Proton Affinity, Ionization Energy, and the Nature of Frontier Orbital Electron Density

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Abstract: A study of the correlation between proton affinity and lowest ionization energy reveals that molecular bases fit into three broad categories: two-electron lone-pair bases, π or σ bond-pair bases, and one-electron bases with relatively high electronic rearrangement energies. A fourth group of bases that cannot be categorized consists of one-electron bases with relatively low electronic rearrangement energies.

The measurement of gas-phase ionization energies and proton affinities has increased greatly in the past 10 years. This is due to the advent of photoelectron spectroscopy,[1] ion cyclotron resonance,[2] and chemical ionization mass spectrometry.[2] The orbital concept in molecular spectroscopy has been considerably strengthened by relating ionization energies to orbital energies by the use of Koopmans' theorem.[3] At the same time, a large amount of work has gone into the calculation of proton affinities by LCAO-MO techniques.[4]

Linear correlations exist between *core* ionization energies and proton affinity as long as the core ionization refers to the atom undergoing protonation in the molecule.[5] It is found that as the core ionization energy increases the proton affinity decreases. There have been attempts to use core ionization energies to predict the site of protonation in molecules.[6] This approach is particularly straightforward for a simple molecule such as CO where the proton affinity for the carbon end of the molecule differs from that of the oxygen end by about 20 kcal/mol.[7] If the proton affinity at two sites differs by only a few kilocalories per mole, this method is less useful.[6b,8]

In a recent review, Kebarle[2b] has classified the proton affinities of molecules into three experimental categories. These are (a) proton affinities of compounds between H_2 (101 kcal/mol) and H_2O (170 kcal/mol), (b) proton affinities of compounds between H_2O and NH_3 (202 kcal/mol), and (c) proton affinities higher than that of NH_3.

It is the purpose of this communication to illustrate that, by correlating *lowest* ionization energy (IE) with proton affinity (PA) for a wide variety of molecules, information can be obtained not only about electron binding energies but also about electron density. Whereas the photon probes the electron binding energy of a molecule B, the proton probes its ability to share electron density in the formation of a $(B-H)^+$ bond. In both cases, the molecule is subjected to its ability to accommodate a positive charge, albeit generated in distinctly different ways. Both processes are a property of the entire molecule and they are adiabatic; that is, electronic and geometrical rearrangements occur during the course of the process. We wish to show that, although PA and IE are both complex properties, an empirical correlation of PA(B) vs. IE(B) for a very wide range of molecules can be interpreted in terms of a simple one-electron molecular orbital model. Such a correlation is found to yield information about the nature of the highest occupied molecular orbital (HOMO) on the molecule B undergoing proton attack. The molecules fall into three broad categories: two-electron lone-pair bases, π or σ bond-pair bases, and one-electron bases with relatively high electronic rearrangement energies. A fourth group of bases that cannot be categorized consists of one-electron bases with relatively low electronic rearrangement energies.

Plot of Proton Affinity vs. Ionization Energy. For an electron donor B the following thermochemical cycle is valid:

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = PA(B) \tag{1}$$

$$BH^+ \rightarrow B^+ + H \qquad \Delta H = D(B^+\text{-}H) \tag{2}$$

$$PA(B) = IE(H) - IE(B) + D(B^+ - H) \tag{3}$$

where IE(H) = 13.598 eV and IE(B) is the first ionization energy of B. The hydrogen atom bond dissociation energy, $D(B^+\text{-}H)$, can be calculated from eq 3. Whereas PA(B) refers to the heterolytic bond cleavage of BH^+, $D(B^+\text{-}H)$ refers to homolytic bond cleavage.

Equation 3 provides a basis for plotting PA(B) vs. IE(B). For a homologous series of molecules it is well known that there is little variation in $D(B^+\text{-}H)$. For example, all tertiary aliphatic amines are found to have $D(B^+\text{-}H) = 93 \pm 1$ kcal/mol.[9] In this case a plot of PA(B) vs. IE(B) produces a straight line with slope of minus one. For wider ranges of compounds, such as $NH_{3-n}(CH_3)_n$ ($n = 0, 1, 2, 3$) and $OH_{2-n}(CH_3)_n$ ($n = 0, 1, 2$), straight-line plots also have been observed.[5b,d] In these cases, however, $D(B^+\text{-}H)$ is not constant and the slope is approximately -0.4 in each case. The fact that a linear correlation is observed indicates that $D(B^+\text{-}H)$ varies smoothly with IE(B). This empirical linear correlation between $D(B^+\text{-}H)$ and IE(B) can be restated as follows: the electron affinity of B^+ is linearly related to the hydrogen atom affinity of B^+. A similar correlation has been observed by Williams and Streitwieser[10] in studying the intrinsic acidity of CH_4, NH_3, H_2O, and HF.

In Table I we present the data and in Figure 1 we illustrate the plot of PA(B) vs. IE(B) for some 35 bases.[11] We have chosen to restrict the data to bases that involve proton attack on simple molecules that contain either first-row or second-row atoms only. The third-row molecules isoelectronic with argon will be discussed at the end of the paper. Furthermore, we have not included the series of methylated nitrogen and oxygen molecules discussed above. Using dotted lines, we have encircled the regions where a large number of oxygen- and nitrogen-containing bases fall on the graph. Trends within these groups of compounds already have been thoroughly examined.[5d,12] In order to examine the broader trends of interest in this paper, these compounds have not been included in the analysis given below.

The data shown in Figure 1 fall into three broad categories which we have designated **1**, **2**, and **3**. According to the frontier orbital theory of Fukui,[13] the proton will attack the HOMO of B. Molecules falling on or near line **1** have a lone pair that is undergoing proton attack. Molecules in category **2** have a σ orbital or a π orbital as the HOMO, and molecules in category **3** have only one electron (of either σ or π type) in the HOMO. The radicals listed in group **4** in Table I are scattered throughout Figure 1 and these will be discussed later. A least-squares analysis of the data produced the following results and correlation coefficients *r*: category **1** (10 points), PA =

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Table I. Proton Affinities and Ionization Energies

molecule	proton affinity, eV (kcal/mol)	adiabatic ionization energy, eV[a]
	Category **1**	
C_5H_5N (pyridine)	9.458 (218.1)[b]	9.27
NH_3	8.773 (202.3)[b]	10.17
$B_3H_6N_3$ (borazine)	8.59 (198)[c]	9.88
HCN	7.628 (175.9)[d]	13.59
CS	7.55 (174)[e]	11.33[f]
H_2O	7.385 (170.3)[b]	12.62
CO	6.03 (139)[b]	14.01
N_2	4.931 (113.7)[b]	15.58
HF	4.86 (112)[g]	16.01
Ne	2.12 (48.9)[h]	21.56
	Category **2**	
C_3H_6 (propene)	7.76 (179)[i]	9.74
C_3H_6 (cyclopropane)	7.76 (179)[j]	10.06
C_6H_6 (benzene)	7.72 (178)[k]	9.25
C_2H_4 (ethene)	6.94 (160)[i]	10.51
SiH_4 (silane)	6.63 (153)[l]	11.66
C_2H_2 (ethyne)	6.59 (152)[i]	11.41
B_2H_6 (diborane)	6.37 (147)[m]	11.38
C_2H_6 (ethane)	6.07 (140)[b]	11.52
CH_4 (methane)	5.559 (128.2)[b]	12.62
H_2 (dihydrogen)	4.38 (101)[b]	15.43
	Category **3**	
Li	8.33 (192)[n]	5.39
C_2H_5	6.3 (145)[a]	8.4
CH_3	5.46 (126)[a]	9.84
CF_3	4.63 (107)[a]	9.25
H	2.67 (61.6)[o]	13.60
	Group **4**	
C_5H_5 (cyclopentadienyl)	9.10 (210)[a]	8.56
C_6H_5 (phenyl)	8.95 (206)[a]	9.20
C_7H_7 (benzyl)	8.6 (198)[a]	7.27
C_3H_5 (allyl)	7.67 (177)[a]	8.07
C_2H_3 (vinyl)	7.39 (170)[a]	8.95
C_2H (ethynyl)	6.98 (161)[p]	12.4[p]
HCO (formyl)	6.72 (155)[p]	8.2[p]
CN (cyanogen)	4.99 (115)[p]	14.5[p]
NO	4.99 (115)[p]	9.26
O_2	4.382 (101.05)[b]	12.06

[a] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, "Energetics of Gaseous Ions", *J. Phys. Chem. Ref. Data, Suppl. 1*, **6** (1977); proton affinities of some radicals also were calculated from this reference by using thermochemical cycle methods. [b] Reference 2b. [c] L. D. Betowski, J. J. Solomon, and R. F. Porter, *Inorg. Chem.*, **11**, 424 (1972); the quoted value is 203 ± 7 kcal/mol, which we have reduced by 5 kcal/mol in line with the new value of $PA(NH_3)$ = 202.3 kcal/mol. [d] R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 2081 (1976). [e] Reference 16. [f] Reference 17. [g] Reference 18. [h] Reference 22. [i] Reference 2a. [j] S.-L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6347 (1972). [k] S.-L. Chong and J. L. Franklin, *ibid.*, **94**, 6630 (1972). [l] T. M. H. Cheng and F. W. Lampe, *Chem. Phys. Lett.*, **19**, 532 (1973). [m] R. C. Pierce and R. F. Porter, *J. Am. Chem. Soc.*, **95**, 3849 (1973). [n] P. Rosmus and W. Meyer, *J. Chem. Phys.*, **66**, 13 (1977). [o] G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, Princeton, N.J., 1950; to the dissociation energy of H_2^+ we have added 0.02 eV to correct for pressure-volume work of the enthalpy. [p] W. T. Huntress, Jr., *Astrophys. J. Suppl. Ser.*, **33**, 495 (1977).

$-0.597\mathrm{IE} + 14.7$, $r = -0.98$, $\sigma_{\mathrm{PA}} = 0.49$, $\sigma_{\mathrm{slope}} = 0.044$, $\sigma_{\mathrm{int}} = 0.6$; category **2** (10 points), PA = $-0.593\mathrm{IE} + 13.3$, $r = -0.97$, $\sigma_{\mathrm{PA}} = 0.28$, $\sigma_{\mathrm{slope}} = 0.053$, $\sigma_{\mathrm{int}} = 0.6$; category **3** (5 points), PA = $-0.686\mathrm{IE} + 11.9$, $r = -0.97$, $\sigma_{\mathrm{PA}} = 0.58$, $\sigma_{\mathrm{slope}} = 0.097$, $\sigma_{\mathrm{int}} = 0.9$.

Several interesting features arise from an analysis of the results in Figure 1.

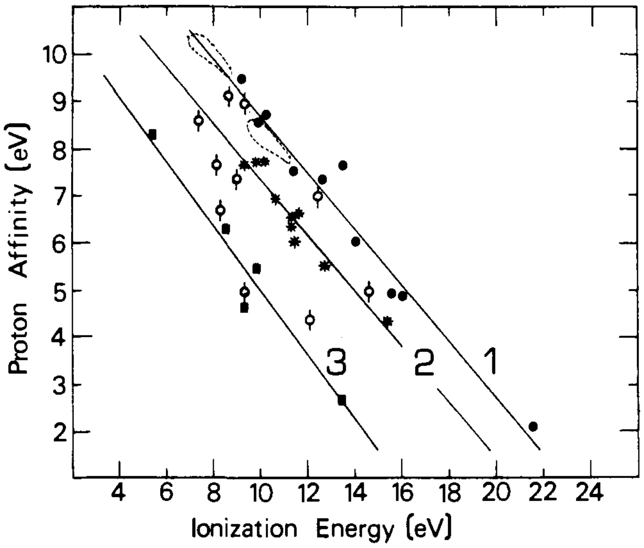


Figure 1. Plot of proton affinity vs. ionization energy for the 35 bases given in Table I. The bases in categories **1**, **2**, and **3** are indicated by closed symbols and those in category **4** by open symbols with vertical line. The upper dashed area encloses some nitrogen bases (ref 12) and the lower dashed area encloses some oxygen bases (ref 5d).

(1) The three lines have nearly the same slope and differ mainly in the constant (intercept). The fact that the slope is not minus one indicates that the homolytic bond dissociation energy does vary within each category. However, since approximate linearity is observed we know that $D(B^+\text{-}H)$ varies relatively smoothly within each category. Given that the slope is approximately −0.6 in each case we can analyze the variation in $D(B^+\text{-}H)$ as follows:

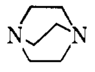
$$\mathrm{PA(B)} = \mathrm{IE(H)} - \mathrm{IE(B)} + D(\mathrm{B}^+\text{-}\mathrm{H})$$

where $D(B^+\text{-}H) = 0.4\mathrm{IE(B)} + C_m$. The constant C_m varies with category m = **1**, **2**, **3** and its values are approximately 1.10, −0.28, and −1.74 eV, respectively. We see that the three categories differ mainly in the value of C_m with the largest values corresponding to the two-electron lone-pair bases, the intermediate values to the σ or π bond-pair bases, and the smallest values to one-electron bases.

(2) At first glance, borazine represents an exception to the categories illustrated in Figure 1. Although borazine often is called "inorganic benzene", its reaction chemistry and frontier orbital electron density are quite different from that of benzene.[14] This difference also is evident in Figure 1 since benzene falls in category **2** and borazine in category **1**. This suggests that the $\pi(e'')$ HOMO in borazine has its electron density largely concentrated on the nitrogen atoms, causing it to behave as a lone-pair electron donor rather than a π-electron donor.

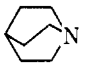
(3) We do not contend that the correlations presented in Figure 1 allow prediction of the *site* of proton attack. However, they do seem to provide an indication of localization of the frontier orbital. For example, HCN lies above the line for category **1** whereas the isoelectronic N_2 molecule lies below the line. This suggests that the lone-pair orbital is more localized in HCN than in N_2. The major reason that HCN lies above the line and N_2 lies below is that the values of $D(B^+\text{-}H)$ for these two molecules do not follow IE(B) as discussed in point (1). The values of $D(B^+\text{-}H)$ for N_2 and HCN are 159 and 176 kcal/mol, respectively. This point is closely connected to the concept of "cation resonance stabilization" observed by Staley and Beauchamp[15] in comparing the homolytic bond dissociation energies of diazabicyclooctane (I) and quinuclidine (II). Perhaps the simplest manifestation of cation resonance

stabilization is provided by the values of $D(B^+-H)$ for HCN and N_2 given above.



I

$D(B^+-H) = 83.3$



II

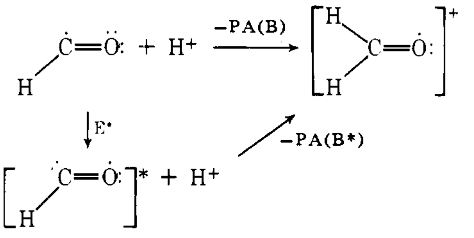
97.4 kcal/mol

(4) The results presented in Figure 1 do suggest that a rough estimate of the proton affinity can be obtained in cases where the IE is known but the PA is unknown. For example, the PA of CS has been estimated to lie between 6.5 and 8.0 eV based upon thermodynamic data.[16] With an experimental IE of 11.33 eV,[17] the curve fit line for category **1** predicts PA(CS) = 8.0 eV. A recent experimental determination gives PA(CS) = 7.56 eV.[16] (Notice that the value of PA for the isovalent CO molecule also lies about 0.4 eV below the line.)

The HF molecule provides another example. Foster and Beauchamp[18] used ion cyclotron resonance spectroscopy to determine PA(HF) = 112 ± 2 kcal/mol (4.86 ± 0.09 eV). Ng et al.[19] have studied the photoionization of $(HF)_2$ to yield H_2F^+ and they determine PA(HF) = 94.3 ± 1.4 kcal/mol (4.09 ± 0.06 eV). These two results differ by about 20%. The correlation for category **1** presented in Figure 1 clearly favors the result of Foster and Beauchamp. The discrepancy between the two experimental values for PA(HF) could be explained if Ng et al.[19] were forming an excited state of H_2F^+ rather than the ground state.

(5) The line drawn for category **3** is based on data for Li, CH_3, C_2H_5, CF_3, and H. These are σ radicals with relatively high electronic rearrangement energies. The term "rearrangement energy" refers to the energy required to produce the base in a state wherein it has a *pair* of electrons in its HOMO. Notice that CF_3 falls considerably below the line, indicating that, although its IE differs little from that of CH_3, it forms a weaker bond with the proton than does CH_3.

(6) The radicals in group **4** consist of HCO, NO, O_2, C_5H_5, C_6H_5, C_7H_7, C_3H_5, C_2H_3, C_2H, and CN. The only common feature of these bases is that they do not seem to fit any of the previous three categories! Both σ and π radicals are found in this group. These bases all have relatively low electronic rearrangement energies which would allow the base to behave as a two-electron donor. Therefore, although the ground state of BH^+ exhibits a two-electron bond for B–H, the energy released upon bond formation has been reduced as a consequence of the energy required to bring about the electronic rearrangement. The protonation of HCO will illustrate this idea.



From this thermochemical cycle we can write

$$PA(B) = PA(B^*) - E^*$$

where E^* is the electronic rearrangement energy of the base B. Consequently, the observed proton affinity, PA(B), is reduced from what it would be for a corresponding two-electron attack, $PA(B^*)$, by the electronic rearrangement energy E^*. Therefore, those bases with a high E^* behave as one-electron bases (category **3**). Bases in group **4** with low values of E^* behave as two-electron bases with proton affinity lower than category **1** or **2** by an amount corresponding to E^*.

The electronic rearrangement energy E^* can be related to a single electronic excitation energy in a qualitative fashion for some molecules. For example, NO and O_2 could behave as two-electron π bases in their $(\pi)^3(\pi^*)^2$: $^2\Pi$ and $(\pi)^4(\pi^*)^2$: $^1\Sigma$ states, respectively. The excitation energies to these states are 5.5 and 1.6 eV, respectively.[20] This is reflected to some extent in Figure 1; NO lies about 3 eV below category **2** whereas O_2 lies only about 2 eV below the category **2**.

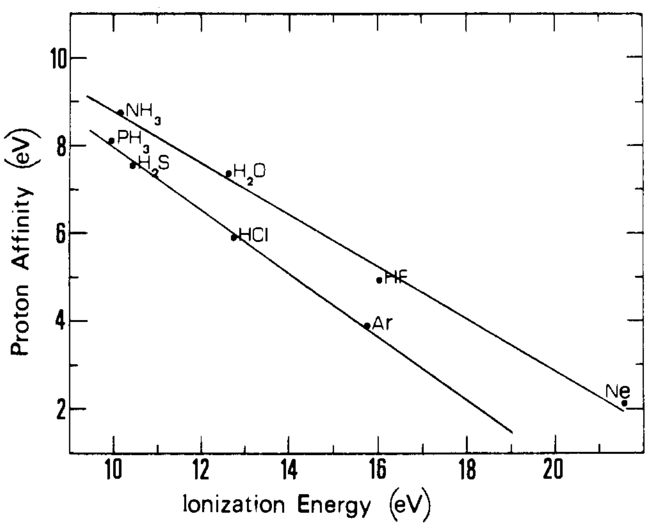


Figure 2. Plot of proton affinity vs. ionization energy for the first- and second-row bases isoelectronic with Ne and Ar.

The radicals CN and C_2H lie below category **1** by about 1 and 1/4 eV, respectively. Correspondingly, their excitation energies $^2\Pi_i \leftarrow {}^2\Sigma$ are only about 1 eV.[21] This corresponds to a low-lying $\pi \rightarrow n$ transition. The other radicals in group **4** also are expected to have low-lying electronic transitions. As a consequence of these low-lying excitation energies, we find no simple relationship between PA and IE for these bases. However, as we have pointed out for NO, O_2, CN, and C_2H, a rough correlation exists between the amount of energy required to form the appropriate two-electron HOMO and the extent to which the PA lies below category **2** (for bond-pair bases) and category **1** (for lone-pair bases).

(7) We have examined the calculations of Kollman and Rothenberg[4a] in an attempt to understand from a theoretical viewpoint the results presented in Figure 1. Their calculations of proton affinity were done within the framework of the Morokuma[4b] energy decomposition analysis. In this method the total proton affinity is described as arising from electrostatic, polarization, and charge-transfer terms. For molecules in category **1**, calculations are reported for NH_3, H_2O, and HF. The electrostatic and charge-transfer terms are by far the dominant factors controlling proton affinity for these lone-pair molecules. However, for molecules in category **2** the largest contribution is provided by the charge-transfer term only. For the molecules H_2, CH_4, and C_2H_4 the charge-transfer energies are 120.5, 103.3, and 114.6 kcal/mol, respectively. However, the *variation* in the proton affinity for these three molecules is controlled more by the electrostatic and polarization terms. The electrostatic energies are −38.3, −36.0, and 9.1 kcal/mol; the polarization energies are 7.3, 36.9, and 41.4 kcal/mol for H_2, CH_4, and C_2H_4, respectively. We conclude that there is no simple theoretical basis underlying the trends observed in Figure 1.

We wish to make two additional points that do not deal directly with the data presented in Table I and in Figure 1.

(1) We have extended the study of PA(B) vs. IE(B) correlations to the isoelectronic series of molecules PH_3, H_2S, HCl, and Ar using the data given by Wolf et al.[22] The regression analysis yields

$$PA = -0.715IE + 15.1,\ r = -0.99$$

The corresponding analysis for NH_3, H_2O, HF, and Ne is

$$\text{PA} = -0.591\text{IE} + 14.7, r = -0.99$$

A plot of PA(B) vs. IE(B) for these eight molecules is presented in Figure 2. Notice that the third-row molecules fall below the second-row molecules. In the language of the hard–soft acid–base theory,[23] this indicates that the proton, being a "hard" acid, interacts more strongly with the "hard" second-row bases than it does with the "soft" third-row bases.

(2) The linear correlation that has been observed between *core* ionization energy and proton affinity was mentioned briefly in the introduction. Those correlations have been observed for molecules in which the proton attack occurs at a given type of atom in a series of molecules (e.g., O or N). We have observed that such a linear correlation also occurs for the isoelectronic series of molecules NH_3, H_2O, HF, and Ne. The 1s-type core ionization energies for these molecules was obtained from the data of Banna and Shirley.[24] The linear regression analysis is

$$\text{PA} = -0.0146\text{IE}_{1s} + 14.9, r = -0.99$$

Notice that the above correlation is very restricted; it does not include the isoelectronic CH_4 molecules which contains no lone-pair electrons. In fact, if we attempt to apply the above correlation to CH_4, we calculate PA(CH_4) = 10.7 eV compared to the experimental value of only 5.5 eV!

Having noticed that both the lowest ionization energy and the core ionization energy correlate with proton affinity for NH_3, H_2O, HF, and Ne, we decided to also carry out a linear regression of the *average valence* ionization energy (AVIE) with proton affinity. We define AVIE by the equation

$$\text{AVIE} = {}^1\!/_4 \sum_i m_i\text{IE}_i$$

The summation on i is over the valence ionization energies and m_i refers to the degeneracy of the ith ionic state. Employing data for IE_i from Banna and Shirley[24] we obtain

$$\text{PA} = -0.622\text{AVIE} + 19.5, r = -0.99$$

In summary, for the molecules NH_3, H_2O, HF, and Ne, we find a very strong linear correlation for lowest ionization energy, core ionization energy, and average valence ionization energy with proton affinity.

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