angle between the CNC and the starting P–N–C(C) planes was increased by steps.

Such calculations have clearly shown that for angles up to ±5°, the fitting of the rotational constants is unaffected. Similar results have been obtained by evaluating ΔP_{cc} for different nonplanar configurations within the error of experimental ΔP_{cc}. A maximum deviation from planarity of 4° has been found. Unfortunately variations of the methyl parameters within the values found by Wollrab[6] for the $HN(CH_3)_2$ molecule yield variations of the same order on ΔP_{cc}, and therefore the present results cannot give any information of a possible departure of the molecule from the semiplanar conformation. This uncertainty could probably be overcome if experimental data for isotopic species like $PF_2N(CH_3)(CD_3)$ were available. However, because of lack of symmetry in the NC_2 group, the spectrum of such a molecule would be made up by the transitions relative to the two possible isomers. Both intensity considerations and the fact that the precalculated spectra of the two isomers show partial overlapping, together with the added complexity due to the vibrational satellites, would make a successful analysis of such a spectrum rather improbable.

Acknowledgments. The authors wish to thank Professor P. Palmieri of this Institute for comments on CNDO results and Professor R. H. Schwendeman of Michigan State University for making available the results on the PF_2NH_2 molecule prior to publication.

An Extension of the *E* and *C* Equation to Evaluate Constant Contributions to a Series of Observed "Enthalpies of Adduct Formation"

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Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received July 11, 1972*

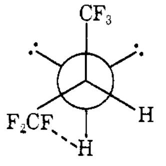
Abstract: When an attempt was made to obtain E_A and C_A numbers for the hydrogen bonding acid 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) by computer-fitting calorimetrically measured enthalpies of interaction of HFIP with various Lewis bases, the fit was much poorer then one would anticipate. The difficulty was believed due to the demonstrated intramolecular hydrogen bonding in HFIP between the hydroxyl proton and the $-CF_3$ fluorine. If one subtracts a constant amount, -1.1 kcal mol^{-1}, to account for the intramolecular interaction, from each of the experimentally measured enthalpies, a suitable fit of the data can be obtained. E_A and C_A parameters of 5.93 and 0.623, respectively, are determined for HFIP. The use of these new parameters, which incorporate the intramolecular interaction, is described. The addition of this constant amount is justified by deriving an *E* and *C* equation to describe competitive equilibria. It is shown that when there is some effect that produces a constant contribution to a series of measured enthalpies toward donors whose E_B and C_B numbers are known, this equation can often be solved for this unknown quantity. The procedure is checked on systems where the constant amount being added can be determined independently. The procedure is invaluable for incorporating systems in which there is intramolecular association into the *E* and *C* scheme. It has the potential of extending this treatment to dimers which must be dissociated to form adducts and whose enthalpy of dissociation is not known. Displacement reactions also fall in the category of reactions containing a constant contribution to measured enthalpies.

In the course of our studies on hydrogen bonding acids, we have had occasion to examine 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, a very interesting acid that has been previously studied extensively as a Lewis acid by Purcell and coworkers.[1,2] Upon attempting to fit their data to our *E* and *C* equation[3]

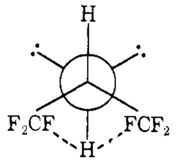
$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

(where E_A and C_A are empirical parameters for acids and E_B and C_B are empirical parameters for bases), we did not get as good a fit as one might expect considering this is a hydrogen bonding acid. We repeated measurements on several of the reported systems, and when we limited the attempted correlation only to our data, the expected fit still did not result.

One of the complications with HFIP is the demonstrated[4] intramolecular hydrogen bonding between the hydroxyl proton and the $-CF_3$ fluorine. In HFIP, two different rotamers are present, a and b. Infrared measurements have been interpreted to indicate that b is the predominant species. The enthalpy of interconversion



a



b

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[1] K. F. Purcell, J. A. Stikeleather, and S. D. Bunk, *J. Mol. Spectrosc.*, 32, 202 (1969).

[2] K. F. Purcell, J. A. Stikeleather, and S. D. Bunk, *J. Amer. Chem. Soc.*, 91, 4019 (1969).

[3] (a) R. S. Drago and B. B. Wayland, *ibid.*, 87, 3571 (1965); (b) R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, 93, 6014 (1971).

[4] J. Murto and A. Kivinen, *Suom. Kemistilehti B*, 40, 14 (1967), and references therein.

Table I. Thermodynamic Data for the System 1,1,1,3,3,3-Hexafluoro-2-propanol–Base

No.	Lewis base (solvent)	$-\Delta H_{\text{exptl}}$, kcal mol^{-1} [c]	$-\Delta H_{\text{calcd}}$, kcal mol^{-1} [b]	K_{exptl}, l. mol^{-1}	Marginal[e] std dev in $-\Delta H$, kcal mol^{-1}	Conditional std dev in $-\Delta H$, kcal mol^{-1}	Marg dev/cond dev	E_B	C_B
1	Ethyl acetate (CCl_4)	5.9 (6.5)[d]	6.01 ± 0.11	37	0.0301	0.0124	2.43	0.975	1.74
2	*N,N*-Dimethylacetamide (CCl_4)	8.2 (8.5)	8.27 ± 0.14	825	0.0342	0.0240	1.42	1.320	2.58
3	Pyridine (*n*-hexane)	9.8 (9.8)	9.54 ± 0.12	731	0.0493	0.0346	1.42	1.165	6.40
4	Quinuclidine (*n*-hexane)	11.3	10.85 ± 0.29	32,322	0.0268	0.0225	1.19	0.704	13.18
5	Tetrahydrothiophene (*n*-hexane)	5.7[a]	6.08 ± 0.12	6.4	0.0457	0.0177	2.58	0.341	7.90
6	Bridged ether (CCl_4)	6.6		86	0.0154	0.00794	1.94		

[a] G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970). [b] These enthalpies are calculated using $E_A = 5.19$ and $C_A = 0.546$. These are the E_A and C_A numbers obtained if no constant is subtracted from the experimental enthalpies to account for intramolecular hydrogen bonding. [c] The heat of solution of HFIP in CCl_4 is endothermic and is 4.78 kcal mol^{-1}. The heat of soultion of HFIP in *n*-hexane is also endothermic and is 5.15 kcal mol^{-1}. [d] Values reported previously.[1,2] [e] The 95% confidence limit in the enthalpy is twice the marginal standard deviation.

is reported to be 0.1 kcal mol^{-1}. The intramolecular hydrogen bonding and rotamer problem caused us to reconsider the application of our *E* and *C* equation to this type of system. In principle, *i.e.*, if accurate enough data can be obtained, we can demonstrate that the enthalpies for intramolecular interactions can be obtained indirectly from enthalpy measurements on acid–base systems by solving the appropriate form of our *E* and *C* equation.

Experimental Section

Purification of Materials. Mallinckrodt Analytical Reagent carbon tetrachloride and Phillips 66 Pure Grade *n*-hexane were dried over Linde 4-A molecular sieves and used without further purifications.

1,1,1,3,3,3-Hexafluoro-2-propanol[2] (Peninsular Chemresearch, Inc.) was purified as previously described.

N,N-Dimethylacetamide (DMA) (Eastman Organic) was twice vacuum distilled at 36 Torr from barium oxide with only the middle fraction being retained in each distillation. The boiling range of the middle fraction of the second distillation was 70–71°. 1-Azabicyclo[2.2.2]octane (quinuclidine) was kindly donated to us by Mallinckrodt Chemical Works, St. Louis, Mo., and was purified by resubliming at ~0.5 Torr and 23° at least three times. Ethyl acetate (Baker Analyzed Reagent) was first dried over Linde 4-A molecular sieves and then was twice distilled over CaH_2 at atmospheric pressure with only the middle fraction being collected in each distillation. The boiling range of the middle fraction for the second distillation was 75.2–75.6°. Pyridine (Baker Analyzed Reagent) was first dried over Linde 4-A molecular sieves and then distilled over CaH_2 at atmospheric pressure. The boiling range of the middle cut taken was 112.0–112.5°. 7-Oxabicyclo[2.2.1]heptane (bridged ether) (Chemical Samples Co.) was first dried overnight over calcium hydride. It was then twice distilled from CaH_2 at atmospheric pressure and only the middle cut was retained in both distillations. The boiling range of the middle cut of the second distillation was 115.5–117.0°.

Because of the hygroscopic nature of the above reagents, all handlings of these materials were performed in a N_2 filled dry bag which had been previously flushed at least twice with dry N_2. The 100-ml round-bottom flasks in which the above reagents were placed were stoppered, wrapped with Parafilm to prevent evaporation and contamination, and stored in a calcium chloride filled desiccator.

Calorimetry. The description of the modified calorimeter and the procedure for performing the experiments and calculating the results have been reported.[5,6] The calorimeter cells and all other glassware used for the calorimetry experiments were dried and flushed with dry nitrogen prior to use. The experiment was performed in such a way that six Lewis base solutions of approximately 0.02, 0.06, 0.10, 0.14, 0.18, and 0.22 *M* were used to fill the 100-ml calorimeter cells. Into each filled cell one injection (~0.1840 ml) of pure 1,1,1,3,3,3-hexafluoro-2-propanol was made. The solvent used in each experiment depended on the Lewis base employed. With pyridine and, quinuclidine, *n*-hexane was used, while with ethyl acetate, *N,N*-dimethylacetamide, and bridged ether, carbon tetrachloride was used.

Results

The thermodynamic data obtained in these studies are summarized in Table I. The experimental data appear immediately following this article in the microfilm edition of this journal.[7] Also reported in Table I is the ratio of the marginal to the conditional standard deviation which we have previously described[8] as a criteria for expressing the uniqueness of the determination of *K* and ΔH. A low ratio ensures that the simultaneous equations which are being solved have a different functional dependence on the two quantities (in this case *K* and ΔH) being solved for.

Discussion

As can be seen from the data in Table I, the agreement between calculated and observed enthalpies is not within the 0.1 kcal mol^{-1} we have come to expect[8b] for good data on hydrogen bonding systems. It was felt that complications arising from intramolecular hydrogen bonding existed. If this is the case, one can immediately eliminate as the source of error in the fit the possibility that the proton–fluorine interaction decreases in direct proportion to the strength of the new donor–hydrogen bond that is formed. Such an effect would be comparable to the usual acid reorganization energies[9] that exist in almost all of the acid–base adducts in the *E* and *C* correlation and the *E* and *C* parameters should be capable of accommodating this effect.

When the hydrogen bond to the fluorine is completely broken upon adduct formation, a conformational change could occur in which the acid fragment of the

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(5) T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967).

(6) M. S. Nozari and R. S. Drago, *ibid.*, 92, 7086 (1970).

(7) The experimental data 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-73-759. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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

(9) D. G. Brown, R. S. Drago, and T. F. Bolles, *ibid.*, **90**, 5706 (1968).

adduct attains the conformation represented in (a). In view of the slight enthalpy of the interconversion of (a) to (b) found in the free acid, this is expected to have an insignificant effect on the measured enthalpy and cannot be the source of the observed discrepancy in the fit.

If the hydrogen bonding interaction of the hydroxyl proton with the fluorine is almost completely broken every time an adduct is formed, all measured enthalpies of interaction of the base with the HFIP hydroxyl group would be less exothermic than the intermolecular interaction by a constant amount; *i.e.*, the constant amount is the enthalpy of the intramolecular interaction. The E and C equation now becomes

$$-\Delta H_{\text{obsd}} = -\Delta H_{\text{AB}} + \Delta H_{\text{C-F}\cdots\text{H}} = (E_{\text{B}} - E_{\text{C-F}})E_{\text{A}} + (C_{\text{B}} - C_{\text{C-F}})C_{\text{A}} \quad (2)$$

In writing eq 2 we have made the tacit assumption that the E and C parameters of HFIP are the same for a linear and bent hydrogen bond. This can be justified because we are making this assumption only to simplify the discussion and do not intend to solve for E_{CF} and C_{CF} parameters. Furthermore the interaction in this case is small.

By using known E_{B} parameters for the bases and trying to fit $-\Delta H_{\text{obsd}}$ to eq 1, we shall assume for simplicity that E_{A} parameters attempt to incorporate the constant $E_{\text{CF}}E_{\text{A}}$ term. If the range of E_{B} values were not very great, it would be possible to accomplish this, *i.e.*, $E_{\text{B}}E_{\text{A}}' \approx E_{\text{B}}E_{\text{A}} + k$ (where the constant is $E_{\text{CF}}E_{\text{A}}$). This cannot be done with a product function, using defined E_{B} values, when the range of E_{B} values for the base employed is large. No constant amount can be added to the true E_{A} term to produce an E_{A}' which always gives the same constant k. Large E_{B} values multiplied by E_{A}' will give a larger k than when small E_{B} values are used. The same arguments would apply to the CC terms. In actual practice, the constant amount, $\Delta H_{\text{C-F}\cdots\text{H}}$, will be distributed over both the EE and CC terms to give the best overall fit of the enthalpies. Consequently, there is considerably more latitude in the way the parameters can be adjusted to pick up the constant enthalpy contribution from the intramolecular interaction. The hope then is, if *accurate data* can be obtained with bases whose E_{B} and C_{B} numbers *are well established,* one can solve for $\Delta H_{\text{C-F}\cdots\text{H}}$, by finding out what value has to be subtracted from $-\Delta H_{\text{obsd}}$ to get an adequate E and C fit. Very accurate data are needed for an approach such as this and it is best to have independent spectroscopic evidence for the existence of the interaction giving rise to the constant enthalpy contribution.

In an attempt to obtain the value of $-\Delta H_{\text{AB}}$ (eq 2) for HFIP adducts which could be meaningfully fit to an E and C equation (eq 1), the intramolecular hydrogen bonding is treated as a systematic error and various estimates of this error were subtracted from the measured $-\Delta H_{\text{obsd}}$ and a fit of the data to eq 1 was attempted. The quality of the fit, indicated by the generalized R factor, $\{\Sigma_n[-\Delta H_{\text{exptl}} - (-\Delta H_{\text{calcd}})]^2/\Sigma_n(-\Delta H_{\text{exptl}})^2\}^{1/2}$, where n refers to the number of bases, is plotted *vs.* the constant value subtracted from the enthalpy in Figure 1. Referring to Figure 1, it can be seen that 1.1 kcal mol^{-1} should be subtracted from the $-\Delta H_{\text{obsd}}$ values to produce a best fit. This analysis assumes that the errors inherent in eq 1 and in the known E_{B} and C_{B} parameters are minimal. In this system we assign this systematic error to the enthalpy of intramolecular hydrogen bonding and it is reasonable that the enthalpy of this interaction should be around -1.1 kcal mol^{-1}. In carrying out this analysis it is critical to employ bases with a wide range of C/E ratios. If an even wider range than that used here could be found, the minimum would probably be more sharply defined.

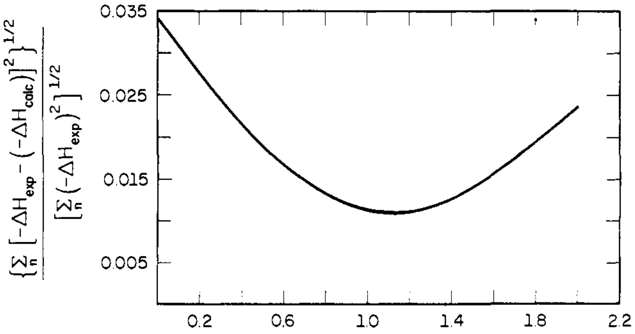

Figure 1. Generalized R factor *vs.* estimate of the magnitude of the C–F$\cdots$H intramolecular interaction.

In order to gain insight into the confidence with which we know this enthalpy of intramolecular hydrogen bonding, a least-squares computer program was developed employing the method reported by Hamilton.[10] Rearranging terms in eq 2 leads to

$$-\Delta H_{\text{obsd}} = E_{\text{A}}E_{\text{B}} + C_{\text{A}}C_{\text{B}} - (E_{\text{A}}E_{\text{C-F}} + C_{\text{A}}C_{\text{C-F}}) \quad (3)$$

or, if one lets $K = -(E_{\text{A}}E_{\text{C-F}} + C_{\text{A}}C_{\text{C-F}})$

$$-\Delta H_{\text{obsd}} = E_{\text{A}}E_{\text{B}} + C_{\text{A}}C_{\text{B}} + K \quad (4)$$

The set of linear equations (4) for several experimental enthalpies may be expressed in matrix notation as

$$-\mathbf{F} = \mathbf{AX} \quad (4a)$$

The **A** matrix is known as the design matrix. Each row of the design matrix, corresponding to an experimental enthalpy, contains an E_{B}, C_{B}, and 1 corresponding to the coefficients of E_{A}, C_{A}, and K of eq 4. The **X** matrix contains the unknowns E_{A}, C_{A}, and K. The **F** matrix contains the experimental enthalpies.

One can solve for the unknowns of the **X** matrix with eq 5.

$$\mathbf{X} = (\mathbf{A}^{\text{T}}\mathbf{A})^{-1}\mathbf{A}^{\text{T}}\mathbf{F} \quad (5)$$

In order to obtain the errors in E_{A}, C_{A}, and K one uses the moment matrix $\hat{\mathbf{M}}_{\text{x}}$. An unbiased estimate of $\hat{\mathbf{M}}_{\text{x}}$ is given by

$$\hat{\mathbf{M}}_{\text{x}} = \frac{\mathbf{V}^{\text{T}}\mathbf{V}}{n-3}(\mathbf{A}^{\text{T}}\mathbf{A})^{-1} \quad (6)$$

where n is the number of experimental enthalpies and **V** is the matrix of differences between the experimental enthalpies and those calculated using the newly found E_{A}, C_{A}, and K parameters. The marginal standard deviations of E_{A}, C_{A}, and K are obtained from the respective square roots of the diagonal elements of $\hat{\mathbf{M}}_{\text{x}}$.

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[10] W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, pp 124–132.

Applying this least-squares treatment to our HFIP model, we found the enthalpy of intramolecular hydrogen bonding to be -1.1 ± 0.3 kcal mol^{-1}. This is the same value which we obtained from the minimum in Figure 1. Indeed, in all the systems reported here the same minimum resulted from the graphical and the computer analyses.

As an additional test of our hypothesis of a "constant correction," we applied both the graphical procedure and the least-squares treatment to two other fluoro alcohols—perfluoro-*tert*-butyl alcohol[11] (PFTB) and trifluoroethanol[12] (TFE)—for which the data summarized in Table II are available in the literature. The intramolecular enthalpy of hydrogen bonding was found to be -1.0 ± 0.4 kcal mol^{-1} for PFTB and -0.1 ± 0.3 kcal mol^{-1} for TFE.

Table II. Enthalpies of Adduct Formation for TFE and PFTB Adducts

	$-\Delta H_{\text{exptl}}{}^{a,c}$ TFE	$-\Delta H_{\text{exptl}}{}^{b,c}$ PFTB
Acetonitrile	4.35 ± 0.2	
Ethyl acetate	4.45 ± 0.2	
Hexamethylphosphoramide	7.67 ± 0.2	
N,*N*-Dimethylformamide	6.10 ± 0.2	
N,*N*-Dimethylacetamide	6.37 ± 0.2	
Dimethyl sulfoxide	6.25 ± 0.2	
Acetone	5.05 ± 0.2	8.0 ± 0.2
Diethyl ether	5.10 ± 0.2	8.3 ± 0.2
Pyridine	7.82 ± 0.2	12.5 ± 0.2
Triethylamine	8.82 ± 0.2	14.3 ± 0.2
Diethyl sulfide	4.7 ± 0.1	7.0 ± 0.2
Tetrahydrothiophene	5.0 ± 0.1	

[a] Reference 12. [b] Reference 11. [c] Enthalpies in units of kcal mol^{-1} in CCl_4 or hexane.

In order to further check and gain confidence in this procedure, the above analysis was extended to data previously reported[3b] for bases interacting with phenol in the solvent CCl_4. By the least-squares treatment an acceptable solution could be obtained if 0.4 ± 0.2 kcal mol^{-1} corrections were made to the experimentally measured enthalpies. It is of interest to point out that in earlier independent studies,[13] we have estimated that any hydrogen bonding of phenol to CCl_4 (which would introduce a systematic error) must be assigned an upper limit of 0.2 kcal mol^{-1} magnitude of interaction. With the data on hand we cannot confidently say that the improvement that would result from subtracting 0.2 kcal mol^{-1} (*i.e.*, making ΔH more negative) would be real. This particular application is questionable since the parameterization of the E_B and C_B values depends heavily on data obtained in CCl_4. The main value of this analysis is to show that the treatment is consistent with the addition of $\sim$0 kcal mol^{-1}.

In an attempt to check this approach further, we decided to examine some data for the hydrogen bonding of *m*-fluorophenol to various donors in the solvents benzene and *o*-dichlorobenzene (ODCB). In the former solvent it was shown that -1.1 kcal mol^{-1} had to be added to the observed enthalpies to produce those measured in the absence of significant solvent contributions while -0.6 kcal mol^{-1} had to be added[13,14] in *o*-dichlorobenzene. Since these are constant contributions to the observed enthalpies which can be described by eq 2, we should be able to independently calculate this quantity by the procedure described above for HFIP. The data employed are summarized in Table III.

Table III. Enthalpies of *m*-Fluorophenol Adduct Formation in Various Solvents

Base	$-\Delta H_{\text{ODCB}}{}^{c}$	$-\Delta H_{\text{benzene}}{}^{c}$	$-\Delta H^{d}$
Ethyl acetate	4.7	4.0	5.2
Dimethyl sulfoxide	6.7	6.1	7.2
Pyridine	7.9[b]	7.3[b]	8.4
Triethylamine	9.3	8.6	9.8
n-Butyl ether	5.7	5.1	6.0
Diethyl sulfide	4.7[a]	4.0[a]	5.2

[a] The predicted solvent correction was added to the value measured in cyclohexane to produce base data for a donor with a large C/E ratio. We could have picked these enthalpies for the set of bases in the last column of Table III and added any constant amount to all of them and then tested our ability to determine this constant. Consequently this assumption is valid. [b] Pyridine has been reported[14] to interact with the solvents benzene and *o*-dichlorobenzene so the value employed here has been corrected for this interaction. [c] Enthalpies in units of kcal mol^{-1}. [d] Enthalpies in units of kcal mol^{-1} in CCl_4 or hexane.

From the results of both the graphical and least-square analyses of the data, we conclude that 1.2 ± 0.2 kcal mol^{-1} would be subtracted from the benzene data and 0.4 ± 0.2 kcal mol^{-1} would be subtracted from the *o*-dichlorobenzene results. These are in good agreement with the reported values of 1.1 and 0.6 kcal mol^{-1}.

It should be pointed out that our method would be of considerable importance when enthalpies for an E and C determination cannot be carried out in "poorly solvating media." A polar solvent which follows ESP[14] may be used to determine the experimental enthalpies. The procedure reported here would then yield the constant correction which gives the gas-phase enthalpy and the appropriate E and C parameters in the inert solvent.

These studies have significant implications in acid–base chemistry for there are many acids, A, which can only be investigated in displacement type reactions, *e.g.*

$$AB + B' \longrightarrow AB' + B \qquad (7)$$

For these systems, the procedure described above has the potential of providing the enthalpy of formation of the AB bond and providing E and C numbers for A even if free A cannot be obtained as, for example, when A is an octahedral transition metal complex that does not form five-coordinate species. It is to be emphasized that very accurate enthalpies employing bases (or acids) with well defined E and C parameters must be used in the procedure.

As a result of these findings we advocate subtracting 1.1 kcal mol^{-1} from all enthalpies measured toward HFIP before using them in eq 1. The corresponding E and C parameters for HFIP are 5.93 and 0.623, respectively. To convert a calculated enthalpy to an observed one, $+1.1$ kcal mol^{-1} would have to be added to

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(11) A. D. Sherry and K. F. Purcell, *J. Amer. Chem. Soc.*, **94**, 1853 (1972).

(12) (a) A. D. Sherry and K. F. Purcell, *ibid.*, **94**, 1848 (1972); (b) A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, 74, 3535 (1970).

(13) M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **94**, 6877 (1972).

(14) R. S. Drago, M. S. Nozari and G. C. Vogel, *ibid.*, **94**, 90 (1972); M. S. Nozari and R. S. Drago, *ibid.*, **94**, 6877 (1972).

Table IV. Enthalpies of Adduct Formation for HFIP Adducts

	$-\Delta H_{\text{exptl}}{}^{a}$	$-\Delta H_{\text{calcd}}{}^{b}$		$-\Delta H_{\text{exptl}}{}^{a}$	$-\Delta H_{\text{calcd}}{}^{b}$
Ethyl acetate	7.5 ± 0.8	6.9 ± 0.1	Pyridine	11.0 ± 0.3	10.9 ± 0.1
Acetonitrile	7.0 ± 0.12	6.1 ± 0.1	Diethyl ether	8.2 ± 0.3	7.8 ± 0.1
Acetone	7.8 ± 0.1	7.3 ± 0.1	Hexamethylphosphoramide	10.9 ± 0.1	11.3 ± 0.2
N,*N*-Dimethylacetamide	9.5 ± 0.4	9.5 ± 0.1	Triethylamine	13.1 ± 2.6	12.8 ± 0.2
Dimethyl sulfoxide	9.8 ± 0.1	9.8 ± 0.1	Tetrahydrofuran	8.0 ± 0.1	8.5 ± 0.1

[a] Experimental values corrected for −1.1 kcal mol^{-1} of intramolecular hydrogen bonding. [b] Calculated using E_A and C_A of 5.93 and 0.623' respectively, and E_B and C_B values from ref 3b, except for HMPA for whch better E and C values of 1.52 and 3.55, respectively, are now available.

the calculated negative value (*i.e.*, it should be made less negative by 1.1 kcal mol^{-1}). Furthermore, it is found that 1.0 kcal mol^{-1} should be subtracted from all experimental enthalpies of PFTB before employing them in eq 1 while for TFE no corrections are necessary. The E and C parameters for PFTB are 7.34 and 0.731, respectively, while those for TFE are 3.88 and 0.451. These E and C parameters should only be used with the E_B and C_B parameters reported in ref 3b. In a recent article, Wiley and Miller[15] failed to realize that since different parameters were fixed to determine the solution to eq 1 in earlier reports,[3a] the parameters from different references cannot be used interchangeably. One must be consistent using only those in ref 3a or 3b with others in the same article. To avoid confusion we recommend disregarding all of the parameters except those in ref 3b.

With these new parameters, it was of interest to check our experimental results and our predicted enthalpies with those reported by Purcell, *et al.*[1,2] We calculated the ratio of marginal to conditional standard deviations from his reported data and found that a wide range of slopes in the K^{-1} *vs.* ΔH plots were generally obtained. However, several of the marginal standard deviations were such as to require large error limits on the data. The results are summarized in Table IV. Two of the systems that miss badly (CH_3CN and THF) are difficult to handle experimentally and could contain systematic errors.

Acknowledgment. The authors acknowledge the generous support of this research by the National Science Foundation and the Paint Research Institute.

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(15) G. R. Wiley and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 3287 (1972).

Solvent Exchange Rates from Iron(III) and Iron(III)–Porphyrin Systems

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Abstract: Solvent exchange rates have been measured by studying the temperature dependence of pmr line widths and chemical shifts for three high-spin iron(III) systems. In *N*,*N*-dimethylformamide (DMF) the $Fe(DMF)_6{}^{3+}$–DMF exchange has $\Delta H^{\ddagger} = 10.1 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -16.5 \pm 3$ cal mol^{-1} deg^{-1}, and the reciprocal of the lifetime of one solvent molecule in the first coordination sphere of iron(III) ($\tau_M{}^{-1}$) is 61 sec^{-1} at 25°. For $\alpha,\beta,\gamma,\delta$-tetraphenylporphineiron(III) in DMF $\Delta H^{\ddagger} = 9.4 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = 3.8 \pm 0.7$ cal mol^{-1} deg^{-1}, and $\tau_M{}^{-1}$ (25°) = 5.4×10^6 sec^{-1}. The $FeTPP^+$ ion in methanol gave $\Delta H^{\ddagger} = 11.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9.0$ cal mol^{-1} deg^{-1}, and $\tau_M{}^{-1}$ (25°) = 3.0×10^6 sec^{-1}; however, the interpretation is subject to some uncertainty and realistic error limits cannot be placed on the parameters. Bulk solvent proton chemical shifts were observed in both $FeTPP^+$ systems and yield values of the hyperfine coupling constants of 3.7×10^6 sec^{-1} for the CH proton in DMF, and 1.4×10^6 sec^{-1} and 1.3×10^6 sec^{-1} for the OH and CH_3 protons, respectively, in methanol.

In previous work it has been noted[1-3] that substitution reactions on a metal ion are considerably faster in the metalloporphyrin complex than in the hexasolvated metal ion. In order to study this rate enhancement further the solvent exchange rates have been measured for iron(III) in *N*,*N*-dimethylformamide (DMF) and for $\alpha,\beta,\gamma,\delta$-tetraphenylporphineiron(III) ($FeTPP^+$) in DMF and methanol.

The general reaction being studied is

$$L_xFeS + S^* \rightleftharpoons L_xFeS^* + S \tag{1}$$

where S and S* are initially coordinated and free solvent molecules and L_x represents any nonexchanging ligand(s). The reaction rate has been followed by studying the temperature dependence of the line widths in the bulk solvent proton nmr spectrum.

Experimental Section

The hexa(*N*,*N*-dimethylformamido)iron(III) perchlorate was prepared by distilling *N*,*N*-dimethylformamide (DMF), under vacuum, into a flask containing hydrated iron(III) perchlorate (Alfa Inor-

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