are, for example

$$\mathrm{Fe(H_2O)_6^{2+}\ (t_{2g}^4e_g^2) + Ru(bipy)_3^{3+}\ (t_{2g}^5) \longrightarrow Fe(H_2O)_6^{3+}\ (t_{2g}^3e_g^2) + Ru(bipy)_3^{2+}\ (t_{2g}^6)}$$

The metal π orbitals of d origin are labeled as t_{2g}, even though the symmetries of the chelated complexes are lower than octahedral. The molecular radii of the chelated complexes are large (6–8 Å).[28] If in the activated complex for electron transfer $Fe(H_2O)_6^{2+}$ is constrained to remain on the periphery of the chelate complex, overlap between d orbitals on the two metal centers may be weak leading to nonadiabatic electron transfer.

It has been suggested that polypyridine ligands may be good "conducting ligands" for electron transfer[41] since their metal complexes characteristically undergo rapid electron transfer. However, as Linck has pointed out[5] rapid electron transfer may occur because ligands like the polypyridines tend to make the two valence states involved in electron transfer more alike by π bonding and not because they provide a low-lying path for electron conduction between metal centers. π and π^* orbitals, basically ligand in character but extensively mixed with metal π-type orbitals, do exist on the peripheries of the complexes;[42,43] however, these orbitals may not provide a useful path for electron transfer into the metal center. Evidence on this point comes from the chemi- and photoluminescence properties of $Ru(bipy)_3^{2+}$ in solution.[44–46] Emission is observed from the lowest charge transfer triplet state (^{3}d–π^*) at ~17.8 kK, essentially independent of the exciting wave length.[46] The observed phosphorescence can be viewed as accompanying intramolecular electron transfer where the phosphorescence lifetime (~0.7

$$^3\mathrm{d}\text{–}\pi^*(t_{2g}^5\pi^*) \longrightarrow {}^1\mathrm{d}\text{–}\mathrm{d}(\mathrm{t}_{2g}^6) + h\nu$$

μsec in room temperature aqueous solution[45]) gives an upper limit on the rate of electron transfer. The same excited state can be reached chemically by reducing $Ru(bipy)_3^{3+}$ with hydrazine in aqueous solution[47] or by $Ru(bipy)_3^{+}$ in acetonitrile.[48] Conceptually the chemiluminescent reactions are very similar to oxidation–reduction reactions involving pentaamminecobalt(III) where ligand-reduced radical anion intermediates have been postulated.[49,50] It is important to note that in the chemiluminescent reactions, electron transfer occurs to ligand π^* orbitals and not through them to metal d orbitals, even though reduction at the metal is far more favorable thermodynamically. For a reductant like $Fe(H_2O)_6^{2+}$, where net reduction of the ligand is not possible thermodynamically, it may also be true that overlap with a π^* (ligand) orbital does not lead to efficient electron transfer to the metal d orbitals in the lifetime of a collision complex. Direct overlap between d orbitals may be a necessary feature of such reactions. The importance of specific chemical interactions with t_{2g} orbitals in the chemistry of ruthenium–ammine complexes has been suggested by Ford and Taube.[51]

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Eliminating Solvation Contributions to the Enthalpy of Adduct Formation in Weakly Polar, Acidic Solvents

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Abstract: A previously reported procedure for eliminating solvation contributions to measured enthalpies in basic solvents has been successfully extended to several adducts in the weakly acidic solvent methylene chloride, CH_2Cl_2. For the donor *N,N*-dimethylacetamide, DMA, and the series of Lewis acids reported here, the enthalpy measured in CH_2Cl_2 differs from that in poorly solvating media by a constant amount, 2.0 ± 0.2 kcal mol^{-1}. The origin of this constant difference has been investigated by measuring the transfer energies of the acids, the base, and the adducts from CCl_4 to CH_2Cl_2.

The extension of our studies of donor–acceptor interactions[1] to a broader range of compounds has been limited by solubility considerations and has made it necessary to employ polar solvents as a reaction medium. Solvents of this nature are no longer "poorly solvating" and, in general, do not produce enthalpies

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

which are comparable to gas-phase data. As a result, our recent efforts have been concentrated on the development of procedures for eliminating solvation contributions to the enthalpies of adduct formation in weakly polar solvents.

In a previous publication from this laboratory,[2] we described a procedure (ESP) for eliminating solvation contributions to enthalpies in basic solvents, which worked exceedingly well on the limited number of systems studied. The essential idea is that if one wishes to compare the donor strength of a series of bases (B, B′, etc.), data can be collected in a basic solvent enabling one to calculate the enthalpy for the displacement reaction

$$\mathrm{BA} + \mathrm{B'} \longrightarrow \mathrm{B'A} + \mathrm{B} \qquad (1)$$

In the displacement reaction, the free acid, A, does not come in contact with the basic solvent and if the interactions of BA, B′, B′A, and B with the solvent are all nonspecific and cancel, the solvation free enthalpy for the reaction

$$\mathrm{B'} + \mathrm{A} \longrightarrow \mathrm{BA'} \qquad (2)$$

can be found by subtracting the solvation free enthalpy for the reaction

$$\mathrm{B} + \mathrm{A} \longrightarrow \mathrm{BA} \qquad (3)$$

from the displacement reaction, eq 1. This approach is particularly valuable if B′ is insoluble in poorly solvating solvents.

Since the enthalpy for the displacement reaction shown in eq 1 is small for hydrogen bonding systems, this quantity is not measured directly. It is obtained indirectly by measuring the enthalpy for the reaction of B and B′ with A in the basic polar solvent. These two enthalpies are then subtracted to produce the value for the displacement reaction; *i.e.*, the species, free A, is eliminated from the reaction. The procedure was tested on systems where both B and B′ could be studied in poorly solvating solvents with both hydrogen bonding and transition metal Lewis acids.[3]

The bases ethyl acetate, dimethyl sulfoxide, and triethylamine all obeyed ESP in the solvents benzene and *o*-dichlorobenzene. Subsequently, it was shown that data in 1,2-dichloroethane had large solvation contributions which could not be corrected by ESP. Pyridine type bases were also shown[4] to interact with the basic solvents benzene and *o*-dichlorobenzene contributing to the failure of ESP on these systems, unless the proper correction for this interaction is made.

The next step in the extension of these ideas should be an investigation in which the acid is varied and the base held constant in weakly acidic solvents. Methylene chloride was chosen as the medium, because it is a weakly acidic solvent in which many substances dissolve that are not soluble in cyclohexane, carbon tetrachloride, benzene, or *o*-dichlorobenzene. The Lewis acids selected for this study represent a range of varying acceptor capabilities. Aliphatic, as well as aromatic, hydrogen bonding acids and a transition metal complex form a cross section of acceptor properties. Our effort was simplified by the fact that the enthalpies of interaction of these acids with the donor DMA had already been determined in poorly solvating solvents. The Lewis acids selected for this study include *m*-fluorophenol,[2] *m*-hydroxybenzotrifluoride,[5] trifluoroethanol,[6] hexafluoro-2-propanol,[7] and bis(hexafluoroacetylacetonato)copper(II).[3] The Lewis base DMA was held constant in this study, the essential displacement reaction becoming

$$\mathrm{BA} + \mathrm{A'} \longrightarrow \mathrm{BA'} + \mathrm{A} \qquad (4)$$

Experimental Section

Aldrich *N,N*-dimethylacetamide (DMA) was distilled at 10 mm over fresh BaO. Baker Analyzed Reagent methylene chloride was stored over anhydrous calcium sulfate for a minimum of 24 hr and distilled from fresh calcium hydride at 40° and atmospheric pressure. The middle fraction was collected and used within 48 hr of distillation. Gas chromatographic analysis demonstrated the water content of the solvent to be negligible (about 3 ppm).

Aldrich 1,1,2,2,2-hexfluoro-2-propanol, ($(CF_3)_2CHOH$), Peninsular ChemResearch *m*-fluorophenol (*m*-FC_6H_4OH), *m*-hydroxybenzotrifluoride (*m*-$CF_3C_6H_4OH$), 2,2,2-trifluoroethanol (CF_3CH_2OH), and hexafluoroacetylacetonatocopper(II) were all purified by previously reported procedures.[2,3,5-7]

Apparatus and Calculations. The description of the calorimeter and the procedure for performing the experiments and calculating the results have been previously reported.[5,8]

Results

Concentrations and heats evolved corrected for the heats of solution of the added reagent in CH_2Cl_2 for the DMA–acid systems under investigation are available in the microfilm edition.[9] The enthalpies of solutions of the various acids in CH_2Cl_2 were all endothermic, whereas that of DMA was exothermic. These values are also available in the microfilm edition.

The concentrations of the hydrogen bonding acids were maintained at less than 0.02 *M* to avoid complications brought about by dimerization of the Lewis acids. Solutions of DMA ranged in concentration from 0.01 to 0.80 *M*. When the acid, $Cu(hfac)_2$, was used, the base concentration was always kept less than that of the acid to avoid formation of the 2:1 adduct. Thus, the concentration of the acid was increased to about 0.05 *M*, while the base concentrations were varied from 0.002 to ~0.05 *M*. Pure $Cu(hfacac)_2$ is extremely hygroscopic, but solvation in CH_2Cl_2 inhibits this to the degree that absorption of H_2O by the solution was not visually detected. Nevertheless, all possible precautions were taken to eliminate moisture (a constant flow of dry nitrogen, passed through a column of Aquasorb, was maintained around the dewar flasks).

Table I summarizes the relevant thermodynamic data. Although the computer-supplied standard deviation in the equilibrium constants were generally quite small, an arbitrary value of 10% deviation was felt to be a more accurate estimate of the error in *K*. A

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

[3] M. S. Nozari and R. S. Drago, *Inorg. Chem.*, **11**, 280 (1972).

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[9] Calorimetric data for DMA–acid systems 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-73-3162. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table I. Summary of Thermodynamic Data for DMA–Acid Systems in CCl_4 and CH_2Cl_2 at 24 ± 1°

Acid	Solvent	K, l. mol^{-1}	$-\Delta H$, kcal mol^{-1}
m-F-C_6H_4OH	CCl_4		7.0 ± 0.2[a]
m-F-C_6H_4OH	CH_2Cl_2	79 ± 8	5.1 ± 0.2
m-$CF_3C_6H_4OH$	CCl_4	768 ± 166[b]	7.3 ± 0.2[b]
m-$CF_3C_6H_4OH$	CH_2Cl_2	40 ± 4	5.4 ± 0.2
CF_3CH_2OH	CCl_4		6.4 ± 0.2[c]
CF_3CH_2OH	CH_2Cl_2	16 ± 2	4.4 ± 0.2
$(CF_3)_2CHOH$	CCl_4		8.5 ± 0.2[d]
$(CF_3)_2CHOH$	CH_2Cl_2	47 ± 5	6.3 ± 0.2
Cu(hfac)$_2$	CCl_4	1650 ± 430	8.0 ± 0.2[e]
Cu(hfac)$_2$	CH_2Cl_2	~4000	5.9 ± 0.2

[a] Estimated from the infrared frequency shift. [b] Reference 5. [c] Reference 6. [d] Reference 7. [e] Reference 10.

Table II. Enthalpies of Reaction for AB + A′ → A′B + A Type Interactions in CCl_4 and CH_2Cl_2 at 24°

Eq no.	AB	+	A′	→	A′B	+	A	$-\Delta H_{CCl_4}$, kcal mol^{-1}	$-\Delta H_{CH_2Cl_2}$, kcal mol^{-1}
4a	m-F-$C_6H_4OH\cdot$DMA		m-CF_3–C_6H_4OH		m-CF_3–$C_6H_4OH\cdot$DMA		m-F-C_6H_4OH	0.3	0.3
4b	m-F-$C_6H_4OH\cdot$DMA		CF_3–CH_2OH		CF_3–$CH_2OH\cdot$DMA		m-F-C_6H_4OH	−0.6	−0.7
4c	m-F-$C_6H_4OH\cdot$DMA		$(CF_3)_2CHOH$		$(CF_3)_2CHOH\cdot$DMA		m-F-C_6H_4OH	1.5	1.2
4d	m-F-$C_6H_4OH\cdot$DMA		Cu(hfac)$_2$		Cu(hfac)$_2\cdot$DMA		m-F-C_6H_4OH	1.0	0.8
4e	m-$CF_3C_6H_4OH\cdot$DMA		CF_3CH_2OH		$CF_3CH_2OH\cdot$DMA		m-$CF_3C_6H_4OH$	−0.9	−1.0
4f	m-CF_3–$C_6H_4OH\cdot$DMA		$(CF_3)_2CHOH$		$(CF_3)_2CHOH\cdot$DMA		m-CF_3–C_6H_4OH	1.2	0.9
4g	m-$CF_3C_6H_4OH\cdot$DMA		Cu(hfac)$_2$		Cu(hfac)$_2\cdot$DMA		m-CF_3–C_6H_4OH	0.7	0.5
4h	CF_3–$CH_2OH\cdot$DMA		$(CF_3)_2CHOH$		$(CF_3)_2CHOH\cdot$DMA		CF_3–CH_2OH	2.1	1.9
4i	CF_3–$CH_2OH\cdot$DMA		Cu(hfac)$_2$		Cu(hfac)$_2\cdot$DMA		CF_3–CH_2OH	1.6	1.5
4j	$(CF_3)_2CHOH\cdot$DMA		Cu(hfac)$_2$		Cu(hfac)$_2\cdot$DMA		$(CF_3)_2CHOH$	−0.5	−0.4

large error was found for the Cu(hfac)$_2$–DMA,[10] as is generally the case for very large equilibrium constants. The error is so large as to make the value of K meaningless, but our main concern is with the enthalpy which becomes very well determined as K approaches infinity.

The computer calculated uncertainty in the enthalpy in all cases was less than 0.1 kcal mol^{-1}; however, other effects (*e.g.*, change in the solvating properties of the solvent as excess base is added) result in our assigning a more realistic error of 0.2 kcal mol^{-1} to the accuracy of the numbers.

Discussion

Elimination of Solvation Procedure (ESP). The primary requirement for our solvation correction procedure is the cancellation of solvation terms in displacement reactions of the type represented by eq 4 in acidic solvents or the ones shown by eq 1 in basic media. In an acidic solvent (eq 4), the base is held constant and the acids (A and A′) are varied. In a basic solvent, the acid is held constant and bases (B and B′) are varied. The constancy of enthalpies for a series of studies represented by eq 1, involving a variety of basic solvents, has been used as support of a cancellation of solvation terms for various systems of donors and acceptors.[2,4] It was further shown that when there is a specific interaction between the solvent and the donor, the solvation terms in eq 1 do not cancel and the enthalpy will not be the same as that in poorly solvating solvents.[4]

In this article, we report the results of our study on the cancellation of the solvation terms in the acidic solvent, CH_2Cl_2, for reactions represented by eq 4. Using the data in Table I, the enthalpies of a series of substitution reaction, similar to eq 4, have been calculated in the solvent CCl_4 and the acidic solvent, CH_2Cl_2

$$m\text{-F-}C_6H_4OH_{(CH_2Cl_2)} + DMA_{(CH_2Cl_2)} \longrightarrow m\text{-F-}C_6H_4OH\cdot DMA_{(CH_2Cl_2)} \quad \Delta H = -5.1 \qquad (5a)$$

$$Cu(hfac)_{2(CH_2Cl_2)} + DMA_{(CH_2Cl_2)} \longrightarrow Cu(hfac)_2\cdot DMA_{(CH_2Cl_2)} \quad \Delta H = -5.9 \qquad (5b)$$

(Table II). The procedure is illustrated for the system in which A and A′ are m-F–C_6H_4OH and Cu(hfac)$_2$, respectively, B is DMA, and the acidic solvent is CH_2Cl_2. Multiplying eq 5a by −1 and adding it to (5b) yields the desired eq 4d which does not contain any free base.

$$m\text{-F-}C_6H_4OH\cdot DMA + Cu(hfac)_2 \xrightarrow{CH_2Cl_2} Cu(hfac)_2\cdot DMA + m\text{-F-}C_6H_4OH \quad \Delta H = -0.8 \qquad (4d)$$

All possible combinations from this study are summarized in Table II. Within the experimental error limit, it appears that the enthalpies of these substitution reactions are independent of whether the solvent is CCl_4 or CH_2Cl_2. As previously shown,[2] the direct implications of such a cancellation require that all enthalpies measured for a DMA–acid system in CH_2Cl_2 will be 2.0 kcal mol^{-1} lower than that in a poorly solvating solvent as long as the acid or complex do not undergo specific interactions with the solvent. In the present case, it is quite possible that CH_2Cl_2 hydrogen bonds to the alcohol oxygen or the hexafluoroacetylacetonate ligands. If this is so, the hydrogen bond strength to these groups must be the same (within ~0.2 kcal mol^{-1}) in the adduct as it is in the free acid. Those acids which have groups attached which are not very basic in the free acid but which accumulate a significant amount of electron density on them in the adduct will not work in our ESP. Boron trifluoride and sulfur dioxide are good candidates for failure of ESP because the fluorines and oxygens, respectively, become quite basic in adducts with strong donors.

We have previously[11] reported data on an acid–base system which fails to obey the ESP relationship presumably for this reason. The enthalpy of formation of the N,N-dimethylacetamide–iodine adduct in CCl_4 is −4.0 kcal mol^{-1}. Accordingly, ESP predicts a value of −2.0 kcal mol^{-1} in CH_2Cl_2 which is in poor agreement with the experimental value of −2.6 kcal mol^{-1}. Alternatively, if the N,N-dimethylacetamide–iodine adduct were incorporated into the systems contained in Table II, they would miss by 0.6 kcal mol^{-1}. The additional −0.6 kcal mol^{-1} observed experimentally is probably

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

(11) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Amer. Chem. Soc.*, **88**, 2717 (1966).

due to a specific interaction of CH_2Cl_2 with the terminal iodine of the complex. In the three-center molecular orbital description of this adduct, the terminal iodine of the adduct is expected to be more basic than the iodine of I_2. Accordingly, if there is hydrogen bonding in the adduct, but not in I_2, the solvation energies will not cancel.

As previously described,[2] ESP provides the basis for a practical procedure of obtaining gas-phase enthalpies. If a given Lewis acid, A, cannot be studied in the gas phase or poorly solvating media, one can determine the enthalpy of the reaction represented by eq 4 in preferably several polar, weakly acidic solvents, such as CH_2Cl_2. A constant enthalpy for the reaction represented by eq 4 in these acidic solvents suggests that the enthalpy is the same as that in a poorly solvating medium (in effect, the constancy suggests one has determined the inert solvent equivalent of the enthalpy for eq 4). The acid A′ is selected so that it can be studied in the gas phase or poorly solvating solvent and the next step involves determination of the enthalpy of the reaction of A′ with the base B in the gas phase (or poorly solvating medium). Subtraction of this enthalpy from that of eq 4 yields the enthalpy of interaction of the acid A′ (insoluble in inert media) with base B in the gas phase or poorly solvating solvent. This procedure opens the door to the study of many acids which are insoluble in the poorly solvating media we have been utilizing to date, but one must be very careful to ensure the absence of specific interactions.

Origin of the Constant Factor. A survey of the thermodynamic data in Table I leads to a critical aspect of the solvent effects study. As mentioned above, the enthalpies of every DMA–acceptor system investigated in CCl_4 were 2.0 ± 0.2 kcal mol^{-1} more endothermic than the corresponding enthalpies in CH_2Cl_2. In general, as long as data for eq 4 are solvation free, any system of Lewis acids with a given Lewis base will have enthalpies of adduct formation which differ by a constant value, when measured in poorly solvating media, and a weakly acidic solvent. In the case of the DMA system, this may be represented by eq 6a (in kcal mol^{-1}).

$$\Delta H_{CCl_4} = \Delta H_{CH_2Cl_2} - 2.0\,(\text{DMA}) \qquad (6a)$$

In general

$$\Delta H_{\text{poorly solvating medium}} = \Delta H_{\text{weakly acidic solvent}} - S'_{\text{base}} \qquad (6)$$

The following thermodynamic cycle aids in understanding the origin of the constant in eq 6 (where ΔH_A, ΔH_B, and ΔH_C represent differences in the enthalpies of solvation from CCl_4 to CH_2Cl_2). This cycle leads to the equation

$$\begin{tikzcd}
A_{(CCl_4)} \arrow[d, "\Delta H_A"] & + & B_{(CCl_4)} \arrow[r, "\Delta H_E"] \arrow[d, "\Delta H_B"] & AB_{(CCl_4)} \arrow[d, "\Delta H_C"] \\
A_{(CH_2Cl_2)} & + & B_{(CH_2Cl_2)} \arrow[r, "\Delta H_D"] & AB_{(CH_2Cl_2)}
\end{tikzcd}$$

$$(\Delta H_E - \Delta H_D) = (\Delta H_A - \Delta H_C) + \Delta H_B \qquad (7)$$

The difference in enthalpies of a reaction in two solvents $(\Delta H_E - \Delta H_D)$ stems from the difference in solvent transfer energies of the base, acid, and adduct. If the enthalpies of interaction of a series of acids are investigated with the same donor in CCl_4 and CH_2Cl_2, ΔH_B will be constant and $(\Delta H_A - \Delta H_C)$ can be evaluated using eq 7. Solvent transfer energies for the acids (ΔH_A) donor (ΔH_B), and 1:1 adducts are presented in Table III. Using the data in Table III, the values for $\Delta H_A - \Delta H_C$, which we shall refer to as k_a', were calculated (Table III). The deviation from the average value of k_a' is also reported. It is significant that in every case the deviation of k_a' from the average value is well within the experimental uncertainties. Thus, the constant in eq 6 arises because every CH_2Cl_2 system investigated differs from the enthalpy measured in CCl_4 by the difference in solvent transfer energy of acid and adduct, k_a', of −0.1 kcal mol^{-1}, and the DMA transfer which amounts to −1.95 kcal mol^{-1}. The constant factor in eq 6 is the algebraic sum of these two values. Since the base is held constant, ESP is a direct result of the constancy of the solvent transfer energies of the Lewis acids and the corresponding adducts formed for a whole series of acids.

Table III. Solvent Transfer Energies of DMA (ΔH_B), Acids (ΔH_A), and 1:1 Adducts (ΔH_C) from CCl_4 to CH_2Cl_2

Species	Solvent transfer energy, kcal mol^{-1}	k_a'[a,b]	$\Delta k_a'$[c]
DMA	−1.95		
m-FC_6H_4OH	−1.49		
m-$FC_6H_4OH \cdot DMA$	−1.5	0.0	0.1
m-$CF_3C_6H_4OH$	−0.9		
m-$CF_3C_6H_4OH \cdot DMA$	−0.9	0.0	0.1
CF_3CH_2OH	−1.7		
$CF_3CH_2OH \cdot DMA$	−1.1	−0.1	0.0
$(CF_3)_2CH_2OH$	−1.9		
$(CF_3)_2CHOH \cdot DMA$	−0.8	−0.3	0.2
$Cu(hfac)_2$	−1.2		
$Cu(hfac)_2 \cdot DMA$	−1.1	−0.1	0.0

[a] $k_a' = \Delta H_A - \Delta H_C$. [b] $k_a'_{(av)} = -0.1$. [c] Δk_a = deviation of individual k_a from $k_{a(av)}$.

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