Justification for the *E* and *C* Equation

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Abstract: By using the same representation for a charge-transfer complex that Mulliken employs to interpret the electronic spectrum of these complexes, it is possible to obtain an expression for the energy of adduct formation. This equation can be simplified by introducing several substantiated approximations to generate an equation of the form of the empirical *E* and *C* equation ($-\Delta H = E_AE_B + C_AC_B$). This equation has been used to successfully correlate and predict enthalpies of adduct formation. In view of the approximations made, the derivation suggests that this equation will not be as successful with data for ionic acids and bases as it was with neutral ones. A new equation results from a more appropriate set of approximations for the ionic systems ($-\Delta H = [(D_A - D_B)^2 + (O_AO_B)]^{1/2}$. The enthalpy data available support the theoretical prediction that ionic acids and bases are more suitably treated with the *D* and *O* equation and neutral acids and bases with the *E* and *C* equation. Generalizations are presented which dictate selection of the appropriate equation.

Previous reports from this laboratory have described an equation for correlating enthalpies of adduct formation[1,2] which was parameterized on the basis of Mulliken's[3] ionic-covalent description of charge-transfer complexes. The equation has the form

$$-\Delta H = E_AE_B + C_AC_B \tag{1}$$

where E_A and E_B crudely relate to tendencies of acids and bases, respectively, to undergo electrostatic bonding and C_A and C_B are similar tendencies to undergo covalent bonding. The many contributions to a complex phenomena, such as forming a covalent bond, are empirically incorporated into the *C* numbers in the parameterization making their a priori calculation difficult. The initial application of this equation to adducts of neutral acids and bases (eq 2) has recently been extended to ionic interactions of the type[4,5]

$$A + B \rightleftarrows AB \tag{2}$$

$$M^+(g) + X^-(g) \rightleftarrows M^{\delta+}X^{\delta-}(g) \tag{3}$$

In the ionic reactions, there are not enough reversals in the order of donor or acceptor strength toward different acids or bases to define a sharp minimum in a series of simultaneous equations of the form of eq 1. Accordingly, several constraints which were consistent with the ionic-covalent interpretation were imposed. However, as mentioned in the report of this work, the *R*-factor ratio[6] of this restricted fit relative to the completely unrestricted fit was not satisfactory. Furthermore, enthalpies involving the proton as the Lewis acid could not be incorporated into the fit.

Theoretical justification for the success of eq 1 is lacking. When it was first introduced,[1] justification for the existence of at least two independent contributions to the bond energy was provided by using the variation method in conjunction with the Mulliken model wave functions to calculate the ground state bond energy of the adduct. The contributions resembled electrostatic (*E*) and covalent (*C*) interactions to the bonding and the energy had a form similar to that of eq 1. Klopman[7] has subsequently shown that eq 1 can be made to be consistent with his perturbation theory approach to intermolecular interactions. In Klopman's approach, the change in energy produced during the interaction of two systems, *R* and *S*, by the partial transfer of electrons from an initially doubly occupied ψ_m of *R* to an initially empty orbital ψ_n of *S* was calculated. The interaction is assumed to occur through atoms *r* (atomic orbitals Φ_δ) of *R* and *s* (atomic orbitals Φ_σ) of *S*. For this interaction

$$\psi_m = \sum_\delta c_\delta{}^m\Phi_\delta \text{ and } \psi_n = \sum_\sigma c_\sigma{}^n\Phi_\sigma$$

Two limiting contributions to the bond energy also result from this treatment. One is termed charge controlled and the other frontier controlled with the former being equivalent to a mainly electrostatic contribution and the latter to covalent bonding. Combination of these two interactions gives rise to an equation of the form

$$-\Delta H = \left[\left(\sum_{\substack{m\\\text{occ}}} (c_r{}^m)^2\right)\left(\sum_{\substack{n\\\text{unocc}}} (c_s{}^n)^2\right)\right]\alpha_{RS} + (c_r{}^m)^2(c_s{}^n)^2\beta_{RS}$$

where α_{RS} and β_{RF} are variable parameters, characterizing the reaction of *R* and *S* in such a way that, when α_{RS} is large and β_{RF} is small, the reaction is charge controlled, whereas, when α_{RF} is small and β_{RF} is large, the reaction is frontier controlled. Equation 1 results by assuming the following equalities

$$\sum_{\substack{m\\\text{occ}}} (c_r{}^m)^2\alpha_R = E_B$$

$$\sum_{\substack{n\\\text{unocc}}} (c_s{}^n)^2\alpha_S = E_A$$

$$(c_r{}^m)^2\beta_R = C_B$$

$$(c_s{}^n)^2\beta_S = C_A$$

and

$$\alpha_R\alpha_S = \alpha_{RS}$$

$$\alpha_R\beta_S = \beta_{RS}$$

Assuming these last two equalities is in effect assuming a product relationship between *R* and *S* in determining the relative importance of charge and frontier contributions and in effect assuming eq 1. Accordingly, this analysis only indicates a way in which the two approaches are consistent. Furthermore, since Klopman's analysis is based upon a perturbation method, the resulting equations are not expected to hold for the large energies associated with many ionic reactions.

We were encouraged to seek a more general relationship between a simplified quantum mechanical description of the bonding and the *E* and *C* equation (eq 1). Reasonable approximations can be incorporated into a crude molecular orbital analysis of this problem to produce the *E* and *C* equation (eq 1). Some of the approximations which are necessary to derive eq 1 for enthalpies of interactions involving neutral acids and bases can be shown to be invalid for the large enthalpies that accompany most ionic reactions (as in eq 3). A new form for an empirical equation for enthalpies of reaction of ionic acids and bases is suggested directly from this analysis. In a subsequent paper, it will be shown that when this new equation is used to empirically fit enthalpy data corresponding to eq 3, the difficulties described in the application of eq 1 to enthalpies of ionic interactions are overcome (i.e., the proton and hydride ion can be incorporated and a good R-factor ratio results).

Calculations

Overlap integrals were evaluated using the Eunice subroutine of a previously described extended Hückel molecular orbital program.[8]

Derivations and Discussion

MO Description of the E and C Equation. The Mulliken molecular orbital formulation of charge-transfer complexes[9] will be used to derive the E and C equation. In order to simplify the mathematics, a basis set is chosen of only two orbitals, ψ_A and ψ_B. ψ_A is taken as the lowest unfilled orbital on the acid, while ψ_B may be considered as the highest filled orbital on the base most capable of donating electron density. When a complex is formed, the two basis orbitals mix to give two new orbitals

$$\begin{aligned}\psi_g &= a\psi_A + b\psi_B \\ \psi_e &= c\psi_A - d\psi_B\end{aligned} \qquad (4)$$

This is shown diagrammatically in Figure 1. In this figure, W_A and W_B are the energy levels of ψ_A and ψ_B, respectively, and W_g and W_e are the two energy levels obtained after the acid-base interaction. The total Hamiltonian for this system is symbolized by $\hat{H}$.

Mulliken has solved the secular determinant for this basis set[9] in order to calculate the energy of the charge-transfer transition in the electronic spectrum. The solution is

$$W(1 - S^2) = (^1/_2)(H_B + H_A) - SH_{AB} \pm \sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_B\beta_A} \qquad (5)$$

where $H_B = \int\psi_B\hat{H}\psi_B d\tau$, $H_A = \int\psi_A\hat{H}\psi_A d\tau$, $H_{AB} = \int\psi_A\hat{H}\psi_B d\tau$, S is the overlap integral ($S = \int\psi_A\psi_B d\tau$), and β_B and β_A are the off-diagonal terms of the secular determinant.

$$\begin{aligned}\beta_A &= H_{AB} - SH_A \\ \beta_B &= H_{AB} - SH_B\end{aligned} \qquad (6)$$

The heat given off in a chemical reaction, $-\Delta H$, is equal to the energy of the original state minus the energy of the final state. The original state consists of 2 electrons in the base orbital, ψ_B, whose energy level is given by the negative of the ionization energy of the base. The final state consists of 2 electrons in the lower energy complex molecular orbital whose energy is given by solving eq 5 for W, using the negative sign for the square root term. The enthalpy measured in terms of 1 electron molecular orbital energies is the difference between two times the energy of the final bonding molecular orbital and the energy of the initial state with 2 electrons on the base. This quantity is given by

$$-\Delta H = -\frac{H_A + H_B}{1 - S^2} + \frac{2SH_{AB}}{1 - S^2} + 2\frac{\sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_A\beta_B}}{1 - S^2} - 2I_B \qquad (7)$$

where I_B is a positive quantity, the ionization energy of the base.

Our approach will involve the introduction of reasonable simplifying assumptions to convert eq 7 into an equation resembling eq 1. The following relationships are reasonable for the interactions to be covered here.

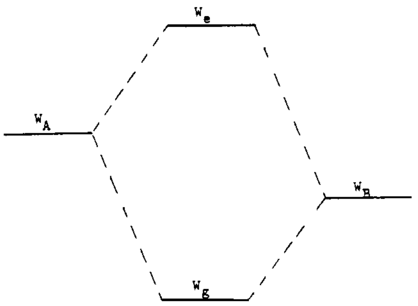

Figure 1. Energy level diagram for a typical acid-base interaction.

$$1 - S^2 \approx 1 \qquad (8a)$$

$$H_{AB} = S(H_A + H_B) \qquad (8b)$$

Equation 8b is simply the Mulliken approximation with C equal to unity.[10,11] Substituting these equations into eq 7 and realizing that $(2S^2 - 1)/(1 - S^2)$ is very close to -1 yields eq 9.

$$-\Delta H = -(H_A + H_B) + 2\sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_A\beta_B} - 2I_B \qquad (9)$$

The following assumptions are applicable to enthalpies of adduct formation involving neutral acids and bases (i.e., of the type shown in eq 2). A treatment of reactions involving ionic acids and bases will follow. The ionization energies, I_B, of typical neutral bases and electron affinities, ϵ_A, of typical neutral acids are about 200 and 55 kcal mol^{-1}, respectively.[12] Typical enthalpies of interaction, $-\Delta H$, are about 10 kcal mol^{-1}.[1,2] Since the interaction is weak, the amount of charge donated by the base to the acid is also fairly small. Therefore, the new energy levels are close to the initial states. Under these conditions, the integrals H_A and H_B can be approximated by a charge corrected ionization energy which, for small changes in charge, can be approximated by a linear function. Therefore

$$H_A = -\epsilon_A(1 - \Delta_A q_B) \qquad (10)$$

$$H_B = -I_B(1 + \Delta_B q_A) \qquad (11)$$

where Δ_A and Δ_B represent the relative change in energy level per unit charge for the acid and base, respectively, q_A is the absolute value of the amount of charge accepted by the acid and for a given adduct equal in magnitude to q_B, the absolute value of the amount of charge donated by the base. For a given base, q_B will depend on the acid. Δ can be thought of as $|(1/E)\ \partial E/\partial q|$ where E is energy and q is charge. Signs have been included in eq 10 and 11 to incorporate the sign conventions for I_B and ϵ_A and to account for the fact that charge is transferred from the base to the acid. I_B, ϵ_A, and ΔH_D, the dissociation energy, are defined as positive numbers, and ΔH, H_A, and H_B are all negative numbers.

We can next simplify eq 9 by using the general expression

$$\sqrt{1 + X} \approx 1 + (X/2) \qquad (12)$$

$$2\sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_A\beta_B} = (H_A - H_B)\left(1 + \frac{2\beta_A\beta_B}{(H_A - H_B)^2}\right) \qquad (13)$$

The square root in eq 9 becomes eq 13. (Squaring both sides of eq 12, we see that the error in the square of eq 12 introduced by using this approximation is equal to $X^2/4$. With the aid of eq 6 and 8b, the error in using the square of eq 13 can be shown to be $[2S^2H_AH_B/(H_A - H_B)^2]^2$. Using the previously mentioned values of electron affinities and ionization potentials in place of H_A and H_B, respectively, and a value of 0.2 for S (which is a generous guess), we find that the relative error in the sqaure root term introduced by this approximation is about 0.2%. Equation 13 is obviously a good approximation for adducts of neutral acids and bases.) Using the relationships in eq 8a, 8b, and 13, eq 9 becomes

$$-\Delta H = -(H_A + H_B) - 2I_B + (H_A - H_B) \times \left(1 + \frac{2\beta_A\beta_B}{(H_A - H_B)^2}\right) = -2H_B - 2I_B + \frac{2\beta_A\beta_B}{(H_A - H_B)}$$

Substituting eq 11 for the first term in the above result yields

$$-\Delta H = +2I_B(1 + \Delta_B q_A) - 2I_B + \frac{2\beta_A\beta_B}{(H_A - H_B)} = +2I_B\Delta_B q_A + \frac{2\beta_A\beta_B}{(H_A - H_B)} \qquad (14)$$

Substitution of the Mulliken approximation (eq 8b) for H_{AB} in eq 6 leads to $\beta_A = \mathrm{K}SH_B$ and $\beta_B = SH_A$, and making these substitutions into eq 14 produces

$$-\Delta H = 2I_B\Delta_B q_A + \frac{2S^2H_AH_B}{(H_A - H_B)} \qquad (15)$$

We can assume that H_A and H_B are functions of the acid and base only in the latter term because the corrections in eq 10 and 11 are small compared to one for neutral adducts. (The term $2I_B\Delta_B q_A$ of eq 14 is ~2-10 kcal mol^{-1} and, since I_B is large, ~200-300 kcal, $\Delta_B q_A$ must be very small.) The denominator in the second term of eq 15 will have a larger contribution from the H_B term than from the H_A term for most of the neutral acids in the E and C correlation (the lowest ionization energy for a base is 181 kcal mol^{-1} for triethylamine while the electron affinity of even the stronger acids, for example, BF_3, is only ~50 kcal mol^{-1}).[12] Thus, $H_A - H_B$ is largely a property of the base and when the last term in eq 15 is replaced by empirical parameters, the $H_A - H_B$ term is incorporated into a base parameter which we shall call C_B'. If H_A does become large enough to be appreciable for a particular acid, the acid parameter, C_A', can be empirically adjusted to compensate. This is comparable to claiming that for neutral adducts the range of values for $H_A - H_B$ can be fit to a product function, X_AX_B. The product, X_AX_B, for a selection of values with $H_B \gg H_A$ can be shown to reproduce $H_A - H_B$ over a range comparable to the ionization potentials and electron affinities of the bases and acids, respectively, incorporated in our fit. (All of the values of $H_A - H_B$ for H_B = 300, 250, 200, and 175 and H_A = 5, 10, 20, 30, 40, 50, and 60 could be fit with a product function X_AX_B to better than 5% and most to 2%. When an H_A value of 75 was included, an 8% miss arose.) If S^2 can also be represented by a product function,[13] the last term of eq 15 has a form $S_AC_A'S_BC_B'$ and the resulting equation

$$-\Delta H = 2I_B\Delta_B q_A + S_AC_A'S_BC_B' \qquad (16)$$

is readily converted into the E and C equation with the equalities

$$2q_A = E_A;\ \Delta_B I_B = E_B;\ C_A = S_AC_A';\ C_B = S_BC_B' \qquad (17)$$

In our parameterization q_A indicates the extent to which a given acid perturbs the energy of the electrons that are on the base and causes them to be held more tightly. This is thus a one-center term. Any small contributions from C of eq 8b not being unity would give an H_A contribution to this term which can also be handled with this product type function in the parameterization of the acid and base parameters. To the extent that E_AE_B consists only of one-center integral approximations and C_AC_B two center, this result is consistent with our earlier claims[1] that the C_AC_B product corresponds to covalency and E_AE_B to ionic bonding. The remaining difficulty with the expressions in eq 16 is that q_A is not a constant, but varies with the donor. However, in view of the slight amount of actual charge transfer in most of these adducts, variations from this effect can be empirically compensated for in the parameterization of the acid and the base, i.e., the product E_AE_B is corrected for this effect by appropriate adjustment of the E_B parameter.

Enthalpies of Interactions of Ionic Acids and Bases. An important difference between reactions of ionic and neutral acids and bases lies in the magnitude of the energies involved. Typical ionization energies for an ionic base range from around 20 to 80 kcal/mol[14] while typical electron affinities for ionic acids range from about 100 to 250 kcal mol^{-1}.[15] (Much more of these fundamental data are available for ionic acids and bases than for neutral ones.) Since typical enthalpies of interaction for ionic systems range from 150 to 250 kcal/mol,[4,5] the interaction is comparable to the original energy levels. Since S will still be small (usually 0.1–0.3), eq 9 will still be valid. We choose to rewrite eq 9 in the following form

$$-\Delta H = -H_A - (H_B + 2I_B) + 2\sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_A\beta_B} \qquad (18)$$

Again, we are confronted with the problems that H_A is not independent of the base nor H_B of the acid. For the neutral adducts, where the enthalpy is at most 20–30 kcal/mol, we employed eq 10 and 11 and showed $H_A - H_B$ could be fit with a product function because H_B was dominant. In the ionic systems, H_A and H_B are often of comparable magnitude. Furthermore, we shall not bother to adjust H_A or H_B with eq 10 or 11 because this is a minor correction for the ionic systems. This can be demonstrated by using eq 10 and 11 to obtain an estimate of the error generated by assuming that H_A is independent of the base and H_B is independent of the acid. In eq 18, the first two terms, $-H_A - (H_B + 2I_B)$, will have an error less than or equal to $-q\epsilon_A\Delta_A + qI_B\Delta_B$, where q is the total charge transferred. For a given acid, q does not vary a great deal from base to base. The difference in the formal charge of carbon in CH_3OH and CH_3-CH_3 (i.e., CH_3^+ reacting with OH^- and CH_3^-) is 0.07 from extended Hückel calculations.[16] Therefore, $q\epsilon_A\Delta_A$ is expected to be very nearly constant for given acids (e.g., CH_3^+) combining with all the bases involved. We would also expect that $qI_B\Delta_B$ will be very nearly constant for a given base. Furthermore, since $-q\epsilon_A\Delta_A$ and $+qI_B\Delta_B$ have opposite signs, the corrections will tend to cancel. Clearly, in the term $-H_A - (H_B + 2I_B)$, the quantities H_A and H_B can be represented by constant empirical parameters of the acid and base with little loss in accuracy relative to the large enthalpies for ionic systems.[17] Again, this is comparable to assuming that the acid–base interactions are inherent properties of the cations and anions and not a function of the individual adducts only. This assumption is inherent in talking about the acidity or basicity of a molecule and has been made in acid–base chemistry for years. We shall subsequently demonstrate that the entire $-H_A - (H_B + 2I_B)$ term can be incorporated into the empirical parameters leading to an even smaller relative error in assuming that $H_A - H_B$ can be reproduced with empirical parameters which are functions of the acid only and the base only. In absolute terms, this error will probably amount to ~5 kcal/mol. An error this large could not be tolerated for small enthalpies of adduct formation of neutral acids and bases. However, for ionic acids and bases, this value is often within the experimental error. It should be pointed out that the fitting of the error generated by this replacement becomes important and must be considered when one attempts to interpret small differences in the parameters (which will be presented in a subsequent paper) for the ionic systems.

One additional difference between the ionic and neutral systems is that we can no longer use eq 13 to simplify the square root term for the ionic systems. Using typical values for ionic systems, the error estimate from using eq 13 increases from a lower value of 4% for many systems to as high as 80% for sodium chloride. Therefore, the simplification in the equation for neutral systems, introduced by using eq 12, is not possible for ionic systems.

We shall proceed with the simplification of eq 18 for ionic systems and define for convenience a quantity "ΔH_c" as follows

$$-\Delta H_c = -\Delta H + H_A + (H_B + I_B) \qquad (19)$$

This definition converts eq 18 into the equation

$$-\Delta H_c = 2\sqrt{\left(\frac{H_A - H_B}{2}\right)^2 + \beta_A\beta_B} \qquad (20)$$

We are still confronted with the problem that β of eq 20 is still a function of both the acid and the base (i.e., eq 6 contains H_{AB}). If one expands β_A and β_B using eq 6 and the Mulliken approximation, $H_{AB} = CS(H_A + H_B)$,[10,18] and substitutes the resulting expressions into eq 20, one obtains

$$-\Delta H_c = \sqrt{(H_A - H_B)^2 + 4[SC(H_A + H_B) - SH_A][SC(H_A + H_B) - SH_B]}$$

Squaring the above equation results in

$$\Delta H_c^2 = (H_A - H_B)^2 + 4S^2C^2(H_A - H_B)^2 - 4S^2C(H_A + H_B)^2 + 4S^2H_AH_B$$

which can be rearranged to

$$\Delta H_c^2 = [1 + 4S^2(C^2 - C)](H_A - H_B)^2 + 4S^2(1 + 4(C^2 - C))H_AH_B \qquad (21)$$

This enables us to rewrite eq 20 as

$$-\Delta H_c = \sqrt{A(H_A - H_B)^2 + BS^2H_AH_B} \qquad (22)$$

where

$$A = (1 + 4S^2(C^2 - C))$$
$$B = 4(1 + 4(C^2 - C))$$

Since C is on the order of unity and S is small, A will be very close to unity. If we express S^2 as $S_A{\cdot}S_B$, we now have eq 23 in terms of two empirical D and O parameters

$$-\Delta H_c = \sqrt{(D_A - D_B)^2 + O_AO_B} \qquad (23)$$

where D refers to quantities arising from the diagonal terms of the Hamiltonian matrix and O refers to off-diagonal contributions. The former are mainly one center in nature and the latter two center. We should emphasize that D_A does not equal H_A. D_A is obtained empirically and has in it contributions previously discussed (see eq 18 and the ensuing discussion leading to eq 20). This same restriction applies to our other parameters.

With regards to the practical application of eq 23, the quantity $-\Delta H_c$ is the remaining complication. From the discussion following eq 18, it can be seen that one should fit the quantity, $-\Delta H + D_A + (D_B + I_B)$, with the right-hand side of eq 23. It must still be determined whether or not the constant parameters of the acids and bases which are outside the square root sign can be incorporated into the parameters under the square root. The approach taken is to attempt a fit of the values of ΔH_D and $-\Delta H$ (for the ionic reaction) to this function. When the right-hand side of eq 23 is used to fit $-\Delta H$, the term $D_A + D_B + I_B$ is being ignored. By fitting ΔH_D it is assumed that this term is equal to the ionization potential of the base minus the electron affinity of the acid. If a good fit is obtained in both instances, it is reasonable to believe that the $(D_A - D_B)$ parameters inside the square root in eq 23 can adjust appropriately to include the contribution from the D parameters on the outside of the square root in eq 18. We find that the dissociation energies can be fit as well as the enthalpies for the ionic reactions (eq 3) by equations of the form of eq 23 in which ΔH_D or $-\Delta H$ is substituted for $-\Delta H_c$, i.e., the equation to be used is

$$-\Delta H = \sqrt{(D_A - D_B)^2 + O_AO_B} \qquad (24)$$

Data on about 100 widely different reactions were fit.

Equation 24 reproduces the enthalpies of the ionic reactions much better than the original E and C fit we have reported.[4] We have shown that quantities which are constant for a given acid or base can be incorporated into the D and O parameters without loss of accuracy. In this connection, the functional form of eq 24 is very much different than that of eq 1. It has been shown[19] that the adducts of neutral acids and bases are so parameterized that a constant contribution to the enthalpy for adducts of neutral acids and bases spoils the data fit to such a degree that this constant contribution can often be independently determined.

It was of interest to determine the ability of the parameters to incorporate the $(1 - S^2)$ quantity that we had neglected earlier. Accordingly, the data on 42 systems whose overlap integrals could be calculated were found to give a range of $1 - S^2$ values from 0.85 to 0.95 and to fit eq 25 as well as eq 24.

$$-\Delta H(1 - S^2) = \sqrt{(D_A'' - D_B'')^2 + O_A''O_B''} \qquad (25)$$

Our theory thus predicts that, depending on circumstances, one must select eq 1 or 24 to predict enthalpies. The next section will indicate the criteria to be employed in making the selection.

Practical Consequences. The theoretical analysis that has just been completed accounts for the failure of eq 1 to produce satisfactory parameters for enthalpies corresponding to the combination of cations and anions. Furthermore, it predicts a form for an equation which is successful in correlating data on these systems. As expected from theory, this new equation (the D and O equation) does not fit enthalpies of interaction of neutral acids and bases as well as the E and C equation.

From an analysis of the approximations used in the above derivations, one can find the conditions under which the E and C equation (eq 1) or the D and O equation (eq 24) should no longer be applicable. The use of eq 11 in the derivation of eq 1 restricts its applicability to prediction of enthalpies of interactions where the amount of electron density transferred from the base to the acid is small enough so that the energy of the acid and base orbitals can be approximated by a linear function of charge. Since in most neutral adducts the amount of charge transfer is expected to be less than 0.5, this is a good approximation. For all of the acid–

base interactions to which eq 1 and 24 have been applied,[2,4] the change in the occupation numbers has been less than unity. One would not expect these equations to predict the enthalpy of a reaction where more than one electron is transferred as, for example, in F^+ reacting with CH_3^- to produce CH_3F.

As mentioned previously, the relative error in the square root term of eq 9 introduced by using eq 13 can be approximated by

$$[2S^2 H_A H_B/(H_A - H_B)^2]^2$$

If an arbitrary upper limit of 5% (0.05) is imposed on the error which will be accepted, the condition that results is

$$2S^2 H_A H_B/(H_A - H_B)^2 \leq \sqrt{0.05} = 0.22$$

Using a value of 0.1 for S (which is a reasonable value for adducts of neutral acids and bases), it is found that

$$H_A H_B \leq 11(H_A - H_B)^2$$

If values of ϵ_A are used to approximate H_A and values of I_B are used to crudely approximate H_B, it can be seen that the above condition holds when ϵ_A and I_B are sufficiently different for a given acid and base. As these two energies become similar, the error involved in using eq 13 becomes larger and eq 1 should not be employed to correlate the experimental enthalpies. The term $S^2/(H_A - H_B)$ of eq 15 can be fit by a product function over only limited ranges, so this will also cause complications as H_A approaches H_B.

The electron affinity of the acid and the ionization energy of the base must fall within a range such that the product of ϵ_A and I_B is less than 11 times the square of the difference between ϵ_A and I_B. Furthermore, if ϵ_A and I_B lie outside the range of acids and bases currently in the system (roughly, 30 to 75 kcal/mol for ϵ_A and 175 to 300 kcal/mol for I_B), caution should be used in extending eq 1 to cover them until it is established that $S^2/(H_A - H_B)$ can be fit to a product function for all the systems in the correlation. The ionic systems do not meet these requirements and accordingly eq 24 will be utilized.

The only theoretical limitation placed on the use of eq 24 occurs as a result of the assumption that H_A and H_B for a given acid or base can be approximated by a constant, i.e., no charge correction term is utilized. As mentioned earlier, the error generated by this approximation is estimated to be a few kilocalories per mole. When this error amounts to a significant fraction of the enthalpy (i.e., enthalpies of adduct formation below about 30 kcal/mol), the E and C equation should be utilized. For enthalpies larger than about 30 kcal/mol, eq 24 may be used quite generally.

Effects Incorporated by the Parameterization. Mulliken's molecular orbital description of the charge-transfer complex, employing only an empty orbital on the acid and a filled orbital on the base, is a vast simplification of the actual changes which occur when an acid and a base form an adduct. For example, the acid and base invariably undergo changes in geometry in the course of adduct formation. Furthermore, in most adducts, the electrons in other orbitals of the acid and base besides the donor and acceptor orbitals are undergoing repulsive interactions. We shall first consider this latter effect as an illustrative example of the various ways whereby the empirical parameterization can incorporate many energetic contributions which may have been ignored in the theoretical treatment.

We have in the correlation acids with only one pair of bonding electrons attached to the acidic center and these are 180° away from the donor lone pair (e.g., hydrogen bonding acids), others with three lone pairs and a bonding pair on the acidic atom (e.g., I_2), still others with nonbonding d electrons, and various combinations of these. The acid's electrons are interacting with bases that have varying numbers of lone pair and bonding pair electrons. These properties of the individual acids and bases must somehow be incorporated into the E and C parameters so as to produce the proper contribution to the measured enthalpy from these effects. This incorporation may be accomplished in the following way. Since the electrostatic attraction is given by a product function, it is reasonable to assume that repulsive interactions might also be represented in this way, i.e., by an $R_A R_B$ term. Thus, it is necessary to show that the E and C equation is in fact equivalent to the equation

$$-\Delta H = E_A'E_B' + C_A'C_B' - R_A R_B \qquad (26)$$

To accomplish this, we shall show that one can modify an E and C number that does not incorporate repulsive effects to include them without changing the form of the E and C equation. Trial and error shows that the following is one way of accomplishing this. Let us define

$$E_A = E_A'' + R_A' \qquad C_A = C_A'' + R_A'$$

$$E_B = E_B'' - R_B' \qquad C_B = C_B'' - R_B'$$

where the double prime indicates the E and C parameters devoid of the repulsive contribution, R_A' and R_B' are the corrections that must be included in E and C to effect the $R_A R_B$ correction. Substituting these new definitions of E and C into eq 1, we have

$$-\Delta H = E_A E_B + C_A C_B = E_A''E_B'' + R_A'E_B'' - R_B'E_A'' - R_A'R_B' + C_A''C_B'' + R_A'C_B'' - R_B'C_A'' - R_A'R_B' = E_B''(E_A'' + R_A') + R_B'(-E_A'' - 2R_A' - C_A'') + C_B''(C_A'' + R_A')$$

Letting $E_B'' = E_B'$, $E_A'' + R_A' = E_A' = E_A$, $R_B' = R_B$, $E_A'' + 2R_A' + C_A'' = R_A$, $C_B'' = C_B'$, and $C_A'' + R_A' = C_A' = C_A$, we obtain eq 26. Thus, it is shown that eq 26 can be made equivalent to the E and C equation with the proper parameterization. Also, note that although there are restrictions on E_A', R_A, and C_A'; these are each multiplied by a parameter (E_B', R_B, or C_B') for which there are no restrictions so the products $E_A'E_B'$, $C_A'C_B'$, and $R_A R_B$ are not fixed.

The quantities C_A'' and C_B'' above were defined as the covalent parameters in the absence of electrostatic repulsion. This quantity is also a complex one. It undoubtedly contains contributions from the quantity referred to in the literature as the *promotion energy*. This is the energy associated with the geometry change a molecule undergoes when it forms an adduct. The early literature[20] considered this to be a constant quantity associated with the energy required for a given acid to be made ready (i.e., bonds lengthened or bent as when BF_3 coordinates to a base) to form an adduct. In a study[21] of the relationship between $-\Delta H$ of adduct formation and the changes in the carbonyl stretching frequency of ethyl acetate upon formation of the adduct, it was shown that such a view of reorganization energy was inconsistent with a large amount of experimental data. It was proposed that the amount of reorganization of the atoms in an acid (or base) that occurs during adduct formation is variable and depends upon the base (or acid) employed. Systems which illustrated a variable amount of reorganization were presented. We did not understand how this information about reorganization could be incorporated into the E and C numbers, but the following discussion indicates one way that this could occur. For convenience, we shall propose that the extent of reorganization is proportional to the covalency in the interaction, i.e., the $C_A C_B$ product is in reality $k_A C_A{}^0 k_B C_B{}^0$. Basically, then, we are claiming that the actual value given for the $C_A C_B$ contribution to the bonding is some fraction of the covalency that would result if no energy were required to rearrange the acid, i.e., $C_A{}^0C_B{}^0$. With C_A, then, given by $C_A{}^0 - k_A'C_A{}^0$ and $C_B = C_B{}^0 - k_B'C_B{}^0$, we obtain

$$C_AC_B = C_A{}^0C_B{}^0 - k_A'C_A{}^0C_B{}^0 - k_B'C_A{}^0C_B{}^0 + k_B'k_A'C_A{}^0C_B{}^0 = (1 - k_A')(1 - k_B')C_A{}^0C_B{}^0 = k_Ak_B\,C_A{}^0C_B{}^0$$

Thus, there could readily be incorporated into the E and C numbers a proportionality constant k_A' for each acid or k_B' for each base which would approach unity when the acid or base is difficult to polarize and approaches zero when it is not. The k' values can be viewed as the slope of a plot of $\Delta E/C^0$ vs. a distortion parameter where ΔE is the energy required for a given distortion. The extent to which a given acid would be polarized in an adduct would depend upon $k_BC_B{}^0$ for the base. Recall that there is no way to factor $k_BC_B{}^0$ out of the C_B number in such a way as to be able to obtain values for k_A or k_B. This discussion should serve to show that any effect which is proportional to covalency or to $-\Delta H$ can be incorporated into our parameters. It should also indicate that the a priori calculation of the E and C parameters from quantum mechanics must await improved methods which enable us to calculate these various effects accurately and sort them out.

It is important to distinguish between a variable reorganization energy and a constant contribution to the enthalpy of a reaction. This latter effect occurs when an associated molecule must be completely dissociated to form an adduct, e.g.

$$B_2H_6 + 2(CH_3)_3N \longrightarrow 2(CH_3)_3NBH_3$$

The energy of dissociation of the diborane dimer makes a constant contribution to ΔH for every 1:1 adduct that diborane forms. The inability of the E and C equation to incorporate this constant value has been used as a means of determining the constant enthalpy value.[19] From this discussion, it should be clear that if an acid existed which had a constant promotion energy it would not fit the E and C equation when studied with a wide range of bases (i.e. varying C_B/E_B).

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(17) By ignoring the charge correction, the term under the square root in eq 18, $((H_A - H_B)/2)$, will have an error less than or equal to one-half the sum of $q\epsilon_A\Delta_A$ and $qI_B\Delta_B$. As stated above, the variation caused by these two terms from a constant empirical value that could be found for the acid or base is not expected to be large. If the terms $\epsilon_A\Delta_A$ and $I_B\Delta_B$ were as large as ϵ_A and I_B, respectively, neglect of these terms would cause a 22% error in $H_A - H_B$ for a range in q equal to 0.07 for $CH_3{}^+$ and its adducts and 0.2 for Cl^- and its adducts. If we replace $H_A - H_B$ with empirical parameters, the error in this term will be averaged out to at most 11%. Furthermore, this is only one of the two terms contributing to ΔH reducing the relative error in the predicted enthalpy still further. However, even more important, this 11% is not a random error. Some bases tend to form adducts which have a large amount of electron transfer and others do not. Certain acids tend to form adducts with greater electron transfer than others. Accordingly, these systematic trends will be incorporated into our parameters when they are simultaneously varied in attempting an empirical fit and our estimate of the potential error is better than 5%.
(18) We could use eq 8b as used previously to obtain eq 15. The result (eq 22) would be identical. However, we present this alternative approach to demonstrate that both eq 15 and 22 would be valid even if the value of C that is used is not exactly unity.
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