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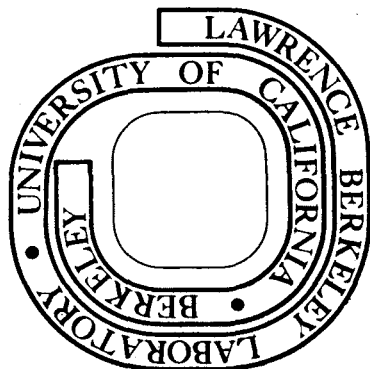
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RELATIVE GAS-PHASE ACIDITIES AND BASICITIES FROM  
A PROTON POTENTIAL MODEL\*

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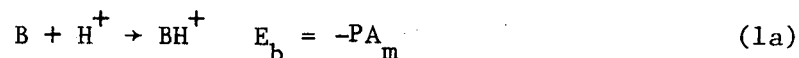
ABSTRACT: A proton-potential model (PPM) calculation of gas-phase proton affinities was used to calculate relative PA values for various molecules and anions. The model, which uses CNDO/2 wave functions, provides separate values of inductive and polarization energies accompanying the gain or loss of 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.

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## 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.<sup>1</sup> These proton affinities PA are the energy  $E_b$  of the reaction



or (minus) the energy  $E_a$  of the reaction



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.



for comparing two bases, or



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.<sup>2</sup>

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.<sup>3-6</sup> 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<sup>7</sup>. 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" 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. Conclusions are briefly summarized in Section V.

## II. Theory

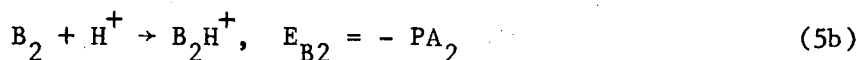
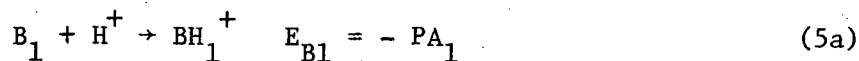
In using the PPM approach to calculate the proton affinity of a reaction  $M + H^+ \rightarrow MH^+$ , the electrostatic potential at the proton site is evaluated from CNDO/2 wave-functions calculated both with and without the proton present. Alternatively we can describe these potentials as the values 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<sup>7-9</sup> that the proton affinity of the above reaction is given to good approximation by

$$PA_N = -\frac{1}{2} [V_N(0) + V_N(1)] = -E_b \quad (3)$$

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

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

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,



to give



we would have

$$\begin{aligned} \Delta E_b(B2-B1) &= E_{B2} - E_{B1} = PA_1 - PA_2 \\ &= \Delta V_N(0) + \Delta R_b, \end{aligned} \quad (7)$$

where

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

and

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

When  $\Delta V$  or  $\Delta R$  is negative, proton transfer reaction (b) tends to proceed to the right, and vice-versa. The  $\Delta V_N(0)$  term represents an inductive effect in the usual chemical nomenclature. The  $\Delta R_b$  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.<sup>10</sup>

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

$$PA_a = -\frac{1}{2}[V_A(0) + V_A(1)] = E_a \quad (9)$$

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

$$\begin{aligned} \Delta E_a &= -\Delta V_A(1) + \frac{1}{2} \Delta[V_A(1) - V_A(0)] \\ &= -\Delta V_A(1) + \Delta R_a \end{aligned} \quad (10)$$



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  $\Delta R_b$  and  $\Delta R_a$  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 Eqs. (1a) and (1b), respectively. For a given pair of molecules  $\Delta R_b$  and  $\Delta R_a$  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  $\Delta R_a$  and  $\Delta R_b$ , from PPM calculations. This is done for alcohols in Section IV.

The details of the proton affinity calculations have been described earlier.<sup>7</sup> 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  $\sim 10 - 20\%$  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<sup>9</sup> to third-row elements. The parameters suggested by Jolly and Perry<sup>11</sup> were used.

### III. Results

Table I lists values of  $\Delta V$  and  $\Delta R$  and derived values of  $\Delta PA$ , calculated by the PPM method, for several groups of similar molecules for which experimental PA values are available. Shifts in PAs among similar molecules (i.e., proton transfer energies) are quoted, rather than absolute PAs. 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.<sup>12</sup> 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<sup>13</sup> and by Hiraoka, et al.<sup>14</sup> McIver, et al. gave proton affinities for anions of aliphatic alcohols, while PA values for aliphatic amines were quoted by Aue, et al.<sup>16</sup> Aliphatic acid and alcohol proton affinities were obtained from Long and Munson<sup>17</sup> and from Beachamp.<sup>18</sup> McMahon and Kebarle gave carbon acid PAs<sup>19</sup>, and McIver and Silvers did the halogenated phenols.<sup>20</sup> Acidities of para-substituted benzoic acids were measured by Yamdagni, et al.<sup>21</sup> and basicities of para-substituted pyridines by Taagepera, et al.<sup>22</sup>

#### 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<sup>5</sup> 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. 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 (Fig. 1). A straight line fits the points to within one Kcal or less, while the standard deviation between theory and experiment is 0.9 Kcal.

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  $\Delta R$  term is typically 20% or less of the  $\Delta V$  term. Within this context the chlorine and fluorine derivatives differ in a significant way. The  $\Delta V$  and  $\Delta R$  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  $\Delta R$  term is negligible, implying that the intrinsically equivalent inductive power of fluorine is not enhanced by deprotonation. This difference is very likely 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. Similar relationships between  $\Delta V$  and  $\Delta R$  are obtained when the CNDO RPM model<sup>12</sup> 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,  $\Delta E_B$ , are 2.8 eV for  $\text{CH}_3\text{F}$  and 1.6 eV for  $\text{CH}_3\text{Cl}$  relative to  $\text{CH}_4$ <sup>23</sup>, the RPM model,

$$\Delta E_B = -\Delta V - \Delta R, \quad (11)$$

- 9 -

gives eV for  $\text{CH}_3\text{F}$  and eV for  $\text{CH}_3\text{Cl}$ .  $\Delta V(\text{F-H})$  and  $\Delta V(\text{Cl-H})$  at the carbon nucleus are -2.7 eV and -2.2 eV for  $\text{CH}_3\text{F}$  and  $\text{CH}_3\text{Cl}$  relative to  $\text{CH}_4$ .  $\Delta R(\text{F-H})$  is -.04 eV and  $\Delta R(\text{Cl-H})$  is .85 eV.<sup>24</sup> Again  $\Delta V$  is considerably larger than  $\Delta R$ ; it determines the direction of the shifts, but  $\Delta R$  is important in determining the difference between 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  $\text{LMM}$  Auger energies in  $\text{GeF}_4$  and  $\text{GeCl}_4$  relative to  $\text{GeH}_4$ , using the relations<sup>25</sup>

$$\Delta E_{\text{LMM}} \approx -\Delta E_{\text{B}} + 2\Delta R \quad (12)$$

$$\Delta E_{\text{B}} = -\Delta V - \Delta R. \quad (13)$$

$\Delta E_{\text{B}}(\text{Cl-H})$  is 2.70 eV,  $\Delta E_{\text{B}}(\text{F-H})$  is 4.65 eV;  $\Delta E_{\text{LMM}}(\text{Cl-H})$  is -.5 eV and  $\Delta E_{\text{LMM}}(\text{F-H})$  is -0.5 eV.<sup>25</sup> In a straight forward manner we find  $\Delta V(\text{Cl-H})$  to be about -3.8 eV or -.95 eV/ligand;  $\Delta V(\text{F-H})$  is -4.35 eV or -1.1 eV/ligand. As previously observed,<sup>25</sup> the relaxation energies are different;  $\Delta R(\text{Cl-H})$  is .28 eV/ligand,  $\Delta R(\text{F-H})$  is -.08 eV/ligand. Here,  $\Delta V(\text{Cl-H})$  is again close to  $\Delta V(\text{F-H})$  and  $\Delta R(\text{Cl-H})$  is 30% of  $\Delta V$ , while  $\Delta R(\text{F-H})$  is much smaller. These are empirical results. It should be noted that the above analyses use electrostatic potential energies, which differ by a minus sign from proton potential energies. Also, our  $\Delta R$  differs from the  $\Delta R$  of reference 25 by a factor of 1/2.

A very different situation is obtained for aliphatic alcohols, acids, and amines in which there are no halogen substituents. With one exception (the  $\text{HCOOH-CH}_3\text{COOH}$  acidity shift), the  $\Delta R$  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 is small: hence the small  $\Delta V$  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  $\Delta V$  and  $\Delta R$  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  $\text{HCO}_2\text{H}$  is more acidic than  $\text{CH}_3\text{CO}_2\text{H}$ , while  $\text{H}_2\text{O}$  is less acidic than  $\text{CH}_3\text{OH}$ .<sup>26</sup> The reason for this difference is clear if the  $\Delta V$  and  $\Delta R$  terms are considered separately. There is a large increase in  $R$  between  $\text{OH}^-$  in which there are few electrons available for screening and  $\text{CH}_3\text{O}^-$ , 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  $\text{CH}_3\text{CO}_2\text{H}$ . Since  $\Delta PA = -\Delta V + \Delta R$  in these comparisons, the sign of  $\Delta PA$  is reversed from alcohols to acids.

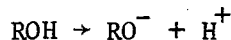
Among the carbon acids the agreement with experiment is variable. If comparisons are restricted to either substituted or unsubstituted hydrocarbons, the relative PA values are predicted quite well. There is a discrepancy of about 20 Kcal between the two sets of molecules, however. With only five points 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

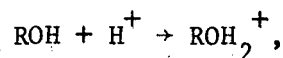
to phenol with experiment,<sup>20</sup> the standard direction is 1.7 Kcal in a quantity with an average value of 3.2 Kcal. For the monochlorophenols these quantities are 4.5 Kcal and 4.53, respectively. Thus the correlation of theory and experiment is quite poor.

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 (Fig. 2). While relaxation effects are most important in the basicity shifts by the  $\text{OCH}_3$  and  $\text{CH}_3$  groups, inductive effects are dominant in acidity shifts by the  $-\text{NO}_2$  and  $-\text{CF}_3$  groups. For para-substitution of  $\text{NO}_2$  or  $\text{CF}_3$  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.

By conceptually separating the  $\Delta\text{PA}$  values into  $\Delta\text{V}$  and  $\Delta\text{R}$  terms, it is possible in certain cases to make empirical estimates of the inductive ( $\Delta\text{V}$ ) and polarization ( $\Delta\text{R}$ ) 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.



or gained in the reaction



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

$$\Delta V_{OX} \approx (e^2/r_{OH}) \Delta q_{OX}$$

$$\approx 13 \Delta q_{OX} \text{ eV.}$$

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,

$$\Delta V(\text{acid proton}, \Delta q_H) = 32 \Delta q_H$$

$$\Delta V(\text{base proton}, \Delta q_H) = 8 \Delta q_H$$

The two components of  $\Delta V$  add to give

$$\Delta V(\text{acid proton}) = 32 \Delta q_H + 13 \Delta q_O$$

$$\Delta V(\text{base proton}) = 8 \Delta q_H + 13 \Delta q_O$$

From CNDO/2 calculations,  $\Delta q_H$  is usually slightly larger than  $\Delta q_O$ . Thus to a good approximation

$$\Delta V(\text{acid proton}) \approx 2 \Delta V(\text{base proton})$$

or

$$\Delta V_A(1) \approx 2 \Delta V_N(0).$$

We have discussed only local contributions to  $\Delta V$ . For molecules with polar substituents the non-local contributions to  $\Delta V$  will lower the above coefficient of 2 toward unity.

The  $\Delta R_a$  and  $\Delta R_b$  terms will be similar. This is a consequence of the approximately linear variation in polarization potential with charge. It is also found approximately to be 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,

$$\Delta PA_a = -\Delta V_A(1) + \Delta R_a$$

$$\Delta PA_b = -\Delta V_N(0) - \Delta R_b$$

with the above approximations ( $\Delta R_a \approx \Delta R_b$ ,  $\Delta V_A(1) \approx 2 \Delta V_N(0)$ ), we find

$$\Delta V_N(0) = -\frac{1}{3} (\Delta PA_a + \Delta PA_b) \quad (14)$$

$$\Delta V_A(1) = -\frac{2}{3} (\Delta PA_a + \Delta PA_b) \quad (15)$$

$$\Delta R_a = \Delta R_b = \frac{1}{3} \Delta PA_a - \frac{2}{3} \Delta PA_b \quad (16)$$

Table II presents, along with CNDO/2 estimates, empirical potential energies  $\Delta V$  and  $\Delta R$  for non-polar alcohols. The experimental data was taken from references 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. They appear to donate more electronic density to the vicinity of the site of protonation.

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



## V. Conclusions

This work has used the proton potential model to proton transfer energies  $\Delta PA$  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  $\Delta PA$  values with experiment was excellent. Separation of  $\Delta PA$  into inductive and polarization terms, an automatic feature of this model, provided unique insight into these two effects.

For other classes of compounds the agreement of  $\Delta PA$  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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Table I. Relative Proton Affinities (kCal/mole)

Species	$\Delta V(\text{theo})$	$\Delta R(\text{theo})$	$\Delta PA(\text{theo})$	$\Delta PA(\text{expt})$	Ref.
<u>Acid anions</u>					
$\text{CH}_3\text{CO}_2^-$	(0)	(0)	(0)	(0)	
$\text{CH}_2\text{FCO}_2^-$	9.5	0.2	-9.3	-10.8	14
$\text{CH}_2\text{ClCO}_2^-$	9.8	-2.3	-12.1	-12.8	13
$\text{CHF}_2\text{CO}_2^-$	17.0	0.4	-16.6	-18.0	14
$\text{CHCl}_2\text{CO}_2^-$	16.4	-3.4	-19.8	-19.8	13
$\text{CF}_3\text{CO}_2^-$	26.6	1.4	-25.2	-25.2	14
$\text{HCO}_2^-$	11.2	5.9	-5.2	-3.2	13
$\text{CH}_3\text{CH}_2\text{CO}_2^-$	-0.2	-1.8	-1.6	-1.2	13
<u>Aliphatic alcohol anions</u>					
$\text{OH}^-$	-	-	27.1	-	a
$\text{CH}_3\text{O}^-$	(0)	(0)	(0)	(0)	15
$\text{C}_2\text{H}_5\text{O}^-$	-2.7	-4.9	-2.2	-1.9	15
$i\text{-C}_3\text{H}_7\text{O}^-$	-5.7	-8.8	-3.1	-3.1	15
<u>Aliphatic amines</u>					
$\text{NH}_3$	(0)	(0)	(0)	(0)	
$\text{CH}_3\text{NH}_2$	1.6	-15.9	14.3	11.4	16
$\text{C}_2\text{H}_5\text{NH}_2$	1.2	-20.8	19.6	14.1	16
<u>Aliphatic acids</u>					
$\text{CH}_3\text{CO}_2\text{H}$	(0)	(0)	(0)	(0)	
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	-1.0	2.6	3.6	2	17

Table I cont'd.

Aliphatic alcohols

$\text{CH}_3\text{OH}$	(0)	(0)	(0)	(0)	
$i\text{-C}_3\text{H}_7\text{OH}$	-2.5	-10.3	12.8	13	18

---

Carbon acid anions

$\text{CH}_3^-$	(0)	(0)	(0)	(0)	
$\text{C}_6\text{H}_5\text{CH}_2^-$	5.5	-30.1	-35.6	-33.1	19

---

Substituted carbon acid anions

$\text{CH}_2\text{CN}^-$	(0)	(0)	(0)	(0)	
$\text{CH}(\text{CN})_2^-$	20.0	-7.6	-27.6	-30.4	19
$\text{CH}_3\text{COCH}_2^-$	-19.5	-12.7	-6.8	-3.0	19

---

Halogenated phenols anions

phenoxy anion	(0)	(0)	(0)	(0)	
a-fluorophenoxy	1.9	1.5	-0.4	-2.8	20
a-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

---

Table I cont'd.

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  $PA(OH^-) > PA(CH_3O^-)$ .

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

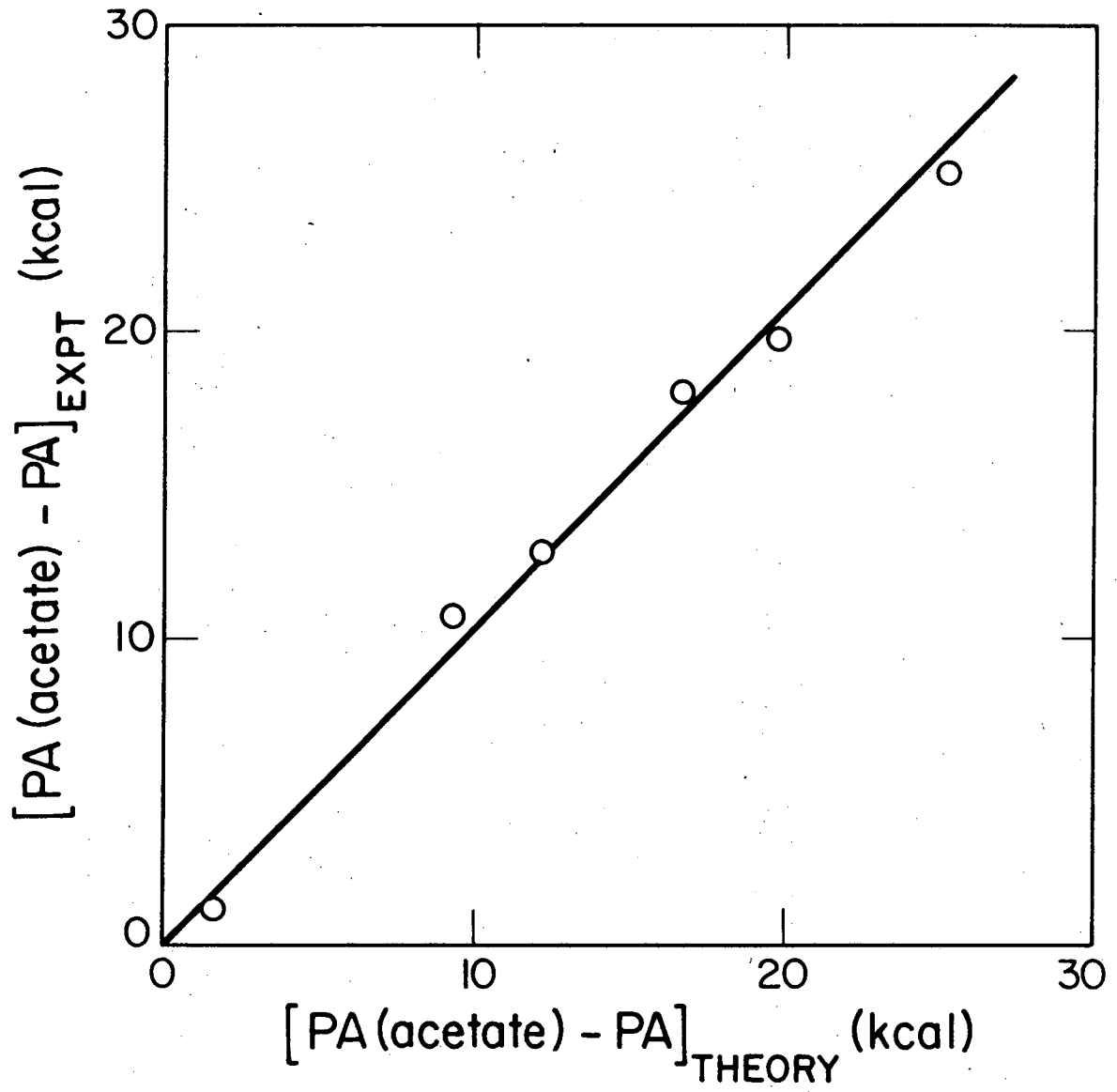
	CNDO/2				Empirical (Eqs. 14 - 16)		
	$\Delta V(0)$	$\Delta V(1)$	$\Delta R_{\text{ANION}}$	$\Delta R_{\text{NEUTRAL}}$	$\Delta V(0)$	$\Delta V(1)$	$\Delta R$
$\text{CH}_3\text{OH}$	0.	0.	0.	0.	0.	0.	0.
$\text{CH}_3\text{CH}_2\text{OH}$	-1.5	-2.7	-4.9	-5.8	-1.6	-3.2	-5.4
$(\text{CH}_3)_2\text{CHOH}$	-2.5	-5.7	-8.8	-10.3	-3.3	-6.6	-9.7

Figure Captions

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

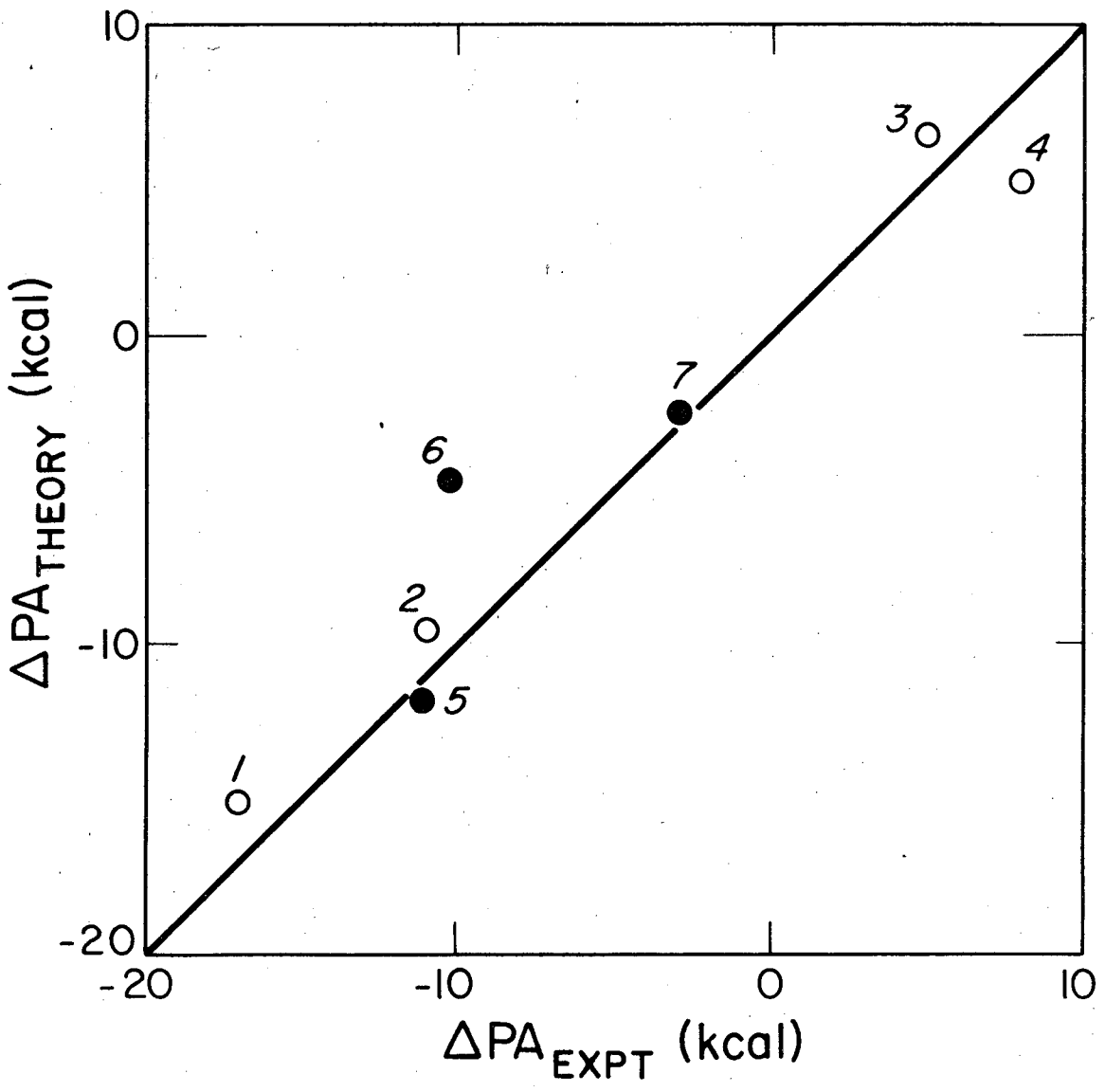
Fig. 2. Relative proton affinities for para derivatives of pyridine (basicities) relative to pyridine (open arches), and of benzoic acid (acidities) relative to benzoic acid itself (filled circles). Points 1 - 4 are respectively p - NO<sub>2</sub>, CF<sub>3</sub>, CH<sub>3</sub>, and CH<sub>3</sub>O<sup>-</sup> pyridine. Points 5 - 7 are respectively p - nitro, cyano-, and fluoro-benzoic acid.





XBL 76I-2019

Fig. 1



XBL 76I-2020

Fig. 2

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