Theoretical Correlation of Substituent Effects on the Acidity of Benzoic Acids in the Vapour Phase with Calculated HOMO Eigenvalues

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Substituent effects on the gas-phase acidity of benzoic acids are shown to have a linear correlation with the substituent effects $\Delta\varepsilon_x$ on the HOMO eigenvalue of the corresponding anions. This calculated property also correlates with substituent effects on gas-phase acidity of phenols, and therefore seems to play a role equivalent to that of Hammett σ constants for the solution properties of the same set of substances.

Catalan and Macias[1] showed that there was a linear relationship between the experimental acidity of *meta-* and *para-*substituted phenols with the theoretical acidity, estimated either as the energy difference between the neutral molecule and the corresponding anion or calculated as the sum of the energy term for the OH bond and the ionization potential of the anion.

This latter relationship was taken into consideration because the heterolytic bond dissociation energy $D(A^- - H^+)$ can be evaluated[2] from equation (1) where $D(A-H)$ is the homolytic bond dissociation energy, $E_A(A)$ is the electronic affinity of the radical A, and IP(H) is the ionization potential of the radical hydrogen. Since $-E_A(A) = $ IP(A^-), ionization potential of the anion A^-, we have equation (2).

$$D(A^- - H^+) = D(A-H) - E_A(A) + IP(H) \qquad (1)$$

$$D(A^- - H^+) = D(A-H) + IP(A^-) + IP(H) \qquad (2)$$

Since IP(A^-) can be fairly well approximated by the negative of the HOMO eigenvalue $\varepsilon(A^-)$ of the anion, it is apparent that a correlation should exist between calculated $\varepsilon(A^-)$ values and the effect of the X substituent on gas-phase acidity as measured[3] by $D(A^- - H^+)$. This latter has been shown to be acceptable with a few assumptions which here can be written $\Delta G^\circ = -D(A^- - H^+)$ and that previous authors[1-3] have shown to hold within a family of compounds.

Taking benzoic acid as the reference compound we can write equation (3). We have tested this equation by direct calculation of the $\varepsilon(A^-)$ eigenvalues of substituted benzoate anions, with the presumption that the substituent effect on $\Delta D(A-H)$ was second order, or negligible. This was found to be the case, and equation (3) is shown to give a linear correlation between $\Delta(\Delta G^\circ)_x$ and $\Delta\varepsilon_x(A^-)$, as reported below.

$$\Delta G^\circ_x - \Delta G^\circ_o = \Delta(\Delta G^\circ)_x = -\Delta D(A^- - H^+) =$$
$$-\Delta D(A-H) + \Delta\varepsilon_x(A^-) \qquad (3)$$

Methods

Geometries of benzoate and substituted benzoates (*m-* and *p-*F, OH, NH$_2$, CH$_3$, and CN) were fully optimized at the STO-3G level within the C_s symmetry by using the GAUSSIAN 80 program[4] with the Murtaugh–Sargent method,[5] yielding bond lengths and angles to ±0.001 Å and 0.5°, respectively. Further calculations were carried out at this optimized geometry employing a 3-21G basis set; this was necessary because of the inadequacy of minimal basis sets to give reliable values of ionization potential for the anions.[6]

Table. Experimental gas-phase $\Delta(\Delta G^\circ)_x$ values at 600 K of substituted benzoic acids (kJ mol^{-1}), HOMO eigenvalues (ε) of the corresponding anions (a.u.), and $\Delta\varepsilon_x$ (kJ mol^{-1})

X	$\Delta(\Delta G^\circ)_x$	ε_x	$\Delta\varepsilon_x$
p-NH$_2$	9.6	−0.1610	2.364
m-NH$_2$	6.3	−0.1632	−3.415
p-CH$_3$	4.6	−0.1611	2.101
m-CH$_3$	2.9	−0.1619	0.000
Unsubstituted	0.0	−0.1619	0.000
m-OH	−5.4	−0.1687	−17.862
p-F	−12.1	−0.1695	−19.963
m-F	−15.9	−0.1713	−24.691
p-OH	−17.2	−0.1641	−5.779
m-CN	−42.7	−0.1820	−52.797
p-CN	−45.6	−0.1835	−56.737

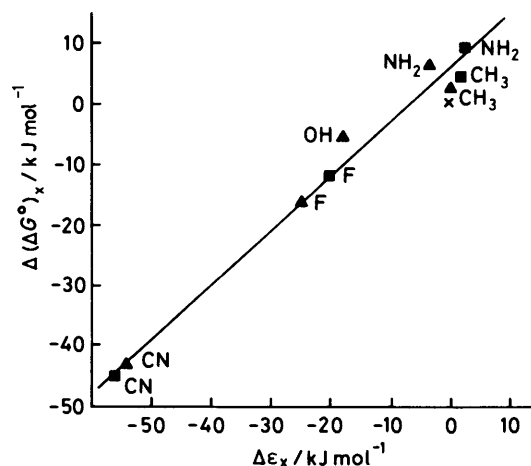**Figure.** $\Delta(\Delta G^\circ)_x$ values of experimental acidity *versus* $\Delta\varepsilon_x$ values for *meta-*(▲) and *para-*(■) substituted benzoate anions (× for unsubstituted benzoate)

3-21G HOMO Eigenvalues along with experimental $\Delta(\Delta G^\circ)$ values for the dissociation of the considered acids in the vapour phase are reported in the Table. Details of the optimized values of geometrical parameters are available in Supplementary Publication No. SUP 56244 (12 pp.).†

Results and Discussion

The plot of $\Delta\varepsilon_x$ *versus* the changes of dissociation free energy values is shown in the Figure. If *p*-hydroxybenzoate is left out,

the linear relationship (4) is obeyed with a correlation coefficient $r = 0.987$, indicating that $\Delta D(A-H)$ is essentially constant within the benzoate anions set.

$$\Delta(\Delta G^\circ)_x = 0.881\ 03\Delta\varepsilon_x + 5.227\ 27\ \text{kJ mol}^{-1} \quad (4)$$

The deviation of p-hydroxybenzoate from the observed correlation is due to the different dissociation process of p-hydroxybenzoic acid in the gas phase, where the corresponding anion has been suggested by McMahon and Kebarle[2] to be the p-carboxyphenolate anion.

Since equation (4) can be interpreted as implying $\Delta(\Delta G^\circ)_x$ to be proportional to $\Delta\varepsilon_x$, which parallels the definition of the Hammett σ constants for acidities in water solution, we have tested if our calculated $\Delta\varepsilon_x$ might play a corresponding role. When gas-phase acidities of substituted phenols are plotted against the benzoate $\Delta\varepsilon_x$ (leaving out the p-hydroxybenzoate), the best-fit equation (5) has $r = 0.981$. McMahon and Kebarle[2]

$$\Delta(\Delta G^\circ)_x = 1.314\ 93\Delta\varepsilon_x + 6.306\ 96\ \text{kJ mol}^{-1} \quad (5)$$

have also shown (Figure 2 of their paper) that an approximate correlation exists between gas-phase acidities of substituted phenols and benzoic acids. In order to make a comparative evaluation of equation (5) we have therefore calculated the correlation coefficient for the corresponding set of benzoic acids and phenols. This also came out to be 0.981, showing that the calculated $\Delta\varepsilon_x$ of benzoic acids is acceptable for predictions at the same confidence level of the experimental data currently available.

Conclusions

We think we have proved that $\Delta\varepsilon_x$, the calculated substituent effect on the HOMO eigenvalue of X-substituted benzoate anions, plays a role for gas-phase acidity similar to that of the σ Hammett constants in solution. There are two points to be made.

The first is that $\Delta\varepsilon_x$ is a property of the anion and not of the neutral molecule. This conclusion is in line with a previous study on the acidity of phenols[7] (carried out with STO-3G basis set and standard model geometry) where the authors concluded that substituent influence on acidity is largely determined by effects on the phenoxide anions.

The second point is that the Hammett constants σ allow us to predict substituent effects on both equilibrium and rate constants. We suggest therefore that, since $\Delta\varepsilon_x$ values have the corresponding role for dissociation equilibrium, they could be useful in predicting substituent effects on gas-phase reaction rates.

Added in proof: After the submission of our manuscript a paper was published by S. Böhm and J. Kuthan (*Int. J. Quantum Chem.*, 1984, **26**, 21) which reported an *ab initio* STO-3G study aimed at interpreting the same experimental data as ref. 2. Their analysis differs from ours in both approach and scope. Their remark (p. 28) that valence MOs correlate badly with experimental substituent effects, contrary to our findings, might depend on the better approximation we used for the basis set and optimization.

References
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