(31) The classical approximation generally underestimates the fraction of activated states, so that s must be taken as an adjustable parameter, smaller than the actual number of oscillators.[30]

(32) T. O. Tiernan in "Ion–Molecule Reactions", J. L. Franklin, Ed., Plenum Publishing Co., New York, N.Y., 1972; M. Henchman, *ibid.*, and references cited therein; J. J. Solomon, M. Meot-Ner, and F. H. Field, *J. Am. Chem. Soc.*, **96**, 3727 (1974); M. Meot-Ner and F. H. Field, *ibid.*, **97**, 2014 (1975).

(33) S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 6174 (1970).

(34) F. A. Long and Z. Margolin, *J. Am. Chem. Soc.* **95**, 2757 (1973); J. Hine, *J. Org. Chem.* **31**, 1236 (1966), *J. Am. Chem. Soc.* **88**, 5525 (1966); see also ref 26.

(35) Kebarle has shown that for some systems there is a correlation between base strength and the strength of the hydrogen bond $B^{-}\cdots HR$. For HOH and a variety of bases with a range of basicities that covers 70 kcal/mol, the strength of the $B^{-}\cdots HR$ bond changes by 14 kcal/mol. If such a correlation applies here, it could lead to relatively small changes in E_R over the small range of base strengths involved.

(36) (a) K. Hiraoka and P. Kebarle, *J. Chem. Phys.* **63**, 394 (1975); (b) F. C. Fehsenfeld, W. Lindinger, A. L. Schmeltkopf, D. L. Albritton, and E. E. Ferguson, *ibid.*, **62**, 2001 (1975).

(37) I. Amdur and G. G. Hammes, "Chemical Kinetics Principles and Selected Topics", McGraw-Hill, New York, N.Y., 1966, p 149.

(38) See ref 27.

(39) We have been able to show that RRKM theory accurately models ionic decompositions: W. N. Olmstead, M. Lev-On, D. M. Golden, and J. I. Brauman, *J. Am. Chem. Soc.*, in press. We have also been able to show that quantum RRK can give results similar to RRKM when the *A* factor is chosen correctly. Nevertheless, there is no assurance that the barrier estimated by RRK is quantitatively correct.

(40) L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Am. Chem. Soc.* **95**, 1057 (1973).

(41) See A. J. Kresge, *Chem. Soc. Rev.* **2**, 475 (1973); *Acc. Chem. Res.*, **8**, 354 (1975).

Relative Gas-Phase Acidities and Basicities from a Proton Potential Model

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Abstract: A proton potential model (PPM) calculation of gas-phase proton affinities was used to calculate relative PA values for various molecules and anions. The model, which uses CNDO/2 wave functions, provides separate values of inductive and polarization energies accompanying the gain or loss of a proton. Agreement with experiment ranges from excellent for acidities of substituted aliphatic acids to poor for certain unsaturated molecules. An approximate method for empirical separation of inductive and polarization effects is presented.

I. Introduction

The Bronsted acidity and basicity of a molecule, which measure that molecule's tendency to lose or gain a proton, are of considerable chemical interest. The increasing availability of accurate experimental values of gas-phase acidities and basicities has stimulated interest in estimating these quantities theoretically. Ab initio calculations with sufficiently large basis sets can predict absolute values of the proton affinities to within a few percent in the Hartree-Fock approximation.[1] These proton affinities (PA) are the energy E_b of the reaction

$$B + H^+ \rightarrow BH^+;\ E_b = -PA_m \qquad (1a)$$

or (minus) the energy E_a of the reaction

$$AH \rightarrow A^- + H^+;\ E_a = PA_a \qquad (1b)$$

Here the subscripts "a" and "m" denote proton affinities of the anions and neutral molecules, respectively. More accurate predictions of the absolute values of E_a and E_b would require very careful ab initio calculations, including electron correlations. Such calculations rapidly become impractical as the molecular size increases.

Relative acidities and basicities can be calculated to satisfactory accuracy using less sophisticated theoretical models. In this approach one tries to calculate the energy of the proton-transfer reaction

$$B + B'H^+ \rightleftarrows B' + BH^+ \qquad (2a)$$

for comparing two bases, or

$$AH + A'^- \rightleftarrows A'H + A^- \qquad (2b)$$

for comparing two acids. If the molecules to be compared lie in a group of molecules with enough similarities, some of the errors in E_b or E_a that arise from theoretical approximations will tend to cancel. Thus, Radom found good agreement with experiment for energies of several proton-transfer reactions involving acidities, using ab initio theory with minimal STO-3G basis sets.[2]

It would be highly desirable to use an intermediate level molecular-orbital theory such as CNDO/2 to estimate energies of proton-transfer reactions. Most of the applications of CNDO/2 for this purpose have been based on difference in total energy, with varying success.[3-6] This approach usually gives the correct order of acidity or basicity, but quantitative agreement with experiment is marginal.

An alternative potential-model approach was derived by Davis and Rabalais.[7] Based on differences in the electrostatic potentials at proton sites, calculated employing CNDO/2 wave functions, this approach is related to the "relaxation potential model" (RPM) used to estimate ESCA shifts. We shall term it the "proton potential model", or PPM. Davis and Rabalais calculated proton affinities of several molecules using the PPM approach. In this paper we report further results based on an improved PPM model. Proton-transfer energies were calculated for several series of molecules and anions, yielding relative acidities or basicities within each series. Our objective was to evaluate the PPM in its applications to a wide range of molecules.

Section II sketches the theory briefly. Results are given in section III. These are discussed in comparison with experiment in section IV. An empirical model of acidities and basicities is discussed in section V. Conclusions are briefly summarized in section VI.

II. Theory

In using the PPM approach to calculate the proton affinity of a reaction $M + H^+ \rightarrow MH^+$, the electrostatic potential at the proton site is evaluated from CNDO/2 wave functions calculated both with and without the proton present. Alternatively we can describe these potentials as the values which would obtain if the proton had a charge of zero as well as +1, i.e., $V_N(0)$ and $V_N(1)$. Here N denotes proton attachment to a *neutral* molecule, and the *V's represent potential energies of +1 charges, rather than electrostatic potentials per se.* It can be shown from arguments based on potential theory[7-9] that the proton affinity of the above reaction is given to good approximation by

$$\mathrm{PA}_N = -\tfrac{1}{2}[V_N(0) + V_N(1)] = -E_b \qquad (3)$$

We have employed the usual sign convention: PA is taken as positive if the bound proton state is favored, but E_b is the energy of the reaction as written. Thus

$$\begin{aligned} E_b &= \tfrac{1}{2}[V_N(0) + V_N(1)] \\ E_b &= V_N(0) + \tfrac{1}{2}[V_N(1) - V_N(0)] \qquad (4) \\ E_b &= V_N(0) + R_b \end{aligned}$$

Here $V_N(0)$ is the electrostatic potential energy at the proton site in the neutral molecule and R_b is the relaxation or polarization energy at this site after the proton is added. For comparing two reactions,

$$B_1 + H^+ \rightarrow B_1H^+;\ E_{B1} = -\mathrm{PA}_1 \qquad (5a)$$

$$B_2 + H^+ \rightarrow B_2H^+;\ E_{B2} = -\mathrm{PA}_2 \qquad (5b)$$

to give

$$B_2 + B_1H^+ \rightleftarrows B_1 + B_2H^+ \qquad (6)$$

we would have

$$\Delta E_b(B2 - B1) = E_{B2} - E_{B1} = \mathrm{PA}_1 - \mathrm{PA}_2 = \Delta V_N(0) + \Delta R_b \qquad (7)$$

where

$$\Delta V_N(0) = V_N{}^{B2}(0) - V_N{}^{B1}(0)$$

and

$$\Delta R_b = \tfrac{1}{2}[V_N{}^{B2}(1) - V_N{}^{B1}(1) - V_N{}^{B2}(0) + V_N{}^{B1}(0)] \qquad (8)$$

When ΔV or ΔR is negative, proton-transfer reaction b tends to proceed to the right, and vice versa. The $V_N(0)$ term represents an *inductive* effect in the usual chemical nomenclature, and is the heat of protonation in the (hypothetical) case of frozen, neutral-state molecular orbitals. The R_b term corresponds to a *polarization* effect to adjust to the added proton. The separation and quantification of these two effects are useful features of the PPM approach. Very similar approaches have recently been published by other workers.[10]

In comparing the acidities of two molecules, we may for each reaction relate the proton affinity of the anion to the energy of the ionization reaction (eq 1b) as

$$\mathrm{PA}_a = -\tfrac{1}{2}[V_A(0) + V_A(1)] = E_a \qquad (9)$$

For the comparison of two acids we would have, by arguments similar to those given above,

$$\Delta E_a = -\Delta V_A(1) + \tfrac{1}{2}\Delta[V_A(1) - V_A(0)] = -\Delta V_A(1) + \Delta R_a \qquad (10)$$

Here $\Delta V_A(1)$ is the relative potential energy of the *added* proton in the neutral species, just as $\Delta V_B(0)$ was the relative potential energy at the protonation *site* in the neutral species for the protonation reaction. The terms ΔR_b and ΔR_a represent relative relaxation or polarization energies at the proton site in the positive or negative ion after the proton is gained or lost, in processes like eq 1a and 1b, respectively. For a given pair of molecules ΔR_b and ΔR_a are usually roughly equal in magnitude, according to the PPM calculations. For some classes of molecules it is possible to predict the relative sizes of $\Delta V_A(1)$ and $\Delta V_B(0)$, as well as those of ΔR_a and ΔR_b, from experiment. This is done for alcohols in section V.

The details of the proton affinity calculations have been described earlier.[7] Some improvements have been made in the present work. Two-center electrostatic r^{-1} integrals involving H 1s and all 2s and 3s functions were evaluated instead of being approximated as e^2/R_{AB}. This reduced the proton affinities ~10-20% in magnitude, but made only negligible changes in relative PA values. Two-center r^{-1} integrals involving 3p functions were also evaluated exactly, extending the p p′ model[9] to third-row elements. The parameters suggested by Jolly and Perry[11] were used.

III. Results

Table I lists values of ΔV and ΔR and derived values of ΔPA, calculated by the PPM method, for several groups of similar molecules for which experimental PA values are available. By "similar molecules" we mean in most cases molecules in which the protonation-site atom and its immediate neighbors are unchanged. In some cases this definition is exceeded, as indicated by the group headings in Table I. Shifts in PA's among similar molecules (i.e., proton-transfer energies) are quoted, rather than absolute PA's. The CNDO/2 level potential models for core-level binding-energy shifts were found to predict shifts among similar molecules well, but not shifts between dissimilar molecules.[12] This is a consequence of cancellation of errors inherent in the CNDO/2 formalism among similar molecules. The same situation obtains for PA calculations in the PPM model.

The PA values for anions of substituted aliphatic acids were compared with experimental values given by Yamdagni and Kebarle[13] and by Hiraoka et al.[14] McIver et al.[15] gave proton affinities for anions of aliphatic alcohols, while PA values for aliphatic amines were quoted by Aue et al.[16] Aliphatic acid and alcohol proton affinities were obtained from Long and Munson[17] and from Beachamp.[18] McMahon and Kebarle gave carbon acid PA's,[19] and McIver and Silvers did the halogenated phenols.[20] Acidities of para-substituted benzoic acids were measured by Yamdagni et al.[21] and basicities of para-substituted pyridines by Taagepera et al.[22]

IV. Discussion

Inspection of Table I shows that the PPM predictions of relative acidities and basicities give agreement with experiment ranging from excellent to only fair. The level of agreement tends to parallel that reported by other workers[5] based on CNDO/2 total energies. Thus, saturated molecules tend to give good results, while discrepancies with experiment are often encountered in unsaturated molecules. We therefore infer that those cases which show only fair agreement with experiment may be attributable to inadequacies in the CNDO/2 theory rather than shortcomings of the potential model itself. It would be interesting to test this hypothesis by combining the PPM approach with ab initio molecular-orbital theory.[27] Because of the wide variation in agreement between the calculated results and experiments, we discuss several classes of molecules separately.

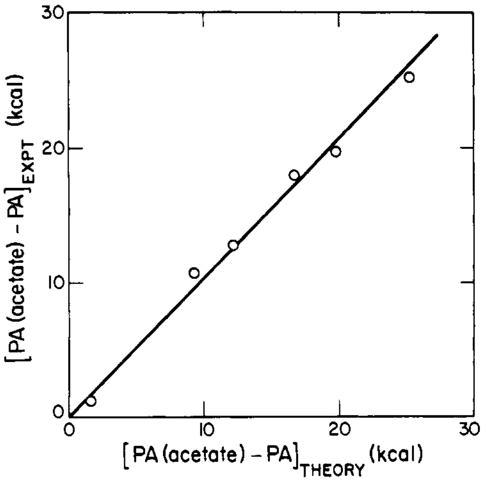
Agreement with experiment is remarkably good for relative acidities of substituted acetic acids (Figure 1). A straight line fits the points to within 1 kcal or less, while the standard deviation between theory and experiment is 0.9 kcal.

Table I. Relative Proton Affinities (kcal/mol)

Species	ΔV(theo)	ΔR(theo)	ΔPA(theo)	ΔPA(expt)	Ref
Acid Anions					
$CH_3CO_2^-$	(0)	(0)	(0)	(0)	
$CH_2FCO_2^-$	9.5	0.2	−9.3	−10.8	14
$CH_2ClCO_2^-$	9.8	−2.3	−12.1	−12.8	13
$CHF_2CO_2^-$	17.0	0.4	−16.6	−18.0	14
$CHCl_2CO_2^-$	16.4	−3.4	−19.8	−19.8	13
$CF_3CO_2^-$	26.6	1.4	−25.2	−25.2	14
HCO_2^-	11.2	5.9	−5.2	−3.2	13
$CH_3CH_2CO_2^-$	−0.2	−1.8	−1.6	−1.2	13
Aliphatic Alcohol Anions					
OH^-	−2.5	24.8	27.3	*a*	7
CH_3O^-	(0)	(0)	(0)	(0)	15
$C_2H_5O^-$	−2.7	−4.9	−2.2	−1.9	15
i-$C_3H_7O^-$	−5.7	−8.8	−3.1	−3.1	15
Aliphatic Amines					
NH_3	(0)	(0)	(0)	(0)	CH_3NH_2
1.6	−15.9	14.3	11.4	16	
$C_2H_5NH_2$	1.2	−20.8	19.6	14.1	16
Aliphatic Acids					
CH_3CO_2H	(0)	(0)	(0)	(0)	
$CH_3CH_2CO_2H$	−1.0	2.6	3.6	2	17
Aliphatic Alcohols					
CH_3OH	(0)	(0)	(0)	(0)	
CH_3CH_2OH	−1.5	−5.8	7.3	7.0	18
i-C_3H_7OH	−2.5	−10.3	12.8	13	18
Carbon Acid Anions					
CH_3^-	(0)	(0)	(0)	(0)	
$C_6H_5CH_3^-$	5.5	−30.1	−35.6	−33.1	19
Substituted Carbon Acid Anions					
CH_2CN^-	(0)	(0)	(0)	(0)	
$CH(CN)_2^-$	20.0	−7.6	−27.6	−30.4	19
$CH_3COCH_2^-$	−19.5	−12.7	−6.8	−3.0	19
Halogenated Phenol Anions					
Phenoxy anion	(0)	(0)	(0)	(0)	
o-Fluorophenoxy	1.9	1.5	−0.4	−2.8	20
o-Chlorophenoxy	4.9	2.5	−2.4	−4.6	20
m-Fluorophenoxy	6.5	0.7	−5.8	−4.8	20
m-Chlorophenoxy	10.0	−0.4	−10.4	−6.1	20
p-Fluorophenoxy	3.7	0.2	−3.5	−2.1	20
p-Chlorophenoxy	9.2	0.1	−9.1	−2.9	20
Benzoate Anions					
$C_6H_5CO_2^-$	(0)	(0)	(0)	(0)	
p-Nitrobenzoate	11.9	0.0	−11.9	−11.1	21
p-Cyanobenzoate	4.1	−0.7	−4.8	−10.3	21
p-Fluorobenzoate	2.8	0.2	−2.6	−2.9	21
Pyridines					
C_5H_5N	(0)	(0)	(0)	(0)	
p-$NO_2C_5H_4N$	−16.4	−1.3	−15.1	−17.0	22
p-$CF_3C_5H_4N$	−10.9	1.4	−9.5	−11.0	22
p-$CH_3C_5H_4N$	2.1	4.3	6.4	5.0	22
p-$CH_3OC_5H_4N$	0.8	4.0	4.8	8.0	22

[a] In ref 26 it was determined qualitatively that $PA(OH^-) > PA(CH_3O^-)$.

Our results indicate that the increase of acidity accompanying chlorine or fluorine substitution in acetic acid arises primarily by increasing V, making the neutral ground-state potential less attractive to the proton. The extent of this effect is apparently about equal for fluorine and chlorine substitution. There are nearly equal contributions to this change in V from both the local and through-space components of the inductive term. That is, the potential at the proton site becomes less attractive both because of a reduction of negative charge on the oxygen *and* because of a less attractive potential component arising through contributions from other atoms. In these molecules the ΔR term is typically 20% or less of the ΔV term. Within this context the chlorine and fluorine derivatives differ in a significant way. The ΔV and ΔR terms reinforce each other in the chlorine derivatives. Upon deprotonation the chlorine derivatives are able to attract more electronic charge from the proton site (relative to acetic acid); i.e., the chlorine atom's inductive strength is effectively increased. In fluorine derivatives the ΔR term is negligible, implying that the intrinsically equivalent inductive power (relative to chlorine) of



XBL 761-2019

Figure 1. Proton affinities, relative to acetate ion, of chloro- and fluoroacetic acids, showing excellent agreement between theory and experiment.

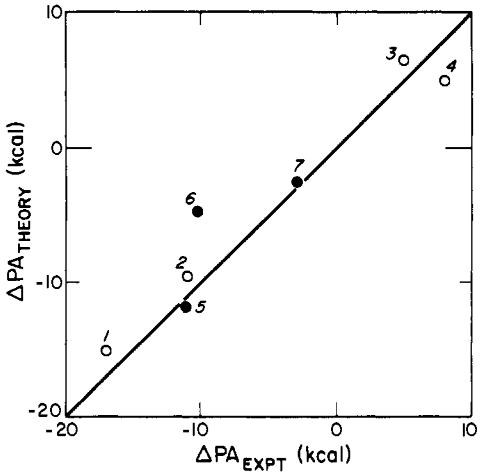


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Figure 2. Relative proton affinities for para derivatives of pyridine (basicities) relative to pyridine (open circles), and of benzoic acid (acidities) relative to benzoic acid itself (filled circles). Points 1-4 are, respectively, p-NO_2, -CF_3, -CH_3, and -CH_3O pyridine derivatives. Points 5-7 are, respectively, p-nitro-, p-cyano-, and p-fluorobenzoic acid.

fluorine is *not* enhanced by deprotonation. This difference is likely to be a consequence of the larger size of the chlorine atom (its more diffuse p orbitals), which allows chlorine to delocalize excess electronic charge more effectively than fluorine. Essentially the same explanation has been given by Kebarle and co-workers.[13,14] Similar relationships between ΔV and ΔR are obtained when the CNDO RPM model[12] is applied to carbon 1s binding energy shifts (essentially the addition of a positive charge to the carbon nucleus) in the halogenated methanes. The observed carbon 1s binding energy shifts, ΔE_B, are 2.8 eV for CH_3F and 1.6 eV for CH_3Cl relative to CH_4;[23] the RPM model,

$$\Delta E_B = -\Delta V - \Delta R \qquad (11)$$

gives 2.74 eV for CH_3F and 1.35 eV for CH_3Cl. ΔV(F-H) and ΔV(Cl-H) at the carbon nucleus are −2.7 and −2.2 eV for CH_3F and CH_3Cl relative to CH_4. ΔR(F-H) is −0.04 eV and ΔR(Cl-H) is 0.85 eV.[24] Again ΔV is considerably larger than ΔR; it determines the direction of the shifts, but ΔR is important in determining the difference between the substituent's fluorine and chlorine.

The halogenated germanes provide a third example of the $\Delta V - \Delta R$ relationships between chlorine and fluorine. Specifically, we will analyze the observed Ge 3d binding energies and Ge_{LMM} Auger energies in GeF_4 and $GeCl_4$ relative to GeH_4, using the relations[25]

$$\Delta E_{LMM} \simeq -\Delta E_B + 2\Delta R \qquad (12)$$

$$\Delta E_B = -\Delta V - \Delta R \qquad (13)$$

ΔE_B(Cl-H) is 2.70 eV, ΔE_B(F-H) is 4.65 eV; ΔE_{LMM}(Cl-H) is −0.5 eV, and ΔE_{LMM}(F-H) is −0.5 eV.[25] In a straightforward manner we find ΔV(Cl-H) to be about −3.8 eV or −0.95 eV/ligand; ΔV(F-H) is −4.35 eV or −1.1 eV/ligand. As previously observed,[25] the relaxation energies are different; ΔR(Cl-H) is 0.28 eV/ligand, ΔR(F-H) is −0.08 eV/ligand. Here, ΔV(Cl-H) is again close to ΔV(F-H) and ΔR(Cl-H) is 30% of ΔV, while ΔR(F-H) is much smaller. These are empirical results. The CNDO/2 PPM order of substituent polarization energies for acetic acids ($Cl \gtrsim CH_3 > H \gtrsim F$) is the same as the empirical order of ref 25 for germanes. It should be noted that the above analyses use electrostatic potential energies, which differ by a minus sign from proton potential energies. Also, our ΔR differs from the ΔR of ref 25 by a factor of ½.

A very different situation is obtained for aliphatic alcohols, acids, and amines in which there are no halogen substituents. With one exception (the $HCOOH$-CH_3COOH acidity shift), the ΔR term is dominant. The reason for this is clear. The aliphatic ligands are not polar, and variations in the inductive power from one such ligand to another are small; hence the small ΔV values. The ability of an alkyl group to screen the proton charge depends largely on its size; through delocalization, the larger groups remove the excess positive (or negative) charge farther away from the site of protonation (or deprotonation).

In most of the aliphatic alcohols and acids ΔV and ΔR have the same sign. Hence, the range of basicities exceeds the acidity range for these compounds ($\Delta PA = -\Delta V - \Delta R$ for basicity, $\Delta PA = -\Delta V + \Delta R$ for acidity).

Turning to the lightest alcohols and acids, we note that HCO_2H is *more* acidic than CH_3CO_2H, while H_2O is *less* acidic than CH_3OH.[26] The reason for this difference is clear if the ΔV and ΔR terms are considered separately. There is a large increase in R between OH^-, in which there are few nuclear centers available for delocalization of charge, and CH_3O^-, in which there are many. No such difference in R is present in the acids, but the V values differ greatly because of the more negative carbonyl oxygen in CH_3CO_2H. Since $\Delta PA = -\Delta V + \Delta R$ in these comparisons, the sign of ΔPA is reversed from alcohols to acids.

Among the carbon acids the agreement with experiment is variable. If comparisons are restricted to either substituted or unsubstituted hydrocarbons, the relative PA values are predicted quite well. There is a discrepancy of about 20 kcal between the two sets of molecules, however. With only five points available at present, a definitive interpretation is not possible.

The calculation predicts acidities of halogenated phenols poorly. Comparing the calculated acidity shifts of the three monofluorophenols relative to phenol with experiment,[20] the standard deviation is 1.7 kcal in a quantity with an average value of 3.2 kcal. For the monochlorophenols these quantities are 4.5 and 4.53 kcal, respectively. We do not know the exact origin of this poor fit.

The relative basicities of para-substituted pyridines and the related acidities of para-substituted benzoic acids are predicted quite well, except for p-cyanobenzoic acid (Figure 2). While relaxation effects are most important in the basicity shifts by

Table II. Inductive and Polarization Effects in Aliphatic Alcohols from an Empirical Model and CNDO/2 Estimates (kcal/mol)

	CNDO/2				Empirical (eq 14–16)		
	$\Delta V(0)$	$\Delta V(1)$	ΔR_{anion}	$\Delta R_{\text{neutral}}$	$\Delta V(0)$	$\Delta V(1)$	ΔR
CH_3OH	0.	0.	0.	0.	0.	0.	0.
CH_3CH_2OH	−1.5	−2.7	−4.9	−5.8	−1.6	−3.2	−5.4
$(CH_3)_2CHOH$	−2.5	−5.7	−8.8	−10.3	−3.3	−6.6	−9.7

the OCH_3 and CH_3 groups, inductive effects are dominant in acidity (and basicity) shifts by the $-NO_2$ and $-CF_3$ groups. For para substitution of NO_2 or CF_3 in pyridines, the through-space components of the inductive effects are insignificant: the inductive effect arises mainly via removal of charge from the nitrogen atom. This behavior contrasts with that of the fluoroacetic acids, for which 50–60% of the inductive effect arises from the through-space component.

V. Empirical Model of Acidities and Basicities

By conceptually separating the ΔPA values into ΔV and ΔR terms, it is possible in certain cases to make empirical estimates of the inductive (ΔV) and polarization (ΔR) effects. Consider the aliphatic alcohols, for example. An alcohol has two proton sites: the acid proton site and the basic proton site, from which a proton is lost in the reaction

$$ROH \rightarrow RO^- + H^+$$

or gained in the reaction

$$ROH + H^+ \rightarrow ROH_2^+$$

respectively. If the R group is altered, the OH group may gain or lose electronic charge by inductive effects. The change in charge on the oxygen atom will shift V equally at the two proton sites by

$$\Delta V_{\text{OX}} \simeq (e^2/r_{\text{OH}})\Delta q_{\text{OX}}$$
$$\simeq 13\Delta q_{\text{OX}}\ \text{eV}$$

The shift at the acid proton site will be enhanced by a change in the electron population on that hydrogen, an effect that is much smaller at the host proton site. Considering the local geometry and the $\langle r^{-1}\rangle$ value for the hydrogen 1s function, it can be shown that, in the point-charge potential model,

$$\Delta V(\text{acid proton}, \Delta q_{\text{H}}) = 32\Delta q_{\text{H}}$$
$$\Delta V(\text{base proton}, \Delta q_{\text{H}}) = 8\Delta q_{\text{H}}$$

The two components of ΔV add to give

$$\Delta V(\text{acid proton}) = 32\Delta q_{\text{H}} + 13\Delta q_{\text{O}}$$
$$\Delta V(\text{base proton}) = 8\Delta q_{\text{H}} + 13\Delta q_{\text{O}}$$

For the range of Δq's $\frac{1}{2} \leq \Delta q_{\text{O}}/\Delta q_{\text{H}} \leq 2$, it is apparent that to a good approximation $\Delta V(\text{acid proton}) \simeq 2\Delta V(\text{base proton})$ or $\Delta V_{\text{A}}(1) \simeq 2\Delta V_{\text{N}}(0)$. From CNDO/2 calculations, Δq_{H} is usually slightly larger than Δq_{O}. We have discussed only local contributions to ΔV. For molecules with polar substituents the nonlocal contributions to ΔV will lower the above coefficient of 2 toward unity.

In contrast, the ΔR_{a} and ΔR_{b} terms will be similar. This is apparently a consequence of the ability of a given substituent group to delocalize an excess or a shortage of electronic charge with about equal facility. At any rate, it is found to be approximately true in the detailed PPM calculations.

Combining the changes in PA values for both acid and base protons of a given alcohol as the R group is varied,

$$\Delta PA_{\text{a}} = -\Delta V_{\text{A}}(1) + \Delta R_{\text{a}}$$
$$\Delta PA_{\text{b}} = -\Delta V_{\text{N}}(0) - \Delta R_{\text{b}}$$

with the above approximations ($\Delta R_{\text{a}} \simeq \Delta R_{\text{b}}$, $\Delta V_{\text{A}}(1) \simeq 2\Delta V_{\text{N}}(0)$), we find

$$\Delta V_{\text{N}}(0) = -\tfrac{1}{3}(\Delta PA_{\text{a}} + \Delta PA_{\text{b}}) \qquad (14)$$

$$\Delta V_{\text{A}}(1) = -\tfrac{2}{3}(\Delta PA_{\text{a}} + \Delta PA_{\text{b}}) \qquad (15)$$

$$\Delta R_{\text{a}} = \Delta R_{\text{b}} = \tfrac{1}{3}\Delta PA_{\text{a}} - \tfrac{2}{3}\Delta PA_{\text{b}} \qquad (16)$$

Table II presents, along with CNDO/2 estimates, empirical potential energies ΔV and ΔR for nonpolar alcohols. The experimental data were taken from ref 15, 17, and 18. Very good agreement is obtained between the CNDO/2 values and the empirical estimates. As expected, the larger substituents have larger polarization energies.

It is expected that this model will extract accurate measures of relative inductive and polarization strengths of nonpolar substituents in alcohols, amines, etc., and qualitative information for very polar substituents, e.g., halogens, in these compounds.

VI. Conclusions

This work has used the proton potential model to calculate proton-transfer energies ΔPA for reactions involving similar molecules. The CNDO/2 formalism was used to provide a molecular-orbital framework. In cases for which the CNDO/2 model is itself successful, e.g., the halogen derivatives of acetic acid, agreement of calculated ΔPA values with experiment was excellent. Separation of ΔPA into inductive and polarization potential terms, an automatic feature of this model, provided unique insight into these two effects.

For other classes of compounds the agreement of ΔPA values with experiment is variable. In general the agreement is quite good if the compounds being compared are similar, but some unsaturated compounds show fairly large discrepancies, perhaps because of deficiencies in the CNDO/2 model.

Finally, a simple method for obtaining empirical polarization energies and inductive potentials is presented and applied to the existing experimental data for aliphatic alcohols.

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References and Notes

(1) A. C. Hopkinson, N. K. Holbrook, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **49**, 3596 (1968).
(2) L. Radom, *J. Chem. Soc., Chem. Commun.*, 403 (1974).
(3) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).
(4) W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970).
(5) M. Graffeuil, J.-F. Labarre, and C. Leibovici, *J. Mol. Struct.*, **22**, 97 (1974).
(6) M. Graffeuil, J.-F. Labarre, and C. Leibovici, *J. Mol. Struct.*, **23**, 65 (1974).
(7) D. W. Davis and J. W. Rabalais, *J. Am. Chem. Soc.*, **96**, 5305 (1974).
(8) L. Hedin and A. Johansson, *J. Phys. B*, **2**, 1336 (1969).
(9) D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972).
(10) (a) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, **96**, 5299 (1974); (b) A. Pullman and P. Brochen, *Chem. Phys. Lett.*, **34**, 7 (1975).
(11) W. B. Perry, T. F. Schaaf, and W. L. Jolly, *J. Am. Chem. Soc.*, **97**, 4899 (1975).

(12) D. W. Davis and D. A. Shirley, *J. Electron Spectrosc.*, **3**, 137 (1974).
(13) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 4050 (1973).
(14) K. Hiraoka, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 6833 (1973).
(15) R. T. McIver, J. A. Scott, and J. H. Silvers, 21st Annual Conference on Mass Spectroscopy and Allied Topics, San Francisco, Calif., May, 1973, Abstract A2 (see ref 2 above).
(16) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4728 (1972).
(17) J. Long and B. Munson, *J. Am. Chem. Soc.*, **94**, 3339 (1972).
(18) J. I. Beachamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(19) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 5940 (1974).
(20) R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, **95**, 8402 (1973).
(21) R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 4035 (1974).
(22) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 1369 (1972).
(23) T. D. Thomas, *J. Am. Chem. Soc.*, **92**, 4184 (1970).
(24) D. W. Davis and D. A. Shirley, unpublished.
(25) W. B. Perry and W. L. Jolly, *Chem. Phys. Lett.*, **23**, 529 (1973).
(26) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 4315 (1971).
(27) Recent ab initio calculations (ref 10b and K. Morokuma and H. Umeyama, *J. Am. Chem. Soc.*, **98**, 4400 (1976)) of methylamine PA values show that ΔPA values arise from CH_3-group polarization, not charge transfer, in agreement with earlier interpretations based on PA–inner shell binding energy correlations and CNDO potential models.[7,10a]

Theoretical Calculation of Steric Effects in Ester Hydrolysis

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Abstract: Steric effects in aliphatic reaction series may be represented quantitatively by E_s values derived empirically by Taft some 20 years ago. $E_s = -\log k_{rel} = -\log k/k_0$ where k is the rate constant for acid-catalyzed hydrolysis of an aliphatic ester RCOOEt and k_0 is the corresponding rate constant for CH_3COOEt. We find that $\log k_{rel} = 0.340 - 0.789\Delta SE$ where ΔSE = steric energy of $RC(OH)_3$ − steric energy of RCOOH. Steric energies were calculated by molecular mechanics using minor modifications of the Schleyer 1973 hydrocarbon force field; ΔSE values closely parallel $\Delta\Delta H_f°$ values, the differences in the corresponding enthalpies of formation. The standard deviation of E_s is 0.24 and the correlation coefficient is −0.98 for 25 esters spanning a range of 4000 in relative rates. Rates have also been calculated for a further group of 20 esters for which only qualitative information is available, and these extend the range of predicted relative rates to about 800 000. While the Taft E_s values have been generally accepted as a measure of steric effects, there has always been a concern that this empirical dissection of steric and polar effects might not be clean. The success of the present theoretical calculations lends strong support to the hypothesis that E_s values do in fact measure steric effects for alkyl groups.

The classical quantitative evaluation of steric effects is based on Taft's treatment of acid-catalyzed hydrolysis of esters.[1,2] It had been pointed out earlier by Ingold that while base-catalyzed hydrolysis is subject to strong acceleration by such electron-attracting groups as chlorine atoms, acid-catalyzed hydrolysis is relatively immune to polar effects.[3] Taft's empirical postulate is that under appropriate restrictions of structural types, $E_s = -\log k_{rel} = -\log k/k_0$ represents a quantitative estimate of steric effects. In this expression k is the rate constant for acid-catalyzed hydrolysis of any ester, RCOOEt, and k_0 the rate constant for the standard, ethyl acetate, under similar conditions. Fortunately E_s values are not very sensitive to reaction conditions. Furthermore, the same E_s values generally correlate esterification rates as well; this implies that K_{eq} is roughly constant in the series. Such is not true for all esters.[4] Taft derived further relationships of the Hammett type to treat polar effects, and the Taft steric–polar relationships have proved to be especially useful in correlating rates of reactions of aliphatic compounds.[1,5] Numerous attempts have been made to relate the Taft E_s values to sizes of groups.[1,5a] These are certainly useful for making rough approximations, and they have the important advantage of simplicity of application. However the ester systems have proved too complex for successful application of a simple analysis.

Recently we have achieved a reasonable degree of success in calculating the magnitude of the steric effects by using hydrocarbon models.[6a] We used an isoalkane $RCH(CH_3)_2$ as surrogate for ester RCOOEt and neoalkane for the tetrahedral intermediate. In fact $\log k_{rel}$ is a quite good linear function of $\Delta\Delta H_f°$. The postulate is that $\Delta\Delta H_f°$, the differences in enthalpies of formation of neoalkanes and isoalkanes in the gas phase at 298 K, will serve as a measure of the energy of steric compression on going from ester to tetrahedral intermediate.

A brief comment is in order about the relationships between steric effects and enthalpy and entropy terms. The concept of a steric correction in collision theory may be approximated by a "cone of approach" treatment, a recent example being Wipke's proposal about carbonyl additions.[7] This is at least in part an entropy factor, and accords closely with the early ideas that polar effects are to be explained by enthalpy of activation and steric effects by entropy of activation. However it has, of course, been clear for some time that steric factors can also affect enthalpy; one of the commonly used measures of strain energy is the departure of an enthalpy of formation from some norm.

The success of hydrocarbon models in treating steric effects in ester hydrolysis shows that this reaction responds primarily to an enthalpy factor. A possible explanation is that steric factors determine the relative concentrations of the tetrahedral intermediates; the overall reaction rates, of course, depend directly on these concentrations. Other reactions may show a greater dependence on cone of approach. For example, SN2 closure to five-membered rings is usually faster than to six-membered rings, but the enthalpic strain energies lie strongly in favor of the six-membered rings.

In the ester hydrolysis there is clearly a favorable cancellation of entropy effects, and also of solvation effects which may comprise both enthalpy and entropy. Evidently conditions at the ester group and at the tetrahedral intermediate are relatively constant from one ester to another, or else the effects are proportional to the steric effects.

Alkane models have one major advantage: the alkane force fields have been relatively well established.[8] They have the