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# Correlations of Gas-Phase Acidities and Basicities with the Electrostatic Field Model

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Abstract: The potential energies of charge–dipole, charge–induced dipole, and dipole–dipole interactions in sets of substituted acetic acids, benzoic acids, phenols, and pyridines were calculated from the classical equations for these interactions and then correlated with the enthalpy changes for the gas-phase dissociations (or proton affinities) of these compounds. The correlation coefficients for the least-squares fit of $\Delta H°$ with the charge–dipole potential energy in the conjugate base (acid) were greater than 0.95 for most of the series. Moreover, the relative magnitudes of the potential energies agreed well with the relative magnitudes of the enthalpy changes. Addition of the charge–induced dipole energy to the charge–dipole energy improved the correlations in sets with low-polarity, polarizable substituents. Hence, the electrostatic field effect can be used to quantitatively correlate the effect of substituents on gas-phase acidities and basicities. Moreover, for systems containing polar substituents, the predominant field effect, indeed probably the predominant substituent effect, is the charge–dipole interaction in the conjugate ion.

The relative gas-phase acidity and basicity data collected over the past decade have been analyzed or correlated with the polarizability (charge–induced dipole field) effect,[1a] molecular orbital theory,[1b] the proton potential model,[1c] the electrostatic potential surrounding a base,[1d] core-ionization energies,[1e] and a variety of other molecular and atomic parameters such as electronegativity, hybridization, bond energies, and electron affinities.[1f] Although the charge–induced dipole field effect is widely invoked, especially in qualitative explanations of the relative acidities or basicities of alkyl homologues,[1a,2] only a few attempts have been made to employ simple classical electrostatic interactions in quantitative correlations. Aue, Webb, and Bowers showed that the charge–induced dipole interaction could account for the difference in proton affinities in a series of four primary alkylamines,[3] while Kollman and Kenyon used the charge–charge interaction to successfully predict the second proton affinities of a series of diamines.[4]

We present here an attempt to evaluate the electrostatic field effects of substituents on the gas-phase dissociation (1) and protonation (2) reaction:

$$X\text{-}A\text{-}H \rightarrow X\text{-}A^- + H^+ \tag{1}$$

$$X\text{-}B + H^+ \rightarrow X\text{-}B\text{-}H^+ \tag{2}$$
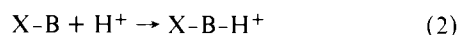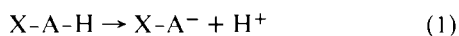
The most important electrostatic interactions between the substituents and the reaction site are the charge–dipole and charge–induced dipole interactions in the conjugate ions of (1) and (2) and the dipole–dipole interaction in the free acid of (1) and the base of (2). These field effects will be most likely to control the relative extents of (1) and (2) when (a) the substituent effects on the A–H and B–H bond energies are minor; that is, when the A or B moieties of a given series of acids or bases moderate the influence of X on the A–H or B–H bond energies; (b) inductive, resonance, and steric substituent effects are small or parallel the field effects; (c) substituent-induced changes in $\Delta S°$ are small.

For the series of compounds studied here the substituent-induced changes in $\Delta S°$ are likely to be negligible[5,6] and therefore the correlation of these field effects with the experimentally determined enthalpies of dissociation and proton affinities should permit an evaluation of the hypothesis that field effects control (in the predictive sense) the relative acidities or basicities within a given series. These correlations should also provide information on the relative importance of the charge–dipole, charge–induced dipole, and dipole–dipole interactions.

The four systems studied include a set (I) of 9 substituted acetic acids, a set (II) of 19 substituted benzoic acids, a set (III) of 13 phenols, and a set (IV) of 10 substituted pyridines. For the acids, the charge–dipole and charge–induced dipole potential energies were calculated for the interaction of the substituents with the negative charge of the conjugate ion, and the dipole–dipole energy was calculated for the interaction of the substituent with the reaction site (COOH for sets I and II, OH for III). For the pyridines, the charge–dipole and charge–induced dipole energies were determined for the substituted pyridinium ion and the interaction of the substituents with the dipole due to the heteroatom was calculated for the substituted base.

The calculations of these field effects were performed with the classical equations for these effects:

$$V_c = \frac{-q\mu \cos \theta}{\epsilon r^2} \qquad V_1 = \frac{-q^2\alpha}{2\epsilon r^4}$$

$$\text{charge–dipole} \qquad \text{charge–induced dipole}$$

$$V_D = \frac{-\mu_1\mu_2(2 \cos \theta \cos \phi - \sin \theta \sin \phi)}{\epsilon r^3}$$

$$\text{dipole–dipole}$$

Table I. Calculated Electrostatic Interactions between Substituent and Reaction Site (kcal/mol)

	V_c	V_1	V_D	$\Delta V_T{}^a$	lit. $\Delta H^{\circ\ b,14}$
		RCOOH (I)			
CF_3	−24.27	−37.52	13.21	−38.5	−25.2
CHF_2	−18.43	−38.01	12.45	−32.4	−18.0
CH_2F	−10.36	−38.43	7.98	−20.3	−10.8
$CHCl_2$	−18.55	−42.88	11.12	−36.1	−19.8
CH_2Cl	−10.48	−40.78	7.23	−22.0	−12.8
CH_2Br	−9.88	−41.44	6.30	−21.1	−13.9
CH_3	0	−36.5	0	0	0
CH_3CH_2	0	−41.32	0	−4.8	−1.2
$CH_3CH_2CH_2$	0	−46.02	0	−4.8	−2.1
		XC_6H_4COOH (II)			
p-NO_2	−7.23	−0.27	1.09	−8.5	−11.2
CN	−7.05	−0.22	1.07	−8.3	−10.3
F	−3.51	−0.042	0.63	−4.1	−2.9
Cl	−3.64	−0.20	0.63	−4.4	−4.45
CH_3	0.79	−0.26	−0.14	0.7	1.05
OH	3.07	−0.11	−0.55	3.6	−4.05
H	0	−0.05	0	0	0
m-NO_2	−9.52	−0.47	1.46	−11.4	−9.0
CN	−9.16	−0.39	1.45	−10.9	−9.6
F	−3.55	−0.07	0.82	−4.4	−3.85
Cl	−3.82	−0.35	0.83	−4.9	−4.7
CH_3	0.82	−0.46	−0.13	0.6	0.7
OH	3.13	−0.19	−0.72	3.7	−1.35
H	0	−0.09	0	0	0
o-NO_2	−9.34	−3.95	4.28	−16.9	−8.8
F	−1.06	−0.60	2.19	−3.1	−2.3
Cl	−1.90	−3.07	2.55	−6.8	−3.8
CH_3	0.33	−3.91	−0.53	−2.3	−0.8
OH	1.01	−1.56	−1.95	2.1	−13.3
H	0	−0.72	0	0	0
		XC_6H_4OH (III)			
p-F	−4.70	−0.07	−0.90	−3.8	−2.1
Cl	−4.76	−0.32	−0.87	−4.1	−2.9
CH_3	1.02	−0.42	0.20	0.5	1.2
$C(CH_3)_3$	1.39	−1.32	0.26	−0.1	−0.6
H	0	0	0	0	0
m-F	−5.05	−0.13	−1.19	−3.8	−4.8
Cl	−5.36	−0.59	−1.17	−4.6	−6.1
CH_3	1.15	−0.78	0.27	0.3	0.5
$C(CH_3)_3$	1.52	−2.42	0.35	−1.1	−0.5
H	0	−0.165	0	0	0
o-F	−16.92	−1.15	−4.48	−12.1	−2.8
Cl	−18.25	−5.20	−4.28	−17.7	−4.6
CH_3	3.91	−6.98	0.92	−2.5	−0.3
$C(CH_3)_3$	5.29	−21.72	1.24	−16.2	−3.4
H	0	−1.46	0	0	0
		XC_5H_4N (IV)			
p-NO_2	17.59	−1.56	3.93	12.5	17.0
CF_3	10.48	−1.52	2.32	7.0	11.0
CH_3	−1.48	−1.50	−0.33	−2.3	−5.0
OCH_3	−8.6	−0.64	−2.37	−6.5	−8.0
H	0	−0.36	0	0	0
o-CN	44.09	−11.30	3.27	33.2	12.5
CF_3	25.98	−12.55	1.65	15.4	9.1
F	27.19	−2.38	8.14	20.3	9.7
Cl	27.03	−8.22	5.91	16.6	6.3
OCH_3	−23.23	−5.61	−6.54	−18.7	−1.1
H	0	−3.65	0	0	0

^{a} $\Delta V_T = V_T(X) - V_T(H)$. ^{b} $\Delta(\Delta H^\circ) = \Delta H^\circ(X) - \Delta H^\circ(H)$.

and are subject to the various approximations (such as the point-dipole assumption) inherent in their derivations.[7,8] For set I μ for the substituent was taken as the bond moment for the carbon-halogen bond,[9] but for the alkyl derivatives μ was assumed to be zero. For sets II–IV μ for each substituent was taken as the dipole moment of the analogous substituted benzene[10] in the gas phase and the center of the moment (for the

Table II. Correlation Coefficients for Correlations of ΔH° with Field Effects^a

system	n^b	V_c	V_1	V_D	V_{c+1}	V_T
RCOOH (I)	9	0.989	−0.221	−0.970	0.961	0.983
$XC_6H_4CO_2H$ (II)						
para	7	0.795	0.448	−0.752	0.797	0.791
para, no OH	6	0.981	0.452	−0.959	0.984	0.981
meta	7	0.944	0.428	−0.898	0.944	0.939
meta, no OH	6	0.994	0.383	−0.989	0.993	0.995
ortho, no OH	6	0.974	0.535	−0.924	0.954	0.993
para + meta^c	11	0.952	0.116	−0.613	0.952	0.947
all^c	16	0.948	−0.002	−0.540	0.885	0.851
XC_6H_4OH (III)						
para	5	0.886	−0.178	0.884	0.935	0.944
meta	5	0.968	−0.339	0.962	0.998	0.992
ortho	5	0.593	0.327	0.578	0.985	0.988
para + meta	9	0.879	−0.267	0.907	0.923	0.916
all	13	0.551	0.158	0.521	0.628	0.596
XC_5H_4N (IV)						
para	5	−0.987	0.570	−0.979	−0.991	−0.993
ortho	6	−0.948	0.513	−0.733	−0.927	−0.945

^{a} Potential energies and ΔH° expressed in kcal/mol. ^{b} Number of derivatives in set. ^{c} OH omitted.

purposes of calculating r) was assumed to be at the center of the C–X bond (X = halogen, CH_3, OH, OCH_3) but at the central atom of the NO_2, $C(CH_3)_3$, CF_3, and CN groups. For the dipole-dipole interaction in the substituted pyridines the dipole moment of pyridine was used as an estimate of the dipole due to the heteroatom. Group polarizabilities[9,11] were employed as α for all substituents except that for the alkyl groups in set I the interaction of each group attached to the α carbon in the extended configuration was considered. The center of the charge in the carboxylate ions in sets I and II was assumed to reside at the midpoint of a line drawn through both oxygens of the COO^- group; the charge centers in the phenolate and pyridinium ions were taken as the oxygen and nitrogen atoms, respectively.[12] The structural parameters necessary for the trigonometric calculation of r were obtained where possible from X-ray data for the molecule or ion in question,[13] or, lacking such data, from appropriate average bond lengths and angles.[13] An appropriate value for the dielectric constant was difficult to determine. In the gas phase it should certainly be low but not necessarily 1.0 due to intervening molecular structure with a higher constant. Because previous calculations[3,4] employing the value of 1.0 produced reasonably good agreement with experimental values, this value was used in all calculations.

The overall effect (V_T) of the field effects on the enthalpies for reactions 1 and 2 can be obtained by subtracting the potential energy of the dipole-dipole interaction (V_D) in the molecular species (X–A–H or X–B) from the sum of the charge-dipole (V_c) and charge-induced dipole interaction (V_1) in the conjugate ion(s) (X–A$^-$ or X–B–H$^+$). Table I contains the calculated values for V_c, V_1, V_D, and $\Delta V_T(V_T(X) - V_T(H))$ as well as literature values[14] of ΔH° (actually $\Delta(\Delta H^\circ) = \Delta H^\circ(X) - \Delta H^\circ(H)$) for the gas-phase dissociations or protonations. (The literature values for set III are actually ΔG°'s, but, because ΔS° is small,[5,6] the difference between ΔG° and ΔH° for these reactions is negligible for the present purposes.)

The correlation coefficients for the least-squares fit of the calculated potential energies with the literature values of $\Delta(\Delta H^\circ)$ are presented in Table II. The correlations with both V_c and V_T are generally quite good, whereas correlations with V_1, the charge-induced dipole interaction, are universally poor. Use of the appropriate angular component[8] of bond polarizabilities[15] to calculate the charge-induced dipole interaction for the acetic acids gave even poorer correlations. That V_1

exerts a significant effect on the correlations of some systems with V_T, however, is most obvious in the phenols (especially the ortho derivatives), where correlations with the sum of the charge–dipole and charge–induced dipole interactions, V_{c+I}, are significantly better than those with V_c alone. This is probably a result of the presence of a larger percentage of low-polarity, moderately polarizable groups (CH_3, $C(CH_3)_3$) in the phenol sets.

For both the substituted benzoic acids and the substituted phenols the correlations of both V_{c+I} and V_T with $\Delta(\Delta H^\circ)$ for the meta and para derivatives considered as one set are at least moderately good. The correlations for *all* the derivatives (ortho, meta, and para considered as one set) for these systems, with the exception of V_c for the benzoic acids, are considerably lower. Since the correlations within each subset (ortho, meta, or para) are good this may be a reflection of the need for a different effective dielectric constant for the ortho subset but it may also be a result of the smaller substituent–reaction site distances (r) in the ortho sets and the consequent decreased validity of the approximate equations employed. It is also interesting to observe the poor correlation obtained for the para- and ortho-substituted benzoic acids when the hydroxy substituent is included in the sets. The deviation of the o-OH derivative is almost certainly a result of intermolecular hydrogen bonding. The anomalous acidity of the p-OH derivative was also noted by Yamdagni, McMahon, and Kebarle, who suggested that the dissociation for this molecule occurs at the OH rather than the COOH group.[14b]

Multiple regression analyses of V_c and V_I with ΔH° and also V_c, V_I, and V_D with $\Delta(\Delta H^\circ)$ were also performed. The fit obtained with both two and three variables, as expected, was generally good, but in most cases not significantly better than the single-variable analyses described above.

Although V_c and V_T correlate well with $\Delta(\Delta H^\circ)$, if field effects do indeed control ΔH°, the effect of substituents on the *magnitude* of the effect should equal their effect on the *magnitude* of ΔH°. An inspection of the data in Table I reveals that for the majority of the derivatives $\Delta(\Delta H^\circ)$ is closer to V_c than to ΔV_T and for six out of the nine sets the difference between $\Delta(\Delta H^\circ)$ and V_c is less than 2 kcal/mol. The ortho sets have the largest discrepancy between $\Delta(\Delta H^\circ)$ and both V_c and ΔV_T; this discrepancy appears to increase as the substituent–

reaction site distance decreases (compare the ortho members of sets II, III, and IV).

Clearly, the electrostatic field effect can be employed quantitatively to correlate and rationalize the effects of substituents on both gas-phase acidities and basicities. Moreover, for systems containing polar substituents the predominant field effect, indeed probably the predominant substituent effect, is the charge–dipole interaction in the conjugate ion.

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