Quantitative Prediction and Analysis of Enthalpies for the Interaction of Gas-Phase Ion–Ion, Gas-Phase Ion–Molecule, and Molecule–Molecule Lewis Acid–Base Systems

Michael K. Kroeger and Russell S. Drago*

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received April 21, 1980*

Abstract: The equation $-\Delta H = e_A e_B + c_A c_B + t_A t_B$, where subscripts A and B refer to acid and base, correlates the enthalpy of Lewis acid–base adduct formation for molecule–molecule (in poorly solvating solvents), gas-phase ion–molecule, and gas-phase ion–ion interactions. The constants obtained for the acids and bases are interpreted in terms of electrostatic, covalent, and electron-transfer nature of the interactions. Trends in the parameters are found to agree with qualitative chemical intuition regarding acid–base properties and a semiempirical justification for adding the electron-transfer term is presented. Several new insights regarding the comparison of gas-phase and solution data are provided. Solution studies often involve displacement reactions or other acid–base species that complicate a direct comparison to gas-phase results. The quantitative correlation can be used to indicate instances where variations may occur in the geometry of acid–base adducts. The existence of bonding contributions other than σ bond formation is also suggested by this correlation.

Previous reports from this laboratory[1-4] have correlated the enthalpies of adduct formation of neutral Lewis acids and bases to the E and C equation

$$-\Delta H = E_A E_B + C_A C_B \tag{1}$$

where E_A and C_A are empirical parameters for acids and E_B and C_B are empirical parameters for bases. The parameters E parallel qualitative ideas about the tendency of the acid or base to undergo electrostatic interactions and the parameters C parallel the tendency of the acid or base to undergo covalent interactions. The E and C equation could be derived from the Mulliken-determined energies of charge-transfer complexes by introducing perturbation-theory types of approximations.[5]

Attempts to correlate enthalpies for the interaction of ionic Lewis acids and bases to eq 1 met with only limited success[6,7] as predicted by the derivation because the energies involved are too large for the perturbation-type approximations to hold. For interactions involving large (>40 kcal/mol) energies, the following equation was derived from theory[5,8] and shown to fit the experimental data within the 1% accuracy expected:

$$-\Delta H = \sqrt{(D_A - D_B)^2 + O_A O_B} \tag{2}$$

where D_A and O_A are empirical parameters for the acids and D_B and O_B are empirical parameters for the bases. The parameters D are related to the diagonal elements of the molecule's molecular orbital (MO) secular determinant and the parameters O are related to the off-diagonal elements of the MO secular determinant. In a crude sense the diagonal elements relate to ionic contributions and the off-diagonal elements to covalent contributions.

Although the fit of eq 2 with experimental data for ionic acids and bases is gratifying, there are several aspects of this equation that are unsatisfactory from the point of view of the practicing chemist. The presence of the square root in the D and O equation makes it difficult to obtain any meaningful decomposition of the total enthalpy into two components (i.e., ionic and covalent). Accordingly, it is difficult to assess the physical meaning of the parameters in terms the chemist commonly uses when discussing bonding (i.e., ionic and covalent interactions). Furthermore, when one attempts to incorporate ion–molecule reactions into eq 2, the neutral molecule D and O parameters obtained are in no way related to their E and C parameters. As a result, the information available from the study of neutral molecule–neutral molecule interactions is of no value in predicting, or understanding, ion–molecule enthalpies. Accordingly, we sought another empirical equation to overcome these objections.

The presence of significant electron transfer is one feature that many of the ion–ion and ion–molecule systems have to a greater extent than molecule–molecule interactions. For example, when CH_3^+ interacts with CH_3^-, a complete electron is transferred in the process and the accompanying energy associated with the electron transfer makes a substantial contribution to the total enthalpy. As mentioned in previous theoretical discussions,[7] the one-center H_A and H_B integrals can no longer be approximated by linear functions when charge transfer is extensive and, accordingly, the E and C equation fails. The simplest method to attempt to account for the electron-transfer contribution to the enthalpy is to add a new term to the E and C equation for these ion–ion and ion–molecule systems and determine empirically if this term can indeed accommodate the electron-transfer energies. There is literature precedent[9,10] for interpreting the enthalpies of ionic interactions in terms of three independent terms: one-center interactions, which can be correlated to electron transfer, and two-center interactions, which can be broken down into two types of contributions (electrostatic and covalent).

The following equation was found to provide a satisfactory fit of the available data

$$-\Delta H = e_A e_B + c_A c_B + t_A t_B \tag{3}$$

where the parameters t indicate the tendency of the acid or base to undergo electron transfer upon adduct formation. The lower case symbols are used to distinguish eq 3 from eq 1. This relation now provides a basis for the unified treatment and prediction of molecule–molecule, ion–molecule, and ion–ion Lewis acid–base interactions. Several interesting insights relative to the interpretation of gas-phase and solution data arise from the treatment. For example, the treatment indicates why the comparison of proton affinities for neutral molecules with pK_B data is not a meaningful exercise, but the comparison of methyl cation affinities with similar processes in solution is more significant. We can demonstrate why proton affinities are improper standards to employ for rationalizing trends in the reactivity of bases toward other ionic

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(1) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1972**, *94*, 6014.
(2) Guidry, R. M.; Drago, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 759.
(3) Drago, R. S.; Parr, L. B.; Chamberlain, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 3203.
(4) Drago, R. S. *Struct. Bonding (Berlin)*, **1973**, *15*, 73.
(5) Marks, A. P.; Drago, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 3324.
(6) McMillan, D. R.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 872.
(7) Jolly, W. L.; Illige, J. D.; Mendelsohn, M. H. *Inorg. Chem.* **1972**, *11*, 869.
(8) Marks, A. P.; Drago, R. S. *Inorg. Chem.* **1976**, *15*, 800.
(9) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 546.
(10) Evans, R. S.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1970**, *32*, 777.

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species. The treatment suggests that Lewis bases containing more than one lone pair interact in a different fashion with alkali cations than with the other acids in the correlation. The analysis is of importance in the design of further studies of ion–molecule reactions because it indicates which ions are similar in their bonding interactions and which systems are really different. Study of the latter combination of ions provides the most meaningful information. These few examples are illustrative of the insights that are potentially obtainable from the correlation.

Calculations

A computer program was developed to find the best-fit *e*, *c*, and *t* parameters to correlate enthalpies with eq 3 by both a gradient-search least-squares method and a "linearized" least-squares method[1,4] for eq 3. Fitting of the data was carried out on a Digital VAX 11/780 computer in double precision.

The following weighting scheme was devised to approximate the uncertainty in experimental enthalpies in the data fit:

$-\Delta H > 350$ kcal/mol then the uncertainty = 8 kcal/mol

$350 > -\Delta H > 250$ kcal/mol then the uncertainty = 6 kcal/mol

$250 > -\Delta H > 150$ kcal/mol then the uncertainty = 4 kcal/mol

$150 > -\Delta H > 75$ kcal/mol then the uncertainty = 2 kcal/mol

$75 > -\Delta H > 20$ kcal/mol then the uncertainty = 1.0 kcal/mol

$20 > -\Delta H > 10$ kcal/mol then the uncertainty = 0.3 kcal/mol

$10 > -\Delta H > 0$ kcal/mol then the uncertainty = 0.15 kcal/mol

This results in an average error of about 2% for most enthalpies. Higher uncertainties were given to single enthalpies when experiment error warranted such an assignment. This weighting scheme is directly related to the error associated with each measured enthalpy. In those systems where steric effects were thought possible (such as with adducts involving $(C_2H_5)_3N$), an uncertainty of 2–4 kcal was assigned. When significant steric effects were expected, the data were omitted from the fit.

As remarked in previous reports, a consistent set of bad data for an acid or base can lead to incorrect parameters. The empirical nature of the approach must be considered as new data becomes available and as attempts are made to incorporate these data into the fit.

Ideally, one would fix the minimum number of parameters in order to obtain a unique solution for a set of simultaneous equations of the form of eq 3, and the data set would provide a meaningful solution that minimized the deviation between the calculated and experimental enthalpies. Unfortunately, the amount of absolute enthalpy data is very limited for the ion–ion and ion–molecule systems and some of the available data has much uncertainty in it. The number of acids and bases that can be incorporated by the model is limited by the scarcity of data involving the interaction of ionic acids with neutral bases, vide infra. These data are necessary to define the value of t_A or t_B.

The following parameters were fixed: $c_{I_2} = 1.2$, $t_{(CH_3)_3COH} = 0.01$, $e_{BF_3} = 2.0$, $t_{SO_2} = 0.01$, $c_{HCCl_3} = 0.01$, $t_{Rb^+} = 0.116$, $t_{Cs^+} = 0.01$, $c_{Cs^+} = 0.073$, $c_{(CH_3)_3C^+} = 0.01$, $c_{NO^+} = 0.01$, $e_{(CH_3)_3N} = 0.745$, $e_{(CH_3)_2S} = 0.024$, $e_{(C_2H_5)_2S} = 0.01$, $e_{cage} = 0.01$, $t_{H_2O(B)} = 0.1$, and $c_{H^-} = -267.005$. The imposition of a model on the system by fixing parameters has been discussed previously.[1,8] The fixed parameters were chosen so that the number of negative parameters in the entire fit would be minimized and so that the fit would also somewhat resemble the *E* and *C* values previously reported.[1,4] For those systems included in the constant *W* analysis[2] (i.e., HFIP, $Al(CH_3)_3$, and $(Rh(COD)Cl)_2$), the previously reported *W* correction was made for the appropriate enthalpies.

Results and Discussion

Data Fit. Fitting 364 enthalpies, including all available and usable ion–molecule interactions, to eq 3 resulted in the *e*, *c*, and *t* parameters for the various ionic and neutral acids and bases reported in Table I. All enthalpies were experimental except Cu^+–$H_2O(A)$ and Cu^+–CH_3OH which were estimated from trends and lower bounds on the absolute values, for C_6H_5OH and I_2 with H_2CO and $(CH_3)_2O$ which were estimated from trends with $(CH_3CH_2)_2O$ and $(CH_3)_2CO$, and I_2 with CH_3OH and HCN which were estimated from trends with $(CH_3CH_2)_2O$ and CH_3CN. The agreement between the enthalpies calculated from the parameters with experimental data is reported in Table II. Because of the difference in the number of systems studied with each different acid or base, variations exist in the certainty of the parameters and in our ability to predict additional enthalpies of interaction from a given system. For many neutral bases, the t_B number is essentially determined only by the proton affinity. Accordingly, these parameters are tentative and are so marked. The interactions of many neutral acids with anions have not been studied, but using known t_B values a reasonable estimate of the t_A value for the neutral acid can be determined from the enthalpies of neutral acid–base interactions. These t_A numbers are labeled as tentative. In order to accurately determine the e_A, c_A, and t_A numbers for a cation, it must be studied with at least one neutral base or with anions whose parameters differ.[11] There are only two classes of anions whose trends of e_B, c_B, and t_B numbers differ: F^-, OH^-, and CH_3O^- comprise the first class whose interactions are dominated by the c_Ac_B term; and Cl^-, Br^-, I^-, CH_3^-, CN^-, NH_2^-, NO_2^-, and H^- comprise the second class whose interactions are dominated by the t_At_B term. Cations were not included in the fit if there were no cation–molecule enthalpies for them. A similar difficulty exists for neutral bases which had no enthalpies of interaction with cations. For neutral acid–base interactions it has already been shown that interactions of neutral acids and bases can be fit to a two-term four-parameter equation. Thus, the addition of a third term is superfluous and the needed parameter cannot be defined from these data. For this reason, neutral bases were not included unless ionic interactions were measured. Since the cations tend to have e_A/c_A, e_A/t_A, and c_A/t_A ratios that differ greatly, the anion parameters do not suffer the same disadvantages as the cations and can be defined from ion–ion enthalpies. The cations may be grouped into classes based on trends of their *e*, *c*, and *t* parameters and enthalpies with F^- and H^-. Class one consists of Li^+, Na^+, K^+, Rb^+, Cs^+, and Sr^+ whose interactions are largely dominated by e_Ae_B and $-\Delta H_{M^+F^-} > -\Delta H_{M^+H^-}$. Class two consists of CH_3^+, $C_2H_5^+$, $(CH_3)_2CH^+$, $(CH_3)_3C^+$, Cu^+, Bi^+, NO^+, and Pb^+ whose interactions contain more significant contributions from c_Ac_B and t_At_B and $-\Delta H_{M^+F^-} < -\Delta H_{M^+H^-}$. Class three contains H^+ and $CpNi^+$ which are similar and whose interactions are dominated by t_At_B.

New acids (or bases) can be added to the system by determining their enthalpies of adduct formation with bases (or acids) whose parameters are known and solving the simultaneous equations for the three unknowns e_A, c_A, and t_A (or e_B, c_B, and t_B). In designing an experiment to study a new acid, the bases (or acids) should be selected to show as large a variation in the *e*, *c*, and *t* parameters (and their ratios) as possible. Sulfur donors should be employed to a much greater extent that has been done in the literature.

The *e* and *c* parameters for neutral species obtained in this fit *cannot* be used interchangeably with the *E* and *C* parameters for eq 1. Each set is internally consistent. The fact that we were able to incorporate the small enthalpies for neutral–neutral systems into a two-term, four-parameter equation (eq 1) is consistent with the finding of a very good fit with those systems in the present

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[11] As an example of the definition of the cation parameters a least-squares e_A, c_A, and t_A fit of Tl^+ for enthalpies with F^-, Cl^-, Br^-, I^-, and H^- yields a reasonably good fit with $e_A = 6.89$, $c_A = 3.33$, and $t_A = 5.81$. Inclusion of a reasonable estimated enthalpy of 25 kcal/mol for the interaction of Tl^+ with H_2O now yields $e_A = 21.66$, $c_A = 1.05$, and $t_A = 1.91$ (reasonable values compared to Bi^+ and Pb^+) with only a very slight worsening of the fit. The problem is that the parameters for the halides are not significantly different (in a three-dimensional space) in determining the least-squares fit.

Table I. *e*, *c*, and *t* Parameters for Lewis Acids and Bases

Lewis acid	no. of enthalpies	e_A (std. dev.)	c_A (std. dev.)	t_A (std. dev.)	Lewis acid	no. of enthalpies	e_A (std. dev.)	c_A (std. dev.)	t_A (std. dev.)
I_2 (iodine)[a]	30	0.231 (0.434)	1.200[b]	0.122 (0.006)	H^+ (proton)	46	8.654 (40.114)	8.554 (8.495)	15.040 (0.552)
C_6H_5OH (phenol)[c]	27	4.561 (3.252	0.274 (0.656)	0.315 (0.012)	Li^+	12	23.066 (0.753)	0.968 (1.278)	1.715 (1.182)
m-FC_6H_4OH[a]	8	4.426 (1.316)	0.291 (0.159)	0.347 (0.014)	Na^+	9	21.798 (0.870)	0.546 (0.280)	1.030 (4.507)
m-$CF_3C_6H_4OH$ (TFMP)[a]	15	4.554 (0.767)	0.352 (0.884)	0.339 (0.010)	K^+	13	21.378 (2.177)	0.148 (0.406)	0.300 (0.714)
$(CH_3)_3COH$	4	3.747 (0.578)	0.408 (0.137)	0.010[b]	Rb^+	7	21.951 (0.490)	0.073 (0.198)	0.116[b]
$(CF_3)_2CHOH$ (HFIP)[a,d]	10	5.214 (0.887)	0.426 (0.261)	0.475 (0.024)	Cs^+[c]	6	21.534 (0.210)	0.010[b]	0.012[b]
$(CH_3)_3SnCl$[a]	5	6.668 (0.561)	0.300 (0.152)	0.307 (0.010)	CH_3^+	18	20.326 (12.700)	3.592 (5.985)	6.627 (0.728)
BF_3 (gas)[c]	5	2.000[b]	1.668 (0.205)	0.914 (0.057)	$C_2H_5^+$[c]	12	26.500 (0.172)	1.547 (0.096)	3.106 (0.252)
$B(CH_3)_3$[a]	6	8.590 (0.391)	1.601 (0.016)	0.292 (0.006)	$(CH_3)_2CH^+$[c]	11	28.080 (0.643)	0.744 (0.476)	1.697 (0.689)
$Al(CH_3)_3$[a,e]	15	16.128 (1.368)	0.685 (0.167)	1.255 (0.037)	$(CH_3)_3C^+$[c]	10	31.931 (2.879)	0.010[b]	0.442 (0.729)
SO_2	5	3.777 (0.249)	0.721 (0.046)	0.010[b]	Sr^+[c]	6	22.494 (0.482)	1.023 (0.534)	1.742 (1.595)
$Cu(hfacac)_2$[a]	5	3.186 (0.162)	1.672 (0.033)	0.235 (0.007)	Cu^+	7	23.621 (23.075)	1.653 (0.828)	3.096 (0.802)
$HCCl_3$ (chloroform)[c]	10	2.247 (0.700)	0.010[b]	0.267 (0.016)	NO^+	11	22.683 (13.655)	0.010[b]	2.867 (0.091)
H_2O	17	1.649 (0.691)	0.372 (0.221)	0.196 (0.022)	Bi^+	7	25.846 (5.920)	0.700 (0.622)	1.513 (0.412)
Co(PPIXDME)[a]	4	3.509 (0.033)	0.472 (0.006)	0.371 (0.002)	Pb^+[c]	6	24.133 (0.223)	0.836 (0.337)	1.659 (0.335)
$(Rh(COD)Cl)_2$[a,f]	5	2.321 (0.090)	1.394 (0.019)	0.457 (0.005)	$(C_5H_5)Ni^+$ ($CpNi^+$)	9	1.977 (3.201)	2.285 (2.335)	3.890 (0.117)
Zn(TPP)[a]	3	5.543 (0.000)	0.442 (0.000)	0.371 (0.000)					

Lewis base	no. of enthalpies	e_B (std. dev.)	c_B (std. dev.)	t_B (std. dev.)	Lewis base	no. of enthalpies	e_B (std. dev.)	c_B (std. dev.)	t_B (std. dev.)
C_5H_5N (pyridine)	16	0.629 (0.163)	5.112 (11.177)	11.486 (9.237)	$C_2H_5C(CH_2O)_3P$ (cage)[c]	4	0.026[b]	7.085 (2.819)	9.782 (0.128)
NH_3 (ammonia)	11	0.694 (0.096)	2.713 (0.906)	11.587 (0.645)	H_2O (A)	11	0.259 (0.106)	10.582 (12.726)	4.417 (0.391)
CH_3NH_2	9	0.786 (0.142)	4.655 (1.347)	11.281 (0.799)	H_2O (B)	6	0.649 (0.018)	19.203 (7.460)	0.100[b]
$(CH_3)_2NH$	9	0.755 (0.075)	6.934 (0.814)	10.574 (0.430)	CH_3OH	6	0.061 (0.255)	2.197 (29.151)	10.684 (0.497)
$(CH_3)_3N$	8	0.745[b]	9.272 (0.181)	9.003 (8.094)	$(CH_3)_2O$	5	0.330 (0.090)	2.170 (0.687)	10.978 (0.602)
$C_2H_5NH_2$[c]	4	0.824 (0.082)	4.866 (0.119)	11.017 (0.218)	H_2CO	4	0.228 (0.069)	1.505 (0.333)	10.285 (0.298)
$(C_2H_5)_2NH$[c]	3	0.579 (0.000)	6.898 (0.000)	10.551 (0.000)	HCN	5	0.727 (0.104)	0.173 (0.143)	11.653 (0.082)
$(C_2H_5)_3N$[c]	5	0.781 (0.047)	8.830 (3.512)	9.786 (0.218)	piperidine[c]	5	0.770 (0.307)	7.223 (4.204)	10.277 (0.611)
CH_3CN (acetonitrile)[c]	8	0.153 (0.107)	0.352 (0.396)	12.230 (0.556)	*N*-methylimidazole[c]	6	0.672 (0.046)	6.854 (1.890)	10.704 (0.526)
$ClCH_2CN$[c]	4	0.085 (0.012)	0.013 (0.135)	11.969 (0.127)	$(CH_2)_5O$ (THP)[c]	5	0.389 (0.183)	2.820 (0.144)	11.132 (0.368)
$HCON(CH_3)_2$ (DMF)[c]	5	0.405 (0.154)	1.665 (0.742)	12.698 (0.915)	$(C_2H_5)_3PO_4$[c]	6	0.475 (0.067)	1.198 (14.417)	13.479 (0.548)
$CH_3CON(CH_3)_2$ (DMA)[c]	9	0.485 (0.146)	2.011 (0.338)	12.803 (3.862)	F^-	16	6.154 (0.148)	34.768 (3.859)	1.108 (39.841)
$CH_3COOC_2H_5$ (EtOAc)[c]	10	0.133 (0.293)	0.892 (11.129)	12.612 (0.614)	Cl^-	19	5.111 (0.317)	2.730 (49.435)	17.508 (57.371)
CH_3COOCH_3 (MeOAc)[c]	8	0.155 (0.026)	0.787 (0.346)	12.384 (0.327)	Br^-[c]	16	4.897 (0.189)	4.863 (63.044)	15.670 (10.132)
$(CH_3)_2CO$ (acetone)	9	0.252 (0.050)	1.463 (0.461)	12.029 (0.466)	I^-[c]	16	4.517 (0.111)	−2.502 (56.694)	19.608 (15.662)
$(C_2H_5)_2O$	8	0.311 (0.348)	2.398 (1.109)	11.587 (1.179)	OH^-[c]	9	6.599 (0.380)	34.817 (164.856)	2.394 (6.465)
$((CH_3)_2CH)_2O$[c]	4	0.400 (0.005)	2.289 (0.057)	11.966 (0.053)	CH_3^-[a]	5	7.564 (0.114)	−8.763 (140.088)	28.476 (3.188)

Table I (*Continued*)

Lewis base	no. of enthalpies	e_B (std. dev.)	c_B (std. dev.)	t_B (std. dev.)
$(CH_2)_4O_2$ (*p*-dioxane)[c]	5	0.317 (0.125)	1.636 (0.341)	11.645 (0.652)
$(CH_2)_4O$ (THF)[c]	8	0.359 (0.081)	3.216 (8.916)	11.160 (0.625)
$(CH_3)_2SO$ (Me_2SO)[c]	14	0.584 (0.040)	2.329 (0.423)	11.969 (10.738)
$(CH_3)_2S$[c]	5	0.024[b]	5.466 (0.307)	9.986 (0.276)
$(C_2H_5)_2S$[c]	6	0.010[b]	5.448 (0.274)	10.210 (0.244)
$(CH_3)_3P$[c]	4	0.870 (0.031)	3.398 (0.106)	12.490 (0.178)
$HC(C_2H_4)_3N$ (quin)[c]	4	0.735 (0.003)	10.546 (0.187)	8.786 (0.009)
CH_3O^- [a]	5	6.756 (0.048)	39.827 (31.704)	−1.298 (0.771)
CN^- [c]	5	5.420 (0.153)	2.585 (2.909)	18.949 (1.648)
NH_2^- [a]	5	6.715 (0.046)	−59.777 (54.765)	56.684 (1.291)
NO^- [a]	5	5.197 (0.024)	−65.781 (24.346)	57.159 (0.645)
NO_2^-	6	5.896 (0.120)	3.396 (0.980)	18.200 (7.597)
H^- [a]	14	5.334 (0.052)	−267.005[b]	175.307 (5.105)

[a] Parameters are tentative due to no ion–molecule enthalpies. [b] The parameter was not allowed to vary. [c] Parameters are tentative due to only one ion–molecule enthalpy. [d] $W'_A = 1.1$. [e] $W'_A = 10.2$. [f] $W'_A = 6.3$.

fit. For those systems in which enthalpies of ionic interactions are not available, we would recommend continued use of the *E* and *C* equation (eq 1) for the prediction and interpretation of data.

The empirical nature of the fit cannot be overemphasized. When there is extensive information about an ion, an incorrect enthalpy can be immediately spotted; for example, assigning the $Bi^+ + F^-$ enthalpy an uncertainty comparable to the other enthalpies results in e_A, c_A, and t_A parameters for Bi^+ which are very similar to those now reported. However, the error in the fit is much larger. This indicates that the $Bi^+ + F^-$ enthalpy plays a very small role in determining e_A, c_A, and t_A for Bi^+ and the BiF enthalpy is clearly incompatible with the rest of the data. When only limited data are available for a particular system, parameters obtained in the fit can be greatly influenced by an incorrect enthalpy and, accordingly, incorrect parameters and predictions will result. The incorrectness will only become obvious when more data become available. This is the meaning of our tentative label.

Equation 3 offers several advantages over both eq 1 and 2. First, two equations (eq 1 and 2) involving eight parameters have been combined into one equation involving six parameters. Second, eq 1 was only partially successful in incorporating ionic enthalpies and completely failed to incorporate the H^+ system.[6] Equation 2 did not allow successful (although a good fit of the data was obtained, the parameters had no physical significance) incorporation of ion-molecule heats, whereas eq 3 now accommodates both the neutral–neutral and ion–ion systems as well as the ion–molecule interactions. As in the case of eq 1, systems have been used in this correlation in which the interaction is expected to involve only σ bond formation.

Error Analysis

Only the conditional standard deviations for the parameters were calculated and are reported in Table I. The conditional standard deviations were calculated for a parameter by assuming all other parameters had their true values.

For some acids and bases the standard deviations of the parameters tend to be high when they have interactions with bases and acids whose *e*, *c*, or *t* parameters are extremely small (cf. F^-, I^-, and CH_3O^-). In calculating the standard deviation for a parameter, e.g., t_B, a small t_A (or any other parameter) value leads to a wide range in possible t_B (or any other corresponding parameter) values that fit a given enthalpy. A very different t_B leads to a large standard deviation for the acid and base parameter even though the fit may be very good.

The reduced χ^2 associated with the entire fit of 364 enthalpies was 0.0512. A typical enthalpy with an uncertainty of 1.000 kcal/mol associated with it had an error of 0.226 kcal/mol associated with the predicted enthalpy. As can be seen, the theoretical enthalpies can be predicted to as good an accuracy as the experimental enthalpies are known. A test of whether or not the parameters constrained were a poor choice is the generalized weighted *R*-factor ratio.[12] For our model there are 364 (the number of enthalpies) − 240 (the number of parameters) = 124 degrees of freedom. The unconstrained fit had a generalized weighted *R* factor of 0.213. The model in which 16 parameters were constrained had a generalized weighted *R* factor of 0.226 which leads to a ratio of 1.0610. On the basis of the *R*-factor ratio test it can be seen that the constrained fit (the model) cannot be rejected at any confidence level. Therefore, it may be concluded that for this data set the model does not contain a poor choice of standards.

Existence of a Transformation Matrix

The problem of selecting a transformation matrix to impose another model on the system, if desired, is not as simple as it was with the *E* and *C* equation.[4,5] With the use of vector notation, a matrix is required such that

$$\mathrm{A}' = \begin{pmatrix} e'_A \\ c'_A \\ t'_A \end{pmatrix} = \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{pmatrix} \begin{pmatrix} e_A \\ c_A \\ t_A \end{pmatrix} = \mathrm{TA} \qquad (4)$$

and

$$\mathrm{B}'^{\mathrm{T}} \begin{pmatrix} e'_B \\ c'_B \\ t'_B \end{pmatrix}^{\mathrm{T}} = \begin{pmatrix} e_B \\ c_B \\ t_B \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} T_{11}^{-1} & T_{12}^{-1} & T_{13}^{-1} \\ T_{21}^{-1} & T_{22}^{-1} & T_{23}^{-1} \\ T_{31}^{-1} & T_{32}^{-1} & T_{33}^{-1} \end{pmatrix} = \mathrm{B}^{\mathrm{T}}\mathrm{T}^{-1} \qquad (5)$$

such that

$$\mathbf{T}^{-1}\mathbf{T} = \mathbf{1} \qquad (6)$$

Vectors **A** and B represent the old acid and base parameters and A′ and B′ represent the new, transformed parameters. In general, an arbitrary selection of nine parameters as standards will not lead to a transformation matrix T. As an example: definition of the matrix elements T_{11}, T_{12}, T_{13}, T_{21}, T_{22}, T_{23}, T_{31}, T_{32}, and T_{33} (i.e., defining *e*, *c*, and *t* using only acids) will lead to a transformation; however, definition of T_{11}^{-1}, T_{21}^{-1}, T_{31}^{-1}, T_{21}, T_{22}, T_{23}, T_{31}, T_{32}, and T_{33} (i.e., definition of *e* with three bases and *c* and *t* with three acids each) will not lead to a solution. Selection of certain combinations of parameters will lead to nonlinear constraints which will overdefine the system. Therefore, one must be extremely careful in choosing parameters as standards. The initial requirement of our model was that the fit resemble the *E* and *C* fit as closely as possible while producing the least amount of negative parameters. Another requirement was that t_A be large for H^+, small for Cs^+, and relatively small for the neutral Lewis acids. The minimization of the fit was monitored and parameters

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(12) For a discussion of the *R* factor ratio test see: Hamilton, W. C. "Statistics in Physical Sciences"; Ronald Press Co.: New York, 1964.

Table II. Enthalpies in the *e*, *c*, and *t* Correlation

Lewis acid	Lewis base	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$, kcal/mol	uncertainty, kcal/mol	ref[a,b]
I_2 (iodine)	C_5H_5N (pyridine)	7.8	7.7	0.15	
	NH_3 (ammonia)	4.8	4.8	0.15	
	CH_3NH_2	7.1	7.1	0.15	
	$(CH_3)_2NH$	9.8	9.8	0.15	
	$(CH_3)_3N$	12.1	12.4	0.30	
	$C_2H_5NH_2$	7.4	7.4	0.15	
	$(C_2H_5)_2NH$	9.7	9.7	0.15	
	$(C_2H_5)_3N$	12.0	12.0	0.30	
	CH_3CN (acetonitrile)	1.9	2.0	0.15	
	$ClCH_2CN$	1.5	1.5	0.15	
	$HCON(CH_3)_2$ (DMF)	3.7	3.6	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	4.0	4.1	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	2.8	2.6	0.15	
	CH_3COOCH_3 (MeOAc)	2.5	2.5	0.15	
	$(CH_3)_2CO$ (acetone)	3.3	3.3	0.15	
	$(C_2H_5)_2O$	4.2	4.4	0.15	
	$((CH_3)_2CH)_2O$	4.3	4.3	0.15	
	$(CH_2)_4O_2$ (*p*-dioxane)	3.5	3.5	0.15	
	$(CH_2)_4O$ (THF)	5.3	5.3	0.15	
	$(CH_3)_2SO$ (Me_2SO)	4.4	4.4	0.15	
	$(CH_3)_2S$	7.8	7.8	0.15	
	$(C_2H_5)_2S$	7.8	7.8	0.15	
	$HC(C_2H_4)_3N$ (quin)	13.9	13.9	0.30	
	CH_3OH	3.9	4.0	0.15	*c*
	$(CH_3)_2O$	4.0	4.0	0.15	*c*
	H_2CO	3.1	3.1	0.15	*c*
	HCN	1.8	1.8	0.15	*c*
	piperidine	10.3	10.1	0.30	*d*
	$(CH_2)_5O$ (THP)	4.9	4.8	0.15	
	$(C_2H_5)_3PO_4$	3.2	3.2	0.15	*e*
C_6H_5OH (phenol)	C_5H_5N (pyridine)	8.0	7.9	0.15	
	NH_3 (ammonia)	7.8	7.6	0.15	
	CH_3NH_2	8.6	8.4	0.15	
	$(CH_3)_2NH$	8.6	8.7	0.15	
	$(CH_3)_3N$	8.8	8.8	0.15	
	$C_2H_5NH_2$	8.6	8.6	0.15	
	$(C_2H_5)_3N$	9.0	9.1	0.15	
	CH_3CN (acetonitrile)	4.6	4.6	0.15	
	$ClCH_2CN$	4.2	4.2	0.15	
	$HCON(CH_3)_2$ (DMF)	6.1	6.3	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	6.7	6.8	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	4.8	4.8	0.15	
	CH_3COOCH_3 (MeOAc)	4.8	4.8	0.15	
	$(CH_3)_2CO$ (acetone)	5.1	5.3	0.15	
	$(C_2H_5)_2O$	6.0	5.7	0.15	
	$((CH_3)_2CH)_2O$	6.2	6.2	0.15	
	$(CH_2)_4O_2$ (*p*-dioxane)	5.6	5.6	0.15	
	$(CH_2)_4O$ (THF)	6.0	6.0	0.15	
	$(CH_3)_2SO$ (Me_2SO)	6.9	7.1	0.15	
	$(CH_3)_2S$	4.6	4.7	0.15	
	$(C_2H_5)_2S$	4.6	4.7	0.15	
	$HC(C_2H_4)_3N$ (quin)	9.0	9.0	0.15	
	$(CH_3)_2O$	5.8	5.6	0.15	*c*
	H_2CO	4.8	4.7	0.15	*c*
	$(CH_2)_5O$ (THP)	6.1	6.0	0.15	
	$(C_2H_5)_3PO_4$	6.7	6.7	0.15	*e*
	Cl^-	27.4	29.6	1.00	*f*
m-FC_6H_4OH	C_5H_5N (pyridine)	8.4	8.3	0.15	
	CH_3CN (acetonitrile)	4.9	5.0	0.15	
	$HCON(CH_3)_2$ (DMF)	7.0	6.7	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	5.1	5.2	0.15	
	$(CH_3)_2SO$ (Me_2SO)	7.3	7.4	0.15	
	$(C_2H_5)_2S$	5.2	5.2	0.15	*d*
	$C_2H_5C(CH_2O)_3P$ (cage)	5.6	5.6	0.15	
	N-methylimidazole	8.5	8.7	0.15	
m-$CF_3C_6H_4OH$ (TFMP)	C_5H_5N (pyridine)	8.5	8.6	0.15	
	CH_3CN (acetonitrile)	4.9	5.0	0.15	
	$ClCH_2CN$	4.4	4.4	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	7.3	7.3	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	5.2	5.2	0.15	
	CH_3COOCH_3 (MeOAc)	5.0	5.2	0.15	
	$(CH_3)_2CO$ (acetone)	5.9	5.7	0.15	
	$(C_2H_5)_2O$	6.5	6.2	0.15	
	$((CH_3)_2CH)_2O$	6.7	6.7	0.15	
	$(CH_2)_4O_2$ (*p*-dioxane)	6.0	6.0	0.15	
	$(CH_2)_4O$ (THF)	6.5	6.5	0.15	

Table 11 (*Continued*)

Lewis acid	Lewis base	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$, kcal/mol	uncertainty, kcal/mol	ref^{a,b}
	$(CH_3)_2SO$ (Me_2SO)	7.4	7.5	0.15	
	$(CH_3)_2S$	5.4	5.4	0.15	
	$(C_2H_5)_2S$	5.4	5.4	0.15	
	$(CH_2)_5O$ (THP)	6.5	6.5	0.15	
$(CH_3)_3COH$	C_5H_5N (pyridine)	4.3	4.6	0.15	
	$(CH_3)_2SO$ (Me_2SO)	3.6	3.3	0.15	
	F^-	38.0	37.3	1.00	*g*
	Cl^-	19.2	20.4	1.00	*f*
$(CF_3)_2CHOH$ (HFIP)	C_5H_5N (pyridine)	9.8	9.8	0.15	
	$(C_2H_5)_3N$	11.5	11.4	0.30	
	CH_3CN (acetonitrile)	5.9	5.7	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	8.2	8.4	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	5.9	6.0	0.15	
	$(CH_3)_2CO$ (acetone)	6.7	6.6	0.15	
	$(C_2H_5)_2O$	7.2	7.1	0.15	
	$(CH_2)_4O$ (THF)	6.9	7.4	0.15	
	$(CH_3)_2SO$ (Me_2SO)	8.7	8.6	0.15	
	N-methylimidazole	11.1	10.4	0.30	*d*
$(CH_3)_3SnCl$	CH_3CN (acetonitrile)	4.8	4.9	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	7.9	7.8	0.15	
	CH_3COOCH_3 (MeOAc)	5.2	5.1	0.15	
	$(CH_3)_2CO$ (acetone)	5.7	5.8	0.15	
	$(CH_3)_2SO$ (Me_2SO)	8.2	8.3	0.15	
BF_3 (gas)	$CH_3COOC_2H_5$ (EtOAc)	13.0	13.3	0.30	
	$(CH_2)_4O$ (THF)	16.8	16.3	0.30	
	$(CH_3)_3P$	18.9	18.8	0.30	
	$(CH_2)_5O$ (THP)	15.4	15.7	0.30	
	F^-	71.0	71.3	1.00	*h*
$B(CH_3)_3$	C_5H_5N (pyridine)	17.0	16.9	0.30	
	NH_3 (ammonia)	13.7	13.7	0.30	
	CH_3NH_2	17.6	17.5	0.30	
	$C_2H_5NH_2$	18.0	18.1	0.30	
	$(CH_3)_3P$	16.5	16.6	0.30	
	$C_2H_5C(CH_2O)_3P$ (cage)	14.4	14.4	0.30	
$Al(CH_3)_3$	C_5H_5N (pyridine)	17.4	17.9	0.30	
	NH_3 (ammonia)	17.4	17.4	0.30	
	CH_3NH_2	19.8	19.8	1.00	
	$(CH_3)_2NH$	20.6	20.0	1.00	
	$(CH_3)_3N$	19.8	19.5	1.00	
	$(C_2H_5)_2NH$	17.1	17.1	0.30	
	$(CH_3)_2CO$ (acetone)	10.1	10.0	0.30	
	$(C_2H_5)_2O$	10.0	11.0	0.30	
	$(CH_2)_4O$ (THF)	12.7	11.8	0.30	
	$(CH_3)_2SO$ (Me_2SO)	18.4	15.8	1.00	
	$(CH_3)_2S$	6.5	6.5	0.15	
	$(C_2H_5)_2S$	6.5	6.5	0.15	
	$(CH_3)_3P$	22.1	21.8	1.00	
	$(CH_3)_2O$	10.1	10.4	0.30	*i*
	$(C_2H_5)_3PO_4$	15.4	15.2	0.30	*j*
SO_2	C_5H_5N (pyridine)	6.0	6.2	0.15	
	$(CH_3)_3N$	9.7	9.6	0.15	
	$CH_3CON(CH_3)_2$ (DMA)	3.3	3.4	0.15	
	Cl^-	22.0	21.4	1.00	*f*
	NO_2^-	25.0	24.9	1.00	*k*
$Cu(hfacac)_2$	C_5H_5N (pyridine)	13.4	13.3	0.30	
	$CH_3CON(CH_3)_2$ (DMA)	8.0	7.9	0.15	
	$(CH_2)_4O$ (THF)	9.1	9.1	0.15	
	$(CH_3)_2SO$ (Me_2SO)	8.5	8.6	0.15	
	N-methylimidazole	16.1	16.1	0.30	*d*
$HCCL_3$ (chloroform)	C_5H_5N (pyridine)	4.9	4.5	0.15	
	$(C_2H_5)_3N$	4.5	4.5	0.15	
	$CH_3COOC_2H_5$ (EtOAc)	3.8	3.7	0.15	
	$(CH_2)_4O$ (THF)	3.6	3.8	0.15	
	$HC(C_2H_4)_3N$ (quin)	4.1	4.1	0.15	
	$C_2H_5C(CH_2O)_3P$ (cage)	2.7	2.7	0.15	
	piperidine	4.6	4.5	0.15	*d*
	N-methylimidazole	4.4	4.4	0.15	*d*
	$(C_2H_5)_3PO_4$	4.4	4.7	0.15	*l*
	Cl^-	15.2	16.2	1.00	*f*
H_2O	C_5H_5N (pyridine)	5.1	5.2	0.15	*m*
	CH_3CN (acetonitrile)	3.0	2.8	0.15	*m*
	$HCON(CH_3)_2$ (DMF)	3.5	3.8	0.15	*m*
	$CH_3CON(CH_3)_2$ (DMA)	4.3	4.1	0.15	*m*
	CH_3COOCH_3 (MeOAc)	3.0	3.0	0.15	*m*
	$(CH_3)_2CO$ (acetone)	3.2	3.3	0.15	*m*
	$(C_2H_5)_2O$	4.0	3.7	0.15	*m*

Table II (*Continued*)

Lewis acid	Lewis base	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$, kcal/mol	uncertainty, kcal/mol	ref[a,b]
	$(CH_2)_4O_2$ (*p*-dioxane)	3.2	3.4	0.15	*m*
	$(CH_3)_2SO$ (Me_2SO)	4.1	4.2	0.15	*m*
	H_2O (A)	5.2	5.2	0.15	*n*
	F^-	23.3	23.3	1.00	*f*
	Cl^-	13.1	12.9	1.00	*f*
	Br^-	12.6	13.0	1.00	*f*
	I^-	10.2	10.4	1.00	*f*
	OH^-	25.0	24.3	1.00	*f*
	CN^-	13.8	13.6	1.00	*f*
	NO_2^-	14.3	14.6	1.00	*k*
Co(PPIXDME)	C_5H_5N (pyridine)	8.9	8.9	0.15	*o*
	$HCON(CH_3)_2$ (DMF)	6.9	6.9	0.15	*o*
	$CH_3CON(CH_3)_2$ (DMA)	7.4	7.4	0.15	*o*
	piperidine	9.9	9.9	0.15	*o*
$(Rh(COD)Cl)_2$	C_5H_5N (pyridine)	7.6	7.5	0.15	*p*
	$(CH_3)_2SO$ (Me_2SO)	3.8	3.8	0.15	*p*
	piperidine	10.1	10.3	0.30	*p*
	N-methylimidazole	9.7	9.7	0.15	*p*
	$(C_2H_5)_3PO_4$	2.6	2.6	0.15	*p*
Zn(TPP)	C_5H_5N (pyridine)	10.0	10.0	0.30	*q*
	$(CH_3)_2CO$ (acetone)	6.5	6.5	0.15	*q*
	$(CH_3)_2SO$ (Me_2SO)	8.7	8.7	0.15	*q*
H^+ (proton)	C_5H_5N (pyridine)	218.1	221.9	4.00	*r*
	NH_3 (ammonia)	202.3	203.5	4.00	*f*
	CH_3NH_2	211.3	216.3	4.00	*f*
	$(CH_3)_2NH$	217.9	224.9	4.00	*f*
	$(CH_3)_3N$	222.1	221.2	4.00	*f*
	$C_2H_5NH_2$	214.0	214.5	4.00	*f*
	$(C_2H_5)_2NH$	222.7	222.7	4.00	*f*
	$(C_2H_5)_3N$	229.0	229.5	4.00	*f*
	CH_3CN (acetonitrile)	186.0	188.3	4.00	*f*
	$ClCH_2CN$	180.9	180.9	4.00	*r*
	$HCON(CH_3)_2$ (DMF)	209.0	208.7	4.00	*f*
	$CH_3CON(CH_3)_2$ (DMA)	213.9	214.0	4.00	*f*
	$CH_3COOC_2H_5$ (EtOAc)	198.1	198.5	4.00	*r*
	CH_3COOCH_3 (MeOAc)	195.4	194.3	4.00	*s*
	$(CH_3)_2CO$ (acetone)	193.9	195.6	4.00	*f*
	$(C_2H_5)_2O$	197.4	197.5	4.00	*f*
	$((CH_3)_2CH)_2O$	203.0	203.0	4.00	*r*
	$(CH_2)_4O_2$ (*p*-dioxane)	192.5	191.9	4.00	*f*
	$(CH_2)_4O$ (THF)	196.4	198.5	4.00	*f*
	$(CH_3)_2SO$ (Me_2SO)	208.2	205.0	4.00	*f*
	$(CH_3)_2S$	197.6	197.2	4.00	*f*
	$(C_2H_5)_2S$	202.6	200.3	4.00	*r*
	$(CH_3)_3P$	223.5	224.5	4.00	*t*
	$HC(C_2H_4)_3N$ (quin)	228.7	228.7	4.00	*f*
	$C_2H_5C(CH_2O)_3P$ (cage)	208.0	208.0	4.00	*r*
	H_2O (A)	170.0	159.2	4.00	*f*
	CH_3OH	182.1	180.0	4.00	*f*
	$(CH_3)_2O$	190.1	186.5	4.00	*f*
	H_2CO	174.6	169.5	4.00	*f*
	HCN	174.2	183.0	4.00	*f*
	piperidine	223.1	223.0	4.00	*r*
	N-methylimidazole	225.1	225.4	4.00	*r*
	$(CH_2)_5O$ (THP)	197.1	194.9	4.00	*f*
	$(C_2H_5O)_3PO$	218.7	217.1	4.00	*f*
	F^-	371.3	367.3	8.00	*u*
	Cl^-	333.3	330.9	6.00	*u*
	Br^-	323.6	319.7	6.00	*u*
	I^-	314.3	312.6	6.00	*u*
	OH^-	390.8	390.9	8.00	*u*
	CH_3^-	416.6	418.8	8.00	*u*
	CH_3O^-	380.0	379.6	8.00	*u*
	CN^-	349.3	354.0	6.00	*u*
	NH_2^-	399.6	399.3	8.00	*u*
	NO^-	342.0	342.0	6.00	*u*
	NO_2^-	354.0	353.8	8.00	*u*
	H^-	400.4	398.9	8.00	*u*
Li^+	NH_3 (ammonia)	39.1	38.5	1.00	*v*
	CH_3NH_2	41.1	42.0	1.00	*v*
	$(CH_3)_2NH$	42.2	42.3	1.00	*v*
	$(CH_3)_3N$	42.1	41.6	1.00	*v*
	H_2O (B)	34.0	33.7	1.00	*v*
	HCN	36.4	36.9	1.00	*v*
	F^-	181.0	177.5	6.00	
	Cl^-	154.0	150.6	4.00	

Table 11 (*Continued*)

Lewis acid	Lewis base	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$, kcal/mol	uncertainty, kcal/mol	ref[a,b]
	Br^-	147.0	144.5	6.00	
	I^-	138.0	135.4	4.00	
	OH^-	184.0	190.0	4.00	
	H^-	165.0	165.1	4.00	
Na^+	NH_3 (ammonia)	29.1	28.5	1.00	*f*
	H_2O (B)	24.0	24.7	1.00	*f*
	F^-	152.0	154.3	4.00	
	Cl^-	133.0	130.9	2.00	
	Br^-	128.0	125.5	4.00	
	I^-	117.0	117.3	2.00	
	OH^-	162.0	165.3	4.00	
	CN^-	139.0	139.1	2.00	*w*
	H^-	148.0	151.0	6.00	
K^+	C_5H_5N (pyridine)	20.7	17.6	1.00	*f*
	NH_3 (ammonia)	17.9	18.7	1.00	*x*
	CH_3NH_2	19.1	20.9	1.00	*x*
	$(CH_3)_2NH$	19.3	20.3	1.00	*x*
	$(CH_3)_3N$	20.0	20.0	1.00	*x*
	H_2O (B)	16.9	16.7	1.00	*x*
	F^-	137.0	137.0	2.00	
	Cl^-	117.0	114.9	2.00	
	Br^-	113.0	110.1	2.00	
	I^-	107.0	102.1	4.00	
	OH^-	144.0	146.9	2.00	
	CN^-	121.0	121.9	2.00	*w*
	H^-	126.0	127.3	4.00	
Rb^+	NH_3 (ammonia)	16.5	16.8	1.00	*y*
	H_2O (B)	16.0	15.7	1.00	*f*
	F^-	136.0	137.8	4.00	
	Cl^-	115.0	114.4	6.00	
	Br^-	110.0	109.7	4.00	
	I^-	105.0	101.2	6.00	
	H^-	118.0	117.7	6.00	
Cs^+	H_2O (B)	14.0	14.2	1.00	*f*
	F^-	133.0	132.9	4.00	
	Cl^-	112.0	110.3	6.00	
	Br^-	106.0	105.7	2.00	
	I^-	97.0	97.5	2.00	
	H^-	114.4	114.3	2.00	
CH_3^+	NH_3 (ammonia)	99.3	100.6	2.00	*v*
	CH_3NH_2	110.3	107.5	2.00	*v*
	$(CH_3)_2NH$	116.9	110.3	2.00	*v*
	H_2O (A)	65.9	72.5	2.00	*v*
	CH_3OH	79.6	79.9	2.00	*v*
	H_2CO	73.0	78.2	2.00	*v*
	HCN	95.5	92.6	2.00	*v*
	F^-	254.0	257.3	6.00	
	Cl^-	227.0	229.7	4.00	
	Br^-	218.0	220.9	4.00	
	I^-	211.0	212.8	4.00	
	OH^-	276.0	275.1	6.00	
	CH_3^-	313.0	311.0	6.00	*z*
	CH_3O^-	270.0	271.8	6.00	
	CN^-	256.0	245.0	6.00	*w*
	NH_2^-	296.0	297.4	6.00	*w*
	NO^-	248.0	248.1	6.00	
	H^-	310.0	311.1	6.00	
$CH_3CH_2^+$	H_2O (A)	37.0	37.0	1.00	*f*
	F^-	220.0	220.3	4.00	
	Cl^-	193.0	194.0	4.00	
	Br^-	185.0	186.0	4.00	
	I^-	177.0	176.7	4.00	
	OH^-	235.0	236.2	4.00	
	CH_3^-	277.0	275.3	6.00	*z*
	CH_3O^-	238.0	236.6	4.00	
	NH_2^-	263.0	261.5	6.00	*w*
	NO^-	214.0	213.5	4.00	
	NO_2^-	218.0	218.0	4.00	
	H^-	272.0	272.7	6.00	
$(CH_3)_2CH^+$	H_2O (A)	22.8	22.6	1.00	*f*
	F^-	201.0	200.6	4.00	
	Cl^-	171.0	175.3	4.00	
	Br^-	163.0	167.7	4.00	
	I^-	155.0	158.3	4.00	
	OH^-	223.0	215.3	4.00	*z*

Table II (*Continued*)

Lewis acid	Lewis base	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$, kcal/mol	uncertainty, kcal/mol	ref[a,b]
	CH_3^-	255.0	254.2	6.00	
	CH_3O^-	217.0	217.1	4.00	*w*
	NH_2^-	241.0	240.2	4.00	
	NO^-	193.0	194.0	4.00	
	H^-	251.0	248.5	6.00	
$(CH_3)_3C^+$	H_2O (A)	11.2	10.3	1.00	*f*
	Cl^-	169.0	171.0	4.00	
	Br^-	160.0	163.4	4.00	
	I^-	150.0	152.9	4.00	
	OH^-	220.0	212.1	4.00	
	CH_3^-	251.0	254.0	6.00	*z*
	CH_3O^-	215.0	215.5	4.00	
	NH_2^-	238.0	238.9	4.00	*w*
	NO^-	191.0	190.6	4.00	
	H^-	246.0	245.2	4.00	
Sr^+	H_2O (B)	34.5	34.4	1.00	*f*
	F^-	182.0	175.9	4.00	
	Cl^-	145.0	148.3	4.00	
	Br^-	133.0	142.4	6.00	
	I^-	124.0	133.2	12.00	
	H^-	153.0	152.2	4.00	
Cu^+	H_2O (A)	35.0	37.3	1.00	*aa*
	CH_3OH	40.0	38.2	1.00	*aa*
	F^-	200.0	206.3	6.00	
	Cl^-	186.0	179.4	4.00	
	Br^-	180.0	172.2	10.00	
	I^-	154.0	163.3	10.00	
	H^-	226.0	227.4	4.00	
NO^+	$CH_3COOC_2H_5$ (EtOAc)	40.7	39.2	1.00	*bb*
	CH_3COOCH_3 (MeOAc)	39.0	39.0	1.00	*bb*
	$(CH_3)_2CO$ (acetone)	40.2	40.2	1.00	*bb*
	$(C_2H_5)_2O$	40.4	40.3	1.00	*bb*
	H_2O (A)	18.5	18.6	1.00	*y*
	CH_3OH	30.2	32.0	1.00	*bb*
	Cl^-	162.0	166.2	12.00	*cc*
	Br^-	158.0	156.1	12.00	*cc*
	I^-	160.0	158.7	12.00	
	CH_3^-	253.0	253.1	6.00	*x*
	NO_2^-	186.0	186.0	4.00	
Bi^+	NH_3 (ammonia)	35.5	37.4	1.00	*y*
	H_2O (A)	22.8	20.8	1.00	*y*
	F^-	152.0	185.1	100.00	
	Cl^-	158.0	160.5	4.00	
	Br^-	154.0	153.7	4.00	
	I^-	149.0	144.7	4.00	
	H^-	217.0	216.1	4.00	
Pb^+	H_2O (A)	22.4	22.4	1.00	*f*
	F^-	178.0	179.4	4.00	
	Cl^-	160.0	154.7	10.00	
	Br^-	152.0	148.2	12.00	
	I^-	147.0	139.5	12.00	
	H^-	196.0	196.4	6.00	
$(C_5H_5)Ni^+$ ($CpNi^+$)	NH_3 (ammonia)	53.0	52.6	1.00	*dd*
	CH_3NH_2	55.9	56.1	1.00	*dd*
	$(CH_3)_2NH$	57.5	58.5	1.00	*dd*
	$(CH_3)_3N$	57.1	57.7	1.00	*dd*
	H_2O (A)	43.1	41.9	1.00	*dd*
	CH_3OH	46.3	46.7	1.00	*dd*
	$(CH_3)_2O$	47.6	48.3	1.00	*dd*
	H_2CO	44.5	43.9	1.00	*dd*
	HCN	48.3	47.2	1.00	*dd*

[a] Unless noted, all neutral–neutral enthalpies are from ref 1. [b] Unless noted, ion–ion enthalpies, dissociation energies, ionization energies, and electron affinities may be found in "Handbook of Chemistry and Physics"; CRC Press, Inc.: Cleveland, 1979. [c] Estimates based on similar enthalpies. [d] Reference 4. [e] Tsubomura, H.; Kliegman, J. M. *J. Am. Chem. Soc.* 1960, *82*, 1314. [f] Reference 14. [g] Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1976, *98*, 1160. [h] Haartz, J. C.; McDaniel, D. H. *J. Am. Chem. Soc.* 1973, *95*, 8562. [i] Henrickson, C H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* 1968, *7*, 1047. [j] Nykerk, K. M.; Eyman, D. P. *Inorg. Nucl. Chem. Lett.* 1968, *4*, 253. [k] Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* 1974, *61*, 3181. [l] Nishimura, S.; Ke, C. H.; Li, N. C. *J. Phys. Chem.* 1968, *72*, 1297. [m] Reference 3. [n] Allen, L. C. *J. Am. Chem. Soc.* 1975, *97*, 6921. [o] Tsubomura, H.; Kliegman, J. M. *J. Am. Chem. Soc.* 1960, *82*, 1314. [p] Li, M. P.; Drago, R. S. *J. Am. Chem. Soc.* 1976, *98*, 5149. [q] Stahlbush, J. R.; Vogel, G. C. *Inorg. Chem.* 1977, *16*, 950. [r] Hodges, R. V.; et al. *J. Am. Chem. Soc.* 1980, *102*, 932. [s] Hudson, R. F.; Greehalgh, R. *J. Chem. Soc. B* 1969, 325. [t] Beauchamp, J. L. *J. Am. Chem. Soc.* 1977, *99*, 5417. [u] Bartness, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* 1979, *101*, 6046. [v] Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1978, *100*, 501. [w] Electron affinity from: Rosenstock, H. M.; et al. *J. Phys. Chem. Ref. Data, Suppl. No. 1* 1977, *6*. [x] Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* 1976, *98*, 6133. [y] Castleman, A. W. *Chem. Phys. Lett.* 1978, *53*, 560. [z] Electron affinity from: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* 1978, *100*, 2556. [aa] Estimates based on data obtained from private communication from B. S. Freiser. [bb] Private communication from B. S. Freiser. [cc] Benson, S. W. *J. Chem. Educ.* 1965, *42*, 502. [dd] Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1976, *98*, 3998.

were accordingly constrained when it appeared they might become negative or that the fit was ceasing to resemble the E and C fit. More experimental data are needed for these cases.

Meaning of the Parameters

Previous papers have provided a theoretical basis for two independent contributions to the enthalpy of adduct formation of charge-transfer complexes.[4,5] The extent of electron transfer from the base to the acid that occurs in these systems is slight and the accompanying energy change in the one-center integrals from such transfer is readily incorporated into the E and C parameters. In the interaction of strong cationic acids (e.g., CH_3^+) with strong anionic bases (e.g., CH_3^-) very extensive electron transfer occurs and the resulting adduct (i.e., C_2H_6) has significant contributions from this effect. For systems of this sort, Kutzelnigg has shown[9] that, under the assumption of validity of the Mulliken approximation, the energy of the chemical bond may be expressed as follows:

$$E = \sum_{\mu} E_{\mu} + \sum_{\mu<\nu} E_{\mu\nu} \tag{7}$$

The total energy of bond formation consists of a sum of one-center and two-center contributions. The sum of energies of the isolated atoms is given by

$$E^0 = \sum_{\mu} E_{\mu}^0 \tag{8}$$

So the bond energy is

$$\Delta E = E - E^0 = \sum_{\mu}(E_{\mu} - E_{\mu}^0) + \sum_{\mu<\nu} E_{\mu\nu} \tag{9}$$

The term $\sum_{\mu}(E_{\mu} - E_{\mu}^0)$ is called "promotion energy" and can be related to electron transfer from the ionic starting materials. The two-center term may be divided into two contributions

$$E = E_{\mu\nu}^{\mathrm{QK}} + E_{\mu\nu}^{\mathrm{interf}} \tag{10}$$

where $E_{\mu\nu}^{\mathrm{QK}}$ represents a quasi-classical Coulomb interaction between the two atoms and $E_{\mu\nu}^{\mathrm{interf}}$ is due to the interference of the AOs of the atoms (i.e., a two-center type of interaction). $E_{\mu\nu}^{\mathrm{QK}}$ can easily be related to e_Ae_B and $E_{\mu\nu}^{\mathrm{interf}}$, which is directly related to the overlap of the AOs between the two atoms, can be related to c_Ac_B. Equation 9 may now be rewritten as

$$\Delta E = \sum_{\mu}(E_{\mu} - E_{\mu}^0) + \sum_{\mu<\nu} E_{\mu\nu}^{\mathrm{QK}} + \sum_{\mu<\nu} E_{\mu\nu}^{\mathrm{interf}} = \sum_{\mu}(E_{\mu} - E_{\mu}^0) + e_Ae_B + c_Ac_B \tag{11}$$

Equating the first summation of eq 11 to t_At_B leads directly to eq 3. For multiatom donors and acceptors, we apply the above consideration to the new bond between the donor and acceptor atom and assume that the changes in the other bonds in the system are proportional to this. Experimental support for this assumption has been offered.[13]

In the context of this derivation, e and c represent the tendency of the systems to undergo electrostatic and covalent interactions, respectively. The trends in the e and c parameters are very similar to those reported earlier for E and C and are consistent with qualitative notions regarding trends in the importance of electrostatic and covalent interactions of adducts.

The consistency of the parameters from the fit with the electrostatic covalent transfer model is seen by agreement between expected trends in these effects and the reported parameters. In agreement with a point charge trend

$$-E = \frac{q_A + q_{B^-}}{4\pi\epsilon_0(r_{A^+} + r_{B^-})} \tag{12}$$

where q_{A^+} and q_{B^-} are the charges on ions A^+ and B^- and r_{A^+} and r_{B^-} are the respective ionic radii, the e_Ae_B products decrease in the order $Cs^+F^- > Cs^+Cl^- > Cs^+Br^- > Cs^+I^-$. The e_Ae_B product constitutes 96% of the total enthalpy for K^+F^-. (Experimental error in the enthalpies precludes comparisons that differ by 2–3%.) The e_Ae_B product for K^+H^- constitutes 90% of the total enthalpy. These trends are consistent with expected trends in the ionic character of the bonds.

The t_At_B products relate to the electron transfer from B to A. If, for the interaction of $A^+ + B^-$, a full electron were transferred, we would expect the following relationship:

$$t_At_B = K_{AB}(\mathrm{IE}_A - \mathrm{EA}_B) \tag{13}$$

where K_{AB} is a scaling parameter dependent upon both A and B, IE_A is the ionization energy of A, and EA_B is the electron affinity of B. For an interaction like $H^+ + H^-$, t_At_B would be large since a full electron is transferred. However, for an interaction like $Cs^+ + F^-$, t_At_B would be very near zero since there is only a very small amount of electron transfer (i.e., the bond is very ionic). For the general interaction $A^+ + B^-$, we would expect the extent of transfer to increase as the electron affinity of A^+ increases and the ionization energy of B^- decreases. That is

$$t_A = K'_A\mathrm{EA}_{A^+} = K'_A\mathrm{IE}_A \tag{14}$$

and

$$t_B = K'_B/\mathrm{IE}_{B^-} = K'_B/\mathrm{EA}_B \tag{15}$$

For the interactions involving a neutral base with an ionic acid, the conventional method of reporting the corresponding energies leads to

$$t_B = K'_B/\mathrm{IE}_B \tag{16}$$

while for the interaction of neutral acids with ionic bases we obtain

$$t_A = K'_A\mathrm{EA}_A \tag{17}$$

where K_{AB}, K'_A, and K'_B are simply scaling parameters or constants. These equations do not predict a direct one-to-one relationship between ionization energy (or electron affinity) and t since the scaling parameter is present in the above equations. Furthermore, the trend is a function of parameter selection and some reversals are expected when these are changed as more information becomes available from good molecular orbital calculations. However, there should be general trends observable so that one can make a rough correlation between the t parameter and ionization energy and electron affinity. As can be seen in the following sequences, the trends in the t values are roughly those expected on the basis of the above equations:

$$\mathrm{IE}_A{:}\quad H^+ \gg CH_3^+ > CH_3CH_2^+ > (CH_3)_2CH^+ \approx (CH_3)_3C^+ > Li^+ > Na^+ > K^+ \approx Rb^+ > Cs^+ \tag{18}$$

$$t_A{:}\quad H^+ \gg CH_3^+ > CH_3CH_2^+ > Li^+ \approx (CH_3)_2CH^+ > Na^+ > (CH_3)_3C^+ > K^+ > Rb^+ > Cs^+ \tag{19}$$

$$1/\mathrm{EA}_B{:}\quad CH_3^- > H^- > NO^- > NH_2^- > CH_3O^- \approx NO_2^- > OH^- > I^- > F^- \approx Br^- > Cl^- > CN^- \tag{20}$$

$$t_B{:}\quad H^- > NO^- \approx NH_2^- > CH_3^- > I^- > CN^- \approx NO_2^- > Cl^- > Br^- > OH^- > F^- > CH_3O^- \tag{21}$$

For both the neutral and anionic bases, the t_B values are in an extremely compressed range. The standard deviations of the parameters must be considered in discussing qualitative trends. For the neutral bases, the range of t_B is so small that it is virtually meaningless to discuss trends due to overlap of the standard deviations. For the anions, halides have small t_B numbers and CH_3^-, H^-, NH_2^-, and NO^- have large t_B numbers.

It must be remembered, however, that there is much more involved in ionic acid–base interactions than simply ionization energies and electron affinities and that some reversals in the sequences would be due to the failure of these simple concepts to include some of the more complicated effects[13] included in the e, c, and t parameters. The general patterns clearly lend evidence to our interpretation of the fit in terms of the crude concepts of covalency, transfer, and electrostatic bonding.

By incorporating a data base including ionic and covalent systems in the same model, extensive electron transfer must occur

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(13) Drago, R. S.; Fisher, K. J. *Inorg. Chem.* **1975**, *11*, 2805.

in some cases, independent of whether one begins with atoms or as in this model ions. It becomes difficult in terms of our present thinking about bonding to distinguish transfer effects from covalency. We think in terms of forming covalent molecules from atoms and ionic compounds from ions. Accordingly, it is difficult to employ semiquantitative guidelines in setting parameters to impose the proper trends. Our breakup of the enthalpy into these two quantities was partially dictated by setting the c_A and c_B parameter for HCl in a manner that gave reasonable trends for the other ions in the fit. It becomes a problem to distinguish between covalency and transfer especially in the case of neutral acid–base adducts where the transfer term was not needed to obtain a good fit with the E and C model. With three terms the parameters are highly correlated and the marginal deviations would be quite large. As a result, the t_At_B products for the neutral systems could change considerably as more good data became available. The t_A values in particular require more anion–neutral acid interactions.

The parameters obtained from this fit are relative because they depend upon the 16 parameters that have been fixed. Thus, *trends* in the parameters are to be compared and *not* their absolute magnitude. In this context a negative parameter should not be considered an antibonding interaction but instead a smaller tendency than a positive number for undergoing this type of interaction.

Insights Provided by The Model

One of the very interesting results of this analysis is the unique nature of H^+ (g) and $C_5H_5Ni^+$ (g) Lewis acids. The parameters of these ions differ from those of any other acid (neutral and ionic) in the correlation more than the parameters for any other pair differ from each other. Thus, proton affinities are a very poor reference set of data to use to infer σ donor basicity trends toward other acids. The proton affinities (and $C_5H_5Ni^+$) have a larger contribution from the t_At_B term than any of the other enthalpies in the correlation and for this reason the proton is the strongest acid in the correlation toward all bases.

The comparison of the gas-phase proton affinities with aqueous solution protonations has attracted the attention of several investigators.[14-16] The gas-phase reaction

$$B + H^+ \rightarrow BH^+ \qquad (22)$$

is very different from the solution reaction

$$B\ (aq) + H_3O^+\ (aq) \rightarrow BH_3O^+\ (aq) \qquad (23)$$

In forming the hydronium ion, electron transfer into the proton has occurred to the extent of 66.4 kcal/mol (the t_At_B product). Thus, when H_3O^+ coordinates to a base as in eq 23, the t_At_B product is expected to be relatively small (<50 kcal mol^{-1}) and the chemistry will be dominated to a greater extent by the e and c parameters of the base than is the case with the proton (eq 22). As a result, it is not valid to compare proton affinities with enthalpies for aqueous solution protonation reactions and attribute the difference to solvation. In this context, it is very misleading to consider H_3O^+ or NH_4^+ as a solvated proton. A full understanding of reaction 23 will involve determination of the enthalpies for the gas-phase reactions of H_3O^+ with several bases in the correlation, including anions, so its e, c, and t parameters can be determined.

Comparison of H^+ and CH_3^+ indicates that these are two different types of interactions with a greater percentage contribution coming from the e_Ae_B and c_Ac_B terms in the latter case. The weaker acidity of $CH_3CH_2^+$ vs. CH_3^+ can also be attributed exclusively to the t_A term (6.627 for CH_3^+ and 3.106 for $CH_3CH_2^+$) and the more electrostatic nature of $C_2H_5^+$. It is interesting to investigate the very large difference between the behavior of CH_3^+ vs. $CH_3CH_2^+$ in the gas phase as compared to a similarity in the behavior of these species in a solution reaction; for example,

$$CH_3OH_2^+ + I^- \rightarrow CH_3I + H_2O \qquad (24)$$

$$CH_3CH_2OH_2^+ + I^- \rightarrow CH_3CH_2I + H_2O \qquad (25)$$

The enthalpies for the monohydration of CH_3^+ and $C_2H_5^+$ are −66 and −37 kcal/mol, respectively, while the enthalpies of interaction of those ions with iodide are −211 and −177 kcal/mol. The CH_3^+ ion is a much stronger acid than $CH_3CH_2^+$ in the gas-phase reactions. When one calculates the enthalpy for the displacement reaction written above, values of −145 kcal/mol and −140 kcal/mol result. Enthalpies for comparison of displacement reactions of this sort are given by $-\Delta H = e_A\Delta e_B + c_A\Delta c_B + t_A\Delta t_B$ where $\Delta e_B = e_{I^-} - e_{H_2O}$, etc. A similar calculation produces values of −161 and −156 kcal/mol for the chloride ion displacement of water from CH_3^+ and $CH_3CH_2^+$, respectively. By referring to the parameters $(CH_3)_2CH^+$ and $(CH_3)_3C^+$ we note that their differences in solution will be less than in the gas phase. This representation of a reaction in water is of course hypothetical and greatly oversimplified but does serve to show that solution reactions of ionic species, which are invariably displacement reactions, can show different behavior than gas-phase results depending on the cancellation of the e, c, and t terms by solvent coordination. Solvation of the coordinated species is an additional factor that complicates the interpretation of the solution results for ionic reactions which cannot be attributed solely to solvation. For reasons exemplified above, it is advantageous to distinguish between coordination and solvation and to consider solvation as effects that occur outside the primary coordination sphere of the reactants. These solvation effects can be further classified as those involving specific interactions (for example, hydrogen bonding) or nonspecific interactions (London dispersion or dipole–dipole).

A parallel has been noted between the gas-phase methyl-cation affinities and enthalpies for the Menschutken reaction[18]

$$B + CH_3I \rightarrow BCH_3^+ + I^- \qquad (26)$$

By comparing the gas-phase enthalpies for $CH_3^+ + I^-$ with those for CH_3^+ plus neutral bases, it becomes clear that the enthalpy for the reaction written above is a large positive number. The driving force is expected to have a large contribution from ion-pairing energy BCH_3^+, I^-, etc. With all bases studied, a constant 211 kcal/mol is required to break the carbon–iodine bond so the reaction as written above will involve the base methyl cation affinity minus the CH_3^+ plus I^- interaction energy. There is no variable displacement reaction as in the comparison of CH_3^+ and $CH_3CH_2^+$ but a constant one that is $-\Delta H = e_{CH_3^+}\Delta e + c_{CH_3^+}\Delta c + t_{CH_3^+}\Delta t$ where $\Delta e = e_B - e_{I^-}$, etc., leading to a constant ΔH_{CH_3I} in all comparisons. Furthermore, solvent coordination does not occur to change the acid species in the solution reaction from what it is in the gas phase as in the H^+, H_3O^+ comparison. The only conditions for a linear relation between the gas-phase methyl-cation affinities and Menschutkin enthalpies is either a constant ion-pairing and solvation energy for the solutions reactions or energies from these effects in solution that parallel the methyl cation affinities.

Additional insights can be obtained from systems that could not be correlated by the e, c, and t equation. Those interactions not included are shown in Table III along with the values calculated by our model. Most of the systems are oxygen donors. The nature of this problem is illustrated in Figure 1 where the proton affinities are compared with the potassium ion affinities.

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(14) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(15) Taft, R. W. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Chapman & Hall: London, 1975; p 31.

(16) Arnett, E. M.; et al. *J. Am. Chem. Soc.* **1972**, *94*, 4724.

(17) (a) Clementi, E. In "Lecture Notes in Chemistry"; Springer-Verlag: New York, Heidelberg, 1976; Vol. 11. (b) Clementi, E. to be published.

(18) Menschutkin, N. *Z. Phys. Chem.* (*Wiesbaden*) **1890**, *5*, 589; **1890**, *6*, 41.

(19) Private communication from Professor H. van den Berger. Reported values for acetic acid dimerization range from −11 to −17.6 kcal mol^{-1}. In a gold-plated cell a value of 14.3 ± 0.8 kcal mol^{-1} was measured that was surface independent. Mathews and Sheets (*J. Chem. Soc. A* **1964**, 2203) report surface-dependent values that extrapolate to −14.2 ± 0.7 kcal mol^{-1} at a zero surface to volume ratio.

Table III. Enthalpies Not Included in the *e*, *c*, and *t* Correlation

Lewis acid	Lewis base	$-\Delta H_{ect}$, kcal/mol	$-\Delta H_{exptl}$, kcal/mol	ref
H^+	C_6H_6		180.1	*a*
Li^+	C_6H_6		37.9	*a*
Li^+	CH_3OH	21.9	38.1	*a*
Li^+	$(CH_3)_2O$	28.5	39.5	*a*
Li^+	H_2CO	24.4	36.0	*a*
Li^+	$(CH_3)_2S$	22.9	32.8	*b*
K^+	C_6H_6		19.6	*c*
K^+	CH_3CN	7.0	24.4	*d*
K^+	$(CH_3)_2CO$	9.2	19.6	*c*
K^+	$(CH_3)_2O$	10.7	20.9	*a*
K^+	$(C_2H_5)_2O$	10.5	22.3	*d*
K^+	DMA	14.5	~31.0	*c*
K^+	DMF	12.7	~31.0	*c*
K^+	Me_2SO	16.4	~34.0	*c*
NO^+	C_6H_6		40.3	*e*

[a] Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1978, *100*, 501. [b] Martinsen, D. P.; Buttrill, S. E. *J. Am. Chem. Soc.* 1978, *100*, 6559. [c] Private communication from P. Kebarle. [d] Reference 14. [e] Private communication from B. S. Freiser.

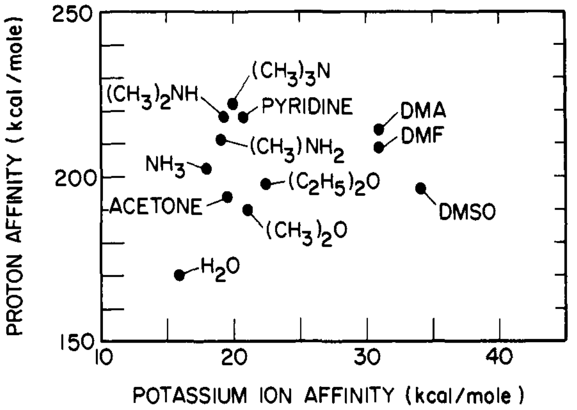

Figure 1. A plot of proton affinity vs. potassium ion affinity for some amines and oxygen donors.

The nitrogen donors manifest one trend and the oxygen donors a second trend. The form of the *e*, *c*, and *t* equation is such that it can accommodate systems whose enthalpies are not linearly related. However, it cannot accommodate the data in Figure 1. For every acid in the correlation, except K^+, nitrogen donor enthalpies are larger than those for the oxygen donors. The *e* and *c* values for $(CH_3)_3N$ are all larger than those for $(CH_3)_2O$, Me_2SO, DMA, and DMF (recall that K^+ is nearly totally dominated by the e_Ae_B term). However, the K^+ affinity for these oxygen donors is substantially greater than that for $(CH_3)_3N$. This apparent contradiction suggests that an alternative bonding mode that we shall label type B (see Figure 2) is involved in the interaction of these oxygen donors with K^+. If we assume the K^+ is located on the twofold axis of the ether, for example, the electrostatic interaction with the net dipole from the two lone pairs would be a maximum but the covalent and transfer energies would be less than when the acid is located on a lone pair (type A, see Figure 2). In the case of K^+ the *c* and *t* values are so small that little covalency or transfer energy is lost if the K^+ interacts on the twofold axis. Thus a slightly larger *e* parameter for this mode of interaction with the ether could lead to a more negative $-\Delta H$ of adduct formation. On the other hand, the c_Ac_B and t_At_B products are significant for the interactions with CH_3^+ and H^+ with the lone pairs and would be less if these acids were on the twofold axis. These contributions make coordination to the lone pair (type A) the preferred interaction with H^+ and CH_3^+. In the case of adducts involving Me_2SO, DMA, and DMF even more electron density exists on the oxygens than in the case of ethers. The location of the K^+ so that it can undergo a symmetrical interaction with this density could result in a very strong electrostatic interaction.

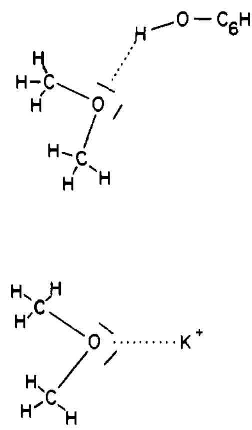

Figure 2. Two possible modes of interaction for oxygen donors: a type A covalent (along a lone-pair axis) interaction shown on top and a type B electrostatic (along the dipole moment axis) interaction.

Note that in Table III $-\Delta H_{ect}$ for acetone, $(CH_3)_2O$, and $(C_2H_5)_2O$, interacting via a lone pair, are all predicted to be less stable by about 10–15 kcal/mol than observed. DMF, DMA, and Me_2SO are predicted to be less stable by about 20–23 kcal/mol. H_2O, which is in the correlation, fits. Based on the argument of bonding along the axis of the dipole moment, we would expect the greatest extra stabilization to occur for the very polar DMA, DMF, and Me_2SO molecules. In DMA and DMF delocalization of the nitrogen lone pair into the π system will increase the negative charge on oxygen enhancing the electrostatic interaction compared to acetone, $(CH_3)_2O$, and $(C_2H_2)_2O$. Water should be least effective in electrostatic interaction because the hydrogen atoms are less inductive than methyl or ethyl substituents leading to less negative charge on oxygen. Therefore, oxygen donors interacting with alkalis would require different e_B, c_B, and t_B numbers than for interactions with neutral acids (like I_2, C_6H_5OH, etc.). As more alkali–oxygen donor interactions become available, their e_B, c_B, and t_B numbers for these bases should be determined for this electrostatic interaction and these separate values used for this vs. lone-pair interactions. For this reason, parameters for two types of interaction are reported for water: a lone-pair type A for interactions with H^+, CH_3^+, CH_3CH^+, $(CH_3)_2CH^+$, $(CH_3)_3C^+$, Cu^+, Pb^+, Bi^+, $C_5H_5Ni^+$, and NO^+ (all relatively covalent and not completely dominated by e_A), and an electrostatic type B for interactions with Li^+, Na^+, K^+, Rb^+, Cs^+, and Sr^+ (all relatively electrostatic with c_A and t_A playing a very minor role). Recent quantum-mechanical calculations[17] have shown that water uses both oxygen lone pairs in binding to monoatomic cations. No reason for the deviation of the K^+–CH_3CN interaction is available at this time but this could also involve a different bonding mode.

The behavior of benzene as a Lewis base is of interest in the context of multiple binding modes. The solution interactions with I_2, phenol, etc., involve electron-pair donation from the π cloud with the acid on the sixfold axis. Interactions with an edge are also possible. Protonation involves σ bond formation to a carbon. Interactions with K^+ and Li^+ are expected to be purely electrostatic. Each of these bonding modes will require a separate set of e_B, c_B, and t_B numbers for benzene to characterize their interactions. We were not able to fit the interactions of benzene with I_2, H^+, Li^+, K^+, and TFMP together to a single set of e_B, c_B and t_B numbers. However, as more ionic data for benzene become available (i.e., Na^+, Rb^+, Cs^+), it may then be possible to obtain electrostatic e_B, c_B, and t_B values for benzene if the same type of interaction persists.

Most of the data used in the neutral–neutral interactions have been determined in poorly solvating solvents. The constancy of the value for the enthalpy of the displacement reaction when

$$BA + B' \rightleftarrows B'A + B \qquad (27)$$

investigated in a series of solvents that do not undergo specific interactions with the bases or adducts has been used to support the position that the essential contribution to the measured enthalpy is from adduct formation. Further support for this position comes from this study because the base parameters can be used to predict data obtained both in the gas phase and in poorly solvating solvents. This statement should not be taken as universally true for all systems in the *E* and *C* correlation. The problem is complicated by our lack of knowledge of the nature and structure of species in solution as well as a poor understanding of subtle, specific solvent-solute interactions.

The direct determination of the neutral-neutral gas-phase enthalpy of interaction is a difficult experiment. For example, the enthalpy of dimerization of formic acid has been investigated in detail[19] and the pitfalls in these studies revealed by this work. The results obtained are, for example, very much dependent upon the surfaces of the containers. When donors with competitive binding sites are used, the comparison of solution and gas phase data is further complicated. It is generally established that the equilibrium constant for donor-acceptor interactions is very different in the gas phase than in CCl_4 or alkanes. If the ratio of the interacting sites on the bases is different under the different sets of conditions, the enthalpies will differ but the cause will not involve a solvation contribution to the enthalpy.

In summary, we have been able to obtain an excellent fit of thermodynamic data to the *e*, *c*, and *t* equation, to provide a theoretical justification for the addition of the $t_A t_B$ term, to obtain parameters that are meaningful in terms of the electrostatic covalent transfer model imposed, and to provide new insights relative to the comparison of solution and gas-phase data.

It must be remembered that the *E* and *C* equation is still the preferred equation when dealing only with neutral-neutral acid-base interactions because of the larger data base. However, as new gas-phase ion-ion, ion-molecule, and molecule-molecule enthalpies become available and as existing enthalpies are corroborated and improved, the *e*, *c*, and *t* equation should eventually be able to satisfactorily replace the *E* and *C* equation.

The data analysis reported here suggests several important criteria for gas-phase ion-molecule experiment design. For example, little information about the coordination tendencies of an acid (or base) will be obtained by studying more than one base (or acid) with similar e/c and c/t ratios. When a new acid is investigated, the bases $(CH_3)_2S$, $(CH_3)_3N$, $(CH_3)_2O$, NH_3, H_2O, $(CH_3)_2CO$, and $(CH_3)_3P$ should be routinely used to best characterize the coordination tendencies of that acid. It would be interesting to have data for H_3O^+ interacting with the above bases. More anion-neutral acid data is sorely needed. Bases in the *E* and *C* correlation[1] that are not listed in Table I should be studied with H^+, K^+, CH_3^+, Li^+, and either Pb^+ or Bi^+. The tentative values reported in Table I should be investigated with the systems needed to complete their characterization. Accurate gas-phase data on neutral acid-neutral base systems are needed in order to understand what is occurring in solutions of poorly solvating solvents. It should be emphasized that these recommendations are independent of the *e*, *c*, *t* model and can be viewed as requirements for fully characterizing the coordination chemistry of acids or bases.

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Study of Methanesulfonates and Trifluoromethanesulfonates. Evidence for Hydrogen Bonding to the Trifluoro Group

O. D. Bonner

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

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Abstract: Osmotic and activity coefficients are reported for the lithium, sodium, and potassium salts of methanesulfonic acid and trifluoromethanesulfonic acid and for the latter parent acid. Nuclear magnetic resonance chemical shift data are reported for ^{19}F vs. ^{13}C nuclei for trifluoromethanesulfonic acid and for its sodium and tetramethylguanidinium salts. The activity coefficient data indicate that the hydronium and tetramethylguanidinium ions, which are capable of hydrogen bonding, do not associate appreciably with the sulfonate group. Both colligative property and NMR data indicate ion pairing to the trifluoro group of the trifluoromethanesulfonate ion.

It was reported by Covington et al.[1] that the measurement of carboxyl ion concentration by Raman spectroscopy enabled the calculation of the ionization constant of aqueous trifluoroacetic acid in the range of 2 to 5 depending on the activity coefficients that were used. Previous measurements, largely based on measurement of hydrogen ion activities, yielded a constant that is a power of 10 lower. After repeating the Raman measurements,[2] we postulated[3] that the anomalous behavior was caused by ion pairing of the hydronium ion to the trichloro group of the trichloroacetate ion. This postulate has received further confirming evidence[4] in that activity coefficient data involving the tetramethylguanidinium ion indicate significant ion pairing of this ion with the trichloroacetate anion but not with the acetate ion. This cation cannot, of course, form covalent bonds with the anions in the manner of the acids. We reported[4] at the same time that the tetramethylguanidinium cation also ion paired with the trifluoromethanesulfonate anion but not with the methanesulfonate ion. The investigation reported in this paper was undertaken for the purpose of (1) determining whether the activity coefficients of the sulfonic acids would indicate the same difference in ion pairing as was found for the tetramethylguanidinium salts and (2) confirming by a different type of evidence (nuclear magnetic resonance) that the association really involved the trihalo group of the molecule.

Experimental Section

The best grades of methanesulfonic acid and trifluoromethanesulfonic acid available from Aldrich Chemical Co. were vacuum distilled and the center fractions retained. Aqueous solutions of these acids were almost

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(1) Covington, A. R.; Freeman, J. G.; Lilley, T. H. *J. Phys. Chem.* **1970**, *74*, 3773-3780.

(2) Bonner, O. D.; Flora, H. B.; Aitken, H. W. *J. Phys. Chem.* **1971**, *75*, 2492-2495.

(3) Bonner, O. D.; Prichard, P. R., *J. Solution Chem.* **1979**, *8*, 113-124.

(4) Bonner, O. D. *J. Solution Chem.* **1980**, *9*, 877-884.