not give a straight line. Since the anion is not shielded from the solvent as it was in the earlier study,[4] we anticipate that in the hydrogen-bonding solvents the ion pair would be more dissociated than in a nonhydrogen-bonding solvent with similar dielectric constant. As was shown in a previous report from this laboratory,[8] we would expect specific interaction of the hydrogen-bonding type to occur between chloroform and $(C_6H_5)_3PCoBr_3^-$. According to the relationship[4]

$$\Delta\nu_{H(1)} = \Delta\nu_p N_p$$

(where all the terms have the usual meaning[4]), the hydrogen-bonding solvents could either decrease the fraction of ions paired together or decrease $\Delta\nu_p$ as a result of an increase in interionic distance. Solvent-separated ion pairs would be counted as dissociated by this technique. In ethylene dichloride, another factor would favor a decrease in $\Delta\nu_{H(1)}$. Molecules of this solvent can exist in the gauche and trans forms. This equilibrium is disturbed by the electric field of the ion in favor of the gauche form[24] (polar form) with the resulting increase in the dielectric constant of the solvent medium in the vicinity of an ion in effect causing the bulk dielectric constant to poorly approximate this solvent's dielectric constant.

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[24] Y. H. Inami, H. K. Bodenseh, and J. B. Ramsey, *J. Amer. Chem. Soc.*, 83, 4745 (1961).

A Procedure for Eliminating and Evaluating Solvent Effects on Thermodynamic Data for Donor–Acceptor Interactions

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Abstract: An elimination of solvation procedure (ESP) is reported which, under appropriate conditions, enables one to study donor–acceptor reactions in polar solvents and predict, from these data, an enthalpy of the adduct formation in the gas phase. The method is tested by predicting enthalpies in poorly solvating media from data in polar solvents. The predicted enthalpies are compared with those directly measured in the nonpolar solvent.

In a series of reports from this laboratory,[1,2] we have been concerned with the interpretation and evaluation of the magnitude of donor–acceptor interactions as manifested by the enthalpy of adduct formation. Enthalpies determined in poorly solvating media, or the gas phase, have been correlated by eq 1 where C_A, E_A

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

and C_B, E_B are empirically determined parameters referring to acceptor and donor, respectively.[1]

Ideally, gas-phase data free from solvation contributions to the enthalpy are desired for evaluation of donor and acceptor strength. However, the difficulty associated with present techniques for gas-phase measurements prevents accumulation of reasonably accurate or extensive amounts of data needed to test the validity of eq 1. Consequently, data obtained in the poorly solvating media (*i.e.*, solvents which do not undergo specific interactions greater than 0.2 kcal mol^{-1} and have dielectric constants equal to or lower than 2.3), carbon tetrachloride and cyclohexane, have been employed. It is well established that solution of gaseous materials in cyclohexane or CCl_4 is accompanied by an interaction between the solvent and solute, *e.g.*, at 21° the enthalpy of vaporization of diethyl ether is 9.39 kcal mol^{-1}, while the apparent molar enthalpy of solution of liquid diethyl ether in CCl_4 is -0.42 kcal mol^{-1}. Combining the above enthalpies leads to an enthalpy of solution of gaseous Et_2O in CCl_4 of -9.81 kcal mol^{-1}. Assuming $(C_2H_5)_2O$ to be monomeric in the gas and in dilute CCl_4 solution, this corresponds to a rather extensive nonspecific solvation energy of diethyl ether by CCl_4. Similar effects are to be expected for the Lewis acid as well as the adduct formed form the interaction of a Lewis acid with the donor diethyl ether. The same type of behavior is also noted in cyclohexane. The only way enthalpy data obtained in poorly solvating media can approach the gas phase is to have a cancellation of solvation terms for products and reactants. Such a cancellation may be possible when solvent–solute interactions are nonspecific and consist mainly of dispersion forces. Under these circumstances, the similarity of the products and reactants would lead one to anticipate a near cancellation of solvation terms. The product is often more polar, so dipole-induced dipole effects would be slightly larger. On the other hand, bond formation reduces the number of solvent molecules that can cluster around the adduct, compared to those around the free acid and base, slightly decreasing the solvation of the adduct compared to the reactants.

Previous reports from this laboratory illustrate the complications which can arise in polar solvents[3,4] or in

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[1] R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, 87, 3571 (1965).

[2] See R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, 93, 6014 (1971), and references therein.

[3] R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *ibid.*, 88, 2717 (1966).

[4] W. Partenheimer, T. D. Epley, and R. S. Drago, *ibid.*, 90, 3886 (1968).

systems in which specific interactions exist, *e.g.*, nitrogen and sulfur donor complexation with CCl_4.[5,6] These studies have led to the generalization that data obtained in methylene chloride, studies involving nitrogen and sulfur donors in CCl_4, and measured enthalpies of very polar donors (such as *N*,*N*-dimethylacetamide) in cyclohexane are not producing results comparable to those expected in the gas phase. Even for the system *N*,*N*-dimethylacetamide in CCl_4, where the average molecular weight is that of a trimer,[4] the data obtained are that of an average trimeric species which could be somewhat different from the results for a monomeric donor in the gas phase. In view of the increased recognition of complications from solvent, it is of considerable importance to investigate in further detail the effect of solvent on the thermodynamic data obtained for acid–base systems. We report here investigations which have led to a procedure for testing the possible cancellation of nonspecific solvation effects in nonpolar and polar solvents. The procedure to be described also has the potential of enabling one to extract data comparable to those obtained in the gas phase from measurements in polar solvents.

We have additional reasons to pursue investigation of solvent effects. Recent attempts to extend our calorimetric studies to new classes of Lewis acids such as transition metal complexes[7] and N–H hydrogen bonding acids,[8] as well as to sulfur[6] and phosphorus donors, have been hampered greatly by the insolubility of compounds in CCl_4 or hydrocarbon solvents. The present study was initiated to test a procedure for converting data obtained in polar solvents to that expected in poorly solvating media. Basically, the idea is to investigate the displacement reaction

$$AB + B' \longrightarrow AB' + B \qquad (2)$$

(where A is the Lewis acid and B and B′ the Lewis bases) in weakly basic, polar solvents. Since the acid remains fully complexed, it cannot undergo specific interactions with the basic solvent. If the interactions of adducts and bases are nonspecific, the solvation of products and reactants might be expected to cancel. On a molecular level, this can be justified if the active site on B undergoes similar nonspecific interactions with the solvent as the active site on B′. Assuming no changes in packing around the remainder of the B or B′ in the adduct or free state and no change around the coordinated phenol, all the other nearest-neighbor interactions should cancel. If the gas phase enthalpy for the reaction

$$A(g) + B(g) \longrightarrow AB(g) \qquad (3)$$

is known, this can be algebraically added to eq 2, producing the gas-phase enthalpy for the reaction

$$B'(g) + A(g) \longrightarrow AB'(g) \qquad (4)$$

if there are no net solvation contributions to eq 2. In this way, a whole series of Lewis bases B′ insoluble in CCl_4 or cyclohexane could be studied in polar solvents, combined with the enthalpy of adduct formation of B in this polar solvent to produce a solvation-free enthalpy (eq 2). Combination of eq 2 with 3 would then lead to the gas-phase equivalent of adduct formation with B′ by eq 4. Similarly, if one wished to investigate a series of different acids, the reaction

$$AB + A' \longrightarrow A'B + A \qquad (5)$$

Table I. Calorimetric Data for *m*-Fluorophenol–Base Systems at 24°

Acid concn, *M*	Base concn, *M*	Total solution vol, ml	Measured heat, cal
m-Fluorophenol	Ethyl acetate	(Carbon tetrachloride)	H′
0.01701	0.5311	110.1	8.788
0.009395	0.6191	110.1	4.980
0.008953	0.2104	110.1	4.137
0.009756	0.1679	110.1	4.210
0.01152	0.1014	110.1	4.293
0.01052	0.05142	110.1	2.844
0.01043	0.05275	110.1	2.795
m-Fluorophenol	Ethyl acetate	(*o*-Dichlorobenzene)	H′
0.01183	0.4090	110.1	4.900
0.01140	0.3153	110.1	4.513
0.01234	0.1541	110.1	3.830
0.01174	0.1102	110.1	3.115
0.01136	0.07560	110.1	2.514
0.01106	0.6065	110.1	4.964
0.01188	0.7140	110.1	5.352
0.01078	1.0414	110.1	5.159
m-Fluorophenol	Ethyl acetate	(Benzene)	H′
0.01464	1.0264	110.1	5.424
0.01366	0.8055	110.1	4.816
0.01618	0.4039	110.1	4.735
0.01535	0.1068	110.1	2.306
0.01203	0.07575	110.1	1.418
m-Fluorophenol	Dimethyl sulfoxide	(Carbon tetrachloride)	H′
0.01735	0.03492	110.2	12.307
0.01535	0.02042	110.1	9.611
0.01645	0.03621	110.2	12.038
0.01396	0.05619	110.4	10.467
m-Fluorophenol	Dimethyl sulfoxide	(*o*-Dichlorobenzene)	H′
0.01567	0.02003	110.1	8.431
0.01593	0.01938	110.1	8.630
0.01572	0.02446	110.1	9.192
0.01525	0.02066	110.1	11.091
0.01669	0.06400	110.1	11.612
0.01733	0.1463	110.1	12.664
0.01775	0.1304	110.1	12.811
m-Fluorophenol	Dimethyl sulfoxide	(Benzene)	H′
0.01573	0.02291	110.1	7.856
0.01609	0.02990	110.1	8.737
0.01503	0.04459	110.1	9.047
0.01692	0.06163	110.1	10.551
0.01614	0.06754	110.1	10.068
m-Fluorophenol	Triethylamine	(*o*-Dichlorobenzene)	H′
0.01464	0.02145	110.1	9.766
0.01424	0.06350	110.1	13.048
0.01494	0.1391	110.1	14.629
0.01514	0.2637	110.1	15.032
0.01601	0.5553	110.1	16.180
m-Fluorophenol	Triethylamine	(Benzene)	H′
0.01565	0.02251	110.1	9.070
0.01637	0.03590	110.1	11.358
0.01598	0.06132	110.1	12.752
0.01595	0.1043	110.1	13.758
0.01577	0.1495	110.1	14.015
0.01610	0.3264	110.1	14.839

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

(6) G. C. Vogel and R. S. Drago, *ibid.*, **92**, 3924 (1970).

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

(8) M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 7086 (1970).

Table II. Apparent Molar Heats of Solution

Dimethyl sulfoxide (in carbon tetrachloride)			Dimethyl sulfoxide (in benzene)			Ethyl acetate (in *o*-dichlorobenzene)			Triethylamine (in benzene)		
mmol[a]	H', cal	ΔH, kcal/mol[b]	mmol[a]	H', cal	ΔH, kcal/mol[b]	mmol[a]	H', cal	ΔH, kcal/mol[b]	mmol[a]	H', cal	ΔH, kcal/mol[b]
1.517	2.743	1.808	1.643	1.801	1.096	1.800	−0.223	−0.124	0.0840	0.0454	0.540
3.070	5.441	1.772	1.776	2.039	1.148	6.200	−0.806	−0.130	1.846	0.978	0.530
4.712	7.734	1.641	2.329	2.488	1.068	15.710	−2.184	−0.139	3.236	1.702	0.526
5.745	9.250	1.610	2.509	2.707	1.079	26.410	−3 777	−0.143	4.828	2.525	0.523
6.347	10.021	1.579	5.722	5.596	0.978				6.380	3.171	0.497
6.747	10.120	1.500	6.423	6.686	1.041				7.694	3.793	0.493
			7.034	6.802	0.967						

[a] Number of moles of solute added to 110.0 ml of solvent. [b] The extrapolated value to zero concentration has been reported in Table III.

Table III. Partial Molar Heats of Solution (ΔH_s, kcal mol^{-1}) of Various Compounds in Different Solvents at High Dilution[a]

	Compd			
Solvent	*m*-Fluorophenol	Dimethyl sulfoxide	Ethyl acetate	Triethylamine
Cyclohexane	4.94 ± 0.06		1.74 ± 0.04	0.26 ± 0.04
Carbon tetrachloride	3.79 ± 0.09	1.89 ± 0.03[a]	0.04 ± 0.01	
o-Dichlorobenzene	2.65 ± 0.05	0.87 ± 0.05	−0.12 ± 0.01[a]	−0.19 ± 0.03
Benzene	1.79 ± 0.06	1.15 ± 0.03[a]	0.11 ± 0.01	0.54 ± 0.04[a]

[a] In these cases, the heats of solution were found to be highly dependent upon concentration, and the reported values are obtained by extrapolation of the data in Table II to zero concentration. In all other cases, over the concentration range studied, the heats of solution remained fairly constant.

could be studied in acidic solvents for a series of different acids A′.

In order to test this approach, the enthalpy of the hydrogen bonding acid *m*-fluorophenol with a series of different donors was studied in benzene, *o*-dichlorobenzene, cyclohexane, and carbon tetrachloride. With these data, the enthalpy of interaction of various donors, B′, calculated by eq 4 in different solvents can be compared with that measured directly in CCl_4 or cyclohexane. The first two solvents mentioned above are basic toward *m*-fluorophenol, whereas the last two have been assumed to be noncomplexing. The solvents also vary in polarity. Cyclohexane and carbon tetrachloride have dielectric constants of 2.02 and 2.24 at 20°, compared to the values of 2.28 and 10.40 for benzene and *o*-dichlorobenzene, respectively. Thus, the solvents chosen represent a range of solvating abilities and different donor strengths. The Lewis bases that were studied include the nitrogen donor triethylamine as well as the oxygen donors dimethyl sulfoxide and ethyl acetate.

Experimental Section

Purification of Materials. Baker Analyzed Reagent carbon tetrachloride, Fisher Certified Reagent cyclohexane, Eastman Organic *o*-dichlorobenzene, and Baker Analyzed Reagent benzene were all dried over Linde 4A molecular sieves and used without any further purifications. Baker Analyzed Reagent dimethyl sulfoxide, Aldrich triethylamine, and Fisher Certified Reagent ethyl acetate were purified as previously described.[7–9] Peninsular ChemResearch *m*-fluorophenol was dried over Linde 4-A molecular sieves for 24 hr and then distilled four times under 24 mm of pressure. Each time only the middle fraction was collected.

The purity was checked by gas chromatographic analysis in all cases. All solutions were prepared in nitrogen-filled dry bags using thoroughly dried glassware. The calorimeter cells were dried and flushed with nitrogen prior to use.

Apparatus and Calculations. The description of the modified calorimeter and the procedure for performing the experiments and calculating the results has been reported.[8–10] The infrared measurements were made with a Perkin-Elmer Model 521 spectrophotometer, equipped with sodium chloride optics and cells. All frequency shifts were checked for concentration dependence.[8]

Results

The concentrations and the measured enthalpies are presented in Table I for various donors, with *m*-fluorophenol, in different solvents. The experimental quantity H' is the total heat evolved, corrected for the heat of solution of the added reagent, at the corresponding concentration. The heats of solution of different donors, as well as *m*-fluorophenol, in various solvents, are reported in Tables II and III. These values were obtained over a range of low concentrations and the reported heats of solution have been determined by extrapolation to infinite dilution, if concentration dependence was observed (Table II). Otherwise, the average values have been reported in Table III. In general, the heat of solution of the acid *m*-fluorophenol is more endothermic than that of the individual bases in the corresponding media.

Table IV contains a summary of the calorimetric results for the interaction of *m*-fluorophenol with various bases in different solvents. The calculated uncertainty limits for the enthalpies, in all cases, were less than +0.1 kcal mol^{-1}, and they were rounded off to ±0.1 kcal mol^{-1}.

Prior to this work, the E and C parameters for *m*-fluorophenol were unknown. Using the enthalpy data in Table IV and the set of newly determined base E and C values,[2] the parameters for this acid were calculated to be 4.42 and 0.506 for E_A and C_A, respectively. The enthalpy of interaction of *m*-fluorophenol with triethylamine in cyclohexane was predicted to be −10.0 ± 0.2 kcal mol^{-1} from these parameters and the E_B and C_B values for triethylamine of 0.99 and 11.1, respectively.[1]

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(9) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3921 (1966).

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

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

	Compd					
	Ethyl acetate		Dimethyl sulfoxide		Triethylamine	
Solvent	K, l./mol	$-\Delta H$, kcal/mol	K, l./mol	$-\Delta H$, kcal/mol	K, l./mol	$-\Delta H$, kcal/mol
Cyclohexane						-10.0 ± 0.2[a]
Carbon tetrachloride	19 ± 1	5.2 ± 0.1	470 ± 71	7.2 ± 0.1		
o-Dichlorobenzene	10.3 ± 0.6	4.7 ± 0.1	321 ± 59	6.7 ± 0.1	158 ± 25	9.3 ± 0.1
Benzene	5.0 ± 0.1	4.0 ± 0.1	254 ± 15	6.1 ± 0.1	120 ± 10	8.6 ± 0.1

[a] Calculated from the *E* and *C* parameters, using eq 1.

Table V. Summary of the Enthalpy of the Reactions for AB + B′ → AB′ + B Type Interactions

Equation no.	Solvent	Compd							$-\Delta H$
		AB	+	B′	→	AB′	+	B	
7a	CCl_4	m-F-$C_6H_4OH \cdot$EtOAc	+	DMSO	→	m-F-$C_6H_4OH \cdot$DMSO	+	EtOAc	2.0
7b	o-$Cl_2C_6H_4$	m-F-$C_6H_4OH \cdot$EtOAc	+	DMSO	→	m-F-$C_6H_4OH \cdot$DMSO	+	EtOAc	2.0
7c	C_6H_6	m-F-$C_6H_4OH \cdot$EtOAc	+	DMSO	→	m-F-$C_6H_4OH \cdot$DMSO	+	EtOAc	2.1
7d	o-$Cl_2C_6H_4$	m-F-$C_6H_4OH \cdot$EtOAc	+	$(C_2H_5)_3N$	→	m-F-$C_6H_4OH \cdot (C_2H_5)_3N$	+	EtOAc	4.6
7e	C_6H_6	m-F-$C_6H_4OH \cdot$EtOAc	+	$(C_2H_5)_3N$	→	m-F-$C_6H_4OH \cdot (C_2H_5)_3N$	+	EtOAc	4.6
7f	o-$Cl_2C_6H_4$	m-F-$C_6H_4OH \cdot$DMSO	+	$(C_2H_5)_3N$	→	m-F-$C_6H_4OH \cdot (C_2H_5)_3N$	+	DMSO	2.6
7g	C_6H_6	m-F-$C_6H_4OH \cdot$DMSO	+	$(C_2H_5)_3N$	→	m-F-$C_6H_4OH \cdot (C_2H_5)_3N$	+	DMSO	2.5

Discussion

An Elimination of Solvation Procedure (ESP). Dramatic effects of solvent on thermodynamic data for acid–base systems are observed in the values summarized in Table IV supporting results previously reported from this laboratory.[3-5] Study of oxygen donors in cyclohexane as solvent has been avoided. The experiments reported in this study have been so designed that it is possible to combine the data in Table IV to produce a whole series of displacement reactions analogous to the general eq 2. The following example of ethyl acetate (EtOAc) and dimethyl sulfoxide (DMSO), interacting with *m*-fluorophenol in CCl_4, illustrates the procedure

$$m\text{-F-}C_6H_4OH_{(CCl_4)} + (CH_3)_2SO_{(CCl_4)} \longrightarrow m\text{-F-}C_6H_5OH \cdot OS(CH_3)_{2(CCl_4)} \quad (6a)$$

$$\Delta H = -7.2 \text{ kcal mol}^{-1}$$

$$m\text{-F-}C_6H_4OH_{(CCl_4)} + \text{EtOAc}_{(CCl_4)} \longrightarrow m\text{-F-}C_6H_5OH \cdot \text{EtOAc}_{(CCl_4)} \quad (6b)$$

$$\Delta H = -5.2 \text{ kcal mol}^{-1}$$

Multiplying eq 6b by −1 and adding it to eq 6a yields the desired eq 7a.

$$(CH_3)_2SO_{(CCl_4)} + m\text{-F-}C_6H_4OH \cdot \text{EtOAc}_{(CCl_4)} \longrightarrow \text{EtOAc}_{(CCl_4)} + m\text{-F-}C_6H_4OH \cdot OS(CH_3)_{2(CCl_4)} \quad (7a)$$

$$\Delta H = -2.0 \text{ kcal mol}^{-1}$$

The results of various other acid–base combinations in different solvents can be similarly treated to produce the displacement reactions summarized in Table V. We are now in a position to test whether or not nonspecific solvation contributions to the enthalpy (dispersion, dipole–dipole, etc.) do cancel, in various basic solvents, when the bases and adducts do not undergo specific interactions with the solvents. Should this be the case, the enthalpy for the reaction described by eq 2 will be independent of the solvent and depend only on the acid and base pairs chosen. The data in Table V provide excellent confirmation of these ideas. The first three sets of equations give constant values for a given pair of bases undergoing the displacement reaction independent of the solvents employed. Even though bases as different in polarity as $(C_2H_5)_3N$, $CH_3C(O)OCH_2CH_3$, and $(CH_3)_2SO$ are involved on opposite sides of the equations, in the polar solvent *o*-dichlorobenzene a cancellation of the solvation energies of the products and reactants occurs producing a displacement enthalpy which is independent of solvent. Such a cancellation now enables the use of more polar solvents such as *o*-dichlorobenzene to extend the range of donors which can be studied toward the acid *m*-fluorophenol. If solvation terms cancel, the CCl_4 equivalent enthalpy for a donor, B″, insoluble in CCl_4, will result from the displacement reaction involving B″ and a soluble base such as EtOAc (eq 8). Using this

$$\text{EtOAc} \cdot m\text{-F-}C_6H_4OH + B'' \xrightarrow{o\text{-}Cl_2C_6H_4} B'' \cdot m\text{-F-}C_6H_4OH + \text{EtOAc} \quad \Delta H = x$$

$$\text{EtOAc} + m\text{-F-}C_6H_4OH \xrightarrow{CCl_4} \text{EtOAc} \cdot m\text{-F-}C_6H_4OH \quad \Delta H = y$$

$$m\text{-F-}C_6H_4OH + B'' \xrightarrow{CCl_4} B'' \cdot m\text{-F-}C_6H_4OH \quad \Delta H = x + y \quad (8)$$

technique for the case where B″ = DMSO, then $x = -2.0$ kcal mol^{-1} and $y = -5.2$ kcal mol^{-1}, yielding $\Delta H = 7.2$ kcal mol^{-1}, an enthalpy value exactly the same as the experimental value. The same result is obtained from eq 7c in benzene. Alternatively, subtraction of the enthalpy of adduct formation of DMSO from eq 7b and 7c produces values of −5.2 and −5.1 kcal mol^{-1} for formation of the ethyl acetate adduct as compared to −5.2 kcal mol^{-1} reported in Table IV.

Examination of the data in Table IV reveals that all of the displacement reactions in *o*-dichlorobenzene, which give the same enthalpies as those in CCl_4 or cyclohexane (Table V), consist of donor–acceptor interactions which, when measured in *o*-dichlorobenzene, are 0.5 kcal mol^{-1} "less" than in poorly solvating media. *Thus, if the acid is held constant in a given polar solvent and a series of bases studied, the assumption that solvation contributions to the general eq 2 cancel is identical with the assumption that the enthalpies mea-*

Table VI. Solvent Transfer Energies (ΔH_C, kcal mol^{-1})

Substance	ΔH_C from solvent I to solvent II $CCl_4 \rightarrow C_6H_{12}$	$CCl_4 \rightarrow$ o-$C_6H_4Cl_2$	$CCl_4 \rightarrow C_6H_6$	$C_6H_6 \rightarrow$ o-$C_6H_4Cl_2$	$C_6H_{12} \rightarrow C_6H_6$	$C_6H_{12} \rightarrow$ o-$C_6H_4Cl_2$
m-F-C_6H_4OH	+1.15	−1.14	−2.00	+0.86	−3.15	−2.29
DMSO		−1.02	−0.74	−0.28		
m-F-$C_6H_4OH \cdot$ DMSO		−1.7	−1.6	+0.0		
EtOAc		−0.16	+0.07	−0.23		
m-F-$C_6H_4OH \cdot$ EtOAc		−0.8	−0.7	−0.1		
$(C_2H_5)_3N$				−0.73	0.28	−0.45
m-F-$C_6H_4OH \cdot N(C_2H_5)_3$				−0.5	−1.5	−2.0

sured in the polar solvent will differ by a constant amount from those measured in an inert medium. The important thing is to ascertain when one can assume that solvation contributions to reaction 2 will cancel, *i.e.*, when specific interactions or unusual solvent effects are absent. When reaction 2 is solvation free, the enthalpy in the nonpolar solvent can be estimated by adding a constant to the value in the polar solvent. For the specific case of m-fluorophenol in o-dichlorobenzene, the equation is

$$-\Delta H_{\text{(poorly solvating media)}} = -\Delta H_{(o\text{-}Cl_2C_6H_4)} + 0.5 \quad (9a)$$

Similar equations can be written for benzene.

$$-\Delta H_{\text{(poorly solvating media)}} = -\Delta H_{(C_6H_6)} + 1.2 \quad (9b)$$

In general

$$-\Delta H_{\text{(poorly solvating media)}} = -\Delta H_{\text{(weakly polar solvent)}} + S \quad (9c)$$

It is of interest to ascertain the source of the constants in eq 9. From the data in Tables III and IV, we can solve for the step labeled ΔH_C in the cycle below, *i.e.*, the enthalpy of transferring the adduct from CCl_4 to o-$Cl_2C_6H_4$ (eq 10), where ΔH_A and ΔH_B are the differences between the heats of solution of the corresponding species in the two solvents, and ΔH_E and ΔH_D are the enthalpies of interaction in the respective media. The transfer energies for several species are summarized in Table VI. Examination of the results shown in Table VI reveal that for both the ethyl acetate and DMSO systems, we find the adduct is solvated about −0.6 kcal mol^{-1} more than the base in o-dichlorobenzene. This coupled with the 1.1 kcal mol^{-1} required to desolvate the phenol gives the constant +0.5 kcal mol^{-1} that must be added to obtain the CCl_4 enthalpy from the one in o-dichlorobenzene. In the absence of specific interactions of the donors with solvent, expectation that solvation energies will cancel when eq 2 is written for m-fluorophenol is tantamount to expecting *that compared to CCl_4 all complexes with m-fluorophenol will be solvated by −0.6 kcal mol^{-1} more than the respective donor* in o-dichlorobenzene. An equivalent way of expressing this is to subtract the enthalpy of formation of the ethyl acetate adduct in CCl_4 from that of the DMSO adduct in o-dichlorobenzene and subtract the energy associated with the transfer of m-fluorophenol from o-dichlorobenzene to carbon tetrachloride. This gives an enthalpy of −2.6 kcal mol^{-1} for the reaction

$$\begin{tikzcd}
B_{(CCl_4)} \arrow[d, "\Delta H_B"] & + & m\text{-F-}C_6H_4OH_{(CCl_4)} \arrow[r, "\Delta H_E"] \arrow[d, "\Delta H_A"] & B\cdot m\text{-F-}C_6H_4OH_{(CCl_4)} \arrow[d, "\Delta H_C"] \\
B_{(Cl_2C_6H_4)} & + & m\text{-F-}C_6H_4OH_{(Cl_2C_6H_4)} \arrow[r, "\Delta H_D"] & B\cdot m\text{-F-}C_6H_4OH_{(Cl_2C_6H_4)}
\end{tikzcd} \quad (10)$$

$$\Delta H_C = -\Delta H_E + \Delta H_A + \Delta H_B + \Delta H_D$$

$$(CH_3)_2SO_{(C_6H_4Cl_2)} + FC_6H_4OH\cdot EtOAc_{(CCl_4)} \longrightarrow (CH_3)_2SO\cdot HOC_6H_4F_{(C_6H_4Cl_2)} + EtOAc_{(CCl_4)}$$

This enthalpy is 0.6 kcal mol^{-1} more negative than the one for the analogous reaction in just CCl_4 or $C_6H_4Cl_2$ (Table V), because the difference in complex and base solvation energy is −0.6 kcal mol^{-1} greater in o-dichlorobenzene than in CCl_4.

In the case of benzene as the solvent, both of the donors are solvated less than in o-dichlorobenzene, while the adducts have similar solvation energies in both solvents. However, solvation of both complexes relative to the free donors is −0.8 kcal mol^{-1} and the main contributions to the larger constant needed to correct benzene data to that in CCl_4 arises from a stronger specific interaction of the phenol with benzene than with o-dichlorobenzene. Thus, the key feature required for cancellation of solvent effects for a reaction similar to (2) is a constant difference in the solvation energy of all donors and the analogous complexes in a given solvent. That is, the solvation energy associated with transferring any complex from solvent I to solvent II, $\Delta H_{C(\text{I to II})}$, minus that for transferring the analogous donor, $\Delta H_{B(\text{I to II})}$, is a constant, k, independent of the complex–donor pair and dependent upon the acid and the solvent.

If ESP can be shown to have general applicability, this should greatly enhance the value of the data determined in polar solvents and increase our understanding of solvation effects and solvent selection for synthesis. Our only claim on the basis of the data now available is that the initial results are encouraging, but a wide range of systems must be examined to ascertain the validity and/or any additional limitations of the ESP.

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