(1), to S_{cc}

$$\Delta a_{\mathrm{N}} = 2S_{cc}A_{\perp}' \qquad (3)$$

where $A_{\perp}'$ is the perpendicular component of the traceless anisotropic tensor.

$$A_{\perp}' = A_{\perp} - A^{\mathrm{iso}} \qquad (4)$$

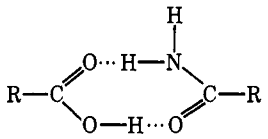
In Tables II and III values of $-\Delta a_{\mathrm{N}}/A_{\perp}'$ are collected by using a value for $A_{\perp}$ of 5 G, taken from ref 22. If we interpret these values, according to eq 2 and 3, giving the element S_{aa} of the average orientation matrix of our radicals, we may try to compare the results with analogous results obtained by Rowell and Phillips in nmr experiments on PAA.[23] They obtained values of S_{aa}, the average orientation matrix element of the PAA molecules referred to the long molecular axis a, for temperatures between 113 and 134°.

In Figure 6 values of S_{aa} at various temperatures are compared for PAA (as obtained from nmr measurements) and for our elongated radicals dissolved in PAA (as obtained from esr measurements).

The orientation of the solute radicals is always less than that of PAA and is larger for more elongated molecules ($n = 2, 3$). Radicals I and VI have the same order of magnitude for S_{aa}, suggesting a major role played by the number of phenyl rings in determining "orientability."

In Figure 7 values of S_{aa} are reported for the same solutes in PBB. Here nmr data for the pure solvent are lacking, but the fact that solute orientation in the nematic phase of PBB is larger than in PAA suggests that orientation of the solvent is also larger.

An apparent anomaly is found in PBB for radical V whose orientation is larger than that of I and VI. This may be an indication of specific interactions between V and PBB. This idea is supported by observations of Rowell and coworkers[23] that indicate large orientation of benzoic acid in *p*-hexyloxybenzoic acid. An interaction analogous to the formation of carboxylic acid dimers



would make the orientation of V more closely approach that of the solvent molecules.

Figure 5 also shows the sudden decrease of S_{aa} below 150° to small negative values. It is possible that this is due to a transition of the solvent from a nematic to a smectic phase. The existence of such phases in higher *p*-alkyloxybenzoic acids has been established,[24] although it was not observed for the butyl case. The direct microscopic observation of such transitions is, however, quite difficult, and it is certain that magnetic resonance is a more sensitive method of detection. Our observations, for example, put the nematic isotropic transition for *p*-butyloxybenzoic acid very close to 165°. The reported value from direct observation is about 5° lower.[24]

Acknowledgment. We thank Dr. P. L. Nordio for many helpful discussions and for some of the measurements.

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A Frequency Shift–Enthalpy Correlation for a Given Donor with Various Hydrogen-Bonding Acids

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Abstract: The determination and estimation of enthalpies of adduct formation for *t*-butyl alcohol with various donors enabled us to incorporate this hydrogen-bonding acid into a linear enthalpy–frequency shift correlation. The wide variation in acidity offered by 1,1,1,3,3,3-hexafluoro-2-propanol, substituted phenols, and butanol provides preliminary evidence for the existence of a linear frequency shift–enthalpy correlation for a given base with various alcohols. These constant-base plots have essentially zero intercept, but the constant-acid plots do not. A theoretical model for the bonding is proposed which is consistent with this observation. The existence of constant-acid and constant-base linear frequency–enthalpy correlations for a series of donors and acceptors requires that a plot of $\Delta\nu_{\mathrm{OH}}$ for phenol *vs.* $\Delta\nu_{\mathrm{OH}}$ for another acid with the same set of bases be linear with zero intercept. The slope of this $\Delta\nu_{\mathrm{OH}}$ *vs.* $\Delta\nu_{\mathrm{OH}}$ line is related to the ratio of the intercepts of this acid and phenol for the constant-acid plots.

Previous articles from this laboratory have dealt with the quantitative evaluation of thermodynamic data for the hydrogen bonding of phenol and various substituted phenols to a series of Lewis bases. Correlations of proton chemical shifts[1] or infrared frequency shifts[2-4] and enthalpies have been sought. A linear relationship between the shift in the frequency of the O–H stretching vibration of phenol, $\Delta\nu_{\mathrm{O-H}}$, and the

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(1) D. P. Eyman and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 1617 (1966).

(2) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817(1962).

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

(4) R. S. Drago and T. D. Epley, *ibid.*, **91**, 2883 (1969).

enthalpy of adduct formation was reported.[4,5] A theoretical justification for the existence of this relationship has been proposed.[6] Within experimental error, the whole series of substituted phenols are characterized by values for ΔH and $\Delta\nu_{\mathrm{OH}}$ which fall on the same line.[4]

Recently a series of enthalpies of adduct formation involving the alcohol 1,1,1,3,3,3-hexafluoro-2-propanol, $(CF_3)_2CHOH$, has been determined calorimetrically.[7] A linear plot of enthalpy *vs.* $\Delta\nu_{\mathrm{OH}}$ was obtained with a slope similar to that of phenol, but with an intercept which is larger. Consequently, it was of interest to study the ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ relationship for a hydrogen-bonding acid which is considerably weaker than phenol.

Thermodynamic data for the hydrogen bonding of *t*-butyl alcohol to several donors have been evaluated by spectroscopic procedures.[8,9] Recent work has demonstrated that in systems of this type, where the equilibrium constant is low, the spectrophotometric technique produces unreliable results.[10,11] This encouraged us to pursue a calorimetric determination of the enthalpy of adduct formation between this alcohol and Lewis bases in order to incorporate this acid into the double-scale enthalpy (E and C) relation and to study its ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ relationship relative to those of $(CF_3)_2CHOH$ and phenol. A linear plot of enthalpy *vs.* $\Delta\nu_{\mathrm{OH}}$ was obtained with similar slope to that of the phenol line but with a very much different intercept. Our results provide us with a third line, and it will be seen that consideration of the slopes and intercepts of these lines gives considerable insight into the hydrogen-bonding interaction. Furthermore, it is found that, if the base is held constant, *t*-butyl alcohol, $(CF_3)_2CHOH$, phenol, and the substituted phenols fall on a straight line when ΔH is plotted *vs.* $\Delta\nu_{\mathrm{OH}}$.

Experimental Section

Purification of Materials. Reagent grade carbon tetrachloride and cyclohexane were stored over Linde 4-A molecular sieves for several days prior to use. *t*-Butyl alcohol was purified by fractional distillation at reduced pressure from BaO and DMSO from CaH_2. Pyridine and N,N-dimethylacetamide (DMA) were purified according to previously described procedures.[3]

Procedure. The calorimetric procedure is essentially the same as that previous reported.[3,4] The only difference is that a twin-cell calorimeter was used in this work instead of a single-cell model. Stock solutions of the alcohol were added to solutions of the base in the calorimeter. The concentration of the alcohol after mixing with the base solution was 0.01 to 0.02 *M*. At these concentrations, self-association of the alcohol is negligible according to infrared evidence.

The infrared measurements were made on a Perkin-Elmer 521 spectrophotometer. The shifts were corrected for any dependence on the concentrations of the acid and base by extrapolating to infinite dilution. The alcohol concentration was 0.01 *M* and sufficient base is added to give a complex peak.

Double-Scale Enthalpy Equation. The double-scale enthalpy equation originally proposed by Drago and Wayland[12] to correlate enthalpies of adduct formation in poorly solvating media is represented by

$$-\Delta H = E_{\mathrm{A}}E_{\mathrm{B}} + C_{\mathrm{A}}C_{\mathrm{B}} \qquad (1)$$

At present, this equation has been demonstrated to apply successfully to 22 different acids and 38 different bases.[13] In this correlation, two empirical constants are determined for each acid (E_{A} and C_{A}) and two for each base (E_{B} and C_{B}) such that when substituted into eq 1, they give the enthalpy of adduct formation for the acid–base pair. The agreement between experimentally determined enthalpies and the calculated ones is within 2% for the 225 acid–base interactions presently in the correlation.

The enthalpy of adduct formation of *t*-butyl alcohol with the weaker donors could not be determined calorimetrically owing to the inaccuracies arising because of the very small enthalpies and equilibrium constants; a small error in the heat of solution of the reagents results in a larger error in the enthalpy of reaction. For these donors, the enthalpies of adduct formation were calculated from eq 1 by using the calorimetrically determined enthalpies to obtain the values of $C_{\mathrm{a}} = 0.287$ and $E_{\mathrm{a}} = 2.04$ for *t*-butyl alcohol.

Results

The heat evolved, corrected for the heats of solution of the reagents, is reported for various concentrations of donor and acceptor in Table I. The equilibrium constant and enthalpy are calculated from these data.[3] The measured enthalpies and those calculated from eq 1 are reported in Table II along with the measured frequency shifts.

Table I. Calorimetric Data for *t*-Butyl Alcohol–Donor Systems

Acid concn, *M* [Acid]	Base concn, *M* [Base]	Total vol, ml (Solvent)	Heat measd, cal
[*t*-Butyl alcohol]	[DMA]	(CCl_4)	
0.01190	0.1052	110	1.472
0.01470	0.2169	110	2.846
0.01123	1.2280	110	3.944
0.01120	0.4258	110	2.872
0.01168	0.8135	110	3.800
0.01055	0.2358	110	2.079
	K = 4.0 (298°K)		
[*t*-Butyl alcohol]	[Pyridine]	(C_6H_{12})	
0.01145	0.3013	110.0	2.499
0.01324	0.4275	109.5	3.420
0.01325	0.6818	109.5	4.139
	K = 2.9 (298°K)		
[*t*-Butyl alcohol]	[DMSO]	(CCl_4)	
0.01516	0.07193	110	2.072
0.01093	0.2163	110	2.769
0.01754	0.1158	110	3.277
0.009348	0.8055	110	3.175
0.01141	0.4480	110	3.503
0.01058	1.0939	110	3.714
	K = 8.2 (298°K)		

Discussion

As was stated in an earlier section, the data in Table II were either directly determined calorimetrically or calculated by use of the E and C correlation. The base parameters used were determined previously from a wide range of donor–acceptor interactions.[13] The utility of this approach in predicting enthalpies for hydrogen bonding systems has been demonstrated.[4] The values of 2.04 and 0.287 for E_{A} and C_{A}, respectively, for *t*-butyl alcohol are reasonable when compared to phenol ($E_{\mathrm{A}} = 4.35$ and $C_{\mathrm{A}} = 0.405$). Classical organic arguments involving phenyl substituents would lead one to predict that phenol would be more polarizable and have a higher OH bond dipole moment than

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(5) W. Partenheimer, T. D. Epley, and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 3886 (1968).

(6) K. F. Purcell and R. S. Drago, *ibid.*, **89**, 2874 (1967).

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(8) E. D. Becker, *Spectrochim. Acta*, 17, 436 (1961).

(9) I. Motogama and C. H. Jarboe, *J. Phys. Chem.*, **71**, 2723 (1967).

(10) R. Foster and I. Horman, *J. Chem. Soc.*, *B*, 171 (1966).

(11) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

(12) B. B. Wayland and R. S. Drago, *ibid.*, **87**, 3571 (1965).

(13) A paper on a refined set of E and C parameters is presently under preparation.

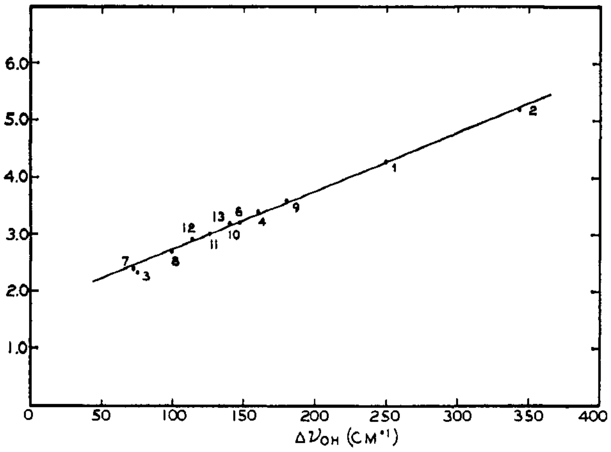

Figure 1. Linear enthalpy–frequency shift plot for butanol adducts. Donors are numbered as listed in Table II.

butanol. The prediction is also made from the *E* and *C* numbers that butanol will be a weaker acceptor than phenol toward all donors, for both the *E* and *C* values are lower. The agreement between predicted and experimental results on the phenyl system and the similarity in the hydrogen bonding interaction of phenol and butanol lead us to believe that reliable enthalpies can be predicted for a wide range of donor–*t*-butyl alcohol interactions by use of the *E* and *C* parameters. This is indeed fortunate in view of the difficulty involved with calorimetric studies with such a weak acid.

Table II. Enthalpies and $\Delta\nu_{OH}$ of Several Bases toward *t*-Butyl Alcohol

Numbering system	Base	$-\Delta H°$, kcal/mol	$\Delta\nu_{OH}$, cm$^{-1\,b}$ (*t*-butyl alcohol)
1	Pyridine	4.3^a	247^c
2	Triethylamine	5.2	344^c
3	Acetonitrile	2.3	77
4	N,N-Dimethylacetamide	3.4	160
5	N,N-Dimethylacetamide	3.8^a	160
6	N,N-Dimethylformamide	3.2	147
7	Ethyl acetate	2.4	73
8	Acetone	2.7	98
9	Dimethyl sulfoxide	3.6^a	183
10	Tetrahydrofuran	3.2	142
11	Diethyl ether	3.0	126
12	*p*-Dioxane	2.9	115
13	Tetrahydropyran	3.2	140
14	Mesitylene		44
15	Toluene		28
16	Benzene		26

^{a} Measured calorimetrically; all others calculated from eq 1. ^{b} Error estimation ±5 cm^{-1}. ^{c} Tetrachloroethylene used as solvent; all other ir shifts measured in CCl_4.

As illustrated in Figure 1, a linear relationship exists between the magnitude of $\Delta\nu_{O-H}$ for a given adduct and its enthalpy of interaction. The equation for the least-squares line is

$$-\Delta H = 0.0106\Delta\nu_{OH} + 1.65 \qquad (2)$$

It is of interest to point out that the intercept is considerably smaller than that for the ΔH *vs.* $\Delta\nu_{OH}$ plot of phenol (2.99), but the slope is comparable (0.0105).

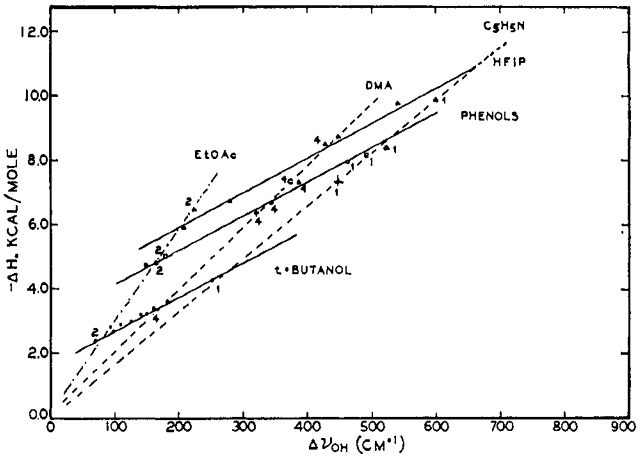

Figure 2. Constant-acid–constant-base frequency shift–enthalpy relations. Solid lines are constant-acid lines. The phenol line also contains values for *p*-*t*-butylphenol (+), phenol (○), *p*-chlorophenol (□), and *m*-trifluoromethylphenol (Δ). The acid butanol is represented by ● and $(CF_3)_2CHOH$ by ▲. The number 1 represents all points on the pyridine constant-base line; 2, ethyl acetate; and 4, N,N-dimethylacetamide. (The pyridine–$(CF_3)_2CHOH$ $\Delta\nu$ is estimated from the $\Delta\nu$ *vs.* $\Delta\nu$ plot of this acid and phenol.)

In Figure 2, the results of enthalpy *vs.* $\Delta\nu_{OH}$ studies are illustrated for several acids. As reported earlier,[4] the various substituted phenols all fell on the same plot of ΔH *vs.* $\Delta\nu_{OH}$. This is illustrated by the middle solid line in the figure. The solid line below this is for the acid *t*-butyl alcohol, whose enthalpies are reported here. The solid line at the top is for the acid 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, studied by a calorimetric procedure by Purcell, *et al.*[7] Each of these lines has essentially the same slope but different intercept and represents experiments in which the acid was held constant and the donors varied.

The dotted lines represent the same data connected *via* a constant base line; *i.e.*, the acid is varied for the same base. Numbers are utilized to represent all of the points on the constant-base line: 1 for C_5H_5N, 2 for EtOAc, and 4 for DMA. On the EtOAc line, for example, number 2 labels the enthalpies for the alcohols HFIP, *p*-chlorophenol, phenol, and butanol toward this donor. The dotted lines have been constructed to show a trend indicating the interrelationship between the constant base lines and the constant-acid lines. It should be noted that while the constant-acid lines have different nonzero intercepts, the constant-base lines have zero intercepts within the accuracy of the measured parameters. Since the four substituted phenol points are so close, one would desire more data before establishing and reporting the slope of the constant-base line. Other constant-base lines can be constructed from the data we have reported, but have not been illustrated to prevent further complicating Figure 2.

The potential existence of these interrelationships has considerable significance both from a practical and theoretical standpoint. With them, it is possible to measure the O–H frequency shifts of any new hydroxyl compound with the three donors in Figure 2 and locate these frequencies on the three straight constant base lines. The points can be connected to produce the constant-acid line whose slope and intercept can then be determined. The enthalpy of interaction of this acid *with all the donors in the phenol correlation* can then be predicted. By use of the E and C correlation, the internal consistency of the enthalpies predicted from the frequency shifts can be checked.

In Figure 3, the change in the O–H stretching frequency of phenol upon complexation to a particular donor is plotted against the change in the O–H stretching frequency of butanol with the same donor. A very interesting relationship can be shown between Figures 2 and 3. The general equations for constant-acid lines and constant-base line are given by eq 3 and 4, respectively, where i refers to the ith acid and j to jth base.

$$\Delta H_{ij} = m_i \Delta\nu_{ij} + n_i \tag{3}$$

$$\Delta H_{ij} = k_j \Delta\nu_{ij} \tag{4}$$

For any two acids, a and b, constant-acid equations are represented by eq 3a and 3b. Then substitution of

$$\Delta H_{\mathrm{a}j} = m_{\mathrm{a}} \Delta\nu_{\mathrm{a}j} + n_{\mathrm{a}} \tag{3a}$$

$$\Delta H_{\mathrm{b}j} = m\Delta_{\mathrm{b}}\nu_{\mathrm{b}j} + n_{\mathrm{b}} \tag{3b}$$

eq 4 into (3a) and (3b) produces

$$\Delta H_{\mathrm{a}j} = k_j \Delta\nu_{\mathrm{a}j} = m_{\mathrm{a}} \Delta\nu_{\mathrm{a}j} + n_{\mathrm{a}}$$

$$\Delta H_{\mathrm{b}j} = k_j \Delta\nu_{\mathrm{b}j} = m_{\mathrm{b}} \Delta\nu_{\mathrm{b}j} + n_{\mathrm{b}}$$

from which

$$k_j = m_{\mathrm{a}} + \frac{n_{\mathrm{a}}}{\Delta\nu_{\mathrm{a}j}} = m_{\mathrm{b}} + \frac{n_{\mathrm{b}}}{\Delta\nu_{\mathrm{b}j}}$$

Rearranging gives

$$\Delta\nu_{\mathrm{a}j} = \frac{n_{\mathrm{a}} \Delta\nu_{\mathrm{b}j}}{(m_{\mathrm{b}} - m_{\mathrm{a}})\Delta\nu_{\mathrm{b}j} + n_{\mathrm{b}}} \tag{5}$$

If $m_{\mathrm{a}} = m_{\mathrm{b}}$, then a plot of $\Delta\nu_{\mathrm{a}j}$ *vs.* $\Delta\nu_{\mathrm{b}j}$ must go through the origin and will have a slope equal to the ratio of the intercepts, $n_{\mathrm{a}}/n_{\mathrm{b}}$. Therefore, *if the constant-acid and constant-base relationships of Figure 2 exists for a new alcohol,* X, a straight-line plot of $\Delta\nu_{\mathrm{OH}}$(X) *vs.* $\Delta\nu_{\mathrm{OH}}$(phenol) with zero intercept must result. Conversely, a straight-line plot of $\Delta\nu_{\mathrm{OH}}$(X) *vs.* $\Delta\nu_{\mathrm{OH}}$(phenol) with zero intercept and the existence of a constant-base line require a $\Delta\nu_{\mathrm{OH}}$(X) *vs.* ΔH(X) relation whose slope is the same as phenol's. The intercept of the constant-acid ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ plot for X can be determined from the slope of the $\Delta\nu_{\mathrm{OH}}$(X) *vs.* $\Delta\nu_{\mathrm{OH}}$(phenol) plot and the known value of the phenol intercept for its ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ plot. When $m_{\mathrm{a}} \pm m_{\mathrm{b}}$, a curved line must result when $\Delta\nu_{\mathrm{OH}}$(X) is plotted against $\Delta\nu_{\mathrm{OH}}$(phenol). Generating synthetic data using the butanol and phenol intercepts, curvature in the $\Delta\nu_{\mathrm{a}j}$ *vs.* $\Delta\nu_{\mathrm{a}j}$ plot is clearly seen when the slopes of the constant acid lines differ by 30%.

When $m_{\mathrm{a}} \approx m_{\mathrm{b}}$, we are then confronted with the problem of distinguishing any differences because of experimental error. When one considers all the complications associated with working in poorly solvating solvents, an error of at least ±0.2 kcal mol^{-1} is to be anticipated between the experimental and true thermodynamic heat. Estimation of the frequency shift for strong donors also introduces considerable error into the relationships reported here because the complex band is very broad and overlaps other absorption bands. It would be impossible to conclude that the slopes of the constant-acid lines reported here are different outside of this combined experimental error. Therefore, none of our conclusions should be expected to hold to any greater degree of accuracy than our combined experimental error. Since the frequency shifts at infinite dilution can be more accurately determined than the enthalpies, the $\Delta\nu_{\mathrm{OH}}$(X) *vs.* $\Delta\nu_{\mathrm{OH}}$(phenol) plot may actually provide more accurate values for the slope and intercept once eq 3 and 4 have been demonstrated to hold within experimental error.

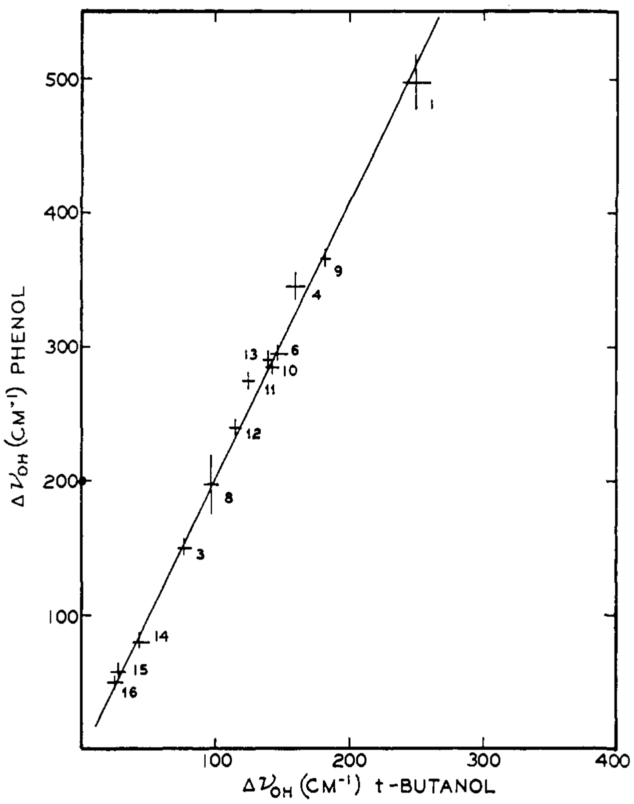

Figure 3. Linear plot of $\Delta\nu_{\mathrm{OH}}$ for phenol adducts *vs.* $\Delta\nu_{\mathrm{OH}}$ for butanol adducts.

From a slope of 2.05 for the line in Figure 3, using eq 5 and $m_{t\text{-butyl alcohol}} = m_{\text{phenol}}$, we predict an intercept of 1.44 for the *t*-butyl alcohol line. From comparable plots, an intercept of 3.4 is predicted for HFIP and 3.16 for *p*-chlorophenol. These are to be compared with measured intercepts of 1.65, 3.6, and 3.08 for *t*-butyl alcohol, HFIP, and *p*-chlorophenol, respectively.

Further insight into the nature of the hydrogen bonding interaction can be obtained by a detailed consideration of Figure 2. We start by asking the question, why should the constant-acid lines have an intercept which varies with its acidity, but the constant-base line have essentially zero intercept? There must be some property of the acid giving rise to the intercept which varies linearly with $\Delta\nu_{\mathrm{OH}}$ along the constant-base line and approaches zero as the acid becomes a poorer acid; *i.e.*, each enthalpy along a constant-base line is composed of two terms, $\Delta H' + n$, where n is a function of the acid that approaches zero linearly as the acid becomes a poorer acid. The value of n is the same for every base point on the linear ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ part of the constant-acid line. (The perturbation made on the intercept by substitution of a single group on the ring of phenol is not great enough for us to detect different intercepts because of experimental error in our measurements.) With this behavior, the constant-base lines can have a zero intercept because n approaches zero as the acid becomes weaker proceeding toward the origin along this line. Each constant-acid line will have an intercept n whose magnitude is a function of its acceptor strength. The total enthalpy for systems on the *linear* part of ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ constant-acid line can then be broken up into three terms

$$-\Delta H = -n_{\mathrm{A}} - \Delta H_{\mathrm{B-HO}} + \delta E_{\mathrm{OH}} \qquad (6)$$

where n_{A} is the constant for a given acid described above, δE_{OH} is the endothermic enthalpy associated with lengthening the O–H bond, and $\Delta H_{\mathrm{B-HO}}$ can be thought of as the residual enthalpy from forming the B–H bond. In order for this line to be straight must $\Delta H_{\mathrm{B-HO}}$ change linearly with δE_{OH} as discussed in the literature.[6] $\Delta H_{\mathrm{B-HO}}$ includes HB bond making as well as the coulombic attraction and repulsion terms.[6,11] Since δE_{OH} has been shown to be a linear function of $\Delta\nu_{\mathrm{OH}}$[6] with zero intercept ($\delta E_{\mathrm{OH}} = k'\Delta\nu_{\mathrm{OH}}$) and since the slopes of the constant-acid plots for all the acids in this study are similar, we can write

$$-\Delta H_{\mathrm{BHO}} = k\Delta\nu_{\mathrm{OH}} \qquad (7)$$

Another way of stating this is if n_{A} were a constant or zero for all alcohols, all acid–base combinations studied here would have fallen on the same line. This is the reported Badger–Bauer proposal.[14] Combining eq 7 with eq 6 and using the relation[6] $\delta E_{\mathrm{OH}} = k'\Delta\nu_{\mathrm{OH}}$, we have given the mathematical expression for reproducing the constant-acid line

$$-\Delta H = -n_{\mathrm{A}} - k\Delta\nu_{\mathrm{OH}} + k'\Delta\nu_{\mathrm{OH}} \qquad (8)$$

or

$$-\Delta H = (k' - k)\Delta\nu_{\mathrm{OH}} - n_{\mathrm{A}}$$

where n_{A} is a constant that varies only with the acid and $k' - k$ is a constant for all systems reported here. In summary, we can write

$$\delta E_{\mathrm{OH}} \propto -\Delta H_{\mathrm{BHO}} \propto \Delta\nu_{\mathrm{OH}} \propto (-\Delta H + n_{\mathrm{A}})$$

With this, we have given the mathematical expression for reproducing the constant-acid line, eq 8. The idea that $-\Delta H_{\mathrm{B-HO}}$ is proportional to δE_{OH} is in keeping with a recent publication from this laboratory[15] suggesting that in general for acid–base reactions, the reorganization energy for a given acid–base system is not a constant but a function of how strong the donor is. In these hydrogen-bonding systems with hydroxyl acids, we can further say that the proportionality constant between promotion energy as manifested by $\Delta\nu_{\mathrm{OH}}$ and the quantity $\Delta H - n$ is about the same for every acid studied because the slopes of the plots are about the same.

Our next concern is the constant-base line. Along this line (eq 4), we have two varying quantities, n_{A} and the $(-\Delta H_{\mathrm{BHO}} + \delta E_{\mathrm{OH}})$ term. We have divided up our energy in such a way that the latter term is linear in ΔH with a zero intercept. Now the only new requirement needed to give a zero intercept to the constant base line is $n_{\mathrm{A}} \propto \Delta H_{\mathrm{B}}$; *i.e.*, for various acids along the constant-base line, the heat is proportional to the intercept going to a value of zero intercept for very weak acids.

Finally, we shall propose a model which is consistent with the behavior of the n_{A} term described above. The effects to be described have not been considered previously in the hydrogen-bonding interaction. It is proposed that n_{A} is related to the maximum amount of electron density that the hydrogen atom can accumulate in an acid–base interaction. In the interaction, the electron density transferred into the acid is distributed between the proton and the OR. The former effect gives rise to the intercept and the latter to the change in $\Delta\nu_{\mathrm{OH}}$ over the linear portion of the curve. In keeping with this, the more electron withdrawing the OR moiety, the less electron density on the proton in the free acid and the greater the n_{A}. This accounts for the fact that the acid intercept approaches zero as the acid becomes weaker along the constant-base line.

It is tempting to speculate on the behavior of the constant-acid plot for weak donors. In order to pass through the point at zero $\Delta\nu_{\mathrm{OH}}$ and zero ΔH, the line must begin curving toward the origin. (The benzene–phenol interaction is about 2.5 kcal mol^{-1} and the shift 50 cm^{-1}.) In this region, the frequency shift is not as responsive to a unit of interaction enthalpy as it is in the straight-line portion and the curve can be represented by the equation

$$\Delta H = \delta n + \delta E_{\mathrm{OH}} + \Delta H_{\mathrm{BHO}}$$

i.e., n_{A} has been replaced by the varying quantity δn because the hydrogen atom has not yet accumulated its maximum charge and δn, the portion of the enthalpy related to placing electron density on the hydrogen atom, has not yet reached its maximum value, n_{A}. Once the proton is nearly saturated with electron density, the curve becomes linear and, throughout this region, most of the additional electron density transferred into the acid is transmitted to -OR with a concomitant weakening of the O–H bond.

The above interpretation is consistent with other observations from this laboratory which have been reported but not completely understood. A linear relationship has been reported between $-\Delta H$ for adduct formation and the Sn^{119}–H coupling constant, $J_{\mathrm{Sn^{119}-C-H}}$, for $(\mathrm{CH_3})_3\mathrm{SnCl}$ adducts.[16] The extrapolation of this line goes through the value for free $(\mathrm{CH_3})_3\mathrm{SnCl}$; *i.e.*, there is no intercept in a ΔJ *vs.* ΔH plot. If the above model is extended to this system, this would imply that there is no range of interaction (ΔH) in which we are essentially adding charge to tin and not polarizing the acid. Instead, the principal mechanism for tin accepting electron density involves polarizing the tin–chlorine dond, placing the negative charge on chlorine, not tin. The isomer shifts reported in a Mössbauer study of $(\mathrm{CH_3})_3\mathrm{SnCl}$ and its adduct[17] are essentially constant indicating relatively little change in the formal charge of tin and supporting our interpretation of the zero intercept in a $\Delta J_{\mathrm{Sn^{119}-C-H}}$ *vs.* ΔH plot.

We have elucidated a fairly stringent set of conditions for a hydrogen-bonding system to obey our correlations. We anticipate that exceptions will be found and interesting aspects about the intermolecular interaction revealed by them. Preliminary results indicate sulfur

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donors do not obey the constant-acid relationships described herein for oxygen and nitrogen donors. Work is underway to elucidate the electronic effects giving rise to this discrepancy.

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Bonding, Proton Transfer, and Diradical Stabilization in Phosphonium Ylides

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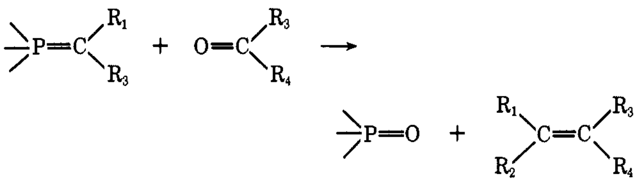
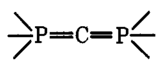
Abstract: The phosphorus–carbon bond of phosphonium ylides is studied with semiempirical molecular orbital calculations. The primary effect of the inclusion of 3d orbitals on phosphorus is the anticipated electron transfer from the ylide carbon to the 3d orbitals, with an accompanying increase in P–C bond order. A novel effect of some significance is the hyperconjugative π-type interaction of CH_2 orbitals in a model H_3PCH_2 with a P 3d orbital of the appropriate symmetry. Intermolecular and intramolecular mechanisms for proton transfer in $(CH_3)_3PCH_2$ are studied. A concerted hydrogen switch involving two molecules is calculated to possess a high activation energy. The potential surface for a concerted intramolecular hydrogen migration leads to a transition state best described as a pentavalent phosphorus derivative. Carbon diradicals should be stabilized by intervening phosphorus or other second-row atoms. This type of stabilization is studied for a hypothetical $CH_2PR_3CH_2$. Such species are potential singlet states and should possess barriers to rotation of CH_2 groups but not of the PR_3 moiety.

Phosphonium ylides or alkylidene phosphoranes, whose electronic structure is commonly described as a resonance hybrid 1, derive much of their current importance from the synthetic utility of the Wittig reaction.[1,2]

1



The ylides are fascinating compounds in their own right, exhibiting a remarkable variety of structural types exemplified by the species 2–5.[3-6]



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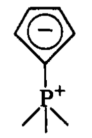

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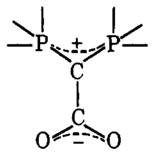

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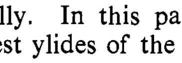

5

The resonance hybrid formulation 1 implies the verifiable existence of double bond character and the less verifiable concomitant participation of phosphorus 3d orbitals in bonding. The presence of partial double bond character is indicated by P–C interatomic distances[7-14] of 1.66–1.74 Å, intermediate between an estimated double bond length of approximately 1.66 Å and single bond lengths of about 1.87 Å.[15,16]

Although p–d π bonding has been examined previously[17-19] and discussed qualitatively in relation to ylides,[2] no attempt has been made before to treat these compounds in detail theoretically. In this paper we report an analysis of the simplest ylides of the type 1. Related to the question of π bonding in ylides is

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