A Four-Parameter Equation for Predicting Enthalpies of Adduct Formation

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Abstract: A computer-fitted set of parameters for acids and bases is presented which accurately correlates over 280 enthalpies of adduct formation. The parameters can be used to predict over 1200 enthalpies of interaction. A matrix formulation of the problem is presented to illustrate the relationship among the various solutions to this problem. Our selection of a particular solution is justified on the basis of our intuitive understanding of the nature of molecular interactions. Means of transforming this solution to any model are presented. The conditions which lead to the Hammett and other two-parameter equations, which are subsets of the four-parameter equation, are derived from the matrix formulation. The fact that the donor number approach proposed by Gutman is not a generalized approach for estimating solvent donor strengths is established mathematically. The relationship of our parameters to the soft-hard acid-base model is discussed, and it can be demonstrated that our approach is not simply a quantitative manifestation of this concept, but the soft-hard concept as it is generally applied is incomplete. Furthermore, it is shown that this incompleteness can often lead to incorrect qualitative predictions of the magnitude of interaction.

A double-scale enthalpy equation was originally proposed to correlate (and predict) the enthalpy of adduct formation in gas-phase or poorly solvating media for several Lewis acid-base systems.[2] This empirical correlation is represented by eq 1. Two

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

empirically determined parameters, E_A and C_A, are assigned to each acid and two, E_B and C_B, are assigned to each base such that when substituted into eq 1, they give the enthalpy of adduct formation for the acid-base pair. E_A and E_B were originally interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interaction and C_A and C_B as the susceptibility of the acid and base, respectively, to form covalent bonds. Equation 1 was found to correlate the enthalpies of interaction of donor-acceptor systems where reversals in donor strength are observed[3] (*e.g.*, oxygen donors interact more strongly with acids like phenol than with I_2, whereas analogous sulfur donors prefer I_2 more than acids like phenol). For several of the systems employed in the qualitative classification of acids and bases as type B or "soft" and type A or "hard,"[4,5] the *E* and *C* equation was in accord with the observation that combination of "like" acids and bases gives the most effective interaction.

At the time eq 1 was proposed, the amount of reliable enthalpy data was very limited. Since then, much enthalpy data have become available, both through direct calorimetric measurement and enthalpy-spectral parameter correlations. A linear relationship for certain types of donors between the shift in the frequency of the O-H stretching vibration of phenols[6-9] and aliphatic alcohols,[10,11] $\Delta\bar{\nu}_{OH}$, and the enthalpy of adduct formation has been reported. A similar correlation has been shown to exist for pyrrole.[12] In addition a linear relationship between the tin-proton nmr coupling constant, $J_{\text{Sn}^{119}\text{-CH}_3}$, and the enthalpy of adduct formation of trimethyltin chloride has been cited.[13] With this large amount of reliable enthalpy data, the *E* and *C* correlation can be extended to many different acids and bases. In this paper, a refined set of *E* and *C* parameters, based upon the newly available enthalpy data, is reported. A computer fit of the data has been employed instead of the hand solution previously utilized. Furthermore, a matrix formulation of eq 1 is discussed which provides considerable insight into the quantitative correlation.

Experimental Section

Infrared Measurements.[14,15] The hydroxyl group frequency shifts, $\Delta\bar{\nu}_{OH}$, were obtained from spectra run on a Perkin-Elmer 521. Sodium chloride liquid cells of various path lengths were used with solvents carbon tetrachloride and tetrachloroethylene (used with amines[15]).

The concentration of the phenol was always kept less than 0.02 *M* to ensure against self-association. The base concentrations, which were always in excess of the acid concentration, were varied over a wide range. Thus, all frequency shifts were checked for concentration dependence and, when necessary, the reported value was obtained by extrapolation to infinite dilution. The experimentally determined shift is converted to an enthalpy using the equation

$$-\Delta H = 0.0103\Delta\nu_{OH}\ (\text{cm}^{-1}) + 3.08$$

and reported as such in Table III (indicated by footnote *n*). This procedure has been demonstrated to be valid for oxygen and some nitrogen donors.[8-11]

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Method of Calculation. The original set of E and C parameters was determined mainly from the enthalpy data of iodine and phenol. Using experimental enthalpies for iodine interacting with a series of alkylamines, eq 1 was solved and empirical values were obtained for the amine E and C parameters by setting $C_A = E_A = 1.00$ for iodine and $C_B = aR_D$ and $E_B = b\mu$ for the amines. Here R_D is the total distortion polarization and μ is the ground-state dipole moment. The four amine parameters were employed with four enthalpies of adduct formation toward phenol to calculate E_A and C_A parameters for phenol, in effect using two enthalpies as checks on the procedure. The parameters for other donors were obtained by using their enthalpy of adduct formation with iodine and phenol, yielding two equations in the two unknowns C_B and E_B for each base. Finally, by using the E_B and C_B parameter for these donors, the correlation was extended to other Lewis acids with several experimental enthalpies remaining to provide checks on the entire procedure.

In an attempt to get the best set of E and C parameters from the large number of enthalpy data presently available, a computer program was written employing a least-squares analysis to find the values of the parameters which give the best fit between the measured enthalpies and those calculated from eq 1. The previously reported values of E and C parameters are used as initial guesses, and corrections to the parameters are calculated from the matrix equation[17]

$$\mathbf{\Delta} = (\mathbf{A'PA})^{-1}\mathbf{PF} \qquad (2)$$

where $\mathbf{\Delta}$ is the vector of corrections to the parameters, A is the matrix of partial derivatives $\partial(-\Delta H_{i_{\mathrm{calcd}}})/\partial(\mathrm{parameter}\ j)$, P is the weight matrix, and F is the vector of residuals, $-\Delta H_{i_{\mathrm{calcd}}} + \Delta H_{i_{\mathrm{obsd}}}$. P is taken to be a diagonal matrix. Since standard deviations for experimental enthalpies are rarely available, the diagonal elements of the weight matrix have been chosen to be $1/(4 - \Delta H_{i_{\mathrm{calcd}}})^2$, a function which seems to give appropriate weights to both large and small enthalpies. Occasionally, when a measured enthalpy has seemed particularly good or bad, a different weight was given to that heat. All enthalpies estimated from constant acid frequency shift relations were weighted as $1/(10 - \Delta H_{i_{\mathrm{calcd}}})^2$.

The corrected parameters are used to calculate a new A matrix and F vector, new corrections are calculated, and the process is repeated until the calculated corrections are essentially zero. As will be shown later, a total of four parameters must be specified in order to determine a unique solution for the E and C numbers; therefore, the following parameters were held fixed and not allowed to vary: iodine $E_A = 1.00$, iodine $C_A = 1.00$, DMA $E_B = 1.32$, diethyl sulfide $C_B = 7.40$.

Results

The parameters calculated for the acids are given in Table I and those for the bases in Table II. The weighted root-mean-square deviation between the experimental enthalpies and those calculated from the parameters in Tables I and II using eq 1 is about 0.016, corresponding to a deviation of about 0.2 kcal/mol for a heat of 8 kcal/mol. The excellent agreement between the experimental enthalpies of adduct formation and the calculated enthalpies for all of the interactions is shown in Table III. Newly determined frequency shifts used to estimate $-\Delta H$ are reported in Table IV.

Accuracy of the Parameters. Included in Tables I and II are marginal standard deviations and conditional standard deviations for each parameter. The method for calculating these numbers is outlined briefly in the Appendix. For a more complete treatment, the reader is referred to ref 16 and 17. The marginal standard deviations are large and reflect the fact that a significant change in one parameter can be compensated for by changes in many of the other parameters so that the heats calculated from all the parameters change very little. Thus, the errors in the parameters are highly correlated and, for example, the C number given for phenol can be too large by 0.213 only if the E number for phenol is too small by nearly 0.51. The marginal standard deviation of a parameter is quite dependent on the extent that the parameter is connected to the standards through enthalpies. Most uses of E and C numbers do not require an exact knowledge of the absolute magnitude of the numbers themselves, but only an accurate knowledge of trends in the numbers, which are, in fact, much more accurately known. The conditional standard deviations given here are standard deviations for each parameter assuming that all the other parameters have their true values. They may be regarded as lower limits to the inaccuracies in the parameters for any use of the parameters. Because of the high correlation in the errors, the appropriate error limits for examining trends in a series of similar numbers are much closer to the conditional standard deviations than to the marginal standard deviations.

One very important use of E and C numbers is the calculation of heats of interaction for systems which have not been examined experimentally. From our knowledge of the standard deviations of the parameters and their correlation coefficients (see the Appendix), we have calculated the expected standard deviations for calculated heats for all possible combinations of all but a few of the acids and bases listed in Tables I and II. For the hydrogen-bonding acids and sulfur dioxide, these predicted standard deviations nearly all lie between 0.1 and 0.3 kcal/mol. For most other systems, the errors are somewhat worse than this, averaging around 0.7 kcal. Of course, the heats for many of these interactions are generally larger, too.

It should be noted that the above treatment of errors does not take into account the effects of any systematic errors in the experimental heats, which might arise, for example, from solvent effects or from the fact that many of the heats were taken from spectroscopic correlations. However, these effects should be smaller than the effects of the larger random errors.

Discussion

Uniqueness of the E and C Parameters. Equation 1 can be rewritten in matrix notation by assigning the acid parameters to a vector $\mathbf{X}_A$ and the base parameters to a vector $\mathbf{Y}_B$, *i.e.*

$$\mathbf{X}_A = \begin{bmatrix} E_A \\ C_A \end{bmatrix} \text{ and } \mathbf{Y}_B = \begin{bmatrix} E_B \\ C_B \end{bmatrix}$$

and allowing the enthalpy of adduct formation, ΔH, to be a scalar function of the vector

$$-\Delta H = \mathbf{Y}_B{}^T\mathbf{X}_A = [E_B C_B]\begin{bmatrix} E_A \\ C_A \end{bmatrix} = E_B E_A + C_B C_A \qquad (3)$$

The series of equations (3) has an infinite number of "best-fit" solutions for E_A, C_A, E_B, C_B, each of which predicts exactly the same ΔH for every interaction. This can be shown by defining a 2 × 2 transformation matrix $\mathbf{A}$ which leads to the new vectors $\mathbf{X}_A'$ and $\mathbf{Y}_B'$ in the following way

$$\begin{aligned} -\Delta H &= \mathbf{Y}_B{}^T\mathbf{X}_A \\ &= \mathbf{Y}_B{}^T[\mathbf{A}^{-1}\mathbf{A}]\mathbf{X}_A \\ &= [\mathbf{A}^{-1T}\mathbf{Y}_B]^T[\mathbf{A}\mathbf{X}_A] \end{aligned}$$

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Table I. Acid Parameters

	Acid	No.[a] of enthalpies	C_A	(Marginal)	(Conditional)[h]	E_A	(Marginal)	(Conditional)
1.	Iodine	39	1.00	(d)	(d)	1.00	(d)	(d)
2.	Iodine monochloride[b]	8	0.830	(0.334)	(0.05)	5.10	(0.62)	(0.10)
3.	Iodine monobromide[b]	3	1.56	(0.31)	(0.09)	2.41	(0.41)	(0.12)
4.	Thiophenol[b,g]	3	0.198	(0.059)	(0.022)	0.987	(0.193)	(0.082)
5.	*p*-*tert*-Butylphenol	5	0.387	(0.161)	(0.014)	4.06	(0.37)	(0.13)
6.	*p*-Methylphenol[c]	6	0.404	(0.166)	(0.021)	4.18	(0.39)	(0.17)
7.	Phenol	34	0.442	(0.170)	(0.010)	4.33	(0.35)	(0.06)
8.	*p*-Fluorophenol	9	0.446	(0.164)	(0.014)	4.17	(0.35)	(0.08)
9.	*p*-Chlorophenol	10	0.478	(0.170)	(0.015)	4.34	(0.37)	(0.11)
10.	*m*-Fluorophenol	10	0.506	(0.173)	(0.015)	4.42	(0.37)	(0.09)
11.	*m*-Trifluoromethylphenol	22	0.530	(0.174)	(0.014)	4.48	(0.37)	(0.08)
12.	*tert*-Butyl alcohol[b]	2 (11)[e]	0.300	(0.102)	(0.028)	2.04	(0.30)	(0.11)
13.	Trifluoroethanol	12	0.434	(0.159)	(0.018)	4.00	(0.33)	(0.06)
14.	Hexafluoroisopropyl alcohol	12	0.509	(0.221)	(0.018)	5.56	(0.46)	(0.08)
15.	Pyrrole[b] (C_4H_4NH)	4 (6)[e]	0.295	(0.100)	(0.013)	2.54	(0.26)	(0.10)
16.	Isocyanic acid[b] (HNCO)	4	0.258	(0.147)	(0.025)	3.22	(0.39)	(0.10)
17.	Isothiocyanic acid (HNCS)	9	0.227	(0.217)	(0.011)	5.30	(0.47)	(0.11)
18.	Boron trifluoride[b,f,i]	5	3.08	(0.36)	(0.07)	7.96	(1.13)	(0.24)
19.	Boron trifluoride (g)[b,f]	4	1.62	(0.44)	(0.06)	9.88	(1.48)	(0.31)
20.	Boron trimethyl[f]	6	1.70	(0.26)	(0.03)	6.14	(0.86)	(0.18)
21.	Trimethylaluminum	18	1.43	(0.67)	(0.02)	16.9	(1.4)	(0.2)
22.	Triethylaluminum[c]	4	2.04	(0.53)	(0.08)	12.5	(1.4)	(0.3)
23.	Trimethylgallium	4	0.881	(0.54)	(0.030)	13.3	(1.5)	(0.4)
24.	Triethylgallium	5	0.593	(0.53)	(0.030)	12.6	(1.2)	(0.2)
25.	Trimethylindium	2	0.654	(0.66)	(0.043)	15.3	(2.5)	(0.5)
26.	Trimethyltin chloride[f]	10	0.0296	(0.312)	(0.0273)	5.76	(0.64)	(0.07)
27.	Sulfur dioxide[b]	6	0.808	(0.043)	(0.020)	0.920	(0.164)	(0.079)
28.	Bis(hexafluoroacetylacetonate)copper(II)[b]	7	1.40	(0.13)	(0.03)	3.39	(0.36)	(0.11)
29	Antimony pentachloride[f]	4	5.13	(0.42)	(0.14)	7.38	(0.85)	(0.24)
30.	Chloroform	10	0.150	(0.138)	(0.009)	3.31	(0.30)	(0.15)
31.	1-Hydroperfluoroheptane [$CF_3(CF_2)_6H$][b]	2	0.226	(0.101)	(0.014)	2.45	(0.35)	(0.15)

[a] Number of heats used to determine the parameters for the specified acid. [b] Tentative value calculated from limited data or data limited to bases with similar *C*/*E* ratios. In latter case, can be confidently used only with bases with *C*/*E* ratios less than 4.0. [c] Tentative value calculated from estimated enthalpies. [d] Parameter is a standard. [e] This number of enthalpies estimated from infrared frequency shifts agree with these parameters. [f] Steric effects commonly encountered. [g] Accuracy of input data estimated to be at best 10%. [h] Marginal and conditional standard derivations. [i] Data from 1,2-dichloroethane displacement reactions.

where

$$\mathrm{A} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$$

The enthalpy in terms of the new vectors $\mathbf{X}_{\mathrm{A}}'$ and $\mathbf{Y}_{\mathrm{B}}'$ is given by

$$-\Delta H = \mathbf{Y}_{\mathrm{B}}'^{\mathrm{T}}\mathbf{X}_{\mathrm{A}}'$$

where

$$\mathbf{X}_A' = \mathbf{A}\mathbf{X}_A; \quad \begin{bmatrix} E_A' \\ C_A' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} E_A \\ C_A \end{bmatrix} \tag{3a}$$

$$\mathbf{Y}_B' = \mathbf{A}^{-1\,\mathrm{T}}\mathbf{Y}_B; \quad \begin{bmatrix} E_B' \\ C_B' \end{bmatrix} = \frac{1}{(a_{11}a_{22} - a_{21}a_{12})} \begin{bmatrix} a_{22} & -a_{21} \\ -a_{12} & a_{11} \end{bmatrix} \begin{bmatrix} E_B \\ C_B \end{bmatrix} \tag{3b}$$

with the conditions that

$$\det \mathbf{A} = a_{11}a_{22} - a_{21}a_{12} \neq 0$$

and the a_{ij}'s have finite values which can be determined. Hence, if one transforms all of the E and C parameters by eq 3a and 3b using an arbitrary matrix **A** (whose inverse exists), one arrives at a new set of parameters which predict the same enthalpies of adduct formation, ΔH.

A is a linear-transformation matrix which allows one to transform from one best-fit solution to another (from the unprimed set to the primed set mentioned above). In order to specify a particular solution (and a unique transformation matrix **A** to get to that solution from some arbitrary solution), four E and C parameters may[18] be chosen and assigned specific values, as long as they are chosen in such a way that the transformation from our arbitrary solution is completely defined and finite; *i.e.*, the four parameters must be chosen so that the elements of **A**, a_{ij}, are completely defined and the determinant of **A** must be *nonzero* in order that $\mathbf{A}^{-1\mathrm{T}}$ exist, $[a_{11}a_{22} - a_{12}a_{21} \neq 0]$. These requirements are not always met for an arbitrary choice of parameters to be fixed. Once a set of parameters is procured which gives a best fit between experimental enthalpies of adduct formation and the ones calculated from eq 3, one can attempt to impose any model on the parameters by finding the transformation matrix **A** which allows one to map the vectors ($\mathbf{X}_A$, $\mathbf{Y}_B$) of one solution (model) respectively onto those ($\mathbf{X}_A'$, $\mathbf{Y}_B'$) of another. Imposing a model corresponds to finding a solution for which the E or C parameters, or some function of them, correspond to some physical property; for example, one may want the E_AE_B product to correspond to the electrostatic interaction or one may want the C_B's to be proportional to the polarizability of the bases. If a transformation matrix which maps one solution onto another does not exist, then the model cannot be imposed on the set of parameters which gives the best fit between experimental enthalpies and those calculated by eq 3.

As mentioned above, the initial model[2] was chosen so as to break the enthalpy of adduct formation into electrostatic and covalent contributions, *i.e.*, $-\Delta H = E_AE_B + C_AC_B$. The fact that more than one solution can exist enables us to *attempt* to break up the enthalpy of adduct formation into a physically meaningful model other than the electrostatic and covalent model initially employed. One apparently obvious break-up of the enthalpy of adduct formation which is of chemical significance would be that of σ and π contributions.

$$-\Delta H = \sigma_A\sigma_B + \pi_A\pi_B \tag{4}$$

The idea here is that reversals occur when there is extensive π back-bonding from the acid to the base. The enthalpy data of phenol and iodine interacting with several alkylamines can be used to test the feasibility of breaking up the enthalpy of adduct formation into σ and π contributions. Since it has presumably no π-bonding capabilities, phenol can be assigned the following parameters and used as the standard: $\sigma_{\text{phenol}} = 1.00$ and $\pi_{\text{phenol}} = 0.0$. Using the phenol–amine enthalpy data, the following equations result in which it is immediately obvious that the amine σ parameter is equal to its enthalpy of interaction with phenol.

NH_3 $\quad -\Delta H = 7.8 = \sigma_B(1.00)$

CH_3NH_2 $\quad -\Delta H = 8.6 = \sigma_B'(1.00)$

$(CH_3)_2NH$ $\quad -\Delta H = 8.6 = \sigma_B''(1.00)$

$(CH_3)_3N$ $\quad -\Delta H = 8.8 = \sigma_B'''(1.00)$

Since alkylamines have no low-energy orbitals for π back-bonding interactions, the iodine–amine enthalpies can be represented by the following equations.

NH_3 $\quad -\Delta H = 4.8 = 7.8\sigma_{I_2}$

CH_3NH_2 $\quad -\Delta H = 7.1 = 8.6\sigma_{I_2}$

$(CH_3)_2NH$ $\quad -\Delta H = 9.8 - 8.6\sigma_{I_2}$

$(CH_3)_3N$ $\quad -\Delta H = 12.1 = 8.8\sigma_{I_2}$

Since there is no solution for σ_{I_2}, the model described by eq 4 is too simple to accurately describe the systems in Table III. In matrix notation, this means that no transformation matrix exists which can transform our present best-fit set of E and C parameters into a set of σ and π parameters.

Two-Parameter Equations. One may question the need of a four-parameter enthalpy equation, *i.e.*, whether describing an acid or base by two parameters is redundant. The following simple matrix algebra shows the conditions whereby a four-parameter model reverts to a less redundant two-parameter equation. Letting **A** be the transformation matrix, E and C represent the parameters for the four-parameter model, and α represent the acid parameters for the two-parameter model, the following equation results.

$$\begin{bmatrix} \alpha \\ 0 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} E \\ C \end{bmatrix}$$

After multiplication, eq 5a and 5b are obtained.

$$Ea_{11} + Ca_{12} = \alpha \tag{5a}$$

$$Ea_{21} + Ca_{22} = 0 \tag{5b}$$

For any two acids i and j, eq 5b yields

$$E_ia_{21} + C_ia_{22} = 0$$

$$E_ja_{21} + C_ja_{22} = 0$$

Rearranging and eliminating a_{22} and a_{21} gives

$$C_i/E_i = C_j/E_j = k \tag{6}$$

Thus, for a transformation from a model describing an acid and base by two parameters each to one describing an acid and base by one parameter each, it is found that the C/E ratio for all the acids (or alternatively all bases) in the two-parameter set must be the

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[18] This is not the only way of specifying a particular solution. For example, one might instead specify three E and C numbers and then require that two amine E numbers be proportional to their dipole moments.

Table II. Base Parameters

Base	No.[a] of enthalpies	C_B			E_E		
		(Marginal)		(Conditional)	(Marginal)		(Conditional)
1. Pyridine	21 (H)	(0.29)	6.40	(0.11)	(0.18)	1.17	(0.02)
2. Ammonia	5 (H)	(0.24)	3.46	(0.16)	(0.07)	1.36	(0.03)
3. Methylamine	5 (H)	(0.30)	5.88	(0.19)	(0.15)	1.30	(0.03)
4. Dimethylamine	4 (H)	(0.46)	8.73	(0.27)	(0.29)	1.09	(0.03)
5. Trimethylamine[d]	7 (H)	(0.58)	11.54	(0.22)	(0.433)	0.808	(0.021)
6. Ethylamine[b]	4 (H)	(0.36)	6.02	(0.21)	(0.18)	1.37	(0.07)
7. Diethylamine[b]	2 (H)	(0.48)	8.83	(0.28)	(0.314)	0.866	(0.045)
8. Triethylamine[d]	9 (H)	(0.57)	11.09	(0.23)	(0.402)	0.991	(0.026)
9. Acetonitrile	11 (C)	(0.10)	1.34	(0.06)	(0.033)	0.886	(0.016)
10. Chloroacetonitrile	6 (C)	(0.16)	0.530	(0.051)	(0.089)	0.940	(0.025)
11. Dimethylcyanamide	7 (C)	(0.16)	1.81	(0.10)	(0.04)	1.10	(0.03)
12. Dimethylformamide	4 (C)	(0.22)	2.48	(0.17)	(0.07)	1.23	(0.05)
13. Dimethylacetamide	13 (C)	(0.14)	2.58	(0.10)	(*c*)	1.32	(*c*)
14. Ethyl acetate	14 (C)	(0.12)	1.74	(0.07)	(0.033)	0.975	(0.017)
15. Methyl acetate	4 (C)	(0.17)	1.61	(0.15)	(0.041)	0.903	(0.032)
16. Acetone	9 (C)	(0.18)	2.33	(0.14)	(0.036)	0.987	(0.018)
17. Diethyl ether[d]	11 (C)	(0.22)	3.25	(0.13)	(0.069)	0.963	(0.017)
18. Isopropyl ether[b,d]	3 (C)	(0.25)	3.19	(0.19)	(0.09)	1.11	(0.06)
19. *n*-Butyl ether[d]	8 (C)	(0.23)	3.30	(0.17)	(0.07)	1.06	(0.03)
20. *p*-Dioxane [$(CH_2)_4O_2$]	6 (C)	(0.20)	2.38	(0.13)	(0.04)	1.09	(0.02)
21. Tetrahydrofuran [$(CH_2)_4O$]	10 (C)	(0.23)	4.27	(0.12)	(0.110)	0.978	(0.021)
22. Tetrahydropyran	4 (C)	(0.27)	3.91	(0.17)	(0.112)	0.949	(0.038)
23. Dimethyl sulfoxide	14 (C)	(0.18)	2.85	(0.10)	(0.04)	1.34	(0.02)
24. Tetramethylene sulfoxide [$(CH_2)_4SO$]	5 (C)	(0.20)	3.16	(0.15)	(0.06)	1.38	(0.04)
25. Dimethyl sulfide	5 (H)	(0.41)	7.46	(0.20)	(0.293)	0.343	(0.021)
26. Diethyl sulfide	10 (H)	(*c*)	7.40	(*c*)	(0.265)	0.339	(0.015)
27. Trimethylene sulfide [$(CH_2)_3S$]	5 (H)	(0.38)	6.84	(0.19)	(0.266)	0.352	(0.021)
28. Tetramethylene sulfide	12 (H)	(0.42)	7.90	(0.13)	(0.313)	0.341	(0.014)
29. Pentamethylene sulfide	5 (H)	(0.41)	7.40	(0.20)	(0.288)	0.375	(0.022)
30. Pyridine *N*-oxide	4 (C)	(0.23)	4.52	(0.16)	(0.11)	1.34	(0.04)
31. 4-Methylpyridine *N*-oxide	5 (C)	(0.25)	4.99	(0.13)	(0.13)	1.36	(0.04)
32. 4-Methoxypyridine *N*-oxide[b]	3 (C)	(0.30)	5.77	(0.19)	(0.18)	1.37	(0.05)
33. Tetramethylurea[d]	3 (C)	(0.24)	3.10	(0.19)	(0.09)	1.20	(0.06)
34. Trimethylphosphine[b]	6 (H)	(0.61)	6.55	(0.18)	(0.219)	0.838	(0.017)
35. Benzene	5 (CorH)	(0.12)	0.707	(0.087)	(0.038)	0.486	(0.025)
36. *p*-Xylene[b]	2 (CorH)	(0.20)	1.78	(0.13)	(0.097)	0.416	(0.036)
37. Mesitylene[b]	3 (CorH)	(0.19)	2.19	(0.11)	(0.109)	0.574	(0.040)

Table II (*Continued*)

	Base	No.[a] of enthalpies	C_B (Marginal)	C_B	C_B (Conditional)	E_B (Marginal)	E_B	E_B (Conditional)
38.	2,2,6,6-Tetramethylpyridine *N*-oxyl[d] ($C_9H_{18}NO$)	7 (H)	(0.50)	6.21	(0.15)	(0.202)	0.915	(0.025)
39.	1-Azabicyclo[2.2.1]octane [$HC(C_2H_4)_3N$]	5 (H)	(0.70)	13,2	(0.31)	(0.518)	0.704	(0.038)
40.	7-Oxabicyclo[2.2.1]heptane ($C_6H_{10}O$)	3 (C)	(0.24)	3.76	(0.15)	(0.10)	1.08	(0.048)
41.	Dimethyl selenide	3 (H)	(0.48)	8.33	(0.20)	(0.344)	0.217	(0.019)
42.	1-Phospha-4-ethyl-1,5,7-trioxabicyclo[2.2.1]octane [$C_2H_5C(CH_2O)_3P$]	3 (H)	(0.73)	6.60	(0.23)	(0.253)	0.515	(0.033)
43.	Hexamethylphosphoramide[b]	5 (C)	(0.11)	1,33	(0.37)	(0.13)	1.73	(0.030)

[a] Number of heats used to determine the parameters for the specified base. The solvent recommended for getting enthalpies for comparison is indicated in parentheses; H stands for cyclohexane or gas phase and C represents carbon tetrachloride or gas phase: M. S. Nozari and R. S. Drago, submitted for publication. [b] Tentative value calculated from data limited to acids with similar *C*/*E* ratios. [c] Parameters considered a standard for the purpose of calculating standard deviations. [d] Steric effects often expected.

Table III

Acid	Base	Heat, kcal/mol Measd	Heat, kcal/mol Calcd	Ref
I_2	C_5H_5N	7.8	7.6	*a*
	NH_3	4.8	4.8	*a*
	CH_3NH_2	7.1	7.2	*a*
	$(CH_3)_2NH$	9.8	9.8	*a*
	$(CH_3)_3N$	12.1	12.3	*a*
	$C_2H_5NH_2$	7.4	7.4	*a*
	$(C_2H_5)_2NH$	9.7	9.7	*a*
	$(C_2H_5)_3N$	12.0	12.1	*a*
	$HC(C_2H_4)_3N$	13.9	13.9	*rr*
	CH_3CN	1.9	2.2	*a*
	$ClCH_2CN$	1.5	1.5	*b*
	$(CH_3)_2NCN$	2.8	2.9	*c*
	$HC(O)N(CH_3)_2$	3.7	3.7	*a*
	$CH_3C(O)N(CH_3)_2$	4.0	3.9	*a*
	$CH_3C(O)OC_2H_5$	2.8	2.7	*a*
	$CH_3C(O)OCH_3$	2.5	2.5	*a*
	$CH_3C(O)CH_3$	3.3	3.3	*a*
	$(C_2H_5)_2O$	4.2	4.2	*a*
	$(C_4H_9)_2O$	4.4	4.4	*ll*
	$(CH_2)_4O$	5.3	5.2	*a*
	$[(CH_3)_2CH]_2O$	4.3	4.3	*ll*
	$(CH_2)_5O$	4.9	4.9	*d*
	$(CH_2)_4O_2$	3.5	3.5	*a*
	$C_6H_{10}O$	4.9	4.8	*ww*
	$(CH_3)_2SO$	4.4	4.2	*a*
	$(CH_2)_4SO$	4.4	4.5	*a*
	$(C_2H_5)_2S$	7.8	7.7	*a*
	$(CH_2)_3S$	7.1	7.2	*e*
	$(CH_2)_4S$	8.3	8.2	*e*
	$(CH_3)_2S$	7.8	7.8	*ll*
	$(CH_2)_5S$	7.8	7.8	*e*
	$(CH_3)_2Se$	8.5	8.6	*ss*
	$[(CH_3)_2N]_2CO$	4.3	4.3	*a*
	C_5H_5NO	5.9	5.9	*f*
	$4\text{-}CH_3C_5H_4NO$	6.3	6.3	*qq*
	$4\text{-}CH_3OC_5H_4NO$	7.2	7.1	*qq*
	C_6H_6	1.3	1.2	*a*
	$p\text{-}(CH_3)_2C_6H_4$	2.2	2.2	*h*
	$s\text{-}(CH_3)_3C_6H_3$	2.9	2.8	*h*
	$C_6(CH_3)_6$	3.7	3.7	*h*
ICl	$CH_3C(O)N(CH_3)_2$	9.2	8.9	*a*
	$CH_3C(O)OC_2H_5$	6.1	6.4	*i*
	$(CH_2)_4O_2$	7.5	7.5	*a*
	$ClCH_2CN$	5.3	5.3	*b*
	$(CH_3)_2NCN$	7.3	7.1	*c*
	C_6H_6	2.8	3.1	*a*
	$p\text{-}(CH_3)_2C_6H_4$	3.6	3.6	*j*
	$s\text{-}(CH_3)_3C_6H_3$	4.7	4.7	*j*
IBr	CH_3CN	4.1	4.2	*b*
	$ClCH_2CN$	3.1	3.1	*b*
	$(CH_3)_2NCN$	5.6	5.5	*c*
C_6H_6SH	C_5H_5N	2.4	2.4	*k*
	$HC(O)N(CH_3)_2$	1.8	1.7	*k*
	C_6H_6	0.5	0.6	*k*
p-tert-$C_4H_9C_6H_4OH$	C_5H_5N	7.2	7.2	*l*
	$(C_2H_5)_3N$	8.3	8.3	*l*
	$CH_3C(O)N(CH_3)_2$	6.4	6.4	*l*
	$(C_2H_5)_2S$	4.2	4.2	*m*
	$(CH_2)_4S$	4.5	4.4	*m*
p-$CH_3C_6H_4OH$	C_5H_5N	7.8	7.5	*l, n*
	$CH_3C(O)N(CH_3)_2$	6.4	6.6	*l, n*
	$CH_3C(O)OC_2H_5$	4.6	4.7	*l, n*
	$(C_4H_9)_2O$	5.9	5.8	*m*
	$(C_2H_5)_2S$	4.3	4.4	*m, n*
	$(CH_2)_4S$	4.6	4.6	*m*
C_6H_5OH	C_5H_5N	8.0	7.9	*l*
	NH_3	7.8	7.4	*o*
	CH_3NH_2	8.6	8.2	*o*
	$(CH_3)_2NH$	8.6	8.6	*o*
	$(CH_3)_3N$	8.8	8.6	*o*
	$C_2H_5NH_2$	8.6	8.6	*o*
	$(C_2H_5)_3N$	9.1	9.2	*p*
	$HC(C_2H_4)_3N$	9.0	8.9	*pp*
	CH_3CN	4.6	4.4	*p*
	$ClCH_2CN$	4.2	4.3	*l, n*
	$(CH_3)_2NCN$	5.4	5.6	*n, u*
	$CH_3C(O)N(CH_3)_2$	6.8	6.8	*p*
	$HC(O)N(CH_3)_2$	6.1	6.4	*q*
	$CH_3O(O)OC_2H_5$	4.8	5.0	*p*
	$CH_3C(O)OCH_3$	4.8	4.6	*l, n*
	$CH_3C(O)CH_3$	5.1	5.3	*p*
	$C_9H_{18}NO$	6.9	6.7	*oo*
	$(C_2H_5)_2O$	6.0	5.6	*q*
	$(C_4H_9)_2O$	6.0	6.0	*m*
	$[(CH_3)_2CH]_2O$	6.2	6.2	*q*
	$(CH_2)_4O$	6.0	6.1	*l*
	$(CH_2)_5O$	6.1	5.8	*l, n*
	$(CH_2)_4O_2$	5.6	5.8	*l, n*
	C_9H_{10}	6.4	6.3	*vv*
	$(CH_3)_2SO$	6.9	7.1	*r*
	$(CH_2)_3SO$	7.2	7.4	*a*
	$(C_2H_5)_2S$	4.6	4.7	*m*
	$(CH_3)_2S$	4.6	4.8	*s*
	$(CH_2)_3S$	4.5	4.5	*s*
	$(CH_2)_4S$	4.9	5.0	*m*
	$(CH_2)_5S$	4.7	4.9	*s*
	$[(CH_3)_2N]_2CO$	6.6	6.6	*l, n*
	C_5H_5NO	7.9	7.8	*t*
	$4\text{-}CH_3C_5H_4NO$	8.4	8.1	*r*
p-FC_6H_4OH	C_5H_5N	7.9	7.7	*l*
	$(C_2H_5)_3N$	9.0	9.1	*l*

Table III (*Continued*)

Acid	Base	Heat, kcal/mol Measd	Heat, kcal/mol Calcd	Ref
	$CH_3C(O)OC_2H_5$	4.9	4.8	*l*
	$(CH_3)_2SO$	6.6	6.9	*tt*
	$(CH_2)_4O$	5.6	6.0	*tt*
	$(C_2H_5)_2O$	5.6	5.5	*tt*
	$[(CH_3)_2N]_3PO$	8.0	7.8	*tt*
	$(C_2H_5)_2S$	4.7	4.7	*m*
	$(CH_2)_4S$	5.0	4.9	*m*
p-ClC_6H_4OH	C_5H_5N	8.1	8.1	*l*
	$(C_2H_5)_3N$	9.5	9.6	*l*
	$CH_3C(O)N(CH_3)_2$	7.0	7.0	*n*
	$CH_3C(O)OC_2H_5$	5.0	5.1	*l*
	$CH_3C(O)CH_3$	5.4	5.4	*n*
	$(C_4H_9)_2O$	6.3	6.2	*n*
	$(CH_3)_2SO$	7.2	7.2	*n*
	$(CH_3)_2NCN$	5.6	5.7	*u*
	$(C_2H_5)_2S$	5.0	5.0	*m*
	$(CH_2)_4S$	5.3	5.2	*m*
m-FC_6H_4OH	C_5H_5N	8.4	8.4	*v*
	CH_3CN	4.9	4.6	*v*
	$CH_3C(O)OC_2H_5$	5.2	5.2	*v*
	$CH_3C(O)N(CH_3)_2$	7.0	7.1	*v*
	$(CH_3)_2SO$	7.3	7.4	*v*
	$(C_2H_5)_2S$	5.2	5.2	*m*
	$(CH_2)_4S$	5.5	5.5	*m*
	$C_9H_{18}NO$	7.5	7.2	*oo*
	$(C_4H_9)_2O$	6.0	6.4	*mm*
	$C_2H_5C(CH_2O)_3P$	5.6	5.6	*pp*
m-$CF_3C_6H_4OH$	C_5H_5N	8.5	8.6	*l*
	CH_3CN	4.9	4.7	*n*
	$ClCH_2CN$	4.4	4.5	*n*
	$(CH_3)_2NCN$	5.8	5.9	*n*
	$CH_3C(O)N(CH_3)_2$	7.3	7.3	*l*
	$CH_3C(O)C_2H_5$	5.2	5.3	*n*
	$CH_3C(O)OCH_3$	5.0	4.9	*n*
	$CH_3C(O)CH_3$	5.9	5.7	*n*
	$(C_2H_5)_2O$	6.5	6.0	*n*
	$[(CH_3)_2CH]_2O$	6.7	6.7	*n*
	$C_9H_{18}NO$	7.5	7.4	*oo*
	$(CH_2)_4O$	6.5	6.6	*n*
	$(CH_2)_5O$	6.5	6.3	*n*
	$(CH_2)_4O_2$	6.0	6.2	*n*
	$(CH_3)_2SO$	7.4	7.5	*n*
	$(CH_2)_4SO$	7.6	7.9	*n*
	$(C_2H_5)_2S$	5.4	5.4	*m*
	$(CH_3)_2S$	5.4	5.5	*s*
	$(CH_2)_3S$	5.4	5.2	*s*
	$(CH_2)_4S$	5.7	5.7	*m*
	$(CH_2)_5S$	5.6	5.6	*s*
	$[(CH_3)_2N]_2CO$	7.0	7.0	*n*
$(CH_3)_3COH$	C_5H_5N	4.3	4.3	*w*
	$(CH_3)_2SO$	3.6	3.6	*w*
CF_3CH_2OH	C_5H_5N	7.8	7.4	*x*
	$(C_2H_5)_3N$	8.8	8.8	*x*
	CH_3CN	4.4	4.1	*x*
	$(C_2H_5)_2O$	5.1	5.3	*x*
	$HC(O)N(CH_3)_2$	6.1	6.0	*x*
	$CH_3C(O)N(CH_3)_2$	6.4	6.4	*x*
	$CH_3C(O)OC_2H_5$	4.4	4.6	*x*
	$CH_3C(O)CH_3$	5.0	5.0	*x*
	$[(CH_3)_2N]_3PO$	7.7	7.5	*x*
	$(C_4H_9)_2O$	5.8	5.7	*n*
	$(CH_3)_2SO$	6.3	6.6	*x*
	$C_9H_{18}NO$	6.2	6.4	*oo*
$(CF_3)_2CHOH$	C_5H_5N	9.8	9.7	*y*
	$(C_2H_5)_3N$	11.5	11.0	*y*
	CH_3CN	5.9	5.6	*y*
	$CH_3C(O)N(CH_3)_2$	8.5	8.6	*y*
	$CH_3C(O)OC_2H_5$	6.5	6.3	*y*
	$[(CH_3)_2N]_3PO$	9.9	10.3	*y*
	$C_9H_{18}NO$	7.9	8.2	*oo*
	$(CH_2)_4S$	5.8	5.9	*m*
	$CH_3C(O)CH_3$	6.7	6.7	*y*
	$(C_2H_5)_2O$	7.2	7.0	*y*
	$(C_4H_9)_2O$	7.9	7.6	*n, y*
	$(CH_3)_2SO$	8.7	8.9	*y*
C_4H_4NH	C_5H_5N	5.0	4.8	*z*
	$(C_2H_5)_3N$	5.9	5.8	*z*
	$(CH_3)_2SO$	4.2	4.2	*z*
	$HC(C_2H_4)_3N$	5.6	5.7	*pp*
$(CH_3)_3SnCl$	CH_3CN	4.8	5.1	*aa*
	$CH_3C(O)N(CH_3)_2$	7.9	7.7	*aa*
	$CH_3C(O)CH_3$	5.7	5.8	*aa*
	$[(CH_3)_2N]_3PO$	10.1	10.0	*aa*
	$CH_3C(O)OCH_3$	5.2	5.2	*g*
	$(CH_3)_2SO$	8.2	7.8	*aa*
	$(CH_3)_2NCN$	6.4	6.4	*u*
	C_5H_5NO	7.8	7.0	*g*
	4-$CH_3C_5H_4NO$	7.9	8.0	*g*
	4-$CH_3OC_5H_4NO$	8.1	8.1	*g*
BF_3 (DCE)	$(CH_3)_2SO$	19.5	19.5	*g*
	C_5H_5NO	24.5	24.5	*g*
	4-$CH_3C_5H_4NO$	26.2	26.1	*g*
	4-$CH_3OC_5H_4NO$	28.5	28.7	*g*
	$C_9H_{18}NO$	26.5	26.4	*oo*
$B(CH_3)_3$	C_5H_5N	17.6	18.0	*bb*
	NH_3	14.3	14.2	*bb*
	CH_3NH_2	18.2	18.0	*cc*
	$C_2H_5NH_2$	18.6	18.6	*bb*
	$(CH_3)_3P$	16.5	16.3	*ss*
	$C_2H_5C(CH_2O)_3P$	14.4	14.4	*pp*
$Al(CH_3)_3$	C_5H_5N	26.7	28.9	*dd*
	NH_3	27.6	28.0	*dd*
	CH_3NH_2	30.0	30.4	*dd*
	$(CH_3)_2NH$	30.8	30.8	*dd*
	$(CH_3)_3N$	30.0	30.2	*dd*
	$(C_2H_5)_2NH$	27.3	27.3	*dd*
	$CH_3C(O)CH_3$	20.3	20.0	*dd*
	$(C_2H_5)_2O$	20.2	20.9	*dd*
	$(CH_2)_4O_2$	22.9	21.9	*dd*
	$(CH_3)_2SO$	28.6	26.8	*ee*
	$(CH_2)_4SO$	28.2	27.9	*ee*
	$(C_2H_5)_2S$	16.7	16.3	*ff*
	$(CH_3)_2S$	16.7	16.5	*ff*
	$(CH_2)_3S$	16.0	15.8	*ff*
	$(CH_2)_4S$	17.0	17.1	*ff*
	$(CH_2)_5S$	17.0	16.9	*ff*
	$(CH_3)_2Se$	16.0	15.6	*bb*
	$(CH_3)_3P$	22.1	23.6	*dd*
$Al(C_2H_5)_3$	C_5H_5N	27.0	27.6	*gg*
	$(C_2H_5)_2O$	18.8	18.7	*gg*
	$(CH_2)_4O$	21.6	20.9	*gg*
	$(CH_2)_4O_2$	18.3	18.5	*gg*
$Ga(C_2H_5)_3$	NH_3	19.2	19.2	*hh*
	CH_3NH_2	19.8	19.8	*hh*
	$(CH_3)_2NH$	18.8	18.8	*hh*
	$(CH_3)_3N$	17.0	17.0	*ii*
	$(CH_3)_3P$	14.5	14.4	*a*
SO_2	C_5H_5N	6.0	6.2	*a*
	$(CH_3)_3N$	10.3	10.1	*jj*
	$CH_3C(O)N(CH_3)_2$	3.3	3.3	*a*
	$(CH_2)_4SO$	4.0	3.8	*a*
	C_6H_6	1.0	1.0	*a*
	s-$(CH_3)_3C_6H_3$	2.2	2.3	*a*
$Cu(hfacac)_2$	C_5H_5N	13.4	12.9	*kk*
	$CH_3C(O)N(CH_3)_2$	8.0	8.1	*kk*
	$CH_3C(O)OC_2H_5$	5.9	5.7	*kk*
	$(CH_3)_2SO$	8.5	8.6	*kk*
	$(CH_2)_4O$	9.1	9.3	*nn*
	$C_9H_{18}NO$	11.7	11.8	*oo*
	$C_6H_{10}O$	8.8	8.9	*nn*
$SbCl_5$	$ClCH_2CN$	9.6	9.6	*oo*
	CH_3CN	13.9	13.4	*oo*
	4-$CH_3C_5H_4NO$	35.4	35.6	*oo*
	$CH_3C(O)OC_2H_5$	15.5	16.1	*oo*
$HCCl_3$	$(C_2H_5)_3N$	4.8	4.9	*yy*
	$(CH_2)_4S$	2.4	2.3	*yy*
	C_5H_5N	4.9	4.9	*yy*
	$(CH_2)_4O$	3.9	3.9	*yy*
	$CH_3C(O)CH_3$	3.6	3.6	*yy*

Table III (*Continued*)

Acid	Base	Heat, kcal/mol Measd	Heat, kcal/mol Calcd	Ref
	$HC(C_2H_4)_3N$	4.3	4.3	*yy*
	$C_2H_5C(CH_2O)_3P$	2.7	2.7	*pp*
	$[(CH_3)_2N]_3PO$	5.9	5.9	*yy*
	$CH_3C(O)OC_2H_5$	3.8	3.5	*yy*
	C_6H_6	2.0	1.7	*yy*
$CF_3(CF_2)_6H$	C_5H_5N	4.3	4.3	*pp*
	$HC(C_2H_4)_3N$	4.7	4.7	*pp*
HNCO	$(C_2H_5)_2O$	3.9	3.9	*xx*
	C_4H_8O	4.2	4.2	*xx*
	CH_3CN	3.2	3.2	*xx*
	C_5H_5N	5.4	5.4	*xx*
HNCS	$(CH_3)_2S$	3.5	3.5	*uu*
	$(C_2H_5)_2S$	3.5	3.5	*uu*
	$(CH_2)_5S$	3.7	3.7	*uu*
	$(CH_2)_4S$	3.6	3.6	*uu*
	$(CH_2)_3S$	3.3	3.4	*uu*
	CH_3CN	4.6	5.0	*uu*
	$(C_2H_5)_2O$	6.3	5.8	*uu*
	$(n\text{-}C_4H_9)_2O$	6.5	6.4	*uu*
	C_4H_8O	6.3	6.2	*uu*
$Ga(CH_3)_3$	$(CH_3)_3N$	21	20.9	*bb*
	$(CH_3)_3P$	18	16.9	*bb*
	$(CH_3)_2Se$	10	10.2	*bb*
$In(CH_3)_3$	$(CH_3)_3N$	19.9	19.9	*bb*
		17.1	17.1	*bb*
$BF_3(g)$	$(CH_3)_3P$	18.9	18.9	*ss*
	$(CH_2)_4O$	16.8	16.6	*ss*
	$(CH_2)_5O$	15.4	15.7	*ss*
	$CH_3COOC_2H_5$	12.8	12.4	*ss*

[a] See ref 2. [b] W. B. Person, *et al., J. Amer. Chem. Soc.*, **85**, 891 (1963). [c] E. Augdahl and P. Klaeboe, *Acta Chem. Scand.*, **19**, 807 (1965). [d] M. Tamres and Sr. M. Brandon, *J. Amer. Chem. Soc.*, **82**, 2134 (1960). [e] M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962). [f] T. Kubota, *J. Amer. Chem. Soc.*, **87**, 458 (1965). [g] J. C. Hill, Ph.D. Dissertation, University of Illinois, 1968. [h] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **77**, 2164 (1955). [i] D. G. Brown, R. S. Drago, and T. F. Bolles, *ibid.*, **90**, 5706 (1968). [j] N. Ogimachi, *et al., ibid.*, **77**, 4202 (1955). [k] R. Mathur, *et al., J. Phys. Chem.*, 67, 2190 (1963). [l] R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, **91**, 2883 (1969). [m] See ref 9. [n] Heats obtained from the appropriate linear ΔH–$\Delta\nu$ relationship and the frequency shifts in Table IV. [o] Frequency shifts from R. S. Drago, *et al., Inorg. Chem.*, **2**, 1056 (1963). [p] T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5570 (1967). [q] M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037, 2096, 3817 (1962). [r] Frequency shifts from T. S. S. R. Murty, Ph.D. Dissertation, University of Pittsburgh, 1967. [s] Estimated from results in ref 9 and $\Delta\nu_{OH}$. [t] Frequency shift from D. Herlocker, *et al., Inorg. Chem.*, **5**, 2009 (1966). [u] Frequency shift from H. F. Henneike and R. S. Drago, *ibid.*, **7**, 1908 (1968). [v] M. Nozari, G. C. Vogel, and R. S. Drago, in preparation. [w] See ref 10. [x] A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, **74**, 3535 (1970). [y] See ref 11. [z] See ref 12. [aa] See ref 13. [bb] F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958). [cc] See ref 27. [dd] C. H. Henrickson, *et al., Inorg. Chem.*, 7, 1047 (1968). [ee] C. H. Henrickson, *et al., ibid.*, 7, 1028 (1968). [ff] C. H. Henrickson and D. P. Eyman, *ibid.*, **6**, 1461 (1967). [gg] E. Bonitz, *Chem. Ber.*, **88**, 742 (1955). The data taken from this reference were corrected for dimerization using the heat of dimerization given in ref *dd* and assuming 90% dimerization of the triethylaluminum. [hh] G. E. Coates, *J. Chem. Soc.*, 2003 (1951). [ii] L. G. Stevens, *et al., J. Inorg. Nucl. Chem.*, **26**, 97 (1964). [jj] J. Grundes and S. D. Christian, *J. Amer. Chem. Soc.*, **90**, 2239 (1968); **93**, 20 (1971); ΔE converted to ΔH. [kk] W. Partenheimer and R. S. Drago, *Inorg. Chem.*, 9, 47 (1970). [ll] Estimated from very similar alkyl-substituted donor; *e.g.*, butyl estimated 0.1 kcal greater than ethyl. [mm] M. S. Nozari and R. S. Drago, to be published. [nn] R. L. Chiang and R. S. Drago, to be published. [oo] Y. Y. Lim and R. S. Drago, to be published. Donor is a free-radical base, 2,2,6,6-tetramethylpiperidine *N*-oxyl. [pp] F. Slejko and R. S. Drago, to be published. [qq] R. C. Gardner and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 139 (1968). [rr] A. M. Halpern and K. Weiss, *J. Amer. Chem. Soc.*, **90**, 6297 (1968). [ss] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963). [tt] E. M. Arnett, *et al., J. Amer. Chem. Soc.*, **92**, 2365 (1970). [uu] T. M. Barakat, *et al., Trans. Faraday Soc.*, **62**, 2674 (1966); **65**, 41 (1969). [vv] E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1684 (1962). [ww] M. Tamres, *et al., ibid.*, **86**, 3934 (1964). [xx] J .Nelson, *Spectrochim. Acta, Part A*, **26**, 109 (1970). [yy] F. Slejko, R. S. Drago, and D. Brown, submitted for publication.

same. Inspection of Tables I and II shows that this condition obviously does not exist in general.

In addition, rearranging eq 6 and combining with eq 5a illustrate that $\alpha_i = k''\alpha_j$. Therefore, a two-parameter model would require that a plot of the enthalpies of adduct formation of one acid *vs.* the enthalpies of adduct formation of another acid for the same series of bases be linear with a zero intercept. The enthalpies of adduct formation for I_2 and phenol with the same series of bases is plotted in Figure 1. These acids have very different *C*/*E* ratios, and their enthalpies of adduct formation cannot be correlated by a two-parameter model. The lack of linearity and a nonzero intercept in Figure 1 support this. Furthermore, a two-parameter, one-term model could not incorporate systems in which reversals in donor–acceptor strength are observed.[3,9] However, it is possible to correlate enthalpies of adduct formation for acids with very similar *C*/*E* ratios, such as hydrogen-bonding acids, using a two-parameter equation. Correlations restricted to one particular type of acid are, of course, only a subset of the overall *E* and *C* correlation.

This brings the discussion to the concept of donor numbers proposed by Gutman[19] to order solvents with regard to their donor strength toward acidic solutes. The conditions under which eq 1 is valid have been clearly emphasized.[2,20] In spite of warnings in the literature about these conditions, the inability of our approach to correlate data in a solvating solvent (1,2-dichloroethane)[21] for an acid in which steric effects are potentially operative (antimony pentachloride) was used to reject the *E* and *C* approach for estimating enthalpies. In its place, the author proposed what amounts to a two-parameter equation. The idea is that when the enthalpy of adduct formation for $SbCl_3$, $SbBr_3$, C_6H_5OH, or I_2 for a series of donors is plotted *vs.* the enthalpies for $SbCl_5$ for the same series of donors, linear plots are obtained. A line for a new acid can be determined by measuring enthalpies for the new acid interacting with two or three donors, and the enthalpies for other donors can be interpolated from this line using the enthalpies of $SbCl_5$ with the donors. Hence, enthalpies for $SbCl_5$ are called donor numbers, and it is claimed that this is the essential property needed to characterize a solvent as a base.

A quick glance at Figure 1 illustrates the fallacy of this approach. Both I_2 and phenol cannot give linear enthalpy plots with $SbCl_5$ unless they give linear plots with each other. The apparent success in the donor-

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(19) V. Gutman, *Coord. Chem. Rev.*, **2**, 239 (1967).

(20) R. S. Drago, *Chem. Brit.*, **3**, 516 (1967).

(21) M. Nozari, G. C. Vogel, and R. S. Drago, *J. Amer. Chem. Soc.*, in press; Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, in press.

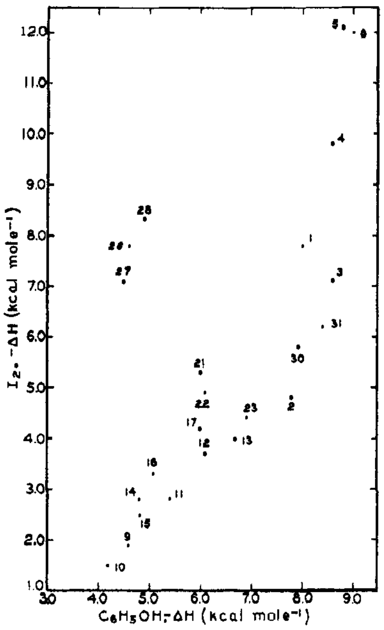

Figure 1. Enthalpies of adduct formation of donors with I_2 plotted *vs.* corresponding enthalpies of adduct formation for phenol with the same series of bases. The numbering of the bases refers to that in Table II.

number lies in utilizing a limited number of donors with similar C/E ratios and using several incorrect enthalpies of interaction with phenol. Clearly, the systems employed as the bases for the donor-number concept do not satisfy the requirements outlined above for a two-parameter equation to be operative. Consequently, the idea upon which the donor-number approach is based is incomplete, and it will work only with acids and bases that satisfy the requirements outlined above for a two-parameter equation.

Relationship of the *E* and *C* and Hammett Equations. The Hammett equation was originally proposed to describe the influence of polar meta or para substitutents on the reactivity of the functional groups of many benzene derivatives.[22] It has been very successful in correlating and predicting relative reaction rates and equilibrium constants. In addition to correlating Gibbs free energy values, ΔG, the Hammett substituent constants, σ, have also been correlated with the infrared stretching frequency shifts of phenols, $\Delta\nu_{OH}$,[9,23,24] and with the enthalpy of adduct formation of phenols with oxygen, nitrogen, and sulfur donors.[8,9] The Hammett substituent constant relationship correlates and predicts enthalpies of adduct formation as well as eq 1 for meta- and para-substituted phenols. Consequently, it is of interest to ascertain how the Hammett equation is related to eq 1 and to determine the conditions whereby the parameters in Tables I and II can be transformed to parameters which obey an equation of the form of the Hammett equation.

The Hammett equation is a two-parameter equation with a constant of the general form $-\Delta H = \sigma\rho - \Delta H^0$ or $-\Delta H + \Delta H^0 = \sigma\rho$, where σ is the Hammett substituent constant and ρ is a parameter assigned to a constant reaction type. In terms of a primed set of E and C parameters, one may write the enthalpy as a function of two vectors

$$-\Delta H = \mathbf{Y}_B{}'^{T}\mathbf{X}_A{}' = E_A{}'E_B{}' + C_A{}'C_B{}'$$

To put this equation in the form of the Hammett equation for a series of substituted phenols, the restriction $-\Delta H_B{}^0 = C_A{}'C_B{}'$ is required, where $\Delta H_B{}^0$ is the enthalpy of adduct formation for a given base with unsubstituted phenol. Now $E_A{}'$ is comparable to σ and $E_B{}'$ is comparable to ρ. Using the transformation equations (3a and 3b), this restriction in terms of the

Table IV. Frequency Shift Data

Acid	Base	$\Delta\bar{\nu}_{OH}$,[a] cm^{-1}
p-$CH_3C_6H_4OH$	C_5H_5N	458 ± 10[b]
	$CH_3C(O)N(CH_3)_2$	336
	$CH_3C(O)OC_2H_5$	147[b]
	$(C_4H_9)_2$	277
	$(C_2H_5)_2S$	245
C_6H_5OH	$ClCH_2CN$	111
	$(CH_3)_2NCN$	222[c]
	$CH_3C(O)OCH_3$	171, 164[c]
	$CH_3C(S)N(CH_3)_2$	308[c]
	$(CH_2)_5O$	294
	$(CH_2)_4O_2$	240
	$(C_4H_9)_2O$	286
	$(CH_3)_2SO$	366
	$(CH_3)_2S$	253[c]
	$(CH_2)_3S$	246
	$(CH_2)_5S$	264[c]
	$[(CH_3)_2N]_2CO$	338[c]
p-ClC_6H_4OH	$CH_3C(O)N(CH_3)_2$	378 ± 10
	$CH_2C(O)C_2H_5$	190 ± 10
	$CH_3C(O)CH_3$	220[b]
	$(C_4H_9)_2O$	310
	$(CH_8)_2SO$	400
m-FC_6H_4OH	C_5H_5N	520 ± 10
	CH_3CN	175
	$CH_3C(O)N(CH_3)_2$	384 ± 10
	$CH_3(O)OC_2H_5$	194
	$(CH_3)_2SO$	402
m-$CF_3C_6H_4OH$	CH_3CN	181
	$ClCH_2CN$	131[c]
	$(CH_3)_2NCN$	260[c]
	$CH_3C(O)OC_2H_5$	207 ± 10
	$CH_3C(O)OCH_3$	182[c]
	$CH_3C(O)CH_3$	280 ± 10
	$CH_3C(S)N(CH_3)_2$	354[c]
	$(C_2H_5)_2O$	328[c]
	$[(CH_3)_2CH]_2O$	348[c]
	$(CH_2)_4O$	331[c]
	$(CH_2)_5O$	334
	$(CH_2)_4O_2$	286
	$(CH_3)_2SO$	416
	$(CH_2)_4SO$	425
	$(CH_3)_2S$	294
	$(CH_2)_3S$	298
	$(CH_2)_5S$	309
	$[(CH_3)_2N]_2CO$	382[c] (398)
$(CF_3)_2CHOH$	$(C_4H_9)_2O$	372 ± 10
	C_6H_6	70
	p-$(CH_3)_2C_6H_4$	78
	s-$(CH_3)_3C_6H_3$	96
	$C_6(CH_3)_6$	135
CF_3CH_2OH	$(C_4H_9)_2O$	254 ± 10

[a] These frequency shifts were measured by the procedure given in the Experimental Section unless otherwise noted. The error limits are ±5 cm^{-1} unless otherwise stated. [b] Measured by Dr. H. F. Henneike in very dilute CCl_4 solutions. [c] Measured by Dr. W. Partenheimer in CCl_4 as solvent. Shift obtained from most dilute solutions.

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(22) J. Shorter, *Chem. Brit.*, **5**, 2969 (1969), and references cited therein.

(23) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(24) C. Laurence and B. Bruno, *C. R. Acad. Sci.*, **264**, 1216 (1967).

unprimed E and C parameters is given by

$$-\Delta H_B^0 = C_A'C_B' = \frac{(a_{21}E_A + a_{22}C_A)(-a_{12}E_B + a_{11}C_B)}{a_{11}a_{22} - a_{12}a_{21}} \quad (7)$$

In addition, for the standard acid, it should be noted that $-\Delta H + \Delta H^0 = \Delta\Delta H = E_A^{0\prime}E_B'$, where $E_A^{0\prime}$ is the new E_A value for the reference acid phenol. Since $\Delta\Delta H$ for phenol is zero, $E_A^{0\prime} = 0 = a_{11}E_A^0 + a_{12}C_A^0$ and

$$a_{11}/a_{12} = -C_A^0/E_A^0 \quad (8)$$

where C_A^0 is the old C_A value for phenol. For eq 7 to be valid for different acids, the term C_A' $(=a_{21}E_A + a_{22}C_A)$ must be constant, since all other terms are independent of the acid. Thus, for acids 1 and 2, it follows that

$$a_{21}E_{A1} + a_{22}C_{A1} = a_{21}E_{A2} + a_{22}C_{A2}$$

$$a_{21}(E_{A1} - E_{A2}) = -a_{22}(C_{A1} - C_{A2})$$

$$-a_{21}/a_{22} = (C_{A1} - C_{A2})/(E_{A1} - E_{A2})$$

or for a series of acids with the unsubstituted phenol as reference

$$-a_{21}/a_{22} = (C_A - C_A^0)/(E_A - E_A^0) \quad (9)$$

Thus, for a series of acids to conform to an equation of the form of the Hammett equation, the ratio given in eq 9 must be a constant for all acids. In addition, for eq 7 to be valid when the base is changed, the expression $(-a_{12}E_{B_i} + a_{11}C_{B_i})/-\Delta H_{B_i}^0$ must be constant. Next, let us consider the base restrictions, if any, on a Hammett-type correlation. Considering any two bases, 1 and 2, the following results are obtained.

$$\frac{-\Delta H_{B1}^0}{-\Delta H_{B2}^0} = \frac{-a_{12}E_{B1} + a_{11}C_{B1}}{-a_{12}E_{B2} + a_{11}C_{B2}} =$$

$$\frac{-E_{B1} + (a_{11}/a_{12})C_{B1}}{-E_{B2} + (a_{11}/a_{12})C_{B2}} = \frac{-E_{B1} - (C_A^0/E_A^0)C_{B1}}{-E_{B2} - (C_A^0/E_A^0)C_{B2}} =$$

$$\frac{-E_A^0E_{B1} - C_A^0C_{B1}}{-E_A^0E_{B2} - C_A^0C_{B2}} = \frac{-\Delta H_{B1}^0}{-\Delta H_{B2}^0}$$

Hence, this condition is always met, regardless of the base E and C parameters.

It would be of interest to see if our E and C parameters for the substituted phenol–base interactions can be transformed into Hammett σ and ρ parameters, *i.e.*, to see how well the constraints of a Hammett treatment are adhered to by our E and C parameters derived from all types of donor–acceptor interactions. Unfortunately, the form of the ratios $(C_A - C_A^0)/(E_A - E_A^0)$, which will be designated R, is such that the uncertainty in these numbers is so large as to make comparisons meaningless. For the sake of completeness, the algebra will be continued for the transformation with the assumption that R is constant for the substituted phenols. From the transformation equation (3a)

$$E_A' = a_{11}E_A + a_{12}C_A$$

Combining this with eq 8, the following is obtained.

$$E_A' = a_{12}(C_A - (C_A^0/E_A^0)E_A) \quad (10)$$

The ρ values are a function of the base and the standard acid selected. From the transformation equation (3b)

$$E_B' = \frac{1}{(a_{11}a_{22} - a_{12}a_{21})}(a_{22}E_B - a_{21}C_B)$$

Dividing by a_{22} and substituting $-R = a_{21}/a_{22}$ yields

$$E_B' = \frac{1}{(a_{11} + a_{12}R)}(E_B + RC_B)$$

Dividing the numerator and denominator by a_{12}, substituting $a_{11}/a_{12} = -C_A^0/E_A^0$, and rearranging yields

$$E_B' = \frac{E_A^0(E_B + RC_B)}{a_{12}(RE_A^0 - C_A^0)} \quad (11)$$

Clearly, given R, a_{12} could be adjusted so that E_A' and E_B' correspond as closely as possible to the known values of σ and ρ.

The experimental values[8] of ρ for $(C_2H_5)_3N$, C_5H_5N, $CH_3CON(CH_3)_2$, $(CH_2)_4S$, and $(C_2H_5)_2S$ are 2.73, 2.01, 1.58, 1.84, and 1.84, respectively. One might expect that ρ is related to basicity, the larger ρ corresponding to the stronger base. Since the enthalpies of adduct formation of these bases with phenol are 9.1, 8.0, 6.8, 4.9, and 4.6 kcal/mol, respectively, the ρ values for this series do not parallel basicity. By considering our four-parameter equation instead of a two-parameter one, the cause of this apparent discrepancy becomes clear. The E_A values for the phenols are very large and, consequently, the large E_B values for the oxygen and nitrogen donors and the small values for sulfur donors determine the order for $-\Delta H$. However, the differences in the E_A values for the substituted phenols are very slight, $\sim 7\%$. The differences in the C_A values are larger, $\sim 30\%$. Consequently, a donor with a large C_B value will emphasize the differences in substituent even though the total $-\Delta H$ may be less. The ρ value measures the sensitivity of the interaction to substituent change and not the basicity, *i.e.*, $\rho = k(E_B + RC_B)$ from eq 11 once a standard acid is selected.

$$(\partial\rho/\partial E_B)_{C_B} = k \text{ while } \partial\rho/\partial C_B = kR$$

Finally, we recall that $\Delta\Delta H = \sigma\rho = E_A'E_B'$. Substituting (10) and (11) for E_A' and E_B' into this expression for $\Delta\Delta H$ yields

$$\Delta\Delta H = \frac{(C_AE_A^0 - C_A^0E_A)(E_B + RC_B)}{RE_A^0 - C_A^0}$$

In view of the large uncertainty in R, it seems likely that we could recompute all of the E and C parameters with the additional requirement that R be constant for all of the substituted phenols without greatly affecting the parameters or the calculated heats.

If a series of bases obeys a Hammett type of treatment toward a constant acid, the above discussion is applicable to this problem also. Now the transformed base parameter E_B' is related to the substituent constant σ and E_A' is related to ρ. The appropriate transformation equations result by simply interchanging the subscripts B and A in all of the above equations. It should also be mentioned that the constancy of $-R$, the requirement for a Hammett-type equation, is a different requirement than the constancy of the C/E ratio for a one-parameter equation. A limited set of data can obey a one-parameter equation and not be amenable to a Hammett type of approach. For example, the parameters of all of the alcohols (aliphatic and aromatic) undergoing a hydrogen-bonding interaction have a fairly constant C/E ratio and give fair agreement with a one-parameter treatment.

Interpretation of the E and C Parameters. As mentioned above, iodine was chosen as the reference acid and assigned parameters $E_A = 1.00$ and $C_A = 1.00$. Consequently, the absolute values of the E and C parameters in Tables I and II are meaningless, but the relative values and trends in a set of E parameters or in the set of C parameters are significant. It should be remembered that the parameters in Tables I and II are not known with equal confidence. The ability of acid parameters to predict accurate enthalpies of interaction when used with accurate base parameters depends upon the number of enthalpies for that acid which were included in the correlation and upon the range of C/E ratios for the bases involved in those interactions. This, of course, also applies to base parameters used with accurate acid parameters. For example, iodine, trimethylaluminum, and phenol have been studied with a large number of bases including bases with very different C/E ratios. Enthalpies predicted using the parameters for these acids should then be very accurate, as long as the base parameters are also well known. Di-*n*-butyl ether is an example of a base for which only enthalpies with hydrogen-bonding acids (with similar C/E ratios) have been measured. Hence, it should be possible to predict good di-*n*-butyl ether enthalpies with other hydrogen-bonding acids. In an attempt to improve our estimate of results with "soft" acids, we have assumed that the di-*n*-butyl ether and diethyl ether enthalpies with iodine are the same within experimental error. The dimethyl and diethyl sulfide enthalpies with iodine were also assumed to be the same.

Our interpretation of these parameters in terms of covalent and electrostatic bond forming tendencies is not proven and can be justified only in terms of our intuitive feelings for these quantities. For example, it is known from classical organic chemistry that substitution of an alkyl group for a hydrogen on a donor atom increases the nucleophilicity of the donor atom. This behavior is manifested in the C parameter for the alkylamines upon successive substitution of alkyl groups on ammonia. As pointed out above and graphically shown in Figure 1, one major success of eq 1 is its ability to correlate donor–acceptor systems where reversals in donor strength are observed, *e.g.*, sulfur and oxygen donors toward phenol and iodine. The magnitudes of the E and C parameters are in accord with our qualitative ideas about these systems.

At present, the correlation contains one transition metal complex, $Cu(HFAcAc)_2$. The results on this complex are very interesting and somewhat unusual for a transition metal in that enthalpies have been obtained in a poorly solvating solvent with nonionic donors,[25] in contrast to the typical stability constant study on a metal cation in some highly polar solvent. It is of considerable interest that a transition metal ion complex can be incorporated into the E and C scheme using the same base parameters that are used to correlate the enthalpies of formation of hydrogen-bonding and charge-transfer adducts.

The E and C correlation contains molecules which undergo drastic changes in their geometry upon adduct formation. Acids like $(CH_3)_3SnCl$, BF_3, and $Al(CH_3)_3$ undergo extensive rearrangement from their structure as free acids when they form adducts. The fact that acids such as these fit into the E and C correlation illustrates the complexity of our E and C numbers. Many effects including the recently reported concept of unit acidity[26] must be evaluated before these numbers are completely understood.

Finally, it should be noted that the E and C parameters for a particular acid or base do not contain information concerning intermolecular steric effects, since these steric effects are a property of the geometry of the adduct and not a property of the individual acid or base. Molecules such as $(CH_3)_3SnCl$, $B(CH_3)_3$, $Al(CH_3)_3$, and $Cu(HFAcAc)_2$ may encounter steric repulsive interaction with certain bases, and the discrepancy between calculated and observed enthalpies gives a quantitative estimate of the magnitude of this effect. Excellent agreement between experimental enthalpies of adduct formation and the calculated ones in Table III for these Lewis acids indicates that steric effects, as manifested through the enthalpy, are minimized with the donors selected for incorporation into this table. However, with donors such as $(C_2H_5)_3N$ and $(C_2H_5)_2O$, which were omitted from the correlation for these acids, it has been suggested that steric effects are present.[2,13,25,27] Table V contains enthalpies calculated using eq 1 which are larger than the experimentally measured enthalpies; the difference is attributed to steric hindrance. In the case of $(CH_3)_3SnCl$ adducts, one would expect the steric interaction to be greater for $(C_2H_5)_2O$ than for $(CH_2)_4O$ from examination of Shulman molecular models.[13] Accordingly, the $(CH_2)_4O$ adduct gives closer agreement between $\Delta H_{\mathrm{calcd}}$ and $\Delta H_{\mathrm{measd}}$.

Table V

Acid	Base	$-\Delta H_{\mathrm{calcd}}$	$-\Delta H_{\mathrm{measd}}$
$B(CH_3)_3$	$(CH_3)_3N$	24.6	17.6
$(CH_3)_3SnCl$	$(C_2H_5)_2O$	5.6	2.2
$(CH_3)_3SnCl$	$(CH_2)_4O$	5.8	5.1
$Al(CH_3)_3$	$(C_2H_5)_3N$	32.7	26.5
$B(CH_3)$	$N(CH_2CH_2)_3CH$	26.7	19.9
$BF_3(g)$	$(C_2H_5)_2O$	14.8	12.4

The Hard–Soft Acid–Base (HSAB) Model. In our original work, we used an ionic–covalent model to interpret the E and C parameters. It has been suggested that our studies can be correlated with the hard–soft model.[4] "Softness" (or "hardness") can be considered[28] as a measure of the *ratio* of the tendency of a species to undergo covalent interaction to the tendency of a species to undergo electrostatic interaction. The relative softness or hardness is depicted in the C/E ratio.[28] It should be emphasized that if our ratio has this meaning, it is because of the model we originally imposed on the solution to the E and C equation.[2] The ratios for the acids and bases can be cal-

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[25] W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).

[26] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

[27] H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

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culated from the data in Tables I and II. If the ratio C/E is comparatively large, the acid or base would be classified as type B, or soft. Conversely, if the ratio is comparatively small, the species is classified as type A, or hard.[28] Inasmuch as the relative ratios of C/E tell the relative importance of the two effects for various donors and acceptors, we agree that the hardness or softness discussed in the HSAB model is given by this ratio.

A qualitative classification of hardness and softness has been presented.[4] This classification divides the Lewis acids in Table I as follows: soft I_2, IBr, etc.; borderline $B(CH_3)_3$, SO_2, $Cu(HFAcAc)_2$; hard H-bonding acids, $Al(CH_3)_3$, $Ga(CH_3)_3$, BF_3, $(CH_3)_3SnCl$. The ratio C/E gives a quantitative order of relative hardness or softness for the various Lewis acids and agrees fairly well with the classification of Pearson.[4] The acids which do not follow the qualitative classification are BF_3 and SO_2. As mentioned above, the parameters for BF_3 were determined from data limited to oxygen donors. The qualitative placing of SO_2 is incorrect and, as will be shown shortly, when strong interactions are compared with weak ones, *the procedures used by Pearson to determine hardness and softness do not give the same result as the C/E ratio because the magnitudes of the C and E numbers which are important in determining the magnitude of an enthalpy are lost in the ratio; i.e.*, a large C divided by a large E can give the same ratio as a small C divided by small E.

The C/E ratios for I_2, IBr, and ICl are 1.0, 0.65, and 0.16, respectively, which is the ordering one would expect from considering ground-state dipole moments and electronegativities. According to the ratio, ICl is as hard as the alcohols which have ratios around 0.1, ranging from the softest, thiophenol, with $C/E = 0.20$, to the hardest, $(CF_3)_2CHOH$, with $C/E = 0.09$.

Table II contains the E and C constants for the donors presently in the correlation. Calculation of the C/E ratio from data in Table II indicates, as it does for the acids in Table I, that a large variety of *different types* of species are present. According to the soft and hard classification, the donors are categorized as follows:[4] soft R_2S, R_3P, benzene; borderline C_5H_5N; hard R_2O, RNH_2, NH_3. This is, in effect, a one-dimensional ranking of bases that goes from soft to borderline to hard. Recalling that the larger the C/E ratio, the softer the species, these qualitative observations agree with the ratios. However, the benzene ratio does not fit into the type B or soft classification, but rather into the type A, or hard, classification. Again, comparing this weak interaction with stronger ones, as in the case of SO_2, leads to an error when the procedures employed by Pearson are employed for a hard–soft ranking. Recently, it has been concluded that classical electrostatic forces make significant contributions to the stability of donor–acceptor complexes and perhaps are of predominant importance for the weak complexes.[29] Since benzene and its methyl derivatives are sacrificial donors,[31] they usually form weak complexes. The E and C parameters of benzene reflect this behavior, but the qualitative HSAB ranking of benzene does not.

In conclusion, the C/E ratios for donors (acids) indicate whether hardness or softness is most important in interactions of a particular donor (acid), but softness or hardness so defined does not enable one to predict even the relative strength of interaction toward a soft or hard acid (base) because, as will be seen below, the magnitudes of the C and E numbers are lost.

Next, we shall describe why the magnitudes of the E and C numbers are not just quantitative manifestations of the HSAB concept, but give insight into intermolecular interactions which are absent in the qualitative soft–soft and hard–hard labeling of interactions. As can be seen from the data in Tables I and II, each acid and base has both a C and an E number which could be thought to correspond to possessing properties of softness and hardness. If this were the case, ammonia, which Pearson labels hard, has a larger C_B value than benzene, which is labeled soft, while dimethylamine which is soft (or borderline) has a larger E_B number than acetonitrile, which is labeled hard. Therefore, toward any hard acid, the soft base $(CH_3)_2NH$ will appear harder than one of the hardest bases in the correlation, CH_3CN. In other words, $(CH_3)_2NH$ is both harder and softer than CH_3CN, leading to the prediction that $(CH_3)_2NH$ will form stronger adducts with both hard and soft acids. Similarly, because of the magnitude of C, the borderline acid, $Cu(HFAcAc)_2$, will always be softer than the soft acid, I_2, when ordered by a soft base. In the original HSAB article, the importance of strength of interaction was recognized as the cause of not getting a complete reversal in donor order when a hard and a soft acid are compared. However, in subsequent HSAB applications in both this and other articles, most authors invariably ignore strength. In the HSAB treatment, one does not find the same substance being ranked as both soft and hard, but instead an ordering that goes from hard to intermediate to soft. Clearly, even though $Al(CH_3)_3$ is hard, its C number is greater than that for I_2, and it should interact more strongly with soft bases than I_2. Whenever weak bases are compared with strong bases (or acids) toward a soft acid (or base), the weak base (or acid) may appear to be not as soft as the strong base even if the weak base is actually softer as manifested in the C/E ratio. Furthermore, since no attempt is made in the HSAB model to factor out the hardness contribtion toward a soft reference acid (*e.g.*, CH_3Hg^+), orders of softness will vary when the reference soft acid is changed if the hard contributions are not identical for both acids. For example, if we consider the interaction of $(C_2H_5)_3N$, $(C_2H_5)_2O$, and $(C_2H_5)_2S$ toward the soft acid, I_2, the softness order would be $(C_2H_5)_3N > (C_2H_5)_2S > (C_2H_5)_2O$. Considering all the interactions and factoring the hard and soft contributions, the C/E ratio gives the order $(C_2H_5)_2S > (C_2H_5)_3N > (C_2H_5)_2O$. The hardness order deduced from interactions with the hard acid phenol is $(C_2H_5)_3N > (C_2H_5)_2O > (C_2H_5)_2S$, which is not the reverse of either soft order. Thus, a perfect order of softness (*i.e.*, one related to the intensity of softness) cannot be obtained from a qualitative examination of the enthalpies unless the E term for the reference soft acid is zero. It should be emphasized that our approach and the HSAB approach are very different because we attempt to factor the total interaction into the electrostatic (hardness) and covalent (softness) components which must accompany nearly all intermolecular

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(29) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New Yok, N. Y., 1969.

interactions. The HSAB approach makes no attempt to factor a given interaction into the two components and assign a magnitude to them. Consequently, the hard–soft description is found to be conceptually incomplete because the magnitude of hardness and softness as manifested by the magnitude of E and C is not taken into account, giving rise to all of the above-described difficulties even in a qualitative application. A substance whose interaction energy comes mainly from the soft–soft term would be labeled soft in the HSAB concept. However, if the intensity of the softness were low, a basically hard material with a significant C term would interact more strongly, in violation of the HSAB rule that "hard prefers hard and soft prefers soft." The absence of listings of the same substances as being both very hard and very soft indicates that this idea is missing from the HSAB concept.[30] The names themselves imply that this is missing because, by definition, if something gets less hard, it gets more soft. If hardness were given by H_A, then softness might be given by $1/H_A$. Consequently, we recommend abandoning the the hard–soft nomenclature because the words imply a two-parameter, two-term approach to acid–base chemistry, *i.e.*

$$-\Delta H = H_AH_B + k[(1H_A)(1H_B)]$$

Subsequent to our publication of the E and C equation, Pearson reported[4] the equation

$$\log K = S_AS_B + \sigma_A\sigma_B$$

which he applied to equilibrium constant data in polar solvents. If solvation effects are constant and the entropy is proportional to the enthalpy, $\log K \sim -\Delta H$, and this would constitute an extension of our model[2] to a new body of data. If we replace log K by $-\Delta H$ and relabel S and σ, eq 1 results. It should be emphasized that this equation is basically our model and not the equation for the HSAB description. The equation in terms of log K was not generally applicable (*i.e.*, constants could not be determined) as we suspected when our program began, because solvation and entropy contributions in polar solvents introduce too many variables for the few parameters. Contrary to claims in the literature,[4] there is no straightforward general connection between log K and ΔH for wide variations in donors and acceptors, as a plot of enthalpy data in Table III and equilibrium constants in the literature will show. Linear relations do exist when the systems treated are limited to a particular set of either acids or bases.

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Appendix

The conventional approach to a nonlinear least-squares problem is to "linearize" the equations by assuming that the current values of the parameters are approximately correct and that the calculated function ($\Delta H_{i\text{calcd}}$ changes linearly with changes in the parameters. Thus, we have

$$\Delta(-\Delta H_{i\text{calcd}}) = E_{\text{A}i}\Delta E_{\text{B}i} + E_{\text{B}i}\Delta E_{\text{A}i} + C_{\text{A}i}\Delta C_{\text{B}i} + C_{\text{B}i}\Delta C_{\text{A}i} \quad (12)$$

(Note that this is valid only if the Δ's are small.) There is one such equation for each experimental heat and there are two parameters for each acid and base, except that four parameters are considered fixed (iodine E and C, DMA E_B, and diethyl sulfide C_B).

Linear least-squares procedures lead to eq 3 for the calculation of the Δ's. When the process has been repeated until the Δ's are zero, the errors in the parameters are given by **Mx**, the variance–covariance matrix for the parameters, which is computed[16] as $\sigma^2 \cdot (\mathbf{A}^T\mathbf{PA})^{-1}$. **A** and **P** are the same as in eq 2 and σ^2 can be estimated as $(\mathbf{F}^T\mathbf{PF})/(n - m)$, where **F** is again the vector of residuals, n is the number of experimental enthalpies, and m is the number of parameters (twice the number of acids and bases minus four). The variance–covariance matrix has as its diagonal elements the variances of the parameters, $(\sigma_i)^2$, that is, the squares of the (marginal) standard deviations. The off-diagonal elements are the covariances of pairs of parameters and can be written $\sigma_i\sigma_j\rho_{ij}$, where σ_i and σ_j are standard deviations of parameters i and j and ρ_{ij} is called the correlation coefficient and can be calculated since the σ's are known from the diagonal elements. For the E and C parameters, many of the ρ's are close to -1 or 1, indicating very high correlations among the parameter errors. To compute the conditional standard deviations, we assume that all of the parameters except one have exactly their true values, so that we have only one variable and the matrix $(\mathbf{A}^T\mathbf{PA})$ is reduced to a single element. The variance of the parameter is then simply σ^2 divided by that element and the standard deviation is just the square root of the variance.

To calculate the variances for calculated ΔH's, eq 12 is squared and the Δ products are replaced by appropriate variances and covariances. Thus, $\sigma^2{}_{\Delta H_i\text{calcd}} = E^2{}_{\text{A}i}\sigma^2{}_{E\text{B}i} + E^2{}_{\text{B}i}\sigma^2{}_{E\text{A}i} + C^2{}_{\text{A}i}\sigma^2{}_{C\text{B}i} + C^2{}_{\text{B}i}\sigma^2{}_{C\text{A}i} + E_{\text{A}i}E_{\text{B}i}\sigma_{E\text{B}i}\sigma_{E\text{A}i}\rho_{E\text{A}E\text{B}i} + E_{\text{A}i}C_{\text{A}i}\sigma_{E\text{B}i}\sigma_{C\text{B}i}\rho_{E\text{B}C\text{B}i} + E_{\text{A}i}\cdot C_{\text{B}i}\sigma_{E\text{B}i}\sigma_{C\text{B}i}\rho_{E\text{B}C\text{B}i} + E_{\text{B}i}C_{\text{A}i}\sigma_{E\text{A}i}\sigma_{C\text{B}i}\rho_{E\text{A}C\text{B}i} + E_{\text{B}i}C_{\text{B}i}\cdot \sigma_{E\text{A}i}\sigma_{C\text{A}i}\rho_{E\text{A}C\text{A}i} + C_{\text{A}i}C_{\text{B}i}\sigma_{C\text{B}i}\sigma_{C\text{A}i}\rho_{C\text{B}C\text{A}i}$. The standard deviation is, as usual, just the square root of the variance. The ρ's used here are usually close to -1, so the estimated standard deviations for the calculated heats are very much smaller than one would expect from the marginal standard deviations of the parameters.

It should be remembered that this treatment assumes that eq 12 is valid. This is true only for small deviations from the true parameters, so a large standard deviation must also be a very inaccurate standard deviation; although we know, in that case, that the parameter in question is bad, we don't know exactly how bad.

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(30) In mathematical terms, the C/E ratio gives the angle the acid or base vector makes with the E axis, but carries no information about the length of the vector which is needed to give $-\Delta H$.