Inorg. Chem. **1993,** *32,* 2473–2479

Addition of New Donors to the *E* and *C* Model

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Received October 1, 1992

The enthalpies of adduct formation of donors with BF_3 measured in CH_2Cl_2 and the free energies of proton transfer from ammonia to nonprotonic, second-row donors in aqueous solution are found to correlate with the *E* and *C* equation. Conditions for fitting data, which are not solvation minimized, to the *E* and *C* model are described, and a complete analysis of the solution contribution to the BF_3 enthalpies is presented. These new acceptor systems and a series of recently reported spectral probes lead to the addition of over 40 new donors to the *E* and *C* data base. The new parameters and a complete listing of the recommended transformed set of parameters are offered here for the first time, providing a complete data base of all known parameters for the *E* and *C* model. New donors are readily added to the correlation by using enthalpies and the probes described in this article. The extension of the *E* and *C* model to these new donors and acceptors facilitates its use as a scale of donor and acceptor strengths in the dual parameter analysis of physicochemical data.

Introduction

In an earlier article,[1] it was shown that a variety of spectral probes could be correlated with the *E* and *C* model.[2] These probes are referred to as spectral acceptors or spectral donors. Such correlations establish the *E* and *C* parameters as a scale for interpreting physicochemical measurements. A successful correlation of a spectral change shows that the dominant contribution made to the spectral shifts arises from the strengths of the σ donor–acceptor interactions and gives an indication of the relative importance of covalent, *C*, and electrostatic, *E*, influences on the shift. Of equal importance is the use of these correlations to add new donors and acceptors into the model. A new donor is added to the *E* and *C* database by measuring the solvation-minimized enthalpies of interaction, $-\Delta H$, of this donor with several of the acids in the database (i.e. acids whose E_A and C_A are known). A series of simultaneous equations of the form

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

are written and solved for the unknowns E_B, C_B, and *W*. *W*, a constant energy contribution, is usually zero for donors. In order to obtain accurate E_B and C_B parameters, it is essential to determine enthalpies for acceptors whose C_A/E_A range is large.[2a]

Equation 2 provides the basis for using the E_B and C_B parameters

$$\Delta\chi = E_A{}^*E_B + C_A{}^*C_B + W^* \qquad (2)$$

as a reference scale of donor strength for the analysis of physicochemical properties. In eq 2, $E_A{}^*$, $C_A{}^*$, and W^* are spectral acceptor parameters with units necessary to give $\Delta\chi$ in the units measured. The E_B and C_B values are the reported, enthalpy-based parameters for the donors. All $\Delta\chi$ values should be expressed in an energy or related (e.g. cm^{-1}) unit. Spectral data involving spectral shifts, $\Delta\chi$, that can be correlated with eq 2 establish this probe as a spectral acceptor. Shifts for the spectral acceptor can be used in conjunction with the enthalpies of adduct formation for various acceptors (eq 1) to determine E_B and C_B for new donors. It is essential for determining accurate E_B and C_B parameters that the spectral probes used provide a good range in the ratios of $C_A{}^*/E_A{}^*$ (e.g. from 0.2 to 3).

In this article the type of acceptors that can be used in eq 2 is extended to enthalpies of complexation of BF_3 in CH_2Cl_2[3] and free energies of proton transfer from ammonia to a series of bases in aqueous solution.[4] Over 40 new donors can be added to the *E* and *C* database by using these new thermodynamic correlations, the spectral acceptors,[1] and enthalpy data with acceptors whose E_A and C_A parameters were published previously.[2]

Results and Discussion

Addition of New Types of Measurements, $\Delta\chi$, into the *E* and *C* Model. 1. BF_3/CH_2Cl_2 Probe. Enthalpies measured in methylene chloride that correspond to eq 3 can be corrected[5] to solvation-minimized enthalpies by adding the measured enthalpy for the interaction of the donor with the CH_2Cl_2 acceptor (eq 4).

$$B\text{- - -}HCHCl_2 + A \rightarrow AB + CH_2Cl_2 \qquad -\Delta H_{meas} \qquad (3)$$

$$B + HCHCl_2 \rightarrow B\text{- - -}HCHCl_2 \qquad -\Delta H_{CH_2Cl_2} \qquad (4)$$

$$\text{net:} \qquad B + A \rightarrow AB \qquad -\Delta H_{cor} \qquad (5)$$

In this discussion, specific solvation (i.e. hydrogen bonding) will be indicated by - - -$HCHCl_2$. Substituting E_A and C_A values[5] of 0.86 and 0.11, respectively, in eq 1 along with reported E_B and C_B values produces the correction for the enthalpy of hydrogen bonding of CH_2Cl_2 to a donor, eq 4. Research establishing E_A and C_A for CH_2Cl_2 indicates[5] that nonspecific solvation makes a negligible contribution to enthalpies of adduct formation

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[1] Drago, R. S.; Vogel, G. C. *J. Am. Chem. Soc.* **1992,** *114,* 9527. See this reference for the meaning and interpretation of $\bar{x}$ (called Δ), percentage fit, and the C_B/E_B range.

[2] (a) Drago, R. S. *Coord. Chem. Rev.* **1980,** *33,* 251–277. (b) Drago, R. S.; Wong, N.; Bilgrien, C.; Vogel, G. C. *Inorg. Chem.* **1987,** *26,* 9–14. (c) For most recent set of *E* and *C* parameters the values in ref 2b should be transformed as described in: Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.* **1990,** *112,* 8953.

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[5] (a) Nozari, M. S.; Jensen, C. D.; Drago, R. S. *J. Am. Chem. Soc.* **1973,** *95,* 3162. (b) Drago, R. S.; Nusz, J. A.; Courtright, R. C. *J. Am. Chem. Soc.* **1974,** *96,* 2802.

0020-1669/93/1332-2473$04.00/0

Table I. BF_3 Adduct Enthalpies in CH_2Cl_2[a]

donor	$-\Delta H_{meas}$[b]	$-\Delta H^{calc}{}_{UC}$[c]	$-\Delta H_{cor}$	$-\Delta H^{calc}{}_{cor}$[d]
$[(CH_3)_2N]_3PO$	28.0	30.1	30.6	32.6
$CH_3C(O)OC_2H_5$	18.1	17.6	19.7	19.1
$(CH_3)_2CO$	18.2	19.8	19.8	21.4
$CH_3C(O)N(CH_3)_2$	26.8	25.0	28.9	27.2
$HC(O)N(CH_3)_2$	26.4	23.7	28.4	25.7
$(CH_3)_2SO$	25.2	26.1	27.5	28.4
$CH_3C(O)OCH_3$	17.5	17.5	19.1	19.1
$O(CH_2CH_2)_2O$	17.7	(20.9)	18.5	(22.7)
$(CH_2)_4O$	21.6	23.1	23.3	24.7
C_5H_5N	30.6	30.2	32.5	32.1
$4\text{-}CH_3C_5H_4N$	32.1	31.6	34.0	33.5
$(CH_3)_3N$	35.0	34.8	36.5	36.3

[a] Units are kcal mol^{-1}. [b] Reference 3. [c] Values of $-\Delta H_{meas}$ are fit producing $E_{A(UC)} = 8.16$; $C_{A(UC)} = 4.44$ with $W = 0$. The % fit is 6.4, $\bar{x}$ is 1.1 kcal mol^{-1}, and C_B/E_B range is 0.56–4.6. The E_B and C_B values previously reported[2c] are employed. [d] Calculated with $E_{A(cor)} = 9.05$, $C_{A(cor)} = 4.52$, and $W = 0$. The % fit is 6.4, $\bar{x}$ is 1.1 kcal mol^{-1}, and the C_B/E_B range is 0.56–4.6. The values in parentheses were omitted from the fit and calculated with the resulting parameter.

measured in this solvent. Accordingly, as long as the donor is fully complexed by CH_2Cl_2, eq 5 is a solvation-minimized enthalpy.

Solvation-minimized enthalpies in CH_2Cl_2, represented by eq 5, result only if the adduct formed does not possess donor groups, X, to which methylene chloride can hydrogen bond. For example, if the measured enthalpy corresponds to eq 6, where A of eq 3

$$MX\text{- -}HCHCl_2 + B\text{- - -}HCHCl_2 \rightarrow B\text{–}M\text{–}X\text{- -}HCHCl_2 + CH_2Cl_2 \quad (6)$$

is replaced by MX, the correction given by eq 4 will not produce solvation-minimized results. Adding eq 6 to eq 4 produces eq 7.

$$B + MX\text{- -}HCHCl_2 \rightarrow BMX\text{- -}HCHCl_2 \qquad \Delta H_{cor} \quad (7)$$

If CH_2Cl_2 hydrogen bonds stronger to B–M–X than to M–X, the measured enthalpy will consist of the solvation-minimized enthalpy plus a net exothermic contribution resulting from solvent hydrogen bonding to the adduct, BMX, minus the hydrogen bonding to the acceptor, MX.

Measured enthalpies[3] of BF_3 adduct formation in CH_2Cl_2 (Table I) are corrected for the donor CH_2Cl_2 interaction and given in Table I as ΔH_{cor}. When the $-\Delta H_{cor}$ values are used in an ECW fit, the values $E_{A(cor)} = 9.05$ and $C_{A(cor)} = 4.52$ are obtained. The data fit is shown under $-\Delta H_{cor}{}^{calc}$. The $C_{A(cor)}/E_{A(cor)}$ ratio is 0.48, $\bar{x}$ is 1.1 kcal mol^{-1}, the percentage fit is 6.4, and the range of C_B/E_B for the donors studied is good.[1]

When the enthalpies corrected for the donor CH_2Cl_2 interaction are compared to those that have been measured in the gas phase (−16.8 kcal mol^{-1} for $(CH_2)_4O$ and −13.0 kcal mol^{-1} for $CH_3C(O)OC_2H_5$), the values measured in CH_2Cl_2 are seen to be more exothermic. This is attributed to specific hydrogen bonding of CH_2Cl_2 to the fluorines of BF_3 in the adducts. Thus, ΔH_{meas} corresponds to a system described by eq 6 with ~7 kcal mol^{-1} of the interaction arising from the stronger hydrogen bonding of CH_2Cl_2 to the adduct than to BF_3. The "corrected" enthalpy values, ΔH_{cor}, of Table I correspond to eq 7 and are not solvation-minimized values.

The fit of the $-\Delta H_{cor}$ data of Table I, which is not solvation minimized, to the E and C model will result only if the enthalpy of hydrogen bonding is proportional to the enthalpy of adduct formation of AB or to either the E_AE_B or C_AC_B contributions.[6] This proposal receives support from X-ray studies of BF_3 adducts that show the bond lengthens and the B–F angles approach tetrahedral as the donor becomes stronger.[7]

Table II. $-\Delta G(BH^+{}_{aq})$[a] Values

donor	$-\Delta G$-(exptl)	$-\Delta G$-(calc)[b]	donor	$-\Delta G$-(exptl)	$-\Delta G$-(calc)[b]
$CH_3C(O)OCH_3$	−18.0	−18.3	$(C_2H_5)_2O$	−15.9	−14.9
$CH_3C(O)OC_2H_5$	−17.3	−18.2	$(CH_2)_4O$	−15.8	(−13.0)
$CH_3C(O)CH_3$	−16.5	−16.7	$O(CH_2CH_2)_2O$	−17.3	−16.2
$CH_3C(O)N(CH_3)_2$	−13.2	−14.7	C_5H_5N	−5.5	−6.7
$(CH_3)_2SO$	−14.7	−13.9	$4\text{-}CH_3C_5H_4N$	−4.4	−5.2
$(CH_2)_4SO$	−14.4	−13.0	$(C_2H_5)_3N$	2.0	1.3
$(CH_3)_3N$	0.750	0.5	quinuclidine	2.6	1.5
$(CH_3)_2S$	22.1	−(10.3)	$(CH_3)_2NH$	−2.1	−(3.8)
CH_3NH_2	1.9	−(7.5)	$(CH_3)_3P$	0.80	(−8.1)

[a] ΔG in kcal mol^{-1} for the aqueous solution reaction $B + NH_4{}^+ \rightarrow BH^+ + NH_3$. Data from ref 4. [b] $E_A{}^G{}_{(UC)} = 2.88$, $C_A{}^G{}_{(UC)} = 4.29$, $W^G{}_{(UC)} = -27.06$. The % fit is 4, the $\bar{x}$ value is 0.9 kcal mol^{-1}, and the C_B/E_B range is 0.6–8.4. The values in parentheses were omitted from the fit and calculated with the resulting parameter.

The utilization of $-\Delta H_{cor}$ to incorporate new donors into the E and C model is complicated by the fact that the E_B and C_B values of a new donor are not known but they are needed to correct for the donor–methylene chloride interaction. However, the measured (uncorrected) enthalpy of reaction in CH_2Cl_2, eq 6, is given by eq 7 minus eq 4. Since eq 7 fits E and C as does eq 4, the difference of these two enthalpies, which is $-\Delta H_{meas}$ (eq 6) must also fit E and C.

$$-\Delta H_{cor} = E_{A(cor)}E_B + C_{A(cor)}C_B$$

$$-(-\Delta H(\text{eq } 4) = 0.86E_B + 0.11C_B)$$

$$\text{net:} \qquad -\Delta H_{meas} = (E_{A(cor)} - 0.86)E_B + (C_{A(cor)} - 0.11)C_Bd$$

Defining $E_{A(UC)} = (E_{A(cor)} - 0.86)$ and $C_{A(UC)} = (C_{A(cor)} - 0.11)$ leads to

$$-\Delta H_{meas} = E_{A(UC)}E_B + C_{A(UC)}C_B \qquad (8)$$

The data fit of $-\Delta H_{meas}$ to eq 8 is shown as column $-\Delta H^{calc}{}_{UC}$ in Table I. The $E_{A(UC)}$ (8.16) and $C_{A(UC)}$ (4.44) parameters given in Table I are essentially equal to $(E_{A(cor)} - 0.86)$ and $(C_{A(cor)} - 0.11)$, respectively. This derivation is important for it shows that $-\Delta H_{meas}$ values for an acceptor measured in interacting solvents can be fit to *ECW* if the solvation energy of the products and/or reactants is proportional to base strength. For our present objective, we have shown that uncorrected BF_3 adduct formation enthalpies measured in CH_2Cl_2 can be used to calculate E_B and C_B for new donors.

2. $-\Delta G$ Proton Transfer in Water. In the previous example, a detailed analysis provided information about the various enthalpy contributions to the reaction in the acceptor solvent. Another

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(6) We can illustrate this for the proportionality with $-\Delta H$, and the E_AE_B or C_AC_B term can be left out if the adduct hydrogen bond contribution parallels only one of these. If the hydrogen bond enthalpy contribution from the specific interaction of CH_2Cl_2 with the coordinated fluorine of the BF_3 adduct is proportional to the E_B and C_B properties of the base bonding to BF_3, the E_B value for the fluorine in the adduct can be written as kE_B and the C_B of the fluorine as $k'C_B$. The base-corrected enthalpies, eq 7, can be expressed as

$$-\Delta H_{cor} = E_AE_B + C_AC_B + 0.86kE_B + 0.11k'C_B = [E_A + 0.86k]E_B + [C_A + 0.11k']C_B = E_{A(cor)}E_B + C_{A(cor)}C_B \quad (A)$$

The enthalpy for eq 7, $-\Delta H_{cor}$, is the measured enthalpy corrected for hydrogen bonding *to the donor*. The $E_AE_B + C_AC_B$ term gives the E and C solvation-minimized BF_3-donor enthalpy of adduction formation, $-\Delta H$. The kE_B and $k'C_B$ terms add the enthalpy of interaction of CH_2Cl_2 hydrogen bonding to the fluorine in the BF_3 adduct assuming that the fluoride basicity in the adduct increases in proportion to the strength of adduct formation. Equation A shows that data can be fit to the E, C, W equation when donor groups in an adduct bond to CH_2Cl_2 in direct proportion to the adduct bond strength. The proportional bonding to the fluoride in the adduct ($0.86k$ and $0.11k'$) is incorporated into the $E_{A(cor)}$ and $C_{A(cor)}$ parameters (eq A) from the data fit; i.e. $E_{A(cor)} = E_A + 0.86k$ and $C_{A(cor)} = C_A + 0.11k'$, where E_A and C_A are the solvent-minimized parameters. Though the data can be fit in eq 1 for this situation, the resulting parameters, $E_{A(cor)}$ and $C_{A(cor)}$, sum two interactions and do not correspond to solvent-minimized enthalpies.

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Table III. Probe Data

Spectral Probes[a]

spectral shift	E_A^*	C_A^*	W^*	C_A^*/E_A^*	$\bar{x}$[a]	n[b]	C_B/E_B range	comments[f]
$\Delta\nu_{OH}(C_6H_5OH)$[c,f]	167.0	108.8	−205	0.65	5[c]	1.2 (2.5)	0.2–16	SD
$\Delta\nu_{OH}(4FC_6H_4OH)$[c]	193	106	−250	0.55	7[c]	1.4 (3)	0.2–16	SD
$\Delta\nu_{OH}(CH_3OH)$[c]	104	69.4	−152	0.67	3[c]	0.95	0.2–16	AD
$\Delta\nu((CH_3)_3COH)$	89.9	55.0	−124	0.61	3[c]	0.95	0.4–2	AD
$\Delta\nu_{IC}(ICN)$[c]	4.4	14.6	−2.0	3.3	3[c]	0.95	0.4–16	HD, ET
$\Delta\nu_{IC}(I_2C_2)$[c]	4.59	6.05	−8.2	1.3	1.3[c]	0.62	0.7–16	AD
$\Delta\nu(I_2)$	1080	1098	−1252	1.0	7[d]	5	0.6–2	AD
$\Delta\Delta\nu(4\text{-}NO_2C_6H_4NH_2)$[d]	−1.06	−0.211	4.23	0.20	0.03[d]	0.2	0.4–4	WD, PD
$\Delta\Delta\nu(4\text{-}NO_2C_6H_5OH)$[d]	−0.683	−0.140	1.14	0.20	0.03[d]	0.2	0.4–2	PD

Enthalpy Probes

$-\Delta H$	$E_{A(UC)}$	$C_{A(UC)}$	$W_{(UC)}$	$C_{A(UC)}/E_{A(UC)}$	$\bar{x}$[a]	n[b]	C_B/E_B range	comments[f]
$-\Delta H_{(UC)}(BF_3/CH_2Cl_2)$[e]	7.23	4.93	0	0.68	0.8[e]	0.5	0.56–4.6	WD, SP
$-\Delta H((CH_3)_3COH)$	1.07 (E_A)	0.692 (C_A)	0 (W)	0.65		0.5	0.2–2.0	

Free Energy Probe

$-\Delta G$	$E_A{}^G{}_{(UC)}$	$C_A{}^G{}_{(UC)}$	$W^G{}_{(UC)}$	$C_A{}^G{}_{(UC)}/E_A{}^G{}_{(UC)}$	$\bar{x}$[a]	n[b]	C_B/E_B range	comments[f]
$-\Delta G(BH^+)$[e]	3.44	4.62	−28.68	1.3	0.9[e]	0.52	0.56–8.4	HD, 3D

[a] See ref 1. $\bar{x}$ is the average absolute difference between the calculated and experimental values. [b] The weight assigned to $-\Delta H(I_2)$ in the data is 10 corresponding to an n value of 0.1. The weight is given by $1/n$. The other probes are given weights corresponding to n values determined by $(\bar{x} \times 0.3)^{1/2}$. The $\bar{x}$ values are calculated using donors in the earlier[1] enthalpy parameter based fit. Any system whose n value is calculated to be less than 0.2 is assigned a value of 0.2. Because of the large numbers involved, $\Delta\nu(I_2)$, the iodine blue shift, is assigned an n-value of 4, and limitations on $\Delta\nu(I_2C_2)$ lead to an n assignment of 0.5. [c] Units: cm^{-1}. [d] Units: 10^3 cm^{-1}. $\Delta\nu$ is the 4-nitrophenol minus the 4-nitroanisole transition or the 4-nitroaniline minus the *N*,*N*-diethyl-4-nitroaniline transition. [e] Units: kcal mol^{-1}. [f] SM, solvation-minimized data must be used. Aliphatic amine, pyridine, and sulfur donors studied in CCl_4 solvent should have 1 kcal mol^{-1} added to the heat and the n increased to 0.4. AD, all donors can be used (spectral shift should be extrapolated to infinite dilution); SD, avoid strong donors ($\Delta\nu > 550$ cm^{-1}) (spectral shift should be extrapolated to infinite dilution; WD, avoid weak donors; PD, avoid π donors; SP, potential steric problems; HD, avoid protonic donors; 3D, avoid sulfur, selenium, and phosphorus donors; ET, avoid ethers.

approach to correlating data in polar, acceptor solvents involves using the measured property without trying to evaluate the individual donor–acceptor contributions. A good fit of the $-\Delta H$ or $-\Delta G$ for the more complex reaction suggests domination of the measured quantity by bond strength considerations. When data for complex reactions are analyzed, it is common to find that certain classes of compounds must be omitted because of complications in some of the contributing energy steps. If these complications can be identified and avoided, the data set has utility for the determination of *E* and *C* for new donors or acceptors in the valid classes. The complications provide interesting insights about chemical reactivity.

The analysis of the free energies of proton transfer between bases in aqueous solution illustrates analysis of a complex reaction. The fit of ΔG for the reaction in eq 9 is shown in Table II.

$$B_{aq} + NH_4{}^+{}_{aq} \rightarrow BH^+{}_{aq} + NH_{3\,aq} \qquad (9)$$

Essentially, we are starting with a large positive free energy of 27.06 kcal mol^{-1} for transferring the proton from NH_3 to "no base" (no base has E_B and $C_B = 0$) as the W^G value. When a base undergoes proton transfer with NH_3, the free energy is reduced from the "no base" value by the donor strength of the base employed. These data are poorly fit by E_B and C_B. The donors that deviate the most are protonic donors and molecules containing third-row (S or P) donor atoms. The difference in the enthalpy and entropy of solvation of B and BH^+ for these systems is not accommodated by $E^*C^*W^*$. When these donors are omitted from the correlation, a good fit results (Table II). $\bar{x}$ is 0.9 kcal/mol^{-1}, and the percentage fit is 4. A large variation exists in the C_B/E_B ratio of the donors studied. In view of the many energetic steps contributing to the displacement reaction in water, it is amazing that the enthalpies and entropies of solvation of so many of these donors are well behaved. The $E_A{}^G{}_{(UC)}$, $C_A{}^G{}_{(UC)}$, and $W^G{}_{(UC)}$ parameters can be used to calculate new E_B and C_B values for any second-row donor that does not contain protonic hydrogen(s) and has a C_B/E_B ratio that falls in the wide range of 0.6–8.4.

Enlarging the *E* and *C* Data Base. With the addition of these probes and the recently reported spectral probes[1] to the *E* and *C* database, experimental data are available to permit the addition of new donors to the model. The large number of new donors added in turn allow the probe parameters to be more accurately determined. Accordingly, the new data are fit to eqs 1 and 2 using a master fit in which the best set of new donor and spectral acceptor parameters are determined from the data. Established, enthalpy-based E_B and C_B parameters[2b] (Table V) are held fixed as are established E_A, C_A, E_A^*, and C_A^* parameters. Table III lists the spectral probes and probe limitations employed in data selection for the master fit. Except for phenol, these parameters have been redetermined by combining all the old data[1] and data for new donors in the master fit. The new donors added are shown in Table IV along with the data fit. The differences in the probe parameters given in the footnotes (Tables I and II) and those in Table III arise because data with more donors are available for the latter set. The experimental data for new donors and the properties calculated from the best fit E_B and C_B parameters for the new donors are given in Table IV using the format: experimental/calculated. Reported data that were omitted from the fit used to solve for E_B and C_B are indicated by placing parentheses around the calculated values.

As can be seen in Table IV, the new data are fit very well by the *E* and *C* model. The E_B and C_B values for the new donors added to the database by fitting the data in Table IV are added to the transformed values[2c] of previously reported donors[2b] in Table V. The largest cause of the differences between these and earlier parameters[2a] results from changing the reference values for I_2 to $E_A = 0.5$ and $C_A = 2.0$. The purpose of this change was

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Table IV. Spectral, Free Energy, and Enthalpy Data for Determining Tentative E_B and C_B Parameters with Data Presented as Experimental/Calculated

donor	$\Delta\nu_{OH}$ for PhOH,[a] [CH_3OH],[b] {4-F0OH}, ⟨t-C_4H_9OH⟩	$-\Delta H_{BF_3}$[c] for CH_2Cl_2 measd	$\Delta\nu_{CI}$ for [ICN],[d] {I_2C_2}[d]	$-\Delta H(I_2)$[e]	$-\Delta H$ (accep)[f]	$-\Delta G(BH^+_{aq})$[g]	$\Delta\nu$ for I_2,[d] {4-NO_2PhNH_2},[h] [4-NO_2PhOH][h]
$CO[N(CH_3)_2]_2$	340/344 (350/348)	26/24.2	[29.5/34.6] {12.0/12.6}	5.2/4.8		−12.5/−12.9	
$(C_2H_5O)_2CO$	145/147	17.0/15.4		2.5/2.5			
$C_6H_5C(O)CH_3$	210/208	17.8/18.1		3.2/3.2	4.7/5.2 (PhOH)	−18.5/−17.4	
$C_6H_5C(O)H$	180/180			2.8/2.8		−18.8/−18.4	
$(C_6H_5)_2CO$	192/188	15.0/17.1		2.1/2.1	4.5/5.1 (PhOH)	−19.4/−19.2	
$C_6H_5C(O)OCH_3$	[76/76]	14.2/15.8		2.2/2.2			
$CH_2(CH_{22}C(O)O$	190/191	18/17.4			4.9/4.9 (PhOH)		[−0.10/−0.13] {2.21/2.28}
$CH_2)_3C(O)NCH_3$	330/333 {339/340}	26.9/23.7			7.0/6.6 (4FPhOH)		{1.41/1.62} [−0.65/−0.56]
$C_6H_5C(O)OC_2H_5$	166/164	14.6/16.2		2.4/2.4			{2.40/2.26}
$CH_2ClC(O)OC_2H_5$	138/138			1.9/1.9			[−0.11/−0.11]
$HC(O)OC_2H_5$	[58/59]	17/14.7		2.1/2.1			
$CH_3CH_2C(O)CH_3$	209/209	18.2/18.2		3.3/3.3		−16.9/−17.2	(2.10/2.20)
$(CH_2)_4CO$	229/229	18.3/19.0	[19/19.9] {8/6.4}		5.8/5.5 (4-FPhOH)		{2.01/1.91}
$(CH_2)_5O$	290/286 [157/157]	20.4/21.6	[25.0/27.2]		6.1/6.1 (PhOH), 6.1/6.1 (4-FPhOH), 6.5/6.6 (3-CF_3PhOH), 15.4/16.4 (BF_3(g))	−15.7/−15.3	{2.08/1.78}
$(n\text{-}Bu)_2O$	[154/161]						{2.18/(1.88)} [−0.39/−0.39]
$[(CH_3)_2N]_3PO$	479/(436) {479/(436)}	28.1/28.1			*i*		
$(CH_3O)_3PO$	305/310 {323/322} [173/172]	20.2/22.5	[26.0/25.8]				
$(C_2H_5O)_3PO$	330/333 [189/186] {341/351}		[26/25.2]	3.2/3.5	6.7/6.9 (PhOH), 6.5/6.9 (4-FPhOH)		{1.30/1.35} [−0.71/−0.73]
$(C_6H_5)_3PO$	415/410 {422/428}		[34/34.0] {14.5/13.8}	4.5/5.2	7.4/7.7 (4-FPhOH), 8.1/8.6[m]		
$(CH_3)_3PO$	464/462 {480/482}		[39/39.6]		7.7/8.2 (4-FPhOH)		
$(C_2H_5)_3PO$	468/468		[41/37.4]	4.8/5.1			
$(n\text{-}C_8H_{17})_3PO$	478/478		[41.5/41.7] {17.5/17.2}				
$(C_6H_5)_3AsO$	540/541		{23.20.9} [53/51.0]	6.7/7.0			
$(C_6H_5)_3PS$	250/251		[54/53.0] {17.5/15.4}	7.3/7.5			
$(C_6H_5)_3PSe$	252/252		[68.5/66.3]	9.2/9.4			
$(C_6H_5)(CH_3)S$	170/170		[44/43.3]	6.1/6.2			
$CH_3S_2CH_3$	150/141 [66/68]		[33.5/34.7] {7.5/8.4}	5.1/5.0			
C_6H_5CN	156/152 [72.5/72.3]	13.3/15.6			3.5/4.6 (PhOH), 12.7/13.8 ($SbCl_5$)		
C_2H_5SCN	123/123		{6.5/6.1}	3.9/3.9			
$(C_6H_5)_2SO$	294/297 {311/304}	19.6/22.0	[29.0/27.6]				
$(C_6H_5)(CH_3)SO$			[30/25.7]	3.2/3.5	6.3/6.4 (4-FPhOH)		
$(n\text{-}Bu)_2SO$	373/370 {384/385}	23.4/25.3					
$C_6H_5NO_2$	67/64	8.6/11.7	[11/10.8]				
$C_6H_5\text{-}N(CH_3)_2$	[244/242] 422/417 {382/393}	26.1/27.8	[58.0/60.0]		5.0/6.9 (4-FPhOH)		
quinoline	494/490 {498/498}		[50/50.4] {20.5/19.7}	7.2/6.9	8.3/8.3 (4-FPhOH)		4380/4383
3-$CH_3C_5H_4N$	497/501 [297/294]	31.3/31.3	[61.5/59.1] {21.0/22.2}	8.3/8.2	7.6/8.1 (PhOH)	−4.9/−5.6[l]	4730/4734
3-ClC_5H_4N	425/419 [239/242]	28.4/27.6	[45.5/48.4]	6.5/6.7	7.2/7.3 (PhOH), 7.0/7.3 (4-FPhOH)	−8.8/−9.0[l]	3920/3916
3-BrC_5H_4N	425/420 {421/417} [239/243]	28.4/27.7	[42/48.3]		7.2/7.3 (4-FPhOH)		3930/3924
3-IC_5H_4N	431/425 [243/246]		[44.0/49.7]				4000/3995
3-CNC_5H_4N	362/357 [202/203]						3390/3390
4-$CH_3C_5H_4N$	500/506 [301/298] {495/498}	32.1/31.6	[61.5/61.3] {22.0/22.9}	8.9/8.5	*j*	−4.4/−5.1[l]	4830/4835
4-$C_2H_5C_5H_4N$	510/508 [299/299]		[62.0/59.9]				4800/4802
4-$OCH_3C_5H_4N$	[308/308]	32.9/32.3				−3.6/−4.9[l]	4920/4921
4-$N(CH_3)_2C_5H_4N$	[352/352]	36.2/35.5			8.8/9.0 (4-FPhOH)	0.8/(−1.6)[l]	5680/5680
4-$CF_3C_5H_4N$	[224/224]					−9.0/−9.3[l]	3780/3780
4-CNC_5H_4N	[216/216]				*k*	−10.1/−10.0[l]	3620/3620

[a] See ref 8, units cm^{-1}. [b] See ref 9, units cm^{-1}. [c] See ref 3, units cm^{-1}. [d] See ref 10, units cm^{-1}. [e] See ref 10, units kcal mol^{-1}. [f] See ref 8, units kcal mol^{-1}. One kcal mol^{-1} is added to $-\Delta H$ for strong nitrogen and sulfur donors measured in CCl_4, calorimetrically. [g] See ref 4, units kcal mol^{-1}. [h] See ref 11, units 10^3 cm^{-1}. See Table III for definition of $\Delta\Delta\nu$. [i] 7.7/7.5 for CF_3CH_2OH; 9.9/10.1 for $(CF_3)_2CHOH$; 11.7/11.4 for $Zn[N[Si(CH_3)_3]_2]_2$; 10.2/9.9 for $Cd[N[Si(CH_3)_3]_2]_2$; 8.0/8.1 for 4-FC_6H_5OH; 10.5/10.7 for $(CF_3)_3COH$. [j] 8.3/8.1 for PhOH; 8.3/8.1 for 4-FC_6H_4OH; 4.6/4.5 for $(CH_3)_3COH$; 13.9/13.7 for $Zn\{N[Si(CH_3)_3]_2\}_2$; 11.1/11.4 for $Cd\{N[Si(CH_3)_3]_2\}_2$. [k] The proton, 210.3/210.5; H_3O^+, 59.8/59.1; and $(H_2O)_2H^+$, 38.7/47.1, were fit with a T value of 0.77 for 4-cyanopyridine. [l] The n value used for these systems in the data fit is 0.51 to accommodate the larger than average miss of pyridine with this probe. [m] $(CH_3)_3SnCl$: Spencer, J. N.; et al. *Organometallics* **1986**, *5*, 118.

to double the E_B scale giving it a larger range. The confidence that can be placed in a reported number is indicated by listing the number of data points used to determine the parameters. The range of C_A/E_A or $C_A{}^*/E_A{}^*$ ratios used to establish a parameter are also important in assessing the accuracy of the parameter. Enthalpy measurements should include acceptors like I_2 and phenol, while spectral acceptors should include I_2C_2, C_6H_5OH, CH_3OH, and $(CH_3)_3COH$. The parameters from the data fit on systems with limited data or limited C/E ratios are reported as preliminary values in Table VI.

Trends in the Parameters. The addition of new donors to the correlation provides additional support for the claim that the parameters have meaning in the context of the electrostatic–covalent model. With iodine arbitrarily chosen[2c] as the reference acid and assigned parameters $E_A = 0.50$ and $C_A = 2.00$, the C values of donors or acceptors cannot be compared directly to the

Table V ^{a}

Enthalpy Acid Parameters

	acid	no. of $-\Delta H$'s	E_A	C_A	W	C_A/E_A
[1]	I_2	42	0.50	2.00		4.0
[2]	IBr	3	1.20	3.29		2.7
[3]	ICl	6	2.92	1.66		0.57
[5]	C_6H_5OH	32	2.27	1.07		0.47
[6]	4-FC_6H_4OH	10	2.27	1.07		0.47
[7]	3-FC_6H_4OH	13	2.35	1.18		0.50
[8]	3-$CF_3C_6H_4OH$	18	2.40	1.21		0.50
[9]	4-ClC_6H_4OH	5	2.30	1.13		0.49
[10]	4-$CH_3C_6H_4OH$	6	2.24	0.98		0.44
[11]	4-*t*-$C_4H_9C_6H_4OH$	5	2.16	0.95		0.44
[12]	CF_3CH_2OH	16	2.07	1.06		0.51
[13]	$(CF_3)_2CHOH$	17	2.89	1.33	–0.16	0.46
[14]	*t*-C_4H_9OH*	6	1.07	0.69		0.65
[15]	$(CF_3)_3COH$	8	3.06	1.88	–0.87	0.61
[16]	$C_8H_{17}OH$	5	0.85	0.87		1.0
[17]	H_2O	9	1.31	0.78		0.59
[18]	$HCCl_3$	6	1.56	0.44		0.28
[19]	C_4H_4NH	5	1.38	0.68		0.49
[20]	C_6H_5SH	3	0.58	0.37		0.64
[21]	HNCO	4	1.60	0.69		0.43
[22]	HNCS	8	2.85	0.70		0.25
[23]	$CF_3(CF_2)_6H$	4	0.80	0.63		0.79
[24]	CH_2Cl_2	12	0.86	0.11		0.13
[30]	$B(CH_3)_3$	6	2.90	3.60		1.2
[31]	$Al(CH_3)_3$	18	8.66	3.68		0.43
[32]	$Al(C_2H_5)_3$	4	6.94	4.19		0.60
[33]	$Ga(C_2H_5)_3$	5	6.95	1.48		0.21
[34]	$Ga(CH_3)_3$	3	6.92	2.28		0.33
[35]	$In(CH_3)_3$	2	6.60	2.15		0.33
[36]	$(CH_3)_3SnCl$	9	2.87	0.71		0.25
[37]	BF_3(g)	4	6.10	2.87		0.47
[38]	SO_2	5	0.51	1.56		3.1
[39]	$SbCl_5$	4	3.64	10.42		2.9
[50]	$[Ni(TFACCAM)_2]_2^b$	8	1.55	1.32		0.85
[51]	$Cu(HFAcAc)_2^b$	9	1.82	2.86		1.6
[52]	$Zn[N(Si(CH_3)_3)]_2$	5	2.75	2.32		0.84
[53]	$Cd[N(Si(CH_3)_3)]_2$	5	2.50	1.83		0.73
[54]	Mo_2PFB_4	5	3.15	1.05		0.33
[55]	ZnTPP	4	2.72	1.45		0.53
[56]	CoPPIXDME	4	2.32	1.34		0.58
[57]	MeCoDMG	6	4.79	3.30	–6.15	0.69
[58]	$Rh_2(CO)_4Cl_4$	6	4.32	4.13	–10.39	0.96
[59]	$[Rh(COD)Cl]_2$	7	2.43	2.56	–5.78	1.1
[60]	$[Pd(\pi\text{-ally})Cl]_2$	4	1.70	2.14	–3.38	1.3

Frequency Shifts Parameters

	acid	no. of shifts	E_A^*	C_A^*	W^*	C_A/E_A
[80]	4-$CH_3C_6H_4OH$	6	169	109	–224	0.65
[81]	C_6H_5OH	21	167	109	–205	0.65
[82]	4-FC_6H_4OH	13	193	133	–250	0.69
[83]	4-ClC_6H_4OH	9	172	106	–183	0.62
[84]	3-FC_6H_4OH	7	184	115	–211	0.63
[85]	3-$F_3CC_6H_4OH$	19	189	122	–220	0.65
[86]	*t*-C_4H_9OH	11	89.9	55.0	–124	0.61
[87]	CF_3CH_2OH	12	150	96.9	–193	0.65
[88]	$(CF_3)_2CHOH$	9	177	112	–142	0.96
[89]	C_4H_4NH	10	88.0	56.4	–110	0.64
[90]	H_2O	9	91.5	50.8	–57.8	0.55
[91]	CH_3OH	37	104	69.4	–152	0.67

Base Parameters

	bases	no. of $-\Delta H$'s	no. of probes	E_B	C_B	C_B/E_B
[1]	NH_3	5H/17G		2.31	2.04	0.88
[2]	CH_3NH_2	5H/13G		2.16	3.12	1.4
[3]	$(CH_3)_2NH$	4H/14G		1.80	4.21	2.3
[4]	$(CH_3)_3N$	7H/14G		1.21	5.61	4.6
[5]	$C_2H_5NH_2$	3H/6G		2.34	3.30	1.4
[6]	$(C_2H_5)_2NH$*	2H		1.22	4.54	3.7
[7]	$(C_2H_5)_3N$	11H/4G	2	1.32	5.73	4.3
[8]	$(CH_2)_5NH$*	6H	1	1.44	4.93	3.4
[9]	$HC(C_2H_4)_3N$	7H/1G		0.80	6.72	8.4
[15]	*N*-CH_3Im	7C/1G		1.16	4.92	4.2
[16]	C_5H_5N	30H/9G	11	1.78	3.54	2.0
[17]	3-$CH_3C_5H_4N$*	2H	7	1.88	3.60	1.9
[18]	3-ClC_5H_4N*	1H	6	1.86	2.88	1.5
[19]	3-BrC_5H_4N*	1H	5	1.87	2.87	1.5
[20]	3-IC_5H_4N*	OH	4	1.83	2.98	1.6
[21]	4-$CH_3C_5H_4N$	6H	7	1.79	3.78	2.1
[22]	4-$C_2H_5C_5H_4N$*	0H	4	1.90	3.64	1.9
[23]	4-$CH_3OC_5H_4N$*	0H	4	1.93	3.73	1.9
[24]	4-$N(CH_3)_2C_5H_4N$*	1H	4	1.82	4.53	2.5
[25]	4-CNC_5H_4N*	3H	3	1.66	2.81	1.7
[26]	quinoline	2H	3	2.28	2.89	1.3
[30]	HCN*	8G		1.19	0.99	0.83
[31]	CH_3CN	13C/13G	8	1.64	0.71	0.43
[32]	$ClCH_2CN$	6C	2	1.67	0.33	0.20
[33]	$(CH_3)_2NCN$	4C	2	1.92	0.92	0.48
[34]	C_6H_5CN*	1C	4	1.65	0.75	0.45
[40]	$H_2C(O)$	9G		1.56	0.10	0.06
[41]	$CH_3C(O)H$	11G		1.76	0.81	0.46
[42]	$CH_3C(O)CH_3$	9C/15G		1.74	1.26	0.72
[43]	$CH_3CH_2C(O)CH_3$	1C	4	1.67	1.24	0.74
[44]	$(CH_2)_4CO$	1C	5	2.02	0.88	0.43
[45]	$C_6H_5C(O)CH_3$	2C	3	1.72	1.15	0.67
[46]	$(C_6H_5)_2CO$	2C	3	2.01	0.55	0.27
[47]	$CH_3C(O)OCH_3$	7C/6G	2	1.63	0.95	0.58
[48]	$CH_3C(O)OC_2H_5$	16C/3G	11	1.62	0.98	0.61
[49]	$CH_3C(O)N(CH_3)_2$	18C	13	2.35	1.31	0.56
[50]	$HC(O)N(CH_3)_2$	8C/1G	6	2.19	1.31	0.60
[51]	$CO[N(CH_3)_2]_2$	1C	5	2.06	1.87	0.91
[60]	$(C_2H_5)_2O$	14C/11G	10	1.80	1.63	0.91
[61]	$(i\text{-}C_3H_7)_2O$	3C/1G	1	1.95	1.66	0.85
[62]	$(C_4H_9)_2O$	8C/3G	6	1.89	1.67	0.88
[63]	$O(C_2H_4)_2O$	6C/3G	7	1.86	1.29	0.69
[64]	$(CH_2)_4O$	14C/5G	7	1.64	2.18	1.3
[65]	$(CH_2)_5O$*	4C	6	2.05	1.38	0.67
[66]	$(CH_3)_2O$	3C/10G		1.68	1.50	0.89
[67]	$(C_8H_{17})_2O$	3C	3	1.77	1.95	1.1
[68]	$(CH_2)_4(CH)_2O$	5C		1.45	2.14	1.5
[75]	H_2S	1H/2G		0.04	1.56	38
[76]	$(CH_3)_2S$	6H/3G	2	0.25	3.75	15
[77]	$(C_2H_5)_2S$	13H/1G	10	0.24	3.92	16
[78]	$(CH_2)_3S$	4H	2	0.38	3.43	9
[79]	$(CH_2)_4S$	29H	10	0.26	4.07	16
[80]	$(CH_2)_5S$	3H	2	0.34	3.81	11
[81]	$CH_3S_2CH_3$*	1H	3	0.55	2.34	4.2
[85]	$(CH_3)_2SO$	18C/2G	11	2.40	1.47	0.61
[86]	$(CH_2)_4SO$	4C	1	2.44	1.64	0.67
[90]	C_5H_5NO	2C/1G		2.29	2.33	0.33
[91]	4-$CH_3C_5H_4NO$	5C		2.32	2.57	1.1
[92]	4-$CH_3OC_5H_4NO$	2C/1G		2.34	3.02	1.3
[93]	$(CH_3)_4C_5H_6NO$	6H		1.46	3.20	2.2
[95]	$(C_6H_5)_3PO$	3C	4	2.59	1.67	0.64
[96]	$(C_2H_5O)_3PO$	3C	3	2.51	1.10	0.44
[97]	$[(CH_3)_2N]_3PO$*	7C	4	2.87	1.52	0.53
[100]	$(CH_3)_3P$	7H/1G		1.46	3.44	2.4
[101]	$C_2H_5C(CH_2O)_3P$	3H		0.71	3.42	4.8
[110]	H_2O^c	17G		2.28	0.10	0.04
[111]	CH_3OH^c	13G		1.79	0.65	0.36
[112]	$C_2H_5OH^c$	12G		1.84	1.09	0.59
[113]	*t*-$C_4H_9OH^c$	6G		1.92	1.22	0.64
[120]	$(CH_3)_2Se$	3H		0.05	4.24	83
[121]	C_6H_6	4C,H/5G		0.70	0.45	0.64
[122]	CH_3Cl^c	5G		2.54	0.10	0.04
[123]	$(C_6H_5)_3PS$	1H	3	0.35	3.65	10

Table V Footnotes

[a] In the column marked number of $-\Delta H$'s for donors, the number preceeding the C or H is the number of solvent-minimized enthalpies used. The letter describes the preferred solvent: H, hexane, or C, carbon tetrachloride. The number preceding "G" indicates the number of gas-phase ion molecules correlated with these parameters. An asterisk placed by a donor indicates the value is tentative because of a limited C/E range for the acceptors used. Improved[2] values over those reported earlier for some donors are contained in Table V. As in any empirical approach, the parameters will change as more data become available. The more systems that are used to determine the parameters, the smaller than change will be. [b] Avoid sulfur, phosphorus, and selenium donors because of repulsions with ligand lone pair electron density. [c] Donor strength for monomers in the gas phase.

Table VI. Preliminary E_B and C_B Values from the Data in Table IV

donor	no. of data pts	E_B[a]	C_B[a]	donor	no. of data pts	E_B[a]	C_B[a]
$(C_2H_5O)_2CO$	3	1.54	0.87	$(C_6H_5)_3AsO$	4	2.63	2.82
$C_6H_5C(O)H$	3	1.67	0.97	$(C_6H_5)_3PSe$	3	−0.38	4.78
$C_6H_5C(O)OCH_3$	3	1.74	0.66	$(C_6H_5)(CH_3)S$	3	0.29	3.00
$C_6H_5COOC_2H_5$	4	1.71	0.77	$CH_2)_3CO)NCH_3$	5	(2.14)	(1.66)
$CH_2CH_2)_2C(O)O$	4	1.62	1.16	$(C_6H_5)(CH_3)SO$	3	2.25	1.21
$CH_2ClC(O)OC_2H_5$	3	1.71	0.52	$C_6H_5NO_2$	3	(1.29)	(0.48)
$HC(O)OC_2H_5$	3	1.58	0.66	3-CNC_5H_4N	3	1.70	2.55
$(CH_3)_3PO$	4	(2.67)	(2.03)	4-$CF_3C_5H_4N$	3	1.60	3.01
$(C_2H_5)_3PO$	3	2.84	1.83	C_2H_5SCN	3	0.82	1.75
$(n\text{-}C_8H_{17})_3PO$	3	2.67	2.18	$(C_6H_5)_2SO$	4	(2.10)	(1.39)
$(CH_3O)_3PO$	5	(2.29)	(1.21)	$C_6H_5N(CH_3)_2$	6	(1.20)	(3.87)
$(n\text{-}Bu)_2SO$	3	(2.41)	(1.59)				

[a] Parentheses indicate parameters from data with a very limited range of C_A^*/E_A^* values. The well-established donor parameters are assigned *n*-values of 0.2 in data fits and the tentative parameters are assigned *n*-values of 0.6.

E values of the donors or acceptors. However, the relative magnitudes of the C_B parameters give an indication of the relative strengths of the covalent bond forming tendencies of the donors. The C_B value is seen to increase, for a series of donors, as the polarizability of a donor atom increases or the ionization energy decreases. This is reflected in the magnitudes of the C_B parameters for $(C_6H_5)_3PO$, $(C_6H_5)_3PS$, and $(C_6H_5)_3PSe$, whose values are 1.67, 3.65, and 4.78, respectively.

It is important not to confuse the strength of the covalent interaction with the covalent nature of the interaction. The covalency in the bond is determined dividing the C_AC_B product by $-\Delta H$. Any change which increases the separation of the energy of the donor and acceptor orbitals decreases the fraction covalency in the bond. This energy separation can be crudely gauged with relative ionization energies, electron affinities, or substituent inductive parameters. This type of comparison for donors and acceptors with well-established parameters consistently gives results in accord with the expected trends. The reader is encouraged to carry out this type of comparison with the reported parameters to gain insights about trends in covalency.

Substitution of an alkyl group for a hydrogen on a donor atom or donor group usually decreases the ionization energy of the molecule and decreases the lone pair dipole moment. When this occurs, an increase in the C_B value and a decrease in the E_B value is observed. Inspection of Table V shows that the trend is pronounced for the R_3N, R_2O, and R_2CO series of compounds.

The addition of new donors enables one to compare trends in donor strength with substituent change in a family of compounds. The results are consistent with expected trends from substituent constant effects. Added insight concerning the mechanism of substituent influence (i.e., covalent or electrostatic) results. The chloromethyl substituent is more electron withdrawing than methyl and functions to decrease the donor strength. In both $ClCH_2CN$ and $ClCH_2(C(O)OC_2H_5$ this decrease occurs by decreasing the C-value.

The donor order of $CH_3CON(CH_3)_2 > (CH_3)_2CO > (CH_3)_2C(O)OCH_3$ will result without exception for all normal σ donor interactions in solvent-minimized systems because the E_B values and the C_B values of the donors both decrease in the order given. Conjugation of the $-N(CH_3)_2$ group makes the amide a better donor than acetone. However, electron withdrawal in the σ system is not compensated for by conjugation with the $-OCH_3$ group making the ester the weakest donor. In general the trends in the parameters are reasonable when considered in the context of the established trends in substituent effects.

It should be noted that the E_B and C_B parameters are determined for systems in which steric effects are absent. Steric effects are a property of the geometry of the adduct and not a property of the individual base or acid. Therefore, the enthalpy calculated from eq 1 or the spectral shift calculated from eq 2 is a measure of the interaction between the acid and base in the absence of steric hindrance. Donors with bulky substituents are expected to show deviations in the calculated and experimental value with the discrepancy giving a quantitative estimate of the magnitude of the steric effect. Steric problems are possible causes of the discrepancies observed in the calculated and experimental enthalpies of adduct formation of BF_3 with $(C_6H_5)_2CO$, $(C_6H_5)_2SO$, $C_6H_5C(O)OC_2H_5$, and $C_6H_5N(CH_3)_2$. Deviations are expected when acceptors such as $B(CH_3)_3$, $(CH_3)_3SnCl$, BF_3, $Al(CH_3)_3$, Cu(hfacac)$_2$, and ZnTPP are studied. The acceptor probes employed here are expected to have minimal steric problems.

***E* and *C* Parameters as a Reactivity Scale.** The large number of donors (or acceptors) in the correlation now permits E and C to be used as a viable scale of donor (or acceptor) strengths. First consider an acceptor system (electrophile) studied with a series of donors. The donor parameters in Table V are used in dual parameter analyses of physicochemical changes an acceptor undergoes as interacting donors are varied. This is accomplished by substituting the measured property for a particular donor into eq 2 along with the donor's E_B and C_B values. Several such equations can be written, one for each donor studied, and solved for unknown E_A^*, C_A^*, and W^* parameters. The donors marked with an asterisk in Table V should be assigned an n-value of 0.6 in the data fit, and all other donors are assigned an n-value of 0.2. A good fit of the calculated and experimental values indicate that the observed changes are dominated by σ donor–acceptor interactions. Any measured quantity that changes as the donor is changed can be analyzed with this approach.

New donors can be added to the E and C data base by measuring the spectral shifts or $\Delta G(BH^+_{aq})$ with probes in Table III and enthalpies with the acceptors in Table V. The weights that should be given to the probes in new donor fits are given by the n-value. This same procedure is used to correlate reactivity studies in which a donor (nucleophile) is held constant and the acceptor varied.

Calculations

The probe E_A^* and C_A^* parameters in Tables I and II are determined by substituting reported data and the corresponding E_B and C_B parameters[2] into eq 2. The resulting series of simultaneous equations is solved for E_A^*, C_A^*, and W^*. In view of the very large number of new systems introduced in this work, a master fit of all the new data in this article and that in ref 1 was carried out. All well-established acceptor probes (e.g., $\Delta\nu_{OH}$ of phenol, $-\Delta H$ of I_2, and $-\Delta H$ of C_6H_5OH) were also held fixed at their transformed reported value. All donors whose E_B and C_B values are well determined[2] were held fixed at their transformed values. The data in ref 1 and Table IV were solved by finding the best fit set of E_A^*, C_A^*, W^*, E_B, and C_B values. A total of 348 physicochemical properties were fit to 31 acceptor unknowns and 92 donor unknowns. For the determination of the donor unknowns, weights assigned to the different acceptors in the fit are given by $1/n$. The value of n for an acceptor is determined by the formula

$$n = [\bar{x} \times 0.3]^{1/2} \tag{10}$$

The n-value of 0.1 is used for $-\Delta H(I_2)$ (average deviation of 0.1 kcal/mol) and all other values are assigned an n-value of 0.2 unless specified otherwise. These weights should be used in new applications aimed at adding new donors. When new acceptors are added, the donors in Table V are assigned n-values of 0.2 and those in Table VI, 0.4. Their use is restricted to acceptors with C/E ratios used to determine the parameters.