

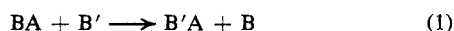
Solvation Contributions to Enthalpies Measured in Methylene Chloride

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Abstract: Data are presented which greatly extend an initial report of a solvent correction procedure for the acidic solvent methylene chloride when the base (*N,N*-dimethylacetamide) was held constant and the acid varied. In this study, correction constants are reported for 11 different bases in methylene chloride. Data for all of the solvation terms in the thermodynamic cycle connecting the adduct formation reaction in CCl_4 to that in CH_2Cl_2 suggest that the principal contribution to the solvent transfer constant (*S*) arises from a specific hydrogen bonding interaction of methylene chloride with the base. The *E* and *C* equation is employed to successfully estimate and correlate the magnitude of the correction constant for the different bases. A molecular interpretation of the reported solvent correction procedure is offered. This molecular model can be used as a guide in predicting when complications from specific interactions may arise. A rebuttal to a recent controversy raised by Olofsson and Olofsson regarding the use of the solvent 1,2-dichloromethane in ESP and to correct to solvation minimized data is presented.

The literature abounds with examples of thermodynamic measurements carried out in polar solvents. As has been pointed out in publications from this laboratory,^{1,2} such data are very difficult to interpret in that they contain appreciable contributions from many different effects. However, experimental limitations (*e.g.*, solubility) often prevent study of certain systems in the poorly solvating solvents CCl_4 or hexane and, therefore, more polar solvents are employed. Consequently, we have been concerned with procedures for correcting thermodynamic data obtained in polar, basic, or acidic solvents to the values that would be obtained in poorly solvating solvents. Our model,³ earlier referred to as ESP (elimination of solvation procedure), is based on the fact³ that if there is no solvation contribution to a series of displacement reactions of the type

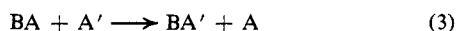


when carried out in a basic solvent, then this is equivalent to requiring that all reactions of the type



carried out in this basic solvent differ from the corresponding solvation-free enthalpy of BA adduct formation by a constant amount. Though some systems have been found in which the enthalpies for eq 1 are not solvent independent, it has been shown³⁻⁵ that sufficient systems are solvent independent to establish ESP as a generally useful, practical means of detecting unusual solvation effects. This has been demonstrated by examining data on comparable acid-base systems obtained in polar and "poorly solvating" solvents.

It has subsequently been shown⁵ that it is possible to apply this model to a series of reactions in acidic solvents when the base is held constant and the acid varied.



(1) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1964).

(2) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973).

(3) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, **94**, 90 (1972).

(4) (a) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, **11**, 280 (1972);
(b) *J. Amer. Chem. Soc.*, **94**, 6877 (1972).

(5) M. S. Nozari, C. D. Jensen, and R. S. Drago, *J. Amer. Chem. Soc.*, **95**, 3162 (1973).

The systems in which the acid is held constant and the base varied in a basic solvent have been better documented than a constant base in acidic solvents. Recently, we have reported⁵ the results of a study in which *N,N*-dimethylacetamide, DMA, was treated with bis-(hexafluoroacetylacetonato)copper(II), $\text{Cu}(\text{hfac})_2$, and a series of alcohols in the acidic, hydrogen bonding solvent, methylene chloride.

In some systems involving basic solvents, the dissolved basic solute, *i.e.*, the Lewis base to be studied, can interact to form a specific complex with a solvent molecule that is destroyed upon addition of a Lewis acid. When this is the case, all acids studied involving this base in this solvent will miss their respective ESP corrections by a constant amount corresponding to the enthalpy required to break up the base-solvent complex. For example, systems of pyridine in benzene invariably miss the individual solvent corrections for the various acids in benzene by ~ 1 kcal mol⁻¹. (In a basic solvent, bases can be varied and the same ESP correction results, but a new correction constant is needed if the acid is changed.) In an acidic solvent the model fails when the Lewis acid complexes to the solvent to a different extent in the adduct than in the free acid. For example, the ESP correction failed for the case of the iodine adduct of DMA in CH_2Cl_2 . Here it can be shown that methylene chloride does not interact with the free acid iodine but probably solvates (possibly *via* a weak hydrogen bond) the more basic, terminal iodine atom in the adduct. Since the formal negative charge on this terminal iodine is a function of the basicity of the donor molecule, we do not anticipate that a constant amount can be added to the correction constants for various base-iodine systems in CH_2Cl_2 . Data on systems of this type, of which BF_3 and the dimeric acids $[(\text{olefin})_2\text{RhCl}]_2$ ⁶ are also expected to be examples (because of hydrogen bonding to the fluorine or chlorine atoms of the adducts), cannot be corrected and acidic solvents should be avoided in their study.

Keeping the above described shortcomings in mind (and avoiding potential complications on other systems suggested by these explanations), we have designed a

(6) W. Parteneimer and E. F. Hoy, *J. Amer. Chem. Soc.*, **95**, 2841 (1973).

Table I. Summary of the Calorimetric Enthalpies

Base	Acid	$-\Delta H^\circ$ in CCl_4 or C_6H_{12} , kcal mol $^{-1}$	$-\Delta H$ in CH_2Cl_2 , kcal mol $^{-1}$	Correction (± 0.2), ^c kcal mol $^{-1}$
$\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$	<i>m</i> - $\text{FC}_6\text{H}_4\text{OH}$	7.0 ± 0.2	5.1 ± 0.1	1.9
	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$	7.3 ± 0.2	5.4 ± 0.2	1.9
	$\text{CF}_3\text{CH}_2\text{OH}$	6.4 ± 0.2	4.4 ± 0.2	2.0
	$(\text{CF}_3)_2\text{CHOH}$	8.5 ± 0.2	6.3 ± 0.2	2.2
	$\text{Cu}(\text{hfac})_2$	8.0 ± 0.2	5.9 ± 0.2	2.1
				Av 2.0 ± 0.2
$\text{C}_3\text{H}_5\text{N}$	<i>m</i> - $\text{FC}_6\text{H}_4\text{OH}$	8.4 ± 0.1	6.3 ± 0.2	2.1
	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$	8.4 ± 0.1	6.3 ± 0.1	2.1
	$(\text{CF}_3)\text{CHOH}$	9.8 ± 0.1	7.3 ± 0.1	2.5
	$\text{Cu}(\text{hfac})_2$	12.9^c	10.6 ± 0.2	2.3
				Av 2.3 ± 0.2
$(\text{CH}_3)_2\text{SO}$	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$	7.4	5.0 ± 0.2	2.4
	$\text{C}(\text{hfac})_2$	8.5 ± 0.3	6.3 ± 0.1	2.2
	$(\text{CF}_3)_2\text{CHOH}$	8.7 ± 0.1	5.5 ± 0.2	Av 2.3 ± 0.2
$\text{HC}(\text{C}_2\text{H}_5)_3\text{N}$	$\text{C}_6\text{H}_5\text{OH}$	9.0 ± 0.1	8.0 ± 0.2	1.0
	$(\text{CF}_3)_2\text{CHOH}$	11.4 ± 0.2	10.1 ± 0.2	1.3
				Av 1.2 ± 0.2
$(\text{CH}_3)_3\text{PO}$	$\text{C}_6\text{H}_5\text{OH}$	7.1 ± 0.1	5.3 ± 0.1	1.8
$(\text{CH}_2)_4\text{SO}$	$(\text{CF}_3)\text{CHOH}$	7.9 ± 0.2	5.7 ± 0.2	2.2
1-Methylimidazole	<i>m</i> - $\text{FC}_6\text{H}_4\text{OH}$	8.5 ± 0.1	6.9 ± 0.1	1.6
$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$	8.7 ± 0.1	6.2 ± 0.1	2.5
Tetrahydrothiophene ^{a, b}	$\text{Cu}(\text{hfac})_2$	5.5^c	4.7 ± 0.2	0.8
		6.0 ± 0.3^b		
$(\text{CH}_3\text{O})_2\text{P}^a$	$\text{Cu}(\text{hfac})_2$	6.9 ± 0.2	6.0 ± 0.1	0.9
$(\text{CH}_3)_2\text{NC}\equiv\text{N}$	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$	5.8 ± 0.3^d	4.2 ± 0.1	1.6
$\text{CH}_3\text{CH}_2(\text{CH}_2)_3\text{P}$	$\text{Cu}(\text{hfac})_2$	6.5 ± 0.1		

^a It is believed that donors with a large *C/E* ratio form more than one isomer in solution with $\text{Cu}(\text{hfac})_2$. Since the isomer distribution in the solvents being compared could vary, it would not be surprising if our methylene chloride solvent correction did not correctly predict the enthalpy difference in the two solvents. ^b ΔH in *o*-dichlorobenzene is -4.6 kcal mol $^{-1}$ for which a solvent correction of -1.4 kcal mol $^{-1}$ leads to a solvation minimized enthalpy of -6.0 kcal mol $^{-1}$. See footnote *a*. ^c In view of potential isomer problems, this system is a questionable check. The solvation minimized enthalpy reported is that calculated from the *E* and *C* correlation. ^d Calculated from the infrared frequency shift (see ref 12). ^e Since the correction compounds the error in two measured enthalpies, we estimate an error of ± 0.2 kcal mol $^{-1}$ in these numbers.

series of experiments which enable us to further test and evaluate the ESP correction in acidic solvents for a whole series of Lewis bases. Furthermore, the results of these studies lead to a new procedure which makes it possible to predict what the ESP correction will be for a new base in the solvent CH_2Cl_2 .

Experimental Section

Purification of Materials. Dichloromethane was stored over calcium sulfate for at least 12 hr, fractionally distilled from calcium hydride, and used within 3 days of purification. Pyridine was fractionally distilled from barium oxide at atmospheric pressure. Dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), and *N,N*-dimethylacetamide (DMA) were distilled from barium oxide at reduced pressures. Hexamethylphosphoramide (HMPA) and 1-methylimidazole were distilled from calcium hydride at reduced pressures. Quinuclidine (1-azabicyclo[2.2.2]octane), reclaimed from its hydrochloride salt, and trimethylphosphine oxide were sublimed at room temperature and 60° , respectively. Hexane, cyclohexane, carbon tetrachloride, benzene, the alcohols, and all other compounds used were purified by previously reported procedures.³⁻⁸

Calorimetry and Calculations. The calorimetric procedures employed and a description of the computer programs used to calculate the enthalpies and equilibrium constants are described elsewhere.⁸

Since most of the acids and bases used in this study are hygroscopic, all solutions were prepared and transferred in a nitrogen-filled glovebag to previously dried glassware. Because of an apparent reaction of pyridine and quinuclidine with methylene chloride (after several hours solutions of these bases yielded a white crystalline material), measurements using these solutions were completed within 20 min of preparation. When the quinuclidine con-

centration was greater than approximately $0.05 M$, inconsistent results were obtained.

Results

The raw data collected in the course of this study are available in the microfilm edition.⁹ Table I summarizes the relevant enthalpies determined in methylene chloride and also lists the value in the appropriate solvent (CCl_4 or C_6H_{12}) which leads to solvent minimized^{4b} results.

The enthalpy of 1-phospha-2,6,7-trioxa-4-ethylbicyclo-[2.2.2]octane (TMPPE) and $\text{Cu}(\text{hfac})_2$ could not be reliably measured in dichloromethane because the equilibrium constant is too small. However, trimethyl phosphite (TMPP) and $\text{Cu}(\text{hfac})_2$ did have a reasonable equilibrium constant in dichloromethane, and the measured enthalpy of this interaction was -6.0 kcal mol $^{-1}$. Unfortunately, the adduct of TMPP and $\text{Cu}(\text{hfac})_2$ was insoluble in cyclohexane, so a direct measurement of the enthalpy in a poorly solvating media could not be carried out. Previous work⁴ in this laboratory has shown that enthalpies of interaction of $\text{Cu}(\text{hfac})_2$ and any Lewis base (that does not interact specifically with the solvent) were 1.4 kcal mol $^{-1}$ less exothermic in *o*-dichlorobenzene (a basic solvent) than those measured in a poorly solvating solvent. The measured enthalpy of adduct formation of $\text{Cu}(\text{hfac})_2$ and TMPP in *o*-dichlorobenzene is -5.5 ± 0.1 kcal mol $^{-1}$ and adding the -1.4 kcal mol $^{-1}$ solvation correction to this enthalpy gives -6.9 kcal mol $^{-1}$ for the solvation minimized enthalpy. The difference between this solvation minimized enthalpy and the enthalpy

(7) R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, **91**, 2883 (1969).

(8) F. L. Slejko, R. S. Drago, and D. G. Brown, *J. Amer. Chem. Soc.*, **94**, 9210 (1972).

(9) See paragraph at end of paper regarding supplementary material.

measured directly in dichloromethane is $0.9 \text{ kcal mol}^{-1}$. This difference ($0.9 \text{ kcal mol}^{-1}$) is in excellent agreement with the correction calculated from the E and C numbers of TMPPE and the E' and C' numbers for dichloromethane to be discussed later. Because of the structural similarity of TMPP and TMPPE, the E and C numbers of TMPPE should be approximately the same as those of TMPP, which are not presently in our E and C correlation. As seen above, enthalpies on both donor systems with the Lewis acid ($\text{Cu}(\text{hfac})_2$) gave similar results.

The enthalpy of adduct formation of $\text{Cu}(\text{hfac})_2$ with tetrahydrothiophene, THTP, does not obey our solvent correction procedures. The enthalpy measured in CCl_4 is $-6.4 \text{ kcal mol}^{-1}$. Earlier studies¹⁰ indicate that THTP interacts with CCl_4 to the extent of $-1.3 \pm 0.3 \text{ kcal mol}^{-1}$ leading to a solvent corrected enthalpy of $-7.7 \pm 0.3 \text{ kcal mol}^{-1}$. With an experimental value in CH_2Cl_2 of $-4.7 \text{ kcal mol}^{-1}$, this would suggest a correction of $3.0 \text{ kcal mol}^{-1}$ in CH_2Cl_2 . An enthalpy of $-4.6 \pm 0.1 \text{ kcal mol}^{-1}$ in *o*-dichlorobenzene leads to a solvent minimized enthalpy of $-6.0 \text{ kcal mol}^{-1}$. This breakdown in ESP on this system is attributed to the possible existence of isomers of the 1:1 adducts. The Lewis base can occupy either an apical or basal position in the expected tetragonal pyramidal geometry of the adduct,¹¹ and both species could exist in solution for this system. If two different complexes formed whose relative amounts varied with solvent, the ESP corrections would not be expected to work.

In addition to the solvents studied above, the $m\text{-CF}_3\text{-C}_6\text{H}_4\text{OH-HMPA}$ interaction was studied in cyclohexane. An enthalpy of $-11.7 \text{ kcal mol}^{-1}$ resulted, compared to a value of -8.7 in CCl_4 . Close examination of the solutions revealed a Tyndall effect in the cyclohexane solution while the CCl_4 solution was perfectly clear. In spite of this fine suspension in the C_6H_{12} solution, an excellent crossing in the K^{-1} vs. ΔH plot was obtained. Apparently, the adduct has very slight solubility and a 1:1 equilibrium involving the adduct in this separate phase pertains. An infrared frequency shift of the $m\text{-CF}_3\text{-C}_6\text{H}_4\text{OH}$ adduct with HMPA was measured in CCl_4 and found to be 532 cm^{-1} . According to a reported correlation,¹² this corresponds to an enthalpy of $-8.6 \text{ kcal mol}^{-1}$ ($\Delta H = 0.0105$; $\Delta\nu_{(\text{cm}^{-1})} = +3.0$), which is in excellent agreement with the calorimetric enthalpy measured in CCl_4 as solvent. To gain further support for CCl_4 being an appropriate solvent for HMPA, this acid-base system was studied in benzene yielding an enthalpy of $-7.6 \text{ kcal mol}^{-1}$. The $\text{DMA-}m\text{-CF}_3\text{-C}_6\text{H}_4\text{OH}$ adduct was studied in benzene and found to produce an enthalpy of $-6.2 \text{ kcal mol}^{-1}$ and the correction constant of $1.1 \text{ kcal mol}^{-1}$ for this acid in the basic solvent. Adding this constant to the $\text{HMPA-}m\text{-CF}_3\text{-C}_6\text{H}_4\text{OH}$ enthalpy in benzene produces $-8.7 \text{ kcal mol}^{-1}$ for the corrected benzene enthalpy in excellent agreement with the CCl_4 result.

The system $(\text{CF}_3)_2\text{CHOH}-(\text{CH}_3)_2\text{SO}$ failed to obey the solvent correction for this donor. The enthalpy

(10) G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970).

(11) D. McMillin, R. S. Drago, and J. A. Nusz, manuscript in preparation.

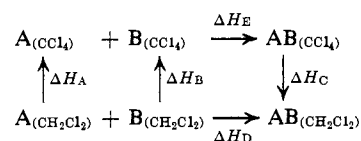
(12) R. S. Drago, N. O'Bryan, and G. C. Vogel, *J. Amer. Chem. Soc.*, **92**, 3924 (1970).

measured in CCl_4 is $-8.7 \text{ kcal mol}^{-1}$, while that measured in CH_2Cl_2 was $-5.5 \text{ kcal mol}^{-1}$ leading to a difference of 3.2 instead of the expected $2.3 \text{ kcal mol}^{-1}$. We are at a loss for an explanation.

Discussion

The ESP procedure, as applied to acidic solvents, requires that enthalpy data in this type solvent for a series of acids with a given base be corrected to data in CCl_4 or hexane by adding a constant. A different constant is required for each different base and the necessary absence of solvation contributions to eq 3 have been discussed. In an earlier study,⁵ a series of acids was studied with the constant base *N,N*-dimethylacetamide in the solvent methylene chloride. With the exception of the acid iodine, all systems studied to date with the base DMA could be corrected to the poorly solvating equivalent (CCl_4 or cyclohexane) enthalpy by adding $-2.0 \text{ kcal mol}^{-1}$ to the enthalpy measured in CH_2Cl_2 as solvent. A reason for the exception on the iodine system has been discussed. As can be seen from the data in Table I, the ESP procedure works well with pyridine, dimethyl sulfoxide, and quinuclidine. The latter bases in Table I were not tested any more extensively with a variety of acids because our approach took on a new perspective (*vide infra*).

Note that, according to this model, each individual base requires a different correction constant. The following thermodynamic cycle indicates the source of all the potential enthalpy contributions to the correction constants listed in Table I and serves to define the symbols for these steps.



The enthalpy of adduct formation measured in methylene chloride, ΔH_D , differs from that measured in the required inert solvents, CCl_4 or cyclohexane, because of noncanceling contributions from the solvent transfer of the acid, base, and complex. If the base is held constant, the enthalpy of transfer of the complex minus that of the acid must also be constant for ESP to work. In the case of the base DMA, values of ΔH_A and ΔH_C were seen⁵ to be the same within $0.1 \text{ kcal mol}^{-1}$ for the adducts of all acids studied. Thus, although the enthalpy of transfer of the various acids used in this earlier study varied from 0.9 to $1.9 \text{ kcal mol}^{-1}$, the solvation differences of the resulting complexes vary to the same extent and the two effects cancel. The solvent correction constant (S) for DMA is seen⁵ to be of the same magnitude as the solvent transfer enthalpy of DMA from CCl_4 to CH_2Cl_2 . This solvent transfer enthalpy includes contributions from the specific and nonspecific interactions of DMA with CH_2Cl_2 . The way to ascertain the relative importance of the specific and nonspecific contributions to this correction would involve a measure of the enthalpy of $\text{DMA-CH}_2\text{Cl}_2$ adduct formation in CCl_4 . Such measurements, involving low equilibrium constants, are extremely difficult to carry out for reasons previously discussed.² Accord-

(13) Table III of ref 6 contains two typographical errors. The ΔH_C values for $\text{CF}_3\text{CH}_2\text{OH}\cdot\text{DMA}$ and $(\text{CF}_3)_2\text{CHOH}\cdot\text{DMA}$ can be calculated from data given in this article to be $1.7 \text{ kcal mol}^{-1}$.

ingly, we shall not attempt to separate the contributions to S .

The next question that arises is how on a microscopic level can we account for the proposal that on many systems the solvation of the complex minus the acid is a constant for a series of adducts in which the base is unchanged and the acid varied. For this discussion, it is convenient to break up the solvation shell around the adduct into the region around the Lewis acid end, referred to as the acid part, and into the part around the Lewis base end, referred to as the base part. The enthalpy of nonspecific solvation of the acid part of the adduct is expected to be less than the nonspecific solvation of the free acid, because at least one molecule of solvent from the shell around the free acid has been lost on forming the adduct. The same argument applies to the base part, but, since the base is held constant, any contribution from this effect is easily incorporated into the constant S for each base. For the acid fragment, any contribution from this loss of solvent can be incorporated into S for the base only in the event of the unlikely result that the quantity is constant for all acids studied. However, in view of the fact that there are a large number of molecules in the solvation shell of the free acid, loss of one or two solvent molecules must be small corresponding to only a small fraction of the total solvation energy of the gaseous acid. If, upon removal of one solvent molecule, there is an increase in the interaction of the remaining individual solvent molecules with the solute, it could be relatively easy to lose a molecule of solvent. Accordingly, a slight increase in the nonspecific solvation of the adduct could partly compensate for the fact that there are fewer solvent molecules around the adduct than around the free acid plus base. If the magnitude of the difference in the nonspecific solvation energy of the adduct acid part and the free acid is not very large, the variation in the magnitude of this quantity for a series of different acids is expected to be even smaller. Furthermore, in using ESP on CH_2Cl_2 , we are comparing the difference in the loss of CCl_4 solvent molecules and the loss of CH_2Cl_2 solvent molecules from the solvation sphere of the solute. Thus, we expect that any small energy term that may exist corresponding to the difference in the nonspecific solvation of the various acids and their respective acid parts in the adduct can be incorporated into S .

For DMA adducts, it was seen⁵ that the difference in the solvent transfer enthalpy of the adduct minus the solvent transfer enthalpy of the acid was approximately zero. Accordingly, the solvent transfer enthalpy of DMA from CCl_4 to CH_2Cl_2 produces the solvent correction. The solvent transfer correction constants (S) and the solvent transfer enthalpies for some of the donors employed in the course of this study are reported in Table II. Fair agreement is seen in several cases. However, it should be emphasized that using solvent transfer enthalpies as an estimate of S is not recommended. If, for example, some base should be less extensively solvated *via* nonspecific interactions in the base fragment than in the free base, the above procedure for estimating S would fail, but determining S as in Table I would incorporate the effect into S and ESP would work (as long as base solvation did not vary when the acid is changed). An additional instance

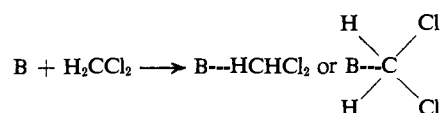
Table II. Solvent Transfer Correction Constants and Solvent Transfer Enthalpies

Base	S	$-\Delta H(\text{CCl}_4 \rightarrow \text{CH}_2\text{Cl}_2)$, kcal mol ⁻¹
$\text{CH}_3\text{C(O)N}(\text{CH}_3)_2$	-2.0	1.95
$\text{C}_6\text{H}_5\text{N}$	-2.2	1.8, ^a 2.5 ^b
1-Methylimidazole	-1.6	3.9
$[(\text{CH}_3)_2\text{N}]_3\text{PO}^c$	-2.5	2.3
$(\text{CH}_2)_4\text{S}^d$	-0.8	1.2

^a Based on an enthalpy of solution of pyridine in CCl_4 of +0.36 kcal mol⁻¹, in CH_2Cl_2 -0.50 kcal mol⁻¹, and ΔH complexation of pyridine and CCl_4 of -0.9 kcal mol⁻¹. ^b Transfer from C_6H_{12} to CH_2Cl_2 . The enthalpy of solution of pyridine in C_6H_{12} is +2.0 kcal mol⁻¹. ^c Enthalpies of solution of HMPA at ~0.03 M in CH_2Cl_2 and CCl_4 are -3.7 and -1.4 kcal mol⁻¹, respectively. ^d Enthalpy of solution of THTP in CH_2Cl_2 is -0.49 ± 0.01 kcal mol⁻¹ over the concentration range 0.02-0.11 M .

whereby S would not agree with the solvent transfer enthalpy of the base would arise when the base is aggregated in one solvent, *i.e.*, CCl_4 or cyclohexane, but not in the other. Under these conditions, the solvent transfer enthalpy will have an endothermic contribution from dissociating the polymeric base, but this effect does not enter in a similar way into S determined as in Table I. When the base is, for example, a dimer in CCl_4 or hexane and the dimer is intact in the adduct, this could have only a minor effect on the measured ΔH . If the base is monomeric in an acidic solvent, when enthalpies in this acidic solvent are subtracted from those in CCl_4 , there will be only minor contributions from the base dimerization to the measured S . However, the solvent transfer enthalpy of the base will include a contribution from the enthalpy of dimerization. Other effects contribute to make obtaining S from solvent transfer measurements dangerous, but, on the other hand, much is to be learned about the nature of these solutions by comparing S , the solvent transfer enthalpy, and the enthalpy of solution of the complex and free acid.

The principle contribution to S in the above systems probably arises from specific interactions of the Lewis base with methylene chloride, *e.g.*



If so, we should be able to correlate and predict these effects with our E and C equation¹⁴ which has been successfully applied to a large number of specific Lewis acid-base adducts.

$$-\Delta H = E_A E_B + C_A C_B \quad (4)$$

The product $E_A E_B$ is crudely related to the electrostatic contribution to the bonding and $C_A C_B$ to the covalent contribution. The E_B and C_B parameters are known for all of the bases used in this study.¹⁴ Accordingly, one can use the S values in Table I as $-\Delta H$ in the above equation and see if one can solve the resulting series of simultaneous equations for E_A' and C_A' values for methylene chloride. Values of $C_A' = 0.01$ and $E_A' = 1.66$ best fit the data. Primes are employed to indicate that the enthalpies may contain a small contribution from nonspecific solvation. When these values for

(14) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

Table III. A Comparison of Measured and Calculated S Values

Base	$-\Delta H_{\text{calcd}}$, kcal mol $^{-1}$	S , kcal mol $^{-1}$	Base	$-\Delta H_{\text{calcd}}$, kcal mol $^{-1}$	S , kcal mol $^{-1}$
CH ₃ C(O)N(CH ₃) ₂	2.2	2.0	Quinuclidine	1.3	1.2
(CH ₃) ₂ SO	2.2	2.3	(CH ₃) ₃ PO	1.8	1.8
C ₃ H ₅ N	2.0	2.2	(CH ₂) ₄ SO	2.3	2.2
1-Methylimidazole	1.6	1.6	(CH ₃) ₂ NC=N	1.8	1.8
[(CH ₃) ₂ N] ₃ PO	2.6	2.5	(CH ₂) ₄ S	0.7	0.8

C_A' and E_A' are substituted into eq 4 along with E_B and C_B of the various bases, the calculated values of the enthalpy summarized in Table III result. The agreement is seen to be excellent for a wide range of bases. The parameters obtained for CH₂Cl₂ suggest that the interactions with methylene chloride are almost completely electrostatic, *i.e.*, mainly dipole-dipole, and the behavior is similar in this regard to that of chloroform ($C = 0.159$, $E = 3.02$). Since there is no obvious difference in the way chloroform and methylene chloride would interact with a base (except in magnitude) that would suggest labeling them differently, we shall call the methylene chloride interaction, hydrogen bonding. The fact that we are able to fit the S values with eq 4 suggests that the solvent corrections for methylene chloride are dominated by specific acid-base interactions. The success of these E' and C' values suggests a similar approach be examined for chloroform and basic, nonpolar solvents.

Recently an attack has been made about our conclusions regarding the use of 1,2-dichloroethane as a solvent for obtaining solvation independent information about acid-base interactions.¹⁵ We reported¹⁶ that in this solvent and with SbCl₅ as the acid, a series of weak bases (with similar C/E ratios) gave a linear relationship between the enthalpy measured in this solvent and that measured in CCl₄ (Figure 1 of ref 16 is a plot of the difference in enthalpies in the two solvents *vs.* the enthalpy in CCl₄). Pyridine *N*-oxide could not be measured directly in CCl₄, but its estimated value did not obey this correlation. Furthermore, we argued that one cannot extrapolate the fact that a proportional relationship existed between $-\Delta H$ of adduct formation and the solvation energy for a series of weak bases (with similar C/E ratios) to strong bases with varying C/E ratios (where the adduct is usually insoluble in CCl₄) (*vide infra*).

Olofsson and Olofsson reported¹⁵ several "new" enthalpies all of which fell on our line (Figure 1, ref 16), but they did not extend the line to stronger bases with varying C/E ratios. Thus, with the same type of experimental result we had reported earlier, these authors saw fit to criticize our reluctance to extrapolate the linear solvation enthalpy plot to strong donors and came out in strong support of using this solvent. However, it is the extrapolation to strong donors that is critical because weak donors can be studied in CCl₄, so there is no need to employ 1,2-dichloroethane.

First, it will be shown that it is impossible for 1,2-dichloroethane to obey ESP, and then we will present arguments to show how tenuous the proportional solvation argument is. It should be clear from the discussion

presented in this article that dichloroethane cannot possibly behave as a basic solvent in ESP for, unless the difference in enthalpy in this solvent and CCl₄ is *constant*, the enthalpy of the displacement reaction cannot be base independent. Thus, one must conclude from the new results¹⁵ as well as the old that dichloroethane cannot behave as a basic, ESP solvent. Since benzene,^{4b} *o*-dichlorobenzene,^{4b} nitrobenzene,¹⁷ and nitromethane¹⁷ all behave as basic solvents in the ESP work toward the same type acid-base systems that do not work in 1,2-dichloroethane, we can look for a molecular interpretation of the different behavior in this latter solvent.

There is agreement between both parties^{15,16} that the existence of *gauche* and *trans* isomers might complicate solvent interactions by inducing the *gauche* isomer in the vicinity of the solute. If this molecular explanation is accepted, a very simple argument leads to our conclusion that 1,2-dichloroethane may give unpredictable solvation energies with strong donors. There are strong bases that are very polar (*i.e.*, have small C/E ratios) and some that are strong but not polar (have large C/E ratios). The very polar base (*e.g.*, pyridine *N*-oxide) can orient the solvent very extensively to the *gauche* form and, as a result, not much more conversion occurs when the adduct is formed. The nonpolar, strong base will not orient the solvent extensively, but if the adduct does, there will be a large "solvation" contribution to the observed enthalpy from this effect. Thus, in the system with the very polar base, there will be extensive solvation of the free polar base that in the acid-base reaction leads to a relatively lower measured enthalpy in dichloroethane than would be obtained if the base were nonpolar but of comparable strength. It is potential uncertainties such as these that cause us to conclude that we cannot find a reliable, general procedure to correct enthalpies measured in 1,2-dichloroethane. The strong base adducts are insoluble in CCl₄. Accordingly, and unfortunately, the uncertainties described are likely to be most significant on systems where 1,2-dichloroethane would have greatest utility.

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Supplementary Material Available. A listing of calorimetric data for various acids and bases will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code numbers JACS-74-2082.

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