$$m_A\mathbf{v}_A = m_A(\mathbf{v}_L + \mathbf{v}_C) + m_S\mathbf{v}_S$$

$$^1/_2 m_A\mathbf{v}_A{}^2 = {}^1/_2 m_A(\mathbf{v}_L + \mathbf{v}_C)^2 + {}^1/_2 m_S\mathbf{v}_S{}^2 \qquad (11)$$

The projection of $\mathbf{v}_C$ on $\mathbf{v}_A$ is

$$v_R = \mathbf{v}_A \cdot (\mathbf{v}_C + \mathbf{v}_L)/v_A = \pm(2E_T/m_A)^{1/2} \qquad (12)$$

where the second equality gives the bounds within which stabilization will occur. By introducing the angle θ between $\mathbf{v}_A$ and the initial A–S line of centers and integrating sin θ with limits given by the simultaneous solution of (11) and (12), we can find the probabilities for reversal, stabilization, and continued outward motion of A.

The reversal probability is

$$P_R = \frac{1 - [(1 - 1/r^2) + (m_A + m_S)(1 + E_T{}^{1/2}/E_A{}^{1/2})/2m_S)]^{1/2}}{1 - (1 - 1/r^2)^{1/2}} \qquad (13)$$

in which E_A is the A recoil energy. Unless

$$2m_S/(m_A + m_S) \geq r^2(1 + E_T{}^{1/2}/E_A{}^{1/2}) \qquad (14)$$

P_R is 0. The probability of stabilization, P_S, is the difference between the square root in the numerator of eq 13—or 1, if P_R is 0—and the same square root with $E_T{}^{1/2}$ replaced by $-E_T{}^{1/2}$, with the result normalized by the same denominator. It fails to exist unless

$$2m_S/(m_A + m_S) \geq r^2(1 - E_T{}^{1/2}/E_A{}^{1/2}) \qquad (15)$$

An average value $\langle r \rangle$, for approximate use in these expressions, can be constructed from the KMA data by setting eq 9 equal to $\langle \Omega \rangle$. Some extrapolation from the KMA computational range may be necessary.

Using Lennard-Jones'[14] σ for σ_S, one finds that among some typical solvents the degree of space filling increases in the order CH_3OH ($\langle r \rangle = 1.3$), C_6H_{14}, C_6H_6, CCl_4, $CHCl_3$ ($\langle r \rangle = 1.1$). There is zero P_R for all these. The minimum E_T/E_A for stabilization is 0.58 for CH_3OH, 0.25 for C_6H_{14}, and 0.02 for CCl_4. If we say that recombination will be avoided if either photofragment escapes the cage, we need roughly $P_S = 0.6$ for I in hexane and $P_S = 0.9$ for I in CCl_4 to match the laboratory data. Both these situations require $E_T/E_A \cong {}^1/_2$, which is unrealistically high. It would require that I's retaining half their initial outward radial kinetic energy after the first collision usually recombine. For all $E_T/E_A \leq {}^1/_2$, the theory incorrectly predicts a very substantial mass effect for our Figure 6a, which should have a very much more efficient cage than in Figure 4a. Confining our attention to the immediate primary events (P_I) does not alter this, although it makes the required E_T more reasonable.

It seems inescapable that we cannot attribute stabilization to a single encounter between photofragment and solvent, and that around three successive encounters will have to be considered. For realistic (not rigid sphere) potentials, it will be preferable to view the situation as a single happening involving about four strongly interacting objects. The difficulties of making a theoretical model of this will be fairly severe.

Hydrogen Bond Interactions with Sulfur Donors

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Abstract: Calorimetric enthalpy data are reported for the reactions of the acids, 1,1,1,3,3,3-hexafluoro-2-propanol and 2,2,2-trifluoroethanol, with six sulfur donors in CCl_4 solution and four donors in hexane solution. Frequency shift data are also reported for the same two acids reacting with eight sulfur donors. Measurement of the heats of solution of each sulfur donor in both CCl_4 and hexane allows us to estimate hexane enthalpies for the two donors whose enthalpies could not be measured directly in hexane. A comparison of oxygen and sulfur donor ΔH *vs.* ΔH and $\Delta\nu$ *vs.* $\Delta\nu$ equations reveals the greater importance of van der Waals repulsions in the sulfur donor reactions. The change in relative slopes of these equations may also be related to the greater importance of covalent contributions (C_aC_b term) to hydrogen bond formation with sulfur donors. The data adhere nicely to linear enthalpy–frequency shift relations which are considerably different from those reported previously for oxygen donors. A comparison of some analogous oxygen and sulfur donor frequency shifts reveals strong P–S π bonding in a series of phosphine sulfides.

Linear enthalpy–frequency shift relationships have been reported for phenol,[2] 1,1,1,3,3,3-hexafluoro-2-propanol[3] (HFIP), 2,2,2-trifluoroethanol[4] (TFE), *tert*-butyl alcohol,[5] and pyrrole[6] with a variety of oxygen and nitrogen donors. Anomalies from this linear behavior have been reported for the enthalpies of reaction of HFIP[3] and phenol[7] with diethyl sulfide, while the spectroscopic shifts (frequency shift *vs.* chemical shift) resulting from the reaction of this donor with HFIP

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(1) National Science Foundation Research Trainee, 1970–1971; abstracted in part from the Ph.D. thesis of A. D. Sherry, Kansas State University, 1971.

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

(3) K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *ibid.*, **91**, 4019 (1969).

(4) A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, **74**, 3535 (1970).

(5) R. S. Drago, N. O'Brian, and G. C. Vogel, *J. Amer. Chem. Soc.*, **92**, 3925 (1970).

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

(7) G. C. Vogel and R. S. Drago, *ibid.*, **92**, 5347 (1970).

Table I. Hydrogen Bond Data for HFIP and TFE with Various Sulfur Donors in CCl_4

Donor	$-\Delta H$,[a] kcal/mol HFIP	$-\Delta H$,[a] kcal/mol TFE	$\Delta\nu$, ± 10 cm^{-1} HFIP	$\Delta\nu$, ± 10 cm^{-1} TFE
1. 1,1,3,3-Tetramethyl-2-thiourea (TMTU)	6.5	4.6	445	290
2. Tributylphosphine sulfide (TBPS)	6.3	4.4	423	273
3. *N,N*-Dimethylthioacetamide (DMTA)	6.0	4.3	430	280
4. Trioctylphosphine sulfide (TOPS)	5.9	4.3	414	272
5. Tetrahydrothiophene (THTP)	5.2	3.9 ± 0.3	361	227
6. Diethyl sulfide (Et_2S)	4.9	3.6 ± 0.3	348	225
7. Triphenylphosphine sulfide (TPPS)	4.6	*b*	312	200
8. Tris(dimethylamino)phosphine sulfide (TDPS)	*b*	*b*	262	177

[a] Error limits ±0.1 kcal/mol unless otherwise designated. [b] See results.

Table II. Measured and Corrected Hexane Enthalpies

Donor	Measured in hexane[a] $-\Delta H_{HF}$	Measured in hexane[a] $-\Delta H_{TF}$	$\delta_{rxn}^{HF\,b}$	$\delta_{rxn}^{TF\,b}$	Corrected enthalpies[a] $-\Delta H_{HF}$	Corrected enthalpies[a] $-\Delta H_{TF}$
1. TMTU			2.2[c]	2.4[c]	8.7	7.0
2. TBPS	8.3	6.6	2.0	2.2	8.3	6.6
3. DMTA			1.8[c]	2.0[c]	7.8	6.3
4. TOPS	7.4	6.0	1.5	1.7	7.4	6.0
5. THTP	6.1, 5.95[d]	5.0, 4.95[d]	0.9	1.1	6.1	5.0
6. Et_2S	5.9, 5.68[d]	4.7, 4.72[d]	1.0	1.1	5.9	4.7

[a] Error limits ±0.1 kcal/mol. [b] δ_{rxn}^{x} defined as difference between CCl_4 and hexane measured enthalpies. [c] From $\delta\Delta H_{AB}$ *vs.* $\delta\Delta H_B$ (see Figure 1). [d] Calculated values from previously known E and C parameters for these acid–base pairs ($-\Delta H = E_aE_b + C_aC_b$).

have been shown to obey the same linear relationships as the oxygen and nitrogen donors.[8,9] In order to determine if the sulfur donors, as a class of "soft" donors, form a completely different enthalpy–frequency shift relationship, and, if so, the reasons for this behavior, the following study was carried out for a variety of sulfur donors and the acids, HFIP and TFE.

Experimental Section

Purification of Chemicals. Eastman Organic Chemicals *N,N*-dimethylthioacetamide (DMTA) and 1,1,3,3-tetramethyl-2-thiourea (TMTU) were purified[10] by vacuum sublimation at 50°: DMTA, mp 74.5°; TMTU, mp 76.0°.

Eastman Organic Chemicals reagent grade tetrahydrothiophene (THTP) and diethyl sulfide were purified by repeated vacuum fractional distillations. Both compounds contained a higher vapor pressure impurity which was usually completely removed after one fractionation. Vapor pressure of pure compounds at 0°: THTP = 21 mm and Et_2S = 15 mm.

Columbia Organics triphenylphosphine sulfide (TPPS) was recrystallized from 1:4 benzene–ethanol to give pure white crystals, mp 160°.

Tris(dimethylamino)phosphine sulfide (TDPS) was prepared according to previously published procedures[11] and was identified by its infrared and proton nmr spectra, bp 68° (1–2 mm).

Trioctylphosphine sulfide was purchased from Eastman Organic Chemicals and generally found pure as obtained, bp 190° (0 mm).

Tributylphosphine sulfide was prepared by refluxing tri-*n*-butylphosphine (Carlisle Chemical Works) with sulfur in toluene. The product was purified by separation of any phosphine oxides on a Florisil chromatography column followed by two vacuum distillations [bp 134–136° (0 mm)]. The pale yellow liquid product was identified by infrared spectroscopy, $n^{20}D$ 1.5018 [lit.[12] values, bp 137–138° (1 mm) and $n^{25}D$ 1.4945].

The solvents, carbon tetrachloride and *n*-hexane, and the alcohols, HFIP and TFE, were purified as described previously.[3,4]

Infrared Measurements. A Perkin-Elmer 457 grating infrared spectrophotometer with a Crystal Laboratories 2.5-cm cell was used to collect the infrared data. The alcohol concentration was generally about 10^{-2} *M* while the base concentrations [0.01–0.05 *M*] were adjusted to obtain spectra with a relatively strong hydrogen bonded OH band and a free OH peak. An expanded frequency scale (2.5 times) was used to obtain accurate values of $\Delta\nu$.

Calorimetry. The calorimetric procedure and the calculation of the enthalpies are similar to that previously reported.[3,4]

Results

Calorimetric enthalpies were measured for the reaction of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with seven sulfur donors and the reaction of 2,2,2-trifluoroethanol (TFE) with six sulfur donors in CCl_4 solution.

Infrared OH frequency shifts were measured for eight sulfur donors with both HFIP and TFE (it should be pointed out that the range of $\Delta\nu$'s is very small (<200 cm^{-1}) from weakest to strongest donor, unlike the large range with oxygen donors). The data are presented in Table I. The large error limits on the measured enthalpies for TFE with tetrahydrothiophene and diethyl sulfide result from extremely small equilibrium constants for these reactions. The HFIP data show a marked decrease in equilibrium constants with the donors, diethyl sulfide and tetrahydrothiophene (from 40–70 to 2–3). With the weaker acid, TFE, a Scott plot for either donor shows scattered points at low base concentrations. Base concentrations from 0.5 to 1.6 *M* were used for both of these donors with TFE to get the enthalpy values found in Table I. The equilibrium constant for the triphenylphosphine sulfide–TFE reaction appears to be large enough to obtain an accurate enthalpy. However, the most concentrated triphenylphosphine sulfide solution we were able to prepare was 0.1 *M* in CCl_4, thus preventing an accurate evaluation of an enthalpy with this acid. Enthalpies were not determined for the reaction of tris(dimethylamino)phosphine sulfide with the two alcohols because we were unable to obtain large enough quantities of the *pure* base to measure an accurate value.

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

[9] K. F. Purcell and A. D. Sherry, *ibid.*, **34**, 177 (1970).

[10] R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Amer. Chem. Soc.*, **86**, 1694 (1964), report sulfur coordination for tetramethylthiourea and *N,N*-dimethylthioacetamide with phenol.

[11] W. E. Slinkard and D. W. Meek, *Inorg. Chem.*, **8**, 1811 (1969), report sulfur coordination of tris(dimethylamino)phosphine sulfide with Co^{2+}.

[12] R. A. Zingaro and R. E. McGlothlin, *J. Org. Chem.*, **26**, 5205 (1961).

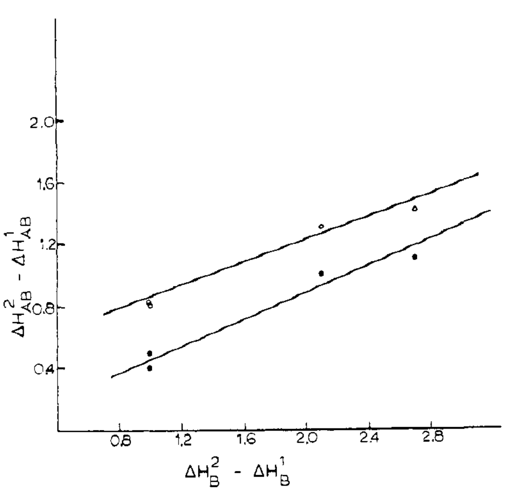

Figure 1. Difference in adduct solvation energies *vs.* difference in base solvation energies for the solvents: 2 = hexane and 1 = CCl_4, ○ = TFE, ● = HFIP.

A recent report[7] indicates there is a specific interaction between sulfur donors and carbon tetrachloride. This would make the enthalpies reported in Table I smaller than the true "gas phase" values. It appears the solvent, *n*-hexane, would be a more suitable solvent for studying sulfur donor reactions. However, two of the donors in this study, tetramethylthiourea and *N*,*N*-dimethylthioacetamide, are only slightly soluble in *n*-hexane while triphenylphosphine sulfide is completely insoluble. Enthalpy values were measured for the other four donors with TFE and HFIP in *n*-hexane and are reported in Table II. In each case, the enthalpy measured in *n*-hexane is larger (more exothermic) than that measured in CCl_4. This is similar to the situation found for pyridine and 2,4,6-trimethylpyridine where a specific interaction with CCl_4 also exists.[13] The differences in the CCl_4 and hexane measured enthalpies, δ_{rxn} ($=\Delta H_{CCl_4} - \Delta H_{\text{hex}}$), appear to increase with increasing donor strength. These values reflect, at least partially, the strength of the CCl_4–donor interactions.[14]

In an attempt to estimate hexane enthalpies for the donors tetramethylthiourea and *N*,*N*-dimethylthioacetamide we also measured the heats of solution at ∞ dilution of each donor in CCl_4 and hexane. These data are found in Table III. The difference in heats of solution, $-\delta_{\Delta H\,\text{sol}}^{CCl_4-\text{hex}}$, also increases with increasing donor strength. However, these values appear larger for trioctyl- and tributylphosphine sulfide than the actual differences found in Table II. This, of course, means that the acid and adduct solvation energies do not cancel on changing solvent. To investigate further we analyze the results in terms of a Hess' law cycle.

Table III. Sulfur Donor Heats of Solution

Donor	$\Delta H_{\text{sol}}^{\infty\,\text{dil}}$,[a] ±0.1 kcal/mol CCl_4	 Hexane	$-\delta_{\Delta H\text{sol}}^{CCl_4-\text{hex}}$
1. TMTU	+4.7	+7.6	2.9
2. TBPS	−0.4	+2.3	2.7
3. DMTA	+4.0	+6.4	2.4
4. TOPS	−0.3	+2.8	2.1
5. THTP	−0.6	+0.4	1.0
6. Et_2S	−0.7	+0.3	1.0
7. TPPS	+5.1	*b*	

[a] All values were found by extrapolating data to ∞ dilution. [b] Too insoluble to measure.

$$\begin{tikzcd}
A(s) + B(s) \arrow[r, "\Delta H_s"] & AB(s) \\
A(g) + B(g) \arrow[u, "\Delta H_A"] \arrow[r, "\Delta H_g"] & AB(g) \arrow[u, "\Delta H_{AB}"']
\end{tikzcd}$$

ΔH_B (upward arrow from B(g) to B(s))

$$\Delta H_s = \Delta H_g - \Delta H_B - \Delta H_A + \Delta H_{AB} \qquad (1)$$

When comparing two solvents (1 and 2)

$$\Delta H_s{}^1 - \Delta H_s{}^2 = (\Delta H_B{}^2 - \Delta H_B{}^1) + (\Delta H_A{}^2 - \Delta H_A{}^1) - (\Delta H_{AB}{}^2 - \Delta H_{AB}{}^1) \qquad (2)$$

Equation 2 indicates that the difference between enthalpies measured in two solvents will be equal to the difference in the heats of solution of the donor in each solvent *only* if the last two terms cancel. This seems to hold for the donors diethyl sulfide and tetrahydrothiophene (*i.e.*, compare $-\delta_{\text{rxn}}$ values in Table II with $-\delta_{\Delta H\,\text{sol}}$ values in Table III). The last two terms do not cancel for trioctyl- and tributylphosphine sulfide. Since the quantities ($\Delta H_A{}^2 - \Delta H_A{}^1$) are known for both acids we can evaluate the terms, ($\Delta H_{AB}{}^2 - \Delta H_{AB}{}^1$). With 2 = hexane and 1 = CCl_4, Figure 1 depicts how the difference in the adduct solvation term varies with the term $\delta\Delta H_b = (\Delta H_B{}^2 - \Delta H_B{}^1)$. The adduct solvation energy difference varies in an essentially linear fashion with $\delta\Delta H_B$ for the latter in the range 1.0 to 2.8 kcal/mol. A smooth variation is expected, though not necessarily linear. That the relationship is linear within 0.1 kcal/mol over $1.0 < \delta\Delta H_B < 3.0$ allows us to estimate the adduct solvation energy difference for tetramethylthiourea and *N*,*N*-dimethylthioacetamide. Knowing all other quantities in eq 2 allows us to compute values for $\Delta H_s{}^2$ for these donors. These are the values which appear in the last two columns of Table II. It is these hexane values, measured in hexane for diethyl sulfide, tetrahydrothiophene, and trioctyl- and tributylphosphine sulfide, and estimated (±0.1 kcal/mol) for *N*,*N*-dimethylthioacetamide and tetramethylthiourea, which are used in the discussion.

Discussion

With sulfur instead of oxygen or nitrogen acting as the donor atom, HFIP and TFE have changed considerably in their hydrogen bonding characteristics. Comparing data for the pairs *N*,*N*-dimethylthioacetamide, *N*,*N*-dimethylacetamide and Et_2S, Et_2O shows that the frequency shifts for each acid do not distinguish between sulfur or oxygen donors while the enthalpy is smaller in each case with the sulfur donor. Yet, by either measure of acidity, OH frequency shifts or enthalpies, HFIP is always a better acid than TFE.

To make comparisons between the "soft" sulfur donors and the "hard" oxygen and nitrogen donors, a comparison must be made between their ΔH_{HF} *vs.* ΔH_{T} plots and their $\Delta\nu_{\text{HF}}$ *vs.* $\Delta\nu_{\text{T}}$ plots. These plots (using ΔH_{corr} values, Table II) are shown in Figures 2 and 3, respectively. The least-squares equations for these lines, with the standard errors at the 95% confi-

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(13) A. D. Sherry and K. F. Purcell, *J. Amer. Chem. Soc.*, **92**, 6386 (1970).

(14) Assuming complete solvation and a specific interaction between a sulfur donor and CCl_4, the stronger sulfur donors should show the greatest donor–CCl_4 interaction.

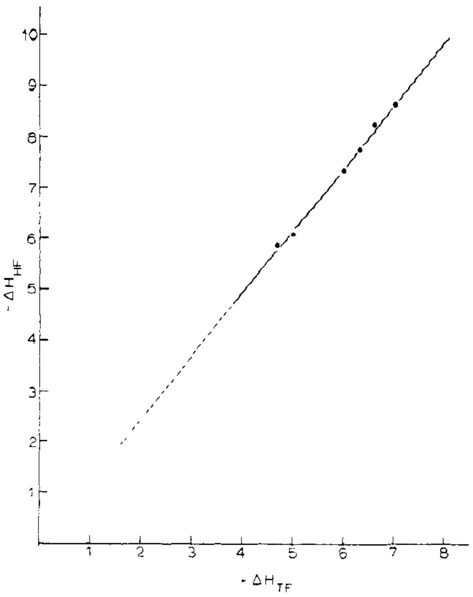

Figure 2. Enthalpies of HFIP *vs.* enthalpies of TFE reacting with a series of sulfur donors.

dence level, are

$$\Delta H_{\mathrm{HF}}\ (\pm 0.1) = 1.26\ (\pm 0.03)\ \Delta H_{\mathrm{T}} - 0.1\ (\pm 0.2) \quad (3)$$

$$\Delta\nu_{\mathrm{HF}}\ (\pm 5) = 1.55\ (\pm 0.06)\ \Delta\nu_{\mathrm{T}} - 3.0\ (\pm 14) \quad (4)$$

The corresponding equations for oxygen and nitrogen donors[4] are

$$\Delta H_{\mathrm{HF}}\ (\pm 0.2) = 1.16\ (\pm 0.04)\ \Delta H_{\mathrm{T}} + 1.1\ (\pm 0.3) \quad (5)$$

$$\Delta\nu_{\mathrm{HF}}\ (\pm 14) = 1.24\ (\pm 0.06)\ \Delta\nu_{\mathrm{T}} + 53\ (\pm 18) \quad (6)$$

The slopes of both sulfur donor equations are larger than the corresponding oxygen and nitrogen donor equations while the intercepts have decreased to values which are essentially zero. The small intercepts indicate that the greater electrostatic or dipolar acidity of HFIP over TFE is masked by the sulfur donors. In an earlier publication,[4] van der Waals repulsions were found more important in the TFE reactions than in HFIP reactions. This is demonstrated with the greater than unity slope of eq 5. Now, with sulfur acting as the donor atom, any van der Waals repulsion difference for these two acids should be greatly magnified. This is reflected in the larger slope of eq 3 over eq 5. This difference in slopes and intercepts can be correlated with the E and C parameters for the two alcohols. The 43% larger E_a of HFIP over TFE (5.88 and 4.12 for HFIP and TFE, respectively) is considerably reduced in importance for sulfur donors which have large C_b's and small E_b's (see below). Hence, the smaller intercept of eq 3 than eq 5 is expected. Similarly, the 19% larger C_a for HFIP (0.64 and 0.54 for HFIP and TFE, respectively) is more significant in the sulfur donor reactions. Consequently, a larger slope is found for the ΔH_{HF} *vs.* ΔH_{TF} line with sulfur donors.

This greater importance of the covalent term and lesser importance of the electrostatic term in the enthalpies of these reactions is also reflected in the α parameters of the single scale enthalpy equation ($\Delta H = \alpha\beta_{\mathrm{B}}$).[4] The α value calculated from the sulfur donor reactions is 1.24 ± 0.02 (defined $\alpha = \Delta H_{\mathrm{HF}}/\Delta H_{\mathrm{TF}}$, where α for TFE = 1.00). This is to be compared with

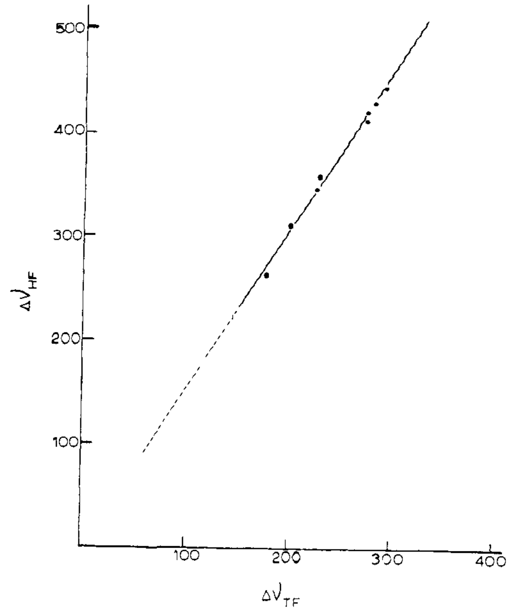

Figure 3. Frequency shifts of HFIP *vs.* frequency shifts of TFE reacting with a series of sulfur donors.

an α value of 1.35 ± 0.06 for the oxygen and nitrogen donor reactions. The decrease in α value in reactions with sulfur donors reflects the decreased importance of the electrostatic term (E_aE_b) to the total enthalpy for HFIP (the 43% larger E_a for HFIP is of only comparable importance to the 19% larger C_a in determining α). It is understandable that the α values for a series of alcohols will depend on the *class* of donors used in defining α. The phrase "single scale" is thus only applicable within a class of donors.[15]

A plot of ΔH *vs.* α for the six sulfur donors is found in Figure 4. The slopes ($\beta_{\mathrm{B}} = \Delta H_{\mathrm{TF}}$ with donor **B**) of these lines are, of course, all smaller than those for the oxygen donor analogs. The lines show excellent linearity through the HFIP and TFE points and through the origin. As the origin is the only check point on this linearity, data with sulfur donors need to be gathered for other hydrogen bonding acids to establish the generality of $\Delta H = \alpha\beta$ for sulfur donors.

When comparing ΔH *vs.* $\Delta\nu$ plots for oxygen and sulfur donors, a large change is seen. These linear plots are compared in Figure 5. The least-squares equations for the sulfur donor data, at the 95% confidence level, are

$$\Delta H_{\mathrm{T}}\ (\pm 0.2) = 0.0319\ (\pm 0.002) \times \Delta\nu_{\mathrm{T}} - 2.4\ (\pm 0.6) \quad (7)$$

$$\Delta H_{\mathrm{HF}}\ (\pm 0.2) = 0.0287\ (\pm 0.002) \times \Delta\nu_{\mathrm{HF}} - 4.2\ (\pm 0.7) \quad (8)$$

Similar plots for oxygen and nitrogen donors gave the following equations[4]

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[15] A referee has pointed out that the E,C equations lead to $\Delta H_{\mathrm{H}} = (C_{\mathrm{H}}/C_{\mathrm{T}})\Delta H_{\mathrm{T}} + E_{\mathrm{B}}(E_{\mathrm{H}} - (C_{\mathrm{H}}/C_{\mathrm{T}})E_{\mathrm{T}})$. Since E_{B} is undoubtedly related to ΔH_{T}, the slope of a ΔH_{H} *vs.* ΔH_{T} plot should differ from the ratio $C_{\mathrm{H}}/C_{\mathrm{T}}$ by some amount. Since ΔH_{T} should be a less sensitive function of E_{B} for sulfur donors than oxygen donors, the slope of ΔH_{H} *vs.* ΔH_{T} for sulfur donors should be less than that for oxygen donors. This approach is difficult to quantify and translate into physical forces but at least shows another view of the relationship between the slopes of ΔH *vs.* ΔH plots and the E,C parameters.

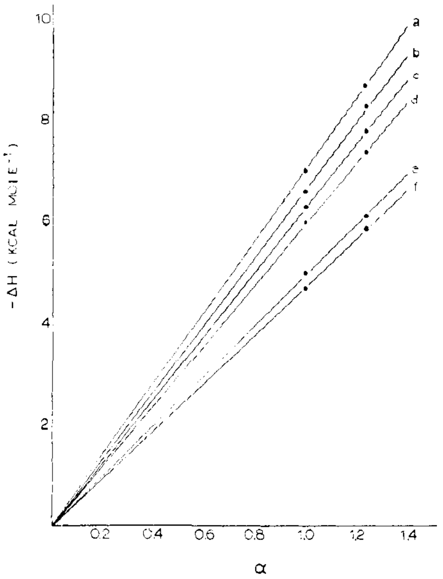

Figure 4. Enthalpy *vs.* hydrogen bonding constant (α) for the following bases: a, TMTU; b, TBPS; c, DMTA; d, TOPS; e THTP; f, Et_2S.

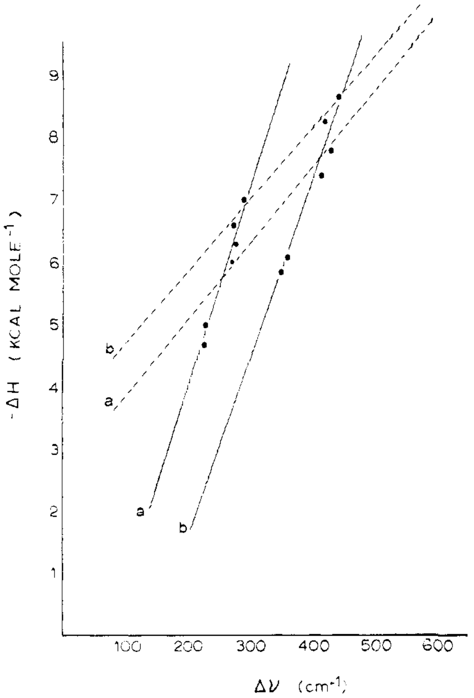

Figure 5. Enthalpy *vs.* frequency shift relations: a = TFE, b = HFIP, solid line = sulfur donors, dashed line = oxygen donors.

$$\Delta H_{\mathrm{T}} (\pm 0.1) = 0.0121 (\pm 0.0005) \times \Delta\nu_{\mathrm{T}} + 2.7 (\pm 0.2) \quad (9)$$

$$\Delta H_{\mathrm{HF}} (\pm 0.2) = 0.0114 (\pm 0.0008) \times \Delta\nu_{\mathrm{HF}} + 3.6 (\pm 0.3) \quad (10)$$

The interpretation of (7) and (8) is difficult because one is comparing two different indices of acid–base interaction. For the oxygen, nitrogen donor class (eq 9 and 10) previous discussion also suggested this difficulty but did indicate that the relative slopes were understandable in terms of relative ΔH *vs.* ΔH and $\Delta\nu$ *vs.* $\Delta\nu$ slopes. The slope difference found for HFIP *vs.* TFE with oxygen, nitrogen donors is amplified by the use of sulfur donors. In eq 4 and 6 the HFIP frequency shifts change at a rate 1.25 (ratio of the slopes of eq 4 and 6) greater for sulfur donors while the HFIP enthalpies change at a rate only 1.09 (ratio of slopes of eq 3 and 5) greater. The result is that the ΔH *vs.* $\Delta\nu$ slope for HFIP with sulfur donors should be ~0.9 that for TFE, as observed. The increased difference in HFIP and TFE slopes is directly attributable to the greater increase in frequency shift slope (eq 6 → eq 4) than in enthalpy slope (eq 5 → eq 3). A possible explanation here is that while both slopes do increase with sulfur donors, the enhanced role of van der Waals repulsions limits the increase in enthalpy slope.

The most interesting feature of eq 7 and 8 is their negative intercepts (both ΔH and $\Delta\nu$ are considered positive quantities). The behavior of the ΔH *vs.* $\Delta\nu$ relationships for sulfur donors is markedly different in the low energy region from that for oxygen, nitrogen donors. Such behavior is expected if it is assumed that van der Waals repulsion is particularly important, relative to dipolar energy, in the weak interaction range as well as over the linear region, as discussed above. The positive intercepts of eq 9 and 10 have been interpreted[4,16] as being due to dipole–dipole attractions between the alcohols and the hard oxygen and nitrogen donors, in the weak interaction region. With the more polarizable sulfur donors, we would expect to find greatly reduced dipole–dipole attractions between the alcohols and the bases (E_aE_b should be very small). This would be consistent with the reduced intercepts of eq 7 and 8. Thus, increasing dipolar attraction over the low energy range is very effectively moderated by increasing van der Waals repulsions, in sharp contrast to the domination by dipolar contributions in this region for oxygen, nitrogen donors.

***E* and *C* Parameters.** We have calculated the *E* and *C* parameters for the donors used in this study and, as expected, find the parameters for these donors to be drastically different from the corresponding hard oxygen and nitrogen donors (*i.e.*, the C_b's are larger and the E_b's are smaller). The C_b parameters decrease steadily (with one exception) from strongest to weakest sulfur donor, while the E_b parameters appear in random order. This emphasizes the importance of the C_b term in determining the strength of a sulfur donor. To discuss the quantitative values of the sulfur donor *E* and *C* parameters is clearly not called for since these values were obtained from only two enthalpies for each donor and, furthermore, only with acids of the hard type.

One interesting observation is the inversion of acid strength of phenol and TFE toward oxygen and sulfur donors. Toward oxygen donors, phenol is a stronger hydrogen bonding acid than TFE.[2,4] However, a comparison of the data in Table II with the phenol data[7] shows TFE to be a stronger hydrogen bonding acid toward THTP and diethyl sulfide. This anomaly could have been predicted from the known *E* and *C* parameters of the two alcohols.[17]

	E_a	C_a
TFE	4.12	0.543
Phenol	4.59	0.537

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[16] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, 23, 1099 (1955).

[17] Private communication from Professor R. S. Drago.

Table IV. Frequency Shifts for Some Oxygen and Sulfur Donors

	Donor	$\Delta\nu_{TFE}$, ± 10 cm^{-1}	$\Delta\nu_{HFIP}$, ± 10 cm^{-1}
1.	Diethyl ether	232[a]	357[b]
	Diethyl sulfide	225	348
2.	*N*,*N*-Dimethylacetamide	277[a]	428[b]
	N,*N*-Dimethylthioacetamide	273	423
3.	Triphenylphosphine oxide	346	475
	Triphenylphosphine sulfide	200	312
4.	Tributylphosphine oxide	414	550
	Tributylphosphine sulfide	280	430
5.	Tris(dimethylamino)phosphine oxide	405[a]	540[b]
	Tris(dimethylamino)phosphine sulfide	177	262

[a] Reference 4. [b] Reference 3.

Toward the hard oxygen donors, the E_a term is predominant while toward the soft sulfur donors, the C_a term predominates.

Comparison of Some Frequency Shifts. A direct comparison of a few analogous oxygen and sulfur donor frequency shifts is possible. The first two pairs of donors in Table IV have the donor atom bonded to a carbon. In this case, frequency shifts make very little distinction between the oxygen and sulfur donor with either alcohol, HFIP or TFE. However, with the next three pairs of donors (the phosphine oxides and sulfides), a large distinction is noticed between the oxide and the sulfide. This may be attributed to a lowering of the basicity of the sulfur donor from P–S d–p π bonding.[18] The difference is the largest in the last pair of donors in which the atoms attached to the phosphorus are all second period atoms in the first instance. The nitrogen atoms are capable of p–d π interaction with phosphorus and thus enhance the basicity of the oxygen atom. With sulfur, on the other hand, strong P–S π bonding is likely to dominate P–N π bonding and the NMe_2 groups appear as mainly electron-withdrawing groups (compare $Me_2N)_3$ PS with $(Bu^n)_3PS$). The relative enhancement of chalcogen basicity should be greater in the case of oxygen.

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Linear Enthalpy–Spectral Shift Correlation for Perfluoro-*tert*-butyl Alcohol

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Abstract: Calorimetric enthalpy data and infrared OH frequency shifts are reported for the acid–base interaction of perfluoro-*tert*-butyl alcohol with a variety of Lewis bases. A reduced adduct solvation by CCl_4 plus an excessive acid solvation leads to lower enthalpies measured in CCl_4 solution than in hexane solution. Reaction enthalpies with six donors in hexane were used to evaluate the E_a and C_a parameters for perfluoro-*tert*-butyl alcohol. Seven other donor enthalpies were calculated using the double scale enthalpy equation. The following correlation was found: $\Delta H\,(\pm 0.2) = 0.0106\Delta\nu + 3.9$. This correlation along with ΔH *vs.* ΔH correlations with 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, and phenol indicates that van der Waals repulsions are of least importance in the perfluoro-*tert*-butyl alcohol reactions. The slopes and intercepts of these relations, like the E_a and C_a parameters, reveal the relative electrostatic and covalent contributions in the formation of a hydrogen bond for each of these alcohols. The data adhere nicely to a single-scale enthalpy equation ($\Delta H_a = \alpha_A\beta_B$) and an α *vs.* σ^* plot. This fit provides good evidence for negligible acid–base steric interactions in the perfluoro-*tert*-butyl alcohol reactions.

During the past few years, linear enthalpy–frequency shift relationships have been reported for a variety of alcohols.[2–7] These reports have led to a better understanding of the hydrogen bond. Two proposed models[4,7,8] reveal the roles of electrostatic forces, covalent forces, and van der Waals repulsions in the total bond energy. The latest publication from our laboratory[7] indicates that since the hexafluoroisopropyl group of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) can remove electron density from the OH group better than the trifluoroethyl group of 2,2,2-trifluoroethanol (TFE), the former more effectively reduces the van der Waals repulsions between the donor electrons and the alcohol oxygen. More recent data[9] with the same two alcohols and sulfur donors substantiates our earlier conclusions.

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