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.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research, Kansas State University, for support of this research.

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

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In this report, we present calorimetric and infrared frequency shift data for the third alcohol in the series of fluoro alcohols, perfluoro-*tert*-butyl alcohol (PFTB). This alcohol is a much stronger hydrogen-bonding acid than the less fluorinated alcohols in this series ($pK_a = 5.2$[10]) and should again test the generality of the linear enthalpy–OH frequency shift relationship. This study also allows a test of the validity of our earlier conclusions[7] concerning the importance of van der Waals repulsions, the generality of the single scale enthalpy equation, $\Delta H = \alpha_A \beta_B$, and the α *vs.* σ^* plots.

Experimental Section

Purification of Chemicals. Most of the donors used in this study were purified by procedures previously reported.[7] In addition, acetone was purified by the method of Perrin[11] through the sodium iodide addition compound. Eastman White Label hexamethylphosphoramide and 2,4,6-trimethylpyridine were refluxed over and distilled from barium oxide (HMPA distilled at reduced pressures). Mallinckrodt Analytical Reagent carbon tetrachloride and hexane were thoroughly dried over Linde 4A molecular sieves and finally passed through a column of Alcoa chromatographic alumina (F-20) in a dry atmosphere box immediately before use. Perfluoro-*tert*-butyl alcohol was prepared by the method of Dear[12] through fluorination of hexafluoro-2-trichloromethyl-2-propanol with antimony pentafluoride, bp 45°.

Infrared Measurements. A Perkin-Elmer 457 grating infrared spectrometer with a matched set of Crystal Laboratories' 2.5-cm sodium chloride cells was used in this study. We often found it advantageous to cancel the solvent bands in the reference beam, especially with the stronger donors which placed the OH hydrogen-bonded band below the CH region. The location of the pyridine adduct OH band was difficult. However, both the ΔH_{PF} *vs.* $\Delta \nu_{PF}$ plot and the $\Delta \nu_{PF}$ *vs.* $\Delta \nu_{TF}$ indicate a shift of about 835 cm^{-1}. The adduct OH bands of γ-collidine and triethylamine were often times obscured by CCl_4 overtone bands. This problem was alleviated by concentration studies and cancellation of the solvent bands. Diaprep Incorporated dimethyl sulfoxide-d_6 was used to obtain the adduct OH frequency shift for DMSO.

Calorimetry. The same calorimeter system as used in the TFE study[7] was used for these measurements. It soon became apparent that PFTB was such a strong alcohol that it would hydrogen bond to minute amounts of H_2O left in the solvents. (Distillation of the solvents did not solve the problem if they were subsequently exposed to the atmosphere.) Thus, the entire calorimeter system, with the exception of the recorder, was placed in a Lab Con Co dry atmosphere box. The heats of solution of PFTB in CCl_4 and hexane were found to be constant in the dry atmosphere box. In the open atmosphere, the heats of solution were always considerably less endothermic. All base solutions were prepared in the drybox immediately after running the solvent through an alumina column. All other techniques are the same as those reported previously.[7]

Least-Squares Treatment of Data. The calculations of the least-squares slopes and intercepts along with the standard error of estimate at the 95% confidence level, standard error in slope, and standard error in intercept were carried out as previously reported.[7]

Results

The heats of solution of perfluoro-*tert*-butyl alcohol (PFTB) in CCl_4 and hexane were determined as a function of concentration. These values are constant (2.86 ± 0.04 kcal mol^{-1} and 3.46 ± 0.04 kcal mol^{-1}, respectively) over the concentration range 0.002–0.02 *M* in PFTB. Since the reaction of PFTB with a base gives off considerable heat, the acid concentrations could usually be kept low (0.005–0.01 *M*) to conserve alcohol.

The work-up of the calorimetric data into ΔH's was performed in the manner used in the trifluoroethanol report.[7] The results are presented in Table I. Calorimetric data were first gathered in the solvent CCl_4.

Table I. Hydrogen-Bond Data for PFTB

	Donor	$-\Delta H$, kcal/mol[b] Hexane	CCl_4	$\Delta \nu$,[a] cm^{-1}
1.	Acetonitrile	6.9[c]	6.4	306
2.	Ethyl acetate	7.3[c]	6.7	320
3.	Acetone	8.0	7.2	380
4.	Diethyl ether	8.3	7.1	480
5.	Tetrahydrofuran	9.2[c]	7.7	506
6.	*N*,*N*-Dimethylformamide	9.5[c]	8.6	510
7.	*N*,*N*-Dimethylacetamide	10.2[c]	8.9	540
8.	Dimethyl sulfoxide	10.6[c]	9.5	578
9.	Hexamethylphosphoramide	12.2[c]	10.5	770 ± 20
10.	Pyridine	12.5	10.3	835 ± 20
11.	2,4,6-Trimethylpyridine	14.1	11.0	968 ± 20
12.	Triethylamine	14.3		980 ± 20
13.	Diethyl sulfide	7.0		

[a] Estimated error ±10 cm^{-1} unless stated otherwise. [b] Estimated error ±0.2 kcal/mol. [c] Calculated using *E* and *C* parameters. For hexamethylphosphoramide, final, generally applicable E_b and C_b values are not known yet. We have computed values for this base from enthalpy data with trifluoroethanol and hexafluoroisopropyl alcohol. Those values are expected to be reliable for hydrogen bonding acids only.

These enthalpies seemed small in comparison to the enthalpies of interaction of the same group of donors with TFE and HFIP in CCl_4. ($-\Delta H$ increased by 1.5–2.5 kcal/mol replacing TFE with HFIP while the changes for PFTB in place of HFIP were only 0.2–0.8. Such behavior might, erroneously, be taken to imply steric interaction between PFTB and donors; see later.) A small enthalpy measured in CCl_4 could be attributed to solvent effects, either an extra large interaction between the PFTB and CCl_4 or a lesser solvation of the PFTB–base adducts than expected. It has recently been suggested that phenol interacts specifically with CCl_4.[13] Thus, it seems possible that the much more acidic PFTB could also interact specifically with CCl_4. The second effect, a small solvation of the acid–base adduct, could also be important since envelopment of the $OH \cdots B$ dipole by the CF_3 groups could account for the smaller enthalpies.

A recent report from this laboratory[14] suggests the trend in adduct transfer solvation energies (hexane → CCl_4) for the HFIP, TFE, pyridine, and γ-collidine acid–base pairs depends on the congestion at the polar O–H–B groupings. These energies (in kcal mol^{-1}) are $TFE \cdot py = -1.48$, $TFE \cdot coll = -0.91$, $HFIP \cdot py = -0.75$, and $HFIP \cdot coll = -0.21$. Using the enthalpy data for PFTB with pyridine and γ-collidine in hexane and CCl_4 from Table I, and ΔH^{PFTB} (hexane → CCl_4) = -0.60 kcal mol^{-1}, adduct transfer solvation energies can be calculated for the PFTB adducts. These are $PFTB \cdot py = -0.09$ kcal mol^{-1} and $PFTB \cdot coll = +1.25$ kcal mol^{-1}. These values indicate that the PFTB adducts are solvated by CCl_4 even less than the HFIP and TFE adducts and support our earlier conclusion that the extent of solvation by CCl_4 depends upon the congestion at the O–H–B groups.[14] Thus, it could be concluded that reduced adduct solvation by CCl_4 is partly responsible for somewhat low ΔH's for PFTB in CCl_4.

The other factor, excessive acid solvation, could also contribute to low heats. That is, the heats of transfer at infinite dilution from hexane to CCl_4 are -0.92,

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(11) D. A. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Elmsford, N. Y., 1966, p 57.

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-0.39, and -0.60 kcal/mol for TFE, HFIP, and PFTB, respectively. Thus, acid solvation is of lesser importance to PFTB than to TFE but of somewhat greater importance to PFTB than to HFIP. It is interesting that a minimum in this quantity occurs with two CF_3 groups. The decreasing acid solvation with increasing substitution of CF_3 groups is indicative of steric congestion near the OH group as CF_3 replaces H, but the minimum suggests that increased OH polarity becomes more important relative to CF_3 group deshielding when the number of CF_3 groups is increased from two to three.

A more pertinent comparison of solvation effects would be the balance between the acid and adduct solvation energies for each acid. To this end, we may compare these quantities for the pyridine and collidine adducts. The results are $\Delta H_{\mathrm{AB}} - \Delta H_{\mathrm{A}}(\text{hexane} \rightarrow CCl_4) = -0.56, -0.36$, and $+0.51$ for TFE, HFIP, and PFTB adducts with pyridine and $+0.01$, $+0.18$, and $+1.85$ for TFE, HFIP, and PFTB with collidine. Assuming the same trends to hold for the other donors in these investigations, the CCl_4 reaction enthalpies for HFIP can be anticipated to be little different ($\sim$0.2 kcal/mol less exothermic) from those in hexane while those for PFTB can be expected to be $\sim$1.5 kcal/mol less exothermic, as far as the change in $\Delta H_{\mathrm{AB}} - \Delta H_{\mathrm{A}}$ is concerned. The marked change from HFIP to PFTB is due to both increased acid and decreased adduct solvations in the latter. This point is clarified by the following equations.

$$\begin{array}{rcll} -\Delta H_{\mathrm{TFE}} + \Delta H_{\mathrm{TFE\cdot py}} &=& +0.92 & -\ 1.48 \\ & & \big\downarrow{\scriptstyle -0.53} & \big\downarrow{\scriptstyle +0.73} \quad = +0.20 \\ -\Delta H_{\mathrm{HFIP}} + \Delta H_{\mathrm{HFIP\cdot py}} &=& +0.39 & -\ 0.75 \\ & & \big\downarrow{\scriptstyle +0.21} & \big\downarrow{\scriptstyle +0.66} \quad = +0.87 \\ -\Delta H_{\mathrm{PFTB}} + \Delta H_{\mathrm{PFTB\cdot py}} &=& +0.60 & -\ 0.09 \end{array}$$

Thus the decrease in adduct solvation appears to be relatively constant (0.7 kcal) as CF_3 replaces H while the acid solvation decreases then increases as CF_3 replaces H. For the change TFE → HFIP the acid and adduct solvation changes offset one another, while for the change HFIP → PFTB they reinforce.

Concern that the unusual solvation effects for the PFTB reactions would complicate later interpretation of alcohol acidity, we subsequently determined reaction enthalpies for six of the donors in hexane. The six donors chosen for these reactions were pyridine, γ-collidine, triethylamine, acetone, diethyl ether, and diethyl sulfide. The first three donors are normally run in hexane to avoid the interactions known to exist between amines and CCl_4,[14,15] while the next two were chosen from those remaining in Table I to avoid the effects of base aggregation in hexane.[3] Diethyl sulfide was chosen to include a "soft" donor enthalpy in the calculation of E_a and C_a. A concentration study of the heats of solution of the oxygen donors used in this study shows that all but acetone and diethyl ether are highly associated in hexane, even at very low base concentrations. Acetone and diethyl ether appear not to associate greatly until their concentration becomes larger than 0.1 *M*. Thus, the base concentrations were kept below 0.1 *M* in the acetone- and diethyl ether–PFTB reactions in hexane to assure an accurate enthalpy. A comparison of the hexane and CCl_4 enthalpies finds the CCl_4 heats low in each case, for the reasons given in the preceding paragraph.

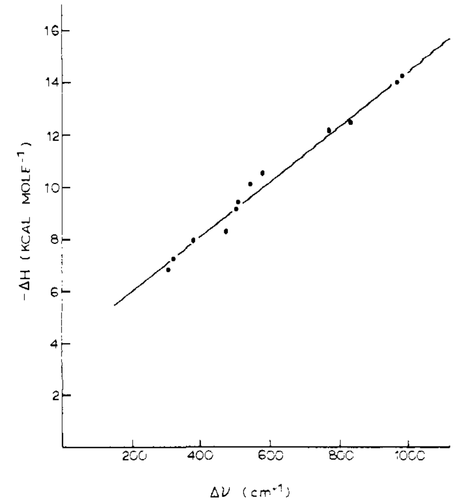

Figure 1. Enthalpy *vs.* frequency shift for PFTB.

Using the six enthalpies measured in hexane and the known base *E* and *C* parameters,[16] the E_a and C_a were calculated for PFTB by a least-squares method (E_a = 6.72 and C_a = 0.849). These values were in turn used to calculate the remaining seven donor enthalpies. These hexane values are used in all equations which follow.

Discussion

As shown in Figure 1, the enthalpy data for perfluoro-*tert*-butyl alcohol (PFTB) generate a linear relationship with the infrared OH frequency shifts. The equation for this line, with the standard error of estimate and standard error in slope and intercept, is

$$\Delta H_{\mathrm{PF}}\ (\pm 0.2) = 0.0106\ (\pm 0.0004) \times \Delta\nu_{\mathrm{PF}} + 3.9\ (\pm 0.3) \quad (1)$$

This may be compared with the similar equations for 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).

$$\Delta H_{\mathrm{HF}}\ (\pm 0.2) = 0.0114\ (\pm 0.0008) \times \Delta\nu_{\mathrm{HF}} + 3.6\ (\pm 0.3) \quad (2)$$

$$\Delta H_{\mathrm{TF}}\ (\pm 0.1) = 0.0121\ (\pm 0.0005) \times \Delta\nu_{\mathrm{TF}} + 2.7\ (\pm 0.2) \quad (3)$$

The larger intercept of the PFTB relationship indicates the greater dipole–dipole attraction between this acid and a weak donor than HFIP or TFE with the same donor. (Note: the difference between PFTB and HFIP is small and marginally significant.) Again, this falls in line with the electron-withdrawing abilities of each of the three groups, PFTB > HFIP > TFE. The slopes of these equations fall in the opposite order of the acid strengths, *i.e.*, TFE > HFIP > PFTB.

To understand the order of slopes, we will adopt the procedure used to compare HFIP with TFE[7] and plot

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

(16) Private communication from R. S. Drago. A complete list of *E* and *C* parameters is to be found in R. S. Drago, *et al.*, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

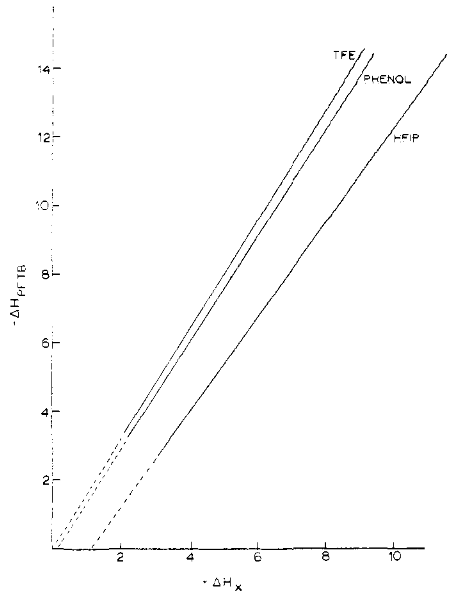

Figure 2. Enthalpy *vs.* enthalpy for TFE, HFIP, and phenol.

ΔH and $\Delta\nu$ for the three alcohols *vs.* the same measure of hydrogen bond acidity of a fourth alcohol, phenol. These equations are

$$\Delta H_{TF}\ (\pm 0.2) = 0.98\ (\pm 0.04) \times \Delta H_{ref} - 0.1\ (\pm 0.3) \quad (4)$$

$$\Delta H_{HF}\ (\pm 0.2) = 1.16\ (\pm 0.05) \times \Delta H_{ref} + 0.8\ (\pm 0.4) \quad (5)$$

$$\Delta H_{PF}\ (\pm 0.3) = 1.60\ (\pm 0.07) \times \Delta H_{ref} - 0.3\ (\pm 0.4) \quad (6)$$

$$\Delta\nu_{TF}\ (\pm 16) = 0.90\ (\pm 0.05)\ \Delta\nu_{ref} - 4\ (\pm 16) \quad (7)$$

$$\Delta\nu_{HF}\ (\pm 9) = 1.11\ (\pm 0.04)\ \Delta\nu_{ref} + 48\ (\pm 10) \quad (8)$$

$$\Delta\nu_{PF}\ (\pm 26) = 1.64\ (\pm 0.09)\ \Delta\nu_{ref} + 37\ (\pm 29) \quad (9)$$

As before, we will assume a model of hydrogen bond formation[7,8] in which the energy of adduct formation may be partitioned into three terms

$$\Delta H = E_{HB} + \delta E_{OH} + V_{OB}{}^{17}$$

The role of the two endothermic terms ($\delta E_{OH} + V_{OB}$) is to control the exothermic term (E_{HB}) in determining the magnitude of the donor–acceptor interaction.

Comparing the slopes of eq 4–6 we find that for a given change in ΔH_{ref}, the changes in ΔH for the three alcohols will be in the order, PFTB > HFIP > TFE (*i.e.*, 1.60 > 1.16 > 0.98). This implies that ($\delta E_{OH} + V_{OB}$) moderates E_{HB} better for TFE than HFIP, and ($\delta E_{OH} + V_{OB}$) moderates E_{HB} better for HFIP than PFTB. Since both E_{HB} and δE_{OH} increase from TFE to HFIP to PFTB, this control of E_{HB} is probably reflected in the greater van der Waals repulsions (V_{OB}) in the TFE reactions than the HFIP or PFTB reactions. Electronegativity arguments alone would predict that the perfluoro-*tert*-butyl group would remove excess charge from the oxygen better than the hexafluoroisopropyl and trifluoroethyl groups. (The alcohol association tendencies imply that the oxygen basicity decreases from trifluoroethanol to perfluoro-*tert*-butyl alcohol.) This leads to a lesser importance of van der Waals repulsions in the PFTB reactions.

A comparison of eq 7–9 shows that for a given change in $\Delta\nu_{ref}$, the change in $\Delta\nu$ for the three alcohols is again in the order, PFTB > HFIP > TFE. Comparing the slopes of the pairs (4) and (7), (5) and (8), and (6) and (9), we expect to find the slopes of the ΔH *vs.* $\Delta\nu$ equations to be in the order, TFE > HFIP > PFTB (*i.e.*, 0.98/0.90 $\gtrsim$ 1.16/1.11 $\gtrsim$ 1.60/1.64). Again, we find that presentation of the data in the form of ΔH *vs.* $\Delta\nu$ equations tends to mask the differences in alcohol acidities as deduced from the slopes of such a presentation. These slopes may, however, reflect the degree of van der Waals repulsions occurring in the reactions of a series of alcohols. A recent test of this is the reactions of TFE and HFIP with a series of the larger, more polarizable sulfur donors.[9] With these donors, where we would expect the van der Waals repulsions to be magnified, the differences in the slopes of the ΔH *vs.* $\Delta\nu$ equations are larger by nearly an order of magnitude than those of the oxygen donor lines.

In analyzing a plot such as ΔH *vs.* ΔH, the Lippincott–Schroeder model[8] suggests that the plot may be divided up into two regions: the region below the linear portion which arises from OH---B electrostatic attractions before appreciable charge transfer sets in and the linear region which arises from enhanced charge transfer or covalent effects. Some recent calculations support this idea.[18] The fact that a plot of ΔH_{PF} *vs.* ΔH_{TF}, ΔH_{HF}, or ΔH_{phenol} gives a zero or negative intercept indicates that the larger electrostatic interaction between PFTB and a weak donor is matched or sometimes more than matched by the larger covalent interaction in the linear portion of the curve. We thus expect to find a larger increase in C_a than in E_a for PFTB relative to any of the other acids. That such expectation was justified can be seen in the following table of E and C values.

	E_a	C_a
PFTB	6.72	0.85
HFIP	5.88	0.64
TFE	4.12	0.54
Phenol	4.59	0.54

The plots of ΔH_{PF} *vs.* ΔH_X (X = HF, TF, Ph) are shown in Figure 2. The HFIP plot has a slope of 1.42 and a negative intercept (−1.68 ± 0.04). Both the slope and intercept result from a 13% larger E_a of PFTB and a 38% larger C_a than HFIP. Comparing PFTB with TFE, we find a 61% larger E_a and a 63% larger C_a for PFTB. This results in a ΔH_{PF} *vs.* ΔH_{TF} plot with a slope of 1.62 and an essentially zero intercept (−0.1 ± 0.3). A similar analysis will predict a slightly negative intercept (−0.3 ± 0.4) for the ΔH_{PF} *vs.* ΔH_{phenol} plot.

This failure of E_a to proportionately increase with C_a for PFTB is also reflected in the intercept of the ΔH *vs.* $\Delta\nu$ plot. The magnitude of this intercept has been interpretated as reflecting the dipole–dipole or electrostatic attractions between an acid and a weak donor. The intercept of this relationship increases from 2.7 for TFE to 3.6 for HFIP, while only increasing to 3.9 for PFTB. The addition of a CF_3 group to TFE increases the intercept 0.9 unit while the addition of the third CF_3 group effects an increase of only 0.3 unit.

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(17) For an explanation of the model and each term, see ref 6.

(18) P. Schuster, *Theor. Chim. Acta*, **19**, 212 (1970); K. MoroKuma and J. R. Winick, *J. Chem. Phys.*, **52**, 1301 (1970); P. A. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969).

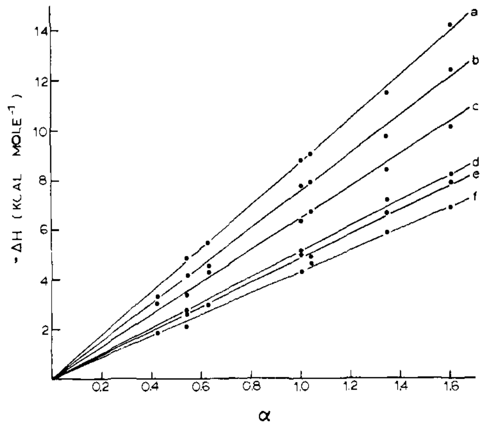

Figure 3. Enthalpy *vs.* hydrogen bonding constant (α) for the following bases: a, triethylamine; b, pyridine; c, *N*,*N*-dimethylacetamide; d, diethyl ether; e, acetone; f, acetonitrile.

The per cent increase in intercept is roughly equal to the per cent increase in E_a.

Single-Scale Enthalpy Relationship. The increased acidity of PFTB provides a good test to the generality of our previously defined single-scale enthalpy relationship, $\Delta H = \alpha_A\beta_B$.[7] Taking TFE as the reference acid, $\alpha_a = \Delta H_a/\Delta H_{TFE}$ and $\beta_B = \Delta H_{TFE}$ with donor B. Previously calculated α_a values are: HFIP = 1.35, phenol = 1.04, TFE = 1.00, *tert*-butyl alcohol = 0.54, and DTBC = 0.42. α_a values calculated from new data are: PFTB = 1.61 (±0.15) and *n*-butyl alcohol = 0.63 (±0.40).[19] A plot of ΔH *vs.* α for seven alcohols and six donors is shown in Figure 3. Good linearity is found[20] and the standard error of estimate of all acids with all bases is 0.10 kcal/mol.

A Taft polar substituent constant, σ^*, has been reported for *n*-butyl (−0.13) and one can also be calculated[21] for perfluoro-*tert*-butyl (+2.76). As a check on the accuracy of the σ^* of PFTB, a plot of pK_a *vs.* σ^* for various acids gives a good fit with the known pK_a of PFTB with σ^* of about 2.76. These two new data points (PFTB and *n*-butyl alcohol) are added to our earlier plot[7] of α *vs.* σ^* for HFIP, phenol, TFE, *tert*-butyl alcohol, and di-*tert*-butylcarbinol in Figure 4. All data points give a good fit with the exception, as before, of the phenol and di-*tert*-butylcarbinol points. The deviations of the latter two points identify the operation of resonance and steric factors for these two acids, respectively. As a result of the fit of PFTB to this relation, it appears that PFTB–donor steric interactions are insignificant. A similar conclusion can be made from the adequacy of the *E* and *C* model in describing PFTB as an acid.

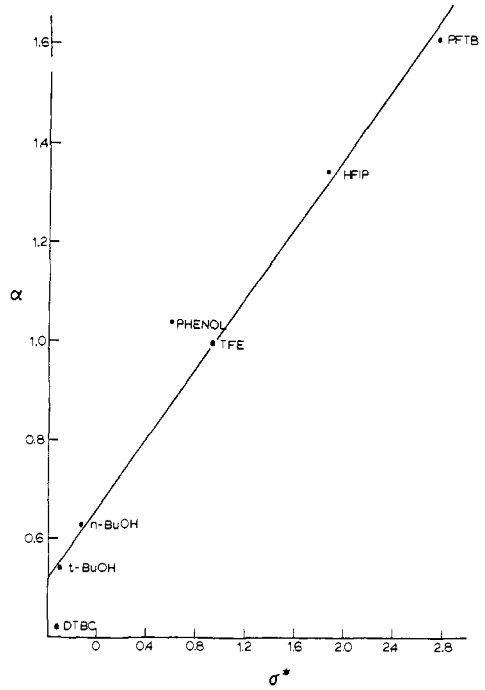

Figure 4. Hydrogen bonding constant (α) *vs.* Taft substituent parameters (σ^*).

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(19) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2365 (1970).

(20) A referee has correctly noted that the single-scale relationship is not unexpected for a class of acids with similar C_a/E_a ratios. In fact, the α values *are* intermediate between the respective ratios of *E* and *C* parameters, as predicted.

(21) J. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 224.