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Regarding the Inherent Dependence of Resonance Effects of Strongly Conjugated Substituents on Electron Demand

R. W. Taft,* J. L. M. Abboud, Frederick Anvia, Michel Berthelot, Mizue Fujio, Jean-François Gal, Allan D. Headley, William G. Henderson, Ilmar Koppel, J. H. Qian, Masaaki Mishima, Mare Taagepera, and Shinichi Ueji

Contribution from the Department of Chemistry, University of California, Irvine, California 92717. *Received August 18, 1986*

Abstract: A generalized treatment of the effects of molecular structure on gas-phase proton-transfer equilibria is reported. The treatment involves the summation of simple product terms for substituent field/inductive, polarizability, and π electron delocalization (resonance) effects. Independently determined substituent parameters are used that are shown to be non-colinear within each acid series analyzed. The treatment reproduces satisfactorily the observed substituent effects on gas-phase proton-transfer equilibria for a wide variety of both aliphatic and aromatic series acids. The reaction parameters follow distinctly different trends with the molecular structures of the acidity series, as expected from theoretical considerations. Well-defined limitations for the treatment have been established. For *strongly conjugated substituents* the simple product term for inherent substituent resonance effects is found to describe well the effects of widely varying changes in π electron demands from the reaction centers.

Long-standing controversies[1] on the effects of π electron demand on substituent π electron delocalization (resonance) effects are based upon experimental observations in solution which are generally complicated by solvent effects.[2,3] We have completed substituent effect studies on the gas-phase proton-transfer acidities of 38 cationic and neutral aliphatic and aromatic series families having a critical selection of substituents.[4] Seldom are there found to be precise general linear free energy relationships between the gas phase and corresponding solution results.[2-4] Nevertheless, the gas-phase results for the most part support the principles of substituent resonance (*R*) and field/inductive (*F*) effects that are frequently presented at the level of introductory courses for substituent effects in solution. The major conceptional additions to substituent effect theory that are provided by the gas-phase results are the following: (a) substituent polarizability (*P*) effects,[5,6] (b) substituent solvation effects,[2-4] and (c) the attenuation in *R*, *F*, and *P* effects that are associated with various acid and solvent structures.[3,4]

The gas-phase substituent acidity effects (expressed as $-\delta\Delta G^\circ$ values) follow with useful quantitative approximation the sum of product functions for each of the three kinds (*R*, *F*, and *P*) of contributions,[3,4] although appropriate modifications (as given below) are required. Linear regression analysis[7] with eq 1 has been utilized, and the requirement of non-colinearity between the independent substituent parameters, σ_R, σ_F, and σ_α (corresponding to the *R*, *F*, and *P* effects, respectively), has been imposed for each of the acidity series analyzed. Values of σ_R, σ_F, and σ_α[4] for typical substituents are given in Table I.

Table I. Typical Substituent Parameters[a]

sub- stituent	σ_R	σ_F	σ_α	sub- stituent	σ_R	σ_F	σ_α
$N(CH_3)_2$	–0.64[b]	0.10	–0.44	$Si(CH_3)_3$	0.02[c]	–0.02	–0.72
$NH(CH_3)$	–0.58	0.12	–0.30	CCl_3	0.02[c]	0.44	–0.70
NH_2	–0.52[b]	0.14	–0.16	CF_3	0.07[c]	0.44	–0.25
OC_2H_5	–0.45[b]	0.25	–0.23	SCF_3	0.10[c]	0.48	–0.64
OCH_3	–0.42[b]	0.25	–0.17	CN	0.10[c]	0.60	–0.46
OH	–0.38[b]	0.30	–0.03	SO_2CH_3	0.12[c]	0.59	–0.62
SCH_3	–0.27	0.25	–0.68	$CON(CH_3)_2$	0.14[c]	0.19	–0.66
F	–0.25	0.44	0.13	CO_2CH_3	0.16[c]	0.24	–0.49
Cl	–0.17	0.45	–0.43	CH_3CO	0.17[c]	0.26	–0.55
t-C_4H_9	–0.07	0.00	–0.75	NO_2	0.18[c]	0.65	–0.26
i-C_3H_7	–0.07	0.00	–0.62	HCO	0.19[c]	0.31	–0.46
CH_3	–0.08	0.00	–0.35	NO	0.26[c]	0.41	–0.25
H	0.00	0.00	0.00	SO_2CF_3	0.21[c]	0.84	–0.58

[a] From ref 4, which gives the source of these (and other) parameters, which are largely independent of any gas-phase acidity measurements. [b] Strongly reduced values necessary for anion forming (neutral) acids, cf. ref 4 for treatment. [c] σ_R = 0.00 for these substituents with π electron acceptor cationic acids.

$$-\delta\Delta G^\circ_{(g)} = \sigma_R\rho_R + \sigma_F\rho_F + \sigma_\alpha\rho_\alpha \tag{1}$$

where ρ_R, ρ_F, and ρ_α are reaction constants (or substituent and reaction type constants[1d,4]) for the substituent *R*, *F*, and *P* effects, respectively.

Emphasis is placed in this report upon the important finding that the π electron delocalization effects of *conjugated* substituents for many varied *gas-phase* aliphatic and aromatic series proton transfer equilibria apparently can be described to good precision by the simple product function $R = \sigma_R\rho_R$. That is, increasing electron demands on conjugated substituent resonance effects are adequately described by increasing values of the reaction constant, ρ_R. The relationship is illustrated in Figure 1 for 14 typical reactions by a plot of $R = -\delta\Delta G^\circ_{obsd} - \sigma_F\rho_F - \sigma_\alpha\rho_\alpha$ vs corresponding σ_R parameters. Structures and *R* and ρ_R values are given in Figure 1 and Tables II–IV. Since only acceptor (+*R*) substituents conjugated to the anionic centers cause enhanced acidities, the points for the neutral acid families (numbers 2–7) of Figure 1 appear in the upper right-hand quadrant. For the cationic acidities (numbers 8–14), the predominant donor (–*R*) substituent conjugation stabilizes the cation so that points for these acidity series in Figure 1 are found in the lower left-hand quadrant, reflecting acid weakening effects.

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[1] (a) Branch, G. E. K.; Calvin, M. *The Theory of Organic Chemistry*; Prentice-Hall: New York, 1941; p 250. (b) Taft, R. W. In Newman, M. S. Ed. *Steric Effects in Organic Chemistry*; John Wiley: New York, 1956; p 595. (c) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970; Chapter 10. (d) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971. (e) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Ibid.* **1972**, *45*, 1210. (f) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1. (g) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; von Nagy-Felsobaki, E.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378. (h) Swain, C. G.; Unger, S. H.; Rosenquist, R. N.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492. (i) Wepster, B. M. *J. Org. Chem.* **1985**, *49*, 1993. (j) Reynolds, W. F.; Topsom, R. D. *J. Org. Chem.* **1985**, *49*, 1989. (k) Charton, M. *J. Org. Chem.* **1985**, *49*, 1997. (l) Mishima, M.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **1986**, *27*, 939, 951. (m) Charton, M. *Prog. Phys. Org. Chem.* **1987**, *16*, 287.

[2] Mishima, M.; McIver, R. T., Jr.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717 and references given therein.

[3] (a) Cf., for example: Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247. (b) Headley, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2347.

[4] Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.

[5] Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 5636, 6301.

[6] Hehre, W. J.; Pau, C.-F.; Headley, A. D.; Taft, R. W.; Topsom, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 1711.

[7] Our computer program was developed by Dr. Ruth M. Doherty using the following: Bevington, P. R. *Data Reduction and Error Analysis for Physical Sciences*; McGraw-Hill: New York, 1969, Chapter 9.

[8] Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 125. A summary of previous results is contained herein.

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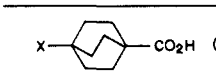
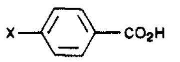
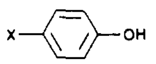
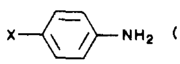
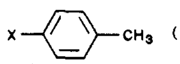
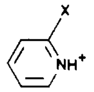
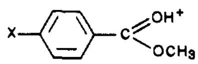
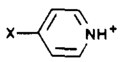
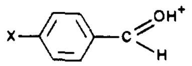
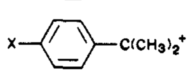
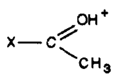
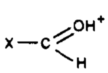
Table II. Results of Linear Regression Analysis Using Equation 1 or an Appropriate Simplified Modification

acidity series[a]	ρ_R	ρ_F	ρ_α	A_0	r	sd	n[b]	r_1	r_2	r_3
 (1)	0	12.9 ± 0.6	−1.1 ± 0.6	0.0 ± 0.3	0.9938	0.4	10	0.212	0.258	0.237
 (2)	14.6 ± 0.7	15.0 ± 0.6	0	−0.2 ± 0.2	0.9972	0.4	11	0.320	0.516	0.226
XC≡CH (3)	44.7 ± 4.6	37.9 ± 1.4	0[f]	0.2 ± 0.6	0.9985	0.6	6	0.231	–	–
 (4)	49.0 ± 1.5	18.6 ± 0.5	0	0.1 ± 0.2	0.9990	0.3	12	0.400	0.205	0.421
 (5)	53.7 ± 1.7	18.9 ± 0.4	0	0.4 ± 0.2	0.9994	0.3	10	0.503	0.592	0.489
 (6)	76.0 ± 2.5	19.9 ± 0.9	0	−0.7 ± 0.5	0.9981	0.6	13	0.478	0.389	0.486
XCH_2CN (7)	152 ± 13	31.8 ± 3.6	0[f]	0.0 ± 1.6	0.9972	1.7	5	0.404	–	–
 (14)	13.3 ± 0.5	27.5 ± 0.5	7.6 ± 0.5	−0.1 ± 0.3	0.9989	0.4	13	0.053	0.152	−0.229
 (13)	18.6 ± 0.5	15.3 ± 0.5	3.1 ± 0.4	−0.2 ± 0.2	0.9981	0.3	15	0.146	0.253	−0.123
 (12)	25.7 ± 0.6	21.8 ± 0.6	5.0 ± 0.5	0.1 ± 0.3	0.9987	0.5	15	0.196	0.158	−0.180
 (11)	31.6 ± 0.7	16.6 ± 0.6	5.0 ± 0.6	0.0 ± 0.3	0.9988	0.5	13	0.322	−0.005	0.114
 (10)	37.5 ± 0.4	19.0 ± 0.6	4.6 ± 0.6	0.2 ± 0.4	0.9992	0.5	12	0.092	0.171	−0.387
 (9)	39.3 ± 0.4	33.6 ± 0.6	20.8 ± 0.6	0.0 ± 0.2	0.9998	0.3	9	0.103	0.169	0.277
 (8)	49.0 ± 0.5	35.4 ± 0.7	25.0 ± 0.5	0.1 ± 0.3	0.9997	0.4	13	−0.009	0.259	−0.033

[a] Numbered as given in Figure 1. [b] Includes H substituent. [c] r_1 is the correlation coefficient for values of σ_R vs σ_F for substituents of each acidity series. [d] r_2 is the correlation coefficient for values of σ_R vs σ_α for substituents of each acidity series. [e] r_3 is the correlation coefficient for values of σ_α vs σ_F for substituents of each acidity series. [f] Dependence on σ_α has been assumed negligible since the number of substituents (and range of σ_α values) is limited for these acidity series. Additional work is in progress to add further critical substituents to test this assumption and the ρ_R and ρ_F values.

Table III. Estimated R Values (π Electron Delocation Effects) for Conjugated Substituents in Gas-Phase Acidities of Neutral Acids (in kcal/mol)[a,h]

	reaction number in Figure 1					
substituent	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]
CF_3	1.0	4.0	3.7	4.4	5.5	
$SOCH_3$			3.9		6.9	
SCF_3			4.6	6.0		
CN	2.0	4.2	5.4	5.8	8.4	16.3
SO_2CH_3			6.0	7.0	10.1	17.0
$CON(CH_3)_2$		6.2				
CO_2CH_3		7.7	7.7	9.0	13.8	23.3
CH_3CO	1.9	7.4	8.4	9.8	13.9	
C_6H_5CO						28.6
NO_2	2.1		8.8	10.1	15.5	
HCO			10.0	10.6	15.2	
SO_2CF_3			10.3	11.3	16.2	
NO			13.0		20.5	
$COCF_3$					19.8	
COCN					21.5	

[a] Obtained from $-\delta\Delta G°_{(g)}$ values given in ref 4 (Table A1) and the eq b–g as follows. For number 7, $-\delta\Delta G°_{(g)}$ values are given in the Experimental section of this work. [b] $R = -\delta\Delta G° - (15.0)\sigma_F$. [c] $R = -\delta\Delta G° - (37.9)\sigma_F$. [d] $R = -\delta\Delta G° - (18.2)\sigma_F$. [e] $R = -\delta\Delta G° - (18.9)\sigma_F$. [f] $R = -\delta\Delta G° - (19.9)\sigma_F$. [g] $R = -\delta\Delta G° - (31.8)\sigma_F$. [h] For acidity series number 1, $R = 0.0 \pm 0.3 = -\delta\Delta G° - (12.9)\sigma_F$ for four $+R$ and five $-R$ substituents.

Table IV. Estimated R Values (π Electron Delocalization Effects) for Conjugated Substituents in Gas-Phase Acidities of Cationic Acids (in kcal/mol)[a]

	reaction number in Figure 1						
substituent	8[b]	9[c]	10[d]	11[e]	12[f]	13[g]	14[h]
$N(CH_3)_2$	−31.3	−25.1	−23.1	−20.4	−15.6		−8.2
$NHCH_3$	−28.8						
NH_2	−25.0	−20.9	−17.3		−13.5	−9.4	−7.4
OC_2H_5	−22.5	−17.7					
OCH_3	−20.1	−16.0	−14.8	−13.4	−10.9	−7.9	−6.2
OH				−11.7		−7.4	
SCH_3				−8.3	−7.2	−4.8	−3.6
F			−9.4	−7.4	−6.1	−4.7	−2.8
Cl			−5.3	−4.4	−4.1	−3.3	−2.6
C_6H_5	−10.5	*i*					
t-C_4H_9		*i*	−2.4	−1.8	−2.0	−1.6	−0.9
i-C_3H_7	−3.2	*i*		−2.1			−1.3
C_3H_7	−4.2						
C_2H_5	−3.1	−2.9		−2.1	−1.8		−0.8
CH_3	−3.1	−3.0	−2.4	−2.5	−1.8	−1.0	−1.2
no. of $+R$ substituents included, cf. ref 3	2	2	4	3	5	4	2

[a] Obtained from $-\delta\Delta G°_{(g)}$ values given in ref 4 (Table A1) and the eq b–h. [b] $R = -\delta\Delta G° - (35.4)\sigma_F - (25.0)\sigma_\alpha$. [c] $R = -\delta\Delta G° - (33.3)\sigma_F - (20.8)\sigma_\alpha$. [d] $R = -\delta\Delta G° - (19.0)\sigma_F - (4.6)\sigma_\alpha$. [e] $R = -\delta\Delta G° - (16.6)\sigma_F - (5.0)\sigma_\alpha$. [f] $R = -\delta\Delta G° - (21.8)\sigma_F - (5.0)\sigma_\alpha$. [g] $R = -\delta\Delta G° - (15.3)\sigma_F - (3.1)\sigma_\alpha$. [h] $R = -\delta\Delta G° - (27.5)\sigma_F - (7.6)\sigma_\alpha$. [h] Omitted from correlation for steric reasons, cf. ref 4.

For acid series number 1, there is (as expected[9]) essentially no R or P substituent effects, so the following simplified relationship applies: $-\delta\Delta G° = \sigma_F\rho_R$. For acidity series numbers 2–7 substituent P effects[5,6] are generally small (this follows from the small values of both σ_α and ρ_α[4]) and the following simplified relationship applies: $R \cong -\delta\Delta G° - \sigma_F\rho_F$. For the cationic acidity series

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[9] (a) Roberts, J. D.; Moreland, W. T., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 2167. (b) Koppel, I.; Mishima, M.; Stock, L. M.; Topsom, R. D.; Taft, R. W., in preparation.

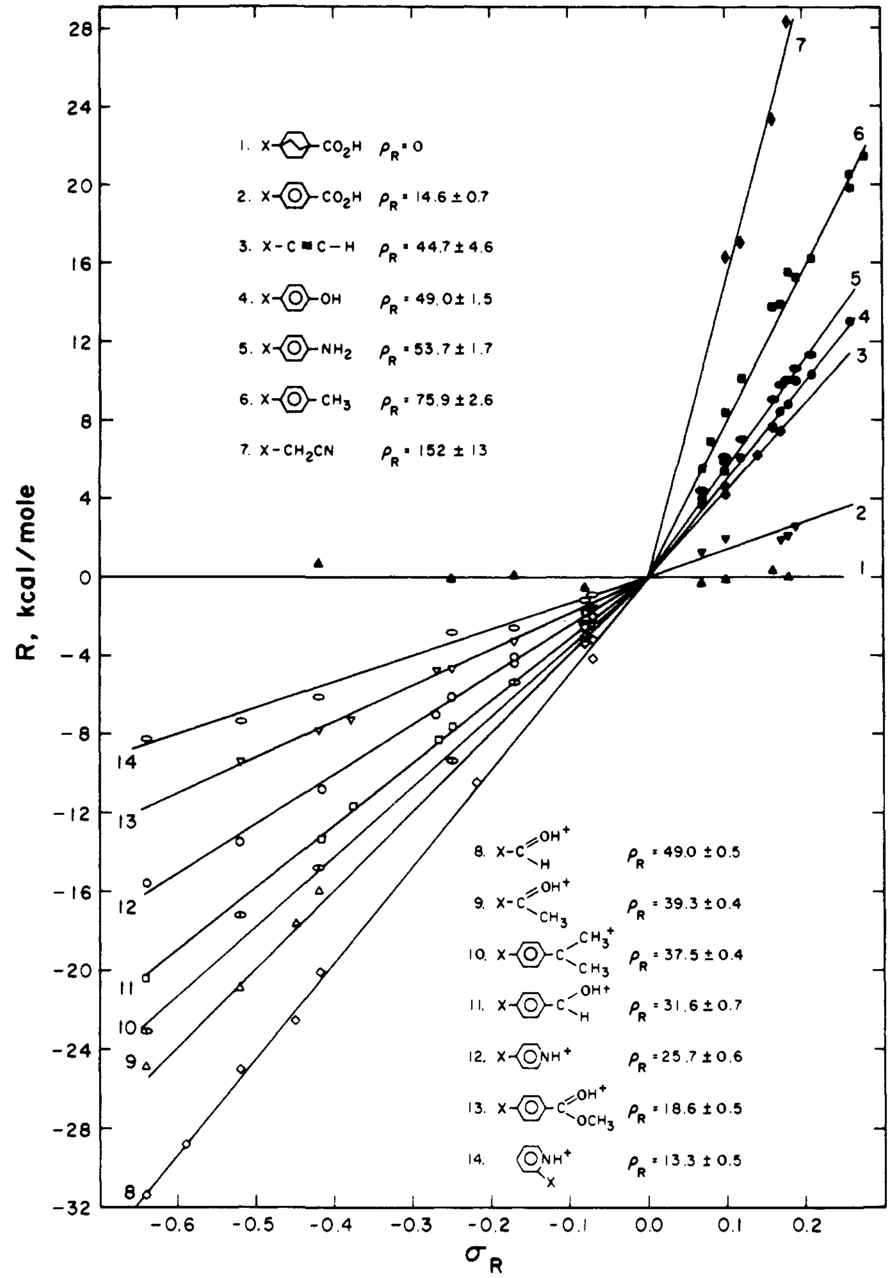

Figure 1. Approximate linear correlations of conjugated substituent π electron delocalization effects by the σ_R parameter for gas-phase proton-transfer equilibria of neutral and cationic acids from both the aliphatic and aromatic series: abscissa, substituent π electron delocalization effect parameter, σ_R (positive sign for π acceptor, negative sign for π donor); ordinate, substituent R value, in kcal/mol, cf. Tables III and IV. Acid structures and slopes (ρ_R values) are given in the insets. R values for some alkyl substituents are not shown to avoid overcrowding.

numbers 8–14, all three terms (R, F, and P) may be significant, but the following class simplifications are found to apply. For normal π electron acceptor ($+R$) substituents of these series, the "no blood from a turnip" condition applies, i.e., $R \cong 0$, and therefore, $-\delta\Delta G° = \sigma_\alpha\rho_\alpha + \sigma_F\rho_F$. This special simplification permits the inclusion of $+R$ with $-R$ substituents in the same data set for evaluation of the crucial ρ_F value, without significant influence being exerted on the evaluation of the R values of the $-R$ substituents. Finally, for all unsubstituted alkyl substituents in all acidity series, $F \cong 0$, so that for these, $R \cong -\delta\Delta G° - \sigma_\alpha\rho_\alpha$. Additional details are given in the following section on experimental data and procedures.

It is important to note that all three kinds of substituent parameters, σ_R, σ_α, and σ_F, are well based in model ab initio calculations carried out by Topsom (in most cases the calculations reproduce the values to within ±0.03).[8] In addition, three other considerations provide strong evidence for the validity of eq 1 and the estimated R values: (i) the correlations by eq 1 are quite precise with overall correlation coefficients of >0.980 and standard deviations within two to three times experimental precisions; (ii) the correlation coefficients for each data set between each pair of independent variables (σ_R vs σ_F, σ_F vs σ_α, σ_R vs σ_α) are less than 0.593, generally significantly less; (iii) the reaction constants, ρ_R, ρ_F, and ρ_α, are quite different functions of the acid structures. These results are summarized in Table II.

The substituent polarizability effect parameter depends upon the total number of electrons present, the effective nuclear charges that act on the electrons, and the effective distances from the charge.[6] These considerations lead to the following sequences of $-\sigma_\alpha$ values: for an isoelectronic sequence, F < OH < NH_2 < CH_3; for alkyl substituents, CH_3 < C_2H_5 < C_3H_7 < i-C_3H_7 < *sec*-C_4H_9 < t-C_4H_9; for halogen substituents F < Cl < Br < I. These and other σ_α substituent effects are in general uniquely different from corresponding σ_R and σ_F parameters. The relatively great fall-off factor with distance for substituent polarizability effects leads to the following observed order of ρ_α reaction parameters: numbers 8, 9, 14 > numbers 13, 12, 11, 10, 6, 5, 4, 2, 1. However, the substituent distance from the deprotonation site is a poor index of quantitative values of ρ_α. The delocalization of partial charges to atoms in close proximity to the substituent results in finite ρ_α

values (as for numbers 10–13). This effect is enhanced in cationic acids by electronegative atoms at the deprotonation (giving $\rho_\alpha(14) < \rho_\alpha(9)$). For neutral acids there is apparently extensive delocalization of π charge of the anion into *para* π acceptor substituents rather than to adjacent atomic positions so that ρ_α values tend to be small for these substituents and acids (numbers 2–7).

Field/inductive effects are longer range and consequently are less sensitive to the spreading of charges into the molecular frameworks. Values of ρ_F are roughly correlated with the minimum number of atoms that intervene between the substituent and the deprotonation site.[4] When conjugation is good, substituent π delocalization effects are less impeded by distance than either *P* or *F* effects (thus $\rho_R(10) > \rho_R(12)$ and $\rho_R(6) > \rho_R(3)$). Further, conjugation with acceptor centers in very close proximity to the donor substituent may even be significantly reduced (e.g., $\rho_R(14) < \rho_R(12)$) because of electrostatic repulsion considerations.[4,10]

In a preliminary report on theoretical treatment of reaction constant parameters,[4] the ρ_R values for a number of series of gas-phase acidity reactions have been found to be in good accord with π charge distributions from ab initio calculations. Specifically, ρ_R is approximately directly proportional to the ab initio π charge density of the unsubstituted parent acid structure at the carbon atom to which the substituent is attached.[4] In work to be reported,[11] this relationship is shown to be quite general. At the present writing, the only gas-phase acidity series for which eq 1 in its properly modified form does not give acceptable precision are those that involve either (i) substituent steric or electrostatic proximity effects[10] or (ii) deprotonation of the atom to which the substituent is attached at an otherwise unsubstituted atomic center (such as XCH_3 acidities). Reactions of the latter kind involve major rather than minor substituent perturbations in π charge density at the atom of substituent attachment. Perturbations of the minor type nevertheless involve very significant ranges in electron demands from the reaction centers. The approximately linear relationships shown in Figure 1 indicate that, for most purposes and for many reactions, a single inherent σ_R scale of substituent π electron delocalization abilities will be appropriate for use.

Experimental and Procedures

Except for acidity series number 7, all gas-phase acidity $-\delta\Delta G°_{(g)}$ values used to obtain the results in Table II are listed in Table A1 of ref 4, together with corresponding values of $-\delta\Delta G°_{(g)}$(calcd) which are obtained from eq 1 with the use of the appropriate substituent parameter values and the reaction constants of Table II. For acidity series number 7 (XCH_2CN) the following $-\delta\Delta G°_{(g)}$ values have been obtained by methods cited in ref 10: CO_2Me (30.9 kcal/mol), CN (35.4 kcal/mol), SO_2CH_3 (35.7 kcal/mol), and C_6H_5CO (37.8 kcal/mol); all values are relative to CH_3CN ($\Delta G°_{acid} = 365.2$ kcal/mol). All results for neutral acidities have been submitted to Prof. J. W. Bartmess who has placed all published and unpublished data on a revised absolute acidity scale that is consistent with the most reliable thermodynamic scale anchor points.[12] In general, the data points within a given acidity series are from a single source. However, for p-$XC_6H_5CO_2H$ (number 2), the points for CF_3, CN, CH_3CO, and CHO are from ref 9b and those for NH_2, OCH_3, F, Cl, CH_3, and NO_2 are from ref 13 (for details of the treatment of this data set of five π donor and five π acceptor substituents see ref 4). For the twelve π acceptor substituents of p-$XC_6H_5CH_3$ (number 6) the data points for CF_3, CN, and CHO were communicated to us by Prof. Bartmess. The other nine data points are based on the present work.

The cationic acidity $-\delta\Delta G°_{(g)}$ values are from literature sources given in ref 3 and the present work. The scale of these acidities has been up-dated and revised, based upon results of ref 14. All values have been submitted to S. G. Lias for inclusion in a revised proton affinity scale for *J. Phys. Chem. Ref. Data.* The data points for acidity series numbers 10, 11, and 13 are from ref 11 and ref 15.

Table II gives the results of linear multiple regression analysis[7] by eq 1 of the data cited therein and above. Further details are given in Tables III and IV and in footnotes to Table II.

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