Comparison of Enthalpies of Hydrogen Bonding Determined by a Gas–Liquid Chromatography Method with Those Obtained by Calorimetric or Frequency Shift Methods

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Abstract: The enthalpies of the hydrogen-bonding interactions between the Lewis base di-*n*-octyl ether and several proton-donor Lewis acids have been determined by calorimetry or infrared frequency shift-enthalpy correlations. These enthalpies compare well with those determined by the Martire-Reidl gas-liquid chromatography method. The average difference between enthalpies determined by the GLC method and the alternative methods is 0.2 kcal/mol.

Several established methods are commonly used for the determination of enthalpies of interaction for acid–base reactions: direct calorimetric measurement, spectroscopic determination of equilibrium constants fitted to the Van't Hoff equation, and infrared frequency shift correlations with enthalpy. More recently, several workers have used gas–liquid chromatography (GLC) for the determination of enthalpy of reaction.[1] One such method developed by Martire and coworkers[2] has been used to determine enthalpies for the hydrogen bonding interaction of proton donors with a nonvolatile ether, thioether, and an amine. Martire has compared equilibrium constants obtained by this pure base method with those obtained by Purnell's additive method[3] and found them to be identical.[4,5] No direct comparison of enthalpies obtained via this GLC method and conventional methods has yet been published, and it has been reported that the equilibrium constants from GLC differ from those obtained by other methods.[5]

In this study we have determined enthalpies for several hydrogen bonding interactions either by calorimetry or infrared frequency shift correlations. These are compared with enthalpies determined by Martire's GLC method. There is good agreement between the GLC method and these other conventional methods for enthalpy determination.

Experimental Section

Materials. Fischer Scientific ACS reagent carbon tetrachloride was dried several days over Linde 4Å molecular sieves prior to use. PCR Incorporated 2,2,2-trifluoroethanol (TFE) was dried over Linde 4Å molecular sieves for GLC work and was fractionally distilled from barium oxide for other determinations. 1,1,1,3,3,3-Hexafluoroisopropyl alcohol (HFIP) was obtained from PCR Incorporated. Other alcohols were Mallinckrodt Analytical Reagent grade. Pyrrole (98%) was obtained from Aldrich Chemical Co. Di-*n*-octyl ether (DOE) and 99% heptadecane were obtained from Chemicals Procurement Laboratories, Inc. Octadecane (OD) (99%) was obtained from the Humphrey Chemical Company. The solid support material used in GLC work was Johns-Manville Chromosorb W, 60–80 mesh, acid washed and DMCS treated.

Gas–Liquid Chromatography. A dual column GLC apparatus was constructed similar to that described by Martire.[2a] However, a Hamilton on column inlet was used, and inlet pressures were measured using a mercury manometer. The stationary phases were *n*-octadecane and di-*n*-octyl ether coated on Chromosorb W. This material was packed into 0.25-in. o.d. copper tubing. Column length was 6.0 ft. Column material was analyzed either by Martire's volatilization method[2a] or by extraction with carbon tetrachloride in a Soxhlet extractor followed by analysis via infrared spectroscopy at 2930 cm^{-1}. Specific retention volumes were calculated from the experimental GLC data using Littlewood's equation.[6]

Correction of specific retention volumes for gas–liquid interfacial effects was done utilizing Martire's equation[2b] in determination of the infinite dilution bulk specific retention volume ($V_g{}^0$) where

$$(V_g{}^0)_d = (V_g{}^0) + kf^{-1} \tag{1}$$

where $(V_g{}^0)_d$ is the specific retention volume extrapolated to infinite dilution to correct for liquid–solid interfacial effects, k is a constant for a given temperature, and f is the percent of liquid phase loading (e.g., 12% w/w OD on chromosorb W).

The GLC equilibrium constant is given by[2a]

$$K = \left[\left(\frac{(V_g{}^0)_B}{(V_g{}^0)_R}\frac{(\tilde{V}_g{}^0)_R}{(\tilde{V}_g{}^0)_B}\right) - 1\right]\frac{(\tilde{V}_g{}^0)_R}{(\tilde{V}_g{}^0)_B}\frac{M_R}{M_B}\frac{1}{[B]} \tag{2}$$

where the *infinite dilution bulk specific retention volumes* ($V_g{}^0$) are as follows: $(V_g{}^0)_B$, acid injected onto base column (DOE); $(V_g{}^0)_R$, acid injected onto reference column (OD); $(\tilde{V}_g{}^0)_R$, volatile alkane injected onto reference column (OD); $(\tilde{V}_g{}^0)_B$, volatile alkane injected onto base column (DOE); and M_R, molecular weight of reference material on column (OD); M_B, molecular weight of base on column (DOE); [B], concentration of base on column (DOE).

Average values for $(\tilde{V}_g{}^0)_R/(\tilde{V}_g{}^0)_B$ and [B] at each temperature have been tabulated by Martire[2b] and were used in the determination of the TFE–DOE enthalpy. These are listed below.

	30°	40°	50°
$(\tilde{V}_g{}^0)_R/(\tilde{V}_g{}^0)_B$	0.987	1.005	1.022
[B], mol l.$^{-1}$	3.299	3.270	3.241

Calorimetry. The calorimetric apparatus has been described previously.[7] In this study our interest is to compare the enthalpies determined by the calorimetric and GLC procedures. The equilibrium constant for the reaction of DOE with TFE in CCl_4 is small necessitating the use of concentrated DOE solutions. Accordingly some procedure is necessary to estimate the nonspecific enthalpy of solution of TFE in solvents of varying composition (i.e., CCl_4–DOE mixtures) in order to calculate an equilibrium constant for the specific reaction. The nonspecific solvation of TFE was estimated by measuring the heat of solution of TFE in ~0.13 mole fraction of *n*-heptadecane in CCl_4. The heat of solution by the acid in other *n*-heptadecane–CCl_4 mixtures was estimated by a linear interpolation of the measured enthalpy of solution of TFE in CCl_4 and that in the 0.13 mole fraction mixture. This heat of solution correction was applied to all H' values measured when TFE was added to CCl_4–DOE mixtures. This was necessary since for systems with low equilibrium constants small errors in the heat of solution of the acid result in large errors in the determined enthalpy.[7] A check of this procedure was made by comparison of the equilibrium constants determined by calorimetric and spectroscopic procedures. The values were found to be the same within experimental error.

Infrared Frequency Shifts. Infrared frequency shifts of the O–H and N–H stretching modes at about 3600 cm^{-1} were measured with a Beckman IR 12 using a matched set of 0.2-mm NaCl solution cells. Initial base concentrations were the same in each cell, varying from about 1.5 to 0.05 M. Frequency shifts were found to be independent of base concentration for the systems studied. All alcohol concentra-

Table I. Calorimetric Data for TFE–DOE

Acid concn, M	Base concn, M	Total vol, ml	Heat measured, cal
0.013 89	0.078 50	105.1	1.676
0.013 89	0.392 4	105.1	4.607
0.013 89	1.177	105.1	6.320
0.013 89	3.319	105.1	7.846

$K = 3.0\ (0.4)$ l. mol^{-1} (297°) $-\Delta H = 5.8\ (0.20)$ kcal mol^{-1}

Table II. Near-Infrared Absorbances for TFE–DOE

Acid concn, M	Base concn M	Absorbance
0.018 48	0.061 44	0.050
0.018 48	0.307 3	0.177
0.018 48	0.921 7	0.280

$K^a = 2.61\ (0.14)$ (301°) $\epsilon = 2.16\ (0.03)$

[a] The spectrophotometric equilibrium constant is estimated to be 3.2 at 297° by using the enthalpy obtained from the calorimetry experiment.

tions were approximately 0.01 M. Frequency shifts were measured to about 3 cm^{-1}. A constant base plot[7] of enthalpy of interaction vs. frequency shift was constructed for the base studied. The enthalpies utilized for this plot were obtained either calorimetrically or by constant acid frequency shift relationships.[8] The TFE and HFIP heats were corrected for the intramolecular hydrogen bonding interaction by adding −0.1 and −1.1 kcal mol^{-1}, respectively.[9]

Spectroscopic Equilibrium Constant. The equilibrium constant for the TFE–DOE system was determined utilizing 10.0-cm Pyrex cells in a Cary 14 recording spectrophotometer in the near-infrared region around 14 000 Å.[10]

Results

The heat evolved when TFE was added to DOE-CCl_4 mixtures, corrected for heats of solution of TFE in analogous mole fractions of CCl_4-heptadecane, is reported for various concentrations of DOE in Table I. Final acid concentrations were 0.014 M. The equilibrium constant and enthalpy are calculated from these data.

Absorbance data in the near-infrared region around 7×10^5 cm^{-1} for the TFE–DOE system at various concentrations are reported in Table II. The equilibrium constant is calculated from these data.

The enthalpies and frequency shift for the O–H or N–H stretch around 3600 cm^{-1} for the various hydrogen bonding systems are presented in Table III. A constant base plot for DOE is presented in FIGURE [/ This linear relationship is based upon enthalpies determined calorimetrically and/or by the constant acid frequency shift vs. enthalpy relationships given in Table IV. Constant base plots have a zero intercept.[7] Enthalpies obtained by the GLC method are also shown on this plot for comparison with the values determined by frequency shift correlations but were not used to determine this relationship. The equation for the DOE constant base plot is

$$-\Delta H(0.1) = 0.0123\Delta\nu \qquad (3)$$

The parameters obtained in the GLC study of the TFE–DOE system are presented in Table V.

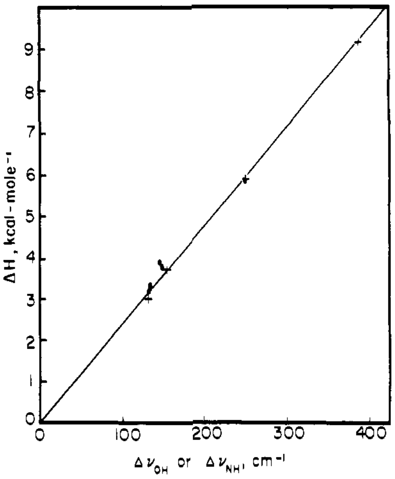

Figure 1. Constant base plot for DOE. Key: ●, GLC enthalpy; +, calorimetric or frequency shift enthalpy.

Table IV. Constant Acid Relationships Used

		Ref
t-BuOH (O,N-donors)	$-\Delta H\ (0.1) = 0.0106\Delta\nu_{OH} + 1.65$	7
HFIP (O,N-donors)	$-\Delta \mathrm{H}\ (0.3) = 0.0115\delta\nu_{OH} + 3.6$	11
TFE(O,N-donors)	$-\Delta \mathrm{H}\ (0.2) = 0.0121\Delta\nu_{OH} + 2.7$	12
Pyrrole (O,N-donors)	$-\Delta \mathrm{H}\ (0.1) = 0.0123\Delta\nu_{NH} + 1.8$	8

Discussion

Enthalpies for acid–base reactions determined by GLC techniques are now being reported in the literature regularly.

Table III. Enthalpies and Infrared Frequency Shifts for Acid–DOE Systems

No.	Acid	$\Delta\nu$, cm^{-1}	ΔH, kcal mol^{-1}	ΔH_{GLC}, kcal mol^{-1}	Dev,[a] kcal mol^{-1}
1	TFE	249	5.9 (0.1)[c,d]	6.0[d] (0.4)	0.1
			5.8 (0.1)[b,d]		0.2
2	HFIP	387	9.2 (0.1)[b,e]		
3	Pyrrole	155	3.7 (0.1)[b]		
4	*t*-BuOH	128	3.0 (0.1)[b]	3.1 (0.10)[g]	0.1
5	*i*-PrOH	135	3.2 (0.1)[f]	3.2 (0.09)[g]	0.0
6	*n*-PrOH	150	3.5 (0.1)[f]	3.8 (0.09)[g]	0.3
7	*n*-BuOH	150	3.5 (0.1)[f]	3.8 (0.08)[g]	0.3
8	*i*-BuOH	147	3.4 (0.1)[f]	3.9 (0.07)[g]	0.5
9	*sec*-BuOH	135	3.2 (0.1)[f]	3.4 (0.09)[g]	0.2

[a] Difference between enthalpy obtained by the GLC method and enthalpy determined from calorimetry or a constant base frequency shift with enthalpy correlation. [b] Determined from constant acid relationship given in Table IV. [c] Determined calorimetrically. [d] Corrected for breaking of the intramolecular hydrogen bond by adding −0.1 kcal mol^{-1} to the observed enthalpy. [e] Corrected for breaking of the intramolecular hydrogen bond by adding −1.1 kcal mol^{-1} to the observed enthalpy. [f] Determined from DOE constant base relationship. [g] From ref 2b.

Table V. GLC Parameters for DOE–TFE[b]

	30°	40°	50°
V_g^0 DOE[a]	397 (1)	232 (1)	141 (2)
V_g^0 OD[a]	10.0 (0.1)	8.4 (0.1)	6. (0.1)
K (l. mol^{-1})	11.99 (0.010)	8.61 (0.014)	7.77 (0.020)
$-\Delta H = 5.9\ (0.4)$ kcal mol^{-1}			

[a] Infinite dilution bulk specific retention volume, ml g^{-1}. [b] Values in parentheses are experimental standard deviations.

Table VI. Observed and Calculated Enthalpies[a,b] for DOE: Acid Systems

Acid	ΔH_{obsd}[d]	$\Delta H_{\mathrm{calcd}}$[d]	Difference[d]
TFE	5.9	5.8	0.1
HFIP	9.2	8.6	0.6
Pyrrole	3.7	3.8	0.1
t-BuOH	3.0	3.3	0.3
$CHCl_3$[c]	3.4	3.8	0.4

[a] Calculated utilizing eq 1 and the tentative values for DOE of $E_B = 1.1$, $C_B = 3.4$. [b] Method given in Table III. [c] From ref 16. [d] In kilocalories per mole.

The method has considerable utility both for the study of weak interactions and gaseous reactants. There has, however, been no direct comparison of the values obtained by the Martire -Reidl GLC method with enthalpies obtained by other independent means. This comparison is made for the hydrogen bonding systems in Table III. The average absolute error in the GLC determination is about 0.2 kcal mol^{-1}. However, consideration of the experimental errors assigned to the GLC method and the errors in the independent determinations leads one to the conclusion that the GLC values are essentially the same as the other determinations within reasonable limits. Thus we feel that it has been shown that Martire's pure base GLC method has an accuracy at least of the order of a typical macrocalorimetric experiment (0.1-0.2 kcal mol^{-1}), with DOE as the liquid phase. The method may be particularly suited to systems in which one of the reactants is a gas where limited solubility of the gas and other experimental complications eliminate the calorimetric method.

Another concern with the pure base method was that working in the pure base as solvent might introduce solvation terms which result in discrepancies between enthalpies obtained via GLC and those obtained calorimetrically in nonpolar solvents such as hexane and CCl_4. Complications from solvation effects are reported for di-*n*-butyl ether in hexane.[13] In this solvent the ether aggregates and solvates but aggregation is not as extensive in CCl_4. From the close agreement between GLC and calorimetric or frequency shift data, it is apparent that complications of this sort are minimized in DOE. Additionally, it has been found that enthalpies determined calorimetrically for the *m*-fluorophenyl-di-*n*-octyl ether system in CCl_4 and hexane are the same.[14] This is taken as further evidence that DOE is not significantly self-associated (on the GLC column) in the pure liquid (in hexane or in CCl_4 in the calorimetric experiment). DOE is acting like an ether oxygen isolated in an alkane solvent by virtue of the long octyl chains. The magnitude of donor-acceptor interactions as manifested by the enthalpy of adduct formation in poorly solvating media or the gas phase has been correlated by eq 4, where $C_A = E_A$, C_B, and E_B are empirically determined parameters referring to acceptor and donor, respectively.[15]

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

We are unable to directly determine E_B and C_B parameters for DOE from our measured enthalpies since the ratio C_A/E_A is approximately the same for the four acids investigated. We have found that for dialkyl ethers the C_B/E_B ratio does not vary much. For example, the following ratios have been determined: diethyl ether, 3.38; di-*n*-butyl ether, 3.12. We have estimated the E_B and C_B parameters for DOE by assuming its C_B/E_B ratio is 3.1 and then utilizing the enthalpies obtained for the various acids with known E_A and C_A values in eq 4. Tentative values for di-*n*-octyl ether obtained by using enthalpies of DOE interaction with each of the first four hydrogen bonding acids in Table VI are $E_B = 1.1$ and $C_B = 3.4$. These are to be compared with values for other alkyl ethers: Et_2O, 0.963, 3.25; *n*-Bu_2O, 1.06, 3.30. Our tentative values are close to those obtained by Martire[16] for DOE: $E_A = 1.11$, $C_A = 3.01$. The calculated enthalpies of hydrogen bonding to DOE using eq 4 and our tentative E_B and C_B values are compared with the experimental results in Table VI. The enthalpy value for hydrogen bonding of DOE to $CHCl_3$ was obtained by Martire[16] in an NMR-GLC study and is in fair agreement with our predicted value. It should be noted that these tentative E_B and C_B values for DOE should only be used for hydrogen bonding systems and even then may not provide the expected agreement (0.1-2.0 kcal/mol) with experimental values.

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