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Evaluation of Models and Effects Contributing to Solvent-Transfer Energies

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Abstract: Large solvation energies accompany the transfer of gaseous materials into nonpolar solvents. Therefore, if meaningful thermodynamic data pertaining to donor–acceptor interactions are to be obtained in these media, a cancellation of product and reactant solvation energies must occur. In a preliminary study, it was shown that the displacement reaction, BA + B′ → B′A + B, was solvent independent in weakly basic solvents for a given acid A with several donors, B, of widely differing strength and polarity as long as the donors did not undergo specific interaction with the solvent. In this article, we show that such a cancellation does not occur when the solvent is 1,2-dichloroethane. Systems involving the donor pyridine also failed to obey our model and this deviation is interpreted in terms of a specific interaction of this donor with CCl_4, benzene, and *o*-dichlorobenzene. The model is successfully extended to the donor *n*-butyl ether in CCl_4 and *o*-dichlorobenzene. The discrepancy in the enthalpy of pyridine–phenol adduct formation in cyclohexane and carbon tetrachloride has been the source of considerable controversy. By eliminating phenol from the displacement reaction, the discrepancy can be attributed confidently to a pyridine–CCl_4 interaction. We offer a procedure for estimating enthalpies of interaction in polar solvents (in the absence of specific interactions) which we feel is superior to a procedure currently offered in the literature for such a purpose.

In a previous report[1] from this laboratory, it was demonstrated that displacement reactions of the general form

$$AB + B' \longrightarrow AB' + B \qquad (1)$$

gave the same enthalpy of reaction in the weakly basic solvents, *o*-dichlorobenzene and benzene, as in the nonpolar solvents so long as the free bases did not specifically interact with the solvent. The terms specific and nonspecific interaction will be used frequently in this article and need to be defined. We propose that a specific interaction requires one substance to be a Lewis acid and the other a Lewis base. The energy of interaction between the two molecules must be lower for an orientation of the molecules in which the donor and acceptor orbitals overlap than for all other orientations. A greater than statistical concentration of this oriented species will result. In the systems studied earlier,[1a] the Lewis acid of eq 1 is *m*-fluorophenol, and B and B′ are various combinations of Lewis bases, such as $(CH_3)_2SO$, $(C_2H_5)_3N$, and $CH_3C({=}O)OC_2H_5$. The generality of this hypothesis was extended to systems involving the Lewis acid bis(hexafluoroacetylacetonato)copper(II).[1b] An essential feature of eq 1 is that there is no free acid available when basic solvents are employed, so any specific acid–solvent interactions are eliminated. An observed constant enthalpy for reactions described by eq 1 occurring in various solvents was interpreted[1] to indicate comparable nonspecific solvation of the products and reactants. It was further demonstrated that the absence of solvation contributions to the thermodynamic data corresponding to eq 1 required that the heat of solvation of any given complex AB minus the heat of solvation of the analogous base was a constant in this solvent, independent of the base employed. In this article, we have now extended the systems studied to include the donors *n*-butyl ether and pyridine. Furthermore, the feasibility of the use of the solvent 1,2-dichloroethane has been explored.

We are now in a position to interpret the discrepancy in the enthalpies of adduct formation obtained in the nonpolar solvents, CCl_4 and C_6H_{12}, for certain donors. For some time,[2-4] we have maintained that pyridine

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[1] (a) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, **94**, 90 (1972); (b) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, **11**, 280 (1972).

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

[3] T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).

[4] M. S. Nozari and R. S. Drago, *ibid.*, **92**, 7086 (1970).

Table I. Summary of Calorimetric Results for Hydrogen-Bond Complexes of *m*-Fluorophenol with Different Bases in Various Solvents at 24 ± 1°

	Compound									
	Ethyl acetate		Dimethyl sulfoxide		Pyridine		Triethylamine		*n*-Butyl ether	
Solvent	K^a	$-\Delta H^b$	K^a	$-\Delta H^b$	K^a	$-\Delta H^b$	K^a	$-\Delta H^b$	K^a	$-\Delta H^b$
Cyclohexane	34 ± 3	6.7 ± 0.1			262 ± 11	8.4 ± 0.1		9.8 ± 0.2[c]	17.0 ± 0.2	6.5 ± 0.1
Carbon tetrachloride	19 ± 1	5.2 ± 0.1[d]	470 ± 71	7.2 ± 0.1[d]	106 ± 3	7.5 ± 0.1			11.1 ± 0.2	6.0 ± 0.1
o-Dichlorobenzene	10.3 ± 0.6	4.7 ± 0.1[d]	321 ± 59	6.7 ± 0.1[d]	116 ± 10	6.9 ± 0.1	158 ± 25	9.3 ± 0.1[d]	7.4 ± 0.1	5.7 ± 0.2
Benzene	5.0 ± 0.1	4.0 ± 0.1[d]	254 ± 15	6.1 ± 0.1[d]	53 ± 2	6.3 ± 0.1	120 ± 10	8.6 ± 0.1[d]		
1,2-Dichloroethane	2.5 ± 0.1	3.7 ± 0.2	73 ± 8	5.4 ± 0.1	32 ± 3	6.4 ± 0.1	82 ± 8	8.8 ± 0.1	3.3 ± 0.1	4.5 ± 0.2

[a] In units of l. mol^{-1}. [b] In units of kcal mol^{-1}. [c] Calculated from the *E* and *C* parameters.[2] [d] From ref 1.

undergoes specific interactions with the solvent carbon tetrachloride, and this causes the enthalpies of formation of pyridine–acid adducts to be low in this solvent. Recently, however, there have been reports contradicting this. Duer and Bertrand[5] have taken the position that hydrogen bonding of phenols to carbon tetrachloride is the main source of difference in the enthalpies of formation of adducts between pyridine and phenols when measured in CCl_4 and C_6H_{12}. The existence of a significant hydrogen-bonding interaction between carbon tetrachloride and hydroxy groups has also been claimed by Fletcher and coworkers.[6] Arnett, *et al.*,[7] have chosen to ignore the significance of pyridine–carbon tetrachloride interaction because of the similarity of the enthalpies measured in carbon tetrachloride and in pure pyridine.

It is the purpose of this report to provide further support for our long-standing opinion and that of others[8] that in carbon tetrachloride there is a significant decrease in the enthalpy of adduct formation with the donor pyridine because of interaction between pyridine and carbon tetrachloride. We also will show that there is no significant specific interaction (*i.e.*, the interaction is less than 0.2 kcal mol^{-1}) between phenols and carbon tetrachloride.

The data collected in this study permit a detailed analysis of the proposal by Christian, *et al.*,[9–11] that the enthalpy of transferring an adduct from solvent I to solvent II, etc., is proportional to the sum of enthalpies of transfer, from solvents I to II, etc., for the acid and the base regardless of whether or not specific interactions exist. It can be shown for the systems described here that our ESP (elimination of solvation procedure) assumption that solvation of the complex minus that of the analogous base, for a whole series of bases in a given solvent remains constant, provides a more accurate model for predicting enthalpies in polar solvents if one accounts for enthalpy contributions from specific interactions of the acid or base with the solvent.

Experimental Section

Purification of Materials. Mallinckrodt Analytical Reagent 1,2-dichloroethane was dried over Linde 4A Molecular Sieves and used without any further purifications. It was noted that if 1,2-dichloroethane was kept over the sieves for more than 3 days, the color of the sieves was changed drastically, indicating a possible interaction. Solvent was kept over the sieves a minimum of 12 hr and a maximum of 36 hr. Aldrich propylene carbonate was dried over the 4A sieves and distilled from barium oxide.

Baker Analyzed Reagent pyridine was kept over barium oxide and fractionally distilled from additional fresh barium oxide. Aldrich *n*-butyl ether was distilled twice from sodium. The purification of all other chemical reagents has been explained elsewhere.[1]

Apparatus and Calculations. The description of the modified calorimeter and the procedure for performing the calorimetric and infrared measurements has been reported.[1,4]

Results

Calorimetric data for *m*-fluorophenol–base systems in various solvents appear immediately following this article in the microfilm edition.[12] The heats of solution of several donors, as well as *m*-fluorophenol, in various solvents has already been reported.[1] The partial molar heats of solution of *m*-fluorophenol and the donors studied here are also reported in a variety of solvents in the microfilm edition.[12]

Table I contains a summary of calorimetric results for the interaction of *m*-fluorophenol with various bases in a range of solvents.

Discussion

As can be seen in Table II, when B is *n*-butyl ether and B′ dimethyl sulfoxide, the enthalpies described by eq 1d′ and 1e′ in CCl_4, $o\text{-}C_6H_4Cl_2$, and $1,2\text{-}Cl_2C_2H_4$ are −1.0 ± 0.2 kcal mol^{-1} in all three cases. When similar reactions are written for *n*-butyl ether being displaced by ethyl acetate (eq 1j′, 1k′, and 1l′ in the above-mentioned solvents), the result is 0.9 ± 0.1 kcal mol^{-1}. The only discrepancy occurs when cyclohexane is the solvent (eq 1i′) and the reason for this will be discussed later.

In an earlier report,[1] we had pointed out that ESP works only in the absence of specific interaction be-

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(5) W. C. Duer and G. L. Bertrand, *J. Amer. Chem. Soc.*, 92, 2587 (1970).

(6) (a) A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, 71, 3742 (1967); (b) A. N. Fletcher, *ibid.*, 73, 2217 (1969).

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(8) L. Sacconi, P. Paolitti, and M. Campolini, *ibid.*, 82, 3828 (1960); (b) K. W. Marconi and D. N. Travers, *Trans. Faraday Soc.*, 62, 2063 (1966); (c) A. D. Sherry and K. F. Purcell, *J. Amer. Chem. Soc.*, 92, 6368 (1970).

(9) S. D. Christian, *J. Phys. Chem.*, 70, 3376 (1966).

(10) J. Grundnes and S. D. Christian, *Acta Chem. Scand.*, 23, 3583 (1969).

(11) S. D. Christian and E. E. Tucker, *J. Phys. Chem.*, 74, 214 (1970).

(12) Colorimetric data and the heats of solution will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6877. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche. The values reported in the third column for the total solution volume represent the total volume of the acid, base, and the solvent which, in each case, is specified in parentheses. The experimental quantity *H′* is the total heat evolved, corrected for the heat of solution of the added reagent, at the corresponding concentration.

Table II. Summary of the Enthalpy of the Reactions for AB + B′ ⟶ AB′ + B Type Interactions

Eq no.	Solvent	AB + B′ ⟶ AB′ + B′	ΔH^b	Ref
1a[a]	C_6H_{12}	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + (C_2H_5)_3N$	1.4	
1b	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + C_6H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + (C_2H_5)_3N$	2.4	
1c	C_6H_6	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + (C_2H_5)_3N$	2.3	
1d	1,2-$C_2H_4Cl_2$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + (C_2H_5)_3N$	2.4	
1e	C_6H_{12}	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $(C_2H_5)_3N$	3.1	
1f[a]	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $(C_2H_5)_3N$	4.6	1
1g[a]	C_6H_6	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $(C_2H_5)_3N$	4.6	1
1h	1,2-$C_2H_4Cl_2$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $(C_2H_5)_3N$	5.1	
1i[a]	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $(C_2H_5)_3N$	2.6	1
1j[a]	C_6H_6	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $(C_2H_5)_3N$	2.5	1
1k	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot(C_2H_5)_3N$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $(C_2H_5)_3N$	3.4	
1l	CCl_4	*m*-F-$C_6H_4OH\cdot$DMSO + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + DMSO	−0.3	
1m	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot$DMSO + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + DMSO	−0.2	
1n	C_6H_6	*m*-F-$C_6H_4OH\cdot$DMSO + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + DMSO	−0.2	
1o	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot$DMSO + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + DMSO	−1.0	
1p	CCl_4	*m*-F-$C_6H_4OH\cdot$DMSO + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + DMSO	2.0	1
1q	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot$DMSO + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + DMSO	2.0	1
1r	C_6H_6	*m*-F-$C_6H_4OH\cdot$DMSO + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + DMSO	2.1	1
1s	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot$DMSO + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + DMSO	1.7	
1t	C_6H_{12}	*m*-F-$C_6H_4OH\cdot$EtOAc + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + EtOAc	−1.7	
1u	CCl_4	*m*-F-$C_6H_4OH\cdot$EtOAc + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + EtOAc	−2.3	
1v	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot$EtOAc + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + EtOAc	−2.2	
1w	C_6H_6	*m*-F-$C_6H_4OH\cdot$EtOAc + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + EtOAc	−2.3	
1x	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot$EtOAc + C_5H_5N ⟶ *m*-F-$C_6H_4OH\cdot C_5H_5N$ + EtOAc	−2.7	
1y	C_6H_{12}	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + [CH_3(CH_2)_3]_2O$	−1.9	
1z	CCl_4	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + [CH_3(CH_2)_3]_2O$	−1.5	
1a′	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + [CH_3(CH_2)_3]_2O$	−1.3	
1b′	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + C_5H_5N \longrightarrow$ *m*-F-$C_6H_4OH\cdot C_5H_5N + [CH_3(CH_2)_3]_2O$	−1.9	
1c′[a]	CCl_4	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $[CH_3(CH_2)_3]_2O$	−1.2	
1d′[a]	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $[CH_3(CH_2)_3]_2O$	−1.0	
1e′	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + DMSO ⟶ *m*-F-$C_6H_4OH\cdot$DMSO + $[CH_3(CH_2)_3]_2O$	−0.9	
1f′	C_6H_{12}	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + (C_2H_5)_3N \longrightarrow$ *m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + [CH_3(CH_2)_3]_2O$	−3.3	
1g′	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + (C_2H_5)_3N \longrightarrow$ *m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + [CH_3(CH_2)_3]_2O$	−3.6	
1h′	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O + (C_2H_5)_3N \longrightarrow$ *m*-F-$C_6H_4OH\cdot(C_2H_5)_3N + [CH_3(CH_2)_3]_2O$	−4.3	
1i′	C_6H_{12}	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $[CH_3(CH_2)_3]_2O$	−0.2	
1j′	CCl_4	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $[CH_3(CH_2)_3]_2O$	0.8	
1k′	*o*-$Cl_2C_6H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $[CH_3(CH_2)_3]_2O$	1.0	
1l′	1,2-$Cl_2C_2H_4$	*m*-F-$C_6H_4OH\cdot[CH_3(CH_2)_3]_2O$ + EtOAc ⟶ *m*-F-$C_6H_4OH\cdot$EtOAc + $[CH_3(CH_2)_3]_2O$	0.8	

[a] Displacement reactions felt to be solvation free (*vide infra*). [b] In kcal mol^{-1}.

tween the solvent and the base. If, however, there are interactions other than the nonspecific ones between the donor B′ and the solvent, then the enthalpy of formation will be more positive (or less negative) when this complex has to be broken to form the B′–phenol complex. Many of the discrepancies in Table II can be explained in terms of the specific interaction of the donors with the solvents; *vide infra*.

On the Question of Phenol Complexing to CCl_4. Pyridine undergoes specific interactions with a variety of nonpolar or weakly basic solvents. The enthalpy of interaction of pyridine with *m*-fluorophenol measured in CCl_4 is ~0.9 kcal mol^{-1} less than in cyclohexane (Table I). Furthermore, examination of Table II indicates that pyridine behaves the same in CCl_4 as in the aromatic solvents (*e.g.*, eq 1l, 1m, 1n; 1u, 1v, 1w; 1z, 1a′) but different than in cyclohexane (*e.g.*, eq 1a, 1b, 1c; 1t, 1u, 1v, 1w). In these displacement reactions, the free *m*-fluorophenol has been eliminated, yet a discrepancy of about 1 kcal mol^{-1} exists. Thus, we can conclude that the difference in the enthalpy of adduct formation in cyclohexane and that in CCl_4, C_6H_6, and *o*-$C_6H_4Cl_2$ is accounted for, without recourse to complexation of the *m*-fluorophenol with carbon tetrachloride. This clearly refutes Duer and Bertrand's[5] as well as Fletcher's[6,7] argument that hydrogen bonding of phenol to carbon tetrachloride is the main source of the ~1 kcal mol^{-1} difference in the enthalpies of pyridine–phenol adduct formation measured in CCl_4 and C_6H_{12}.

Specific Complexation of Pyridine by Various Solvents. With hydrogen bonding of phenol to CCl_4 eliminated as the source of the discrepancy, it now remains for us to determine whether or not the enthalpy measured in cyclohexane or that measured in the other solvents is the solvation energy minimized enthalpy. This is the essence of our differences with Arnett, *et al.*[7] Before addressing ourselves to this question, we shall first examine the behavior of other donors in CCl_4 and cyclohexane. We have previously shown that when the polar oxygen donor *N,N*-dimethylacetamide was studied in cyclohexane, the enthalpy determined was much larger than that in CCl_4. Furthermore, it was shown that the enthalpy in cyclohexane was close to that measured in the pure polar base as solvent. This led to the proposal that aggregation of the free donor and excess donor about the complex in cyclohexane gave rise to a solvation energy contribution comparable to that in the pure solvent. Examination of the data in Table I indicates similar behavior for all the oxygen donors studied, as larger enthalpies are invariably found in cyclohexane compared to CCl_4. Extension of these ideas to pyridine as a donor would lead one to predict that aggregation about the complex by pyridine in cyclohexane would lead to the same enthalpy in pyridine as solvent.

Since this enthalpy is the same as that determined in CCl_4, there is no way to account for the needed solvation contribution to the enthalpy in cyclohexane if we assume the CCl_4 enthalpy to be solvation minimized. A reasonable explanation which accounts for all the data involves our original proposal of a pyridine–CCl_4 complex lowering the enthalpy from that expected. This proposal then requires that there be comparable interactions of pyridine with benzene and *o*-dichlorobenzene. There is support for pyridine–pyridine interactions from matrix isolation studies which showed the existence of very stable pyridine dimers.[13] We also have previously called attention to the spectroscopic evidence for pyridine interacting with CCl_4.[3]

At this time, it is of interest to determine if the reaction of pyridine with aromatic solvents is characteristic of the nitrogen lone pair of amines as is the case for interactions with carbon tetrachloride. The absence of specific interactions involving triethylamine and these aromatic solvents can be illustrated with eq 1a, 1b, and 1c. If we correct 1b and 1c for the -0.9 kcal mol^{-1} interaction of pyridine with these solvents, and we then subtract the pyridine–phenol enthalpy of adduct formation in cyclohexane, we obtain the negative of the enthalpy for the interaction of triethylamine with *m*-fluorophenol in cyclohexane. This indicates the absence of any specific interactions involving triethylamine and these solvents. Furthermore, if the ethyl acetate–phenol enthalpy of adduct formation in CCl_4 is subtracted from eq 1f and 1g, the value obtained is the negative of that for forming the trimethylamine adduct in cyclohexane. This indicates the absence of enthalpy contributions from specific interactions of triethylamine with the aromatic solvents. It also supports the proposal that the enthalpy determined in CCl_4 for the ethyl acetate adduct is solvent minimized. The same general approach can be used in eq 1i and 1j with the DMSO enthalpy in CCl_4 and with *n*-butyl ether in 1f′. Subtraction of these oxygen donor enthalpies in CCl_4 from all pyridine enthalpies in benzene and *o*-dichlorobenzene produces an enthalpy which misses that for the pyridine–phenol adduct in cyclohexane by 0.9 kcal mol^{-1}. Thus, a consistent interpretation of these data is obtained by employing enthalpies measured under conditions we have previously defined.

It is important to have established the correct solvent for determining the enthalpy of adduct formation for the pyridine adducts because many of the systems which Arnett, *et al.*,[7] used to dispute a reported enthalpy–infrared frequency shift correlation were based on pyridine type donors. The findings here provide further support for our selection of solvent for the enthalpy data used to establish this relationship for various oxygen and nitrogen donors. It is appropriate at this time to comment on two other donors, anisole and dibenzyl ether, which these authors claim disputes our enthalpy–frequency shift relationship. It is indeed surprising that anisole would be used as a base to check the validity of the enthalpy–frequency shift relationship. It has been clearly shown[14] that anisole forms two complexes with phenol—an n-donor oxygen complex and a π-donor ring complex. The fact that has been overlooked is that the calorimetrically determined ΔH measured in pure base for this system is an equilibrium constant weighed average of the enthalpies of adduct formation for the ring and n-donor site. This enthalpy will, obviously, be lower than that predicted from the frequency shift of the n-donor site. Interestingly enough, these authors report two complexes with dibenzyl ether in their infrared studies and again misinterpret their measured enthalpy and try to compare it with that obtained from a frequency shift for an n-donor site.[15]

1,2-Dichloroethane as a Solvent. One notes in general that the systems studied in the solvent 1,2-dichloroethane do not give the same values for the displacement reaction as those thought to be solvation free (see footnote *a* in Table II). The systems described in eq 1d, 1k, and 1h′ all miss badly. Some insight into the problem can be obtained by evaluating how the enthalpies measured in 1,2-dichloroethane would have to be corrected to get "solvent-free" displacement reactions. There are a large number of solutions to this problem, so only the relative values are meaningful. The enthalpies of adduct formation would have to be made 0.1 kcal mol^{-1} more negative for *n*-butyl ether, 0.3 kcal mol^{-1} for DMSO, and 0.4 kcal mol^{-1} for pyridine if no change is assumed for ethyl acetate. The triethylamine interaction would have to become 0.4 kcal mol^{-1} more positive. It is difficult to find a single factor to account for these discrepancies. The trend does not parallel that expected for an acid–base interaction (hydrogen bonding) with the solvent, for $(C_2H_5)_3N$ is out of line in this regard. We undertook an infrared study of *N*,*N*-dimethylacetamide and 1,2-dichloroethane in CCl_4 and could find no evidence for a hydrogen-bonding interaction. The solvating properties of 1,2-dichloroethane are complicated by the equilibrium between staggered and eclipsed forms. The corrections required above are thus some complicated combination of a varying proportion of these two forms solvating the free donors and complexes such that the enthalpy of solvation of the complex minus the enthalpy of solvation of the free base is not constant as it was shown to be in systems where the ESP procedure works. These results are consistent with a previous study of $SbCl_5$ adducts,[16] in which we stated that 1,2-dichloroethane should be avoided as a solvent for studies of acid–base interaction because of extensive and unpredictable contributions to the enthalpies of adduct formation from solvation.

Estimation of the Magnitude of Solvation. In this and earlier papers,[1,3,17–19] we have taken the general approach of factoring the contributions to solvation

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(15) Professor P. v. R. Schleyer has called our attention to pronounced asymmetry in the infrared spectrum of the phenol–acetone adduct which he attributes to two complexes. With such a weak n-donor oxygen, this is quite reasonable. However, the difference in the peak maxima are within 75 cm^{-1} or 0.6 kcal mol^{-1} of each other. Thus, an average enthalpy is at least within 0.3 kcal mol^{-1} of the n-donor site. Consequently, the equilibrium constant, averaged enthalpy, and average $\Delta\nu_{OH}$ fall on our $-\Delta H$ *vs.* $\Delta\nu_{OH}$ correlation line.

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Table III. Transfer Energies for Acids, ΔH_A, Bases, ΔH_B, and Adducts, ΔH_c, from Solvent I to Solvent II, kcal mol^{-1}

Substance	$CCl_4 \longrightarrow C_6H_{12}$	$CCl_4 \longrightarrow$ *o*-$C_6H_4Cl_2$	$CCl_4 \longrightarrow C_6H_6$	$C_6H_6 \longrightarrow$ *o*-$C_6H_4Cl_2$	$C_6H_{12} \longrightarrow C_6H_6$	$C_6H_{12} \longrightarrow$ *o*-$C_6H_4Cl_2$	$C_6H_{12} \longrightarrow$ 1,2-$C_2H_4Cl_2$	$CCl_4 \longrightarrow$ 1,2-$C_2H_4Cl_2$	*o*-$C_6H_4Cl_2 \longrightarrow$ 1,2-$C_2H_4Cl_2$	$C_6H_6 \longrightarrow$ 1,2-$C_2H_4Cl_2$
m-Fluorophenol	+1.15	−1.14	−2.00	+0.86	−3.15	−2.29	−3.18	−2.03	−0.89	−0.03
DMSO		−1.02	−0.74	−0.28				−2.20	−1.18	−1.46
m-Fluorophenol· DMSO		−1.7	−1.6	0.0				−2.4	−0.8	−0.8
EtOAc	+1.70	−0.16	+0.07	−0.23	−1.63	−1.86	−1.98	−0.28	−0.12	−0.35
m-Fluorophenol· EtOAc	+1.4	−0.8	−0.7	−0.1	−2.1	−2.2	−2.2	−0.8	0.0	−0.01
Pyridine	+1.65	−0.20	−0.36	+0.16	−2.01	−1.85	−2.00	−0.35	−0.15	+0.01
m-Fluorophenol· pyridine	+1.9	−0.7	−1.2	+0.4	−3.1	−2.6	−3.2	−1.3	−0.5	−0.1
Et_3N				−0.73	+0.28	−0.45	+0.31		+0.76	+0.03
m-Fluorophenol· Et_3N				−0.6	−1.7	−2.2	−1.9		+0.4	−0.2
n-Butyl ether	+0.60	0.16				−0.44	+0.61	+1.21	+1.05	
m-Fluorophenol· *n*-butyl ether	+1.2	−0.7				−1.9	−0.6	+0.7	+1.4	

from specific and nonspecific interactions. We have attempted to evaluate the magnitudes of these effects by completing thermodynamic cycles connecting the reaction in polar media to that in poorly solvating media.[1] Recently this approach was criticized[20] because of the difficulty associated with determining thermodynamic data for specific solvent–solute interactions in pure donor or hydrogen-bonding solvents. It should be pointed out that when specific interactions involving a base or acid and the solvent molecule are studied in CCl_4 as solvent and graphically presented by a reported procedure,[21] the data collected in the pure acid molecule as solvent can be combined with that obtained in CCl_4. Good intersections of this curve with the curves for data in CCl_4 support using the thermodynamic data in CCl_4 to estimate specific interactions in the pure donor solvent or hydrogen-bonding solvent. Good intersections often do not result but did in our reported cases.

In place of completing the thermodynamic cycle described above, a different approach for treating solvation effects, that reported earlier by Christian,[9–11] was recommended.[20] It is claimed that by utilizing this approach one can predict thermodynamic data in a range of solvents as long as the specific interactions are not large—large being defined[20] as greater than the hydrogen bonding of CH_2Cl_2 to amides (~2 kcal mol^{-1}) since Christian's approach was proposed[20] for this system. This approach is based on the assumption that the enthalpy, $\Delta H°$, of transferring a solute AB from solvent I to II is given by

$$\underset{I \longrightarrow II}{\Delta H°_{AB}} = \alpha(\underset{I \longrightarrow II}{\Delta H°_A} + \underset{I \longrightarrow II}{\Delta H°_B}) \tag{2}$$

where $\Delta H°_A$ and $\Delta H°_B$ are the enthalpies of transfer from solvents I to II for the acid and base, respectively. The quantity α is a constant for a given acid–base pair which is not strongly dependent upon either the temperature or choice of solvents. It is relatively straightforward to convert[9–11] this to an identical equation involving free energies in which $\Delta H°$ is simply replaced by $\Delta G°$. Much of the reported[9–11] work has involved $\Delta G°$.

In our acid–base studies, we have primarily focused our attention on the enthalpy of adduct formation. The free energy is a more complex quantity to interpret, often showing variation with solvent under conditions where the enthalpy remains unchanged and sometimes giving opposite trends in a series of compounds to those obtained from the enthalpies. The successful correlation of enthalpies in terms of the *E* and *C* parameters[2] has further encouraged us to concentrate on enthalpies of interactions, and we shall use enthalpy data to test the basic assumption upon which Christian's model is based—the cancellation of enthalpies assumed by eq 2. We do not advocate the extension of ESP to free-energy data. The data in Table III can be used to calculate the α values of eq 2 and these are reported in Table IV. Several systems work out such that the enthalpy of transferring the adduct is very low, and α cannot be satisfactorily estimated from such data because of experimental error. All of our α's were evaluated from systems where the transfer enthalpy of the complex, as well as the sum of the transfer enthalpies of the donor and the acceptor, was at least 0.5 kcal mol^{-1}. We have used the α determined in this way along with enthalpies of transfer of A and B (Table III) which are known very accurately to calculate the complex transfer enthalpy, ΔH_c (I → II) (our ΔH_c corresponds to $\Delta H°_{AB}$ of eq 2). These values are reported in Table IV along with the experimental values. Of the 38 systems reported, 16 miss outside of a generous estimate of the precision of ±0.2 kcal mol^{-1}. This is in sharp contrast with our Δk values (deviation from *k*) which are all less than 0.2 kcal mol^{-1}. This is not a strictly valid comparison for we have rejected several systems in our analysis but have done so for a reason. What is most discouraging about the model based on eq 2 is our inability to understand why it misses so badly in some cases. Such understanding would permit rejection of some of the data. For example, why should the transfer energy of the triethylamine complex from benzene to *o*-dichlorobenzene be predicted so poorly? In other instances where the phenol is known to be interacting specifically with one of the solvents, *e.g.*, benzene, and not with the other, *e.g.*, cyclohexane, the transfer

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Table IV. Comparison of the ΔH_c Values Obtained from α with That of the ESP Constant, K

Complex	α_{av}[a]	ΔH_c calcd	Solvent	ΔH_c measd	$\lvert(\Delta H_c)\rvert$[b]	k_{measd}[c]	Δk[d]
m-F-$C_6H_4OH\cdots OS(CH_3)_2$	0.6	−1.3	$CCl_4 \longrightarrow o\text{-}C_6H_4Cl_2$	−1.7	0.4	−0.7	0.0
		−1.6	$CCl_4 \longrightarrow C_6H_6$	−1.6	0.0	−0.9	0.1
		+0.3	$C_6H_6 \longrightarrow o\text{-}C_6H_4Cl_2$	0.0	0.3	+0.3	0.1
		−2.5	$CCl_4 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−2.4	0.1	e	
		−1.2	$o\text{-}C_6H_4Cl_2 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.8	0.4	e	
		−0.9	$C_6H_6 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.8	0.1	e	
m-F-$C_6H_4OH\cdots$EtOAc	0.5	−0.6	$CCl_4 \longrightarrow o\text{-}C_6H_4Cl_2$	−0.8	0.2	−0.6	0.1
		−1.0	$CCl_4 \longrightarrow C_6H_6$	−0.7	0.3	−0.8	0.0
		+0.3	$C_6H_6 \longrightarrow o\text{-}C_6H_4Cl_2$	−0.1	0.4	+0.1	0.1
		−2.1	$C_6H_{12} \longrightarrow o\text{-}C_6H_4Cl_2$	−2.2	0.1	f	
		−2.4	$C_6H_{12} \longrightarrow C_6H_6$	−2.1	0.3	f	
		+1.4	$CCl_4 \longrightarrow C_6H_{12}$	+1.4	0.0	f	
		−2.6	$C_6H_{12} \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−2.2	0.4	e	
		−1.2	$CCl_4 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.8	0.4	e	
		−0.5	$o\text{-}C_6H_4Cl_2 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	0.0	0.5	e	
		−0.2	$C_6H_6 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.1	0.1	e	
m-F-$C_6H_4OH\cdots n$-$(Bu)_2O$	0.6	−0.6	$CCl_4 \longrightarrow o\text{-}C_6H_4Cl_2$	−0.7	0.1	−0.9	0.2
		−1.6	$C_6H_{12} \longrightarrow o\text{-}C_6H_4Cl_2$	−1.9	0.3	−1.5[f]	
		+1.0	$CCl_4 \longrightarrow C_6H_{12}$	+1.2	0.2	+0.6[f]	
		−1.5	$C_6H_{12} \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.6	0.9	e	
		−0.5	$CCl_4 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	+0.7	0.2	e	
		+0.1	$o\text{-}C_5H_4Cl_2 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	+1.4	1.3	e	
m-F-$C_6H_4OH\cdots$py	0.6	−0.8	$CCl_4 \longrightarrow o\text{-}C_6H_4Cl_2$	−0.7	0.1	−0.5	0.2
		−1.4	$CCl_4 \longrightarrow C_6H_6$	−1.2	0.2	−0.8	0.0
		+0.6	$C_6H_6 \longrightarrow o\text{-}C_6H_4Cl_2$	+0.4	0.2	+0.2	0.0
		−3.1	$C_6H_{12} \longrightarrow C_6H_6$	−3.1	0.0	2.0[g]	0.0
		−2.5	$C_6H_{12} \longrightarrow o\text{-}C_6H_4Cl_2$	−2.6	0.1	1.7[g]	0.1
		+1.7	$CCl_4 \longrightarrow C_6H_{12}$	1.9	0.2	1.1[g]	
		−3.1	$C_6H_{12} \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−3.2	0.1	e	
		−1.4	$CCl_4 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−1.3	0.1	e	
		−0.0	$C_6H_6 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.1	0.1	e	
		−0.6	$o\text{-}C_6H_4Cl_2 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.5	0.1	e	
m-F-$C_6H_4OH\cdots Et_3N$	0.68	−1.9	$C_6H_{12} \longrightarrow o\text{-}C_6H_4Cl_2$	−2.2	0.3	−1.8	0.0
		−2.0	$C_6H_{12} \longrightarrow C_6H_6$	−1.7	0.3	−2.0	0.0
		−2.0	$C_6H_{12} \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−1.9	0.1	e	
		+0.1	$C_6H_6 \longrightarrow o\text{-}C_6H_4Cl_2$	−0.6	0.7	+0.1	0.1
		0.0	$C_6H_6 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	−0.2	0.2	e	
		−0.1	$o\text{-}C_6H_4Cl_2 \longrightarrow 1,2\text{-}C_2H_4Cl_2$	+0.4	0.5	e	

[a] α_{av} is determined from only cases in which both ΔH_c and $\Delta H_A + \Delta H_B$ are equal to or greater than 0.5 kcal mol^{-1} because experimental error makes the number meaningless in other cases. [b] The difference between ΔH_c measd and ΔH_c calcd from eq 2. [c] $k_{measd} = \Delta H_c$ measd $- \Delta H_B$ for a given adduct which according to ESP should be constant for all adducts of a given acid for a given pair of solvents. [d] $\Delta k = k_{measd} - k_{av}$ where k_{av} is determined for a given acid and transfer between a pair of solvents for different bases. The k_{av} values for systems in which specific interactions are absent are as follows: $CCl_4 \rightarrow o\text{-}C_6H_4Cl_2$, $k = -0.7$; $CCl_4 \rightarrow C_6H_6$, $k = -0.8$; $C_6H_6 \rightarrow o\text{-}C_6H_4Cl_2$, $k = 0.2$. [e] 1,2-Dichloroethane does not obey ESP (see text). [f] Nonideal system involving an oxygen donor in cyclohexane. [g] Corrected for specific interaction of free pyridine with the solvent of 0.9 kcal mol^{-1}.

energy of the complex is predicted unbelievably well (*e.g.*, the pyridine complex from C_6H_{12} to C_6H_6). In this transfer from $C_6H_{12} \rightarrow C_6H_6$, there are known specific hydrogen-bonding interactions between the aromatic solvent and the phenol that should make the denominator in the α calculation too large by ~2 kcal mol^{-1}. On the other hand, this hydrogen bonding to the solvent should partially cancel in the transfer from o-$C_6H_4Cl_2 \rightarrow C_6H_6$, but α for these transfers with the Et_3N and DMSO adducts is not accurately predicted. When solvent transfers involve o-dichlorobenzene → 1,2-dichloroethane, for n-butyl ether complex, we obtain a ΔH_c which is off by 1.3 kcal mol^{-1}. A similar transfer for the pyridine complex misses by only 0.1 kcal mol^{-1}. Clearly, one cannot rationalize these discrepancies by completely neglecting specific interactions as has been proposed.[20] On the other hand, then, invoking them after α is determined makes many of the systems in Table IV difficult to understand. We conclude that solvation effects cannot be ignored and thus used with confidence if the existence of errors of the order of magntitude of 0.3 kcal or greater cannot be understood and thus anticipated.

In the place of the model based on eq 2 for predicting enthalpies in polar solvents, we propose tentatively an approach which is suggested by the ESP reported earlier.[1] In order to predict enthalpies of interaction of different bases with a given acid in a polar solvent, the solvents selected should be basic ones which do not undergo specific interactions with the bases to be studied. For a given acid in a given solvent, it has been shown for several systems that

$$-\Delta H \text{ (poorly solvating media)} = -\Delta H \text{ (weakly polar solvent)} + S$$

The constant S which is a measure of the difference between the enthalpy measured in that solvent and the one in an inert media[1] can be determined. If the enthalpy, for a given donor, in a nonpolar solvent is known or can be predicted from the E and C correlation, the constant, S, derived from the above type study in the polar solvent with a limited number of bases can be used to predict the enthalpy in the polar solvent for the given donors. No more measurements are required in this approach than by use of eq 2. The constant S must be determined for every acid in every solvent but then can be used for many different bases. The constant α must be determined for each acid–base pair and then reportedly can be used in many solvents. If the acid is to be varied in our procedure, acidic solvents which do not undergo specific interactions with the acid can be used with the base held constant. It should be emphasized that we make no claims for using our model to predict solvent effects on free energies. Furthermore, we anticipate it will fail when data in cyclohexane are employed if the adducts, acceptors, and/or donors are so polar that they are extensively associated in this solvent but not in the others that they are transferred to. Furthermore, our approach should not be employed when the adduct formed is itself a Lewis base that can undergo specific hydrogen bonding interactions with the solvent being employed. For these reasons, we have not considered the system $(CH_3)_3NSO_2$, which has been extensively studied.[10] These oxygens are expected to be at least as basic as those in an organic sulfone[22] and the adduct may be extensively associated in cyclohexane.

It would be of interest to apply eq 2 to those systems which we have considered ideal as far as the absence of specific interactions are concerned. The test of eq 2 is obtained by having data on a given adduct in widely different solvents. Since the test of ESP involves widely different bases in a given solvent, our effort has been directed along these latter lines and our data do not provide a good test of eq 2. Clearly, one must avoid systems which involve specific interactions in solving eq 2 for α. Otherwise, these complications get absorbed by the α value along with other effects making the interpretation of the α values difficult.

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Sterically Indifferent Triplet Energy Transfer[1]

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Abstract: Stern–Volmer $k_q\tau$ values for 2,5-dimethyl-2,4-hexadiene or 2-chloronaphthalene quenching of the type-II reactions of α,α-dimethylvalerophenone and for pyrene quenching of β,β-dimethyl-α-ketobutyrophenone show the same dependence on solvent viscosity as previously observed for the sterically unhindered valerophenone. This observation of "diffusion-controlled" quenching indicates that *tert*-alkyl groups do not significantly hinder energy transfer from carbonyl compounds. Comparison of these results with others in the literature suggests that the interaction distance between donor and acceptor in solution is on the order of 4 Å, long enough to preclude large steric effects.

The subject of steric hindrance in triplet energy transfer needs clarification. Hammond and his coworkers have concluded in several papers[3–6] that such steric hindrance can be important, presumably because of a decrease in the orbital overlap necessary for exchange interactions.[7] Nonetheless, several workers have performed standard Stern–Volmer quenching experiments in order to determine the excited state lifetimes of *tert*-alkyl ketones[8–10] and have decided against the possibility of steric hindrance by assuming "diffusion-controlled" rate constants for energy transfer. Since *tert*-alkyl ketones are well known to be highly resistant to nucleophilic attack on their carbonyl groups, conventional intuition added to Hammond's earlier conclusions surely would have predicted steric hindrance to energy transfer involving *tert*-alkyl ketones.

Since we also were interested in the photochemistry of some *tert*-alkyl ketones,[11] as well as in the topic of energy transfer, we have performed a few simple experiments which demonstrate that exothermic energy transfer from the triplets of *tert*-alkyl ketones remains diffusion controlled.

Results

We have utilized the type-II photocyclizations of α,α-dimethylvalerophenone (**1**)[9b,11] and of 3,3-dimethyl-1-phenyl-1,2-butanedione (**2**)[12] to monitor any steric hindrance to energy transfer. We performed standard quenching studies on the two reactions, using 2-chloronaphthalene and several dienes, particularly 2,5-dimethyl-2,4-hexadiene, to quench **1** and pyrene and anthracene to quench **2**. Linear Stern–Volmer plots

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