1}}\cdots\alpha{-}\beta \rightleftarrows \beta{-}\alpha\cdots\mathrm{X{-}G{-}B^{\nu-1}}\cdots\alpha{-}\beta + \mathrm{H{-}G{-}B{-}H^{\nu}}\cdots\beta{-}\alpha \qquad (19)$$

where X is represented as having a basic center (alternately, an acidic center may also be appropriately represented) and α–β specificies the acidic (either protonic or nonprotonic) and the basic centers of the solvent molecules, respectively.

For oxygen and nitrogen bases (B = O, N) specific ionic solvation energies tend to be much greater than that for neutral group solvation. This predominant ionic solvation opposes the direction favored by the gas-phase reaction. For example, if X is an electron-withdrawing substituent in phenol, p-X-C_6H_4-$O^-\cdots\alpha$–β solvation stabilization is reduced compared to that for C_6H_5-$O^-\cdots\alpha$–β,[5] and equilibrium 19 will be shifted to the left compared to the corresponding equilibrium (eq 18). The converse applies if X is electron donating. In either case, the solvent effect $K_{(19)}/K_{(18)}$, is less than unity (frequently much less); that is, the subsituent effect of X is reduced in solution compared to the gas phase.

Solvation of the neutral molecule acid or base center produces the same result, a reduced substituent effect in solution compared to the gas phase. This may be seen, for example, in the phenol with an electron-withdrawing group, for which p-X-C_6H_4-$OH\cdots\beta$–α solvation stabilization is greater than that of C_6H_5-$OH\cdots\beta$–α. The result is that equilibrium 19 is shifted to the left compared to the corresponding equilibrium 18, and again $K_{(19)}/K_{(18)} < 1$.

Specific solvation of the X at a basic center is favored for the anionic conjugate base compared to that for the corresponding neutral acid and specific solvation of an acidic center of a substituent is favored in the cationic conjugate base compared to that of the neutral base. Considering para-substituted phenol acidities to illustrate the consequences of substituent solvation, for example, a basic substituent will be more stabilized by external solvation in β–$\alpha\cdots p$-X-$C_6H_4O^-\cdots\alpha$–β than in β–$\alpha\cdots p$-X-C_6H_4-$OH\cdots\beta$–α. If X is an electron-withdrawing substituent (e.g., NO_2), the consequence of this specific solvation of the substituent is an acid-strengthening or increased electron-withdrawing effect. That is, equilibrium 19 is shifted to the right compared to the corresponding (hypothetical) equilibrium in which X is not solvated. Solvation of a basic net electron-donating substituent (e.g., p-OCH_3) will also shift equilibrium 19 to the right, giving an apparent reduced electron-donating effect. With weakly solvated base centers $-B{:}^-$ or acidic centers $-BH^+$, as for carbon acids and bases with extensive charge delocalization, specific substituent solvation effects may become the predominant solvent effects.[7,9a,17]

Additional considerations are important in applying this generalized scheme. First, solvent self-association competes favorably with solute–solvent association due to the mass law (relatively high solvent concentration) and entropy effect considerations.[35a] Therefore, as specific solvation of a solute center is weakened, a limit will be reached in which this interaction is no longer competitive with solvent self-association and abruptly will no longer be observed. Further, the differential in corresponding specific solute solvation between the right- and left-hand sides of equilibrium 19 will tend to be reduced toward zero as the strength of these interactions decreases. That is, both of the above considerations lead to cancellation of weak specific solvation effects on equilibrium 19.

The generalized scheme may be adapted to any solvent system which permits equilibrium 19 to occur with completed dissociated ions. The use of a solvent effect treatment,[36] e.g., $\delta\Delta G°_{\mathrm{solvation}} = s\pi^* + a\alpha + b\beta$, for correlation of or prediction of these general solvent effects seems appropriate.

If the solvent does not support complete dissociation of ions, the scheme is still qualitatively applicable by replacing the solvent α–β interactions with those of the generally much stronger counterion acid (M^+) or base (A^-).[7]

Finally, it must be remembered that nonspecific solvent effects may alter the position of equilibrium in a proton-transfer reaction in solution compared to the gas phase. These nonspecific solvation effects are indicated by simple electrostatic equations (e.g., ion–dipole, dipole–dipole, and charge-induced–dipole interactions) to involve a constant reduction factor in the substituent effect energies for a given reaction in solution—namely, the ratio of the effective dielectric constants in the gas and solution phases. For solution reactions involving completely dissociated ions, the dielectric factor has been considered to reduce substituent effects by at least a factor of twofold or greater. However, recent studies on the aqueous solvent effects of dipolar substituents on the acidities of primary ammonium ions indicate that the observed reduction factor is due almost entirely to the effects of specific rather than nonspecific solvation.[9b,c] On the other hand, the effects of aqueous solvent on the acidities of pyridinium ions with dipolar three and four substituents have been shown to involve important contributions from both specific and nonspecific solvation effects.[6]

The Effects of Aqueous Solvent on Phenol Acidities. The effects of meta and para substituents on the gas-phase acidities of phenols plotted vs. the corresponding effects on acidities of phenols in water (25 °C) (from Table I) are shown in Figure 6. A five- to sevenfold aqueous solvent attenuation factor[2,3,5] is apparent in Figure 6. However, our detailed substituent study reveals that this is by no means a precise factor since the linear correlation of all data points in Figure 6 is not precise compared to well-behaved LFE relationships. Further, as we shall see, a least-squares fit for Figure 6 would give an inappropriate slope since scatter is not random. Figure 6 does show that a limited LFE relationship of very satisfactory precision holds for the non-HBA acceptor substituents, m-CH_3, m- and p-Cl, m- and p-CF_3, m-CN, and m-NO_2. For apparently coincidental reasons (as we will show) the points for the p-NH_2, p-$N(CH_3)_2$, and p-OCH_3 (but not m- and p-F) substituents may also be included in this precise limited LFE relationship. The linear correlation for these substituents is:

$$\delta\Delta G°_{(\mathrm{g})} = (6.56)\delta\Delta G°_{(\mathrm{aq})} - 0.1 \qquad (20)$$

the average deviation of calculated $\delta\Delta G°_{(\mathrm{g})}$ values from eq 20 is ±0.4 kcal/mol covering a range of 17.6 kcal/mol (the range of $\delta\Delta G°_{(\mathrm{aq})}$ values is 2.45 kcal/mol) and the correlation coefficient is 0.998. The points for p-CH_3 and p-F deviate upward in Figure 6 both by 1.6 kcal/mol whereas the points for all other substituents deviate downward by 0.8 to 5.5 kcal/mol. Many of the latter deviations, except for m-F (and the 0.9 kcal/mol deviation for m-Cl), may be attributed (cf. subsequent discussion) largely to the substituent HBA effects. The behavior displayed in Figure 6 provides no evidence of significant polarizability effects of meta

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[34] The detailed formalism presented has not been given previously but the main ideas are implicit in earlier discussions, e.g., ref 4c,d, 7–9, and R. W. Taft, in "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, Chapter 2.

[35] (a) R. W. Taft and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, 1723 (1979); (b) cf. M. J. Kamlet, M. E. Jones, R. W. Taft, and J. L. M. Abboud, *ibid.*, 342 (1979).

[36] Cf. M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

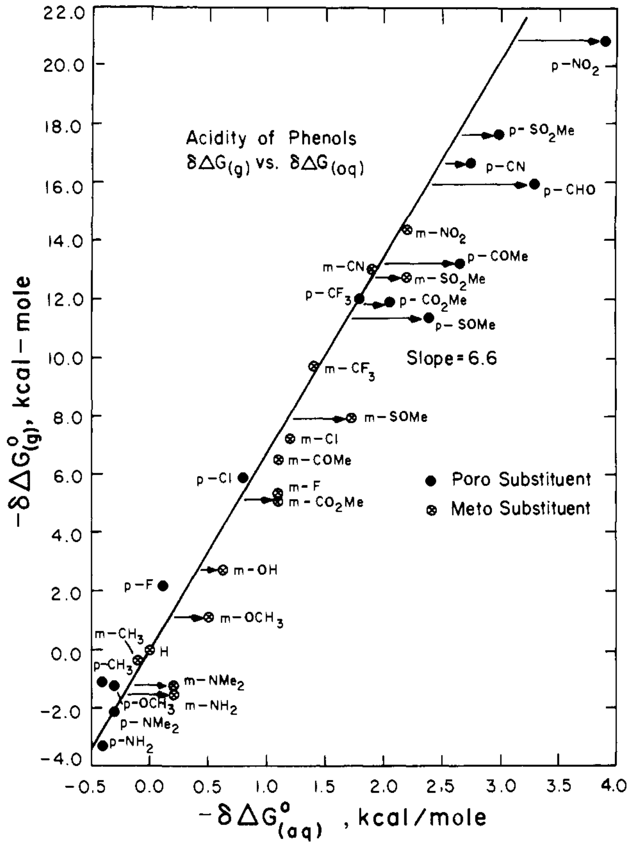


Figure 6. Acidity of phenols, Gas phase vs. aqueous phase: ordinate, $-\delta\Delta G^\circ_{(g)}$ (kcal/mol); abscissa, $-\delta\Delta G^\circ_{(aq)}$ (kcal/mol).

Table IV. Comparison of Inherent σ Values from Equation 17 with Those from Aqueous Solution

	$\sigma_{m(g)}$	$\sigma^n_{m(aq)}$[a]	$\sigma^-_{p(g)}$	$\sigma^-_{p(aq)}$[a]
$N(CH_3)_2$	−0.09[c]	−0.05	−0.16[c]	−0.22
NH_2	−0.07	−0.04	−0.17	−0.27
OCH_3	0.06	0.08	−0.06	−0.13
CH_3	−0.02	−0.07	−0.06	−0.12
F	0.27	0.34	0.12	0.15
Cl	0.36	0.37	0.30	0.26
H	0.00	0.00	0.00	0.00
CF_3	0.48	0.47	0.59	0.56
$SOCH_3$	0.39	0.52	0.57	0.73[b]
CN	0.65	0.61	0.83	0.99
SO_2CH_3	0.64	0.68	0.88	1.05
CO_2CH_3	0.26	0.32	0.59	0.74
CH_3CO	0.33	0.38	0.66	0.82
NO_2	0.72	0.71	1.04	1.23
CHO	0.43		0.79	0.98

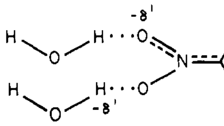
[a] From ref 33, unless otherwise noted. [b] From O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, Chapter 1. [c] With polarizability effect correction, cf. Table I.

and para substituents on the gas-phase phase acidities, except for hydrocarbon substituents and heteroatom substituents which have a high hydrocarbon content (e.g., $N(CH_3)_2$ and C_6H_5CO—cf. subsequent discussion).

The slope of Figure 6 (6.56) gives the substituent effect attenuation factor for aqueous solvent which results from the combined effect of strong specific solvation of the phenoxide ions,[5] the dielectric constant factor for nonspecific solvation, and the specific solvation of the phenols.

Effects of Specific Solvation of Substituents. The select meta and para substituents have little or no HBA effects from aqueous solvent.[11,16] That is, hydrogen bonding to these substituents is sufficiently weak[11,16] that there is little or no contribution to their effects on aqueous acidity[4d] resulting from a significant *differential* in the energy of the hydrogen bond to the substituent between the substituted phenol and its corresponding phenoxide ion. For substituents with weak hydrogen-bond-acceptor propensities, this result (as noted in the previous section) is strongly aided by preferential self-association rather than solute–solvent hydrogen bonding.[35a] All of the other meta substituents (e.g., $SOCH_3$, CH_3CO, $N(CH_3)_2$) involve appreciable substituent HBA effects in aqueous media.[4d,11] Accordingly, the σ^n_m(aq) values for these substituents all tend to be more positive than the corresponding inherent σ_m(g) values which are calculated from eq 17 (cf. Table IV). Indeed, it had been shown previously that the σ_I value for these substituents, which is the predominant contributor to the corresponding σ_m value, is increased from 0.03 to 0.13 units by hydrogen-bonding effects of weakly protonic solvents.[11]

It follows from eq 17 and 20 that the aqueous phase σ^-_p(aq) values for weak or non-HBA acceptor +R para substituents, e.g., p-CF_3, are essentially identical with the corresponding inherent σ^-_p(g) values (obtained from eq 17—cf. Table IV). On the other hand, as indicated by the deviations shown in both Figures 5 and 6, hydrogen-bond-acceptor +R para substituents have σ^-_p(aq) values which are significantly larger than the corresponding inherent σ^-_p(g) values (cf. Table IV). It is incompatible with substituent effect theory that σ^-_p values should be more enhanced for solvated phenoxide ions (i.e., for the aqueous phenol acidities) than for unsolvated phenoxide ions (i.e., for the gas-phase phenol acidities). Consequently, the previously generally held view that σ^-_p(aq) values represent the inherent internal π-electron-acceptor ability of +R substituents must be incorrect. Instead, σ^-_p(aq) values are shown to involve a complex composite of field/inductive, internally enhanced π-electron delocalization and specific substituent HBA solvation-assisted resonance effects. Thus, for example, the oxyanion character endowed by conjugation upon the oxygen atoms of the p-NO_2 substituent converts a very weak or negligible HBA substituent (m-NO_2) to a relatively strong HBA substituent (p-NO_2), as represented by the schematic structure I.



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The magnitudes of the spcific substituent solvation enhancements in phenol acidities in aqueous solution (shown by the horizontal arrows in Figure 6) may be estimated by rearranging equation 20

$$\delta\Delta G^\circ_{(aq)}(\text{calcd}) = (\delta\Delta G^\circ_{(g)} + 0.1)/6.56 \qquad (20')$$

That is, eq 20′ gives the aqueous substituent effect on phenol acidity estimated for the unsolvated substituent. The specific hydrogen-bond-acceptor solvation effect on the aqueous acidity is obtained as the difference between the observed $\delta\Delta G^\circ_{(aq)}$ value and that calculated from eq 20′. The values obtained in this manner are given in Table VIII and may be seen to be of reasonable magnitudes for substituent HBA effects. For HBA meta substituents, the enhancements in acidity range from 0.12 kcal/mol for m-CH_3CO to 0.58 kcal/mol for m-$SOCH_3$ (corresponding to increased σ_m(aq) values of 0.04 to 0.18 units). For HBA +R para substituents, the enhancements in acidity range from 0.24 kcal/mol for p-CN to 0.88 kcal/mol for p-CHO (corresponding to increased σ^-_p(aq) values of 0.08 to 0.28 units). Thus, Table VIII illustrates those substituents for which specific solvation has a significant acid-strengthening effect on aqueous phenol acidities and for which similar specific solvation effects may be expected in analogous systems (Table VIII lists a few typical additional results).

It is important to recognize that the specific solvation effects for the +R para substituents are not related σ^-_p values. Thus, while both σ^-_p(g) and σ^-_p(aq) values increase in the order $SOCH_3$ < CO_2CH_3 < $CHCO_3$ < CHO < CN < SO_2CH_3 < NO_2, the HBA specific solvation effects increase in a very different order CN < CO_2CH_3 < SO_2CH_3 < CH_3CO < $SOCH_3$ < NO_2 < CHO. In a later section it will be shown that this order of specific

Table V. Field/Inductive Effects (F) of Para (and Meta) Substituents for Phenol Acidities in the Gas and Aqueous Phases (kcal/mol)

X	$F_{(g)}{}^{p}$ [a]	$F_{(aq)}{}^{p}$ [b]	$F_{(g)}{}^{p}/F_{(aq)}{}^{p}$
CH_3			
H	0.0	0.0	
$N(CH_3)_2$	−0.5	−0.5	1.0 (HBAE)[c]
NH_2	−1.5	−0.5	3.0 (HBAE)
CO_2CH_3	−3.5	−1.0	3.5 (HBAE)
OCH_3	−4.5	−0.9	5.0 (HBAE)
CH_3CO	−4.8	−0.9	5.3 (HBAE)
CHO	−6.6		
$SOCH_3$	−6.9	−1.7	4.1 (HBAE)
OH	−7.8	−1.2	6.5
CF_3	−9.0	−1.4	6.4
Cl	−9.0	−1.4	6.6
F	−9.8	−1.6	6.1
SO_2CH_3	−11.6	−2.1	5.5 (HBAE)
CN	−12.1	−1.8	6.7
NO_2	−12.8	−2.0	6.4

[a] Obtained by using eq 29 with $K = 1.00$ and $\alpha = 0.60$ for −R and 0.20 for +R substituents. [b] Obtained by using eq 29 with $K = 1.00$ and $\alpha = 0.34$ for −R and 0.10 for +R substituents. [c] HBAE denotes significantly lower $F_{(g)}{}^{p}/F_{(aq)}{}^{p}$ ratio than 6.4 due to substituent hydrogen-bond acceptor effects in aqueous solution.

solvation effects correlates much better with inherent resonance effects.

Applicability of σ^-_p(g) Values to Solution Processes. Forceful additional evidence in support of the interpretation of Figure 6 as involving solvent-assisted resonance effects for HBA +R para substituents is provided by the demonstrated applicability of the inherent σ^-_p(g) values to appropriate solution equilibria (and other processes).

The acidities of meta- and para-substituted anilinium ions in water at 25 °C plotted vs. σ^-_m(g) and σ^-_p(g) values of Table IV gives most of the same qualitative features that are shown in Figures 5 and 6. The magnitudes of specific substituent HBA acceptor effects obtained as for aqueous phenol acidities are also recorded in Table VIII. However, as expected by the previous arguments, the acidities of meta- and para-substituted *N*,*N*-dimethylanilinium ions in nitromethane solution[37] at 25 °C are satisfactorily correlated by the inherent σ^-_p(g) values[38]

$$\log(K/K_0) = (3.70)\sigma^-_{(g)} + 0.06;\ n = 6;\ r = 0.991 \quad (21)$$

based upon H, *m*-Cl, *m*-F, *p*-CF_3, *p*-CO_2CH_3, *m*- and *p*-NO_2, and *p*-CN. Furthermore, the acidities of meta- and para-substituted thiophenols in 48% aqueous C_2H_5OH, 25 °C,[39] are also correlated with excellent precision by σ^-_p(g) values

$$\log(K/K_0) = (2.52)\sigma^-_{(g)} + 0.09;\ n = 10;\ r = 0.993 \quad (22)$$

as compared with $r = 0.979$ using σ^-_p(aq) values. These correlations are shown in Figure 7. The ^{1}H-SCS for the phenolic hydrogen of meta- and para-substituted phenols in *N*,*N*-dimethylformamide[40] (or dimethyl sulfoxide) solutions also correlate with good precision to the σ^-_p(g) values for +R substituents:

$$^1\text{H-SCS} = (1.66)\sigma^-_{(g)} - 0.02;\ n = 18;\ r = 0.985 \quad (23)$$

compared with $r = 0.959$, using σ^-_p(aq) values. Figure 8 shows this correlation. In a subsequent paper we report numerous high-precision correlations of appropriate rate data for electron-rich aromatic systems by the simple Hammett equation, using σ^-_p(g) values for +R substituents.

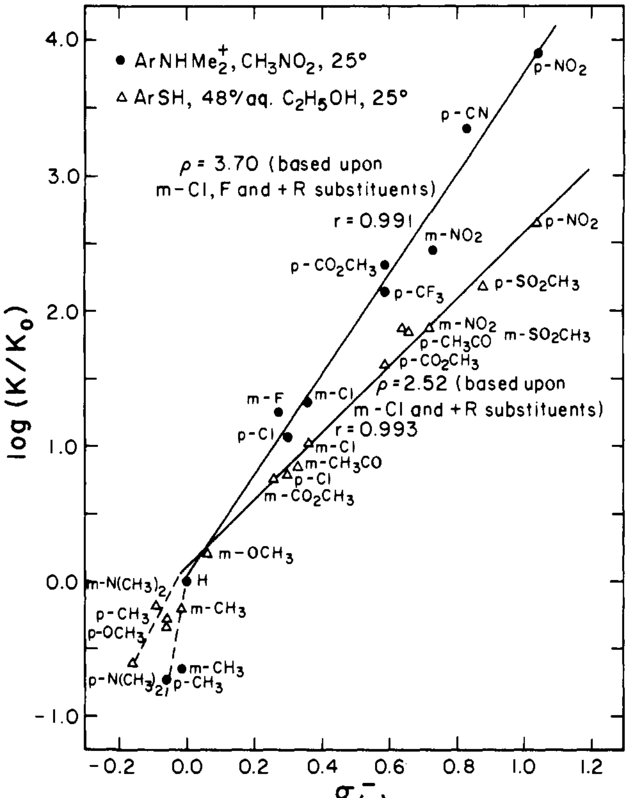

Figure 7. Hammett plot using inherent $\sigma^-_{(g)}$ values for acidities of meta- and para-substituted *N*,*N*-dimethylanilinium ions in nitromethane solution (25 °C) and of thiophenols, 48% aqueous ethanol solution (25 °C): ordinate, log (K/K_0); abscissa, $\sigma^-_{(g)}$.

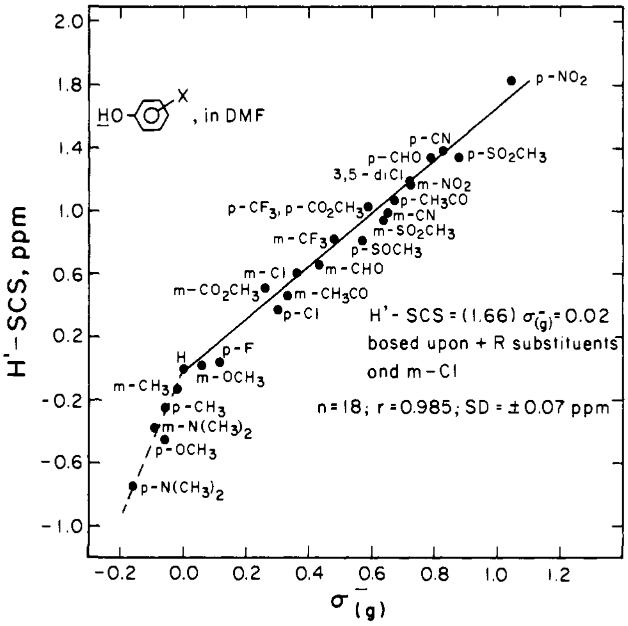

Figure 8. Hammett plot of phenolic OH hydrogen substituent chemical shifts in *N*,*N*-dimethylformamide solution using inherent $\sigma^-_{(g)}$ values: ordinate, ^{1}H-SCS (ppm); abscissa, $\sigma^-_{(g)}$.

The above correlations establish as have no previous ones the great relevance of gas-phase proton-transfer equilibria to appropriate chemical processes in solution. The correlations of the thiophenol acidities with inherent σ^-_p(g) values deserves particular comment. There is evidence that the hydrated thiophenate ion group is a substantially weaker π-electron donor than is the hydrated phenoxide ion group.[41] Consequently, the hydrogen

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[37] B. A. Korolav and B. I. Stepanov, *Izo Uyssh. Uchab Zaved Khim. Tekhnol.*, **11** (10), 1193 (1968).

[38] There is insufficient data for +R meta substituents to make this data set discriminating between better fit to σ^-_p(g) or σ^-_p(aq) values. However, the fact that the results for the *p*-CF_3, *p*-CO_2CH_3, *p*-CN, and *p*-NO_2 substituents are more precisely linear with the σ^-_p(g) values favors this correlation. Additional data for this series would be valuable.

[39] (a) G. Schwarzenbach and H. A. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934); (b) G. Schwarzenbach and E. Rubin, *ibid.*, **22**, 360 (1939); (c) F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 6019 (1953); (d) F. G. Bordwell and P. J. Bouton, *ibid.*, **78**, 856 (1956).

[40] Y. Tsuno, M. Fujio, Y. Takai, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **45**, 1519 (1972).

Table VI. Inherent σ_I Values

	$XCH_2NH_3^+$ [a]	$XC_5H_4NH^+$ [b]	XC_6H_4OH [c]	SCS[d] $XC_6H_4CH{=}CH_2$	SCS[e] $XC_6H_4(H,F)$	inherent best value	Charton[f] hydroxylic solvent value
$Si(CH_3)_3$	−0.10			−0.10	−0.10	−0.10	−0.11
CH_3	−0.04	−0.01		0.00	−0.04		−0.01
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CH_2{=}CH$	0.01			0.03		0.02	0.11
$N(CH_3)_2$	0.05	0.07	0.03	0.12	0.06	0.06	0.17
NH_2			0.08	0.10	0.12	0.10	0.17
$HC{\equiv}C$	0.17			0.24		0.20	0.29
CO_2CH_3		0.16	0.18		0.20	0.17	0.32
OCH_3		0.21	0.23	0.27	0.27	0.25	0.30
CH_3CO		0.19	0.24	0.21	0.20	0.22	0.30
CHO			0.33		(0.27)	0.32	
$SOCH_3$			0.35		(0.49)	0.36	0.50[g]
CF_3	0.43	0.39	0.45	0.41	0.42	0.43	0.40
Cl		0.50	0.46	0.46	0.46	0.46	0.47
F		0.52	0.49	0.48	0.50	0.50	0.54
SO_2CH_3			0.58		0.60	0.58	0.59
CN	0.57	0.57	0.60	0.59	0.56	0.58	0.57
NO_2		0.65	0.64	0.66	0.65	0.65	0.67

[a] Based upon gas-phase acidities of substituted methylammonium or monosubstituted trimethylammonium ions with polarizability effect corrections–cf. ref 9. [b] Obtained from $F_{(g)}^{p}$ values for gas-phase pyridinium ion acidities, ref 4d; $\sigma_I = F_{(g)}^{p}/-20.0$. [c] Obtained from $F_{(g)}^{p}$ values of Table V; $\sigma_I = F_{(g)}^{p}/-20.0$. [d] Values obtained in hydrocarbon solvents for ^{13}C and ^{1}H substituent chemical shifts of styrenes, private communication, Professor W. F. Reynolds. [e] Values suggested in ref 12 based upon ^{13}C and ^{19}F substituent chemical shifts of substituted benzenes in hydrocarbon solvents. Values in parentheses are particularly uncertain. [f] M. Charton, *Prog. Phys. Org. Chem.*, 13, 119 (1981). [g] Reference 15.

Table VII. *R* Values Obtained for Phenol Acidities from Equation 30

	σ^0_R [a]	$R_{(g)}^{p}$	$R_{(g)}^{m}$	$R_{(aq)}^{p}$	$\sigma^-_{R(g)}$
F	−0.31	7.5	4.5	1.46	−0.38
OCH_3	−0.42	5.8	3.4	1.17	−0.29
NH_2	−0.50	4.8	2.9	0.89	−0.24
$N(CH_3)_2$	−0.55	3.6	1.2	0.75	
Cl	−0.18	3.1	2.1	0.60	−0.17
CH_3	−0.13	1.8	1.1	0.35	−0.09
H	0.00	0.0	0.0	0.00	0.00
CF_3	0.08	−2.9	−0.6	−0.42	0.15
$SOCH_3$	0.07[b]	−4.5	−0.9	−0.71	(0.23)
CN	0.08	−4.5	−0.9	−0.98	0.23
SO_2CH_3	0.12	−6.0	−1.2	−0.94	0.30
CO_2CH_3	0.16	−8.2	−1.6	−1.08	0.41
NO_2	0.15	−8.1	−1.6	−1.87	0.41
CH_3CO	0.16	−8.5	−1.7	−1.74	0.43
CHO	0.22	−9.2	−1.9	−2.3	0.46

[a] From ref 12, unless otherwise designated. [b] Unpublished result of W. Adcock, J. Bromilow, and R. W. Taft.

bonding of water to potential HBA para substituents (e.g., p-NO_2) is evidently sufficiently weak that is does not compete well enough with solvent self-association for substituent specific solvation assisted resonance (SSSAR) effects to be observed in the aqueous thiophenol acidities. Furthermore, the excellent correlation of these acidities with the inherent $\sigma^-_p(g)$ values indicates that the limiting values of enhanced substituent parameters which give the scale for internal stabilization of electron-rich aromatic systems by π-electron delocalization tend to be reached under conditions that have been regarded as relatively mild electron enhancement from the reaction center. That is, "electron demand" is markedly less for hydrated thiophenolate ion than for unsolvated phenoxide ion, yet $\sigma^-_p(g)$ values are applicable to both. This conclusion is well supported by the above correlations of the phenolic hydrogen H^1-SCS for meta- and para-substituted phenols in DMF (or Me_2SO) and the correlation of the acidities of meta- and para-substituted anilinium ion in nitromethane with the $\sigma^-_p(g)$ values from gas-phase acidities of phenols.

It thus appears that many (if not most) of the enhancements that have previously been ascribed to increased electron demand (i.e., increased π donation from the reaction center) are not due to this cause at all, but instead are the result of variable stabilization due to specific solvation-assisted resonance (SSSAR) effects.

For π-electron-donor (−R) substituents, HBA effects are not the dominant consideration in the substantial difference found between corresponding $\sigma^-_p(g)$ and $\sigma^-_p(aq)$ values (Table IV). The p-N(CH$_3$), p-NH_2, and p-OCH_3 substituents, as well as the p-CH_3 and p-Cl substituents, all have more negative $\sigma^-_p(aq)$ than $\sigma^-_p(g)$ values—a result inconsistent with the expectations of substituent HBA effects. Further, the values of $\sigma^-_p(g) - \sigma^-_m(g)$, which at least approximately must provide a measure of the relative π-electron-donor (−R) effects on the gas-phase phenol acidities, are in an unusual nonconventional order: F (−0.15) < OCH_3(−0.12) < NH_2 (−0.10) < $N(CH_3)_2$ (−0.07) < Cl (−0.06) < CH_3 (−0.04). It will also be noted that Figures 7 and 8 tend to be bilinear with smaller slopes for −R than for +R para substituents. Further analysis of the remarkable results for −R substituents is usefully postponed awaiting the discussion of a separation of the field/inductive and resonance effects of substituents.

Additional Evidence for Specific Substituent Solvation Assisted Resonance Effects. The acidities of nitromethane and acetone in water have been estimated[9a] by appropriate comparisons with gas-phase acidities to be increased in aqueous solution by very much larger SSSAR effects (15.7 and 14. pK_a units, respectively) than those obtained in Table VIII for aqueous p-nitro- and p-acetylphenols. This result is one expected from the much stronger direct-resonance interactions and the much weaker specific solvations of the reaction centers for the substituted methyl carbanion ions than for the corresponding phenoxide ions.

Cohen[42] has found, however, that there is a proportionately large increase in the acidifying effect of a p-NO_2 substituent in 2,6-di-*tert*-butylphenols. With steric hindrance to solvation of the phenoside center, the HBA solvation (SSSAR) effect of the conjugated p-NO_2 substituent is markedly increased. For example, in 50% aqueous ethanol the ρ value for para-substituted 2,6-di-*tert*-butylphenols based upon CH_3 and Br substituents (which have no HBA effects) is 3.90, from which one calculates a σ^-_p value for the p-NO_2 substituents of 1.72 (0.68 units greater than the intrinsic value and 0.49 units greater than the Hammett value for para-substituted phenols). The SSSAR effect is sufficiently dramatic that even though 2,6-di-*tert*-butylphenol is a 3.1 pK_a units weaker acid than phenol, p-nitro-2,6-di-*tert*-butylphenol is a 0.5 pK_a units stronger acid than p-nitrophenol.[42] Rochester[43]

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(41) R. W. Taft and J. W. Takshys, Jr., *J. Am. Chem. Soc.*, **87**, 4387 (1965), and unpublished results.

(42) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

has reported similar pK_a behavior in methanol.

There is also spectroscopic evidence that the hydrogen-bond-acceptor propensity of the nitro group is increased from insignificance to significance as the result of the enhanced resonance interaction with an electron-rich center. The ultraviolet $\pi \rightarrow \pi^*$ transition for *N,N*-diethyl-3-nitroaniline (nonconjugated NO_2) shows no effects of hydrogen bonding with water or alcohols.[28] On the other hand, *N,N*-diethyl-4-nitroaniline (conjugated NO_2) has a $\pi \rightarrow \pi^*$ transition with readily detectable hydrogen-bond-acceptor effects at the *p*-NO_2 group in these solvents.[14] The *p*-nitrophenoxide ion shows similar (but larger) hydrogen-bonding effects of the *p*-NO_2 substituent in its electronic absorption spectrum.[13,44]

Separation of Field/Inductive and Resonance Effects. We turn next to a more detailed examination of the meta- and para-substituent effects on the gas-phase acidities of phenols which is obtained by employing the method of Taft and Lewis to separate the observed effects into contributions from the field/inductive (*F*) effects and the π-electron-delocalization (resonance, *R*) effects. In the method of Taft and Lewis[32] the effects of a meta- and para substituent in a given series of acids is taken as the sum of its field/inductive effects, *F*, and its resonance effect, *R*, i.e.,

$$\text{for meta} \qquad \delta\Delta G^\circ_{(m)} = F^m + R_m \tag{24}$$

$$\text{for para} \qquad \delta\Delta G^\circ_{(p)} = F^p + R^p \tag{25}$$

Further, the ratio of the *R* effect for the given substituent at the meta relative to the para position is taken to be a constant,[45] α (generally a fraction ranging from ~0.2 to 0.6), for the given substituent class (+R or –R), i.e., $R^m = \alpha R^p$. The ratio of the *F* effect at the meta relative to the para position is also taken to be a constant (frequently unity or very near to it), i.e., $F^m = KF^p$. From these assumptions one obtains the following expressions for separation of *F* and *R* effects:

$$\delta\Delta G^\circ_{(p)} = F^m/K + R^m/\alpha \tag{26}$$

or

$$\alpha\delta\Delta G^\circ_{(p)} = \frac{\alpha}{K}F^m + R^m \tag{27}$$

from which

$$\delta\Delta G^\circ_{(m)} - (\alpha)\delta\Delta G^\circ_{(p)} = F^m\left(1 - \frac{\alpha}{K}\right) \tag{28}$$

therefore

$$F^p = F^m/K = \frac{\delta\Delta G^\circ_{(m)} - (\alpha)\delta\Delta G^\circ_{(p)}}{K - \alpha} \tag{29}$$

and

$$R^p = \delta\Delta G^\circ_{(p)} - F^p = \frac{K\delta\Delta G^\circ_{(p)} - \delta\Delta G^\circ_{(m)}}{K - \alpha} \tag{30}$$

Equations 29 and 30 have been applied to the ab initio MO calculations of acidities of meta- and para-substituted phenols and values of F^p and R^p were obtained using $K = 1.00$ and $\alpha = 0.35$ for both +R and –R substituents.[18] The resulting F^p values correlate well with the σ_I scale of field/inductive effects.

The prediction from the ab initio MO calculations that reasonable F^p values may be obtained with the use of eq 29 is confirmed by the experimental $\delta\Delta G^\circ{}_{(g)}{}^m$ and $\beta\Delta G^\circ{}_{(g)}{}^p$ values of Table I. The best results are obtained from the experimental gas-phase results, using $K = 1.00$ and $\alpha = 0.20$ for +R and 0.60 for –R substituents (as obtained by trial and error methods). The reason for the different α values used with the theoretical calculations appears to be related to systematic errors already noted in connection with the discussion of Table II. The $F_{(g)}{}^p$ values obtained are listed in Table V.

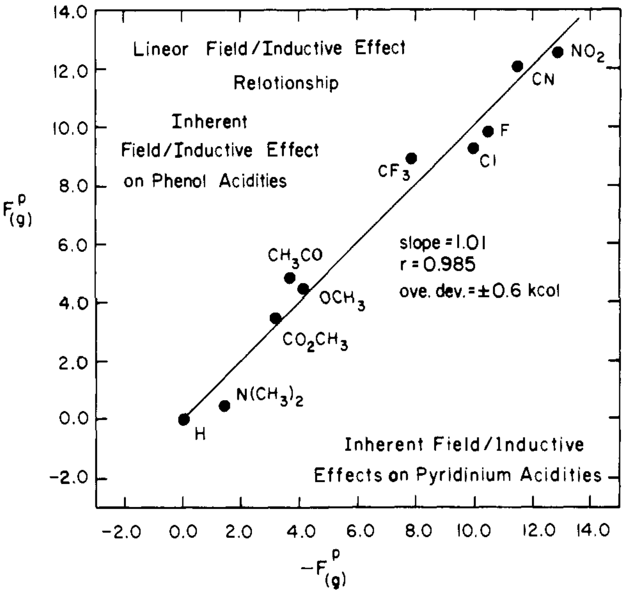

Figure 9. Linear field/inductive effect relationships: ordinate, $-F_{(g)}{}^p$, phenol acidities (kcal/mol); abscissa, $-F_{(g)}{}^p$, pyridinium ion acidities (kcal/mol).

Field/Inductive Effects Relationships. Figure 9 plots the $F_{(g)}{}^p$ values for the gas-phase phenol acidities vs. the corresponding $F_{(g)}{}^p$ values obtained previously[4d] from the experimental values for the gas-phase acidities of meta- and para-substituted pyridinium ions. In contrast to the substantial scatter exhibited in the corresponding plot of $\delta\Delta G^\circ{}_{(g)}$ values (Figure 4), Figure 9 shows a good linear correlation between the field/inductive effect contributions to the $\beta\Delta G^\circ{}_{(g)}$ values for these reactions. The correlation equation is: $F_{(g)}{}^p(\text{ArOH}) = (1.01)F_{(g)}{}^p(\text{pyrH}^+)$; the average deviation is ±0.6 kcal/mol and $r = 0.985$. Considering the manner in which errors can accumulate in the application of eq 29, this is very satisfactory precision.

Table V also gives aqueous $F_{(aq)}{}^p$ values obtained from the aqueous phenol acidities through the application of eq 29 with $K = 1.00$, $\alpha = 0.34$ for –R and 0.10 for +R substituents.[32] Corresponding $F_{(g)}{}^p$ and $F_{(aq)}{}^p$ values are linearly correlated by the equation: $F_{(g)}{}^p = (6.4)F_{(aq)}{}^p$, with an average deviation of +0.3 kcal/mol for a range of 12.6 kcal/mol in $F_{(g)}{}^p$ values, provided that only non-hydrogen-bonding or very weak hydrogen-bond-acceptor meta substituents are included (i.e., based upon CF_3, Cl, F, CN, and NO_2 substituents). This result, together with a similar one for pyridinium ion acidities,[4d] may be taken to indicate that field/inductive effects of meta and para subsitutents are quite precisely linear between the gas and solution phases in the absence of specific solvation of substituents. The slope (6.4) of this relationship is a measure of the extent of charge dispersal resulting from (a) specific solvation of the phenoxide ion, (b) nonspecific dielectric solvation (ion–dipole interaction reduced by the effective dielectric constant of water), and (c) (to a smaller extent) specific solvation of the reaction center in the uncharged acid or base.

The deviant substituents in phenol acidities from the relationship $F_{(g)}/F_{(aq)} = 6.4 \pm 0.3$ are: $N(CH_3)_2$, NH_2, CO_2CH_3, CH_3CO, OCH_3, $SOCH_3$, and SO_2CH_3, all hydrogen-bond acceptors.[11,16] These substituents have $-F_{(aq)}{}^p$ values which are greater than those calculated by the above relationship (i.e., $F_{(g)}/F_{(aq)}$ ratios are significantly less than 6.4, cf. Table V, by 0.1 to 0.6 kcal/mol. In σ_I units (i.e., dividing by $\rho_I(\text{aq}) = -3.2$ (kcal mol^{-1})/σ unit) these deviations correspond to increased values[11] from hydrogen-bond-acceptor effects of ~0.05 to 0.20 units ($SOCH_3$ has the most increased σ_I value). Thus the increases in $\sigma^n{}_m(\text{aq})$ values due to substituent hydrogen-bond-acceptor effects (Table VI) are essentially due to the increases in the corresponding σ_I values.

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[43] C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, **65**, 1004 (1969).

[44] R. W. Taft, M. J. Kamlet, and J. L. M. Abboud, *Bull. Chem. Soc. Jpn.*, submitted.

[45] For the aqueous acidities of phenols (and similar solution processes) the assumption of a precise α constant for all +R para substituents is inconsistent with the evidence presented herein for SSSAR effects with oxyanionic substituents, e.g., *p*-NO_2 (which would consequently have smaller α values) as opposed to *p*-CF_3 and *p*-SF_5 substituents which do not give such effects. However, in practice the application of α = 0.1 or 0.2, for example, has only very minor effect on F^p values obtained from eq 6.

Table VIII. Specific Hydrogen Bond Acceptor Solvation Enhancements in Aqueous Solution (kcal/mol)

	$\delta\Delta G^\circ_{(g)}$	$\delta\Delta G^\circ_{(aq)}$	$\delta\Delta G^\circ_{(aq)}$-(calcd)[a]	$\delta_{HBA}\Delta G^\circ_{(aq)}$-(ArOH)[b]	$\delta_{HBA}\Delta G^\circ_{(aq)}$-($ArNH_3^+$)[c]
		Meta Substituents			
CH_3CO	−6.5	−1.10	−0.98	−0.12	−0.08
SO_2CH_3	−12.8	−2.16	−1.93	−0.23	−0.10
CO_2CH_3	−5.1	−1.08	−0.76	−0.32	−0.33
OCH_3	−1.1	−0.48	−0.15	−0.33	
NH_2	1.4	−0.15	0.23	−0.38	
$N(CH_3)_2$	1.2	−0.20	0.20	−0.40	
$SOCH_3$	−7.8	−1.75	−1.17	−0.58	
		Para Substituents			
CN	−16.6	−2.76	−2.52	−0.24 (−1.2)[d]	−0.58
CO_2CH_3	−11.7	−2.05	−1.77	−0.28 (−1.0)[d]	−0.51
SO_2CH_3	−17.6	−3.01	−2.67	−0.34	−0.63
CH_3CO	−13.3	−2.66	−2.01	−0.65 (−1.9)[d]	−0.64
$SOCH_3$	−11.4	−2.39	−1.72	−0.67	
NO_2	−20.9	−3.89	−3.17	−0.72 (−3.5)[d]	−0.65
CHO	−15.8	−3.27	−2.39	−0.88 (−2.5)[d]	−0.77

[a] $\delta\Delta G^\circ_{(aq)}(\text{calcd}) = (\delta\Delta g^\circ_{(g)} + 0.1)/6.56$. [b] $\delta_{HBA}\Delta = \delta\Delta G^\circ_{(aq)} - \delta\Delta G^\circ_{(aq)}(\text{calcd})$. [c] For anilinium ion acidities in aqueous solution, $\delta_{HBA}\Delta G^\circ_{(aq)} - \delta\Delta G^\circ_{(g)}(\text{ArOH})/4.94$. [d] For acidities of 2,6-di-*tert*-butylphenols in 50% aqueous EtOH $\delta_{HBA}\Delta G^\circ_{(aq)} = [\log(K/K_0) - (3.90)\sigma^-_{p(g)}](-1.36)$.

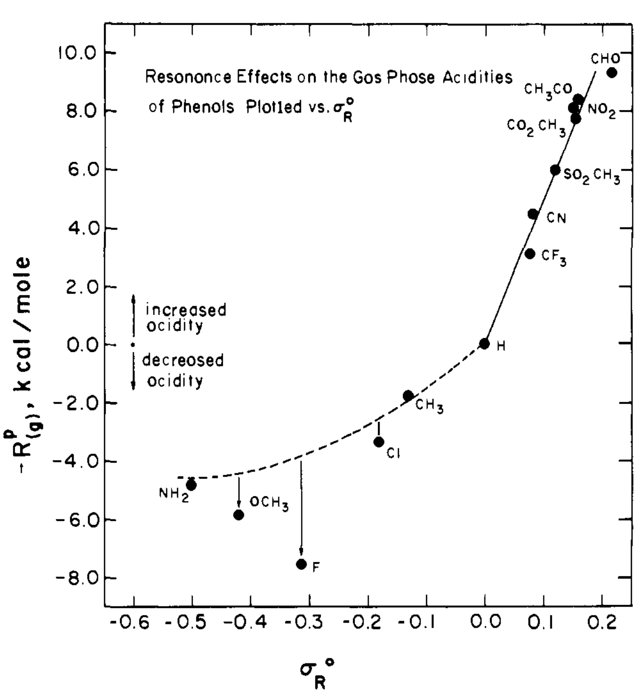

Figure 10. Resonance effects of para substituents on the gas-phase acidities of phenols plotted vs. the σ°_R parameter: ordinate, $-R_{(g)}^p$ (kcal/mol); abscissa, σ^0_R.

The linear field/inductive effect relationship of Figure 9 may be used as the basis for defining inherent σ_I values which are free from the effects of solvent–substituent hydrogen bonding or other interactions. Table VI lists the current best values for inherent σ_I parameters, which are largely based on gas-phase acidity data. Comparison is also given in Table VI with a recent tabulation[46] of σ_I values obtained from hydroxylic solvents.

Resonance Effect Relationships. Next we examine the resonance effects obtained from the use of eq 30, i.e., $R = \delta\Delta G^\circ - F$. The values of $R_{(g)}^p$, $R_{(g)}^m$, and $R_{(aq)}^p$ obtained are given in Table VII. There are several striking features of the gas-phase R values. First, the NO_2 substituent is not inherently a particularly strong π-electron acceptor. The para-substituent resonance effects on the gas-phase phenol acidities are about 8.3 kcal/mol for NO_2,[47] CO_2CH_3, and CH_3CO, increasing to 9.3 kcal/mol for the CHO substituent. This is exactly the same feature as shown by σ^0_R parameters obtained recently from ^{13}C substituent chemical shifts of monosubstituted benzenes in dilute cyclohexane solutions.[12] Thus, although there are much enhanced resonance effects (in absolute magnitudes) in the gas-phase phenol acidities (note in Table VII that the $R_{(g)}^p$ values are 4–7 times greater than the corresponding $R_{(aq)}^p$ values), the p-NO_2 substituent in the gas phase does not show the large relative enhancement as a π-electron acceptor that it does in aqueous solution.

In Figure 10 are plotted values of $R_{(g)}^p$ vs. the σ^0_R values referred to above[12] for all of the substituents, i.e., both −R and +R types. For the +R substituents there is a remarkably good linear correlation: $R_{(g)}^p = -0.3 - 46.1\ \sigma^0_R$; average deviation = ±0.6 kcal/mol; $r = 0.972$. For −R substituents, Figure 10 shows a distinct V shape. We believe that the latter behavior is due to two contributing factors. First, repulsive π-electron saturation resulting from the interaction of the para-R substituent with the π-charge built up at the para carbon from the even stronger −R phenoxide center tends to give a strong leveling effect as represented in Figure 10 by the curve shown. This is indeed the behavior anticipated from the theoretical STO-3G calculations.[18a] Second, the downward deviations from this curve, which increase in the sequence $NH_2 < Cl < OCH_3 < F$, result from para π-electron repulsion effects[48] (which are not adequately treated at the STO-3G level of approximation). In the unsolvated phenoxide ion the great extent of delocalization of π electronic charge to the para carbon position[18a] we believe gives rise to major para π-electron repulsion effects, which are expected to follow the above sequence. This consideration is evidently still a major effect for the solvated phenoxide ion since $R_{(aq)}^p$ values follow the same trends (note that the ratio of $R_{(g)}^p/R_{(aq)}^p$ from the results given in Table VII is ~5.1 for all of the −R substituents). The behavior is not indicated to be an artifact of the assumed application of eq 29 and 30 because, as shown in Figure 9 and Table VI, these substituents give $F_{(g)}^p$ values which are well-behaved. An additional factor which may contribute to reduced $R_{(aq)}$ compared to the corresponding $R_{(g)}$ values for −R substituents is hydrogen bonding between the electron-rich benzene ring and water molecules.[35b]

Gas-phase phenol acidities appear to be appropriate[17] for the definition of inherent $\sigma^-_{R(g)}$ parameters. Making the arbitrary assumption that $\rho_I = \rho_R = -20.0$ kcal/σ unit, one obtains $\sigma^-_{R(g)} = -R_{(g)}^p/-20.0$. The values of the inherent $\sigma^-_{R(g)}$ parameters (which are free from substituent HBA effects) are also recorded in Table VII. Comparison of $\sigma^-_{R(g)}$ values for +R substituents with corresponding σ^-_R values from hydroxylic solvents[15] shows that only the p-CF_3 and p-CO_2CH_3 substituents are unaffected by significant substituent HBA resonance effects. It is also worthy

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(46) M. Charton, *Prog. Phys. Org. Chem.*, **13**, 119 (1981).

(47) The R value obtained from STO-3G calculations[18a] for the difference in acidities of p-nitrophenol with a planar and an orthogonal NO_2 substituent is 7.2 kcal/mol, in reasonable accord with the empirical value.

(48) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules", Methuen, London, 1963.

of note for these substituents that the ratio $R_{(g)}^{p}/R_{(aq)}^{p} = 7.3 \pm 0.3$ is greater than $F_{(g)}^{p}/F_{(aq)}^{p}$ ($= 6.4 \pm 0.3$, indicating that there is a small enhancement factor for resonance effects of unsolvated +R para substituents with the unsolvated compared to the solvated phenoxide center.

Additional Limitations of the $\sigma\rho$ Relationship. In the analysis of gas-phase and aqueous-solution acidities of meta- and para-substituted pyridinium ions,[4d] it was found that the aqueous solvent attenuation factor for resonance effects is substantially greater from the meta than the para position. The same result is found for phenol acidities. That is, the ratios of $R_{(g)}^{m}/R_{(aq)}^{m}$ are 9 or greater for all substituents as compared with $R_{(g)}^{p}/R_{(aq)}^{p}$ ratios of only 4–7. Alternately, this effect is seen in the greater gas-phase α values $= R^{m}/R^{p}$ of 0.60 for −R and 0.20 for +R substituents compared to the aqueous values of 0.35 for −R and 0.10 for +R substituents, respectively. It was suggested[4d] that the indirect meta resonance effects are more subject to the greater effective dielectric constant in aqueous solution than are the direct para resonance effects.

It is important to note that the behavior discussed above means that the simple Hammett equation cannot be strictly valid for both the gas and aqueous phases, even in the absence of effects of specific substituent solvation. The point is well illustrated by the fluorine substituent which has relatively large values of R^{m}, R^{p}, F^{m}, and F^{p} in both phases. The constraint of the simple Hammett equation is that $\rho = \rho_I = \rho_R$ from which $\lambda_{(g)}^{p}/\lambda_{(aq)}^{p} = \lambda_{(g)}^{m}/\lambda_{(aq)}^{m}$, where $\lambda^{p} = \rho_R^{p}/\rho_I^{p}$ and $\lambda^{m} = \rho_R^{m}/\rho_I^{m}$. However, the F values of Table V and the R values of Table VII for the fluorine substituent give: $\lambda_{(g)}^{p}/\lambda_{(aq)}^{p} = (R_{(g)}^{p}/R_{(aq)}^{p})(F_{(aq)}^{p}/F_{(g)}^{p}) = 0.84$ whereas $\lambda_{(g)}^{m}/\lambda_{(aq)}^{m} = (R_{(g)}^{m}/R_{(aq)}^{m})(F_{(aq)}^{m}/F_{(g)}^{m}) = 1.48$. The consequence of this departure from the simple Hammett relationship is seen clearly in the plot of $\delta\Delta G°_{(g)}$ vs. $\delta\Delta G°_{(aq)}$ values (Figure 6). The point for the *p*-F substituent deviates upward in this plot by 1.6 kcal/mol, since there is greater solvent attenuation of the field/inductive than of the resonance effect. On the other hand, the point for the *m*-F substituent deviates downward by 2.2 kcal/mol because of the greater solvent attenuation in the meta resonance effect. Similar, but less pronounced, behavior is also seen in Figure 6 for the points for *m*- and *p*-Cl substituents.

The +R substituent specific solvation assisted resonance effects for the aqueous phenol acidities may be estimated by subtracting $R_{(g)}^{p}/7.4$ from $R_{(aq)}^{p}$ values given in Table VII. The SSSAR effects obtained in this manner increase in the order CF_3, CO_2CH_3 < $SOCH_3$, SO_2CH_3 ≪ CN ≪ CH_3CO < NO_2 < CHO, which correlates roughly with the inherent $\sigma^-_R(g)$ values. Further work is in progress to determine the best manner to incorporate SSSAR effects in substituent parameter treatments.

The limited LFE relationship between the relative acidities of meta- and para-substituted anilinium ions and corresponding meta- and para-substituted phenols in H_2O (25 °C) (Figure 3) may now be understood. The apparent relative enhancements in effects in phenol compared to anilinium ion acidities for the *p*-NO_2, *p*-CHO, and *p*-CH_3CO substituents result from relatively greater SSSAR effects. Para substituents with weak or negligible HBA resonance effects[11,49] follow an approximate LFE relationship, i.e., SO_2CF_3, SO_2CH_3, CN, SF_5, CF_3. Field-induced resonance effects preferentially stabilize −R para-substituted anilinium ions,[4d] accounting, together with some HBA and electron repulsion substituent effects in the hydrated phenoxide ions, for the deviations for *p*-NH_2 and *p*-OCH_3 substituents.

Charge-Induced Dipole Stabilization Effects in the Gas-Phase Acidities. McIver and Silvers[2] found that while the methyl substituent increases the gas-phase acidity of phenol in the ortho position, acidity is decreased by this substituent in the meta and para positions. Further, the *tert*-butyl substituent increases gas-phase acidities at all three positions. The present results confirm and extend these findings. The gas-phase acidity increases regularly in the sequence: $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$. The incremental increases in this sequence are meta, ~0.3 kcal/mol < para, ~0.6 kcal/mol < ortho, ~1.2 kcal/mol. These results are accounted for by predominant ion-induced dipole stabilization of the phenoxide ion with increasingly polarizable alkyl groups.[50] A much ovver-simplified calculation according to the electrostatic equation, $E = -\alpha q^2/2Dr^4$, using a full electronic charge at oxygen, a distance of 2.82 Å units between this charge and the center of the substituent, $D = 2$, and $\alpha = 0.4 \times 10^{-24}$ H and 2.2×10^{-24} cm^3 for each CH_3 group,[51] indicates an approximately 1.5 kcal/mol incremental increase in proton acidity for the above sequence at the ortho position. At the meta and para positions such a calculation gives increments of approximately 0.2 kcal/mol and approximately 0.1 kcal/mol, respectively. These results, while artificial on a quantitative basis, do confirm the qualitative expectations of the polarizability effects on gas-phase phenol acidities. The greater observed effects at the para rather than the meta position are readily understood in terms of the substantial delocalization of π charge to the former position.[18a]

Destabilization of the unsolvated phenoxide ion by generally second-order electron-releasing alkyl-substituent effects is clearly indicated by the acid-weakening effects of the *m*- and *p*-CH_3 substituent.[2] It is difficult to estimate by how much the observed acid-weakening effects are reduced by the opposed polarizability effects but presumably by no more than several tenths of a kcal/mol. Nevertheless, this uncertainty makes the application of eq 29 and 30 very crude for the methyl substituent. As noted earlier, there is no indication, however, of appreciable polarizability effects for the other meta and para substituents, except for the $N(CH_3)_2$ and C_6H_5CO substituents, which have a high hydrocarbon content. The gas-phase acid-strengthening polarizability effects of the $N(CH_3)_2$ substituent can be estimated by taking the difference between the observed effects of the *i*-C_3H_7 and CH_3 substituents. This procedure gives corrected values of +1.7 and +3.1 kcal/mol for the meta and para positions, respectively, and these figures have been used in the applications of eq 29 and 30. The corrected values for the *m*- and *p*-$N(CH_3)_2$ substituents within experimental error are the same as those obtained for the *m*- and *p*-NH_2 substituents, respectively.

It may be noted that the observed effect of a *p*-*t*-C_4H_9 substituent appears to provide an excellent test for a specifically solvated aromatic anion. This substituent is acid strengthening in the gas phase due to its predominant charge-induced dipole stabilization of the unsolvated anion. However, with the charge dispersal which accompanies specific hydrogen-bonding (or other strong dipolar) solvation, there is no significant polarizability effect observed in solution for a specifically solvated anion.[5b] Thus only acid-weakening F and R effects apply, and there is a reversal in acidity order between the gas phase and solution (*p*-*t*-C_4H_9 phenol is a weaker acid than phenol in water, for example).[43]

Additive and Nonadditive Substituent Effects. Strictly additive behavior is observed for the gas-phase acidities of 3,5-dichlorophenol ($\delta\Delta G° = -14.4$ kcal/mol) and 2-methyl-4-nitrophenol ($\delta\Delta G° = -20.8$ kcal/mol). On an additive basis, the increased acidities compared to phenol are −14.2 and −21.2 kcal/mol, respectively. On the other hand, the gas-phase acidities of 3-methyl-4-nitrophenol ($\delta\Delta G° = -19.2$ kcal/mol) and 3,4,5-trichlorophenol ($\delta\Delta G° = -17.9$ kcal/mol) are significantly nonadditive. The 1.2 kcal/mol smaller acidity than additive for the former compound indicates approximately a 15% steric inhibition of resonance effect for the NO_2 substituent.[52] The 2.2 kcal/mol smaller acidity than additive for the latter compound is less clearly explained, but may be associated with activation of increased π-electron repulsion from the *p*-Cl substituent induced by the electron-withdrawing effects of the adjacent (3,5) chlorine atoms.

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(49) Cf. in particular Figure 2 of ref 9a.

(50) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 5636, 6501 (1968).

(51) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976).

(52) Cf. for example, R. W. Taft and H. D. Evans, *J. Chem. Phys.*, **27**, 1427 (1957), and B. Wepster, *Recl. Trav. Chim. Pays-Bas* **76**, 335, 357 (1957).