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A Method for the Analysis and Prediction of Gas-Phase Ion-Molecule Enthalpies

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Abstract: Solution-based E_B and C_B parameters are applied to fit gas-phase ion-molecule enthalpy changes, greatly extending the range of systems covered and consequently the utility of the E and C model. Several significant insights result from the data fit. The use of E_B and C_B parameters to fit enthalpy changes for cations coordinating to Lewis bases in the gas phase supports earlier proposals that the solution enthalpies used to obtain E and C values have minimal solvation contributions. The reported analysis provides a direct link between conventional Lewis acid-base interactions and gas-phase ion-molecule reactions. The trends in the fraction of covalent and electrostatic contributions (C_AC_B/E_AE_B) to most reactions $M^+(g) + B(g) \rightleftharpoons MB^+(g)$ are seen to parallel base HOMO and acid LUMO energies. The trends in the covalent, electrostatic, and transfer terms for the amines reacting with the proton are in good agreement with similar quantities from literature ab initio calculations on these systems. Comparison of gas-phase interaction energies of a series of bases with a new ion to those for the proton, or to other ions, as a reference is found to be a questionable procedure because different donor orders result for acids that are significantly more electrostatic or covalent in their interaction than the reference. On the other hand, an ECT analysis with the parameters reported here provides a quantitative estimate of σ donor strength, and when deviations do occur they signal the existence of unusual effects in the gas-phase chemistry, e.g. repulsive effects, π-back bonding, or adduct geometry variation from multiple donor coordination sites. Insights relative to the proper design of a gas-phase experiment are also provided by this analysis. If the C/E ratio of all the bases studied is the same, the covalent and electrostatic nature of the cation cannot be determined no matter how large the data set. These data will plot up linearly with the proton affinity, and the ion will be incorrectly interpreted as being similar. The C_B and E_B values reported here should be employed to select different bases for study in a properly designed experiment. This analysis demonstrates that care must be exercised in using gas-phase cation enthalpies to analyze solution data (e.g. proton affinities and pK_B). In the case of gas-phase interactions, the enthalpy is dominated by a transfer term that is largely cancelled out in the solution phase where displacement reactions usually occur. The transfer contribution is very large for the proton and makes proton affinities poor reference acids to employ for the interpretation of solution chemistry.

Introduction

Solution enthalpy changes upon adduct formation between neutral molecule, Lewis acids, and bases

$$A + B \rightleftharpoons AB$$

can be fit to the E, C, W equation with considerable success:[1,2]

$$-\Delta H = E_AE_B + C_AC_B - W \qquad (1)$$

Proper solvent selection,[1] to avoid specific acid-base interactions of the solvent with the reactants and products, produces enthalpy changes ($-\Delta H$) with minimal solvation energy contributions because nonspecific solvation of the products and reactants cancels out. The basis for eq 1 is Mulliken's description of charge-transfer complexes. The E_A and C_A parameters parallel qualitative notions of the acid's tendency to undergo electrostatic and covalent bonding, respectively, and E_B and C_B are the corresponding base parameters. The term W, which usually is zero, is a constant contribution to the enthalpies of reaction for a particular acid (or base) that is independent of the bases (or acids) reacting. For example, in the case of the dimeric acid $Rh_2(CO)_4Cl_2$, reacting to form B-$Rh(CO)_2Cl$ adducts, W corresponds to the enthalpy of cleaving the dimer. The E and C portion of the equation corresponds to the exothermic interaction of the donor with the monomeric acid. Since the amount of energy required to cleave the dimer will be the same regardless of the donor, the constant contribution must be accommodated in eq 1 by the W term.

The ECW model provides a basis for determining expected trends in Lewis acid-base coordination strength for normal, σ-bonded systems. Substitution of the reported, empirical ECW parameters into eq 1 predicts the enthalpy of adduct formation for over 2000 adducts with an expected accuracy of ±0.2 kcal mol^{-1} or to 1% for larger enthalpies. When larger deviations in calculated and experimental values exist, they signify the presence of additional bonding effects and provide a quantitative basis for invoking steric effects, π-back-bonding donation, etc. in the interpretation of data. Once deviations are found, experiments can be designed to probe these interpretations[2] and the guess work is taken out of invoking such explanations.

Unfortunately, ionic species are insoluble in poorly solvating solvents, so solution data with minimal solvation contributions are not available to quantify the acidity or basicity or ions with the ECW model. The advent of ICR and other related high-pressure techniques has produced a wealth of data for ion-molecule reactions in the gas phase.[3-12] The enthalpies for binding many of the bases in the ECW studies have been measured toward the proton, lithium, trimethyltin, nickel(II) cyclopentadienide, etc. cations. This technique allows one to obtain thermodynamic data

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concerning bond strengths without the added complexity of solvent effects and thus has the potential of providing valuable insights concerning the electronic factors influencing coordinate bond strength and facilitating the understanding of solvation contributions to reactivity.

In most of the literature on gas-phase ion–molecule systems, data for a new ion are compared by plotting the enthalpies against proton affinities or some other reference acid with the absence or existence of a linear relationship noted. Often electronic interpretations are offered for the systems that deviate. We have shown[13] that such an analysis can be misleading for neutral addition compounds. A straight line will result for a plot of enthalpies of two different acids reacting with a series of different bases only if the C_A/E_A ratios of the acids are comparable.[14] Deviations from such plots caused by differences in the covalent contribution to the σ bonding in the acids (i.e. different C/E ratios) have been incorrectly concluded to result from steric effects or π-back-bond stabilization for neutral addition compounds.[13] Furthermore, if all the bases used in a study of two different acids have similar C_B/E_B ratios, a straight line enthalpy plot will result even if the acids differ appreciably in the importance of the covalent interaction,[15] and the incorrect conclusion that the acids are similar would have been made. When this plot of data with similar bases is used to predict enthalpies for interactions for a new, more (or less) covalent acid from known enthalpies of the reference acid, incorrect estimates will result for those bases that have a different C_B/E_B ratio than those used in the plot. Similar problems are expected in plots of gas-phase data for cation versus proton affinities when the C_A/E_A ratio of the cation differs from that of the proton.

The long-recognized need of a quantitative model for the interpretation of gas-phase ion–molecule interactions has prompted several attempts to analyze gas-phase ion–molecule data.[16,17] The E and C equation ($W = 0$) does not provide a reasonable fit. The gas-phase enthalpies are much larger and additional contributions besides E and C are present in the measured enthalpies. For example, cations in the gas phase have significant enthalpies of interactions with Ar, Xe, Kr, CH_4, etc. Since there is no detectable interaction of I_2 or C_6H_5OH with these molecules, their E_B and C_B values must be near zero. In the latest[16c] analysis of gas-phase ion–molecule data, the E and C model was modified for gas-phase ions with the addition of a new term $t_a t_b$ to accommodate these added effects:

$$-\Delta H = e_a e_b + c_a c_b + t_a t_b \qquad (2)$$

Here e_a, c_a, e_b, and c_b are gas-phase counterparts of the terms in eq 1. The lower case letters are employed to emphasize that the resulting empirical parameters are not compatible with the E and C parameters from the neutral acid–base fit. The $t_a t_b$ term takes into account the changes in the one-center energy contribution to the total energy that occur when a base coordinates to a cation. The cation (M^+) gains electron density at the expense of the base via the electron transfer that occurs upon coordination. The driving force for the electron transfer comes from the stabilization of this electron density on the cation. Furthermore, the proximity of the base to the cation modifies the one-center nuclear–electron interactions in the cation and the base. A quantum mechanical description of this effect is offered by Kutzelnigg,[18] who also breaks the σ bond energy up into three independent terms. Added support for eq 2 comes from the derivation of an expression of this form from the quantum mechanical expression of the energy of the acid–base interaction.[19] The $t_a t_b$ contributions are minimal in molecule–molecule interactions because the extent of electron transfer to the neutral acid is small and the small energy change that occurs in the corresponding one-center terms upon coordination is readily incorporated into E and C.

The gas-phase data available at the time of the last reported fit[16c] obeyed eq 2 very well; however, several shortcomings were observed. Most of the ions were similar, making it difficult to find a unique minimum in the data fit. Insights about coordination from trends in the e, c, and t parameters could not be obtained because the parameters are not uniquely determined. The poor definition of the parameters does not allow one to predict enthalpies on new systems with confidence.[5] Further, direct comparison of the e, c, and t parameters of ions with the neutral fit E and C parameters is not possible. A matrix transformation that converts e_b, c_b, and t_b to E_B and C_B has been found;[15b] however, the reverse transformation utilizing the better determined E and C values is not possible. Thus, the enthalpies for the neutral systems provide no information for the cation–neutral base fit. As a consequence of these shortcomings, the ect model has been of little utility in the analysis of gas-phase ion chemistry.

Recently,[20] it was reported that eq 1 could be used to fit the gas-phase data for the proton and hydrated proton species by using reported[2] E_B and C_B parameters from the neutral acid–base data fit and incorporating the transfer term for these ionic systems into a constant W that is unique for each cationic acid. The resulting fit provides a new interpretation for the anomalous basicity order observed in water for the alkylamines. This approach is extended here to encompass a wide range of cations, as well as several new neutral bases. The resulting data fit overcomes the shortcomings discussed above for the ect fit. In addition, previously unrecognized, novel electronic effects that exist in these gas-phase acid–base interactions are identified.

Calculations

The calculation was carried out with use of a previously described[16c] least-squares program to find the best fit parameters that produce the enthalpy when substituted into the equation being studied. The contribution that a particular enthalpy value makes to the fit is determined by the inverse of the square of the weight assigned. For example, an enthalpy with a weight of 1 influences the fit 12 times more than one with a weight of 3.5. In the gas-phase ion–molecule fit, the weighting of the enthalpies is assigned as follows:

(a) A neutral acid–neutral base adduct enthalpy involving bases (acids) with known E and C values is given a weight of 1.0. The value is increased to 2 when the neutral base (acid) E and C parameters are tentative or the error in the enthalpy is greater than 0.2 kcal mol^{-1}. If small steric effects are suspected a weight of 2.5–4 is used. Those systems with large steric effects are omitted.

(b) The enthalpy value for a neutral base, whose E_B and C_B values are known,[2] reacting with a cation is given a weight of 3.5. This value is increased to 4.0 when the base parameters are tentative and to 5.0 when the E and C parameters of the base are unknown.

(c) The enthalpies for gas-phase systems, where the acid or base enthalpy is far removed from any others studied with that ion (e.g. K^+ DMSO), or for systems where the estimated error in the measurement is large, are given a weight of 7–10 depending on the error.

Two different equations were tested to determine their ability to reproduce the data in a least-squares fit. Equation 1 is referred to as the ECW fit. The second equation is of the form

$$-\Delta H = E_A E_B + C_A C_B + R_A T_B \qquad (3)$$

The capital letters are employed to indicate that the known E_B and C_B values reported[2] for the neutral acid–neutral base system are employed and held fixed in the fit to eq 3. Since the EE and CC products are divided up by the fixed, reported E_B and C_B values, the resulting acid parameters are compatible with the ECW data set of neutral acids and bases. The symbol R_A is used to indicate that the acid (A) is the receptor in the electron-transfer interaction, and T_B indicates that the base (B) is the transmitter. The relevant enthalpy data used in these fits are contained in the accompanying microfilm Table M-1.

The experimental enthalpies were fit initially to eq 1 with each cation

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Table I. Listing of Acid and Base Parameters

(A) Acid Parameters

	E	C	R	C/E		E	C	R	C/E
H^+	45.00	13.03	130.21	0.29	K^+[c]	3.78	0.10[e]	20.79	0.03
CH_3^+	19.70	12.61	55.09	0.64	NO^+[c]	0.1[e]	6.86	45.99	68.65
Li^+	11.72	1.45	24.21	0.12	NH_4^+[c]	4.31	4.31	18.52	1.00
Mn^+	16.69	2.70	51.25	0.16	$(CH_3)_2NH_2^+$[c]	3.21	0.70	20.72	0.22
H_3O^+	13.27	7.89	20.01	0.59	$(CH_3)_4N^+$[c]	1.96	2.36	8.33	1.20
$(H_2O)_2H^+$	11.39	6.03	7.36	0.53	$C_5H_5NH^+$[c]	1.81	1.33	21.72	0.73
$(H_2O)_3H^+$	11.21	4.66	2.34	0.42	$(C_2H_5)_3NH^+$[c]	2.43	2.05	11.81	0.84
$(H_2O)_4H^+$[c]	10.68[d]	4.11	−3.25	0.38	$(CH_3)_3NH^+$[c]	2.60	1.33	15.95	0.51
$(CH_3)_3Sn^+$	7.05	3.15	26.93	0.45	Mg^+[a]	11.70	2.64	54.15	0.23
$(C_5H_5)Ni^+$	11.88	3.49	32.64	0.29	Al^+[a]	10.10	5.38	51.85	0.53
$(CH_3)NH_3^+$[b]	2.18[d]	2.38	20.68	1.09					

(B) Base Parameters

base[f]	E_B	C_B	T_B	C/E	base[f]	E_B	C_B	T_B	C/E
NH_3[g]	2.31	2.04	0.56	0.88	$(CH_2)_4O$	1.64	2.18	0.75	1.33
CH_3NH_2[g]	2.16	3.12	0.59	1.45	$(CH_2)_5O$	1.70	2.02	0.74[h]	1.19
$(CH_3)_2NH$[g]	1.80	4.21	0.64	2.33	$(C_2H_5)_2S$	0.24	3.92	1.10[h]	16.3
$(CH_3)_3N$[g]	1.21	5.61	0.75	4.63	$(CH_3)_2SO$	2.40	1.47	0.65	0.61
$C_2H_5NH_2$[g]	2.35	3.30	0.54	1.41	C_5H_5NO	2.29	2.33	0.67[h]	1.02
$C_5H_{10}NH$	1.47	4.79	0.75	3.26	4-$CH_3OC_5H_4NO$	2.34	3.02	0.64[h]	1.29
$(C_2H_5)_3N$	1.32	5.73	0.76	4.34	$(CH_3)_3P$	1.46	3.44	0.90[h]	2.36
$HC(C_2H_4)_3N$	0.80	6.72	0.83[h]	8.40	$(CH_3)_2O$	1.68	1.50	0.73	0.89
CH_3Im	1.16	4.92	0.86[h]	4.24	$(CH_3)_2S$	0.25	3.75	1.07	15.09
C_5H_5N[g]	1.78	3.54	0.73	1.99	CH_3OH	1.80	0.65	0.70	0.36
4-$CH_3C_5H_4N$	1.74	3.93	0.73[h]	2.26	C_2H_5OH	1.85	1.09	0.70	0.59
3-$CH_3C_5H_4N$	1.76	3.72	0.74[h]	2.11	C_6H_6	0.70	0.45	0.81	0.64
3-ClC_5H_4N	1.78	2.81	0.75[h]	1.58	H_2S[i]	0.04	1.56	1.13	
CH_3CN	1.64	0.71	0.83	0.43	HCN[i]	1.19	0.10[j]	0.90	
$CH_3C(O)CH_3$	1.74	1.26	0.80	0.72	H_2CO[i]	1.56	0.10[j]	0.76	
$CH_3C(O)OCH_3$	1.63	0.95	0.86	0.58	CH_3Cl[i]	2.54	0.10[j]	0.23	
$CH_3C(O)OC_2H_5$	1.62	0.98	0.89	0.60	CH_3CHO[i]	1.76	0.81	0.74	
$HC(O)N(CH_3)_2$	2.19	1.31	0.74[h]	0.60	H_2O[i]	2.28	0.10[j]	0.43	
$(C_2H_5)_2O$	1.80	1.63	0.76	0.91	CN-C_5H_4N[i]	1.72[j]	2.49	0.77	
$(i\text{-}C_3H_7)_2O$	1.95	1.66	0.74[h]	0.85	$(CH_3)_3COH$[i]	1.92	1.22	0.71	
$(n\text{-}C_4H_9)_2O$	1.89	1.67	0.75	0.88	C_6H_5CN[i]	1.75	0.62	0.85	
$O(CH_2CH_2)_2O$	1.86	1.29	0.71	0.69					

[a] Valid predictions are expected for bases with C/E ratios less than 1.2. [b] Valid predictions are expected for bases with C/E ratios greater than 1.2. [c] Predictability uncertain because of limited data set or compounding of error. [d] E and R are highly correlated. [e] Parameter was fixed because a limited data set led to a negative value. [f] If not indicated otherwise the bases in this table have E_B and C_B values determined[2] from the fit of neutral acid–neutral base adducts. They have been transformed with the matrix given in the text. See ref 2 for the names corresponding to these formulae. [g] The E_B and C_B values for these bases were previously reported as tentative.[2] These new parameters have been determined by combining all the gas phase and solution data. [h] The E_B and C_B values for these bases are well determined.[2] The T_B values are tentative for they have been determined from limited data—often only a proton affinity. [i] The values for these bases are tentative because only limited enthalpy data are available. [j] The parameter was forced or fixed to overcome negative or meaningless results.

having a different constant W value. This fit was run several times to find suspect systems, i.e. those whose enthalpy seemed to be in error and those that had unusual electronic effects, for example, donors with multiple coordination sites, π-back-bond stabilization, vide infra. Relatively few suspect systems were found. These were eliminated and a final fit of the data to eq 1 was carried out.

In the final constant W fit, patterns existed in the small deviation of calculated and experimental enthalpies for many of the cations. For a given cation, the most covalent bases ($C/E > 1.5$) in the fit deviated in a negative direction from the calculated value while the least covalent ($C/E < 1.5$) deviated in a positive direction. These patterns are eliminated and a better fit of the data is obtained by using eq 3 in the least-squares fit.

The W values from the constant W fit were used as the initial estimate of the R_A values for the fit to eq 3. Rather than force the data to fit an assigned R_A equal to W, a hypothetical base was defined called T-base whose $E_B = 0$, $C_B = 0$, and $T_B = 1$. The W value calculated from our previous fit for a polyatomic cation was used as an "enthalpy" for the reaction of this cation with T-base in the data fit of all the enthalpies. The calculated "enthalpy" for this interaction is the new R_A enabling us to modify the initial R_A value, which was set equal to W, to best fit the enthalpy data. This approach enables the value of R_A to vary from the W value if a better fit of the enthalpy data set can result. The new, best fit calculated R_A value from the preceding fit was used as the input enthalpy for R_A reacting with T-Base in the subsequent fit. This procedure was repeated until the calculated R_A values for these ions agreed with the input value to at least better than 3%. The cations K^+ and NO^+ as well as the bases HCN, H_2O, CH_3Cl, and H_2CO gave negative parameters for E or C because of a limited data set with these donors. These values were fixed at 0.1 in the final fit and the parameters labeled tentative. In the final fits, all data that had been left out of the earlier fits because of the possible existence of unusual bonding effects but whose enthalpies were correctly calculated by the E, C, and T parameters were added. Several reported bases,[2] whose parameters from neutral acid–base studies were tentative because of limited data ($(CH_3)_2O$, NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$) were refit after adding all the known[2,21,22] neutral–neutral enthalpies for these bases to the fit.

After a series of iterations to obtain the best data fit, one further constraint was added to the final fit. The C value of the proton was pressured with C-base to give a C_AC_B product for CH_3NH_2 equal to the polarization energy calculated by Umeyama and Morokuma (U-M)[23] from an ab initio calculation of $CH_3NH_3^+$. The E value was pressured with E-base to give their calculated electrostatic energy. In view of limited data for $C_2H_5NH_2$, the C_B value was set to give the U-M polarization (PL) contribution and the E_B value of 4-cyanopyridine was fixed at a slightly lower value than that for pyridine. No significant decrease in the quality of the fit resulted and we report this as our final fit. Any ion or neutral molecule whose parameter is constrained is indicated in Table I. More experiments are suggested on these systems.

We report in Table I the ECT parameters from the final least-squares minimization of the data set reported in Table M-1. We report in Table II those systems, in the fit whose calculated enthalpies miss the experimental value by more than 3 kcal mol^{-1}. This value is selected because gaps in the ladders used to determine the enthalpies as well as the possible contributions from entropy to the position of a base in the ladder can lead to errors of this magnitude in the data set.

The systems indicated in Table II are omitted from the fit. These systems are analyzed separately and the results described.

Table II. Systems Whose Calculated and Experimental Enthalpies Miss by More Than 3 kcal mol^{-1}

acid	base	$-\Delta H_{exp}$	$-\Delta H_{calc}$
Li^+	NH_3	39.1	43.6[b]
NH_4^+		25.0	29.12[a]
$N(CH_3)_4^+$	CH_3NH_2	8.7	16.51[a]
$(H_2O)_4H^+$	C_5H_5N	26.7	32.16[b]
$(H_2O)_3H^+$	$4CNC_5H_4N$	27.6	32.7[b]
$(H_2O)_4H^+$		18.8	26.1[b]
CH_3^+	HCN	95.5	74.3[a]
$CpNi^+$		48.3	43.9[a]
$CpNi^+$	CH_3CN	53.9	49.1[a]
H^+	H_2O	166.5	159.1[a]
H_3O^+		31.5	39.5[a]
$(H_2O)_2H^+$		20.0	29.7[a]
$(H_2O)_3H^+$		17.0	27.0[a]
$(H_2O)_4H^+$		15.0	23.3[a]
K^+	$(CH_3)_2SO$	35.0	22.7[a]
H^+	C_6H_6	181.3	142.8[a]
Li^+		37.9	28.5[a]
H^+	CH_3Cl	166.98	145[a]
H^+	$CH_3C(O)N(CH_3)_2$	216.6	217[c]
H_3O^+		66.8	56[c]
$(H_2O)_2H^+$		47.6	40[c]
$(H_2O)_3H^+$		36.9	34[c]
$(H_2O)_4H^+$		29.1	28[c]

[a] Enthalpy not used (or highly weighted) in the parameter fit and calculated from E, C, and T values from Table I. Cause for the deviation is provided in the discussion. [b] These enthalpies are used in the fit but miss by more than 3 kcal/mol. [c] The proton enthalpy was fit by using E_B and C_B from ref 2 leading to a T_B value of 0.72 for $CH_3C(O)N(CH_3)_2$. The reason for this approach and the deviations are discussed in the text.

Results and Discussion

The ECW Fit. The ECW fit will be discussed briefly because it provides important insights for the ECT fit and demonstrates the need for a R_AT_B term. In applying eq 1 to gas-phase ion-molecule data, W has a new meaning for a cation interacting with a neutral base. The W term can be viewed as converting the gas-phase reaction to a displacement reaction of the form

$$M^*B^{\bullet+} + B \rightarrow M^*B^+ + B^\bullet$$

In this reaction $B^\bullet$ is a base whose E and C values are 0, but which has a transfer term for a given cation that is an average of that for all the bases studied.

The enthalpy changes used for Al^+ or Mn^+ are those for displacement reactions in which CH_3OH is displaced from Al^+ and CH_3SH from Mn^+. The W values for these ions correspond to the E and C component of the displacement enthalpy of binding CH_3OH from Al^+ and CH_3SH from Mn^+. The data fit well but no information is available about the transfer term contribution to the W for these ions because it is largely cancelled out in the displacement reaction. In a similar vein, endothermic, constant energy rearrangements of bonds and water molecules in $H(H_2O)_n^+$ species upon adduct formation are included in W, along with the transfer term, making it difficult to separate these energies.

In order to fit the proton affinities to the experimental precision, two different groupings of donors were required for the ECW fit. The first category contains those bases whose C_B values are less than 1.5 and the second those whose values are greater than 1.5. Those donors that belong to the second group have a lower ionization energy and transfer more electron density to the proton upon complexation than those in the first set. The same type of variation in the transfer term is probably operative for other cations in the data set, but the magnitude of the W value is small enough that an average value can be used to fit the data to reasonable precision. In the case of the proton, where the W value is large, different average values are needed for the two groups.

Since the stabilization from transfer into an acid should be related to the ionization energy of this acid, the W values for monatomic ions from the ECW fit were plotted vs the ionization energy (IE) of the atom (Figure 1) leading to a smooth curve whose equation (forced to go through the origin) is given by

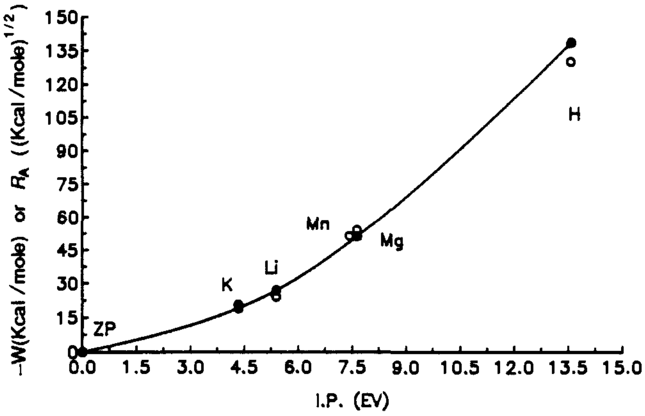

Figure 1. Plot of R_A and W versus the ionization energy of the atom. The line represents W and has units of kcal mol^{-1}, and the open circles represent R_A.

$$0.5431E^2 + 2.3581E - 0.446 \tag{4}$$

The Al^+ and Mn^+ ions were left off since these are relative heats and not absolute heats. The ionization energies of two polyatomic cations in the fit (CH_3^+ and NO^+) are well-known but not included in this plot. The ionization energy of the methyl radical corresponds to a planar molecule forming a planar cation. The W value is expected to differ because it corresponds to electron transfer into an orbital of a pyramidal $\sim sp^3$ carbon in the methyl cation adduct. The NO^+ ion is also omitted from the plot because the ionization energy corresponds to removal of an electron from a π^* orbital and base coordination to NO^+ involves interaction with an $\sim sp^2$ hybridized orbital on the nitrogen.

A significant prediction regarding absolute energies can be made from the relationship in Figure 1. Using the W value for Al^+ calculated from the ionization energy (Figure 1) and adding the W value from the fit for $Al(CH_3OH)^+$ enables one to add -61.0 kcal mol^{-1} to the $Al(CH_3OH)^+$ displacement enthalpies to calculate absolute energies for the gas-phase reaction of Al^+. In a similar fashion, absolute enthalpies for Mn^+ can be obtained from $Mn(CH_3SH)^+$ by adding -64.4 kcal mol^{-1} to the displacement enthalpy. These absolute enthalpies are used in the final fit.

In spite of the insights gained from the ECW analysis, disturbing features remain. Requiring two donor categories for the proton is not satisfying and suggests that an average W is not adequately accommodating the transfer term. For several ions, patterns exist in the deviation between calculated and experimental enthalpies as the base is varied suggesting that the transfer term is being overestimated for weak oxygen donors and underestimated for sulfur donors. We can allow variation in this term for a given acid binding to different bases by using eq 3 instead of eq 1, setting $R_A = W$ and letting T_B vary. The least-squares data fit of this equation is referred to as our ECT fit.

Fit to the ECT Equation. In the initial ECW and ECT fit, several of the C_A parameters obtained were negative. This is due to the values selected to fix the four required parameters to obtain a unique solution of the data set in the neutral acid-neutral base fit.[2a] Fixing these parameters imposes the ionic-covalent model, and negative values indicate that the electrostatic contribution to the bonding was overestimated in the initial assignment. We have previously shown that transformation matrices exist[1a] that permit a parameter transform without changing the fit of calculated and experimental energies for any of the adducts. After considerable trial and error, it was found that only a small window existed for transformation parameters that led to positive values for all of the well-determined acid and base E and C values. The reported transformation leads to a new set of parameters that are all positive and enables us to eliminate negative parameters in future analyses as being meaningless. In the course of making this change we also decided to set the iodine parameters at $C_A = 2.0$ and $E_A = 0.5$. This change expands the E_B scale so that it covers a range comparable to the other parameters. New acid parameters E_A and C_A are obtained from the older set $E°_A$ and

$C°_A$ by expanding the matrix

$$\begin{pmatrix} 0.50 & 0 \\ 0.11 & 1.89 \end{pmatrix} \begin{pmatrix} E°_A \\ C°_A \end{pmatrix} = \begin{pmatrix} E_A \\ C_A \end{pmatrix}$$

New base parameters are obtained from

$$\frac{1}{0.945} \begin{pmatrix} 1.89 & -0.11 \\ 0 & 0.5 \end{pmatrix} \begin{pmatrix} E°_B \\ C°_B \end{pmatrix} = \begin{pmatrix} E_B \\ C_B \end{pmatrix}$$

Only the new parameters will be used in this and subsequent publications.

As described in the experimental section, the $R_A T_B$ term is introduced to accommodate variation in the transfer term for a given acid as the base is varied. The W value for the cation in the earlier ECW fit required this to be constant for each cation. The solid circles in Figure 1 show the starting W values obtained from the ECW fit and the open circles are the final best fit R_A parameters from the ECT fit. The two sets of parameters are seen to be similar. The T_B values of the bases vary allowing for variation in the $R_A T_B$ term for a given cation as the base is changed. This flexibility leads to a considerable improvement in the data fit (Table M-1) to eq 3 over that observed with eq 1. The smooth curve relating R_A and IE in Figure 1 for monatomic cations supports our interpretation of the transfer term.

The final fit of 387 enthalpies, solved for 63 unknown acid parameters and 78 base parameters, led to the ECT parameters listed in Table II. Tentative acid (or base) parameters are indicated for those systems in which the range and number of bases or acids studied is limited. All of the bases in the reported[2] neutral acid–neutral base fit whose proton affinities are the only gas-phase ion data available have been listed and the T_B value marked tentative.

The gas-phase cation–neutral base enthalpies calculated from the empirical parameters and the experimental enthalpies are compared in Table M-1. Sample results comparing calculated and experimental enthalpies for the H^+, CH_3^+, Li^+, $(CH_3)_3Sn^+$, and $NiCp^+$ are illustrated in Table III. The quality of the fit for the cations is not as good as that reported for the neutral acid–base adducts.[2] The precision for most gas-phase enthalpies is 2 kcal mol^{-1} with experimental enthalpy values that are much larger than those for neutral adducts. However, for most ions the maximum range of enthalpy differences for a given ion with the various bases studied (i.e. largest ΔH minus the smallest ΔH) is $\sim$18 kcal mol^{-1}. The 2 kcal mol^{-1} error for this range of enthalpy values corresponds to a precision of about 11%. In the original fit of neutral acids and bases, a precision of $\sim$0.2 kcal mol^{-1} in a 10 kcal mol^{-1} range of enthalpy differences provides a precision of 2%. Thus, the parameters for a new base are better determined with neutral adducts and when available[2,21] these enthalpies are given more weight in the data fit. Additional complications also exist and contribute to error in the gas-phase data. Often the gas-phase enthalpies are derived from equilibria (i.e. ΔG) for the displacement of one base from the cation by another. The assumption is made that the entropy contributions are constant for the series of base adducts. Minor variations in entropies could cause some of the observed deviations in the data set. The relative ΔG values are obtained by constructing a ladder of increasing base strength. When a large difference in basicity exists between two bases in the ladder, nearly complete displacement of the weaker base occurs. A small error in measuring the concentrations of the minor species leads to a large error in ΔG.

The acid–base adducts whose experimental and calculated enthalpies miss by more than 3 kcal mol^{-1} are listed in Table II. The exceptions to the fit and the insights they provide about coordination are discussed in the following sections.

Table III. Sample Data Fit for Some Better Determined Cations

acid	base	$-\Delta H_{exp}$	$-\Delta H_{calc}$	dev
H^+	CH_3NH_2	214.10	214.30	0.20
	C_5H_5N	220.80	221.41	0.61
	$(C_2H_5)_3N$	232.30	232.44	0.14
	H_2S	170.20	169.76	−0.44
	HCN	174.20	172.24	−t.96
	NH_3	204.00	203.48	−0.52
	H_2CO	171.70	170.20	−1.50
	CH_3Cl	166.98	144.99	−21.99
	CH_3OH	181.90	180.86	−1.04
	CH_3CN	188.40	190.80	2.40
	CH_3CHO	186.60	186.81	0.21
	C_2H_5OH	188.30	188.42	0.12
	$(CH_3)_2O$	192.10	190.60	−1.50
	$(CH_3)_2NH$	220.60	218.84	−1.76
	$(CH_3)_2CO$	196.70	199.53	2.83
	$(CH_3)_3N$	225.10	225.25	0.15
	$(C_2H_5)_2O$	200.20	200.69	0.49
	H_2O	166.50	159.10	−7.40
	$(CH_3)_2S$	200.60	199.47	−1.13
	$(CH_3)_2SO$	211.30	211.42	0.12
	$CH_3C(O)OCH_3$	197.80	198.32	0.52
	$C_2H_5NH_2$	217.00	218.25	1.25
	$CH_3C(O)OC_2H_5$	200.70	201.07	0.87
	$(C_4H_9)_2O$	203.70	204.05	0.35
	$(CH_2)_4O_2$	193.80	193.22	−0.58
	$(CH_2)_4O$	198.80	200.29	1.49
	$(CH_3)_3COH$	193.70	195.08	1.38
	C_6H_5CN	195.90	197.61	t.71
	$4CN\text{-}C_5H_4N$	210.30	210.49	0.19
Li^+	C_5H_5N	44.00	43.70	−0.30
	HCN	36.40	35.91	−0.49
	H_2CO	36.00	36.79	0.79
	CH_3Cl	36.00	35.38	−0.62
	CH_3CN	43.00	40.29	−2.71
	CH_3CHO	41.30	39.87	−1.43
	$(CH_3)_2O$	39.50	39.62	0.12
	$(CH_3)_2CO$	44.50	41.71	−2.79
	$(CH_3)_3N$	42.10	40.49	−1.61
	$(CH_3)_2S$	32.80	34.27	1.47
	CH_3OH	38.10	39.03	0.93
	$(CH_3)_2NH$	42.20	42.65	0.45
	CH_3NH_2	41.10	44.05	2.95
	NH_3	39.10	43.60	4.50
	H_2O	34.00	37.12	3.12
CH_3^+	CH_3NH_2	116.00	114.23	−1.77
	H_2S	82.40	82.94	0.54
	NH_3	103.00	102.10	−0.90
	H_2CO	73.00	73.74	0.74
	CH_3OH	84.00	82.29	−1.71
	H_2O	68.00	69.52	1.52
	CH_3Cl	62.00	63.72	1.72
	$(CH_3)_2NH$	122.00	123.66	1.66
$(CH_3)_3Sn^+$	CH_3NH_2	42.10	40.87	−1.23
	$(C_2H_5)_3N$	45.70	47.70	2.00
	NH_3	36.90	37.80	0.90
	CH_3OH	32.60	33.64	1.04
	CH_3CN	37.50	36.09	−1.41
	C_2H_5OH	34.80	35.30	0.50
	$(CH_3)_2NH$	42.20	43.11	0.91
	$(CH_3)_2CO$	37.40	37.92	0.52
	$(CH_3)_3N$	45.60	46.41	0.81
	H_2O	25.70	27.82	2.12
	$CH_3C(O)OCH_3$	38.40	37.78	−0.62
	$C_2H_5NH_2$	44.10	41.35	−2.75
	$(CH_3)_3COH$	36.60	36.57	−0.03
$CpNi^+$	CH_3NH_2	55.90	55.71	−0.19
	NH_3	53.00	52.85	−0.15
	H_2CO	44.50	43.63	−0.87
	CH_3OH	46.30	46.56	0.26
	CH_3CHO	47.01	48.07	1.06
	C_2H_5OH	48.20	48.59	0.39
	$(CH_3)_2O$	47.60	49.12	1.52
	$(CH_3)_2NH$	57.50	56.88	−0.62
	$(CH_3)_2CO$	51.40	51.34	−0.06
	$(CH_3)_3N$	57.10	58.44	1.34
	$(C_2H_5)_2O$	51.60	51.75	0.15
	H_2O	43.10	41.28	−1.82
	$(CH_3)_2S$	51.80	50.98	−0.82
	$(CH_3)_3COH$	50.79	50.33	−0.46

Insights from the Fit. The cation and base parameters are listed in Table I. Tentative values are assigned to certain cations (and

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(22) Laurence, C.; Berthelot, M.; Helbert, M.; Sraich, K. *J. Phys. Chem.* **1989**, *93*, 3799.

(23) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 4400.

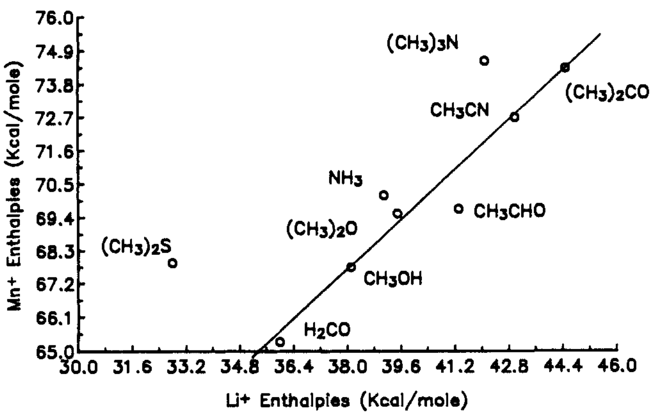

Figure 2. Plot of the enthalpy of interaction of a series of bases with Mn^+ vs those for the proton (the least-squares line is drawn omitting $(CH_3)_3N$ and $(CH_3)_2S$).

bases) because a limited data set exists or because the C_B/E_B ratios of the bases studied are similar. These systems are indicated with footnotes *c* and *d* in Table I. In further gas-phase studies of these systems, we strongly encourage the use of $(CH_2)_4S$ in gas-phase experiments along with a selection of other bases to give a wide range of T_B, C_B, and E_B values. Prediction of enthalpies for cations (or bases) assigned tentative parameters should be limited to bases (or acids) whose C/E ratio is similar to those used in the fit of the tentative systems.

The parameters that are firmly established show reasonable trends. Most of these cations have a C/E ratio indicative of an essentially electrostatic interaction ($C/E \leq 0.2$) except for Me_3Sn^+, CH_3^+, $CH_3NH_3^+$, and H_3O^+. Thus, in many experiments one is changing the cation but in effect studying similar coordination chemistry. The bonding to Li^+ and K^+ is essentially electrostatic with the E_A value for Li^+ being larger than that for K^+ as expected on the basis of the size of the ion. The C_A/E_A ratio indicates that the K^+ interaction is more electrostatic than that for Li^+. Estimating the Li^+ and K^+ HOMO–LUMO energy gap from the ionization energy of Li and K atoms leads to a larger energy gap and the prediction of a more electrostatic interaction for the latter ion. The fractional electrostatic contribution to the enthalpy, $E_AE_B/(C_AC_B + E_AE_B)$, is calculated to be larger for K^+ than for Li^+. In keeping with the smaller size of Mn^+, a larger E_A number results than for K^+. Furthermore, the bonding is more covalent for Mn^+ than for K^+ as expected from the HOMO–LUMO gap estimated from the IE of the atoms. On the basis of the ionization energy, the Mn^+ LUMO is expected to be closer in energy to the ligand HOMO than that of Li^+, and accordingly the interactions are found to be more covalent. The larger electrostatic interaction for Mn^+ does not follow charge-size considerations and probably results from ineffective shielding of the positive nuclear charge by rearrangement of the d electrons of Mn^+ in the 3-d orbitals. It is interesting to note that these insights are not possible from methods of data analysis that involve plotting the enthalpies of interaction with a cation versus the proton affinity. Figure 2 is a plot of the Li^+ and Mn^+ enthalpy change upon coordination to the same base. Most bases fall on the straight line as would be expected from a similar C/E ratio (0.12 and 0.16, respectively) for the ions. The two bases with the largest C_B value deviate from the line in the direction expected for more covalency from the larger C_A/E_A ratio of Mn^+. In this context it is interesting to note that the linear plot of the H^+ vs $NiCp^+$ enthalpies reported by Beauchamp[9a] results because both ions have the same C/E ratio.

Toward Li^+ and K^+, acetone is more basic than trimethylamine and comparable in basicity to pyridine. This is in contrast to the proton order of $(CH_3)_3N > C_5H_5N > (CH_3)_2CO$ and reflects the dominance of the trend by the largely electrostatic interaction with Li^+. The transfer contribution for these bases toward a given acid is comparable.

The ECT values for the proton indicate that the proton affinity has substantial contributions from the electrostatic, covalent, and transfer terms. Which effect is dominant will depend on the E_B, C_B, and T_B values of the base to which it coordinates. In keeping with its small size, the E_A value is the largest found. The fractional covalent contribution in the proton interaction with bases, $C_AC_B/(C_AC_B + E_AE_B)$, is intermediate between that of Li^+ and CH_3^+. On the basis of the HOMO–LUMO gap between the donor and acceptor, one expects covalency to increase in the order $Li^+ < CH_3^+ < H^+$. However, the small overlap integral of the hydrogen 1s orbital compared to the carbon sp^3 reverses the order predicted on the basis of energy. With these illustrations, we leave it to the reader to make further comparisons of HOMO–LUMO trends for the data in Table I to gain the full impact of this analysis.

The data fit of the proton was E-based and C-based to fit Umeyama and Morokuma's estimate[23] of the electrostatic (ES) and polarization (PL) contribution (Table IV) in methylamine. Except for ethylamine in which there is limited data, the other amines are not constrained. The results obtained for the other amines are in excellent agreement with the U–M calculation. The trends of PL parallel C_AC_B, ES parallels E_AE_B, and CT (change transfer) parallels R_AT_B as shown in Table IV. The results are in complete agreement with the U–M conclusion that though the E_AE_B contribution is large "the order of importance of components in the alkyl substituent effect (i.e. the trend found) for the proton affinity is $PL(C_AC_B) > CT(R_AT_B) \gg ES(E_AE_B)$". We also agree with the U–M conclusion[23] for the oxygen donors that "$ES(E_AE_B)$ and $CT(R_AT_B)$ are more important contributors to the stabilization than $PL(C_AC_B)$". Furthermore, our results also show that the trend in the alkyl-substituent effect in both the oxygen and nitrogen series is "found to be controlled mainly by the $PL(C_AC_B)$ term". We note much larger changes in the E_AE_B contribution for amine protonation with methyl substitution than U–M. This is compensated by a larger change in the R_AT_B contribution in the opposite direction. We also note that compared to U–M, our analysis puts more of the energy for protonation of methanol and dimethyl ether into R_AT_B instead of C_AC_B. It can be appreciated that there are many ways to group and decompose the intermolecular interaction energy from a molecular orbital calculation just as one can transform the wave function from a localized to a delocalized picture. It is gratifying that in spite of this complication, the essential conclusions of our empirical approach are in agreement with those of the theoretical analysis.

The coordination of donor molecules to monatomic cations producing new cationic acids leads to a significant decrease in the R_A values of the resulting polyatomic cation. The R_A values for H_3O^+, $CH_3NH_3^+$, and other ammonium ions are considerably smaller than that of the proton. Similarly, the R_A value of $CpNi^+$ is considerably below the value expected for Ni^+ on the basis of its ionization energy (Figure 1). The $(CH_3)_3Sn^+$ cation also has a much smaller R_A value than monatomic cations. Since naked cations are seldom encountered in solution and since the lowered R_AT_B contribution of ligated ions is largely cancelled out in displacement reactions, one must use considerable caution in extrapolating gas-phase results to solution reactions. It is clearly misleading to lump all of the different effects that exist in gas-phase and solution data into a term called solvation. Admittedly, definitions are arbitrary, but terms become useless when they encompass a great many different effects. As described[20] in a reanalysis of the gas-phase and solution acidity of toluene and methanol, it is further essential to compare the same species and the same reaction in the two phases.

In neutral acid–neutral base systems, it has been shown that a straight-line plot of the enthalpies for two different acids reacting with a series of bases results if the C_A/E_A ratio of the two acids is comparable.[15] The proton has a C/E ratio of 0.29 which is similar to that of chloroform ($C/E = 0.30$). In plotting the proton affinities versus limited data for the chloroform enthalpies, R_A is reflected in a large intercept at a zero chloroform enthalpy and deviations occur in the plot for those bases in which the R_AT_B term of the proton does not change linearly with ΔH. Thus, we note that when ion–molecule enthalpies are plotted vs those for neutral–neutral systems, a constant C/E ratio is not a sufficient criterion for a straight line. In plots of gas-phase enthalpies for

Table IV. Comparison of ab Initio and ECT Estimates of the Energy Contribution to the Protonation of Alkylamines

base	PL[a]	C_AC_B	ES[a]	E_AE_B	CT[a]	R_AT_B	$-\Delta H$		
							UM[a]	ECT	exp
NH_3	27.4	26.6	99.8	104.0	88.3	72.9	221	204	204
CH_3NH_2	40.2	40.7[c]	96.5	97.2[c]	91.7	76.8	230	214	214
$C_2H_5NH_2$[b]	45.4	43.0	94.6	105.7	93.0	70.3	233	219	217
$(CH_3)_2NH$	53.1	54.9	91.2	81	95.1	83.3	236	219	221
$(CH_3)_3N$	65.4	73.1	84.9	54.5	98.6	97.7	240	225	225
$(CH_3)_2O$	54.4	19.5	72.9	75.6	76.9	95.1	201	190	192
CH_3OH[b]	43.5	8.5	76.4	81	74.5	91.2	194	181	180
H_2O[b]	25.9	1.3	82.1	102.6	71.7	56.0	185	160	166

[a] PL is the Umeyama Morakuma (U–M) polarization term, ES their electrostatic term, and CT their charge-transfer term. [b] Tentative parameters. [c] The proton *C* and *E* was pressured with C-base and E-base to give agreement of these numbers with the U–M result for this base.

a series of bases bonding to one ion versus that for the interaction of the corresponding bases with a second ion, the required linearity of R_AT_B vs $R_A'T_B$ will make a constant C/E ratio for the two ions the requirement for a linear plot.

In a recent article, the methyl cation affinities were plotted versus the proton affinities. Deviations from linearity imply that two different types of methyl cation interactions[10] exist since two different lines are drawn. Our results predict that a nonlinear plot is expected because the C_A/E_A ratios of these two ions are very different. The importance of covalency in the bonding is very different for H^+ and CH_3^+ causing reversals in the orders of donor strength.

Exceptions from the Fit. The systems that are not correlated by our model are listed in Table II where the calculated enthalpy and experimental enthalpy are reported. The fit of the enthalpies for the K^+ is among the poorest in the correlation. Two of the bases selected have ethyl groups attached to the donor atom leading to potential complications upon coordination from entropy terms. The other bases have enthalpies that are grouped around 22 kcal mol^{-1}. The laddering gap makes it difficult to accurately measure an equilibrium constant for $(CH_3)_2SO$ because it almost completely displaces all the other bases studied. Uncertainty also exists in the $(CH_3)_3N$ enthalpy for it is nearly completely displaced by all bases. As a result of these complications, the K^+ parameters are tentative and the miss of DMSO in Table II for this ion is accounted for.

The enthalpy values for donor binding to the species $(H_2O)_nH^+$ are calculated indirectly from hydration of the onium ions (BH^+) by combining the following equations for gas-phase reactions

$$BH(H_2O)_{n-1}{}^+ + H_2O \rightarrow BH(H_2O)_n{}^+$$

$$+ [B(g) + H(H_2O)_{n-1}{}^+ \rightarrow BH(H_2O)_{n-1}{}^+]$$

$$+ [(H_2O)_nH^+ \rightarrow H_2O + H(H_2O)_{n-1}{}^+]$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$B(g) + (H_2O)_nH^+(g) \rightarrow BH(H_2O)_n{}^+(g)$$

Thus, the errors in the hydrated proton species are cumulative as n increases. Data for $n > 4$ are omitted from the fit, and the ECT analysis of these systems is reported in Table M-2. Errors in Table II for $(H_2O)_nH^+$ (n = 3 and 4) are attributed to the compounding of experimental error.

The existence of π-back-bond stabilization in the $NiCp^+$ adducts of HCN and CH_3CN is also noted. It is significant that these enthalpy changes do not fit the linear plot of $NiCp^+$ enthalpies (C/E = 0.29) versus those of H^+ (C/E = 0.29) but deviate in the direction expected for added stabilization in the $NiCp^+$ adduct. The Mn^+ adducts with these bases were initially omitted from the fit because of possible contributions from this effect. The good agreement between experimental and calculated results for Mn^+ with these bases suggests that π-back-bonding from Mn^+ to nitriles does not occur to a significant extent. These systems were added to the final fits. Coordination of the Cp group to Ni^{2+} reduces its formal positive charge below +1, resulting in a greater radial extension of the d orbitals than exists in Mn^+. The greater radial extension leads to better overlap with the empty π^* orbitals of the nitrile ligands and stabilization from π-back-bonding results.

The systems in which water coordinates to $(H_2O)_nH^+$ show marked deviations. The symmetry of the adducts is such that the positive charge is delocalized over all the protons in the molecule and the typical electrostatic ion–dipole interaction involved in the coordination of water to other cations may be diminished in these adducts. It is also found that base adducts of $(H_2O)_nH^+$ [i.e., $(H_2O)_nH\text{-}B^+$] have different geometries than the $(H_2O)_nH\text{-}(H_2O)^+$ structure. Different E_A and C_A values would be needed for $(H_2O)_nH^+$ depending on the geometry of the adduct formed.

An interesting pattern of deviations is noted in symmetrical B--H^+--B systems, e.g. $(H_2O)_2H^+$, $(NH_3)_2H^+$, $(CH_3NH_2)_2H^+$, and $((CH_3)_2NH)_2H^+$. In all instances, the calculated value is greater than that observed experimentally and the magnitude of the deviation decreases as the number of protons on the donor atom decreases. Those systems are all expected to have a double well in the potential energy surface. The $CH_3^+\text{-}CH_3Cl$ adduct as well as other $(H_2O)_nH^+$ systems may have a similar effect operative. This could lock in a minima in which the acidic X–H^+ bond is not lengthened to the extent it is in other adducts and the acid behaves as though it is weaker. Such a proposal is pure speculation at present. It is offered to illustrate how the ECT approach can be used to spot patterns in deviations and suggest further experimentation. In this example, the study of the deuterated analogues would be of considerable interest if exchanged systems could be sorted out.

The $CH_3^+\text{-}HCN$, $H^+\text{-}C_6H_6$, and $Li^+C_6H_6$ systems deviate from expected behavior. This is attributed to the complications arising from different possible donor sites in the molecules and lack of information about the geometry of the adduct. One would anticipate that $CH_3\text{-}CN\text{-}H^+$ would be more stable than $H\text{-}CN\text{-}CH_3^+$ and rearrangement may have taken place. In a similar fashion, Li^+ and the H^+ may coordinate to C_6H_6 by forming a σ-bonded complex leading to an sp^3 carbon and carbonium ion, i.e., species while the other acids coordinate to the intact π-system.

The donor *N,N*-dimethylacetamide has well-determined E_B and C_B parameters so all that needs to be determined in eq 3 is T_B. A consistent value cannot be found to fit H^+ and $(H_2O)_nH^+$ (n = 1, 2). If we proposed that the H^+ coordinates to nitrogen and the H_3O^+ to oxygen, the resulting value of T_B for the H_3O^+ enthalpy predicts a $-\Delta H$ for the proton coordinating to oxygen that is larger than the experimental value. Since no known favorable entropy effect exists for nitrogen coordination, this interpretation is not acceptable and oxygen coordination is required. When T_B is calculated for the H^+ coordinating to oxygen (T_B = 0.72), the calculated value for H_3O^+ is much lower than the experimental result. This suggests that extra stabilization exists for H_3O^+. Either H_3O^+ coordinates more strongly to nitrogen or the H_3O^+ plane of hydrogens is perpendicular to the amide plane with one hydrogen of H_3O^+ coordinating to the nitrogen end of the three-center amide π-system and a second hydrogen coordinating to the oxygen end.

This leaves only $(CH_3)_4N^+\text{-}CH_3NH_2$, H^+CH_3Cl, and $H_3O^+\text{-}HCN$ as unexplained exceptions out of the over 200 cation–neutral base systems included in the fit. These could be due to the existence of other unusual effects in the acid–base interaction that may be revealed as more data become available to indicate patterns in the deviations or to faulty data.

Amine Basicities and the Hydronium Series. The ECT analysis leads to the same conclusion as reported previously[20] concerning the inadquacy of using the proton affinity as a step in an energy cycle and attributing differences between it and the energy change upon aqueous protonation to solvation. In the present study, the trend of the proton affinities upon methyl substitution is dominated by the covalent and transfer term, i.e., the C_B and T_B values. The gas-phase hydronium ion is also a poor model for the aqueous proton because its C/E ratio of 0.59 causes the covalent contribution (C_AC_B) to be even more important than in the case of the proton in determining the differences in the amine enthalpies toward this species. As additional waters are added to the H_3O^+ up to $(H_2O)_4H^+$, the LUMO energy increases and the C/E ratios are observed to decrease. The R_A values also decrease and the R_AT_B term makes minor contributions to the differences in the amine enthalpies of bonding to $(H_2O)_nH^+$ with $n > 1$. The values of the parameters for $(H_2O)_4H^+$, $(H_2O)_5H^+$, and $(H_2O)_6H^+$ are suspect because of cumulative errors. The pK_B order is essentially the order of the E_B parameter of the amines. This order will result for the gas-phase hydrated proton species when $C_A/E_A \le 0.2$ for values of $T_B \sim 10$ or less. Extrapolation of the trend in the known C_A/E_A values for $(H_2O)_nH^+$ ($n = 1, 2, 3$) suggests this will occur in the gas phase with $n \ge 6$ as reported previously. Thus, the conclusions discussed in the previous paper[20] still apply and the interested reader is referred to this reference for a discussion of the insights regarding amine basicity that have resulted from the ECT analysis.

ECT Values for New Bases. The bases involved in this study are divided into four groups in Table I: (1) those whose E_B and C_B values are well-established from solution data and T_B is well-established; (2) those with tentative C_B and E_B values from solution studies whose values are now better established by adding gas-phase data that also define T_B well; (3) those whose E_B and C_B values are well-established from solution studies but whose T_B is obtained from limited data, often only a proton affinity; and (4) tentative parameters from limited data. The trends in the C_B and E_B parameters for the bases in categories 1 and 2 have been discussed in the literature. It is of interest to look for trends in the T_B values. One notes that, in the family of nitrogen donors, T_B increases as the ionization energy decreases. More transfer from the base to the cation leads to a large R_AT_B product. Accordingly, sulfur and phosphorus donor also have large T_B values. In contrast to the above trends with ionization energies, polar oxygen donors with larger ionization energies than the amines have large T_B values, suggesting that negative charge in the vicinity of the cation also increases the R_AT_B value. The trend of increasing T_B upon substitution of H by CH_3 observed with the amines is also observed for the series H_2O, CH_3OH, and $(CH_3)_2O$. The same trends are observed in the U-M ab initio calculation.

Because of the percentage error in the range of enthalpies (error in $-\Delta H/[\text{largest } (-\Delta H) - \text{smallest } (-\Delta H)]$) and because of the similarity in the C/E ratio of the gas-phase ions, it is difficult to obtain C_B and E_B values for a new donor molecule from only gas-phase data. Many of the new bases used in this fit are volatile in solution and difficult to handle in these studies, e.g. H_2CO, $(CH_3)_2O$, CH_3CHO, HCN, and H_2S. Water is an especially difficult problem. The enthalpy for $(CH_3)_2NH_2^+$ interacting with H_2O in the gas phase is 15.0 kcal mol^{-1} while that for gaseous water dimer $(H_2O)_2$ interacting with this cation is 23.5 kcal mol^{-1}. In solution, it is impossible to carry out equilibrium or enthalpy measurements under conditions where water is a monomer. Even in dilute, weakly-solvating solvents a distribution of aggregates will exist. The parameters for methanol and ethanol are the best determined of these bases for they have been studied with CH_3^+, $(CH_3)_3Sn^+$, $CpNi^+$, and H_3O^+ providing acids with a substantial range of E_A, C_A, and R_A values. However, because of hydrogen bonding in solution leading to aggregates, the use of these parameters in solution may not be valid. The formaldehyde and acetaldehyde parameters can be used to predict enthalpies with confidence toward cationic acids with a C/E ratio less than 0.13. Benzonitrile should be studied with neutral acids or $(CH_3)_3Sn^+$ and CH_3^+ and their parameters recalculated. Until more cationic, gas reference acids with C/E ratios greater than 1.0 are found, the bases H_2S, HCN, H_2CO, CH_3Cl, and H_2O should be avoided in future work whose goal is to characterize the acidity of new cations. Several alternative selections are available[2] from donors in the neutral acid–neutral base E and C fit. To facilitate their use, we report bases in Table I with well-determined E_B and C_B parameters from solution studies and a tentative T_B from limited gas-phase ion data (often only a proton affinity).

Conclusion

Over 250 gas-phase, cation–molecule enthalpies of adduct formation have been quantitatively interpreted with an electrostatic–covalent–transfer (ECT) model. This illustrates a direct relationship between typical Lewis acid–base interactions and gas-phase ion–molecule interactions. The shortcomings of comparing enthalpy data for a new cation by plotting it versus proton affinities are discussed. In place of this analysis, our E_B, C_B, and T_B parameters afford a scale of basicity that enables one to uniquely characterize the σ-bond acidity of a cation. Cations can be compared in terms of the contribution that electron transfer, covalent, and electrostatic bonding makes to their fundamental acid–base interaction. Relative covalent contributions to the coordinate bond are seen to parallel base HOMO and acid LUMO energies. The electrostatic term follows charge/size trends, and the transfer term parallels ionization energies. The proton affinity is seen to be a poor model for solution chemistry because of the domination of the gas-phase enthalpy differences by the R_AT_B term. Prediction of the enthalpy of interaction of hundreds of systems that have not been studied can be made. The model provides a means of determining when unusual effects are operative in gas-phase coordination chemistry, e.g. repulsive effects, π-back-bond stabilization, or different adduct geometries. The analysis provides an experimental guide for the proper selection of reactants in the design of an experiment that are critical to obtaining a meaningful comparison of acids or bases. For example, Al^+ is not characterized with the nine bases studied because they all have similar C_B/E_B ratios. In contrast, Li^+ is well-defined with ten bases. Finally, the utilization of E_B and C_B values for bases in fitting the gas-phase data supports our claim that the enthalpies used in the E and C fit[2] are relatively free of solvation energy contributions.

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Registry No. $NH_4^+\cdot NH_3$, 50939-42-9; $N(CH_3)_4^+\cdot CH_3NH_2$, 129916-53-6; NH_4^+, 14798-03-9; $(H_2O)_4H^+\cdot C_5H_5N$, 129916-54-7; $(H_2O)_4H^+$, 12501-73-4; $(H_2O)_3H^+$, 23108-28-3; $(H_2O)_2H^+$, 22206-74-2; H_3O^+, 13968-08-6; CH_3NH_2, 74-89-5; $(H_2O)_3H^+\cdot 4CN\text{-}C_5H_4N$, 129916-55-8; $(H_2O)_4H^+\cdot 4CN\text{-}C_5H_4N$, 129916-56-9; $CH_3^+\cdot HCN$, 64709-60-0; $CpNi^+\cdot HCN$, 60507-88-2; NH_3, 7664-41-7; $CpNi^+CH_3CN$, 60508-21-6; $(H_2O)_5H^+$, 26719-17-5; CH_3OH, 67-56-1; $K^+\cdot (CH_3)_2SO$, 71699-14-4; $H^+\cdot C_6H_6$, 38815-08-6; $Li^+\cdot C_6H_6$, 60926-51-4; $(CH_3)_2O$, 115-10-6; $(CH_3)_2NH$, 124-40-3; $H^+\cdot (CH_3)_2CO$, 43022-03-3; $(CH_3)_3N$, 75-50-3; $H^+\cdot (C_2H_5)_2O$, 17009-83-5; H_2O, 7732-18-5; $H^+\cdot (CH_3)_2S$, 18683-32-4; $H^+\cdot (CH_3)_2SO$, 26428-06-8; $H^+\cdot CH_3C(O)OCH_3$, 39014-36-3; $C_2H_5NH_2$, 75-04-7; $H^+\cdot CH_3C(O)OC_2H_5$, 39014-41-0; $H^+\cdot (C_4H_9)_2O$, 17009-85-7; $H^+\cdot (CH_2)_4O_2$, 71815-79-7; $H^+\cdot (CH_2)_4O$, 27659-93-4; $H^+\cdot (CH_3)_3COH$, 20468-51-3; $H^+\cdot C_6H_5CN$, 56683-68-2; $H^+\cdot 4CN\text{-}C_5H_4N$, 37449-63-1; $Li^+\cdot C_5H_5N$, 57450-23-4; $Li^+\cdot HCN$, 66084-42-2; $Li^+\cdot H_2CO$, 53259-65-7; $Li^+\cdot CH_3CN$, 19511-74-1; $Li^+\cdot (CH_3)_2O$, 53259-64-6; $Li^+\cdot (CH_3)_2CO$, 63602-70-0; $Li^+\cdot (CH_3)_3N$, 87311-90-8; $Li^+\cdot (CH_3)_2S$, 127540-40-3; $Li^+\cdot CH_3OH$, 63602-73-3; $Li^+\cdot (CH_3)_2NH$, 87311-89-5; $Li^+\cdot (CH_3)NH_2$, 83928-28-3; $Li^+\cdot NH_3$, 52472-72-7; $Li^+\cdot H_2O$, 51518-07-1; $(CH_3)_3Sn^+\cdot CH_3NH_2$, 129732-15-6; $(CH_3)_3Sn^+\cdot (C_2H_5)_3N$, 129732-16-7; $(CH_3)_3Sn^+\cdot NH_3$, 64710-03-8; $(CH_3)_3Sn^+\cdot CH_3OH$, 129732-17-8; $(CH_3)_3Sn^+\cdot CH_3CN$, 129732-14-5; $(CH_3)_3Sn^+\cdot C_2H_5OH$, 129732-13-4; $(CH_3)_3Sn^+\cdot (CH_3)_2NH$, 129732-12-3; $(CH_3)_3Sn^+\cdot (CH_3)_2CO$, 129732-11-2; $(CH_3)_3Sn^+\cdot (CH_3)_3N$, 129732-10-1; $(CH_3)_3Sn^+\cdot H_2O$, 129732-09-8; $(CH_3)_3SN^+\cdot CH_3C(O)OCH_3$, 129732-08-7; $(CH_3)_3SN^+\cdot C_2H_5NH_2$, 129732-07-6; $(CH_3)_3Sn^+\cdot (CH_3)COH$, 129732-06-5; $CpNi^+\cdot CH_3NH_2$, 60508-22-7; $CpNi^+\cdot NH_3$, 60508-20-5; $CpNi^+\cdot H_2CO$, 111846-75-4; $CpNi^+\cdot CH_3OH$, 60507-91-7; $CpNi^+\cdot CH_3CHO$, 60507-85-9; $CpNi^+\cdot$

C_2H_5OH, 60507-87-1; $CpNi^+\cdot(CH_3)_2O$, 60507-94-0; $CpNi^+\cdot(CH_3)_2NH$, 60508-24-9; $CpNi^+\cdot(CH_3)_2CO$, 60508-14-7; $CpNi^+\cdot(CH_3)_3N$, 60508-23-8; $CpNi^+\cdot(C_2H_5)_2O$, 60508-18-1; $CpNi^+\cdot H_2O$, 111846-73-2; $CpNi^+\cdot(CH_3)_2S$, 60508-19-2; $CpNi^+\cdot(CH_3)_3COH$, 60508-16-9; $H^+\cdot CH_3Cl$, 65967-47-7; $H^+\cdot CH_3NH_2$, 17000-00-9; $H^+\cdot C_5H_5N$, 16969-45-2; $H^+\cdot(C_2H_5)_3N$, 17440-81-2; $H^+\cdot H_2S$, 18155-21-0; $H^+\cdot HCN$, 21107-92-6; $H^+\cdot H_2CO$, 18682-95-6; $H^+\cdot CH_3OH$, 17836-08-7; $H^+\cdot CH_3CN$, 20813-12-1; $H^+\cdot CH_3CHO$, 18682-96-7; $H^+\cdot C_2H_5OH$, 18639-79-7; $H^+\cdot(CH_3)_2O$, 17009-82-4; $H^+\cdot(CH_3)_2NH$, 17000-01-0; $H^+\cdot(CH_3)_3N$, 16962-53-1; $H^+\cdot C_2H_5NH_2$, 16999-99-8; $H^+\cdot CH_3C(O)N(CH_3)_2$, 52754-55-9; $H_3O^+\cdot CH_3C(O)N(CH_3)_2$, 129916-57-0; $(H_2O)_2H^+\cdot CH_3C(O)N(CH_3)_2$, 129916-58-1; $(H_2O)_3H^+\cdot CH_3C(O)N(CH_3)_2$, 129916-59-2; $(H_2O)_4H^+\cdot CH_3C(O)N(CH_3)_2$, 129916-60-5; $CH_3^+\cdot H_2S$, 18683-23-3; $CH_3^+\cdot H_2CO$, 23653-97-6; $CH_3^+\cdot CH_3Cl$, 24400-15-5.

Supplementary Material Available: Tables of calculated and experimental enthalpies for systems used in the final data fit and for hydrated proton systems omitted from the final data fit (20 pages). Ordering information is given on any current masthead page.

Duocarmycin–Pyrindamycin DNA Alkylation Properties and Identification, Synthesis, and Evaluation of Agents Incorporating the Pharmacophore of the Duocarmycin–Pyrindamycin Alkylation Subunit. Identification of the CC-1065–Duocarmycin Common Pharmacophore

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Abstract: A demonstration and subsequent study of the DNA covalent alkylation properties of duocarmycin A and duocarmycin C_1 and C_2 (pyrindamycin B and A, respectively) are detailed and have led to the identification of two high affinity binding sites [5′-d(A/TAA$\underline{\text{A}}$)-3 and 5′-d(A/TTT$\underline{\text{A}}$Pu)-3′] within a full set of available alkylation sites [5′-d(AA$\underline{\text{A}}$)-3′ > 5′-d(TT$\underline{\text{A}}$)-3′ > 5′-d(TA$\underline{\text{A}}$)-3′ > 5′-d(AT$\underline{\text{A}}$)-3′] that proceeds through 3′-adenine N-3 alkylation of the duocarmycin A activated cyclopropane similar to the (+)-CC-1065 covalent alkylation of DNA. The synthesis of **10** (CI-TMI) incorporating the parent 1,2,7,7a-tetrahydrocycloprop[1,2-*c*]indol-4-one (CI) alkylation subunit of duocarmycin is described and the results of its comparative evaluation (in vitro cytotoxic activity and DNA covalent alkylation properties) demonstrate that **10** constitutes an agent bearing the minimum potent pharmacophore of the duocarmycin DNA alkylation subunit and the common pharmacophore of the duocarmycin–CC-1065 alkylation subunits.

Two independent efforts have disclosed the isolation, structure determination, and preliminary evaluation of a new class of antitumor antibiotics now including duocarmycin A[2–4] (**2**), duocarmycin B_1 and B_2 (**3** and **4**),[6] duocarmycin C_1[3–5] (**5**, pyrindamycin B[7]), and duocarmycin C_2[3] (**6**, pyrindamycin A[7])[8] (Figure 1). The structural similarities between the duocarmycins and (+)-CC-1065 (**1**)[9–13] suggest that the agents may be acting by a common or related mechanism initiated with the irreversible covalent alkylation of DNA. Herein, we report full details of studies that provide a demonstration of the formation of duocarmycin–DNA covalent adducts in a reaction analogous to that observed with (+)-CC-1065[9] and report the comparative DNA binding properties of duocarmycin A, C_1, C_2 and (+)-CC-1065 (**1**) that provide support for the potential that the agents may be acting by a common mechanism derived from the irreversible covalent alkylation of DNA.

The preparation of **10** incorporating the parent 1,2,7,7a-tetrahydrocycloprop[1,2-*c*]indol-4-one (CI)[14,15] left-hand subunit of the duocarmycins and (+)-CC-1065 is detailed as is that of the stable precursors **7–9**[19] (Scheme I). A recent demonstration[15] of the comparable DNA alkylation selectivity of racemic (±)-*N*-BOC-CI (**11**) and (+)-*N*-BOC-CPI (**12**) that has proven distinct from that of (+)-CC-1065[16] coupled with the results of a study of the comparative DNA binding properties and cytotoxic activity of **7–12** with that of the duocarmycins detailed herein illustrate that **10** embodies the required, but not necessarily optimal, structural and functional features of the duocarmycin left-hand subunit that is responsible for their DNA alkylation properties. That is, **10** represents an agent bearing the minimum pharma-

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