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Solvent Effects and Their Relationship to the *E* and *C* Equation

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Abstract: We report a calorimetrically determined enthalpy for the interaction of the weak base benzene with *m*-fluorophenol. This result is compared with that obtained by a reported pure base method. Using these data we are able to obtain E_B and C_B parameters for benzene that can be used to predict the solvent correction term for enthalpies obtained in benzene as a solvent. The success of this approach further substantiates the validity of our elimination of solvation procedure (ESP). Other approaches to the prediction of solvent effects are demonstrated to be unreliable by using new and recently reported data. The modified E_B and C_B numbers for benzene now enable us to incorporate systems into the correlation which were previously reported to constitute failures. We have also been able to obtain an independent test of the *E* and *C* approach by using reported data from another laboratory on water as a Lewis acid. E_A and C_A parameters for water are obtained.

The influence of solvation on chemical reactivity has been studied with increasing interest in recent years. It is now recognized that in many systems solvation is as important a factor in understanding chemical reactivity as the electronic properties of the reactants. Accordingly, we have been interested in the development of quantitative models for correcting enthalpies obtained in basic or acidic solvents to the results one would obtain in carbon tetrachloride or an alkane.[1-5] An elimination of solvation procedure (ESP) has been proposed as a method for eliminating contributions to the enthalpy from specific solvent interactions.[1] This procedure has been shown to work for both acidic and basic solvents. For the acidic solvent methylene chloride, the approach has been extended to the point where the solvent correction term is found to be due mainly to specific interactions which can be predicted using a modified form of the *E* and *C* equation.[6] The enthalpies of adduct formation, ΔH, are related to the *E* and *C* parameters by

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

where E_A and C_A are empirically determined parameters for the acid, and E_B and C_B are for the base. The *E* terms are related to the propensity to undergo electrostatic interactions and the *C* terms are related to the propensity to undergo covalent interactions. Over 300 enthalpies have been correlated using this equation[7] and over 2000 can be predicted.

In this paper we present an analysis of the elimination of solvation procedure using the basic solvent benzene. The ESP approach has previously been applied to enthalpy data in benzene solutions and solvent correction terms have been obtained.[1,3,5] We have obtained reliable solvent-minimized enthalpy data for the specific interaction of benzene with the acid *m*-fluorophenol. Using these data we are able to determine new E_B and C_B values for benzene, which we feel are more reliable than those previously published.[7] Incorporating these values into eq 1 allows us to predict the solvent correction terms for various acids. These values are in agreement with experimentally determined solvent correction terms.

These new results enable us to analyze recent criticisms of the predictive value of the *E* and *C* equation. This discussion includes a determination of E_A and C_A parameters for water and a complete list of some of the more recently determined *E* and *C* parameters. Finally, a comparison is made between the ESP approach and the possible use of a *G*-value method[8] to correct enthalpies to the solvent-minimized value.

Experimental Section

Purification of Materials. Aldrich *m*-fluoroanisole (MFA) was distilled at reduced pressure (10–15 mm) from barium oxide. The following reagents were purified as previously described: Mallinckrodt Spectrar pyridine[3] and cyclohexane;[1] Aldrich tetrahydrothiophene (THTP),[9] 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP),[10] and *N,N*-dimethylacetamide (DMA);[4] PRC *m*-fluorophenol (MFP);[1] Fisher spectrograde carbon tetrachloride;[1] Fisher Certified dimethyl sulfoxide (Me_2SO);[6] Phillips 66 pure grade *n*-hexane;[5] Eastman Organic *o*-dichlorobenzene (ODCB);[1] Allied reagent grade dimethylformamide (DMF).[9]

Apparatus. Infrared measurements were made on a Perkin-Elmer 467 grating infrared spectrophotometer, using a matched set of 1-mm NaCl cells. The frequency shifts were checked for concentration dependence of base and phenol concentrations. The description of the modified calorimeter and the procedures for performing the experiments and determining ΔH and *K* have been previously described.[11]

Procedures. The benzene/MFP enthalpies were determined calo-

Table I. Calorimetric Data for the Solution of MFP and MFA[a] in Various Benzene-CCl_4 Mixtures

Concn of benzene, M	H'-$(MFP)_{C_6H_6/CCl_4}$[b]	H'-$(MFA)_{C_6H_6/CCl_4}$[b]	$-H'_{AB}$[b,c]
0.00	−3.34	−0.43	
1.12	−2.40	−0.43	0.94
2.81	−2.21	−0.32	1.02
5.62	−1.98	−0.22	1.14
8.44	−1.73	−0.16	1.34
11.24[d]	−1.57	−0.09	1.43

[a] In all cases the concentration of MFP and MFA is 0.00845 M. The total volume is 100.1 mL. [b] Values of H' are given in calories and are accurate to ±0.01 cal. [c] Calculated using eq 2; see text for explanation. [d] This is the molarity of a pure benzene solution.

rimetrically by injecting either *m*-fluorophenol or *m*-fluoroanisole into solutions of benzene in carbon tetrachloride. H' for each concentration of benzene was calculated using eq 2. These H' values were analyzed by a computer program[11] to obtain K and ΔH. The procedure for determining E_B and C_B parameters has been previously described.[7]

The frequency shifts used in the determination of G values were measured by dissolving the reference compound in the solvent of interest and running its infrared spectrum. G values are assigned[12a] to a solvent on the basis of the position of a carbonyl or sulfonyl infrared absorption band for three reference solutes with the G value in CH_2Cl_2 arbitrarily assigned as 100 to fix the scale. The reference solutes are benzophenone,[12b] *N,N*-dimethylformamide,[12b] and dimethyl sulfoxide.[12c]

Results

The concentrations of benzene employed, the heat evolved upon addition of *m*-fluorophenol to these solutions, and the enthalpy of solution of a similar concentration of *m*-fluoroanisole (MFA) in these solutions are listed in Table I. The quantity H'_{AB} is defined by

$$H'_{AB} = [H'(MFP) - H'(MFA)]_{C_6H_6/CCl_4} - [H'(MFP) - H'(MFA)]_{CCl_4} \quad (2)$$

This equation is explained in the Discussion.

Table II lists the equilibrium constants and enthalpies calculated from data in Table I.

A measured G value of 104 is found for *o*-dichlorobenzene. The carbonyl band of benzophenone and the sulfonyl band of dimethyl sulfoxide occur at lower frequency in nitrobenzene than in bromoform (G value 118). However, the carbonyl band position of *N,N*-dimethylformamide is the same in nitrobenzene as in methylene bromide (G value 108). We assign a range of 105–120 for the G value of nitrobenzene.

Discussion

Elimination of Solvation Procedure (ESP). Our procedure for eliminating specific solvent contributions from thermodynamic data can be employed with acidic or basic solvents; however, for simplicity of discussion, the ideas will be illustrated using basic solvents. In basic solvents, the enthalpy of adduct formation for a series of bases (B,B′) interacting with an acid (A) is measured calorimetrically. Adduct formation reactions of the type

$$\begin{aligned} A + B &\rightarrow AB \\ A + B' &\rightarrow AB' \end{aligned} \quad (3)$$

studied in basic solvents can be combined (subtract that for B from that for B′) to produce the displacement reaction

$$AB + B' \rightarrow AB' + B \quad (4)$$

Table II. Calculated Values of K and ΔH for Benzene and MFP

Data sets[a]	K	$-\Delta H$[c]	Marg/cond[b]
A (std method)	0.07	2.2 ± 0.1	1.97
B ($[B]_{max}$ = 11.24 M)	1.44	1.7 ± 0.1	1.69
C ($[B]_{max}$ = 8.44 M)	1.9	1.6 ± 0.1	1.78
D ($[B]_{max}$ = 5.62 M)	3.4	1.4 ± 0.1	1.96
E (pure base method)		1.7 ± 0.1	

[a] A is the result obtained when H' for dissolution of MFP in the benzene/carbon tetrachloride mixture is corrected by the heat of solution of MFP in pure carbon tetrachloride, i.e., $H'_{AB} = H'_{C_6H_6/CCl_4} - H'(MFP)_{CCl_4}$. This is the standard method for determining enthalpies for systems with large K's in dilute base solutions. $[B]_{max}$ refers to the maximum benzene concentrations used in determination of K and ΔH. Data sets B, C, and D are the results obtained when eq 2 is used to determine H'_{AB}. B represents a calculation using all five data points, C uses data from 1.12, 2.81, 5.62, and 8.44 M benzene solutions, D uses data from the 1.12, 2.81, and 5.62 M solutions. It should be noted that data sets B–D represent increasing carbon tetrachloride solvent character. Data set E represents a calculation of the enthalpy using only the data obtained in the pure base in which a correction is made for the heat of solution of the acid in pure CCl_4 (i.e., Arnett's pure base method).[8] [b] This is the ratio of the marginal standard deviation to the conditional standard deviation. Lower values indicate more reliability in the results; values above 3.0 indicate the calculated results may not be meaningful. See ref 13 for a full explanation for definitions and selection of these criteria. [c] Units are kilocalories per mole.

When there is no specific interaction[36] of the solvent with B, B′, AB, and AB′, it is expected for nonpolar and slightly polar solvents that the nonspecific solvation of the products and reactants will cancel. Thus, by eliminating the free acid from the reaction in a basic solvent, the enthalpy for the displacement reaction (eq 4) will be similar (±0.2 kcal mol^{-1}) in basic solvents to that in CCl_4 or an alkane. A cancellation of solvent effects is also expected if the base or coordinated acid undergoes comparable specific interactions with the solvent in the products and reactants. The method has been shown to be valid in the solvents benzene, *o*-dichlorobenzene, and nitrobenzene when applied to a large series of bases.[1-5] The solvent 1,2-dichloroethane was selected for study because it was not expected to work with ESP. An explanation has been offered to rationalize this.[6] The ESP approach has also been shown to work in acidic solvents such as methylene chloride.[4,6] However, it has been shown to break down in an acidic solvent when the acid has basic sites whose basicity is enhanced by adduct formation over that in the free acid.[14]

It has been found that for all systems where the enthalpies for a series of displacement reactions in any given solvent are similar (±0.2 kcal mol^{-1}) to those obtained under solvent-minimized conditions, the equation

$$\Delta H_{\text{(poorly solvating media)}} = \Delta H_{\text{(basic or acidic solvent)}} - S \quad (5)$$

is also satisfied. Here S is a constant for a given acid (or base) in a given solvent and is independent of the base (or acid) employed. The constant S is simply the difference between the measured enthalpy for adduct formation in carbon tetrachloride or an alkane and that in a basic (or acidic) solvent such as benzene (or methylene chloride).

To determine the source of this constant correction term, S, consider the following thermodynamic cycle (Scheme I),

Scheme I

$$\begin{tikzcd} A_{CCl_4} \arrow[d, "\Delta H_A"] & + & B_{CCl_4} \arrow[d, "\Delta H_B"] \arrow[r, "\Delta H_D"] & AB_{CCl_4} \arrow[d, "\Delta H_C"] \\ A_{C_6H_6} & + & B_{C_6H_6} \arrow[r, "\Delta H_E"] & AB_{C_6H_6} \end{tikzcd}$$

where ΔH_A, ΔH_B, and ΔH_C are the differences in the enthalpy of solvation in going from weakly interacting solvent such as CCl_4 to the basic solvent benzene (the so-called transfer enthalpies) and ΔH_D and ΔH_E are the observed enthalpies of adduct formation in the respective solvents. This means that

$$\Delta H_D = \Delta H_E - (\Delta H_C - \Delta H_B - \Delta H_A) \qquad (6)$$

The solvent correction term, S, is thus given by:

$$S = (\Delta H_C - \Delta H_B) - \Delta H_A \qquad (7)$$

If this term is to be a constant for a given acid with a whole series of bases, then the term $(\Delta H_C - \Delta H_B)$ must be either small or a constant for all of the bases and their respective complexes.

If in benzene and methylene chloride the solvent correction term is an enthalpy arising mainly from specific interactions, it should be possible to predict this enthalpy, that is, the solvent correction term, using the E and C equation (eq 1). This prediction has been successful for the solvent methylene chloride under conditions where ESP holds.[6] Using the E_B and C_B values for the various bases employed, E' and C' values were obtained for methylene chloride. Primes are used to indicate that these enthalpy values may contain some minor contribution from nonspecific solvation interactions. With minor effects, the E' and C' values calculated for methylene chloride should be close to the E_A and C_A values for this acid. Unfortunately, methylene chloride is such a weak acid that we have not been able to obtain E_A and C_A directly. It is desirable to find a system where we can compare the actual enthalpy for specific adduct formation and the solvent correction term. We have been able to do this with the basic solvent benzene.

We selected the acid *m*-fluorophenol (MFP) for these studies because it is a strong hydrogen-bonding acid that has given consistently good results. The solvent correction term for the acid *m*-fluorophenol in benzene was previously reported to be 1.2 kcal mol^{-1}.[1] It was felt that this acid gave us the best hope of obtaining good enthalpy data with the weak base, benzene. In order to obtain measurable heats in the calorimeter, it was necessary to use quite high concentrations of benzene in carbon tetrachloride solution (see Table I). If the standard procedures for dilute solution measurements are used, that is, if one uses H'_{AB} values corrected for the heat of solution of MFP in pure CCl_4, values of $K = 0.7$ L mol^{-1} and $-\Delta H =$ 2.2 kcal mol^{-1} are obtained. However, with such concentrated solutions of base, we were concerned with the effect of the change in solvating properties on the individual determinations. The severity of this problem was demonstrated by a changing heat of solution of the noninteracting compound, *m*-fluoroanisole (MFA), in the various solutions reported in Table I. To correct for this effect, we attempted to factor out the enthalpic contribution from specific interactions associated with phenol dissolving in a mixed solvent (C_6H_6/CCl_4) by using the noninteracting compound *m*-fluoroanisole as a model for *m*-fluorophenol. Equation 2 was then used to calculate a corrected H'_{AB} value. The first term of the equation, $[H'(\mathrm{MFP}) - H'(\mathrm{MFA})]_{C_6H_6/CCl_4}$, is the difference in the enthalpies of solution of MFP and MFA in the C_6H_6/CCl_4 mixture. This difference is an attempt to correct the observed heat evolution upon addition of MFP to the mixed solvent for specific solvation effects by using MFA as a model compound that does not hydrogen bond to benzene. The second term, $[H'(\mathrm{MFP}) - H'(\mathrm{MFA})]_{CCl_4}$, accounts for the endothermic breakup of the intramolecularly hydrogen-bonded phenol upon going into solution. We are in effect transferring the phenol and MFA from dilute solution in CCl_4 to the C_6H_6/CCl_4 mixture and attempting to factor out the enthalpy due to hydrogen bonding, that is, the H'_{AB} value. These corrections are patterned after those made in the pure base method employed by Arnett et al.,[8] but the overall approach differs. The pure base method usually employs the pure base as a solvent and ΔH is calculated from one concentration. The tacit assumption is made that the hydrogen-bonding acid is fully complexed in the pure base solvent. We use the H'_{AB} values obtained to calculate ΔH and K simultaneously. The results for the interaction of benzene and MFP are given in Table II, where it can be seen that there is still a concentration dependence in the calculated enthalpy values. Using the three most dilute solutions (data set D), an enthalpy of -1.4 ± 0.1 kcal mol^{-1} results with an excellent marginal to conditional deviation of 1.96. However, in view of the observed concentration dependence, we feel that the true, solvent-minimized, enthalpy is even lower. A linear extrapolation from a plot of the calculated enthalpy vs. the highest benzene concentration of the solution used in calculating that enthalpy yields a value of -1.1 kcal mol^{-1} at zero benzene concentration. Thus, we feel that -1.1 ± 0.1 kcal mol^{-1} is a reasonable estimate of the benzene–MFP enthalpy. The value of -1.1 kcal mol^{-1} is considerably different (~40%) from the value of -1.7 kcal mol^{-1} obtained using only the pure base data (data set E, Table II).

From the data in Table II we are unable to determine whether the observed concentration dependence for this system results from an actual dependence of the thermodynamic data on the benzene concentration, or if we are simply not adequately correcting for the changing solvent properties using the model compound MFA.

The agreement of the solvent-minimized benzene–MFP enthalpy in dilute solution (-1.1 ± 0.1 kcal mol^{-1}) with the solvent correction term in pure benzene (-1.2 ± 0.1 kcal mol^{-1}) indicates that the observed concentration dependence for the benzene–MFP data results from a failure of the model compound to correct accurately for solvation contributions to the enthalpy. The extrapolation we carried out is justified even though the model compound correction is not accurate because, as can be seen from eq 2 and Table I, the model compound correction becomes less important as the benzene concentration decreases (that is, the difference in $H'(\mathrm{MFA})_{CCl_4}$ (-0.43) and $H'(\mathrm{MFA})_{C_6H_6/CCl_4}$ becomes smaller). The agreement in these two numbers further suggests that, for this type of hydrogen-bonding system in pure benzene, the nonspecific solvation of the products and reactants are comparable to those in CCl_4 or hexane.

***E* and *C* Parameters.** The previously published E and C values for benzene[7] were empirically determined from literature values for enthalpies of adduct formation of benzene with I_2, $CHCl_3$, ICl, and SO_2. In view of the known difficulties associated with obtaining thermodynamic data on weak complexes, there could be sizable errors in these numbers. The enthalpy for the hydrogen bonding of *m*-fluorophenol to benzene suggests that some of these values and thus the reported empirically determined E_B and C_B values for benzene are incorrect. We report tentative E and C parameters based only on the above enthalpy with MFP and the reported value of -1.5 kcal mol^{-1} for I_2.[15] Values for benzene of $E_B = 0.11$ and $C_B = 1.4$ result. We also suspect that the reported E_B and C_B values for mesitylene and xylene[7] are incorrect for similar reasons.

Since nonspecific interactions in benzene are comparable to our solvation-minimized conditions, the E_B and C_B values obtained for benzene can be used to predict the solvent correction term (that is, the specific interaction) for various acids in benzene solution. Such an approach requires that the acid be fully complexed by the benzene solvent. Consider, for example, the benzene solvent correction terms for hexafluoro-2-propanol (HFIP)[5] and *m*-trifluoromethylphenol (TFMP) (see Table III). Using the reported E_A and C_A values for these acids and the above E_B and C_B values for benzene, we calculate specific hydrogen-bonding interactions of -1.5 and -1.2 kcal

Table III. Enthalpy Data for the Acid *m*-Trifluoromethylphenol

Base	Solvent	$-\Delta H$, kcal mol^{-1}	K, L mol^{-1}	Ref
DMA	CCl_4	7.3 ± 0.1	768	11
DMA	C_6H_6	6.2 ± 0.1	213	*a*
HMPA	CCl_4	8.6 ± 0.1		*b*
HMPA	C_6H_6	7.6 ± 0.1	3632	*a*

[a] Calculated using data obtained by J. Nusz in this laboratory. [b] Calculated from the E and C equation, using $E_A = 4.5$, $C_A = 0.53$ for *m*-trifluoromethylphenol, and $E_B = 1.5$, $C_B = 3.6$ for HMPA.

Table IV. Benzene Solvent Correction Terms

Acid	$-S_{meas}$, kcal mol^{-1}	$-S_{calcd}$,[a] kcal mol^{-1}
MFP	1.2[b]	1.1
HFIP	1.7[c]	1.5
TFMP	1.1[d]	1.2

[a] Calculated using the following equation: $-S_{calcd} = E_A E_{benzene} + C_A C_{benzene}$. [b] Reference 1. [c] Reference 5. [d] See Table III.

mol^{-1} (see Table IV). Thus, in these hydrogen-bonding systems, the S value has, within experimental error, its source in the specific complexation of the acid to the benzene. The $-S$ value for iodine, −0.70, does not agree with the −1.5 kcal mol^{-1} of adduct formation.[15] However, the benzene-iodine equilibrium constant is so low that the iodine is not fully complexed in pure benzene. When corrections are made for incomplete complexation by treating the system as a competing equilibrium,[16] we again find that the full contribution to S (within experimental error) is the specific complexation of the iodine to the benzene.

The success of the E and C equation for predicting solvent corrections in benzene solution is very encouraging. It further substantiates the widespread applicability of the E and C approach to thermodynamic data. Several other tests of the E and C equation can now be made.

Arnett et al.[8] claimed that by studying a para-substituted phenol they could "test the E and C approach". Studies that do test the E and C approach are important. However, the selection of a para-substituted phenol to test the E and C equation is a poor choice. There are several meta- and para-substituted phenols in the E and C correlation and it has been shown that their enthalpies of adduct formation with bases obey the Hammett equation.[11] Since it has been shown mathematically that the Hammett equation is a special case (with more stringent conditions) of the E and C equation,[7] should the E and C equation fail, the Hammett equation must fail. Failure of the Hammett equation is very unlikely for a series of para-substituted phenols undergoing a hydrogen-bonding interaction involving the hydroxyl proton. Some other data in the literature can also be reexamined in the context of this discussion. Table V lists some enthalpies reported in the literature for a series of substituted phenols forming hydrogen-bonded adducts with *N,N*-dimethylacetamide (DMA). The equilibrium constants were determined using infrared spectroscopy and the enthalpy from the temperature dependence of K.[17] The experimental values are listed under $-\Delta H$ measured, the enthalpies from the Hammett equation are listed under $-\Delta H$ Hammett equation, using our previously reported[11] ρ' value of 1.6 for this system, and the enthalpies are predicted from our reported constant base-frequency shift correlation[18] under $\Delta\nu_{OH}$. There is excellent agreement between the enthalpies predicted from $\Delta\nu_{OH}$ and ρ'. With the exception of the first five values, the agreement between the reported values and our predicted ones (from ρ' and $\Delta\nu_{OH}$) is excellent. As explained in the footnote to Table IV, the first five values are unreasonable, being inconsistent with calorimetric literature data, infrared frequency shifts, and the Hammett correlation of the rest of the reported data. This may have resulted from an incorrect assumption made by Stymne et al.[17] in their workup of the spectral data, where it was assumed that the complexed phenol and free phenol bands did not overlap. This assumption is quite unnecessary and probably introduces error into the systems where the complex band is shifted the least. Infrared bands are notorious for long tailing. Whatever the cause, the Hammett equation (ρ'), the $\Delta\nu_{OH}$ correlation, and the calorimetric enthalpy determinations suggest that the enthalpies for the first five acids listed in Table V are incorrect. In contrast to these systems, there is excellent agreement between the *m*-trifluoromethylphenol values obtained by calorimetry[11] and infrared spectroscopy[19] and excellent agreement for *all* of the other systems reported in Table V. We had earlier reported that plots of $\Delta H°$ vs. $\Delta\nu_{OH}$ for a given base with a series of acids should have a zero intercept. The reported failure of the authors' data to do so[17] results from the error in the enthalpies on the low enthalpy end of the line. The enthalpies from the Hammett equation and $\Delta\nu_{OH}$ have a zero intercept within experimental error.

Table V. Measured and Predicted Enthalpies (kcal mol^{-1}) of Adduct Formation of *N,N*-Dimethylacetamide with a Series of Substituted Phenols

		$-\Delta H$		
Substituent	Hammett[d] constant, σ	Meas[a,19]	Hammett eq[a,11]	$\Delta\nu_{OH}$[a,20]
p-OCH_3	−0.11	5.7[c]	6.6	6.3
m-$N(CH_3)_2$	−0.27	5.6[c]	6.4	6.4
p-CH_3	−0.17	5.7[c]	6.5	6.3
m-CH_3	−0.07	5.9[c]	6.7	6.3
H	0	5.8[b]	6.8	6.5
p-F	0.06	6.8	6.9	6.7
p-Cl	0.23	6.8	7.2	7.1
p-Br	0.23	7.0	7.2	7.0
m-F	0.35	7.1	7.4	7.2
m-Cl	0.40	6.7	7.4	7.3
m-Br	0.40	7.3	7.4	7.3
m-CF_3	0.42	7.3	7.4	7.4
p-CN	0.66	8.3	7.9	8.2
m-CN	0.56	7.6	7.7	7.8
m-NO_2	0.71	7.7	7.9	7.9
p-NO_2	0.78	8.2	8.0	8.1

[a] In units of kilocalories per mole. [b] This number must be in error. It differs from our measured calorimetric value of −6.8 kcal mol^{-1} and, as Arnett et al.[8] state, the *p*-fluorophenol and phenol data are very close. The infrared *p*-fluorophenol value is −6.8 kcal mol^{-1}. [c] These enthalpies are unreasonable because with these σ values the enthalpies for these acids cannot possibly differ very much from the calorimetric value of −6.4 kcal mol^{-1} for *p-tert*-butylphenol (σ value of ~−0.2). [d] From J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963.

It will be very important to find systems where the E and C equation fails, for these failures will give insight into bonding effects other than those included in the E and C equation.[20] However, a higher probability of finding exceptions will occur by investigating systems that are not expected to obey the Hammett equation. Recent data[21] on the Lewis acidity of water provides such a test because it cannot be put on a phenol Hammett plot. Working with dilute solutions of water in CCl_4, McTigue and Renowden obtained the thermodynamic and spectroscopic data reported in Table VI for a series of bases in the E and C correlation.[21] From this one obtains values for water of $E_A = 2.45 \pm 0.24$ and $C_A = 0.33 \pm 0.08$ for a C_A/E_A ratio of 0.13. Thus, the E_A and C_A numbers for water are lower

Table VI. Frequency Shifts,[21] Calculated and Experimental[21] Enthalpies for Various Adducts of Water

	E_B	C_B	$\Delta\nu_{OH}$, cm^{-1}	$-\Delta H$,[b] kcal mol^{-1}	$-\Delta H_{calcd}$[c] (E and C)
1. C_5H_5N[a]	1.17	6.40	292	5.1	5.0
2. $(CH_3)_2SO$	1.34	2.85	242	4.1	4.2
3. $(C_2H_5O)_3PO$	1.36	1.81	240	4.0	3.9
4. $CH_3CON(CH_3)_2$	1.32	2.58	213	4.3	4.1
5. $HCON(CH_3)_2$	1.23	2.48	198	3.5	3.8
6. $(C_2H_5)_2O$	0.963	3.25	197	4.0	3.4
7. $O(CH_2CH_2)_2O$	1.09	2.38	170	3.2	3.4
8. $(CH_3)_2CO$	0.987	2.33	165	3.2	3.2
9. CH_3COOCH_3	0.903	1.61	134	3.0	2.7
10. CH_3CN	0.886	1.34	135	3.0[d]	2.7
11. $(CH_2CH_2)_2SO_2$			138	2.9	

[a] Reported value in CCl_4 is 17.1 kJ mol^{-1} × (1 kcal mol^{-1}/4.18 kJ mol^{-1}) = 4.08 kcal mol^{-1}. To this is added 1.0 kcal mol^{-1} to correct for the pyridine/CCl_4 interaction, giving 5.1 kcal mol^{-1}. [b] Probable error is 10%. [c] Calculated using $E_A = 2.45$ and $C_A = 0.33$ for water. [d] Obtained from the frequency shift–enthalpy correlation reported here.

than those for phenol ($E_A = 4.33$ and 0.422), but are close to those of 2-methyl-2-propanol ($E_A = 2.04$ and $C_A = 0.300$). The enthalpy values predicted from the E and C parameters are also listed in Table VI and are seen to be in excellent agreement with the experimental values. Errors of 10% are reported for the experimental enthalpies. The reported frequency shifts of water upon hydrogen bonding to these various bases obey a frequency shift–enthalpy correlation similar to those reported earlier for other hydroxyl acids.[18] The relation is of the form:

$$-\Delta H\ (\text{kcal mol}^{-1}) = 0.0126\Delta\nu_{OH}\ (\text{cm}^{-1}) + 1.20 \quad (8)$$

The average deviation from the line is about 0.2 kcal mol^{-1} and the largest 0.5 kcal mol^{-1}. A straight line plot of $\Delta\nu_{OH}$(water vs. $\Delta\nu_{OH}$(trifluoroethanol) is obtained as is predicted from the mathematical relationships[18] of the two constant acid lines. A zero intercept was not obtained. The data were found to fall on previously reported[18] constant base plots for other hydroxyl compounds.

We have reported several new E and C parameters in this paper. The E and C parameters are empirically obtained; thus, as more experimental data become available, the values of the parameters are improved. Every time a new result is obtained, the least-squares fit of all the E and C parameters should be redone. However, this is not feasible because of the proliferation of E and C values that differ slightly for the same systems. Accordingly, we determine new values for an acid (or a base) by using previously obtained parameters for the bases (or acids) and the observed enthalpies and solving for the new or refined E and C values by solving equations for two unknowns. Reference 26 contains the most recent compilation of E and C parameters. In Table VII we summarized the new and refined values that have been obtained since that time.

The prediction of solvation contributions to enthalpy data is the goal of the ESP method. Arnett et al.[8] have reported linear correlations for the heat of formation of phenol–base adducts with the spectrophotometrically derived G values for the various solvents to estimate solvation contributions. However, only three or four points (solvents) were used in these correlations. A G value approach has its real test by studying a limited number of bases interacting with a given acid in a large number of different solvents. Accordingly, we have determined some solvent G values and made some further tests of this correlation (see Table VIII). As can be seen in Figure 1, in which the data of Table VIII are plotted, the correlation between the enthalpy and G values does not lead to a quantitative correlation or prediction of solvent effects on this system. This conclusion is in agreement with the report by Spencer et al.[27] that the correlation between G values and enthalpies is poor. In contrast, the ESP approach works well on all of the data in Table VIII. Therefore, we must conclude that the ESP approach is a superior means of estimating solvation contributions to enthalpic data than one based on G values.

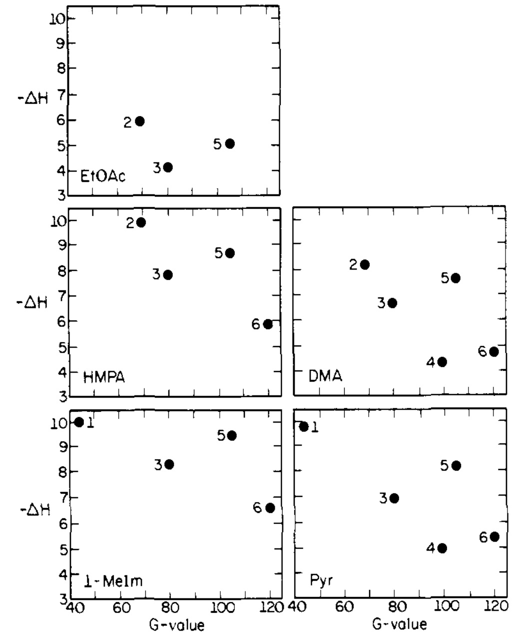

Figure 1. Enthalpy of adduct formation vs. G value of solvent for HFIP–base adducts. Data are taken from Table VIII: 1 = n-hexane, 2 = carbon tetrachloride, 3 = benzene, 4 = nitromethane, 5 = o-dichlorobenzene, 6 = nitrobenzene. Enthalpy units are kcal mol^{-1}.

The validity of the ESP approach has enabled us to detect certain interactions between components involved in an acid–base study that were not suspected a priori. For example, all of our ESP work can be consistently interpreted by invoking an interaction between pyridine and CCl_4.[3] Early work from this laboratory on the phenol–pyridine system in CCl_4 and hexane solvents was interpreted to indicate that the donor pyridine interacted with the solvent CCl_4 to the extent of ~1.0 kcal mol^{-1} of pyridine.[11] The direct determination of such a small enthalpy for a system with a low equilibrium constant cannot be accurately carried out. Thus, the ~0.3 kcal mol^{-1} report of Morcom and Travers[28] on the results of a Raman study of this system was interpreted to provide support for the existence of such an interaction and to be consistent with a magnitude of ~1.0 kcal mol^{-1} of pyridine. We have subsequently shown that such an assumption leads to a consistent interpretation of all[1-6] our ESP results. Furthermore, only data obtained in cyclohexane (or alkanes) leads to results which are consistent with those predicted by the E and C equation for the interaction of pyridine with a large number of Lewis acids.

In the absence of a direct measurement of the thermodynamic data for the pyridine–carbon tetrachloride interaction, the above interpretation has been challenged, in effect, challenging the validity of ESP and the E and C equation. Arnett et al.[8] used the G value correlation, which we disputed above, as evidence that there was no specific interaction between pyridine and CCl_4. Duer and Bertrand[29] claimed that the low value for the pyridine–phenol enthalpy in CCl_4 compared to cyclohexane was due to hydrogen bonding between phenol and CCl_4. Recently, however, Bertrand and Burchfield[30] studied the interaction of pyridine and $CHCl_3$ in CCl_4 solution. Using our dilute solution method, they obtained an enthalpy for the interaction of pyridine and chloroform of −3.3 kcal mol^{-1} in

Table VII. Refined or New *E* and *C* Parameters

Acid or base	C_A	E_A	C/E	Ref
$(CF_3)_3C\text{-}OH$ (PFTB)	0.816 ± 0.07	5.82 ± 0.71	0.14 ($W = 0.65$)	*a*
$Cu(hfac)_2$	1.32 ± 0.02	3.46 ± 0.06	0.39	22
"$(CO)_2RhCl_2$"[c]	2.02 ± 0.05	8.72 ± 0.32	0.23 ($W = 11.3$)	23
"$(COD)RhCl_2$"[c]	1.25 ± 0.04	4.93 ± 0.25	0.25 ($W = 6.3$)	14
$Cd[N(Si(CH_3)_3)_2]_2$	0.79 ± 0.07	4.74 ± 0.29	0.17	24
H_2O	0.33 ± 0.08	2.45 ± 0.24	0.13	*d*
CH_2Cl_2	0.01[e]	1.66[e]	0.006	6
Base[b]	C_B	E_B	C/E	Ref
4-Picoline (H)	6.47 ± 0.1	1.26 ± 0.03	5.1	24
$(EtO)_3PO$ (C)	1.81	1.36	0.74	22
7-Oxabicyclo[2.2.2]heptane (C)	4.11 ± 0.09	0.887 ± 0.02	4.6	*f*
Di-*n*-octyl ether[g] (C or H)	3.4		1.1	3.1
Benzene (C or H)	1.4	0.11	12.7	*d*
(The xylene and mesitylene parameters in ref 26 are incorrect. These are unknown.)				

[a] These values were redetermined employing literature data for pyridine, triethylamine, and diethyl sulfide in the solvent hexane along with oxygen donors in CCl_4 (A. D. Sherry and K. F. Purcell, *J. Am. Chem. Soc.*, **94,** 1853 (1972)). [b] The (C) or (H) refer to solvents of choice; carbon tetrachloride or alkanes, respectively. [c] The enthalpy calculated is that of half the dimer reacting with base, i.e., *W* must be added to the calculated heat to obtain the experimental ΔH in units of kilocalories per mole of adduct. [d] This work; see text. [e] These are actually solvent correction values, previously reported as E' and C'. The enthalpies employed may contain a small contribution from nonspecific solvation. [f] These E_B and C_B values were determined using the following enthalpies of adduct formation: −7.73 (HFIP); −5.8 (C_6H_5OH); −8.8 ($Cu(hfac)_2$); −4.94 kcal mol^{-1} (I_2). [g] Tentative; use with acids with a small (~0.1) *C/E* ratio only.

Table VIII. Solvent Enthalpy Data for HFIP

		$-\Delta H^b$				
Solvent	G^a	EtOAc	HMPA	DMA	1-MeIm	Py
1. *n*-Hexane	44				10.0[d]	9.78
2. Carbon tetrachloride	69	5.92	9.9[c]	8.23		
3. Benzene	80	4.09	7.78	6.67	8.32	6.93
4. Nitromethane	99		4.30			4.89
5. *o*-Dichlorobenzene	105	5.05	8.66	7.58	9.44	8.20
6. Nitrobenzene	120 ± 5		5.91	4.70	6.57	5.34

[a] *G* values for solvents 5 and 6 were measured here and others are from ref 5. [b] Enthalpies are from ref 5 except where noted. Units are kilocalories per mole. [c] Reference 10. [d] Calculated using eq 1 and $W = 1.1$ kcal mol^{-1}.

CCl_4 solution. Comparison of this value to the enthalpy of formation in cyclohexane[19] of −4.6 kcal mol^{-1} of adduct shows a difference of 1.3 kcal mol^{-1} of pyridine reacted. When comparing any two measurements in CCl_4 and cyclohexane with possible errors[31] of ±0.2 kcal mol^{-1} in each, this result is certainly consistent with our reported interactions of ~−1.0 kcal mol^{-1}. Since it seems unlikely that the enthalpy of hydrogen bonding of the much weaker acid chloroform to CCl_4 would be the same as the value claimed for the interaction of phenol and CCl_4, Bertrand's result clearly provides strong support for our claim of an interaction between pyridine and CCl_4 to the extent of ~1.0 kcal. Further support comes from a study of the enthalpy of formation of the pyridine-iodine adduct in cyclohexane and carbon tetrachloride. A lower value by 0.5 kcal mol^{-1} is obtained in CCl_4. In an attempt to provide further support for the absence of significant phenol-CCl_4 interaction, an oxygen donor was sought which would not be expected to aggregate extensively in alkanes. Di-*n*-octyl ether was selected and the enthalpies of adduct formation with phenol determined[32] in CCl_4 and *n*-hexane. Though the equilibrium constants differed, the enthalpies were the same in both solvents and in agreement with an enthalpy of −7.2 kcal mol^{-1} estimated from the $\Delta\nu_{OH}$ value measured in CCl_4 of 411 cm^{-1}. These results and this discussion are not intended to imply that a phenol-CCl_4 hydrogen bonding interaction does not exist, but only that if it does, it is small (~0.2 kcal mol^{-1} of phenol).

In a recent spectrophotometric study of the complexation of guaiacol by pyridine, the same enthalpy of adduct formation was reported in cyclohexane and CCl_4. This was presented as evidence that a phenol-CCl_4 interaction was occurring. However, since large error limits were obtained, the results in this study are not accurate enough to draw any conclusion concerning a pyridine-CCl_4 interaction. Although raw data are not reported, with such a small enthalpy and equilibrium constant, there is no way a substantial fraction of the acid can be complexed for the reported concentrations. The errors introduced when this is the case have been described recently in the literature.[33] We have previously analyzed such systems[26] and describe how different results could arise from a calorimetric and spectrophotometric evaluation of the data. The most important conclusion that can be drawn from the above discussion is that if one is to employ ESP or *E* and *C*, and reap the predictive benefits therefrom, ~1 kcal mol^{-1} must be added to the enthalpy of any system involving the donor pyridine in CCl_4.

One final aspect of the problem remains to be considered. In an important experiment, Tucker and Christian[34] were able to measure accurately the gas-phase enthalpy of complexation of trifluoroethanol to acetone. A $\Delta E°$ value for adduct formation of −6.79 kcal mol^{-1} was reported which corresponds to a $-\Delta H°$ of 6.2 ± 0.1 kcal mol^{-1}. This is 1.1 ± 0.3 kcal mol^{-1} higher than the enthalpy measured in CCl_4 solution of −5.1 ± 0.2 kcal mol^{-1}. The selection of acetone for this study was unfortunate because it has been reported[35] that in solution ketones form two types of 1:1 hydrogen-bonded complexes using the π system in one type and a lone-pair oxygen donor orbital in the other. In solution the enthalpy measured is an average of both adducts. Since it is well established that K's are very different in the gas phase than in solution, a different ratio of the two types of complexes in the gas phase and in solution could lead to a difference in enthalpy that is independent of solvation by CCl_4. Furthermore, if in nonpolar, nonbasic solvents (previously called "inert" by us, but more appropriately called innocent), the base were aggregated (say, an average molecular weight of a dimer), our E_B and C_B parameters would be for this dimer. If the base were a monomer in the gas phase, different E_B and C_B parameters might apply, and any differences could not be attributed to solvation by CCl_4. For this reason, we have been very careful to specify the solvents that should be employed to study the various bases in the E and C correlation. If the degree of aggregation were constant in a series of nonpolar solvents, the E and C parameters for the aggregate would be more relevant to the chemistry in solution than those of the individual molecules. If E_B and C_B changed with aggregation and different degrees of aggregation exist in different solvents, ESP will not work. Clearly, the combination of gas-phase and ESP studies are important for they can provide us with clues to the nature of the species in solution. Furthermore, if for *most* of the bases and acids in the E and C correlation the enthalpy in the gas phase were to differ from that in our innocent solvents by a constant amount, the data in solution would be related to the properties of the isolated donors and acceptors.

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(36) By specific interactions, we mean those where there are orientations of the solute and solvent molecules in which the donor and acceptor orbitals of the two overlap to a greater extent than for other orientations. This implies that a complex exists whose energy is lower than other orientations of the two molecules.

Calculations of Rotatory Strengths in Chiral Chromophores: Cisoid Conjugated Dienes

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Abstract: Observation of the chiroptical effects of dissymmetrically disposed substituents has led us to reexamine the circular dichroism of the lowest $\pi \rightarrow \pi^*$ transition in nonplanar conjugated dienes. Oscillator and rotatory strengths of some skewed dienes with allylic substituents have been calculated, using both the CNDO/S and the CNDO/2 methods without configuration interaction. The CNDO/S method reproduces very well the experimental variation of the circular dichroism with changes in the allylic substituent. The reasons for the extreme sensitivity of the rotatory strength to the substituents are explored. Rotatory strengths for twisted butadiene are compared with those for model planar diene systems which are dissymmetrically substituted. The calculations confirm that the effect of the sense of twist does not always outweigh the effect of dissymmetric substituents.

Some years ago, an analysis of the relationship between the inherent diene chirality of nonplanar cisoid conjugated dienes and the sign of the Cotton effect associated with their lowest energy $\pi \rightarrow \pi^*$ transition led to the proposal of what has become known as the "diene chirality rule".[1] The rule states that a cisoid conjugated diene exhibits a positive or a negative circular dichroism (CD) depending on whether the diene is twisted about the central bond in a right- or left-handed sense (Figure 1), respectively. The sign of this band is attributed solely to the sense of helicity of the diene, and takes no account