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Linear Enthalpy–Spectral Shift Correlations for 1,1,1,3,3,3-Hexafluoro-2-propanol¹

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Abstract: Calorimetric (enthalpy), OH frequency shift, and hydrogen-bond chemical shift data are reported for the 1,1,1,3,3,3-hexafluoro-2-propanol acid–base interaction with a variety of Lewis bases. The following quantitative correlations are found: $\Delta H (\pm 0.2) = (0.0115)\Delta\nu + 3.6$ and $\Delta H (\pm 0.3) = (0.886)\Delta + 3.6$. The comparison of the data for the fluoro alcohol with those for phenol show the former to be the stronger hydrogen-bonding acid, regardless of the experimental quantity used to measure acidity. Several reliable linear correlations are found which can be used to compare the sensitivities and determine the compatibility of the three indices of acid–base interaction. The linear relationships, and in particular the nonzero intercepts, have been interpreted by an elaboration of the Lippencott–Schroeder model for hydrogen bonding. Application of this model to our data and that for phenol demonstrates the competitive relationship between OH elongation and HB formation for each experimental parameter. The role of R, in ROH, in controlling the balance between these two processes is brought out by this analysis and is shown to be different for the three experimental quantities. The enthalpy data are used to characterize the acidity of the fluoro alcohol in terms of the *E*, *C* parameters of Drago and Wayland; the *E* and *C* values are useful in a discussion of the low enthalpy found for the soft donor diethyl sulfide. An attempt is made to determine the acidity leveling of the fluoro alcohol by diethyl sulfide, but the three experimental indices of acidity are found to be of different sensitivities to this leveling.

The question of the generality of linear enthalpy–spectroscopic shift (OH frequency and proton-shielding constant lowering) relations for hydrogen-bonding acids has yet to be fully explored. Such relations have been determined^{2,3} for phenol and some substituted phenols. Such relations, and their generality, are important not only for their utility in measuring acid and base strengths but also for their theoretical implications and, through the latter, for the development of a better understanding of the hydrogen-bond phenomenon.

Apparently crucial to confirmation of such a relation is the determination of enthalpies by some technique other than the spectroscopic methods so often used.³

(1) Taken in part from the Master of Arts thesis of J. A. Stikeleather, Wake Forest University, 1967.

(2) (a) W. Partenheimer, T. D. Epley, and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 3886 (1968); (b) D. P. Eyman and R. S. Drago, *ibid.*, **88**, 1617 (1966).

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

In this report we present calorimetric data for the hydrogen-bonding acid 1,1,1,3,3,3-hexafluoro-2-propanol (abbreviated HFIP) with a series of nitrogen and oxygen donors and the soft donor diethyl sulfide. This alcohol was chosen for study because it is structurally considerably different from phenol and is expected to be a much stronger hydrogen-bonding acid than the aromatic alcohol. The alcohol forms an isolable 1:1 adduct with tetrahydrofuran⁴ and presumably other donors and its $pK_a^{H_2O}$ is reported⁴ to be 9.3, compared with 25 for 2-propanol and 9.9 for phenol.

Experimental Section

Purification of Chemicals. The fluoro alcohol, 1,1,1,3,3,3-hexafluoro-2-propanol, was obtained at 99% minimum purity from Columbia Organic Chemicals Co. and was further purified by dis-

(4) W. J. Middleton and R. V. Lindsey, Jr., *ibid.*, **86**, 4948 (1964).

Table I. Hydrogen-Bond Data for HFIP and PhOH

Donor	$-\Delta H$, kcal/mole		$\Delta\nu$, cm^{-1}		Δ , ppm	
	HFIP	PhOH	HFIP	PhOH	HFIP	PhOH ^b
1. Diethyl sulfide	5.1 \pm 0.1	4.6 ^{b,c}	254 \pm 10	250 ^b	3.47	2.89
2. Acetonitrile	5.9 \pm 0.1	4.7 ^a	208 \pm 10	150 ^a	3.02	2.49
3. Ethyl acetate	6.5 \pm 0.1	4.8 ^a	224 \pm 10	164 ^a		
4. Acetone	6.7 \pm 0.1	4.9 ^a	280 \pm 10	193 ^a	3.46	2.91
5. Diethyl ether	7.2 \pm 0.1		357 \pm 10	279 ^b	4.25	3.71
6. N,N-Dimethylacetamide	8.5 \pm 0.1	6.8 ^a	428 \pm 10	345 ^a	5.12	4.36
7. Dimethyl sulfoxide	8.7 \pm 0.1		449 \pm 10	359 ^b		
8. Pyridine (CCl ₄)	8.4 \pm 0.1					
(hexane)	9.8 \pm 0.1	8.0 ^a		465 ^a	7.23	6.12
9. 2,4,6-Trimethylpyridine (CCl ₄ ; hexane)	9.8 \pm 0.1		542			
10. Hexamethylphosphoramide	9.9 \pm 0.1		540 \pm 10			
11. Triethylamine (CCl ₄)	10.0 \pm 0.1					
(hexane)	11.5 \pm 0.1	9.1 ^a	1038	556 ^a	9.32	7.07

^a Reference 3. ^b Reference 1b. ^c Similar values are reported for *t*-Bu₂S and *n*-Bu₂S in R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *J. Am. Chem. Soc.*, **86**, 3227 (1964).

tillation at atmospheric pressure from barium oxide. The boiling point of the middle cut that was collected was 58.2 \pm 0.2°. All distillations were carried out with a spinning-band column of about 52 theoretical plates.

Baker Analytical Reagent acetonitrile, ethyl acetate, acetone, tetrahydrofuran, and pyridine, Eastman White Label diethyl sulfide and triethylamine, Mallinckrodt Analytical Reagent diethyl ether, and Brother's Chemical Co. 2,4,6-trimethylpyridine (*s*-collidine) were refluxed over barium oxide for several hours and distilled from fresh barium oxide at atmospheric pressure with only the middle cuts held for use.

Baker Analytical Reagent N,N-dimethylacetamide and dimethyl sulfoxide and Aldrich Chemical Co. hexamethylphosphoramide were all refluxed over and distilled from barium oxide at reduced pressure (generally about 10 mm).

Fisher ACS carbon tetrachloride and methylene chloride and Baker Analytical Reagent *n*-hexane were stored over Linde 4A sieves for at least 1 week before use.

Baker Analytical Reagent potassium chloride was dried at 160° for 1 week before use and Baker Analytical Reagent sulfuric acid was used without further purification.

Infrared Measurements. A Perkin-Elmer 621 high-resolution, grating infrared spectrophotometer with a matched set of Crystal Laboratories' long path length (2.5 cm) sodium chloride cells was used to collect the infrared data. The advantage in using these cells is that the alcohol and base concentrations can be kept at about 10⁻³ *M*. At this concentration any absorption due to polymerization of the alcohol was eliminated.

Carbon tetrachloride was used as the solvent for all bases in this study because it has no absorption in this region that cannot be cancelled without loss of sensitivity; *n*-hexane cannot be used for some of the donors without sensitivity loss. Fortunately the fluoro alcohol does not show unwanted absorption over most of this region (3600–2500 cm⁻¹). Concentrations of acid and base were chosen in each case to give an easily measured OH band without complications from alcohol polymerization and solvent effects⁵ and to allow cancellation of base absorption bands with the reference cell.

An expanded frequency scale was used in which the region under study was spread linearly over a 67-cm length of chart paper. The Perkin-Elmer frequency marker was used to calibrate the spectra at 10-cm⁻¹ intervals.

No pains were taken to determine the exact concentration of the alcohol and bases used in these studies. Generally, a solution of the base in carbon tetrachloride was prepared by adding about 15 μ l of base to a 50-ml volumetric flask and diluting to the mark. A portion of this solution was used to fill the reference cell and another portion to fill the sample cell containing about 3 μ l of alcohol (density⁶ 1.62 g cm⁻³). The base concentration was chosen in each case to give a per cent transmittance of the shifted OH band between 30 and 60.

Proton Resonance Measurements. The proton resonance spectra were obtained in methylene chloride solution with TMS as the

(5) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).

(6) Allied Chemical Corp., General Chemical Division, unpublished research data

internal reference. The instrument was a Varian A-60 spectrometer equipped with a variable-temperature unit. The solution concentrations of acid and base were calculated from the calorimetric enthalpy and free-energy results to give nearly complete adduct formation in each case at about 0°. Spectra were recorded as a function of base concentration and temperature (to -50°). The techniques used were very similar to those used previously⁷ for studies of trifluoroethanol.

Calorimetry. Enthalpy data were collected calorimetrically with a thermistor calorimeter fashioned after that reported by Arnett.⁸ The general procedure was to successively inject 100- μ l samples of the alcohol into 200-ml solutions of the Lewis base.

Results

Frequency Shifts. The infrared spectrum of a dilute (0.005 *M*) carbon tetrachloride solution of the free alcohol in the OH-stretching region exhibits two nearly resolved and sharp bands of almost equal intensity at 3608 and 3572 cm⁻¹. The peaks may well be due to rotational isomers involving "free" and/or intramolecularly hydrogen-bonded hexafluoro-2-propanol.⁹ We have taken the 3608-cm⁻¹ band to be the reference OH fundamental in calculating the frequency shifts (see Discussion). In keeping with our observation of a doubled OH fundamental, which is typical of secondary aliphatic alcohols,¹⁰ we observed a doubled CH fundamental at 2970 and 2940 cm⁻¹. Both lines are fairly narrow and nearly completely resolved. The frequency shifts for the donors used in these studies are listed in Table I.

The spectral data for pyridine and triethylamine deserve special comment. For these donors the "bonded" OH frequency falls below 3000 cm⁻¹ in a region obscured by a multitude of alcohol and base CH vibrations. The bonded OH absorption bands are broad and the maximum absorbance wavelength for the pyridine adduct cannot be located. The absorption maximum for the HFIP-triethylamine adduct can be located at about 2570 cm⁻¹. This corresponds to a frequency shift of some 1040 cm⁻¹—far too large a value to adhere to any of the relations to be discussed. Our attempts to cancel base absorption in this region by using matched absorption cells have failed because it appears the triethylamine CH absorption bands do

(7) K. F. Purcell and S. T. Wilson, *J. Mol. Spectry.*, **24**, 468 (1967).

(8) E. M. Arnett, W. G. Bentrude, J. J. Burkner, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

(9) J. Murto and A. Kivinen, *Suomen Kemistilehti*, **B**, **40**, 14 (1967).

(10) R. Piccolini and S. Winstein, *Tetrahedron Letters*, **4** (1959).

not occur at the same frequencies in the sample and reference cells. We are presently investigating the possibility that there is some mixing of OH and CH motions which could lead to excessive depression of the OH frequency. By way of contrast, the enthalpy and chemical shift data to be discussed indicate nothing at all unusual about the HFIP-triethylamine interaction.

Proton Chemical Shifts. A dilution study of the HFIP proton resonance energy in methylene chloride at room temperature indicates (Figure 1) less self-association of HFIP than has been found for trifluoroethanol⁷ or phenol.¹⁵ The proton chemical shift remains constant at 3.1 ppm until the alcohol concentration exceeds 0.2 *M* and then only slowly increases with concentration. The CH resonance signal is a septet ($J_{FH} = 6$ cps) at 4.5 ppm down from TMS and is concentration independent.

The results of the adduct chemical shift measurements are given in Table I. These are values recorded at -50° relative to the monomeric alcohol resonance of 3.1 ppm; that is, the adduct chemical shifts relative to TMS at -50° are 3.1 ppm larger than reported in the table. The chemical shift values for the carbonyl donors and pyridine have been corrected for paramagnetic shielding (1.0¹¹ and 1.1 ppm,¹² respectively) of the proton which results from donor molecule diamagnetic anisotropy.

Calorimeter Calibration. Accuracy of the calorimeter and the associated techniques was determined by measurement of the heat of solution of potassium chloride in water (endothermic) and the partial molal heats of solution of sulfuric acid in water (exothermic). The heat of solution of potassium chloride over the concentration range 0.01–0.02 *M* was found to be 4.19 ± 0.02 kcal/mole to be compared with the literature value¹³ of 4.185 ± 0.001 .

Enthalpies of formation of sulfuric acid–water solutions, taken from NBS Circular No. 500 (part I), were used to calculate the reference heats of dilution. Giauque¹⁴ has also reported precision calorimetric results for the heats of dilution of sulfuric acid solutions in water. An average error of 1.8% for eight acid concentrations covering a range from 0.015 to 0.044 *M* was encountered and is due, in part, to errors in determination of the acid solution densities and in interpolation of the enthalpies of formation from the NBS tables.

Thermodynamics of HFIP Adduct Formation. The most meaningful definition of the enthalpy of hydrogen-bond formation is the change in enthalpy from the

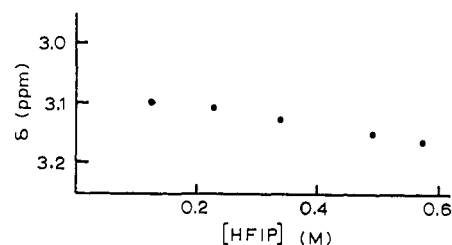


Figure 1. Chemical shift dilution study of HFIP.

reaction of the acid and base to give the adduct, all species in the gas phase. A Born–Haber cycle relating this reaction to the calorimetric heat of reaction is given in Scheme I, where $\Delta H(g)$ = gas-phase enthalpy of reaction, ΔH_2 = heat of solvation of gaseous alcohol, ΔH_3 = heat of solvation of base, ΔH_4 = heat of solvation of adduct, ΔH_5 = heat of solution of liquid alcohol, Q = measured heat of reaction, Q' = heat of reaction with both reactants in solution. (All ΔH_n involving gaseous species must be corrected for Δ_n .)

$$\Delta H(g) = Q' + \Delta H_2 + \Delta H_3 - \Delta H_4$$

$$\Delta H(g) = Q - \Delta H_5 - (\Delta H_4 - \Delta H_2 - \Delta H_3) \quad (1)$$

$$\Delta H(g) \simeq Q - \Delta H_5 = Q' \quad (2)$$

Equation 1 results from a straightforward application of Hess' law to the Born–Haber cycle, and eq 2 results from the assumption that the heats of solvation of the acid, base, and adduct will nearly cancel. This assumption was studied by Drago^{1b,15} and found to be reasonable for "nonsolvating" solvents like carbon tetrachloride and hexane. An interesting point here is that it may be possible to determine every term on the right side of eq 1 for many of these acid–base pairs since their adducts with hexafluoro-2-propanol can be distilled⁴ and, therefore, the adducts may be sufficiently stable in the gas phase to allow direct determination of ΔH_4 . It might also be possible to determine $\Delta H(g)$ directly from gas-phase measurements.

The heat of solution of the liquid alcohol, ΔH_5 , was determined in both carbon tetrachloride and hexane as a function of concentration. The values were determined to be 4.77 ± 0.01 and 5.16 ± 0.03 kcal/mole, respectively, up to a concentration of 0.01932 *M* (equivalent to four successive 100- μ l additions of alcohol to 200 ml of CCl_4). The measured acid–base heats, Q , were then corrected by one or the other of these values to give Q' , the heat associated with the middle leg of the Born–Haber cycle.

Since there is an equilibrium between the reactants and hydrogen-bonded adduct, one must allow for incomplete formation of the adduct in calculating $\Delta H(g)$. If ΔH ($\Delta H(g)$ above) is the heat of formation of 1 mole of adduct, then the concentration of the adduct can be written¹⁵

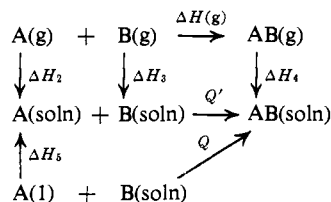
$$C = Q'/v\Delta H \quad (3)$$

where v is the solution volume in liters, Q' is in calories, and ΔH is in calories per mole of adduct. By making approximations similar to those in deriving the well-known Scott equation,¹⁶ the equilibrium constant expression may be rearranged to give eq 4, in which A_0

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

(16) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

Scheme I



(11) P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959).

(12) B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectry.*, **10**, 117 (1963).

(13) G. Somson, J. Coops, and M. W. Tolk, *Rec. Trav. Chim.*, **82**, 321 (1963).

(14) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

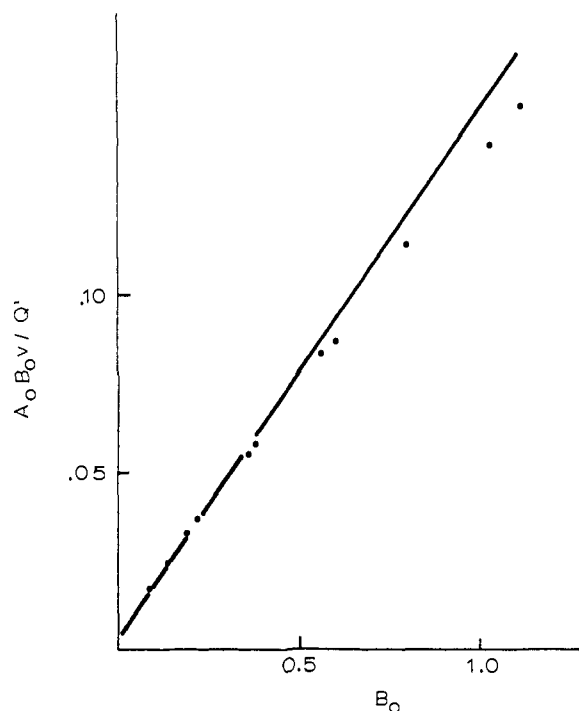


Figure 2. Scott method of obtaining K and ΔH for the acetone data.

is the initial alcohol concentration and B_0 is the initial base concentration.

$$\frac{A_0 B_0 v}{Q'} = \frac{B_0}{\Delta H} + \frac{1}{\Delta H} \quad (4)$$

This provides a graphical method for determining ΔH .

Person¹⁷ has critically examined the pitfalls in using the Scott method to determine K and ΔH from spectrophotometric data. Applying a similar analysis to eq 4, we have chosen the ranges of A_0 and B_0 in our measurements so that both K and ΔH , or at least ΔH , can be accurately determined.

The Scott plot of our acetone data is shown in Figure 2. This plot illustrates a complication not discussed by Person. At higher base concentrations (above 0.35 M in acetone), there is considerable deviation of the data points from linearity in a direction corresponding to increasing ΔH . The reason behind the deviation at high base concentration is reasonably linked to the increasing solvating properties of the solvent-base mixture with increasing base concentration. A similar, but less pronounced, phenomenon was observed for most of the other bases also. Enthalpies for each system were calculated, therefore, using only data points for which B_0 is less than that concentration at which solvation energies appear to become important. The data used in these calculations are given in Table II.

We ultimately resorted to use of the rigorous method described by Bolles and Drago¹⁸ for determining K and ΔH .

$$K^{-1} = \frac{Q'}{v\Delta H} + \frac{A_0 B_0 v \Delta H}{Q'} - (A_0 + B_0) \quad (5)$$

(17) W. B. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965).

(18) T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965).

Table II. Calorimetric Data for the Reaction of Hexafluoro-2-propanol with Various Bases

Base	Solvent	A_0 , ^a M	B_0 , M	v , ml	$-Q'$, cal
Diethyl sulfide	CCl_4	0.01921	0.05550	201.2	02.83
		0.01848	0.4021	209.1	10.78
		0.01835	0.4651	210.6	11.75
		0.01774	0.7609	217.9	13.66
Acetonitrile	CCl_4	0.01644	1.383	235.0	15.99
		0.01452	0.1005	201.1	13.02
		0.01445	0.1977	202.1	14.63
		0.01437	0.2993	203.2	15.50
Ethyl acetate	CCl_4	0.01430	0.3929	204.2	15.80
		0.01410	0.5466	207.0	16.44
		0.01297	0.02551	200.5	07.26
		0.01291	0.07613	201.5	09.15
Acetone	CCl_4	0.01281	0.1511	203.0	13.16
		0.01876	0.2978	206.0	21.72
		0.01819	0.4469	212.4	23.11
		0.01915	0.1131	201.8	21.27
Diethyl ether	CCl_4	0.0191	0.1593	202.4	22.53
		0.0190	0.2156	203.5	23.44
		0.0190	0.2391	203.6	23.51
		0.0237	0.1674	203.5	27.58
Tetrahydrofuran	CCl_4	0.0189	0.1993	204.2	22.59
		0.0187	0.2967	206.4	23.91
		0.0186	0.3641	207.9	24.45
		0.0184	0.4716	210.3	25.77
Dimethylacetamide	CCl_4	0.0192	0.1309	201.6	23.68
		0.0186	0.3142	207.4	25.35
		0.0184	0.5780	209.9	26.13
		0.00953	0.05207	200.5	15.25
Dimethyl sulfoxide	CCl_4	0.00951	0.1076	201.0	15.71
		0.00946	0.1952	202.0	15.94
		0.00948	0.09720	201.5	15.99
		0.00948	0.09906	201.6	15.78
Pyridine	CCl_4	0.01255	0.4461	207.2	22.60
		0.01244	0.5521	209.0	22.39
		0.01092	0.03199	200.5	16.93
		0.01453	0.06381	201.0	23.94
γ -Collidine	CCl_4	0.00726	0.07652	201.2	12.01
		0.01438	0.1895	203.1	24.29
		0.00960	0.1895	203.1	16.29
		0.01274	0.2514	204.1	21.64
Hexamethylphosphorotriamide	CCl_4	0.01921	0.06862	201.1	38.25
		0.01916	0.1064	201.7	37.98
		0.00477	0.1555	202.5	9.47
		0.01926	0.02298	200.6	32.41
Triethylamine	CCl_4	0.01903	0.1148	203.1	36.75
		0.01874	0.2285	206.2	37.17
		0.01922	0.04050	201.0	36.42
		0.00959	0.05820	201.4	18.16
Triethylamine	CCl_4	0.01896	0.1508	203.8	37.49
		0.01881	0.2166	205.5	37.87
		0.01291	0.03723	201.5	26.32
		0.01287	0.07402	202.1	26.55
Triethylamine	C_6H_{14}	0.00705	0.1125	203.2	14.43
		0.01927	0.02727	200.5	32.46
		0.01921	0.04173	201.2	42.91
		0.01201	0.1144	203.3	43.82
		0.01889	0.1596	204.6	44.10

^a Total alcohol concentration after four successive additions of 100 μ l of HFIP.

The results of the application of this method to the acetone data are given in Figure 3. Once again, the effect of high base concentration, in giving intersections at higher ΔH values, is evident. Bolles and Drago¹⁸ give a detailed discussion of the application of eq 5 and its limitations.

Table I gives the values of ΔH obtained by a least-squares fitting procedure^{18,19} of eq 5 for all the bases used in these studies. The error limits on ΔH , for a

(19) K. Conrow, D. Johnson, and R. E. Bowen, *ibid.*, **86**, 1025 (1964).

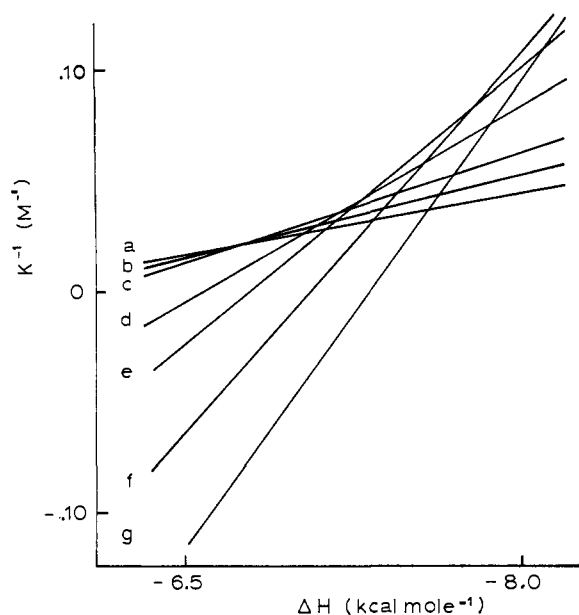


Figure 3. Bolles-Drago method of obtaining K and ΔH for the acetone data. Acetone concentration: a, 0.113, b, 0.159, c, 0.215, d, 0.399, e, 0.584, f, 0.824, g, 1.054.

sharpness of fit¹⁹ ≥ 20 , were computed to be much less than ± 0.1 kcal/mole but are given as ± 0.1 in Table I as realistic estimates of the true accuracies of the measured ΔH .

Since triethylamine and perhaps pyridine, are known²⁰ to react or strongly interact with carbon tetrachloride, their heats of reaction with hexafluoro-2-propanol were also determined in *n*-hexane. The ΔH values for these donors in hexane are given in Table I along with ΔH in carbon tetrachloride. It is readily apparent that carbon tetrachloride is not an "inert" solvent for these donors. Interestingly, *s*-collidine gives the same enthalpies in carbon tetrachloride and hexane.

Finally, it should be mentioned that the Scott method gives ΔH values within 0.1 kcal/mole of those obtained from eq 7.

Discussion

That the data for HFIP generate linear enthalpy-frequency shift and enthalpy-chemical shift relations is evidenced by the plots given in Figures 4 and 5. The least-squares equations for these lines are

$$\Delta H (\pm 0.3) = (0.886)\Delta + 3.6 \quad (6)$$

$$\Delta H (\pm 0.2) = (0.0115)\Delta\nu + 3.6 \quad (7)$$

(The signs in these equations result from using the absolute values of ΔH , $\Delta\nu$, and Δ . Δ is defined as the chemical shift of the hydrogen-bonded adduct relative to the free alcohol, and the data for carbonyl donors and pyridine have been corrected for donor molecule anisotropy contributions to Δ .) The data in Table I show that replacement of phenyl by the hexafluoro-2-propyl group increases Δ , ΔH , and $\Delta\nu$ with a given donor. It appears that the properties of the hydroxyl group which are responsible for the linear relations are not sufficiently altered by substitution of hexafluoro-2-propyl for phenyl to destroy the linear relations. It

(20) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **62**, 2063 (1966).

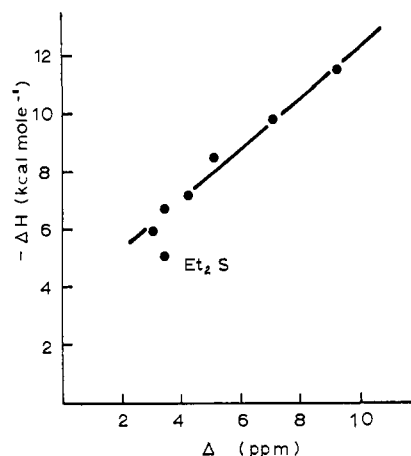


Figure 4. Enthalpy vs. hydrogen-bond chemical shift for HFIP.

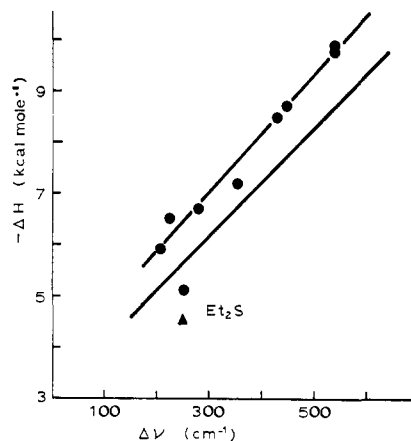


Figure 5. Enthalpy vs. frequency shift relations for: ●, HFIP; —, phenols.

would also appear from these data that greatly increasing the electron-attracting ability of the substituent only mildly increases both the slope and intercept of the enthalpy-frequency shift relation. For comparison, the slope of relation 7 for various phenols (Figure 5) is reported^{1a} to be 0.0103, and the intercept is 3.1. The nonzero intercept in the relations 7 for HFIP and the phenols indicates a change for each acid, with increasing adduct interaction, in the relative values (ratio) of ΔH and $\Delta\nu$. At some point fairly soon (*i.e.*, $\Delta\nu < 200$ cm^{-1}) in progressively increasing acid-base interaction the frequency shift becomes (relative to the enthalpy) more responsive to the presence of the donor and this introduces (as yet experimentally unverified) curvature in the relationship which in turn leads to a nonzero intercept along the enthalpy axis.

Such a relationship^{21,22} between enthalpy and frequency has been predicted by Lippencott and Schroeder from a semiempirical theory of hydrogen-bond formation. According to their model, the results of which are shown in Figure 6, the enthalpy is a more gently increasing function of the acid-base interaction (oxygen-donor distance) than is the frequency shift.

According to the assumptions of the Lippencott-Schroeder model, the energy of adduct formation may

(21) E. R. Lippencott and R. Schroeder, *J. Chem. Phys.*, **23**, 1099 (1955).

(22) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2874 (1967).

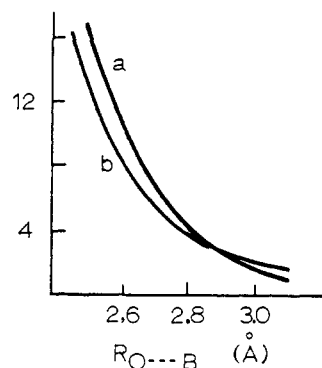


Figure 6. Lippencott-Schroeder relations of $-\Delta H$ and $\Delta\nu$ vs. oxygen donor distance: a, $\Delta\nu$ in units of hundreds of cm^{-1} ; b, $-\Delta H$ in units of kcal/mole.

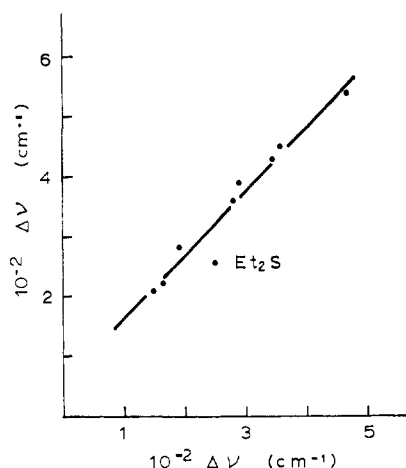


Figure 7. Frequency shifts of HFIP vs. those of phenol.

be partitioned into four contributions: the (endothermic) OH bond breaking, the (exothermic) HB bond making, the (exothermic) OB coulombic attraction resulting from B to OH charge transfer, and the (endothermic) OB van der Waals repulsion. In what follows, we will refer to the first of these as δE_{OH} , the second and third collectively as E_{HB} , and the last as V_{OB} . The observed OH frequency depression also has at least two contributions:⁷ the depression of the OH frequency as a result of OH bond breaking and an effect which opposes the frequency depression and which results from HB bond making and mixing, in the bonded OH normal mode, of OH and HB motions. The first we will refer to as δK_{OH} and the latter as K_{HB} . Referring to Figure 6, the sharpness with which ΔH increases with increasing acid-base interaction is a balance between the rates of change of δE_{OH} , E_{HB} , and V_{OB} and, while all terms should increase with increasing acid-base interaction, of the three, E_{HB} must show the sharpest increase. The role of the other two (endothermic) terms is to moderate the rate of increase of E_{HB} and, as noted by Lippencott and Schroeder, the van der Waals term should show the most sensitive variation with R_{OB} when the latter is in a range for effective hydrogen-bond formation. These considerations serve to qualitatively account for the gentle increase of ΔH with decreasing R_{OB} . With regard to the OH frequency shift, δK_{OH} is necessarily larger than K_{HB} to produce the observed depressions of the OH frequency. The role

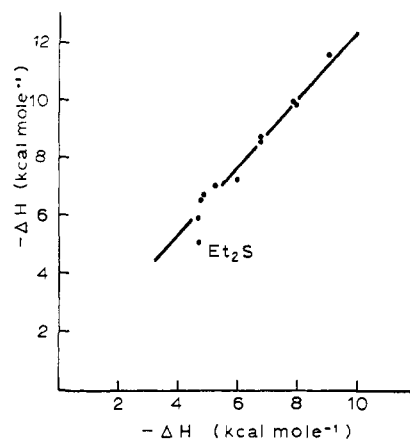


Figure 8. Enthalpies of HFIP vs. those for phenol.

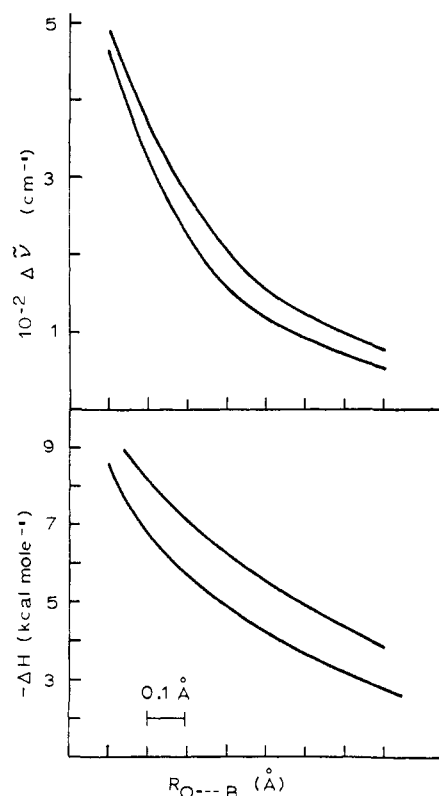


Figure 9. Lippencott-Schroeder curves for two alcohols of different acidities; upper curve of each pair for HFIP.

of K_{HB} is to moderate the rate of decrease of δK_{OH} . The curves in Figure 6 imply that, relatively speaking, K_{HB} is a poorer moderator of δK_{OH} than is $(\delta E_{\text{OH}} + V_{\text{OB}})$ of E_{HB} . This accounts for the relatively sharp break in the $\Delta\nu$ vs. R_{OB} curve. This relative change in sensitivities of ΔH and $\Delta\nu$ occurs in the weak interaction range (near 2 kcal/mole in the Lippencott-Schroeder graph) and accounts for the nonzero intercepts observed for relation 1 with both HFIP and phenol and substituted phenols. According to the Lippencott-Schroeder model, the break in $\Delta\nu$ vs. R_{OB} occurs at the same OB distance as the break in a plot of r_{OH} vs. R_{OB} .

We have attempted to construct ΔH vs. R_{OB} and $\Delta\nu$ vs. R_{OB} curves for HFIP and PhOH which retain the qualitative characteristics of the Lippencott-Schroeder curves (Figure 6) and which will nearly quantitatively reproduce the experimental linear relations depicted in

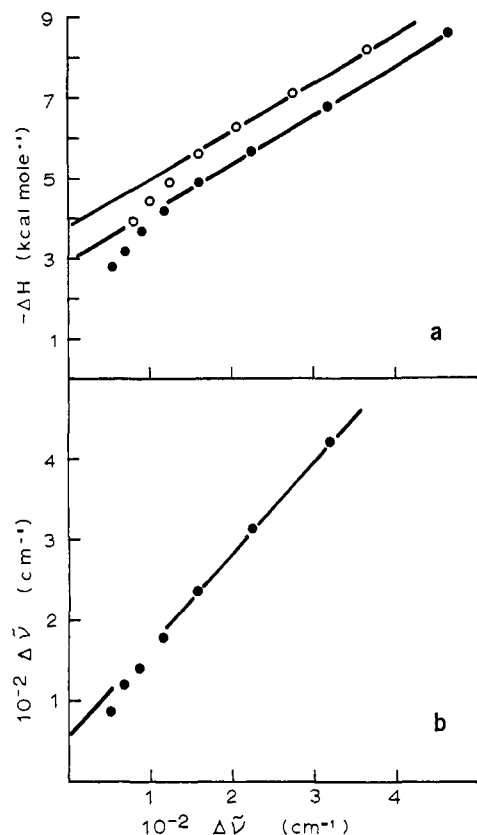


Figure 10. (a) ΔH vs. $\Delta\nu$ as predicted from Figure 9: \circ , HFIP; \bullet , PhOH. (b) $\Delta\nu^{hf}$ vs. $\Delta\nu^{ph}$ as predicted from Figure 9.

Figures 5, 7, and 8. These ΔH and $\Delta\nu$ vs. R_{OB} curves are given in Figure 9. The theoretical counterparts of Figures 5, 7, and 8 are presented in Figures 10a, 10b, and 11, respectively. (The derivation of Figures 10a, 10b, and 11 from Figure 9 and the construction of the latter are discussed below.) The success of this approach can be judged from a comparison of experimental and theoretical slopes and intercepts in Table III. Fine adjustment of the curves in Figure 9 could be made which would give even better agreement than shown in Table III.

Table III. Comparison of Experimental and Theoretical Relations

Relation	Slope		Intercept	
ΔH vs. $\Delta\nu$				
Expt	0.012 ^a	0.010 ^b	3.6 ^a	3.1 ^b
Theory	0.012 ^a	0.012 ^b	3.9 ^a	3.0 ^b
ΔH^{hf} vs. ΔH^{ph}				
Expt	1.16		0.7	
Theory	1.14		1.0	
ΔH^{hf} vs. $\Delta\nu^{ph}$				
Expt	1.05		64	
Theory	1.13		60	

^a HFIP. ^b Phenol.

Our finding that the ΔH vs. R_{OB} and $\Delta\nu$ vs. R_{OB} curves for the stronger acid must be placed above, with more gentle changes of slope, those of the weaker acid is necessary to achieve agreement with the experimental relations. The implications of this are: *with a given donor at a given distance* from the two alcohols (1) ΔH

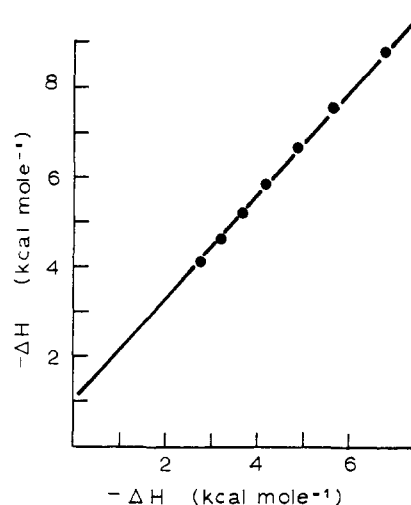


Figure 11. ΔH^{hf} vs. ΔH^{ph} as predicted from Figure 9.

and $\Delta\nu$ are larger for the more acidic acid if for no other reason than the expected higher proton charge of the stronger acid which should result in a more exothermic acid-base interaction *and* greater OH-bond elongation or breaking; (2) K_{HB} and $(\delta E_{OH} + V_{OB})$ are more effective moderators for the stronger acid since in the stronger acid the oxygen (negative) and proton (positive) charges are presumably larger which in turn could make $(\delta E_{OH} + V_{OB})$ and K_{HB} (disproportionately) larger. These statements are in no way incompatible with any of the experimental data at hand and are conclusions in that they are necessary to the successful interpretation of those data.

Now the experimental relationships in Figures 5, 7, and 8 arise from data for the same series of donors, but each donor presumably moves closer to the oxygen of the stronger acid than to the oxygen of the weaker acid. We must allow for this difference in synthesizing Figures 10a, 10b, and 11 from Figure 9. We have no way, however, of *a priori* determining this difference in OB distances and, as a reasonable estimate, we have taken the difference to be 0.05 Å. The curvature and relative positions of the lines in Figure 9 have been drawn, subject to this estimate of the difference in R_{OB} for the two alcohols with each donor, to give semi-quantitative agreement with the intercepts and slopes of the experimental relations. The necessity of approximating the difference in R_{OB} for the same donor with the two acids prevents a rigorous determination of the curves in Figure 9. However, the condition that $R_{OB}(\text{HFIP}) < R_{OB}(\text{PhOH})$ (1) requires separate ΔH and $\Delta\nu$ curves for the two alcohols and (2) requires that the HFIP curves lie above, with more gentle slope changes with changing R_{OB} , those of PhOH. Since we also have no quantitative information concerning the magnitudes of R_{OB} for PhOH, the abscissa of Figure 9 is unmarked. This is of no great importance to our discussion of the relative $\Delta\nu$ changes and ΔH values for the two alcohols interacting with the same series of donors.

Figures 10a, 10b, and 11 have been generated by quantitatively transferring points from Figure 9 to the appropriate axis systems. Fine adjustment of the curves in Figure 9 to give even better fits of experimental and calculated relationships seems unnecessary in view of our goal of obtaining only a qualitative

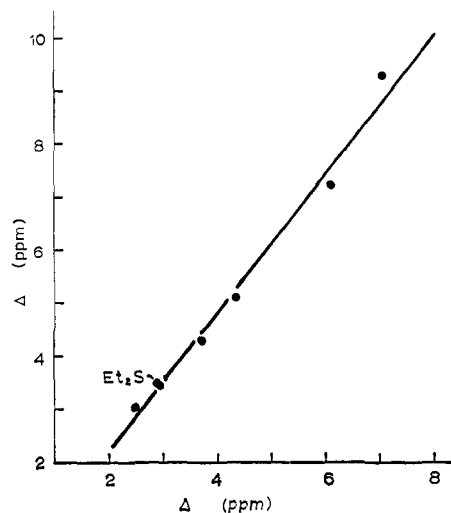


Figure 12. Hydrogen-bond chemical shifts of HFIP vs. those of phenol.

interpretation of Figures 5, 7, and 8 and the degree of freedom associated with estimating ΔR_{OB} .

To summarize, we have adopted the successful model of Lippencott and Schroeder and found that the important features of our experimental correlations can be understood by writing $\Delta H = E_{HB} + (\delta E_{OH} + V_{OB})$ and $\Delta\nu = \delta K_{OH} + K_{HB}$. The importance of the second term in each of these expressions lies in their moderation of each first term. For a given alcohol, K_{HB} is a poorer moderator of δK_{OH} than is $(\delta E_{OH} + V_{OB})$ of E_{HB} . In comparing two alcohols of different acidity, it appears necessary to conclude that the effectiveness of moderation by these terms is greater for the stronger acid.

A similar rationale can be applied^{7,23} to understand the nonzero intercept of the enthalpy-chemical shift relation 6. The observed Δ may, to a first approximation, be considered to be the result of proton deshielding from OH breaking and proton shielding from HB making and B to H charge transfer. A comparison of HFIP with phenol on the basis of this relation is not possible at this time. Although a linear relation has been reported^{1b} for phenol, recent calorimetric measurement of the enthalpies for several of the (weaker) donors used in that correlation has shown³ some of those enthalpies to be in error. The more reliable enthalpies indicate that a larger intercept and smaller slope than previously found for relation 6 is to be expected.

In both relations 6 and 7 and the corresponding ΔH - $\Delta\nu$ relation for phenol, there is an anomaly associated with the soft donor diethyl sulfide. Although HFIP appears as the stronger acid with the hard oxygen and nitrogen donors, its acidity is nearly leveled to that of phenol by the soft sulfur donor when enthalpies are used as the indicator of acid strength (Figure 8). We have computed the E and C parameters^{24a} for HFIP using only the oxygen and nitrogen donor enthalpies and find the following values: $E = 7.34$ and $C = 0.57$.

(23) K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, submitted for publication.

(24) (a) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965). (b) These E , C values for Et_2S differ only slightly from those of ref 24a, and have been computed from the enthalpy data for I_2 , PhOH , and 1,1,1-trifluoroethanol. The parameters of ref 24a for Et_2S are, according to Professor Drago, not particularly accurate.

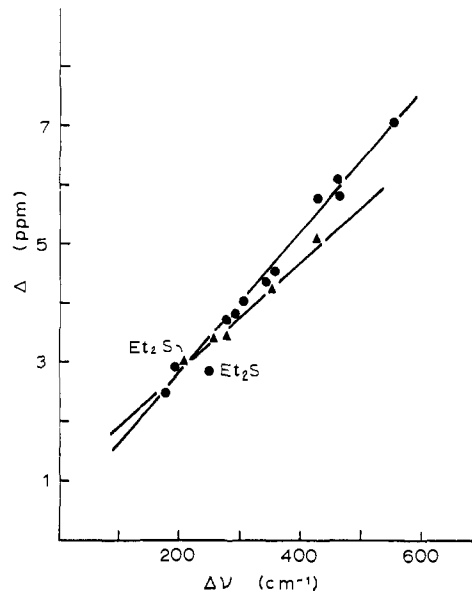


Figure 13. Chemical shift-frequency shift relations for: ●, phenol; ▲, HFIP.

These E , C values can then be used with the E , C parameters^{24b} (0.09, 7.69) for diethyl sulfide to compute a value of $-\Delta H = E_a E_b + C_a C_b = 0.7 + 4.4 = 5.1$ to be compared with the experimental value of 5.1. A similarly accurate replication of the experimental enthalpy can be obtained for phenol ($E = 4.45$, $C = 0.56$). It is apparent that hydrogen-bonding acids are hard acids,^{24a} and the greater acidity of HFIP is associated with its larger "electrostatic" binding ability which, however, is of little consequence with the donor diethyl sulfide. Thus the diethyl sulfide-alcohol interaction seems to arise nearly entirely from the "polarizability" mechanism, and since this property is the same for HFIP and phenol, the adduct enthalpies with the sulfide donor are nearly indistinguishable.

This anomaly or leveling is not restricted to enthalpies, however. As shown in Figure 7, the leveling effect is also observed for the frequency shift. It is intriguing that there is no anomaly associated with the chemical shift-chemical shift correlation shown in Figure 12. As discussed elsewhere,²³ the chemical shifts of these acids when interacting with diethyl sulfide should be corrected by about 0.5 ppm for sulfur atom paramagnetic anisotropy. In Figure 13, such a correction eliminates the anomaly for phenol but requires a leveling of $\Delta\nu^{\text{hf}}$ by 75 cm^{-1} . This is just the leveling indicated in Figure 7! The spectroscopic indices of acidity may therefore be consistently interpreted in terms of a leveling of only $\Delta\nu^{\text{hf}}$ (and not $\Delta\nu^{\text{ph}}$, Δ^{hf} , or Δ^{ph}) by 75 cm^{-1} . If only $\Delta\nu^{\text{hf}}$ has been leveled by 75 cm^{-1} , Figure 5 indicates that ΔH^{hf} has been leveled more (2.2 kcal/mole) than ΔH^{ph} (1.0 kcal/mole). Enthalpy leveling by these amounts is quantitatively consistent with the deviate position of the diethyl sulfide data in Figures 4 and 8. Thus an internally consistent estimate of the acidity reversal effect of diethyl sulfide can be achieved with the following levelings: ΔH^{hf} , 2.2, ΔH^{ph} , 1.0; and $\Delta\nu^{\text{hf}}$, 75 cm^{-1} . We hasten to point out that leveling must be measured relative to some norm of behavior. In the preceding estimates, the norms of behavior are the hard donor

correlations and the chemical shift relation of Figure 12. One conclusion is certain: Δ , ΔH , and $\Delta\nu$ exhibit sensitivities to the leveling property of diethyl sulfide which are not in keeping with their relative sensitivities to the hard donors. It is a distinct possibility that soft donors generate different linear relations than do the hard donors.²⁵ We plan an extensive study of this possibility with the fluoro alcohols.

The *apparent* absence of leveling when the chemical shifts are used to measure the acidities of HFIP and phenol and the failure of $\Delta\nu^{\text{ph}}$ (and $\Delta\nu$ of trifluoroethanol with diethyl sulfide^{7,23}) to exhibit leveling are incompletely understood by us at this time. Hopefully, further investigations will shed more light on these observations or suggest alternate interpretations.

It is interesting that 2,4,6-trimethylpyridine (*s*-collidine) and pyridine give the same enthalpies and that the former gives the same enthalpy in carbon tetrachloride and hexane. Both these observations can be interpreted in terms of steric hindrance in the interaction of *s*-collidine with HFIP and carbon tetrachloride. Molecular models of the HFIP-*s*-collidine adduct show that steric bumping of the methyl and trifluoromethyl groups is likely.

In closing we would like to comment on the possibility of intramolecular bonding in HFIP and its effect on the linear relations discussed above. We believe such intramolecular bonding would not destroy the linearity of any of these relations, when the nonintramolecularly bonded monomer is taken as the reference for the ΔH , $\Delta\nu$, and Δ . One study⁹ of the OH fundamental region of the monomer alcohol suggests that the two OH fundamental bands result from two intramolecularly bonded forms of HFIP and that the enthalpy difference

(25) R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *J. Am. Chem. Soc.*, **86**, 3227 (1964).

between these two forms is negligible (<0.1 kcal/mole). There is apparently no nonbonded monomeric alcohol present in carbon tetrachloride solution at or below room temperature. In our frequency shift measurements we note no change in the relative intensities of the two OH fundamentals of the monomeric acid in equilibrium with the adduct and could find no evidence in any of the spectra of doubling of the adduct absorption band. We therefore assume that the adduct contains the acid with its nonintramolecularly bonded structure and that ΔH , $\Delta\nu$, and Δ should be corrected by constant amounts which reflect the effect of intramolecular bonding on each. (These quantities may be thought of as *constant* acid reorganization energies and spectral shifts.) Such corrections would have the effects of increasing the intercepts of relations 6 and 7 by amounts nearly equal to the ΔH of intramolecular bonding since the corresponding frequency shift and chemical shift corrections are expected to be very small. For example, in 2,2,2-trifluoroethanol, the intramolecular hydrogen-bonding enthalpy and frequency shift are estimated²⁶ to be 3.3 kcal/mole and 20 cm^{-1} . If such values are appropriate to HFIP, the intercepts of relations 6 and 7 will be increased to about 7 kcal/mole, indicating, relative to phenol, a very marked substituent effect. We are presently attempting to measure this intramolecular enthalpy and frequency shift in order that we may fully ascertain the substituent influence of the hexafluoro-2-propyl group.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank the National Science Foundation for an Undergraduate Research Participation Grant for S. D. Brunk.

(26) P. J. Kruger and H. D. Metee, *Can. J. Chem.*, **42**, 340 (1964).