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Acidities of OH Compounds, Including Alcohols, Phenol, Carboxylic Acids, and Mineral Acids[1]

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Abstract: The gas-phase acidities of a significant variety of alcohols, haloalcohols, phenol, carboxylic acids, and mineral acids are reproduced by an empirical theoretical treatment of substituent (X), polarizability (P), field/inductive (F), and π electron delocalization (R, resonance) effects in XOH. The substituent parameters for each of these effects are distinctly noncolinear. A standard deviation of 0.8 kcal/mol has been obtained for acidities covering a range of 50 powers of 10. All three kinds of substituent effects are indicated to be in general of major significance. π Electron donor substituents require separate treatment. The 17.6 powers of 10 gas-phase acidity of phenol greater than that of cyclohexanol is estimated to be primarily due to its 11.7 powers of 10 π electron delocalization effect. On the other hand, the 22.5 powers of 10 gas-phase acidity of acetic acid greater than that of ethanol is estimated to be primarily due to the stabilization of the acetate ion by the electrostatic interaction of the acetyl group dipole which contributes 14.0 powers of 10. The treatment supports the ideas that coiling of straight chain alkoxides in the gas phase increases the alcohol acidities by 0.8–3.4 powers of 10 and that negative C–H hyperconjugation in gaseous alkoxides increases acidities by ca. 0.1 kcal/mol/α-C–H. The results of similar analysis of acidities in dimethyl sulfoxide and in aqueous solutions is also presented. Comparisons of both gas phase and solution acidities of the XOH compounds with the correspondingly substituted phenols (p-XC_6H_4OH) strongly suggests that lone pair–lone pair electronic repulsions in XO^- anions decrease the importance of the X substituent π electron acceptor effects relative to the corresponding electrostatic field/inductive effects.

The proton dissociation energies of OH acids are of long standing utility and theoretical interest.[2-4] Absolute values of many of these energies in the gas phase are available from relatively recent studies of proton-transfer equilibria coupled with benchmark thermochemical values.[5] These results provide intrinsic structural effects, free of solvent and counterion influences. The relative gas-phase acidities within many diverse families of acids have been described satisfactorily by appropriate combinations of substituent dipolar field/inductive, π electron delocalization, and polarizability (F, R, and P, respectively) effects obtained from linear regressions with the corresponding substituent parameters, σ_F, σ_R, and σ_α.[6,7] The directions and magnitudes of these effects within each family of acids are determined by how the substituent interactions change between the acid and conjugate base forms. The treatment has been shown to hold generally for substitution at a fixed carbon position in either a saturated or an unsaturated chain or cycle. Acidity series in which the carbon position is tetrahedral, trigonal planar, or linear are included.[6,7]

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In this paper we report the application of the above parameters to an empirical theoretical treatment to XOH acids in which substituents X (with some well-defined limitations) are attached directly to the oxygen atom from which proton dissociation occurs.[8] The available gas-phase data for the XOH family involve a significant variety of covalently bound π electron acceptor (+R) substituents replacing the hydrogen atom of the water molecule. Solution acidities for the XOH family have also been similarly analyzed, and the results are compared with the corresponding gas-phase results.

Acidity increases for XOH acids are due to much stronger substituent interactions (each of the above three kinds) with O^- of XO^- than with OH of XOH. For all of the available data, dipolar substituents are oriented with their positive ends toward oxygen, stabilizing in particular XO^- by a dipole-charge interaction (positive F effect). Similarly, XO^- is stabilized by charge-induced dipole interactions with polarizable X substituents[9] (positive P effect). π electron acceptor (+R) substituents interact to preferentially stabilize the more donor O^- than the less donor OH. Therefore, according to the sign convention for the substituent parameters,[7] as σ_F and σ_R values become more positive and σ_α values become more negative, acidities are increased. There are equilibrium data available for only two π donor (−R) substituents. These data are treated separately since acid weakening repulsive lone pair–lone pair interactions[21] occur between the substituent and the O^- center.

XOH Acidities in the Gas Phase. The absolute gas-phase acidities ($\Delta G^\circ_{\mathrm{acid}}$) values for the XOH acids have been taken from the Lias, Bartmess et al. table[5b] and (relatively small) statistical corrections applied. Generalized eq 1 gives the gas-phase proton dissociation reaction corresponding to $\Delta G^\circ_{\mathrm{acid}}$:

$$\mathrm{XOH}_{(g)} \rightleftarrows \mathrm{XO}^-_{(g)} + \mathrm{H}^+_{(g)} \qquad (1)$$

The generalized proton-transfer reaction of eq 2 gives the acidity increasing effect ($-\delta\Delta G^\circ_{(g)}$) of the substitution of X for an H atom of water:

$$\mathrm{XOH}_{(g)} + \mathrm{OH}^-_{(g)} \rightleftarrows \mathrm{XO}^-_{(g)} + \mathrm{H_2O}_{(g)}$$

$$-\delta\Delta G^\circ_{(g)} = \Delta G^\circ_{\mathrm{acid}}(\mathrm{H_2O}) - \Delta G^\circ_{\mathrm{acid}}(\mathrm{XOH}) \qquad (2)$$

Table I lists $\Delta G^\circ_{\mathrm{acid}}$ and $-\delta\Delta G^\circ_{(g)}$ values for 25 acids with widely varying +R substituents. The observed results are shown in Table I (by the comparison between observed and calculated values) to be described by eq (3) (or 3′) to within the precision of the experimental results:

$$\Delta G^\circ_{\mathrm{acid}}(\mathrm{XOH}) = 384.5 \pm 0.5 + \sigma_\alpha\rho_\alpha + \sigma_F\rho_F + \sigma_R\rho_R = 384.5 \pm 0.5 + (23.4 \pm 0.8)\sigma_\alpha - (73.4 \pm 0.9)\sigma_F - (72.8 \pm 2.0)\sigma_R \qquad (3)$$

$$-\delta\Delta G^\circ_{(g)} = (-23.4 \pm 0.8)\sigma_\alpha + (73.4 \pm 0.9)\sigma_F + (72.8 \pm 2.0)\sigma_R \cong -\delta\Delta H^\circ_{(g)} \qquad (3')$$

$$n = 25,\ R^2 = 0.999,\ \mathrm{sd} = 0.8,\ T\delta\Delta S^\circ_{(g)} = \pm 0.6\ \mathrm{kcal/mol}^{5b}$$

Values of the substituent parameters σ_α, σ_F, and σ_R are from ref 7, except for values given in parentheses which are obtained from additive relationships given in this reference (and the σ_R values for the alkyl and the phenyl substituents which have been obtained as described in a later section). The success of eqs 3 and 3′ is remarkable because of the magnitudes of the substituent effects resulting from direct substitution at oxygen as well as the variety of sources of the data.[5] Equations 3 and 3′ are strongly supported because the absolute values of the reaction constants ρ_α and ρ_F (23.4 ± 0.9 and 73.4 ± 0.9, respectively) obtained from the linear multiple regression analysis are precisely those predicted from relationships established by the earlier treatment[7] for the more distant substituents in the $\mathrm{XCH_2OH}$ acid family. The validity of these equations is also strongly supported by the following statistical requirements: (a) the independent variables (the three kinds of substituent parameters) show a high degree of nonlinearity: $R^2(\sigma_\alpha \text{ vs } \sigma_F) = 0.025$; $R^2(\sigma_\alpha \text{ vs } \sigma_R) = 0.003$; $R^2(\sigma_F \text{ vs } \sigma_R) = 0.316$; (b) in contrast, the overall $R^2 = 0.999$, and sd = 0.8 kcal/mol; (c) when any term in eq 3′ is dropped, marked decreases in R^2 and increases in sd result. Thus, for example, with the $\sigma_\alpha\rho_\alpha$ term removed, $R^2 = 0.957$ and sd = 4.6 kcal, with the $\sigma_R\rho_R$ term removed, $R^2 = 0.957$ and sd = 6.0 kcal, and with both of these terms removed, $R^2 = 0.929$ and sd = 7.5 kcal.

For the individual substituents the estimated values of the three kinds of substituent effects ($P = -23.4\sigma_\alpha$, $F = 73.4\sigma_F$, and $R = 72.8\sigma_R$) are also given in Table I. The following points are to be noted. The values of P, R, and F for the various substituents cover large ranges (0–20 kcal/mol for P and R and 0–48 kcal/mol for F) for the total range of $-\delta\Delta G^\circ_{(g)}$ values of 68.5 kcal/mol (or ~50 $\mathrm{p}K_\mathrm{A}$ units). Depending upon the substituent, any one of the three kinds of substituent effects may be predominant. For example, for aliphatic alcohols, 2-fluoroethanols, and phenol, the substituent P effect is predominant; for the polyfluoro alcohols and the carboxylic acids, F effects (*not R for the carboxylic acids*) are predominant. The much greater acidity of nitrous acid than that of hexafluoroisopropyl alcohol is indicated to be due predominantly to the greater R effect of the NO than the $(\mathrm{CF_3})_2\mathrm{CH}$ substituent.

Robust Character of Eq 3. σ_R^- Parameters of Alkyl and Phenyl Substituents. Several additional lines of evidence support the robust character of eq 3. For example, if all of the acids of Table I are excluded (including phenol) for which one or more substituent parameter values have been estimated (as indicated by the parenthetic values in Table I), the following correlational results are obtained:

$$\Delta G^\circ_{\mathrm{acid}} = 384.5 \pm 0.6 + (23.5 \pm 0.9)\sigma_\alpha - (73.3 \pm 1.1)\sigma_F - (72.9 \pm 2.6)\sigma_R \qquad (4)$$

$$n = 17,\ R^2 = 0.999$$

Equation 4 differs in no significant way from eq 3.

The negative σ_R^+ values for alkyl substituents given in ref 6 and 7 apply only for hyperconjugative interactions with π electron-deficient centers and clearly are not applicable for hyperconjugative acceptor interactions with the π donors OH and (particularly) O^-. Theoretical calculations and measured deuterium isotope effects on the gas-phase acidity of $\mathrm{CH_3OH}$ have indicated[10] that in the unsolvated, highly charge localized and strongly π donor alkoxide ion there are small negative C–H hyperconjugative effects. This conclusion has been further supported by a study of branching and straight chain effects in the gas-phase acidities.[11] That is, σ_R^- values should be small positive values for the alkyl substituents with α-C–H bonds. By consideration of the magnitude of the σ_R value of 0.07 for the $\mathrm{CF_3}$ substituent (due to negative C–F hyperconjugation) the small positive σ_R values given in Table I ($\sigma_R = 0.01/\alpha$-CH in the alkyl substituent) were assumed. If instead $\sigma_R = 0.00$ is taken for all alkyl and substituted alkyl substituents, the following correlational results are obtained:

$$\Delta G^\circ_{\mathrm{acid}} = 383.1 \pm 0.7 + (22.9 \pm 1.1)\sigma_\alpha - (72.6 \pm 1.3)\sigma_F - (68.6 \pm 2.6)\sigma_R \qquad (5)$$

$$n = 25,\ R^2 = 0.998,\ \mathrm{sd} = 1.0$$

While eq 5 is of very slightly poorer precision than eq 3, the ρ_α, ρ_F, and ρ_R reaction parameters of eq 3 and 5 are the same within the errors of the estimates. The same situation prevails when the correlation is run with the 17 acids used to obtain in eq 4. These results show not only the robust character of eq 3 but also strongly support the σ_R value of 0.22 used for the phenyl

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Table I. Gas-Phase Acidities of X–OH Acids, Including Alcohols, Phenol, Carboxylic Acids, and Mineral Acids

acid	X	ΔG°_{acid}[a]- (obs)	ΔG°_{acid}[b]- (calc)	σ_α[c]	σ_F[c]	σ_R[c]	P[d]	F[e]	R[f]	$-\delta\Delta G^\circ$- (calc)[g]	$-\delta\Delta G^\circ$- (obs)[g]
1. H_2O	H	384.5	(384.5)	0.00	0.00	0.00	(0.0)	(0.0)	(0.0)	0.0	(0.0)
2. CH_3OH	CH_3	374.0	374.1	−0.35	0.00	0.03	8.2	0.0	2.1	10.3	10.5
3. C_2H_5OH	C_2H_5	371.4	371.6	−0.49	0.00	0.02	11.5	0.0	1.4	12.9	13.1
4. C_3H_7OH	C_3H_7	369.4	370.4	−0.54	0.00	0.02	12.6	0.0	1.5	14.1	15.1
5. i-C_3H_7OH	i-C_3H_7	368.8	369.3	−0.62	0.00	0.01	14.5	0.0	0.7	15.2	15.7
6. t-C_4H_9OH	t-C_4H_9	368.0	367.0	−0.75	0.00	0.00	17.5	0.0	0.0	17.5	16.5
7. s-C_4H_9OH	s-C_4H_9	367.6	367.9	−0.68	0.00	0.01	15.9	0.0	0.7	16.6	16.9
8. $CH_3O(CH_2)_2OH$	$CH_3O(CH_2)_2$	366.8	365.8	(−0.52)	(0.07)	0.02	12.2	5.1	1.4	18.7	17.7
9. c-$C_6H_{11}OH$	c-C_6H_{11}	(366.1)[h]	366.0	−0.76	0.00	0.01	17.8	0.0	0.7	18.5	18.4
10. t-$C_4H_9CH_2OH$	t-$C_4H_9CH_2$	366.0	367.4	−0.67	0.00	0.02	15.7	0.0	1.4	17.1	18.5
11. $F(CH_2)_2OH$	$F(CH_2)_2$	363.5	363.3	(−0.47)	(0.12)	0.02	11.0	8.8	1.4	21.2	21.0
12. $C_6H_5CH_2OH$	$C_6H_5CH_2$	363.4	363.0	−0.70	0.05	0.02	16.4	3.7	1.4	21.5	21.1
13. F_2CHCH_2OH	F_2CHCH_2	359.2	357.8	(−0.45)	(0.20)	0.02	10.5	14.7	1.5	26.7	25.3
14. CF_3CH_2OH	CF_3CH_2	354.1	355.4	(−0.46)	(0.23)	0.02	10.8	16.9	1.4	29.1	30.4
15. C_6H_5OH	C_6H_5	342.3	342.2	−0.81	0.10	(0.22)	19.0	7.3	16.0	42.3	42.2
16. CH_3CO_2H	CH_3CO	340.7	340.2	−0.55	0.26	0.17	12.9	19.1	12.3	44.3	43.8
17. HCO_2H	HCO	338.0	337.2	−0.46	0.31	0.19	10.8	22.7	13.8	47.3	46.5
18. $(CF_3)_2CHOH$	$(CF_3)_2CH$	338.3	338.4	(−0.57)	(0.44)	0.01	13.3	32.3	0.7	46.3	46.2
19. t-$C_4H_9CH_2CO_2H$	t-$C_4H_9CH_2CO$	337.7	336.9	(−0.69)	(0.26)	(0.17)	16.1	19.1	12.4	47.6	46.8
20. $C_6H_5CO_2H$	C_6H_5CO	332.6	333.3	−0.75	0.28	0.18	17.6	20.5	13.1	51.2	51.9
21. HNO_2	NO	330.1	329.6	−0.25	0.41	0.26	5.9	30.1	18.9	54.9	54.4
22. $CF_3CH_2CO_2H$	CF_3CH_2CO	327.3	327.3	(−0.60)	(0.39)	0.20)	14.0	28.6	14.6	57.2	57.2
23. $(CF_3)_3COH$	$(CF_3)_3C$	324.0	323.8	(−0.68)	0.61	0.00	15.9	44.8	0.0	60.7	60.5
24. HNO_3	NO_2	317.1	317.6	−0.26	0.65	0.18	6.1	47.7	13.1	66.9	67.4
25. CF_3CO_2H	CF_3CO	316.0	317.0	−0.51	0.50	0.26	11.9	36.7	18.9	67.5	68.5

[a] ΔG°_{acid}(obs) values from ref 5b, with statistical corrections applied (in kcal/mol). [b] $\Delta G^\circ_{acid}(calc) = 384.5 \pm 0.5 + (23.4 \pm 0.9)\sigma_\alpha - (73.4 \pm 0.9)\sigma_F - (72.8 \pm 2.0)\sigma_R$; $r = 0.999$ sd = 0.8; [$r(\sigma_\alpha$ vs $\sigma_F) = 0.157$; $r(\sigma_\alpha$ vs $\sigma_R) = 0.050$; $r(\sigma_F$ vs $\sigma_R) = 0.562$]. [c] Substituent constants in parentheses are estimated based upon well-established fall-off relationships (ref 6 and 7, $\sigma_{F(C-X)} = 1/1.95\sigma_{F(X)}$ and $\sigma_{\alpha(C-X)} = 1/2.30\ \sigma_{\alpha(X)}$.[7] For alkyl and phenyl σ_R values see text. All other values are from refs 6 and 7. [d] Substituent polarizability effect $(-23.4 \pm 0.9)\ \sigma_\alpha$. [e] Substituent field/inductive effect = $(73.4 + 0.9)\sigma_F$. [f] Substituent π electron delocalization effect = $(72.8 \pm 2.0)\sigma_R$. [g] For $XOH + OH \rightleftharpoons XO^-, H_2O$; $-\delta\Delta G^\circ = \Delta G^\circ_{acid}(H_2O) - \Delta G^\circ_{acid}(XOH) = P + F + R$. [h] Value for $(C_2H_5)_2CHOH$.

substituent when it is fully conjugated with an unsolvated powerful donor reaction center,[12] such as O^-, NH^-, or CH_2^-.

Theoretical calculations for the fully conjugated vinyl substituent indicate that it is unique in having its π donor and π acceptor ability vary linearly from one extreme to the other with π-electron demand.[13,14] Calculations have not been made for the fully conjugated phenyl substituent, but it is reasonable to assume that it behaves in a similar fashion to the vinyl substituent. That is, since $\sigma_R^+ = -0.22$ for C_6H_5 fully conjugated with highly deficient π electron centers,[15] it can be assumed with highly electron rich π centers that $\sigma_R^- = +0.22$ will be applicable (as has been used in Table I and eq 3). The value of $\sigma_R^- = 0.22$ for the phenyl substituent also appears to apply satisfactorily in describing the gas-phase acidities of aniline relative to ammonia[12] and toluene relative to methane.[12]

Since the original draft of this paper, the measurements given in the Experimental Section have been carried out by the bracketing technique to obtain the ΔG°_{acid} value for CF_3OH. The value found is 341 ± 2 kcal/mol. This acid provides an excellent test of eq 3 since the CF_3 substituent parameters $\sigma_\alpha = -0.25$, $\sigma_F = 0.44$, and $\sigma_R^- = 0.07$ have been well confirmed by numerous other gas-phase proton-transfer equilibria results.[7] With these parameters eq 3 gives $\Delta G^\circ_{acid} = 340.5$ kcal/mol. No revision is indicated for eq 3 based upon these experimental results for CF_3OH.

A referee has pointed out that eq 3 should be applicable to ΔG°_{acid} for $CH_2{=}CHOH$, which is available from $\Delta G^\circ_{acid} = 359.0$ for CH_3CHO minus the free energy of tautomerization of ca. +9 kcal/mol,[5b] i.e., $\Delta G^\circ_{acid} \cong 350.0$ for $CH_2{=}CHOH$. Unfortunately, tested σ_F and σ_R^- values for the $-CH{=}CH_2$ substituent are not available, although $\sigma_\alpha = -0.50$ has been obtained.[7] With use of the last value and (probably as an upper limit) the σ_F and σ_R^- values of C_6H_5 for $CH{=}CH_2$, the rough estimated value of ΔG°_{acid} obtained from eq 3 is $\geqslant 349.0$ kcal/mol.

Why Are Phenols and Carboxylic Acids More Acidic Than Corresponding Alcohols? The results obtained by eq 3 provide new evidence regarding the recent discussions on the question of why phenol is a stronger acid than cyclohexanol and acetic acid is stronger than ethanol.[17-19] It will be seen in Table I that the values of P are nearly the same for each of these pairs of acids (P = 18–19 kcal for the former pair and P = 12–13 kcal for the latter pair). Consequently, changes in the P effect are of little or no importance in these two pairs of relative acidities. The R value (16 kcal) for phenol indicates that π electron delocalization in phenoxide ion is the predominant cause of its greater inherent acidity, while the F value (7 kcal) is significant but of secondary importance. On the other hand, the R value of acetic acid (12 kcal compared to 1 kcal for ethanol) is significant, but in this case R is clearly of secondary importance compared to the predominant electrostatic field/inductive effect (F = 19 kcal for acetic acid compared to 0 kcal for ethanol). These compelling results in part both agree and disagree with the conclusions recently put forward.[17-19]

Cyclization or Coiling Effects in Gaseous Alkoxide Ions. Table I does not include 23 available acidity data[5b] for aliphatic alcohols. Instead only a representative selection of such acids was made for Table I so as not to skew the correlational results. Table II gives the results of applying eq 3 to these 23 aliphatic alcohols and two other acids with heteroatoms for which the σ parameters

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Table II. Comparison of Additional Observed and Calculated Values of ΔG°_{acid} (in kcal/mol)

X–OH	$-\sigma_\alpha{}^a$	$\Delta G^\circ_{acid}{}^b$(obs)	$\Delta G^\circ_{acid}{}^c$(calc)
1. *i*-BuOH	0.61	368.8	368.1
2. c-$C_6H_{11}CH_2OH$	0.68	367.1	367.1
3. *t*-$C_5H_{11}OH$	0.82	366.4	365.3
4. *i*-Pr(Me)CHOH	0.76	366.4	366.0
5. Et_2CHOH	0.75	366.1	366.2
6. $Pr(Me)_2COH$	0.85	365.5	364.6
7. *i*-Pr(Et)CHOH	0.82	364.9	364.7
8. *t*-Bu(Me)CHOH	0.82	364.5	364.7
9. *i*-PrCHOH	0.88	364.1	363.2
10. *t*-Bu(Et)CHOH	0.88	363.4	363.2
11. *t*-Bu(*i*-Pr)CHOH	0.94	362.2	361.8
12. *t*-Bu_2CHOH	1.00	361.0	360.4
13. $Me(CH_2)_3OH$	0.57	368.6	369.7
14. $Et(CH_2)_3OH$	0.58	367.3	369.5
15. *i*-$Pr(CH_2)_3OH$	0.58	366.5	369.5
16. $Pr(CH_2)_3OH$	0.58	366.5	369.5
17. $Bu(CH_2)_3OH$	0.59	365.9	369.2
18. $Pe(CH_2)_3OH$	0.59	365.2	369.2
19. $Hex(CH_2)_3OH$	0.59	364.6	369.2
20. *i*-$Pr(CH_2)_2OH$	0.61	366.9	368.8
21. *t*-$Bu(CH_2)_2OH$	0.63	365.9	368.3
22. $Et_2(Me)COH$	0.89	365.3	363.7
23. Et_3COH	0.98	364.3	361.6
24. $CF_3CH(Me)OH^d$	0.60	353.7	353.5
25. $EtCO_2H^e$	0.60	340.3	339.0

[a] From ref 7 or estimated as given in footnote (c) of Table I. [b] From ref 5b. [c] From eq 3. [d] σ_R and σ_F values taken to be the same as for CF_3CH_2OH (cf. Table I). [e] σ_R and σ_F values taken to be the same as for CH_3CO_2H (cf. Table I).

can be reliably estimated. For the 12 short chain branched alcohols (first entries in Table II), the agreement between calculated and observed ΔG_{acid} values is truly excellent (this is also true for alcohols nos. 2–7 and 10 of Table I). There are nine alcohols (entry nos. 13–21 of Table II) with straight chains capable of giving cyclization of the very polarizing alkoxide O^- to form a five-membered (or larger) ring with an end polarizable CH_3 (or higher alkyl) substituent. The observed values of ΔG°_{acid} for these are smaller (there is greater acidity) than that calculated from 1.1–4.6 kcal/mol, as expected from cyclization or coiling effects.[11] These alcohols are listed in Table II as $R(CH_2)_3OH$ or $R'(CH_2)_2OH$. Thus, the only exceptional values are for $(C_2H_5)_2C(CH_3)OH$ and $(C_2H_5)_3COH$ (entry nos. 22 and 23) which have reported values[11] that are 1.6 and 2.7 kcal/mol, respectively, less acidic than calculated. Entry nos. 24 and 25 are a fluoroalcohol and an aliphatic carboxylic acid for which the σ values can be reliably estimated. Satisfactory agreement between observed and calculated ΔG°_{acid} values has been obtained for these. There are about 10 other ΔG°_{acid} values available[5b] for OH acids in the same functional categories as these last two compounds. However, reliable parameter estimates are not available, although crude estimates of these generally give calculated values that are in agreement with experimental results within a few kcal/mol.

Gas-Phase Acidities Involving Effects of –R Substituents. The gas-phase acidity for HOOH is $\Delta G^\circ_{acid} = 369.0$ (statistical correlation). Taking for the OH substituent $R = 0$,[20] since there are no acceptor orbitals for either OH or O^-, and $P = (-0.03)(-23.4) = 0.7$ kcal and $F = (0.30)(73.4) = 22.0$ kcal, one obtains a ΔG°_{acid}(calc) value of 361.8 kcal/mol for HOOH. This value is 7.2 kcal/mol less (more acidic) than the experimental value. This is the correct order of magnitude for the figure expected from the decreased acidity caused by increased lone pair–lone pair repulsion in HOO^- compared to HOOH.[21] The gas-phase acidity of $(C_2H_5)_2NOH$ is 364.0.[5b] By using $\sigma_\alpha = -0.56$ and $\sigma_F = 0.10$ for $N(C_2H_5)_2$ and (again) $R = 0$, the value calculated by eq 3 is 364.1 kcal/mol.

This good agreement is not expected since lone pair–lone pair repulsion in Et_2NO should cause an increase in ΔG°_{acid} that is significantly above the estimated value. It may be inferred that there are low-energy conformations that place the ethyl substituents in close proximity to the O^-, thus increasing the P effect well beyond that estimated by the σ_α value of –0.56. Thus enhanced anion stabilization perhaps coincidentally matches the anion lone pair–lone pair repulsion destabilization, giving agreement between calculated and observed values. Gas-phase acidities of FOH and ClOH have been calculated from bond dissociation energies and radical electron affinities. However, the combined experimental errors of these measurements appear to lead to uncertainties in ΔG°_{acid} values of as much as 10 kcal/mol or more. These *D*–EA values are 357 for HOF and 352 for HOCl.[5b] Koppel[8] (1985) has corrected proton affinities from structure optimized ab initio calculations at several levels of theory with corresponding experimental values available from gas-phase equilibrium studies. The correlation equations have been used to predict the gas-phase acidities of HOF and HOCl. The predictions consistently indicate considerably larger difference in the acidities of these two acids than is given by the above *D*–EA values. By using eq 3 with $R = 0$ and $\sigma_F = 0.44, 0.45$; $\sigma_\alpha = 0.13, -0.43$ for F and Cl, respectively,[7] ΔG°_{acid} values have been calculated, and then 7.0 kcal/mol has been added to both as a rough estimate of the effects of lone pair–lone pair repulsions in the anions. This procedure gives estimated ΔG°_{acid} values of 362.0 and 348.0 kcal/mol for HOF and HOCl, respectively. The agreement obtained by these methods is as good as can be expected in view of the various uncertainties that are involved.

XOH Acidities in Dimethyl Sulfoxide Solution. The following acidities of XOH relative to H_2O have been measured in dimethyl sulfoxide,[22] i.e., $-\delta\Delta G^\circ_{(Me_2SO)}$ values (with statistical ion-pairing and homoconjugate formation corrections) for X are as follows: H, 0.0; CH_3, 3.7; C_2H_5, 2.6; *i*-C_3H_7, 1.9; CF_3CH_2, 12.2; C_6H_5, 19.5; CH_3CO, 27.4; $(CF_3)_3C$, 28.6; C_6H_5CO, 28.6; SOPh, 34.0; NO, 33.5; CF_3CO, 38.9; SO_2Ph, 41.8. The correlation of these 13 values by an equation of the form of eq 3′ gives eq 6. Compared to eq 3′ for the gas-phase acidity, there is a decrease in R^2 from 0.999 to 0.978 and an increase in sd from 0.8 to 2.6 kcal/mol (even though $-\delta\Delta G^\circ_{Me_2SO}$ values are generally significantly smaller than corresponding values of $-\delta\Delta G^\circ_{(g)}$). Since neither effects due to OH, X, nor O^- solvation by Me_2SO are specifically treated, the poorer fit is expected. However, reaction constants in eq 6, even when the large errors of the estimates, are reasonable in the sense that the signs remain the same as in eq 3′, and all ρ's are decreased in magnitude—with the largest decrease for ρ_α.[23]

$$-\delta\Delta G^\circ_{(Me_2SO)} = -1.5 \pm 1.8 - (7.5 \pm 3.3)\sigma_\alpha + (45.4 \pm 3.7)\sigma_F + (59.3 \pm 7.9)\sigma_R \quad (6)$$

$$n = 13,\ R^2 = 0.9781,\ \text{sd} = 2.6\ \text{kcal}$$

More significant correlations of the $-\Delta G^\circ_{(Me_2SO)}$ values are obtained by separation of the acids into two groups. The first set involves anions having little or no resonance stabilization but with relatively strong solvation due to charge localization at O^-. The second set involves anions with relatively strong resonance stabilized anions but with poorer solvation energies.[24]

The results for the first set are given by eq 7 and for the second one by eq 8:

$$-\delta\Delta G^\circ_{(Me_2SO)} = 0.8 \pm 1.1 - (3.5 \pm 2.7)\sigma_\alpha + (41.8 \pm 2.6)\sigma_F \quad (7)$$

$$n = 6,\ R^2 = 0.992,\ \text{sd} = 1.2\ \text{kcal}$$

σ_R has been taken as zero for all members since the range of σ_R is only 0.00–0.03, too small to define a reliable ρ_R value. For this set X = H, CH_3, C_2H_5, *i*-Pr, CF_3CH_2, and $(CF_3)_3C$.

$$-\delta\Delta G^\circ_{(Me_2SO)} = 15.3 \pm 0.5 + (45.7 \pm 1.4)\sigma_F \quad (8)$$

$$n = 7,\ R^2 = 0.996,\ \text{sd} = 0.5\ \text{kcal}$$

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(20) Cf.: ref 13.

(21) Taft, R. W.; Anvia, F.; Taagepera, M.; Catalān, J.; Elguēro, J. *J. Am. Chem. Soc.* **1986**, *108*, 3237.

(22) Cf.: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(23) Koppel's treatment, cf. ref 8 for **1983** and **1988**, gives essentially the same ratio(s) of corresponding coefficients.

(24) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

Table III. Summary of Reaction Constant Parameters for XOH and *p*-XC_6H_4OH Acidity Series (Conjugated +R Substituents)

acidity series	ρ_α	ρ_F	ρ_R	σ_R/ρ_F	n	R^2	sd
$XOH_{(g)}$	−23.4 ± 0.9	73.4 ± 0.9	72.8 ± 2.0	0.99 ± 0.03	25	0.999	0.8
p-$XC_6H_4OH_{(g)}$	0.0	18.6 ± 0.5	49.0 ± 1.5	2.63 ± 0.11	12	0.998	0.3
$XOH_{(Me_2SO)}$	−7.5 ± 3.3	45.0 ± 3.7	59.0 ± 7.9	1.31 ± 0.21	13	0.978	2.6
p-$XC_6H_4OH_{(Me_2SO)}$[a]	0.0	7.0 ± 0.3	12.9 ± 1.6	1.84 ± 0.24	13	0.998	0.2
$XOH_{(aq)}$	0.0	25.0 ± 2.3	39.0 ± 4.3	1.56 ± 0.22	16	0.964	1.6
p-$XC_6H_4OH_{(aq)}$[b]	0.0	3.1 ± 0.3	5.4 ± 1.7	1.74 ± 0.57	13	0.984	0.2

[a] Values from eq 11, taken from ref 7. [b] Values from eq 12, taken from ref 7.

For this set X = CH_3CO, PhCO, PhSO, NO, CF_3CO, $PhSO_2$, and Ph.

For the first acid series with charge localized anions, the substituent polarizability effects are indicated by eq 7 to be nearly completely attenuated by the anion solvation. The value of ρ_α in eq 7 is hardly statistically significant at the 95% confidence level,[23] and in eq 8 neither ρ_α nor ρ_R have statistically significant values. The Me_2SO solvent attenuation factor for ρ_F is given by eq 3 and 8 as 73.4 ± 0.9/45.7 ± 1.4 = 1.6 ± 0.2.[23] This is similar but smaller (as expected[24]) than the value previously obtained for para-substituted phenols[7] of 18.6 ± 0.5/7.0 ± 0.3 = 2.7 ± 0.3.

As the σ_R value of X increases, gas-phase acidity is increased by the inherent R effect, but in Me_2SO solution there is a reduction in acidities caused by decreasing anion solvation as more charge is delocalized away from the O^- center. For the stronger π acceptor substituents (with σ_R greater than ~0.15), new oxyanionic solvation sites in X are created (the SSAR effect),[7,25] and this solvation tends to restore the total anion solvation energy. The consequence of all of the above factors appears to be the large near constant value of 15.3 ± 0.5 kcal/mol in eq 8. That is, the substituent resonance effects in Me_2SO with their accompanying effects on anion solvation energy are large but (in contrast to the corresponding gas-phase *R* values) are now nearly constant for all of the strong π acceptor substituents. It is interesting to note in Table I that for the gas-phase acidities, *R* = 12–19 kcal/mol for such acids; i.e., the gas-phase *R* values center for moderate-to-strong π acceptors at ca. the 15 kcal/mol value found in Me_2SO acidities. The F effect values for the Me_2SO acidities of these XOH acids all exceed 12 kcal/mol, except for C_6H_5, for which it is 4.6 kcal/mol. Thus, the R effect remains the dominant effect for phenol acidity in Me_2SO, and the F effect remains the dominant effect for CF_3CO_2H. However, both the F and R effects for the Me_2SO acidity of CH_3CO_2H appear to be quite similar.

XOH Acidities in Aqueous Solution. Sixteen substituents for which parameters and corresponding $-\delta\Delta G°_{(aq)}$ acidities relative to water are available in aqueous solution[3,26] give equation 9:[27]

$$-\delta\Delta G°_{(aq)} = -0.4 \pm 0.7 + (25.2 \pm 2.3)\sigma_F + (39.2 \pm 4.3)\sigma_R \tag{9}$$

$$n = 16,\ R^2 = 0.964,\ \text{sd} = 1.6$$

There is no term in σ_α in eq 9 (the error of the estimated ρ_α is found to be more than 3 times greater than the value of ρ_α). With even greater dispersion of the anion charge into water than Me_2SO, substituent polarizability effects for oxyanions are completely attenuated.[7] Values of both ρ_F and ρ_R, however, remain significant although decreased, so that both acidities increase in the following order: aqueous < Me_2SO < gas phase.[23] This result has also been found earlier[7] for the distant substituents of the para-substituted phenol family of acids.

It is to be noted by comparing eq 3′ with eq 9 for aqueous acidities (as well as with eq 6 for Me_2SO acidities) that anion solvation is indicated to lead to particularly large uncertainties in the values of the reaction constant ρ_R. The consideration of only acids for which X is a relatively strong π acceptor gives eq 10, in which values of both the approximately constant *R* term and the ρ_F reaction parameter are reduced in water to ca. one-half those of the corresponding terms in Me_2SO[23] (i.e., in eq 8).

$$-\delta\Delta G°_{(aq)} = 6.6 \pm 1.1 + (28.4 \pm 2.9)\sigma_F \tag{10}$$

$$n = 9,\ R^2 = 0.937,\ \text{sd} = 1.3$$

These were obtained by using X = Ph, CH_3CO, HCO, $ClCH_2CO$, C_6H_5CO, NO, CO_2H, CF_3CO, and NO_2.

Results Revealed by Comparison of Reaction Parameters. Table III compared the values of the reaction constants, ρ_α, ρ_F, and ρ_R, obtained previously[7] for *p*-XC_6H_4OH acidities with the corresponding values reported herein for the XOH family. The substituents in each family are limited to π electron acceptor substituents.

The strong attenuation in substituent polarizability effects with distance and with solvation of oxide center is shown by the fact that the ρ_α values of Table III are statistically significant only for the XOH family in Me_2SO and (particularly) in the gas phase.

However, the important new finding shown in Table III for conjugated substituents is that although both ρ_F and ρ_R values increase as the substituent is brought to the point of direct attachment to OH (by eliding C_6H_4 of *p*-XC_6H_4OH to give X–OH), the ratio, ρ_R/ρ_F, is actually decreased quite significantly. Since the substituent electrostatic F effect is relatively long range in character, the greater increase of F than corresponding R effects with the decreasing distance is at first surprising. However, an analogous result has been previously observed.

For the gas-phase acidities of 4-substituted pyridinium ions compared to corresponding 2-substituted pyridinium ions, the ρ_R/ρ_F ratios are (25.7 ± 0.6)/(21.8 ± 0.6) = 1.18 ± 0.04 and (13.3 ± 0.5)/(27.5 ± 0.5) = 0.48 ± 0.02, respectively. A similar decrease in the ρ_R/ρ_F ratio takes place with the corresponding aqueous acidities.[7] The results have been interpreted[28] in terms of electrostatic repulsions associated with π electron delocalization between the −R substituent and the NH^+ reaction center. The −R substituent becomes positively charged, and a repulsion is developed between the positive force fields of the substituent and the reaction center. The repulsion plays a minor role from the 4-position, but it is quite significant at the 2-position.

An analogous explanation accounts for the results in Table III. There is less effect of electrostatic repulsion between the O^- force field and the negative force field developed by the π electron acceptor (+R) substituent at the distant ring para position than when it is at the directly attached (XOH) position. Consequently, ρ_R/ρ_F is greater for *p*-XC_6H_4OH than for XOH as a result of this kind of lone pair–lone pair electronic repulsion.

The important SSAR effects involved in the proton-transfer acidities of the *p*-XC_6H_4OH family have been treated by replacing the $\sigma_\alpha\rho_\alpha$ term by a $\Delta\sigma_R\rho_s$ term.[7] The following eqs 11 and 12 give very much more precise descriptions of Me_2SO and aqueous acidities of the *p*-XC_6H_4OH family[7] than are given by eqs 6 and 9,

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(25) Mishima, M.; McIver, R. T., Jr.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1981**, *106*, 2717.

(26) Brown, H. C.; McDaniel, D. H.; Häflinger, O. *Determination of Organic Structures by Physical Methods*; Academic Press: 1955; p 567.

(27) The $-\delta\Delta G°_{(aq)}$ values used to obtain eq 9 are as follows: X = H, 0.0; CH_3, 0.0; $C_6H_5CH_2$, 0.8; $Cl(CH_2)_2$, 2.3; CF_3CH_2, 4.9; $(CF_3)_2CH$, 9.1; $(CF_3)_3C$, 14.5; C_6H_5, 8.2; CH_3CO, 15.4; HCO, 16.8; C_6H_5CO, 16.1; NO, 17.3; CO_2H, 16.5; CF_3CO, 22.2; NO_2, 23.7; $ClCH_2CO$, 17.9. The σ_α values used are those given in Table I; the estimated σ_α values used for $(CH_2)_2Cl$, CO_2H, and $ClCH_2CO$ are −0.58, −0.41, and −0.67, respectively. The σ_F(aq) values[7] used were as follows: C_6H_5, 0.12; CH_3CO, 0.30; HCO, 0.32; C_6H_5CO, 0.30; CO_2H, 0.32; $ClCH_2CO$, 0.19; all other σ_F values are those given in Table I. For the first seven of the 16 substituents, σ_R is taken to be 0. For CO_2H and $ClCH_2CO$, the values used were 0.18 and 0.19, respectively, and all other σ_R values are those given in Table I.

(28) Reference 7, pp 38, 39, 43, 62, and 65.

$$-\delta\Delta G^\circ_{\mathrm{Me_2SO}} = 0.0 \pm 0.2 + (7.0 \pm 0.3)\sigma_F + (12.9 \pm 1.6)\sigma_R + (17.5 \pm 1.2)\Delta\sigma_R \quad (11)$$

$$n = 13,\ R^2 = 0.998,\ \mathrm{sd} = 0.2$$

$$-\delta\Delta G^\circ_{(\mathrm{aq})} = 0.01 \pm 0.20 + (3.1 \pm 0.3)\sigma_F + (5.4 \pm 1.7)\sigma_R + (6.5 \pm 1.2)\Delta\sigma_R \quad (12)$$

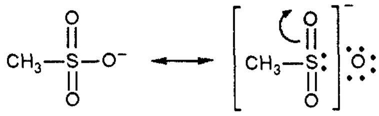
$$n = 13,\ R^2 = 0.984,\ \mathrm{sd} = 0.2$$

Values of ρ_R/ρ_F from eqs 11 and 12, 1.84 ± 0.24 and 1.74 ± 0.57, respectively, are both larger than that (0.99 ± 0.03) for the XOH gas-phase acidities. These results also support the above idea of lone pair–lone pair repulsions reducing the ρ_R value for XOH acidities. An equation in the form of eqs 11 and 12 fails to apply to XOH family acidities in solution. This is in accord with the earlier discussion of eq 8 and 10. In simply indicates that $\Delta\sigma_R$ (SSAR effect) parameters apply well only for solvated π electron acceptor substituents acting at relatively remote distances. In XO^- anions, the substituent oxygen atoms (e.g., for NO_2) become an integral part of the principal solvation center of the anion. In contrast, in ambient anions (e.g., p-$XC_6H_4O^-$) there are with the SSAR substituents two quite distinct solvation sites, both p-X and O^-.

Some Possible Limitations. The present treatment of XOH gas-phase acidities does not apply to X–NH_2 and X–CH_3 family acidities.[12] Strongly electron-withdrawing substituents increase acidity less than is predicted. The discrepancies are more severe for the X–CH_3 than the X–NH_2 family. This is a resonable expectation since R effects increase with increasing π donating ability of the anion center, i.e., in the order $-O^- < NH_2^- < CH_3^-$. Strong π electron acceptor substituents will therefore increasingly reduce the anionic center charge, with increasing reductions in the X–NH_2 and X–CH_3 family ρ_F and ρ_α reaction constants. This corresponds to reduced acidities. The large electronegativity of oxygen is evidently responsible for maintaining the necessary integrity of the XO^- anion center that is required for eq 3 to be a useful approximation (that is, with ρ_α, ρ_F, and ρ_R remaining reasonably constant through the entire XOH family).

Stronger π electron acceptor substituents than those appearing in Table 1, therefore, may lead to weaker acidities than are predicted by eq 3. Two possible candidates are $HOC(CN){=}C(CN)_2$ and $HOSO_2CN$, for which the relevant estimated values[29,30] of σ_α, σ_F, and σ_R for the former are −0.88, 0.72, and 0.27 and for the latter −0.67, 0.99, and 0.27, respectively, leading by eq 3 to predicted ΔG_{acid} values of 291.5 and 276.5, respectively.

An additional matter will be noted from consideration of the structures for the strong π acceptor substituents of Table I. All of these substituents involve C, N, and O as acceptor sites. There are no data available for the second long row of periodic elements, that is for substituents, e.g., SO_2CH_3, SO_2CF_3, or SO_2CN. We have attempted preliminary measurements on the first of these but do not as yet have adequate standards developed to obtain a quantitative ΔG_{acid} value. For CH_3SO_2OH and CF_3SO_2OH the predicted ΔG_{acid} values from eq 3 and the σ values of ref 7 are 318.0 and 293.9 kcal/mol, respectively. These predictions are in qualitative agreement with acidity orders obtained by Viggiano, Paulson, and Henchman.[31] However, our preliminary results indicate that methanesulfonic acid probably has ca. 3 kcal/mol greater acidity than the value (318.0) obtained by eq 3. σ bond resonance such as



may act to stabilize anions like those above and increased their acidity beyond that predicted by eq 3. There is one data in ref 5b for a weak π acceptor from the second long row of the periodic table, i.e., $X = Si(C_2H_5)_3$ with $\Delta G^\circ_{\mathrm{acid}} = 353.6$ kcal/mol. By using[7] $\sigma_\alpha = 1.18$, $\sigma_F = -0.02$, and eq 3, one calculates $\sigma_R = 0.08$ for $Si(C_2H_5)_3$. This value appears larger than expected,[7] but neither σ_R for this nor for the $Si(CH_3)_3$ substituent have been well tested by gas-phase proton-transfer equilibria. Clearly, it is highly desirable to obtain quantitative results for acids of this kind.

Experimental Section

Details of the gas-phase acidities of $HC(CF_3)_2OH$ and $(CF_3)_3COH$ given in Table I and ref 5b have not been reported previously. By using the method described previously,[32] the latter compound was found to be 1.1 ± 0.2 kcal/mol stronger than 4-CNC_6H_4OH (having $\Delta G^\circ_{\mathrm{acid}} = 325.3$)[5b] and 0.1 ± 0.1 stronger than difluoroacetic acid (having $\Delta G^\circ_{\mathrm{acid}} = 323.8$),[5b] giving $\Delta G^\circ_{\mathrm{acid}} = 324.0 \pm 0.2$. The former compound was determined to be 0.3 ± 0.2 kcal/mol greater than 2-FC_6H_4OH (having $\Delta G^\circ_{\mathrm{acid}} = 339.0$)[5b] and 1.5 ± 0.2 kcal/mol stronger than $(CH_3CO)_2CH_2$ (having $\Delta G^\circ_{\mathrm{acid}} = 336.7$),[5b] giving $\Delta G^\circ_{\mathrm{acid}} = 338.4 \pm 0.3$ kcal/mol.

Indications from unpublished previous work (cf. ref 8) supported the unreliability of the $\Delta G^\circ_{\mathrm{acid}}$ value for CF_3OH estimated from D–EA values that have relatively large uncertainties.[5b] Since this acid was of particular interest, its $\Delta G^\circ_{\mathrm{acid}}$ value has been determined by the bracketing method. The $^-OCF_3$ anions were generated by electron impact from $(CF_3)_2O_2$ by using low-energy (1–2 eV) electrons and reacted with the following series of acids having $\Delta G^\circ_{\mathrm{acid}}$ values between 343 and 328 kcal/mol: p-$CH_3C_6H_4OH$ ($\Delta G^\circ_{\mathrm{acid}} = 343.4$), $CH_2(CO_2C_2H_5)_2$ ($\Delta G^\circ_{\mathrm{acid}} = 342.3$), CH_3CO_2H ($\Delta G^\circ_{\mathrm{acid}} = 341.5$), NC–C_2H($\Delta G^\circ_{\mathrm{acid}} = 341.1$), $3,5$-$(CF_3)_2C_6H_4NH_2$ ($\Delta G^\circ_{\mathrm{acid}} = 340.6$), 2-FC_6H_4OH ($\Delta G^\circ_{\mathrm{acid}} = 339.0$), $(CH_3CO)_2CH_2$ ($\Delta G^\circ_{\mathrm{acid}} = 336.7$), 3-$CF_3C_6H_4OH$ ($\Delta G^\circ_{\mathrm{acid}} = 332.4$), $CH_2(CN)_2$ ($\Delta G^\circ_{\mathrm{acid}} = 328.5$). Two reaction channels were observed:

$$CF_3O^- + HA \rightarrow (1)\ CF_3OH + A^-$$

$$CF_3O^- + HA \rightarrow (2)\ F_2CO + FHA^-$$

with (2) being the major channel for all of the above acids. However, the minor channel showed an excellent correlation with the $\Delta G^\circ_{\mathrm{acid}}$ values for all of the above HA's. Namely, for the ΔG acids above 342.0, no A^- was observable, and for those below 341.0, A^- was observed in each case. For CH_3CO_2H and NCC_2H with $\Delta G^\circ_{\mathrm{acid}}$ values between 341.1 and 341.5, observation of A^- was difficult and uncertain, both because of the interference from the major channel but also from the formation of homodimers A^-–HA of the OH acid. Ejection of A^- revealed the presence of no A···HF only for HA = p-$CH_3C_6H_4OH$ and $CH_2(CO_2C_2H_5)_2$; some was observed for all of the other stronger acids. All of these observations are satisfactorily consistent with a value of $\Delta G^\circ_{\mathrm{acid}}$ for CF_3OH of 340.7 ± 1.5 kcal/mol.

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[29] Values of σ_F and σ_R for substituents such as SO_3H, SO_2F, SO_2CF_3, SO_2CN, $C(CN){=}C(CN)_2$, $C(CF_3)_3$, $C(CN)_3$, and others are available from F NMR chemical shifts of meta- and para-substituted fluorobenzenes.[3σ] A table giving values of these parameters for nearly 300 substituents is given by the following: Hansch, C.; Leo, A.; Taft, R. W. To be submitted for publication.

[30] (a) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. H.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *35*, 709, 1346. Equations are as follows: $\sigma_F = 0.16 \pm (0.137) \int_H^{m-X}$; $\sigma_R = (0.0295) \int_{m-X}^{p-X}$ for +R substituted fluorobenzenes, and $\sigma_R = (0.0357) = \int_{m-X}^{p-X}$ for −R substituted fluorobenzenes (cf. above references).

[31] (a) Viggiano, A. A.; Paulson, J. F.; Henchman, M. J. Private communication. (b) The estimated $\Delta G^\circ_{\mathrm{acid}} = 293.3$ kcal/mol for CF_3SO_3H is in good agreement with that calculated using $D_{(A-H)} \cong 102.$ kcal/mol and $EA_{(CF_3SO_3\cdot)} = 5.4$ eV given by the following: Herd, R.; Smith, D.; Adams, N. G. *Int. J. Mass Spectr. Ion Processes* **1989**, *91*, 177.

[32] Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.