J. Phys. Chem. A **2003,** *107,* 11517−11524

# Proton Donor Is More Important Than Proton Acceptor in Hydrogen Bond Formation: A Universal Equation for Calculation of Hydrogen Bond Strength

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*Received: May 25, 2003; In Final Form: September 28, 2003*

Analysis shows that proton donor is more important than proton acceptor in determining hydrogen bond formation and strength, and a clear explanation is given for this. Within one system, hydrogen bond strength, $\Delta H$, can be calculated by $\Delta H = kx - \alpha$, where $k$ and $\alpha$ are constants and $x$ is the ratio of proton affinities of the acceptor [PA(A)] to the donor [PA(D)]. If the proton donor is fixed and the proton acceptor is varied when one system is fit into the linear function, the $k$ and $\alpha$ so obtained are functions of donor's proton affinity, PA(D). Therefore, it is possible to obtain a universal equation to calculate hydrogen bond strength in a variety of systems. One example has the form of $\Delta H = a\text{PA(D)} + dx + c\text{PA(A)} + e$, where $a$, $c$, $d$, and $e$ are constants. This equation has been tested with more than 300 hydrogen bond pairs with positive charge. The average absolute error for the test is 1.9 kcal/mol. Other forms of the universal equation have also been discussed.

## Introduction

Hydrogen bonding is one of the important interactions between molecules in biology and chemistry.[1] The hydrogen bond can be roughly categorized as weak bonding, usually having a bond strength below 10 kcal/mol and forming between two neutral partners, or strong bonding, usually having a bond strength from 10 to 50 kcal/mol and forming between a neutral molecule and a charged partner, either positive or negative.

Different approaches have been and are being used to better understand and predict hydrogen bonding strength. One of the approaches is based on fitting experimental values, which usually provides useful equations for predicting the actual bond strength. The present study falls into this category, on the basis of the understanding of the different significances of a hydrogen bond donor and acceptor.

A hydrogen bond forms between a proton donor that provides the proton and a proton acceptor that accepts the proton. Although both a donor and an acceptor must be provided to form a hydrogen bond, the relative importance may be different in controlling the bond strength. Little attention has been paid to this difference, although understanding their difference has both theoretical and practical significances. For calculations of a limited number of hydrogen bond strengths with an equation, the different roles of proton donor and acceptor may not be obvious, whereas for an equation that can be used "universally" to calculate bond strengths for a large number of hydrogen bonds, much attention should be paid to the donor's property, according to this study.

For calculation of hydrogen bond strength, many studies aim to relate the bond dissociation energy (bond strength), $\Delta H$, to a difference between proton affinities, $\Delta$PA, of the partner bases or a difference between acidity of the partner acids. Proton affinity (PA) is defined as a negative enthalpy of the following reaction:[2]

$$\mathrm{B} + \mathrm{H}^+ = \mathrm{BH}^+$$
$$\mathrm{PA(B)} = -\Delta H_{\mathrm{rxn}} \tag{1}$$

Acidity of an acid, $\Delta H_{\mathrm{acid}}$, is defined as the enthalpy of the following reaction:[3]

$$\mathrm{AH} = \mathrm{A}^- + \mathrm{H}^+$$
$$\Delta H_{\mathrm{acid}} = \Delta H_{\mathrm{rxn}} \tag{2}$$

Because the acidity of an acid equals the proton affinity of the acid's conjugate base, $\mathrm{A}^-$, in this report, we use the proton affinity of the conjugate base to represent the acidity of the acid.

Hydrogen bond strength has been linearly correlated to the difference of proton affinities of proton donor and proton acceptor[4] for the system D−H···A:

$$\Delta H = \mathrm{De} - b[\mathrm{PA(D)} - \mathrm{PA(A)}] \tag{3}$$

where De and $b$ are constants obtained from fitting experimental data, PA(D) is the proton affinity of the donor, and PA(A) is the proton affinity of the acceptor. The equation is usually used for a limited number of hydrogen bond strengths where the donors (or the acceptors) are limited by chemical similarities or by the same category of molecules. When the donors (or acceptors) are changed to another category, the constants De and $b$ must be changed accordingly. In most cases of fitting experimental data into eq 3, PA(D) is a variable and PA(A) is fixed,[4−9] whereas in other cases both PA(D) and PA(A) are variables.[9−12] When the acceptor's PA is fixed, eq 3 can also be written as a function of only the donor's PA:[13] $\Delta H = \mathrm{De}' - b\mathrm{PA(D)}$. In one case,[11] PA(D) is fixed and PA(A) is a variable. The constant $b$ in the literature varies from 0.16 to 0.5, depending on the systems.

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10.1021/jp035446r CCC: $25.00

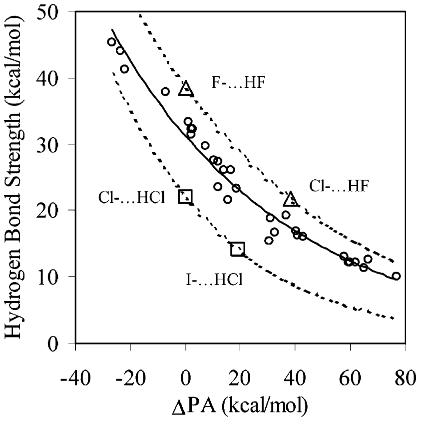

**Figure 1.** Exponential plot of hydrogen bond strength, Δ*H*, as a function of ΔPA for the X···HOR and X···HX systems, where X stands for $F^-$, $Cl^-$, $Br^-$, or $I^-$ anions. The X···HOR data (circles) are from refs 17 and 18 and the additional four points (triangle for HF donor and square for HCl donor) are from ref 19.

In the linear eq 3, all the PA(D) values are larger than the PA(A)'s; otherwise, a negative Δ(PA) would be found. The De value may be thought of as the hydrogen bond dissociation energy when the donor and the acceptor are the same ($AH^+$···A). The De value has also been related to an average of the dissociation energies of the symmetrical dimmers $D_{AHA}$ and $D_{DHD}$.[14] Although a calculation can be done on the basis of the average dissociation energy, De in this treatment is no longer a constant for a series of chemicals in a system. Although the constant De has been given a physical significance, constant *b* has not been clearly explained. Equation 3 was also written as an equation with three fitting constants,[15] where both PA's are variables:

$$\Delta H = \mathrm{De} - b\mathrm{PA(D)} + b'\mathrm{PA(A)} \qquad (4)$$

In eq 4, the constant *b* is different from constant *b*′. In anticipating that proton donor is more important than proton acceptor in hydrogen bond formation, the constant *b* has been assigned to be 1.5 times constant *b*′.[16] With [1.5PA(D) − PA(A)] as the parameter, hydrogen bond strength has been fitted into a linear equation (similar to eq 3, not shown here) or into an exponential equation[16]

$$\Delta H = C_1 \exp\{-C_2[1.5\mathrm{PA(D)} - \mathrm{PA(A)}]\} \qquad (5)$$

where $C_1$ and $C_2$ are fitted constants. It was claimed that the fitting with the above exponential function was better than the linear fitting. In the early publications,[17,18] the same author proposed that an exponential equation should be used in fitting a large range of hydrogen bond strength Δ*H* as a function of ΔPA for halogen anions (X) interacting with oxygen type donors (X···HOR) as

$$\Delta H = 32 \exp(-0.0156|\Delta\mathrm{PA}|)\ \mathrm{kcal/mol} \quad \text{for } \Delta\mathrm{PA} > 0 \quad (6)$$

$$\Delta H = -\Delta P\mathrm{A} + 32 \exp(-0.0156|\Delta\mathrm{PA}|)\ \mathrm{kcal/mol} \quad \text{for } \Delta\mathrm{PA} < 0 \quad (6')$$

where ΔPA = [PA(D) − PA(A)]. Although this exponential relation can be used in large ranges of ΔPA and Δ*H*, it is limited to X···HOR type complexes (where X = $F^-$, $Cl^-$, $Br^-$, $I^-$) and cannot be extended to other proton donor systems unless the numerical constants ($C_1$ and $C_2$) have been changed. In Figure 1, eq 6 of the original published set of data[17,18] is plotted with addition of another 4 points cited from the literature. It is interesting to see that for other proton donors, HF and HCl, the fitting curves shift away from the curve that is obtained from donors of the HOR type, even though all the acceptors in the figure are X type, and for the new four points, the donor and acceptor atoms are both halogens. Therefore, it seems that one equation can only be used in one system, either a linear equation or an exponential equation.

In all the fitting equations above, each set of fitted constants (De and *b*; De, *b*, and *b*′; or $C_1$ and $C_2$) can only be applied to a limited number of hydrogen bonds of similar molecules. If we group the number of the hydrogen bonds that can be fitted into one of the equations above with a specific set of constants as one system, there is no equation that can be used across different systems for calculation of hydrogen bond strengths, whatever the equation form is, to our best knowledge. This paper attempts to define an equation that can be used for different systems, namely, a "universal equation".

## Model Analysis

As explained in the Introduction, when eq 3 is used in the literature, PA(A) is set as a constant, whereas PA(D) is varied (using different donors DH) in most cases. Under this condition, the constant De in eq 3 is thought of as the hydrogen bond strength of AH···A, where the A has the smallest proton affinity within all the donors (because ΔPA > 0). In this treatment, De is related to the property of the acceptor.

We believe that when PA(D) is a constant and PA(A) varies (using different acceptors), the linear equation should also hold, and then De is the hydrogen bond strength of DH···D and is determined by the proton donor only. Because PA(A) is used as a variable, we can let it approach zero, i.e., an acceptor having a zero affinity to a proton. Physically, a hydrogen bond does not form ($\Delta H = 0$) when PA(A) = 0. (Note: physically, letting PA(D) → 0 is meaningless at a constant PA(A) for hydrogen bonding.)

Mathematically, when $\Delta H = 0$ at PA(A) = 0, *b* = De/PA(D). Then, *b* is the fraction of PA(D) that contributes to the hydrogen bonding (because De < PA(D)) if PA(D) is set as a constant. Equation 3 would be reduced to $\Delta H = \mathrm{De}\cdot x$, where $x$ = PA(A)/PA(D). As will be seen later, real experimental data fitting leads to the form

$$\Delta H = kx - \alpha \qquad (7)$$

where *k* and α are nonzero constants. The use of the proton affinity ratio, *x*, instead of difference, ΔPA, is another point of view for understanding *relative* contributions of the donor and acceptor to the hydrogen bonding. Because the formation of a hydrogen bond can be thought as a competing result, it is the relative power of "pulling" the proton that controls the H-bond formation and strength, not their absolute values. A better way to describe the "relative" pulling power is to use the PA ratio. Another advantage of using the PA ratio is that the ratio is always positive, which is easily treated, mathematically.

We prefer that, in calculation of the proton ratio in eq 7, PA(D) is set as a constant and PA(A) is varied. The proton in a hydrogen bond is usually not symmetrically shared by two bases. It generally sits closer to the donor base than to the acceptor base. Intuitively, the proton chemistry, and therefore, hydrogen bond strength, should be influenced more by the donor base than by the acceptor base. In an extreme case where a donor is too strong (high PA donor), the proton will not show its "positive character" to an acceptor and the hydrogen bond will not form, no matter how strong the acceptor is. Thus, the De in eq 3 derived from AH···A in a treatment where PA(A) is fixed is less relevant (if not irrelevant) to the hydrogen bonds from these (high PA) donors. However, setting PA(D) as a constant actually fixes the partial positive character of the proton that is available to all possible acceptors. Then, De obtained from DH···D is relevant to all acceptors that form a hydrogen bond with the donor, D. Therefore, setting PA(D), instead of PA(A), as a constant would be more meaningful. More advantages will be seen later.

When $\Delta H = 0$ in eq 7, $x_o = \alpha/k$, where $x_o$ is the intercept of the linear line with $x$-axis. The $x_o$ signifies a critical ratio of proton affinities. Above the ratio, $x_o$, a hydrogen bond starts to form. When $0 < \mathrm{PA(A)/PA(D)} < x_o$, a hydrogen bond cannot form, even though the PA(A) has a very large value, namely, is electronegative enough. The critical value, $x_o$, is independent of acceptors (at $x_o$ there is no acceptor to bind with the donor); it is only dependent on the property of the proton donor, most likely on proton affinity of the donor.

The constant $k$ signifies how much the original proton owner, D, allows A to share the proton. A low PA donor allows an acceptor to share more of the proton to form a stronger hydrogen bond, which means a high $k$ value, whereas a high PA donor will allow an acceptor to share less of the proton to form a weak H-bond, which means a low $k$ value. Therefore, the constant $k$ is dependent only on the donor's PA, which can be seen in the following reasoning. At $x = 1$, $\Delta H$ is the hydrogen bond strength of DH···D, which is only dependent on the donor. At $x = x_o$, $\Delta H = 0$, which is independent of any acceptor. Thus, the slope, $k$, between the two points ($x = 1$, $x = x_o$) must also be dependent only on the donor. The constant $k$ can be called hydrogen bond forming potential of a donor. However, if PA(A) is set as a constant in the ratio, the physical meaning of $k$ is dependent on both donor and acceptor.

This analysis leads to a hypothesis that when PA(D) is set as a constant, both $k$ and $\alpha$ in eq 7 are dependent only on donor's properties, independent of acceptor. Therefore, there would be a chance to unify different systems into one universal equation (by writing $k$ and $\alpha$ as functions of donor's properties). Let us further assume that both $\alpha$ and $k$ are also linear functions of the proton affinity of a proton donor D as

$$k = c\mathrm{PA(D)} + d \qquad (8)$$

$$-\alpha = a\mathrm{PA(D)} + e \qquad (9)$$

Substituting eqs 8 and 9 into eq 7 leads to

$$\begin{aligned}\Delta H &= (c\mathrm{PA(D)} + d)x + a\mathrm{PA(D)} + e \\ &= a\mathrm{PA(D)} + dx + c\mathrm{PA(A)} + e \qquad (10)\end{aligned}$$

Equation 10 will be tested later. [The treatment would be similar when relations other than linearity of $k$ and $\alpha$ with PA(D) are used, as long as they are functions of "only PA(D)"].

If PA(D) is a variable and PA(A) is a constant in eq 7, the constant $k$ and $\alpha$ will be dependent on both donor and acceptor. Consequently, it is not possible to lead to the universal eq 10. Because eqs 3 and 7 are mathematically transferable, if $k$ and $\alpha$ are dependent only on the properties of proton donor, De and $b$ of eq 3 should also depend only on the properties of proton donor when PA(D) is a constant in every one system. However, one would not reach the same symmetrical form of (10) from eq 3, even though PA(D) is chosen to be a constant.

We deduced eq 10 with the assumptions that linear eq 7 is true and both $k$ and $\alpha$ are also linearly related to PA(D). However, if an exponential equation (or any other forms of equations), is used in place of eq 7 with a constant PA(D) and variable PA(A), the preexponential factor and the exponent should also be a function of only the donor's properties, and another universal equation can be derived.

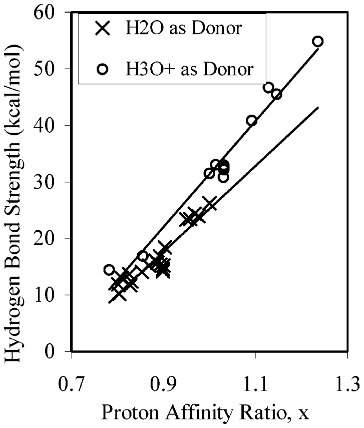

**Figure 2.** Hydrogen bond strength as a function of the ratio of proton affinities of acceptor to donor, $x$, where $H_3O^+$ or $H_2O$ is the proton donor. Acceptors for $H_3O^+$: ether, alcohol, acid, aldehyde, $H_2O$, $CH_3CN$, $CO_2$, HCN, $N_2O$, $NH_3$. Acceptors for $H_2O$: ionized acid, alcohol, phenol, halogen, $CN^-$, $SH^-$, $OH^-$, $NO_2^-$, $HSO_4^-$, $NO_3^-$, $PO_3^-$.

## Data Collection and Treatment

To test the hypothesis that a universal equation can be found to calculate the hydrogen bond strengths in different systems, we need the data of hydrogen bond strength, base proton affinity, and acid acidity (conjugate base proton affinity). Fortunately, the information of proton affinity has been compiled by Hunter and Lias[2] up to 1997, the acidity of acids can be found[3] up to 1986. The hydrogen bond dissociation energy was complied by Keesee and Castleman[19] up to 1986. In this paper, most of the data were taken from the three compilations. For the proton affinity, we took the data from the compilation without discrimination because a single value for a chemical was found in the reference. However, there are often several values cited in the compilation and in other literature for one hydrogen bond strength. In these cases, we took the value that fits the equation best, or their average. All the data were claimed in a gas state by the original authors or editors. The data collection by no means is exhausted, and it is only for testing the possibility to have a universal equation for hydrogen bond calculations.

When a set of data for a system with a same donor (or an acceptor) has less than 3 points, the data were not used. In the linear fitting process, certain obvious outliers have been deleted if there are additional reasons to do so, such as a carbon acid (RC−H) that cannot be fitted with an oxygen type acid (RO−H), or if there are multiple accepting base atoms in an acceptor and the data source did not clearly indicate which one was the accepting base, which may form multiple hydrogen bonds. In a couple of systems, when it is more appropriate, the linear fitting is only for specific types of bases, which is indicated in the tables.

## Result and Discussion

### 1. Comparison of Neutral Donors and Positive Donors of Same Molecules.

*(A) Bond Strength Difference of Cationic and Neutral Donors.* Typical linear fitting of the hydrogen bond strength as a function of the ratio of proton affinities of the acceptor to donor is shown in Figure 2 for water. Two sets of data are plotted in the figure: $H_2O$ as donor and $H_3O^+$ as donor. The figure shows that for a same proton affinity ratio, $H_3O^+$ as

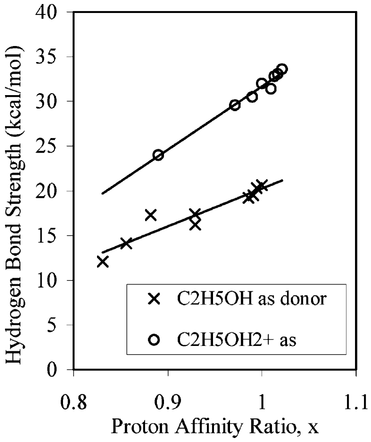

**Figure 3.** Hydrogen bond strength as a function of the ratio of proton affinities of acceptor to donor, where $C_2H_5OH_2^+$ or $C_2H_5OH$ is the proton donor. Acceptors for $C_2H_5OH_2^+$: alcohols, acids, $H_2O$. Acceptors for $C_2H_5OH$: ionized alcohol, halogen ions, $CN^-$, $SH^-$.

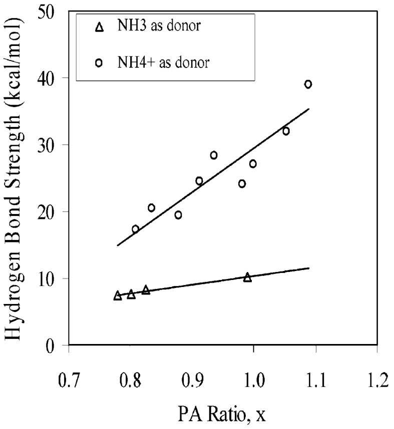

**Figure 4.** Hydrogen bond strength as a function of the ratio of proton affinities of acceptor to donor, where $NH_4^+$ or $NH_3$ is the proton donor. Acceptors for $NH_4^+$: $(CH_3)_2NH$, $CH_3NH_2$, $CH_3NC$, $NH_3$, *n*-$C_3H_7CN$, $CH_3CN$, benzene, $H_2O$, HCN. Acceptors for $NH_3$: halogen ions and $NH_2^-$.

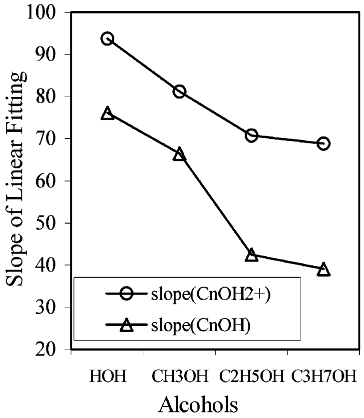

**Figure 5.** Slopes of the linear fitting as a function of carbon number in alcohols.

the donor forms hydrogen bonds ($H_2OH^+\cdots A$) that are stronger than that formed with $H_2O$ as the donor ($HOH\cdots A^-$). That the hydrogen bond of cationic complex [$OH^+\cdots O$] is stronger than that of anionic complex [$OH\cdots O^-$] was noticed before.[7] The authors explained the strength difference by the high PA of the anions, which lead to a larger $\Delta$PA than that of cationic complex. With use of the PA ratio in this study, we find that the same ratio (e.g, $x = 1$) results in different hydrogen bond strengths for the cationic and anionic complexes. Therefore, a new explanation must be sought. Obviously, in the cationic complex, the positive donor provides “more proton” (partial positive charge) than the neutral donor in the anionic complex, whereas the anionic acceptor in the anionic complex has a stronger proton accepting ability (lone pair characters) than the neutral acceptor in the cationic complex. These are the two main differences; but which is more important? In a “D−H−A” system, the partial positive charge provided by H is much less (deficit) than the lone pairs of electrons provided by both D and A. It is usually the one in shortage (deficit) that controls the sensitivity of a whole system. In the D−H−A system, it is the partial positive charge that controls the increase of the hydrogen bond strength. The different strengths by donor $H_2OH^+$ and donor HOH clearly indicate that a donor’s ability of donating “more proton” (providing more positive charge) is more important than the acceptor’s ability of accepting the proton, so hydrogen bonding is largely determined by the proton-donating ability of the donor.

This is true not only in comparing positive and neutral donors but also in comparing two donors having the same type of charge. It was shown[20,21] that there was a positive correlation between the partial positive charge on the proton and the hydrogen bond strength in systems of $RNH^+\cdots OH_2$. Therefore, a stronger hydrogen bond in a cationic system (than in the anionic system) would be no surprise, even at $x = 1$, where the relative power of the donor and the acceptor to “pull” the proton is the same. Two more examples are shown in Figure 3 and Figure 4 for ethanol and ammonia as donors. The explanation for the relative bond strengths of the cationic complexes and the anionic complexes should be the same as that for water.

*(B) Different Slopes, k, of Positive and Neutral Donors.* It is also noted from the figures that the slopes of the linear line for the positive donors are larger than that for the neutral donors. This indicates that the positive donors have a higher potential to form stronger hydrogen bonds with acceptors (a higher slope means a larger increase for same acceptor difference). In the neutral donor systems, the donor (with large PA) would be reluctant to provide proton for an acceptor to share and any increase in an acceptor’s power to “pull” proton (acceptor’s PA) is largely “wasted”, which leads to a small *k* value for the donor. (Neutral donors have much higher PA’s than the cationic donors.) This again shows that the donor’s ability of releasing partial positive charge is more important than acceptor’s ability of accepting the proton.

*(C) Slope Change with Donor Sizes.* Comparison of Figures 2 and 3 shows that the difference between the positive donor and the neutral donor is increased from water to ethanol. Figure 5 shows the linear fitted slopes as a function of carbon numbers for both protonated alcohols and neutral alcohols. It is known that the alkyl is an electron-pushing group. A strong electron-pushing group increases the electron density of the oxygen for the large size alcohol, which leads to the high PA of the alcohol and low proton donating ability. Therefore, the bigger the alcohol, the weaker the hydrogen bond formed and the smaller the slope *k* value. It is also noticed that the difference of the slopes between the positive donor and the neutral donor increases as a function of alcohol size. If we define a relative charge difference as the difference of the partial positive charges between the positive donor and the neutral donor divided by the partial positive charge, the relative charge difference increases as the alcohol size increases, which indicates that the large slope difference between positive and neutral donors in the big alcohol is due to less partial charge available to acceptors. (When there is no difference for the fitted slopes between

($DH\cdots A^-$) and ($DH_2^+\cdots A$), the partial positive charge of the proton and the lone pair of electrons would be equally important in hydrogen bonding).

In short, the hydrogen-bonding strength is mainly controlled by the proton-donating ability of the donors, and less controlled by the proton-accepting ability (proton affinity) of acceptors, because proton character (or partial positive charge) is more important in hydrogen bond strength than the lone pair character of acceptors for most hydrogen bonds. For example, an increment in proton-donating ability (a decrease in donor's PA) contributes much more to hydrogen bond strength than the same increment in proton-accepting ability (an increase in acceptor's PA). A similar phenomenon was noticed in other research[16] where the author used a larger coefficient before the donor's PA than that before acceptor's PA for double linear correlation of hydrogen bond strength, and the difference was accounted for by the asymmetry of the proton to the two basic partners. The asymmetry is actually a result of the difference of the two PA's, not the cause of the PA difference. The fact that the hydrogen bond strength is more sensitive to the donors than to the acceptors is true not only for the strong interaction systems in this study but also for weak systems involving weak C−H donors.[22,23]

**2. Comparing Fixed Donor and Fixed Acceptor in Positively Charged Systems.** To save space, we will only list the results from the fitting data into eq 7 in the following tables. In these tables, the donor (or acceptor) chemical formula, which is the same for one fitting system, number of data points, slope $k$, intercept ($-\alpha$), and correlation coefficient ($R^2$) are given for each donor (or acceptor) system. In the last column, a value of ($\alpha/k = x_o$) is given, which represents the intercept of the linear line with $x$-axis.

Table 1 lists 33 fitted results for positively charged donor systems. Its positive charge is created by receiving a proton, before its participation in a hydrogen bond formation. As discussed in eq 7, the slope, $k$, can be thought of as the ability or potential of a donor to form an H-bond with certain acceptors: the larger the $k$ value, the stronger the H-bond formed with an acceptor. Although the $\alpha$ value has no physical reality, the ($\alpha/k$) value is a critical value of $x$, assigned as $x_o$. Above $x_o$, a hydrogen bond starts to form, whereas when $0 < x < x_o$, for the donor, there is no hydrogen bond formed, even though an acceptor has a very large proton affinity. An acceptor that cannot form a hydrogen bond with one donor may form a strong hydrogen bond with another donor, depending on the donor's $x_o$ values. $x_o$ increases when the donor proton affinity decreases for the positive donors, as shown in Table 1.

It is seen from Table 1, that the slope $k$ increases with a decrease of the donor proton affinity. This is consistent with the conclusion that the stronger donating ability of a donor (low PA) results in higher potential to form a strong hydrogen bond.

To see if there is any difference between setting the donor as a constant and setting the acceptor as a constant, we also fitted eq 7 with an acceptor being fixed (from the same data pool). Table 2 lists the results of fitting eq 7 for a fixed acceptor with varying positively charged donors for 30 systems. (Note, the $x$ value is always the ratio of acceptor PA/donor PA.) The average fitting is as good as those listed in Table 1, as seen by the correlation coefficients in the two tables

However, the correlation is poor ($R^2 = 0.185$) between the slope $k$ values and the acceptor PA in Table 2 where the acceptor is constant in each system, whereas the correlation is good ($R^2 = 0.921$) between the fitted $k$ values and donor PA where the donor is a constant in each system (Table 1), as can be clearly seen from the plots in Figure 6. This indicates that the proton affinity of a donor is more important than that of an acceptor for a correlation among different systems.

**TABLE 1: Fitting $\Delta H = kx - \alpha$ for Systems with Fixed Cationic H Donors (Varying Neutral Acceptors)[a]**

| H donor | no. of points | donor PA | $k$ | $\alpha$ | $R^2$ | ($\alpha/k$) |
|---|---|---|---|---|---|---|
| $H_3O^+$ | 12 | 165 | 93.7 | 62.3 | 0.967 | 0.665 |
| $HCNH^+$ | 4 | 170 | 92.9 | 61.4 | 0.986 | 0.661 |
| $H_2COH^+$ | 3 | 170 | 96.0 | 66.6 | 0.750 | 0.693 |
| $CH_3OH_2^+$ | 7 | 180 | 81.0 | 50.0 | 0.929 | 0.617 |
| $CH_3CHOH^+$ | 6 | 184 | 73.2 | 42.1 | 0.915 | 0.575 |
| $C_2H_5OH_2^+$ | 8 | 186 | 69.4 | 37.9 | 0.975 | 0.546 |
| $CH_3CNH^+$ | 4 | 186 | 84.9 | 51.8 | 0.906 | 0.610 |
| $HCOOCH_3H^+$ | 3 | 187 | 78.2 | 47.6 | 0.999 | 0.608 |
| $CH_3C(OH)_2^+$ | 6 | 187 | 72.4 | 42.3 | 0.992 | 0.584 |
| $n$-$C_3H_7OH_2^+$ | 6 | 188 | 68.8 | 37.5 | 0.997 | 0.544 |
| $n$-$C_4H_9OH_2^+$ | 3 | 189 | 75.3 | 43.9 | 0.964 | 0.583 |
| $(CH_3)_2OH^+$ | 9 | 189 | 66.7 | 36.1 | 0.961 | 0.541 |
| $i$-$C_3H_7OH_2^+$ | 4 | 190 | 68.1 | 36.0 | 0.982 | 0.529 |
| (1,4-dioxane)$H^+$ | 6 | 191 | 74.6 | 43.7 | 0.981 | 0.585 |
| $(CH_3)_2COH^+$ | 15 | 194 | 71.5 | 40.3 | 0.939 | 0.563 |
| c-$C_4H_8OH^+$ | 5 | 196 | 68.5 | 37.1 | 0.824 | 0.542 |
| $(CH_3)(C_2H_5)COH^+$ | 3 | 198 | 56.8 | 26.4 | 0.999 | 0.464 |
| $(C_2H_5)_2OH^+$ | 8 | 198 | 60.4 | 29.8 | 0.970 | 0.494 |
| $(C_2H_5)_2COH^+$ | 9 | 200 | 55.6 | 25.0 | 0.968 | 0.449 |
| $CH_3NCH^+$ | 4 | 200 | 67.4 | 40.6 | 0.746 | 0.603 |
| ($n$-$C_3H_7)_2OH^+$ | 4 | 200 | 54.7 | 25.0 | 0.857 | 0.456 |
| $NH_4^+$ | 10 | 204 | 61.5 | 32.1 | 0.828 | 0.521 |
| (c-$C_3H_5)_2COH^+$ | 3 | 210 | 52.8 | 25.1 | 0.999 | 0.474 |
| (aniline)$H^+$ | 3 | 211 | 36.1 | 17.4 | 0.986 | 0.481 |
| $CH_3NH_3^+$ to O | 24 | 215 | 41.8 | 14.1 | 0.866 | 0.338 |
| $CH_3NH_3^+$ to S | 6 | 215 | 43.5 | 21.4 | 0.890 | 0.491 |
| $(CH_3)_2NH_2^+$ | 6 | 222 | 27.2 | 4.8 | 0.891 | 0.174 |
| $C_5H_5NH^+$ | 5 | 222 | 42.2 | 15.0 | 0.976 | 0.355 |
| $(CH_3)_3NH^+$ | 8 | 227 | 24.0 | 2.4 | 0.830 | 0.101 |
| $(C_2H_5)_3NH^+$ | 5 | 235 | 25.9 | 3.5 | 0.814 | 0.135 |
| sum or average | 199 | 197 | 62.8 | 33.9 | 0.923 | 0.499 |

[a] Note: the donor PA is in kcal/mol.

Figure 7 plots the correlations of the fitted intercepts, $\alpha$, with the donor's PA (from Table 1) and that with the acceptor's PA (from Table 2). Again, the correlation between $\alpha$ and the donor's PA is better ($R^2 = 0.904$) than that between $\alpha$ and the acceptor's PA ($R^2 = 0.22$), further supporting the above point of view. The correlation between $x_o$ and the donor's PA ($R^2 = 0.811$) is also better than that between $x_o$ and the acceptor's PA ($R^2 = 0.248$) (see Tables 1 and 2, but not plotted).

The intuitive reason the donor is more important in forming a hydrogen bond has been explained by the higher importance of partial positive charge in the proton than electron lone pairs in the two bases in previous sections. Although both kinds of fitting (either donor or acceptor is fixed) lead to good linear lines with similar correlation coefficients for individual systems, the two kinds of fitting result in different correlations from one system to the other. The donor's PA can correlate different systems much better than that of the acceptor's PA. When an acceptor is fixed in fitting a linear line, the slope and the intercept are functions of both the acceptor and donor (the main controlling factor, donor property, cannot be neglected at any kind of fitting), whereas when a donor is fixed, the slope and the intercept are functions of only the donor.

**3. Comparing Fixed Donor and Fixed Acceptor in Negatively Charged Systems.** In last section, all the hydrogen bonding systems bear a positive charge. It was concluded that the proton donor controls the hydrogen bond formation, strength, and fitting constants more than the acceptors, and thus the positively charged donor should be fixed in fitting each system, to correlate (compare) among different systems.

**TABLE 2: Fitting $\Delta H = kx - \alpha$ for Systems with Fixed Neutral H Acceptors (Varying Cationic H Donors)[a]**

| H acceptor | no. of points | acceptor PA | $k$ | $\alpha$ | $R^2$ | $(\alpha/k)$ |
|---|---|---|---|---|---|---|
| $H_2O$ to S | 8 | 165 | 51.9 | 30.1 | 0.958 | 0.579 |
| $H_2O$ to O & N | 58 | 165 | 56.9 | 27.5 | 0.933 | 0.483 |
| $CF_3CH_2OH$ | 3 | 167 | 41.3 | 13.3 | 0.560 | 0.323 |
| $H_2S$ | 4 | 168 | 47.4 | 26.9 | 0.789 | 0.568 |
| HCN | 16 | 170 | 56.6 | 27.7 | 0.897 | 0.489 |
| benzene | 4 | 179 | 26.4 | 4.2 | 0.873 | 0.158 |
| $CH_3OH$ | 8 | 180 | 91.7 | 60.4 | 0.945 | 0.659 |
| $CH_3CHO$ | 4 | 184 | 148 | 116.1 | 0.999 | 0.784 |
| $C_2H_5OH$ | 10 | 186 | 73.1 | 41.8 | 0.958 | 0.572 |
| $CH_3CN$ | 10 | 186 | 98.1 | 66.0 | 0.970 | 0.672 |
| $HCOOCH_3$ | 4 | 187 | 75.5 | 43.7 | 0.877 | 0.579 |
| $CH_3COOH$ | 7 | 187 | 76.0 | 45.8 | 0.971 | 0.602 |
| $n$-$C_3H_7OH$ | 7 | 188 | 85.2 | 53.9 | 0.900 | 0.632 |
| $n$-$C_4H_9OH$ | 5 | 189 | 54.0 | 22.5 | 0.957 | 0.416 |
| $(CH_3)_2O$ | 11 | 189 | 97.1 | 66.4 | 0.936 | 0.684 |
| $i$-$C_3H_7OH$ | 5 | 190 | 90.6 | 59.0 | 0.852 | 0.651 |
| 1,4-dioxane | 4 | 191 | 63.0 | 32.1 | 0.774 | 0.509 |
| $t$-$C_4H_9OH$ | 3 | 192 | 83.3 | 51.4 | 0.999 | 0.618 |
| $(CH_3)_2CO$ | 10 | 194 | 76.8 | 45.8 | 0.961 | 0.597 |
| $CH_3COOCH_3$ | 3 | 196 | 74.9 | 45.0 | 0.997 | 0.600 |
| tetrahydrofuran | 4 | 196 | 108.1 | 76.2 | 0.847 | 0.705 |
| $(CH_3)(C_2H_5)CO$ | 4 | 198 | 68.8 | 38.0 | 0.970 | 0.553 |
| $(C_2H_5)_2O$ | 9 | 198 | 87.7 | 57.1 | 0.954 | 0.652 |
| $(C_2H_5)_2CO$ | 7 | 200 | 70.5 | 39.9 | 0.966 | 0.566 |
| $CH_3NC$ | 4 | 200 | 47.3 | 21.8 | 0.804 | 0.460 |
| $(n$-$C_3H_7)_2O$ | 5 | 200 | 63.9 | 33.7 | 0.886 | 0.528 |
| $NH_3$ | 9 | 204 | 111.5 | 82.7 | 0.982 | 0.742 |
| $CH_3NH_2$ | 3 | 215 | 119.5 | 94.9 | 0.812 | 0.795 |
| $(CH_3)_2NH$ | 4 | 222 | 177.4 | 154.4 | 0.969 | 0.87 |
| aniline | 3 | 225 | 40.3 | 25.1 | 0.648 | 0.625 |
| sum or average | 236 | 191 | 78.8 | 50.1 | 0.898 | 0.589 |

[a] Note: the acceptor PA is in kcal/mol.

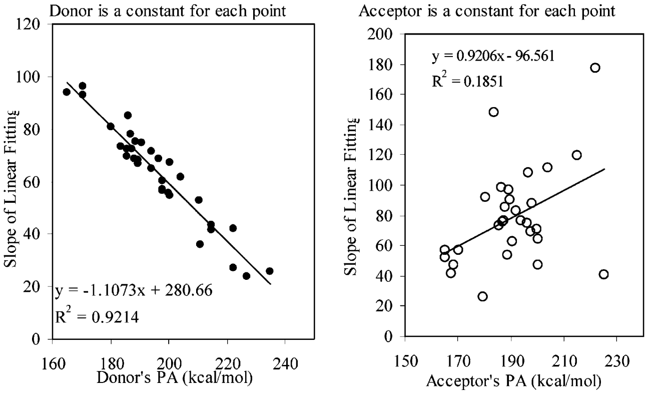

**Figure 6.** Plots of $k$ as a function of donor or acceptor PA for comparison. Left: donor is fixed and from Table 1. Right: acceptor is fixed and from Table 2.

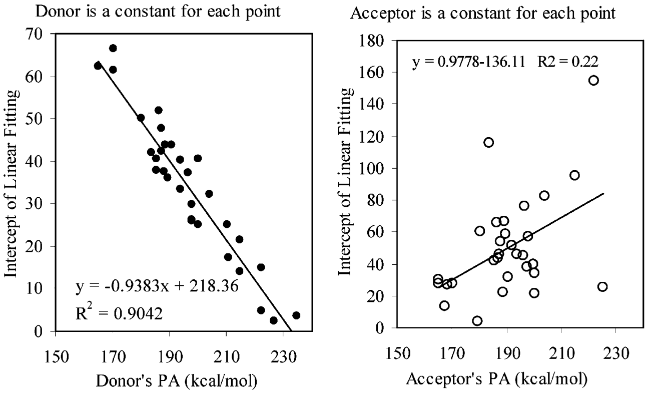

**Figure 7.** Plots of $\alpha$ as a function of donor or acceptor PA for comparison. Left: donor is fixed and from Table 1. Right: acceptor is fixed and from Table 2.

**TABLE 3: Fitting $\Delta H = kx - \alpha$ for Systems with Fixed Neutral H Donors (Varying Anionic Acceptors)[a]**

| H donor | no. of points | donor PA | $k$ | $\alpha$ | $R^2$ | $(\alpha/k)$ |
|---|---|---|---|---|---|---|
| $CH_3COOH$ | 5 | 349 | 161 | 131 | 0.936 | 0.82 |
| $CH_3OH$ | 18 | 381 | 66 | 43 | 0.893 | 0.65 |
| $H_2O$ | 22 | 391 | 76 | 51 | 0.893 | 0.67 |
| HCN | 5 | 351 | 177 | 151 | 0.719 | 0.86 |
| HCOOH | 4 | 346 | 163 | 129 | 0.976 | 0.79 |
| HF to O, N | 6 | 371 | 143 | 115 | 0.990 | 0.78 |
| $i$-$C_3H_7OH$ | 4 | 375 | 129 | 95 | 0.998 | 0.74 |
| $n$-$C_3H_7OH$ to X | 4 | 376 | 130 | 96 | 0.987 | 0.74 |
| $n$-$C_3H_7OH$ to O | 3 | 376 | 132 | 111 | 0.928 | 0.84 |
| $t$-$C_4H_9OH$ to X | 3 | 375 | 133 | 99 | 0.996 | 0.74 |
| $C_2H_5OH$ to O | 4 | 381 | 103 | 82 | 0.931 | 0.8 |
| $C_2H_5OH$ to X, SH, CN | 6 | 381 | 105 | 77 | 0.729 | 0.73 |
| $C_6H_5OH$ | 3 | 349 | 167 | 137 | 0.915 | 0.82 |
| $NH_3$ to X | 3 | 404 | 17 | 6 | 0.998 | 0.35 |
| sum or average | 90 | 372 | 122 | 94 | 0.921 | 0.74 |

[a] Note: X stands for halogen bases; O, for oxygen related bases. PA values are acidities of their conjugate acids in kcal/mol.

**TABLE 4: Fitting $\Delta H = kx - \alpha$ for Systems with Fixed Anionic Acceptor (Varying Neutral Donors)**

| H donor | no. of points | donor PA | $k$ | $\alpha$ | $R^2$ | $(\alpha/k)$ |
|---|---|---|---|---|---|---|
| $Br^-$ | 7 | 324 | 111 | 86 | 0.804 | 0.77 |
| $C_2H_5O^-$ | 3 | 378 | 88 | 61 | 0.835 | 0.69 |
| $C_6H_5O^-$ | 3 | 349 | 110 | 83 | 0.984 | 0.75 |
| $CH_3CO{-}Ala{-}OCH_3\ (N^-)$ | 4 | 355 | 121 | 95 | 0.918 | 0.78 |
| $CH_3COO^-$ | 7 | 349 | 98 | 71 | 0.885 | 0.73 |
| $CH_3O^-$ | 3 | 381 | 194 | 165 | 0.996 | 0.85 |
| $Cl^-$ | 23 | 333 | 128 | 96 | 0.927 | 0.75 |
| $CN^-$ | 5 | 351 | 48 | 28 | 0.866 | 0.59 |
| $F^-$ | 21 | 371 | 130 | 98 | 0.741 | 0.75 |
| $HCC^-$ | 3 | 379 | 123 | 103 | 0.600 | 0.83 |
| $HCOO^-$ | 4 | 345 | 185 | 150 | 0.930 | 0.81 |
| $I^-$ | 9 | 314 | 77 | 52 | 0.976 | 0.68 |
| imidazole$^-$ | 3 | 352 | 102 | 77 | 0.961 | 0.75 |
| $NO_2^-$ | 3 | 340 | 86 | 58 | 0.983 | 0.68 |
| $NO_3^-$ | 3 | 325 | 57 | 33 | 0.840 | 0.58 |
| $SH^-$ | 4 | 351 | 71 | 49 | 0.964 | 0.69 |
| $t$-$C_3H_7O^-$ | 4 | 371 | 53 | 33 | 0.800 | 0.62 |
| $t$-$C_5H_{11}O^-$ | 5 | 373 | 97 | 76 | 0.980 | 0.79 |
| sum or average | 114 | 352 | 104 | 79 | 0.888 | 0.73 |

One may also be interested in systems with a neutral donor, which donates its proton to anionic bases. Table 3 lists the results of fitting into eq 7 for systems with a fixed neutral donor and varied acceptors (anionic bases). The $x$ in the table is the ratio of proton affinities of acceptor to donor. The table gives the acidity for each donor (system), which is the proton affinity of its conjugate base, in kcal/mol. The fitting gives slope, $k$, intercept, $\alpha$, and the correlation coefficient for each system. The last column shows the $(\alpha/k)$ value, which is the intercept of the fitting line with the $x$-axis. When the acidity ratio $x$ equals $(\alpha/k)$, the hydrogen bond strength is zero. Table 4 lists the results of fitting eq 7 for systems with a fixed anionic base, the acceptor, and varied neutral donors. The average correlation coefficient $R^2$ is 0.89 in Table 3, and 0.90 in Table 4. There is almost no difference for the fitting quality between Table 3 and Table 4 for each individual line. However, when we look at the fitted constant $k$ and $\alpha$, as a function of proton affinity of the donor or acceptor, we find that there is a good correlation between the fitted constants ($k$ and $\alpha$) and the donor's PA (acidity), whereas there is almost no correlation between the fitted constants and the acceptor's PA. This is clearly seen in Figures

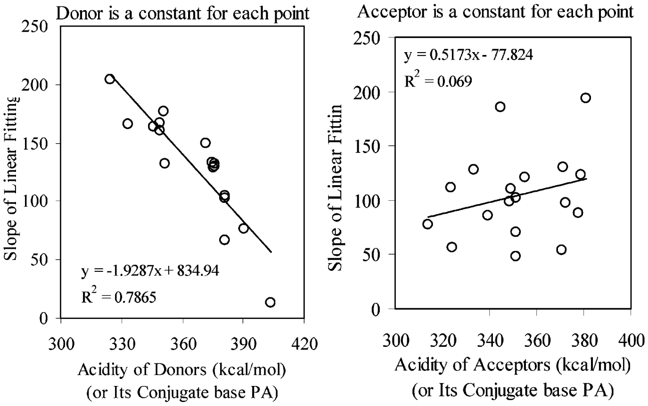

**Figure 8.** Plots of *k* as a function of donor (conjugate base) or acceptor PA for comparison. Left: donor is fixed (from Table 3). Right: acceptor is fixed (from Table 4).

7 and 8. The results are very similar to what we have found in a previous section for cationic hydrogen bond systems.

The same reasoning for the cationic systems is applicable to the anionic systems: The donor property controls the hydrogen bond formation, strength, and fitting constants ($k$ and $\alpha$) more than the acceptors, and the fitting with the donor being fixed leads to the consistency from one system to another.

**4. About the Universal Equation: Equation 10.** Because the linear fitted constant $k$ and $\alpha$ are also uniquely dependent on the donor PA, as shown in Figures 6−9, we may write one equation for all the positively charged donor systems, by substituting the linear equations for $k$ and for $\alpha$ in Figures 6 and 7 for the donor fixed plots into eq 7, which leads to eq 10. For the positively charged systems, eq 10 has the form

$$\Delta H = 0.938\mathrm{PA(D)} - 1.107\mathrm{PA(A)} + 280.6x - 218.4 \quad (11)$$

Equation 11 can be used to calculate the hydrogen bond strength for most (if not all) of the cationic complex. To calculate a hydrogen bond strength, one substitutes the donor and acceptor PA values into the equation, where $x = \mathrm{PA(A)}/\mathrm{PA(D)}$. The hydrogen bond strength calculated by eq 11 is given in kcal/mol.

Using eq 11, we recalculated the hydrogen bond strength for each of 199 hydrogen bond pairs in Table 1 and another 101 pairs that were not included in Table 1 because some sets of data have less than 3 points. All 300 calculated hydrogen bond strengths are plotted against their experiment values in Figure 10. Ideally, we should obtain an equation of $\Delta H_{\mathrm{calc}} = \Delta H_{\mathrm{exp}}$ in Figure 10. The linear line in Figure 10 has a nonzero intercept (about 2 kcal/mol), which should be related to the error limits of the experimental data and the calculation, and the slope is about 0.9, which is less than 1, indicating that the calculated $\Delta H$ is slightly smaller than the experimental values, on average. The averaged absolute difference between calculated and experimental H-bond strengths is 1.9 kcal/mol, which is close to the experimental uncertainty, with consideration of the experimental data that are from a variety of sources and methods. The largest difference between calculated and experimental bond strengths occurs for the pairs $NH_4^+\cdots C_2H_2$ and $CH_3CNH^+\cdots HCH_2Br$. Large errors for the calculations occur most of the time in a complex involving a carbon base and occasionally occur in a complex involving a −CN group. However, there is no pattern of chemically related underestimation or overestimation of the calculated hydrogen bond strengths, and therefore, except for the carbon base, the errors may be related to a variety of sources and different methods used for the measurements.

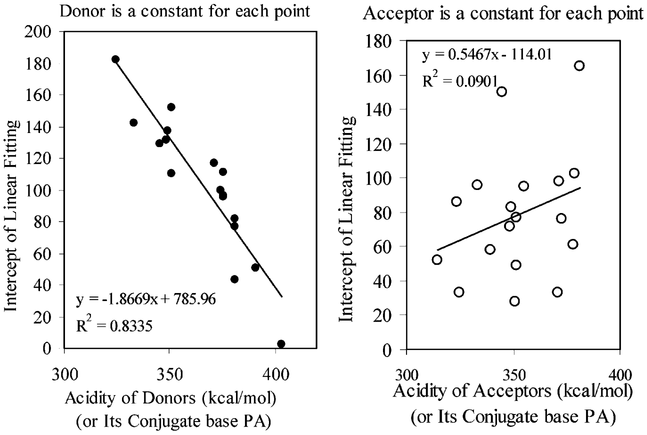

**Figure 9.** Plots of intercept, $\alpha$, as a function of donor (conjugate base) PA or acceptor PA for comparison. Left: donor is fixed (from Table 3). Right: acceptor is fixed (from Table 4).

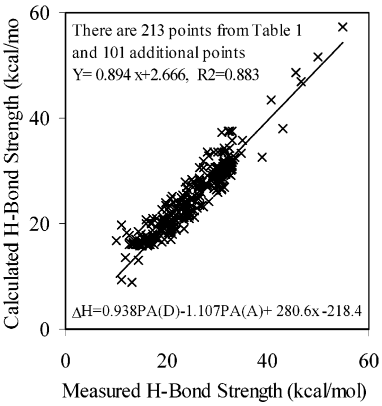

**Figure 10.** Correlations between calculated hydrogen bond strength (by eq 11) and the experimental hydrogen bond strength for all (316) positively charged pairs.

A similar treatment of Table 3 leads to a universal equation for calculation of negatively charged hydrogen bond strength:

$$\Delta H = 2.138\mathrm{PA(D)} - 2.366\mathrm{PA(A)} + 1001\mathrm{x} - 889.6 \quad (12)$$

where PA(D) is the neutral donor's acidity, PA(A) is the anion base's proton affinity, and $x = \mathrm{PA(A)}/\mathrm{PA(D)}$. To calculate an anionic complex bond strength, one substitutes PA(A) and PA(D) into eq 12 and the bond strength is given in kcal/mol. Using eq 12 we recalculated the hydrogen bond strengths for each of the 90 H-bond pairs in Table 3 and another 35 pairs that were not included in Table 3 because some donors have less than 3 acceptors available. The calculated hydrogen bond strength by eq 12 and the experimental measurement value can be related by $\Delta H_{\mathrm{calc}} = 0.998\Delta H_{\mathrm{exp}} - 0.50$ (kcal/mol) with a correlation coefficient of $R^2 = 0.801$, The averaged absolute difference between the calculated and the experimental bond strengths is about 3.2 kcal/mol, which is not as good as that for a cationic complex (eq 11), probably because of the smaller database of Table 3. The largest differences (errors) of the calculations occur in complexes involving a carbon base, such as $HCC^-$, or $C_6H_5CC^-$ and $F^-$ as acceptors. Otherwise, there is no pattern of chemically related underestimation or overestimation of the calculated hydrogen bond strengths, and therefore, the error may be related to a variety of sources and methods used for the measurements.

**5. An Exponential Form of the Universal Equation.** In Figure 1, the original author fitted the exponential curve for $Cl^-$, $I^-$, and $F^-$ as the acceptors, where the donors are all R−OH

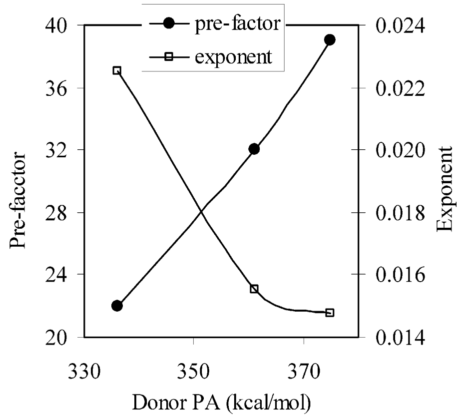

**Figure 11.** Correlation of the prefactor and exponential constant with the donor's PA value (data from Table 5).

**TABLE 5: Constants Fitting into Exponential Function from Figure 1 with ΔPA as the Variable**

| donors | PA | prefactor | exponent |
|---|---|---|---|
| HF | 375 | 39 | 0.0148 |
| ROH | 361 | 32 | 0.0156 |
| HCl | 336 | 22 | 0.0228 |

type of neutral molecules. When we keep the acceptor bases, $Cl^-$ and $F^-$, to be the same, and use HF or HCl as donor, the exponential fitted curves shift to the left and right from the original curve. This indicates that the donor controls the fitted curve constants: preexponential factor and the exponent. For example, from HF to HCl the fitted curves have a large shift (from left to right), whereas from $Cl^-$ to $F^-$ as the acceptor all the data fall on to a curve. Assuming we can fit the HF and HCl donor systems in Figure 1 in an exponential function (although only two points), we will obtain another two sets of prefactor and exponent. The fitted constants are listed in Table 5, together with the original author's fitted constants. The average acidity (anion proton affinity) for all the donors of ROH used by the author[17,18] is 361 ± 15 kcal/mol, which is also listed in Table 5 for donor RO−H.

Plots of prefactor and exponent as a function of the donor's PA from Table 5 are shown in Figure 11. It is seen that the donor PA is well related to the prefactor and the exponent by exponential functions in the figure. This figure supports the hypotheses that the prefactor and the exponent can be written as functions of "only the donor's PA". When we substitute the two new functions (prefactor and exponent as functions of the donor's PA) from Figure 11 into the hydrogen bond strength function (eq 6), we have a chance to shift all the points into one curve:

$$\Delta H = f(\text{donor PA}) \exp(-g(\text{donor PA})|\Delta \text{PA}|) \qquad (13)$$

where $f$(donor PA) and $g$(donor PA) are functions of the donor proton affinity. We do not give the real forms for the functions $f$ and $g$, because fitting with the limited 3 points is less meaningful. However, we do show the possibility of unifying all three curves in Figure 1 into one curve.

## Conclusions

1. Analysis shows that the hydrogen bond strength is a linear function of the proton affinity ratio ($x$) of proton donor to acceptor as $\Delta H = kx - \alpha$, where $k$ and $\alpha$ are constants.

2. Comparing plots of hydrogen bond strengths for cationic donor (neutral acceptor) and neutral donor (anionic acceptor) shows that the cationic donor has a stronger bond strength and is more sensitive to $x$ than the neutral donor, which is explained by the sensitiveness of the strength to less partial positive charge.

3. The analysis also leads to a conclusion that the proton donor controls the bonding strength more than the acceptor.

4. $k$ and $\alpha$, from fitting the above equation, are correlated well with the donor's PA value from one system to another, if the donor PA is a constant for each of the systems; however, a poor correlation is produced with the acceptor PA for different systems if the acceptor PA is a constant for each of the systems. This is true for both positive donors (to neutral acceptor) and neutral donors (to negative acceptor).

5. Therefore, it is possible to express the constants $k$ and $\alpha$ as functions of donor proton affinity by two linear relations, and substituting the two relations into the hydrogen bond strength equation leads to a universal equation for a variety of systems.

$$\Delta H = a\text{PA(D)} + dx - c\text{PA(A)} + e$$

where $a$, $d$, $c$, and $e$ are constants. The equation was tested with measured bond strengths with an average error (kcal/mol) of 1.9 for cationic bond pairs and 3.2 for anionic bond pairs.

**Acknowledgment.** I thank Dr. Hongyu Wang for his help, encouragement, and much useful advice. I also thank Dr. Jinru Bian for his help, encouragement, and useful comments during my literature search and writing. Thanks are also due to Dr. Terry Thomas for his useful discussions and to many people who helped me, especially the librarians in Delaware University Library.

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