

“Basicity.” A Comparison of Hydrogen Bonding and Proton Transfer to Some Lewis Bases^{1,2}

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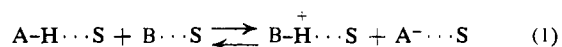
Abstract: Hydrogen bond enthalpies (ΔH_f 's) for the interaction of *p*-fluorophenol with 65 bases have been determined calorimetrically, using two independent methods wherever feasible. Heats of protonation (ΔH_i 's) in fluoro-sulfuric acid for these bases have been measured also. ΔH_f and ΔH_i are used to compare the energetics of hydrogen bonding and proton transfer in solution, and it has been found that no single relationship exists to correlate protonation and hydrogen bonding, but that separate lines are necessary for different functional groups. If ΔH_i is plotted vs. ΔH_f , points representing data for basic types such as amides, phosphoroxy compounds, pyridines, sulfides, and sulfoxides fall on separate parallel lines. Solvent effects on ΔH_f are discussed especially with regard to recent attempts to correct for them. ΔH_f is correlated with various acid-base solvation parameters and we find that Gutmann's donicity numbers, Drago's *E* and *C* parameters, or $\Delta\nu$ values (the Badger-Bauer relationship) can be used to estimate reasonable ΔH_f values, often within about 0.5 kcal/mol of our experimental results. ΔH_f values and independently measured equilibrium constants for hydrogen bond formation (K_f 's) are used to consider the extrathermodynamic relations between ΔG_f° , ΔH_f° , and ΔS_f° . Neither ΔG_f° nor ΔS_f° showed any general correlation with ΔH_f° , but some of the data could be resolved into separate trends for different groups of bases. Moreover, large changes in ΔG_f° and ΔH_f° for pyridines, sulfoxides, amides, and phosphoroxy compounds are found to be nearly independent of entropy changes. The relation of current theories of the hydrogen bond is examined and attention is drawn to conceptual fuzziness in the definition of hydrogen-bonded systems. In conclusion, the advantages of using proton affinities in the gas phase as a primary reference point for discussing “basicity” are cited.

For at least 2 centuries students of chemical affinity have recognized two fundamental classes of compounds, acids and bases.^{3,4} Not content to define the two classes purely in terms of their mutual interaction, a long and prestigious line of natural philosophers including Lavoisier, Davy, Berzelius, Liebig, Ostwald, Arrhenius, and Brønsted has attempted to identify the essential atom or function which was inherently responsible for “acidity” or “basicity.” In 1923 G. N. Lewis proposed the unifying concept which has organized this entire field ever since. “A basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom. An acid substance is one which can employ a lone pair from another molecule to complete its stable grouping.”⁵ By supplementing Lewis' definitions with such terms as *heterolysis*, *coordination*, *electrophile*, *nucleophile*, and *solvation*, his concepts have been able to encompass most of the modern electronic theory of chemical reactions.⁶

However, despite the enormous power of the Lewis valence theory to explain and predict molecular interactions, there is still no single quantifiable property which can be used as a general guide to “basicity” or “acidity.” In principle, if the electron density on the donor atom could be determined, this would be the ultimate measure of the inherent basicity of an isolated

function. Yet, if such a property were readily available, we now know (see below) that even in the gas phase, where solvation is not a complicating factor, there is no general qualitative relationship for the interaction of such Lewis acids as boron halides, the bare proton and carbenium ions⁷⁻¹⁰ with a variety of bases carrying different functional groups. In condensed phase chemistry, where acid-base interactions are most commonly encountered, the enormous discrepancies between the orders of reactivity of different types of acids with a given series of electron donors are even more dramatic. Various attempts have been made to classify acid-base behavior by introducing new variables.¹¹⁻¹³ However, recourse to multiparameter treatments merely formalizes the fact that “acidity” and “basicity” are terms which only have operational meaning within the complex relationships of specific acid-base interactions.

The transfer of a proton from one base¹⁶ (A^-) to another (B) in solvent (S) is the most general and impor-



tant reaction in chemistry.¹⁷ Both the forward and

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(1) This work has been supported by NSF Grant GP-6550-X and OSW Grant 14-30-2570 for which we are most grateful.

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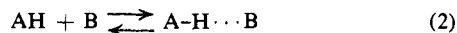
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reverse reactions must occur through transition states which are very similar to (and which may be preceded by) hydrogen-bonded complex formation.¹⁸⁻²⁰ Furthermore, the solvation of the four species shown in eq 1 and various subsidiary ion pairs (e.g., B-H⁺...A⁻) which may be present generally occurs primarily through hydrogen bonds. It is therefore natural that many authors have naively considered it obvious that a close relationship should exist between proton transfer (eq 1) and hydrogen bonding (eq 2). Reaction 2 is probably a



good model for the initial stages leading to the transition state in eq 1. However, in eq 1 strong bonds are made and broken; and charges are created, neutralized, and solvated; so that the structural and energy differences between products and reactants must be vastly different from those represented in eq 2.

The first serious attempt, of which we are aware, to correlate hydrogen bonding with proton transfer was that of Gordy and Stanford²¹ in 1940. Using Hammett's newly devised estimates for the p*K*_a's of protonated weak bases as a measure for reaction 1 they found a rather good correlation of these data with infrared frequency shifts, Δ*ν*, produced by the interaction of the same bases with CH₃OD. Subsequent scrutiny by Tamres, *et al.*,²² weakened the case for a general correlation and a thoughtful study by Joris and Schleyer²³ examined the difference between Δ*ν* and p*K*_a as measures of "basicity."

In several previous publications we have drawn attention both to the problems with using Δ*ν* as a criterion of hydrogen bond strength²⁴ and to the shortcomings of many p*K*_a estimates obtained by the Hammett indicator method as reliable measures of protonation energies.¹⁷ We have proposed the heat of protonation (Δ*H*_i) in fluorosulfuric acid (HSO₃F) as a direct and simple quantitative measure for comparing Lewis bases in reaction 1 and, in collaboration with Professors R. Taft and P. v. R. Schleyer, have developed several methods for comparing the thermodynamics of the interaction of bases with a common hydrogen bonding acid (AH = *p*-fluorophenol) in eq 2. Several more recent reports^{25,26} suggested that within the limited data of our preliminary studies, major systematic differences exist between the energetics of hydrogen bonding and proton transfer for bases of different functional groups.

The present article is a full report on our determination of heats of ionization (Δ*H*_i) in HSO₃F and heats of hydrogen bonding (Δ*H*_f) with *p*-fluorophenol (PFP) in carbon tetrachloride at 25° for 65 Lewis bases carrying a variety of functional groups. To our knowledge, this is the most extensive comparative study of hydrogen bonding and proton transfer that has yet been carried

out. The relationship between the two properties will be examined and they will be compared with other "basicity" parameters in order to assess the value of current theoretical approaches.

Experimental Section

Materials. All of the compounds used in this study were commercially available. Their sources, details of purification, and evidence for their purity are presented in Mitchell's thesis.²

Generally liquids were dried, using an appropriate agent, and then distilled through a 20-in. vacuum-jacketed column packed with glass helices and rated at six theoretical plates. If higher resolution was required, a 24-in. Nestor-Faust spinning band column was used. Solids were recrystallized to a constant melting point (usually two or three recrystallizations) and dried in a vacuum oven or a drying pistol. Refractive indices were measured using an Abbé refractometer thermostated at 25°. Melting points were obtained using a Thomas-Hoover melting point apparatus. All compounds were purified until their properties agreed well with accepted literature values.

Carbon tetrachloride ("Baker Analyzed" reagent) was distilled from calcium hydride, stored over a large bed of Linde molecular sieves (size 4A, 4 × 8 beads), and used with 2 weeks of purification. Karl Fischer titration, using a Photovolt automatic titrator, showed that random samples of the carbon tetrachloride used generally contained less than 0.001% water.

Fluorosulfuric acid was purified as before.¹⁷

Nuclear Magnetic Resonance Measurements. Nmr spectra were determined for fluorosulfuric acid solutions of the bases used in this study. These demonstrated that the protonation process was simple and complete; furthermore, it provided additional proof for the identity and purity of the compounds. In many cases spectra could be matched against those reported by Olah²⁷ and Gillespie²⁸ for the conjugate acids of the bases under study in HSO₃F. In all cases the spectra were constant for at least a period corresponding to that required for the calorimetric measurement of Δ*H*_f and could be readily interpreted in terms of the expected onium ion.²

Nmr spectra were determined with a Varian A-60 nmr spectrometer. All chemical shifts (δ) were reported in parts per million (ppm) downfield from TMS at 60 MHz, using internal CH₂Cl₂ (δ 5.30 ppm) as a secondary standard in fluorosulfuric acid. Samples of the protonated bases for nmr observation were prepared by slowly adding the internal standard and about 50 mg of base to a rapidly stirred solution of 0.5 ml of HSO₃F in a 2-dram vial at room temperature. These solutions were then transferred quickly *via* pipet to an nmr sample tube whose plastic cap had been punctured to prevent buildup of pressure.

The observation of simple conversion to protonated species under conditions used for the nmr studies (0.1-1.0 *M*; 40°) is taken as good evidence for similar behavior under the conditions of the calorimetric measurements (*ca.* 10⁻³ *M*; 25°).

Enthalpy Measurements. The solution calorimeter was essentially that described originally by Arnett, *et al.*²⁹ Its application to hydrogen bonding (Δ*H*_f) measurements²⁴ and heats of protonation (Δ*H*_i)¹⁷ was as we have previously reported.

Precision and Accuracy of Calorimetric Measurements. The precision of the heat measurements is dependent primarily on the magnitude of the recorder pen deflection. The size of this deflection itself depends upon such factors as the amount of base used, the amount of proton donor used, the Δ*H*_f and *K*_f of hydrogen bond formation, the heat capacity of the calorimetric system, and the heat of solution of the solute in the solvent.

The errors involved in the measurements are reported here at the 95% confidence level.³⁰

When using the high dilution method (method I),²⁴ the errors in the calculated heats of hydrogen bond formation can be as large as 0.4-0.5 kcal/mol for weak bases with low *K*_f's (e.g., 3,5-dichloropyridine; *K*_f = 6.4)³¹ where the heats produced are small. In the case of strong bases (e.g., phenyl methyl sulfoxide; *K*_f = 140),

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Table I. Measured Partial Molar Heats of Solution Used to Derive Enthalpies of Hydrogen Bonding in Carbon Tetrachloride (ΔH_f) and of Ionization in Fluorosulfuric Acid (ΔH_i). Bases in This and Table II Are Arranged in Order of Increasing ΔH_i .

Base	$-\Delta\bar{H}_{\text{HSO}_3\text{F}}$, kcal/mol	$\Delta\bar{H}_{\text{CCl}_4}$, kcal/mol	$\Delta\bar{H}_s$ of PFP ^a in base, kcal/mol	$\Delta\bar{H}_s$ of PFA ^b in base, kcal/mol
1. Thionyl chloride	Endothermic	+0.58 ± 0.04	+4.51 ± 0.20	-0.63 ± 0.06
2. Dimethyl sulfate	2.69 ± 0.04 ^c	+2.59 ± 0.03 ^c	+3.88 ± 0.07	+0.39 ± 0.05
3. Phosphoroxchloride	4.4 ± 0.1	+0.39 ± 0.03	+2.46 ± 0.04	-0.14 ± 0.02
4. Diphenyl sulfide	7.4 ± 0.5 ^d	+0.18 ± 0.03	+5.15 ± 0.14	+0.25 ± 0.04
5. Tetramethylene sulfone	9.6 ± 0.2 ^c	+2.21 ± 0.05	+2.06 ± 0.08	0
6. Dichlorophenylphosphine oxide	9.9 ± 0.3	+0.84 ± 0.05	+1.63 ± 0.05	-0.09 ± 0.02
7. Chloromethyl methyl sulfide	11.4 ± 0.2	+0.45 ± 0.01	+4.73 ± 0.13	+0.31 ± 0.01
8. Anthrone	12.7 ± 0.3 ^f	+6.5 ± 0.4 ^f		
9. Acetonitrile	12.8 ± 0.2	+1.81 ± 0.10		
10. Phenyl methyl sulfide	12.8 ± 0.2	+0.36 ± 0.03	+4.77 ± 0.14	+0.13 ± 0.03
11. <i>o</i> -Dichlorobenzene	14.1 ± 0.3	+0.37 ± 0.01	+5.96 ± 0.12	+0.15 ± 0.01
12. Propylene carbonate	14.6 ± 0.1	+3.15 ± 0.08	+2.01 ± 0.10	+0.23 ± 0.04
13. Diethyl chlorophosphate	14.7 ± 0.3	+0.77 ± 0.02	+0.57 ± 0.02	-0.19 ± 0.03
14. Dimethyl sulfite	14.9 ± 0.2	+1.08 ± 0.05	+2.24 ± 0.10	0
15. Diethyl carbonate	16.2 ± 0.2	+0.19 ± 0.03	+1.81 ± 0.09	-0.30 ± 0.02
16. Cyclopentanone	17.3 ± 0.1 ^f	+0.32 ± 0.02 ^f	+0.14 ± 0.06	-0.68 ± 0.05
17. Ethyl acetate	17.4 ± 0.1 ^f	+0.014 ± 0.004 ^f	+1.13 ± 0.09 ^g	-0.46 ± 0.04 ^g
18. Cyclohexanone	18.1 ± 0.1 ^f	+0.09 ± 0.01 ^f	+0.23 ± 0.01	-0.42 ± 0.02
19. Acetone	18.3 ± 0.1 ^f	+0.79 ± 0.02 ^f	+0.38 ± 0.05	-0.34 ± 0.03
20. Triphenylphosphine oxide	18.8 ± 0.2	+4.15 ± 0.23		
21. Di- <i>n</i> -butyl sulfide	18.9 ± 0.1	-0.41 ± 0.03	+3.23 ± 0.05	+0.36 ± 0.01
22. <i>N,N</i> -Dimethyltrifluoroacetamide	19.2 ± 0.1	+1.67 ± 0.04		
23. Diethyl ether	19.5 ± 0.7 ^e	-0.42 ± 0.01 ^e	+0.41 ± 0.09 ^g	-0.35 ± 0.04 ^g
24. Diethyl sulfide	19.5 ± 0.3	-0.54 ± 0.02	+2.77 ± 0.08	+0.09 ± 0.02
25. Trimethyl phosphate	19.6 ± 0.1	+0.76 ± 0.03	-0.21 ± 0.03	-0.08 ± 0.02
26. Tetrahydrofuran	20.2 ± 0.2 ^e	-0.60 ± 0.02 ^e	-0.17 ± 0.01 ^g	-0.75 ± 0.01 ^g
27. Tetrahydrothiophene	20.2 ± 0.2	-0.55 ± 0.05	+2.60 ± 0.12	0
28. Phenyl methyl sulfoxide	20.2 ± 1.0 ^d	+4.96 ± 0.13		
29. Triethyl phosphate	20.6 ± 0.2	+0.02 ± 0.05	-0.18 ± 0.03	+0.10 ± 0.03
30. 1,4-Dioxane	21.7 ± 0.2	-0.16 ± 0.01	+1.01 ± 0.09 ^g	-0.22 ± 0.01 ^g
31. Diethyl ethylphosphonate	23.6 ± 0.3	-0.64 ± 0.09	-1.95 ± 0.09	-0.80 ± 0.06
32. <i>N</i> -Methylformamide	25.1 ± 0.3	+4.5 ± 0.10	0 ^g	+0.11 ± 0.02 ^g
33. 2,6-Dimethyl- γ -pyrone	25.2 ± 0.2 ^f	+6.23 ± 0.24		
34. <i>N,N</i> -Dimethylchloroacetamide	25.5 ± 0.2	+1.86 ± 0.06		
35. 3,5-Dichloropyridine	26.4 ± 0.3	+4.28 ± 0.06		
36. Dimethyl sulfoxide	26.5 ± 0.2	+1.76 ± 0.04	-0.66 ± 0.03 ^g	+0.22 ± 0.01 ^g
37. Trimethylphosphine oxide	27.0 ± 0.6	+5.23 ± 0.09		
38. 1,2-Dimethoxyethane	28.3 ± 0.2	-0.27 ± 0.05	-0.29 ± 0.05	-0.85 ± 0.02
39. <i>N,N</i> -Dimethylbenzamide	28.4 ± 0.2	+0.71 ± 0.02		
40. <i>N,N</i> -Dimethylformamide	28.6 ± 0.1	+0.76 ± 0.02	-1.13 ± 0.08 ^g	-0.49 ± 0.02 ^g
41. Di- <i>n</i> -butyl sulfoxide	28.9 ± 0.5	+0.60 ± 0.09		
42. Tetramethylene sulfoxide	29.1 ± 0.1	+0.39 ± 0.02	-2.21 ± 0.07	-0.88 ± 0.04
43. Pyridine <i>N</i> -oxide	29.1 ± 0.3	+4.28 ± 0.41		
44. 2-Bromopyridine	29.2 ± 0.3	+0.96 ± 0.03	+0.70 ± 0.03	+0.18 ± 0.01
45. 2-Chloropyridine	30.7 ± 0.3	+0.96 ± 0.04	+0.51 ± 0.03	+0.13 ± 0.03
46. <i>N</i> -Methyl-2-pyrrolidone	31.3 ± 0.4	0	-1.02 ± 0.04	-2.09 ± 0.08
47. <i>N,N</i> -Dimethylacetamide	31.6 ± 0.1	+0.41 ± 0.02	-1.76 ± 0.11 ^g	-0.65 ± 0.01 ^g
48. 3-Bromopyridine	34.4 ± 0.4 ^e	+0.23 ± 0.03 ^e		
49. Quinoline	35.6 ± 0.2	+0.46 ± 0.01	-1.14 ± 0.06 ^g	0 ^g
50. Pyridine	38.2 ± 0.2 ^e	+0.36 ± 0.02 ^e	-1.01 ± 0.06 ^g	+0.06 ± 0.01 ^g
51. 1,1,3,3-Tetramethylurea	38.2 ± 0.7	-0.56 ± 0.05		
52. 4-Methylpyridine	39.1 ± 0.3	-0.05 ± 0.01	-1.53 ± 0.04 ^g	-0.27 ± 0.01 ^g
53. 2,6-Dimethylpyridine	41.0 ± 0.2 ^e	+0.27 ± 0.08	-2.31 ± 0.07	-0.16 ± 0.05
54. 2,4,6-Trimethylpyridine	42.9 ± 0.2	-0.23 ± 0.03	-2.34 ± 0.09	-0.29 ± 0.05
55. Quinuclidine	45.2 ± 0.2	+0.57 ± 0.03 ^h		
56. Triethylamine	49.8 ± 0.1 ^e	-0.64 ± 0.08 ^e	-2.31 ± 0.05 ^g	+0.28 ± 0.01 ^g
57. Phenyl phosphorodichloridate			+2.12 ± 0.04	+0.10 ± 0.03
58. Hexamethylphosphoramide			-4.12 ± 0.08	-1.71 ± 0.05

^a PFP is *p*-fluorophenol. ^b PFA is *p*-fluoroanisole. ^c Unpublished results of Dr. John V. Carter. ^d Compound undergoes slow exothermic reaction in HSO₃F. ^e Reference 17. ^f E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970). ^g Reference 24. ^h Inert solvent used was *o*-dichlorobenzene.

which produce larger heats, the standard deviation in the ΔH_f values are of the order of ± 0.1 – 0.2 kcal/mol.

The standard deviation in ΔH_f values, using the pure base method (method II),²⁴ which essentially involves pooling four heats of solution³² is ± 0.10 – 0.15 kcal/mol. Wherever feasible, at least seven replica measurements of the heat of solution of the base were made in each acid solution. In several cases of particular importance using method I for ΔH_f determination, two or three independent

repetitions were made at each acid and base concentration. Further, to verify the reproducibility of the results, some of the measurements were repeated after a time lapse of from 3 months to 1 year, using freshly purified materials.

Systematic errors were avoided by frequent checks of the calorimeter against well-accepted values for the heat of solution of KCl³³ or ethanol³⁴ in water.

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Results

In Table I, we present the measured thermochemical values for 58 Lewis bases necessary to derive enthalpies of hydrogen bond formation (ΔH_f) between *p*-fluorophenol and these bases in carbon tetrachloride as solvent at 25°. Corresponding data to determine heats of protonation (ΔH_i) in fluorosulfuric acid are also given. In Table II the derived results are listed and in some cases compared with independent estimates. Other relevant properties will be presented in appropriate sections of the Discussion section. The methods used to determine ΔH_f and ΔH_i have been described in detail elsewhere. However, considerable experience has been gained in our laboratory and elsewhere since the methods were originally suggested and a few comments about their reliability are now in order.

I. Hydrogen-Bonding Enthalpies, ΔH_f . Most of the new data presented in this paper were obtained by one or both of the methods which we described in two previous publications.^{24,35}

Since one of the goals of this project was an extensive test of the consistency of the methods with each other and with reliable published values, both methods were used whenever feasible. In a few cases further comparison is made with values determined in this laboratory by Mr. John Kulluk using thermometric titration (see Discussion).

Method I: The High Dilution Method. If a small quantity of a base B is injected into a dilute solution of the hydrogen bonding acid AH (or conversely, the acid is injected to a dilute solution of the base) to produce a 1:1 complex C, the observed heat of interaction, ΔH_{obsd} , is related to the enthalpy of hydrogen bond formation (ΔH_f) by the expression

$$\Delta H_{\text{obsd}} = \Delta H_f [C] V \quad (3)$$

where V = volume in liters of the solution in the calorimeter and $[C]$ = molar concentration of the complex formed at equilibrium which is calculated from the equilibrium constant K_f . Our values of K_f were mainly derived from the direct determinations of our collaborators, Taft [using ^{19}F nmr²⁵] and Schleyer [using infrared spectroscopy²⁴]. Data were treated as before.²⁴ Provided that pure, dry materials are used, the most important experimental problem with this method is the instrumental one of detecting the effect of changing concentration on AH, B, or C in systems so dilute that the hydrogen-bonding acid AH is not associated. Very weak complexes of low K_f may require such high concentrations of AH and B in order to obtain measurable amounts of C that association of AH or B occurs or special medium effects arise. This can be a particularly difficult problem when ΔH_f and K_f are to be obtained from the same set of thermometric titration data.³⁶⁻⁴⁰ In the present study $[\text{AH}]$ and $[\text{B}]$ were generally varied between (2 and 15) $\times 10^{-3}$ M. In no case did either

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concentration exceed 0.025 M. Detailed tabulations and calculations for determination of ΔH_f of compounds listed in Table II by the high dilution method are given in E. J. M.'s thesis (obtainable through University microfilms).

We have shown previously²⁴ that ΔH_f when determined by method I is very sensitive to errors in K_f , especially if K_f is low. In order to side-step the determination of K_f altogether, method II was previously proposed and partially tested.

Method II: The Pure Base Method. When a small increment of a hydrogen-bonding acid (AH) is injected into a large excess of pure base B, one may dichotomize the enthalpy of solution into two hypothetical terms—that due to formation of the 1:1 complex $\text{A-H}\cdots\text{B}$ and that due to all other thermochemically significant terms which do not involve hydrogen bonding between AH and B. Provided that there are no strong specific association or solvation contributions to this latter term it should be approximated by the heat of solution of a model compound M which is as similar as possible in structure to AH save that it does not carry the same acidic hydrogen bonding function.

Furthermore, the heats of solution for both the model compound and the hydrogen bonding acid must be referred back to a common "inert" solvent. When they are injected into the pure base as a solvent, the observed heat of solution is the sum of the heat of solution which it might be expected to give in an inert solvent and the heat due to special interaction with the base. To correct the heats of solution of the acid and the model compound, carbon tetrachloride was used as the reference inert solvent.

The measurement of ΔH_f is then a matter of determining: (1) $\Delta \bar{H}_s$ of the acid A in pure base, (2) $\Delta \bar{H}_s$ of the model M in pure base, (3) $\Delta \bar{H}_s$ of the acid A in the reference solvent, and (4) $\Delta \bar{H}_s$ of the model M in the reference solvent. Then, $(\Delta H_f)_{\text{AH}\cdots\text{B}} = (\Delta \bar{H}_s^{\text{A}} - \Delta \bar{H}_s^{\text{M}})_{\text{base}} - (\Delta \bar{H}_s^{\text{A}} - \Delta \bar{H}_s^{\text{M}})_{\text{CCl}_4}$. Sample calculations and further explanations can be found in references.^{2,24,35,41}

In the Discussion section we will comment on how well this method has stood up to scrutiny since it was originally proposed.

II. Heats of Ionization in HSO_3F ; ΔH_i . The heat of protonation or ionization in fluorosulfuric acid was chosen as a widely applicable criterion of Brønsted basicity.¹⁷ ΔH_i corresponds simply to the heat of transfer of the base from infinite dilution in an "inert solvent" (usually carbon tetrachloride) to infinite dilution in HSO_3F , *i.e.*, $\Delta H_i = \Delta \bar{H}_s^{\text{HSO}_3\text{F}} - \Delta \bar{H}_s^{\text{CCl}_4}$. The method itself has been discussed extensively in the original article¹⁷ and requires no further comment here. At present, standard free energies of ionization are known for only a few very weak bases in this acid²⁸ so that no ΔS_i° have been determined in this medium. We will compare ΔH_i against aqueous pK_a data in Discussion section II.

Discussion

I. Hydrogen Bonding. A. The Determination and Use of Hydrogen-Bonding Energies.

Pauling⁴² has

(41) T. S. S. R. Murty, Ph.D. Thesis, University of Pittsburgh, 1967.

(42) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Table II. Derived Data for ΔH_i and ΔH_f and Comparison with Literature Values

Base	$-\Delta H_i^a$, kcal/mol	$-\Delta H_f^b$, kcal/mol	$-\Delta H_i^c$, kcal/mol	$-\Delta H_f$ (lit.), ^d kcal/mol
1. Thionyl chloride			1.17 ± 0.23	
2. Dimethyl sulfate	5.3 ± 0.1		2.82 ± 0.10	
3. Phosphoroychloride	4.8 ± 0.1		3.71 ± 0.08	
4. Diphenyl sulfide	7.6 ± 0.5		1.41 ± 0.19	
5. Tetramethylene sulfone	11.8 ± 0.2		4.25 ± 0.11	3.6 ^e
6. Dichlorophenylphosphine oxide	10.7 ± 0.3		4.59 ± 0.08	
7. Chloromethyl methyl sulfide	11.9 ± 0.3		1.89 ± 0.15	
8. Anthrone	19.2 ± 0.7 ^f	5.6 ± 0.4 ^g		
9. Acetonitrile	13.6 ± 0.3	4.2 ± 0.2		4.65 ± 0.06 ^h
10. Phenyl methyl sulfide	13.2 ± 0.2		1.67 ± 0.19	
11. <i>o</i> -Dichlorobenzene	14.5 ± 0.3		0.50 ± 0.14	
12. Propylene carbonate	17.8 ± 0.3		4.53 ± 0.13	
13. Diethyl chlorophosphate	15.5 ± 0.3		5.55 ± 0.07	
14. Dimethyl sulfite	16.0 ± 0.2		4.07 ± 0.12	
15. Diethyl carbonate	16.4 ± 0.2		4.20 ± 0.10	
16. Cyclopentanone	17.3 ± 0.1 ^f		5.50 ± 0.09	
17. Ethyl acetate	17.4 ± 0.1 ^f		4.74 ± 0.12 ^g	4.77 ± 0.1 ^h
18. Cyclohexanone	18.1 ± 0.1 ^f	5.8 ± 0.2 ^g	5.66 ± 0.07 ^g	
19. Acetone	18.3 ± 0.1 ^f		5.59 ± 0.08	4.94 ± 0.05; ^h 5.3 ⁱ
20. Triphenylphosphine oxide	20.9 ± 0.3	7.4 ± 0.1		7.5 ^j
21. Di- <i>n</i> -butyl sulfide	18.5 ± 0.1		3.44 ± 0.08	4.19 ^k
22. <i>N,N</i> -Dimethyltrifluoroacetamide	20.9 ± 0.1	3.2 ± 0.2		3.6 ^l
23. Diethyl ether	19.5 ± 0.7 ^m	5.6 ± 0.1 ^g	5.57 ± 0.12 ^g	5.41 ^k
24. Diethyl sulfide	19.0 ± 0.3		3.63 ± 0.11	3.6 ± 0.1 ⁿ
25. Trimethyl phosphate	20.4 ± 0.2	6.5 ± 0.1	6.44 ± 0.09	5.7 ^j
26. Tetrahydrofuran	19.6 ± 0.2 ^m	5.6 ± 0.1 ^g	5.75 ± 0.08 ^g	5.30 ± 0.06 ⁿ
27. Tetrahydrothiophene	19.7 ± 0.2		3.71 ± 0.13	3.7 ± 0.1 ^m
28. Phenyl methyl sulfoxide	25.2 ± 1.0	6.3 ± 0.1		
29. Triethyl phosphate	20.6 ± 0.2	6.5 ± 0.1	6.59 ± 0.09	5.9 ^e
30. 1,4-Dioxane	21.5 ± 0.2		5.10 ± 0.11 ^g	5.0 ^e
31. Diethyl ethylphosphonate	23.0 ± 0.4		7.46 ± 0.12	
32. <i>N</i> -Methylformamide	29.6 ± 0.4	5.5 ± 0.1 ^g	6.44 ± 0.08 ^g	5.3 ^e
33. 2,6-Dimethyl- γ -pyrone	31.2 ± 0.3 ^f	6.9 ± 0.2		
34. <i>N,N</i> -Dimethylchloroacetamide	27.4 ± 0.3	6.9 ± 0.3		
35. 3,5-Dichloropyridine	30.7 ± 0.3	5.4 ± 0.3		
36. Dimethyl sulfoxide	28.6 ± 0.2	6.6 ± 0.1 ^g	7.21 ± 0.08 ^g	
37. Trimethylphosphine oxide	32.2 ± 0.7	7.7 ± 0.2		8.1 ^o
38. 1,2-Dimethoxyethane	28.0 ± 0.3		5.75 ± 0.10	
39. <i>N,N</i> -Dimethylbenzamide	29.1 ± 0.4	6.9 ± 0.2		5.2 ^e
40. <i>N,N</i> -Dimethylformamide	29.5 ± 0.2	6.6 ± 0.1 ^g	6.97 ± 0.11 ^g	6.35 ^p
41. Di- <i>n</i> -butyl sulfoxide	29.5 ± 0.6	6.9 ± 0.1		
42. Tetramethylene sulfoxide	29.5 ± 0.1		7.64 ± 0.11	7.0 ^q
43. Pyridine <i>N</i> -oxide	33.4 ± 0.5	7.5 ± 0.2		7.9 ± 0.5 ^r
44. 2-Bromopyridine	30.2 ± 0.3		5.83 ± 0.09	4.76 ^s
45. 2-Chloropyridine	31.7 ± 0.3		5.93 ± 0.07	4.82 ^t
46. <i>N</i> -Methyl-2-pyrrolidone	31.3 ± 0.4	7.0 ± 0.2	7.38 ± 0.12	6.3 ^e
47. <i>N,N</i> -Dimethylacetamide	32.0 ± 0.1		7.44 ± 0.13	6.84 ± 0.1, ^h 6.8 ^z
48. 3-Bromopyridine	34.6 ± 0.3 ^m	6.2 ± 0.2 ^g		
49. Quinoline	37.0 ± 0.2	7.35 ± 0.1 ^g	7.47 ± 0.09 ^g	7.2 ^t
50. Pyridine	38.6 ± 0.3 ^m	7.1 ± 0.1 ^g	7.40 ± 0.09	7.2 ^t
51. 1,1,3,3-Tetramethylurea	37.6 ± 0.7	7.8 ± 0.2		
52. 4-Methylpyridine	39.0 ± 0.3	7.3 ± 0.1 ^g	7.59 ± 0.08 ^g	7.3 ^t
53. 2,6-Dimethylpyridine	40.7 ± 0.3 ^m	7.8 ± 0.3	8.36 ± 0.12	7.2 ^s
54. 2,4,6-Trimethylpyridine	42.7 ± 0.2	7.9 ± 0.1	8.46 ± 0.11	7.5 ^s
55. Quinuclidine	45.8 ± 0.7	9.5 ± 0.2 ^u		
56. Triethylamine	49.1 ± 0.2 ^m		8.92 ± 0.09 ^g	9.1 ^v
57. Phenyl phosphorodichloridate			4.29 ± 0.08	
58. Hexamethylphosphoramide		8.0 ± 0.1 ^g	8.72 ± 0.11 ^g	8.1 ^e
59. Diphenyl sulfoxide		6.2 ± 0.3		
60. Triphenyl phosphate		6.7 ± 0.2		
61. Trimethylamine <i>N</i> -oxide		8.8 ± 0.3 ^w		

^a Heat of transfer of the base from CCl_4 to HSO_3F , $\Delta\bar{H}_{\text{HSO}_3\text{F}} - \Delta\bar{H}_{\text{CCl}_4}$. ^b Heat of hydrogen bond formation to *p*-fluorophenol in CCl_4 measured using method I, the dilute solution method. ^c Heat of hydrogen bond formation to *p*-fluorophenol in the pure base as solvent (method II). ^d Literature values for the interaction of the phenol with these bases. The values can be compared directly with those for the interaction of PFP with bases (ref 41). ^e D. P. Eyman and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 1617 (1966). ^f E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970). ^g Reference 24. ^h T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967); R. S. Drago and T. D. Epley, *ibid.*, **91**, 2883 (1969). ⁱ W. C. Duer and G. L. Bertrand, *ibid.*, **92**, 2587 (1970). ^j G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14**, 1485 (1960). ^k R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *J. Amer. Chem. Soc.*, **86**, 3227 (1964). ^l R. L. Middaugh, R. S. Drago, and R. Niedzielski, *J. Amer. Chem. Soc.*, **86**, 388 (1964). ^m Reference 17. ⁿ G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970). These authors maintain that this value is "too low" due to an exothermic interaction between the solvent (CCl_4) and the base. It should be noted, however, that their value is in close agreement with our value which was obtained using a method in which the base and CCl_4 do not come in contact. ^o M. D. Joesten and R. S. Drago, *J. Amer. Chem. Soc.*, **84**, 3817 (1962). ^p D. Neerincx, A. van Audenhaege, and L. Lamberts, *Ann. Chim. (Paris)*, **4**, 43 (1969). ^q R. S. Drago, B. Wayland, and R. L. Carlson, *J. Amer. Chem. Soc.*, **85**, 3125 (1963). ^r T. Kubota, *J. Amer. Chem. Soc.*, **88**, 211 (1966). ^s T. Kitao and C. H. Jarboe, *J. Org. Chem.*, **32**, 407 (1967). ^t T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962). ^u Solvent used was *o*-dichlorobenzene. ^v S. Singh and C. N. R. Rao, *Can. J. Chem.*, **44**, 2611 (1966). ^w Solvent used was dichloromethane. ^x B. Styme, H. Styme, and G. Wettermark, *J. Amer. Chem. Soc.*, **95**, 3490 (1973).

provided a useful description of the hydrogen bond by stating "that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms—so that it may be considered to be acting as a bond between them." During the past 4 or 5 decades an enormous literature has developed⁴³⁻⁴⁷ documenting intensive efforts to define exactly the "conditions" for this attraction, to quantify these "rather strong forces" and to understand the nature of this peculiar bond in quantum mechanical terms. At its lower limit the strength of the hydrogen bond shades into the weak forces (dispersion, dipole-dipole, etc.) which operate between all molecules which carry covalent bonds to hydrogen. At its upper limit, attraction of a covalent hydrogen for a second atom becomes so great that proton transfer occurs.

Ordinary hydrogen bonds between neutral oxygen and nitrogen compounds have energies between 3 and 10 kcal/mol. Because of their great importance to many areas of applied and biological chemistry, particular effort has gone into attempts to isolate and measure the strengths of hydrogen bonds between the common organic functions bearing acidic hydrogen and those with basic lone pair electrons.

It is important to appreciate that the use to which hydrogen bonding data may be put by applied chemists or biochemists is quite different from that by theoreticians. The former will have a greater need for knowing the interaction energies of somewhat complex model compounds in condensed phases—the latter usually prefer simplified systems in the gas phase. For the most part our approach has been the former one although as we shall see below, solvent effects on hydrogen-bonding energies are mostly small and probably can be estimated within 5% in most cases.

It is also important to realize that there is both an experimental and even conceptual lower limit below which it becomes a matter of taste whether or not one chooses to say a "hydrogen bond" exists between two molecules. Thus if we consider the complex between chloroform and trimethylamine and progressively replace the chlorines on the former atom with hydrogens until it is methane, we pass by stages from a system with a fairly strong hydrogen bond to one without one. At what stage does the hydrogen bond become a normal weak dipole-dipole attraction; in CH_2Cl_2 or CH_3Cl ?

As an operational thermochemical definition we have arbitrarily chosen to say that a hydrogen bond exists between A-H and B if under similar conditions the enthalpy of interaction is at least 1 kcal/mol greater than the comparable interaction which is found between B and A-X where A-X is the best possible model for A-H if the A-H bond were a normal C-H bond incapable of engaging in specific intermolecular hydrogen bonding.⁴⁸ The use of the "pure base method" clearly

(43) (a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960; (b) *Annu. Rev. Phys. Chem.*, **22**, 347 (1971).

(44) D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959.

(45) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding," Van Nostrand-Reinhold, New York, N. Y., 1971.

(46) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).

(47) A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 69 (1968).

(48) The problem of defining hydrogen bonding energy is thus equivalent to that for aromaticity and depends on the model one chooses to represent behavior of the system in the absence of H-bonding (or aromaticity).

involves the appropriate choice of such models and also assumes that solvent effects on hydrogen bonded systems should be small. We will now consider the present status of both of these matters.

1. Solvent Effects on ΔH_f . Even if one is ready to say that all of the interaction energy between AH and B in the complex $\text{AH} \cdots \text{B}$ is due to hydrogen bonding considerable care must still be exercised in determining the energy of forming this complex in solution. The generally recognized conditions for such a careful study are that neither AH nor B should be associated to an energetically significant degree (no solute-solute interactions) and that there should not be significant solvent-solute interactions between the medium and AH or B which are peculiar to that solvent. (Chloroform would be a poor solvent for studying the interaction of phenols with bases.) Therefore the solvent must interact strongly enough with AH and B to dissociate their molecules, but must not do this through strong specific interactions. These and related problems are described clearly by Drago, *et al.*⁴⁹ If specific solvation forces have to be overcome in the formation of $\text{AH} \cdots \text{B}$ from AH and B, this would introduce a spurious endothermic term causing the stability of the complex to be underestimated. Ultimately there will always be some interactions which are idiosyncratic to any solute-solvent pair; our problem is not so much that of identifying specific interactions but of deciding on how large they must be to deserve special attention.

Despite the importance of the hydrogen bond there have been few extensive systematic studies of solvent effects on hydrogen bond energies. Allerhand and Schleyer⁵⁰ have reported a careful investigation of solvent effects on several infrared O-H \cdots O frequencies in 21 nonbasic solvents and the gas phase. They found that medium effects were sometimes quite large and did not follow current theories of solvent shifts.⁵⁰ Osawa and Yoshida obtained similar results with fewer solvents and concluded that the solvent shifts were mainly ascribable to dipole-dipole forces.⁵¹

A reasonable approach for relating hydrogen bonding energies in different solvents has been advanced by Christian and his colleagues.⁵²⁻⁵⁵ They propose that the energy of transfer of $\text{A-H} \cdots \text{B}$ from one solvent to another is proportional to the sum of the transfer of AH and B. This has not been tested adequately but comparison of his association constants for the pyridine-water complex in various solvents⁵² with Allerhand's and Schleyer's *G* values⁵⁰ shows the same qualitative ordering. Four values of $\log K$ for pyridine- I_2 complex (Figure 1) even give a close linear correlation with *G*. For the present purposes a useful application of Christian's equation is seen in Figure 2 where heats of hydrogen bonding of phenol (see Table III) with various bases in cyclohexane are plotted against ΔH_f for the same complex in carbon tetrachloride as solvent.

(49) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, **94**, 90 (1972).

(50) A. Allerhand and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 371 (1963).

(51) F. Osawa and Z. Yoshida, *Spectrochim. Acta*, **23**, 2029 (1967).

(52) S. D. Christian, J. R. Johnson, H. E. Afisprung, and P. J. Kilpatrick, *J. Phys. Chem.*, **70**, 3376 (1966).

(53) S. D. Christian, K. O. Yeo, and E. E. Tucker, *J. Phys. Chem.*, **75**, 2413 (1971).

(54) S. D. Christian, R. Frech, and K. O. Yeo, *J. Phys. Chem.*, **77**, 813 (1973).

(55) S. D. Christian, *J. Amer. Chem. Soc.*, **91**, 6514 (1969).

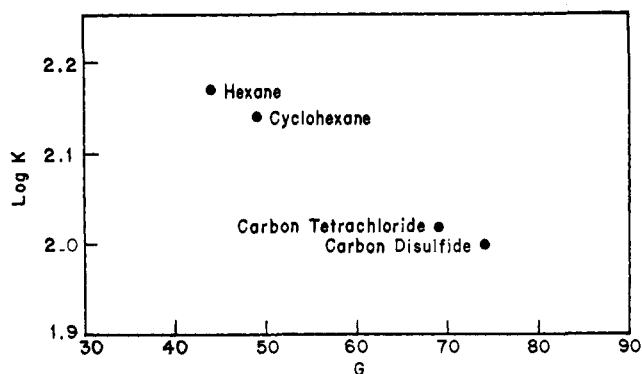


Figure 1. Log K for pyridine- I_2 complex vs. G values.

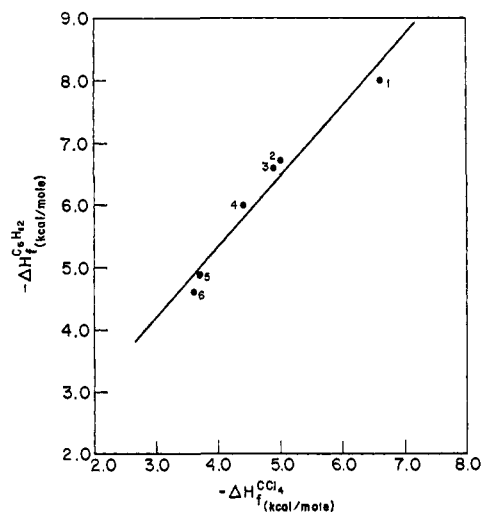


Figure 2. Heats of hydrogen bond formation measured in cyclohexane vs. heats measured in CCl_4 ; numbers refer to Table III.

Table III. Solvent Effects on Heats of Hydrogen Bonding between Phenol and Various Bases

Base	$-\Delta H_f^{C_6H_{12}}$	$-\Delta H_f^{CCl_4}$	Ref
1. Pyridine	8.00 ± 0.1	6.6 ± 0.2	<i>a</i>
2. THF	6.7 ± 0.1	5.0 ± 0.2	<i>a</i>
3. Acetone	6.6 ± 0.1	4.8 ± 0.2	<i>b</i>
4. 1,4-Dioxane	6.0 ± 0.05	4.4 ± 0.1	<i>b</i>
5. Tetrahydrothiophene	4.9 ± 0.1	3.7 ± 0.1	<i>b</i>
6. Diethyl sulfide	4.6 ± 0.1	3.6 ± 0.1	<i>b</i>

^a L. Lamberts, *Z. Phys. Chem. (Frankfurt am Main)*, **73**, 159 (1970). ^b G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970).

Figure 3 uses data from Drago's⁵⁶ work (see Table IV) to illustrate the same point. In Figure 4 enthalpy data from the work of Nozari and Drago are plotted against Schleyer's G values.

Some of the strongest evidence that solvent effects on hydrogen bonding energies are usually modest and systematic is provided by the rather good success of the pure base method described below. Taft²⁵ has also noted the small effect of solvent effects on K_f for a few cases of hydrogen bonds from hydroxyl acids.

2. Present Status of the Pure Base Method (See Re-

(56) M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **94**, 6877 (1972). An extension of this work appeared after the present article was submitted: R. M. Guidry and R. S. Drago, *J. Phys. Chem.*, **78**, 454 (1974). For a very recent test of criticisms by these authors, see G. Olofsson and I. Olofsson, *J. Amer. Chem. Soc.*, **95**, 7231 (1973).

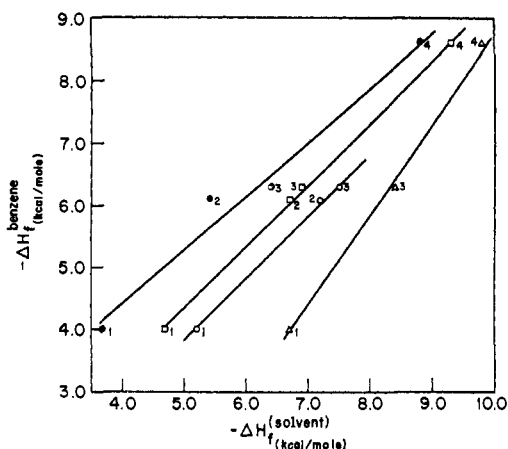


Figure 3. Heats of hydrogen bond formation in various solvents vs. heats measured in benzene; numbers refer to Table IV; (●) ΔH_f in 1,2-dichloroethane; (□) ΔH_f in *o*-dichlorobenzene; (○) ΔH_f in carbon tetrachloride; (Δ) ΔH_f in cyclohexane.

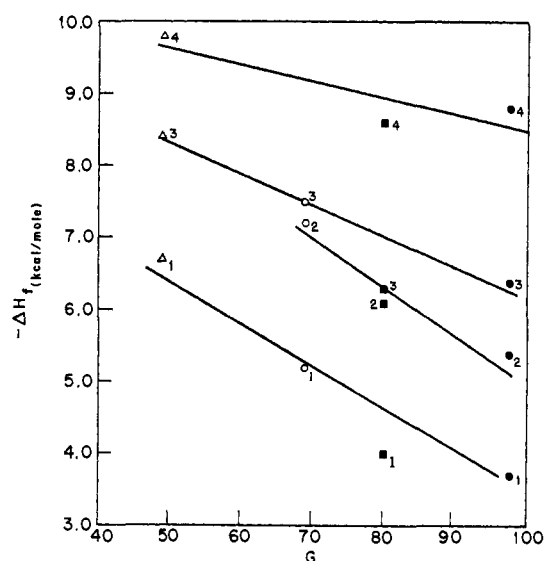


Figure 4. Heats of hydrogen bond formation in various solvents vs. G values; numbers refer to Table IV: (●) ΔH_f in 1,2-dichloroethane; (○) ΔH_f in carbon tetrachloride; (Δ) ΔH_f in cyclohexane; (■) ΔH_f in benzene.

sults for a Restatement of the Method). This simplistic approach for estimating hydrogen bonding enthalpies was proposed by us^{24,35,41} to deal with cases where K_f was so small or hard to obtain that the high dilution method would lead to gross errors in ΔH_f . We were skeptical of its reliability.²⁴ After preliminary tests with about ten bases whose ΔH_f values had been reliably determined by other methods, we were pleasantly surprised to find that it worked rather well. Compounds with large K_f 's will usually be highly polar or polarizable and thus should impose relatively large solvent effects on ΔH_f so that one would expect the pure base method to be at its worst in just those circumstances where large K_f 's make the high dilution method to be at its best and there is no need for the pure base method. Thus the two methods complement each other and could hardly be expected to match exactly across a wide range of K_f 's or ΔH_f 's. Nonetheless, for 15 compounds in Table II the average difference between the methods is 0.4 kcal/mol in our hands and the average difference

Table IV. Solvent Effects on Heats of Hydrogen Bonding between *m*-Fluorophenol and Various Bases^a

Base	$-\Delta H_f^{\text{cyclohexane}}$	$-\Delta H_f^{\text{CCl}_4}$	$-\Delta H_f^{\text{1,2-dichlorobenzene}}$	$-\Delta H_f^{\text{benzene}}$	$-\Delta H_f^{\text{1,2-dichloroethane}}$
1. Ethyl acetate	6.7 ± 0.1	5.2 ± 0.1	4.7 ± 0.1	4.0 ± 0.1	3.7 ± 0.2
2. Dimethyl sulfoxide		7.2 ± 0.1	6.7 ± 0.1	6.1 ± 0.1	5.4 ± 0.1
3. Pyridine	8.4 ± 0.1	7.5 ± 0.1	6.9 ± 0.1	6.3 ± 0.1	6.4 ± 0.1
4. Triethylamine	9.8 ± 0.2		9.3 ± 0.1	8.6 ± 0.1	8.8 ± 0.1
5. <i>n</i> -Butyl ether	6.5 ± 0.1	6.0 ± 0.1	5.7 ± 0.2		4.5 ± 0.2

^a All data taken from ref 56.

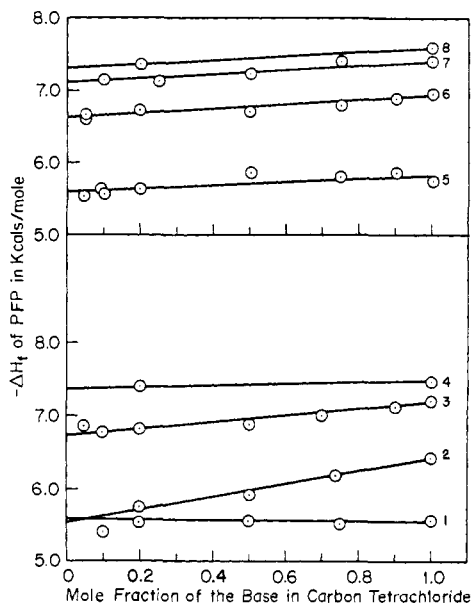


Figure 5. A plot of mole fraction of base in carbon tetrachloride vs. $-\Delta H_f$ in kcal/mol at each concentration: (1) diethyl ether as the base, $-\Delta H_f^\infty$ dilution = 5.6 ± 0.1 kcal/mol; (2) *N*-methylformamide, 5.5 ± 0.1 kcal/mol; (3) dimethyl sulfoxide, 6.7 ± 0.1 kcal/mol; (4) quinoline, 7.35 ± 0.1 kcal/mol; (5) tetrahydrofuran, 5.6 ± 0.1 kcal/mol; (6) dimethylformamide, 6.6 ± 0.1 kcal/mol; (7) pyridine, 7.1 ± 0.1 kcal/mol; (8) 4-methylpyridine, 7.3 ± 0.1 kcal/mol.

for 29 compounds between our pure base values and literature values (for phenol) is 0.5 kcal/mol. Most of the comparisons are for hydrogen bonds above 5 kcal/mol in strength. The most serious discrepancies are for the formamides which are very polar or for several pyridines whose K_f 's are low and dubious.

Many polar Lewis bases have a tendency to associate through dipole-dipole interactions in "inert" solvents such as carbon tetrachloride or hydrocarbons.⁵⁷⁻⁶¹ This can introduce errors from solute-solute interactions in applying high dilution methods to bases of low K_f . Bertrand and Duer⁶² have suggested that errors in the pure base method caused by association or a poor choice of the model compound can be considerably reduced by eliminating the use of an inert reference solvent and comparing directly the heats of transfer of A-H and the model compound from one pure base to another. Apparently differences between model compounds are

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

(58) M. Rabinowitz and A. Pines, *J. Chem. Soc. B*, 1110 (1969).

(59) T. F. Lin, S. D. Christian, and H. E. Aßsprung, *J. Phys. Chem.*, **71**, 968 (1967).

(60) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications, New York, N. Y., 1964, Chapter XI.

(61) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths, London, 1959.

(62) W. C. Duer and G. L. Bertrand, *J. Amer. Chem. Soc.*, **92**, 2587 (1970).

emphasized in the inert solvents. Lamberts⁶³ showed in the cases of acetone, dioxane, and pyridine (see below) that ΔH_f values relative to tetrahydrofuran were not only insensitive to the choice of model compound (anisole vs. toluene) but also to the choice of solvent (carbon tetrachloride vs. cyclohexane). For many applications in solution chemistry especially in comparing the strengths of hydrogen bonds in biological systems absolute estimates of ΔH_f are not needed.⁶⁴ In such cases the evidence so far available indicates that the heat of transfer for the acid from one pure base to another corrected by the heat of transfer of a reasonable model compound (of size and shape similar to AH) should give an estimate of relative ΔH_f within 5%.

A means for improving the agreement between the pure base method and high dilution method is shown in Figure 5.⁶⁵ The combined heats of transfer for PFP and PFA from pure base are plotted for a series of binary mixtures of the base with carbon tetrachloride and the resulting line extrapolated to infinite dilution of the base. This approach can only be used for systems which are completely complexed across the range of solvent concentrations. If K_f is low and complexing is weak, a curve rather than a straight line will result. By using the pure base ΔH_f value and eq 3 it is possible to estimate [C] at various points on the curve and hence K_f . Iteration gives values for K_f and ΔH_f which agree rather well with those derived by other means.⁴¹ Table V shows that for the bases listed, the extrapolated inter-

Table V. Comparison of ΔH_f 's for PFP with Various Bases Using Dilute Solution Method and the Pure Base Method Extrapolated to Infinite Dilution

Base	$-\Delta H_f$, kcal/mol		
	a	b	c
Pyridine	7.2 ± 0.2	7.1 ± 0.1	7.40 ± 0.09
Quinoline	7.5 ± 0.2	7.35 ± 0.1	7.47 ± 0.09
4-Methylpyridine	7.4 ± 0.2	7.3 ± 0.1	7.59 ± 0.08
Tetrahydrofuran	6.0 ± 0.3	5.6 ± 0.1	5.75 ± 0.08
Diethyl ether	5.6 ± 0.3^d	5.6 ± 0.1	5.57 ± 0.12
Dimethyl sulfoxide	6.8 ± 0.2	6.7 ± 0.1	7.21 ± 0.08
Dimethylformamide	6.7 ± 0.2	6.6 ± 0.1	6.97 ± 0.11

^a Dilute solution method (method I).²⁴ ^b Pure base method extrapolated to infinite dilution. ^c Values in pure base (method II).²⁴ ^d K_f used for this base is determined from calorimetric data alone. K_f 's used for the other bases are measured by ir.²⁴

cept is within experimental error of ΔH_f as determined in CCl_4 by the high dilution methods. Table VI confirms that the high estimates of ΔH_f obtained for these bases by the pure base method are related to the polarity of the medium.

(63) L. Lamberts, *Z. Phys. Chem. (Frankfurt am Main)*, **73**, 159 (1970).

(64) I. M. Klotz and S. B. Farnham, *Biochemistry*, **7**, 3879 (1968).

(65) This section is taken from ref 41.

Table VI. Estimate of Solvent Effects on ΔH_f for PFP as Proton Donor with Various Bases

Base	Dielectric constant at 25°	$-\Delta H_f$ in pure base, kcal/mol	$-\Delta H_f^\infty$ at infinite dilution (extrapolated), kcal/mol	$-\Delta\Delta H_f$, kcal/mol
Diethyl ether	4.22	5.57 ± 0.12	5.6 ± 0.1	0
Tetrahydrofuran	7.39	5.75 ± 0.08	5.6 ± 0.1	0.15 ± 0.13
Quinoline	9.22	7.47 ± 0.09	7.35 ± 0.1	0.12 ± 0.14
Pyridine	12.3	7.40 ± 0.09	7.1 ± 0.1	0.30 ± 0.14
Dimethylformamide	36.7	6.97 ± 0.10	6.6 ± 0.1	0.37 ± 0.14
Dimethyl sulfoxide	48.9	7.21 ± 0.08	6.7 ± 0.1	0.41 ± 0.13
<i>N</i> -Methylformamide	182.4	6.44 ± 0.08	5.5 ± 0.1	0.94 ± 0.13

Table VII. Thermodynamic Parameters for the Hydrogen-Bonded Complex of PFP with Various Bases

Base	K_f^{298} , l./mol	$K_f^{298,a}$, l./mol	$-\Delta G_f^\circ$, kcal/mol	$-\Delta H_f^\circ$, kcal/mol	$-\Delta H_f^\circ,^a$, kcal/mol	$-\Delta S_f^\circ$, eu
8. Anthrone	17.6 ± 0.2 ^b		1.70 ± 0.01	5.6 ± 0.4 ^b		13.1 ± 0.1
9. Acetonitrile	7.5 ^c		1.43	4.2 ± 0.2 ^e	4.7	9.3 ± 0.7
17. Ethyl acetate	12.3 ± 0.4 ^b		1.49 ± 0.02	4.74 ± 0.12 ^{b,d}		10.9 ± 0.3
18. Cyclohexanone	20.5 ± 0.9 ^b		1.79 ± 0.02	5.8 ± 0.2 ^b		13.4 ± 0.7
19. Acetone	15.4 ^e		1.60	5.59 ± 0.08 ^d	5.5	13.4 ± 0.3
20. Triphenylphosphine oxide	1456 ± 80 ^b		4.32 ± 0.01	7.4 ± 0.1 ^b		10.3 ± 0.3
21. Di- <i>n</i> -butyl sulfide	1.8 ^e		0.36	3.44 ± 0.08 ^d		10.3 ± 0.3
22. <i>N,N</i> -Dimethyltrifluoroacetamide	26 ^e		1.60	3.2 ± 0.2 ^f		5.4 ± 0.7
23. Diethyl ether	10.3 ± 1.0 ^b		1.38 ± 0.05	5.6 ± 0.1 ^b		14.2 ± 0.3
24. Diethyl sulfide	1.3 ^e		0.15	3.63 ± 0.11 ^d		11.7 ± 0.3
25. Trimethyl phosphate	296 ^e		3.37	6.5 ± 0.1 ^f		10.5 ± 0.3
26. Tetrahydrofuran	17.7 ± 0.5 ^b		1.70 ± 0.2	5.6 ± 0.1 ^b	5.3	13.1 ± 0.3
28. Phenyl methyl sulfoxide	140 ^e		2.92	6.3 ± 0.1 ^f		11.2 ± 0.3
29. Triethyl phosphate	540 ^e		3.73	6.5 ± 0.1 ^f		9.4 ± 0.3
32. <i>N</i> -Methylformamide	90 ± 6 ^b		2.67 ± 0.3	5.5 ± 0.1 ^b		9.5 ± 0.3
33. 2,6-Dimethyl- γ -pyrone	318 ^e		3.40	6.9 ± 0.2 ^f		11.7 ± 0.7
34. <i>N,N</i> -Dimethylchloroacetamide	48 ^e		2.68	6.9 ± 0.3 ^f		15.5 ± 1.0
35. 3,5-Dichloropyridine	6.9 ^e		1.14	5.4 ± 0.4 ^f		14.3 ± 1.3
36. Dimethyl sulfoxide	346 ± 8 ^b	442	3.46 ± 0.02	6.6 ± 0.1 ^b	6.0	10.9 ± 0.3
37. Trimethylphosphine oxide	3090 ^e		4.74	7.7 ± 0.2 ^f		10.1 ± 0.7
39. <i>N,N</i> -Dimethylbenzamide	166 ^e		3.02	6.9 ± 0.2 ^b		13.0 ± 0.7
40. <i>N,N</i> -Dimethylformamide	116 ± 3 ^b	128	2.81 ± 0.01	6.6 ± 0.1 ^b	6.10	12.7 ± 0.3
41. Di- <i>n</i> -butyl sulfoxide	400 ^b		3.53	6.9 ± 0.1 ^f		11.3 ± 0.3
43. Pyridine <i>N</i> -oxide	576 ^e		3.75	7.5 ± 0.2 ^f		12.6 ± 0.7
44. 2-Bromopyridine	8.7 ^e		1.28	5.83 ± 0.09 ^d		15.3 ± 0.3
46. <i>N</i> -Methyl-2-pyrrolidone	235 ^e		3.22	7.0 ± 0.2 ^f		12.7 ± 0.7
47. <i>N,N</i> -Dimethylacetamide	260 ± 12 ^b		3.29 ± 0.03	7.44 ± 0.11 ^{b,d}	7.10	13.9 ± 0.3
48. 3-Bromopyridine	20.3 ± 0.9 ^b		1.78 ± 0.03	6.2 ± 0.2 ^b		14.8 ± 0.7
49. Quinoline	72.3 ± 1.0 ^b		2.54 ± 0.01	7.35 ± 0.1 ^b		16.1 ± 0.3
50. Pyridine	76.2 ± 1.1 ^b		2.56 ± 0.01	7.1 ± 0.1 ^b	6.6	15.2 ± 0.3
51. 1,1,3,3-Tetramethylurea	186 ^e		3.10	7.8 ± 0.2 ^f		15.8 ± 0.7
52. 4-Methylpyridine	109 ± 5 ^b	111	2.78 ± 0.03	7.3 ± 0.1 ^b	6.9	15.2 ± 0.3
53. 2,6-Dimethylpyridine	135 ^e		2.91	7.8 ± 0.3 ^f		16.4 ± 1.0
54. 2,4,6-Trimethylpyridine	200 ^e		3.13	7.9 ± 0.1 ^f		16.0 ± 0.3
55. Quinuclidine ^b	420 ^e		3.58	9.5 ± 0.2 ^f		19.8 ± 0.7
56. Triethylamine	85.2 ± 1.9 ^b		2.63 ± 0.2	8.92 ± 0.09 ^{b,d}		21.0 ± 0.3
58. Hexamethylphosphoramide	3600 ^b		4.85 ± 0.02	8.0 ± 0.1 ^b	8.3	10.6 ± 0.3
59. Diphenyl sulfoxide	105 ± 1 ^b		2.76 ± 0.01	6.2 ± 0.3 ^b		11.5 ± 1.0
60. Triphenyl phosphate	54 ^e		2.35	6.7 ± 0.2 ^f		14.6 ± 0.7
61. Trimethylamine <i>N</i> -oxide ⁱ	3680 ^j		4.84	8.8 ± 0.3 ^f		13.3 ± 1.0
62. 4-Dimethylaminopyridine	407 ^{f,k}		3.56	8.4 ± 0.2 ^f		16.2 ± 0.7
63. 2-Butanone	15.6 ± 0.5 ^b		1.63 ± 0.02	5.20 ± 0.13 ^{b,d}		12.0 ± 0.3
65. Cyclopropylamine	44 ± 2 ^b		2.24 ± 0.1	7.5 ± 0.3 ^e		17.6 ± 1.0
66. <i>N,N</i> -Dimethylamino-3-propionitrile	17.1 ± 0.9 ^b		1.68 ± 0.3	5.8 ± 0.1 ^b		13.8 ± 0.3

^a Determined by Mr. John Kulluk using a thermometric titration technique.³⁶ ^b Reference 24. ^c Reference 41. ^d ΔH_f determined by the pure base method (II). ^e Reference 25. ^f ΔH_f determined by the dilute solution method (I). ^g Reference 31. ^h *o*-Dichlorobenzene was used as solvent. ⁱ Dichloromethane was used as solvent. ^j T. Kubota, *J. Amer. Chem. Soc.*, **89**, 459 (1967). ^k This value was revised by Taft^g from that reported in ref 25, and ΔG_f° , ΔH_f° , and ΔS_f° have been recalculated to conform with the revised equilibrium constant. They supplant the values reported in Table V of ref 24.

3. Concerning the Choice of Solvent for Hydrogen-Bonding Studies. Were it not for the fact that most important hydrogen bonding energies are in the range of 5–8 kcal/mol, solvent effects of ± 0.5 kcal/mol could be considered insignificant. We have seen above that for condensed phase comparisons the pure base method

gives good estimates of relative ΔH_f 's and Figures 1–4 suggest that through suitable solvent parameters it may be possible to make some corrections for medium changes, although the data correlated here are too few to be more than suggestive.

Drago and his colleagues⁶⁶ have employed substitu-

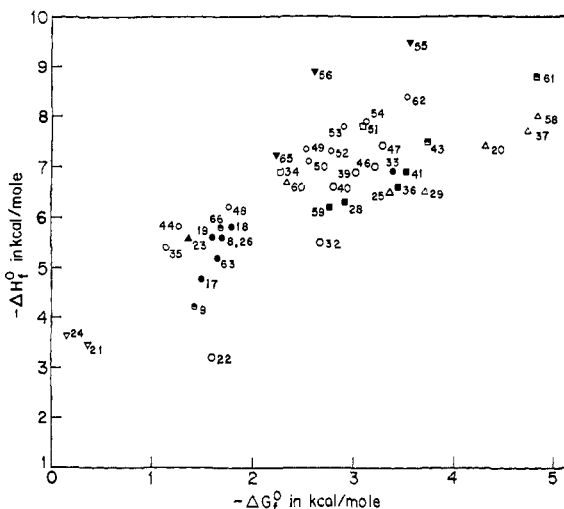


Figure 6. Plot of ΔH_f° for PFP with various bases vs. ΔG_f° for PFP with the bases; numbers for data points correspond to numbers listed in Table VII, e.g., data point 8 refers to anthrone.

tion reactions in order to eliminate the contribution from AH in various solvents in a manner similar to that used by Bertrand and Duer in pure bases.⁶² Using the complexing of *m*-fluorophenol with five Lewis bases (DMSO, ethyl acetate, di-*n*-butyl ether, pyridine, and triethylamine) in five nonpolar solvents they have found that the majority of the 30 displacements studied by them met their criteria of being "solvation free" within ± 0.2 kcal/mol. In some cases, such as the aggregation of amides in cyclohexane, there is a reasonable model for discrepancies. In others, such as those where 1,2-dichloroethane is the solvent, the results did not fit their model and unexplainable factors were inferred.

In our opinion it is not surprising that such discrepancies arise or that they are unexplainable. Even if we assume that all of the reported enthalpies of complexing and solution are both *accurate* and *precise* to within 0.1 kcal/mol, we do not see how it is possible to account for or predict solvent-solute interactions for these diverse systems within 0.3 kcal/mol of the theoretical gas phase value. We even doubt that it is physically significant to assign the gas phase interaction energy between the common organic bonding acids and bases completely to the "hydrogen bond" within 0.3 kcal/mol considering the conceptual looseness of the term to which we have referred.

Finally we would like to respond briefly to criticisms which Drago, *et al.*,^{56,67,73} have raised regarding the use of carbon tetrachloride to study the hydrogen bonding to pyridines. Referring originally to the study of Morcom and Travers⁶⁶ who determined the enthalpy of complexing of pyridine with this solvent as 0.3 kcal/mol, Drago and his colleagues have gradually raised this to 0.9 kcal/mol⁵⁶ in order to account for failures of this system to fit their correlations. By similar indirect methods Purcell⁶⁷ has suggested that the interaction energy is 1.9 kcal/mol. As can be seen from Figures 1-5 there is nothing especially abnormal about pyridine in carbon tetrachloride compared to other solvent-base systems. Furthermore, the results of Lamberts⁶³ and

Bertrand⁶² do not show it to be unique. Until there is direct objective evidence for large abnormal interactions between pyridine and carbon tetrachloride we see no reason to set it apart from other common systems since many of them also show singularities of 0.3 kcal/mol or more.

B. Thermodynamic Parameters for Hydrogen-Bonded Complexes of PFP; Extra Thermodynamic Relations. Relations between ΔG_f° , ΔS_f° , and ΔH_f° . Table VII lists the thermodynamic parameters calculated for the hydrogen-bonded complexes of *p*-fluorophenol with 44 bases. This extends and updates our previous tabulation.²⁴ The values for the standard free energy of hydrogen bond formation to PFP, ΔG_f° , have been calculated from the spectrophotometric equilibrium constants determined by our collaborators.^{24,25} Consequently, the ΔH_f° and ΔS_f° data listed in Table VII are based on essentially independent enthalpy and free energy measurements. Therefore, their correlation⁶⁸ can be attempted without much likelihood⁶⁹ that we might only be generating the rough contours of two sets of numbers (ΔH° , ΔG° , or ΔS°) obtained from the same set of experimental data.

None of the data presently available from other published studies of which we are aware is based on entirely independent determinations of ΔG_f° and ΔH_f° for the estimation of ΔS_f° . The great majority has employed the van't Hoff equation to determine ΔH_f and ΔS_f° from the temperature coefficient of K_f (or ΔG°). In the last decade, the development of solution calorimetry, particularly titration calorimetry, has generated a variety of approaches for estimating K_f and ΔH_f from the concentration dependence of the observed heat of interaction between titrants—in this case AH and B.^{36-38,41} Both the van't Hoff method and the thermometric titration methods are somewhat vulnerable in principle since the same data are being used to determine two variables so that errors can develop in both.^{39,40}

We have previously noted good agreement between our results using independent ΔG_f° and ΔH_f° with high quality van't Hoff data and with Drago's thermometric titration data. In Table VII several measurements determined in our laboratory by Mr. John Kulluk using the continuous thermometric titration technique of Izatt and Christensen³⁶ are presented for comparison and give support for the validity of both methods (provided, of course, that concentrations are low and other experimental requirements are met).

The results presented here for 44 bases with a single hydrogen bonding acid are the most extensive set of such data yet available and generally support our previous conclusions regarding the relationships of ΔG_f° , ΔH_f , and ΔS_f° on half as many compounds.

Thus, large changes in ΔG_f° and ΔH_f° for pyridines, sulfoxides, amides, and phosphoroxy compounds are nearly independent of entropy changes. The value of ΔS_f° is essentially constant within each of these classes of bases. This leads to the behavior shown in Figure 6, where ΔG_f° and ΔH_f° are correlated by a series of crudely parallel lines, each of about unit slope, correlating free energy with enthalpy for the pyridines, sulfoxides, phosphoroxy compounds, and amides. For

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

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

(69) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 232 (1964).

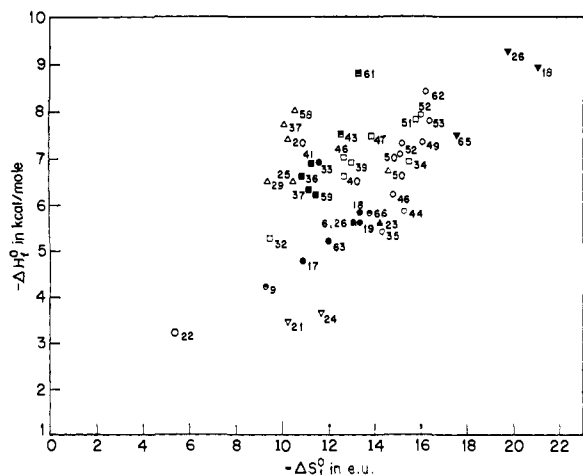


Figure 7. Plot of ΔH_f° for PFP with various bases *vs.* ΔS_f° for PFP with the bases; numbers for data points correspond to numbers listed in Table VII, *e.g.*, data point 8 refers to anthrone: (□) amides, (○) pyridines, (Δ) phosphoroxo compounds, (▽) sulfides, (■) sulfoxides, (●) carbonyl compounds, (▲) ethers, (▼) amines, (⊞) *N*-oxides, (⊙) nitriles.

most of these compounds studied, the entropies of complexing are grouped within ± 3 eu of -15 eu, the main contribution of which is probably the loss of translational entropy on complexation. A few which show unusually low ΔS_f° 's are compounds such as *N*-methylformamide or *N,N*-dimethyltrifluoroacetamide which might be especially subject to association or relatively strong solvation. We note that the pyridine bases have relatively high ΔS_f° values thus giving further evidence against specific solvation compared to the other compounds.⁵⁶

In their 1960 review of hydrogen bonding, Pimentel and McClellan^{43a} presented evidence supporting a monotonic relationship between ΔH_f° and ΔS_f° for hydrogen bond formation. This proposed relation was rationalized on the basis that a "higher value of $(-\Delta H)$ implies stronger bonding, with a more restricted configuration in the polymer, hence greater order, leading to a larger value of $(-\Delta S)$." At that time, data pertinent to this proposal were sparse and largely uncertain. Our data for ΔS_f° and ΔH_f° , listed in Table VII and plotted in Figure 6, indicate quite clearly that, in general, a straight line correlation between ΔS_f° and ΔH_f° does not hold, although a trend is clear.

More recently, Murthy and Rao⁴⁷ and Pimentel and McClellan^{43b} have partially reviewed the literature data (primarily van't Hoff calculations from spectroscopy) and have concluded that ΔS_f° and ΔH_f° for the interaction of phenol with various bases could be resolved into a series of straight lines, each correlating entropy with enthalpy for ethers, carbonyl bases, amines, and amides. An examination of Figure 7 shows that the carbonyl bases, ethers, amines, and nitriles do define a reasonably linear correlation between ΔH_f° and ΔS_f° , and consequently, of course, a rough linear correlation holds between ΔG_f° and ΔH_f° . Phosphoroxo and sulfoxo compounds give relatively positive ΔS_f° values while pyridines and sulfoxides show relatively large entropy loss upon complexing compared to other compounds of similar ΔH_f° . Unfortunately, there are not enough data for each of these types of bases so that a rigorous comparison of our data with the proposals made by

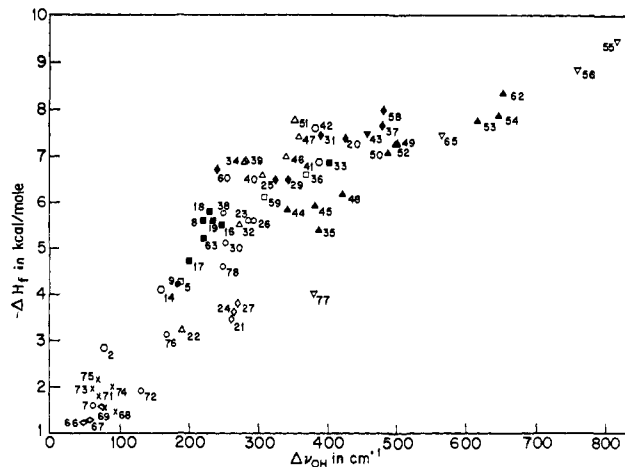


Figure 8. Plot of ΔH_f for PFP with various bases *vs.* $\Delta\nu_{OH}$ for PFP with the bases; numbers for data points correspond to numbers listed in Table VIII; *e.g.*, data point 2 refers to dimethyl sulfate: (◇) aromatics, (×) alkyl halides, (○) ethers, (□) sulfoxides, (Δ) amides, (◇) sulfides, (▽) amines, (●) nitriles, (■) carbonyl bases, (▲) pyridines, (◆) phosphoroxo compounds, (▼) *N*-oxides.

Murthy and Rao and Pimentel and McClellan could be made.

A recent complementary study by Styme, Styme, and Wettermark⁷⁰ of the hydrogen bonding of 17 phenols with a single base (dimethylacetamide) in CCl_4 shows nearly constant ΔS_f° within -10 to -12 eu. Their value for PFP of -12 ± 1.4 eu is not significantly different from ours (-13.9 ± 0.3).

C. The Badger-Bauer (ΔH_f *vs.* $\Delta\nu$) Relationship. The proposal of Badger and Bauer⁷¹ that a linear correlation might exist between ΔH_f and the infrared shift ($\Delta\nu$) produced by a hydrogen bond has only been subject to rigorous testing recently. Although high quality $\Delta\nu$ values have been available for several decades, an extensive data base of reliable ΔH_f values has only developed in the last 10 years. There is now nearly unanimous agreement^{43, 44, 47, 70} that no *general* linear correlation exists. However, for closely related compounds (such as those of a single functional group) interacting with the same AH⁷⁰ good correlations (standard deviation of $\Delta H_f \approx 0.1$ kcal/mol) are found.

In Table VIII are listed what we consider to be the best estimates of $\Delta\nu_{PFP}$ for 65 bases in this study. In Figure 8 their correlation with ΔH_f is tested.

Some of these bases, for example, those containing an aromatic system as well as an electronegative atom and carbonyl bases, contain more than one potential hydrogen bonding site, so that their position on Figure 8 may be deceptive. Where more than one $\Delta\nu_{OH}$ has been obtained for a compound, we have followed convention and used the largest $\Delta\nu_{OH}$ value for comparison with ΔH_f . Considering the small number of these bases which have been shown to have more than one $\Delta\nu_{OH}$ value, and also the large difference in wavelength between the two $\Delta\nu_{OH}$ values found for most of these bases, it is unlikely that this practice would greatly affect the general relationship between ΔH_f and $\Delta\nu_{OH}$. Clearly, if the purpose of ΔH_f - $\Delta\nu$ correlations is the

(70) B. Styme, H. Styme, and G. Wettermark, *J. Amer. Chem. Soc.*, **95**, 3490 (1973).

(71) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

Table VIII. Other Properties of Bases

Base	$\Delta\nu,^a$ cm^{-1}	E_B^b	C_B^b	$-\Delta H_f,^c$ (calcd) kcal/mol	Donicity, ^d kcal/mol	$pK_a,^{ij}$	P.A., ^e kcal/mol
1. Thionyl chloride					0.4		
2. Dimethyl sulfate	77 ^{f,g}						
3. Phosphoroychloride					11.7		
5. Tetramethylene sulfone	186 ^{f,h}				14.8		
6. Dichlorophenylphosphine oxide					18.5		
8. Anthrone	218 \pm 5						
9. Acetonitrile	184 ^{f,i}	0.886	1.34	4.3	14.1	-10.0 ^j	186 ^k
12. Propylene carbonate					15.1		
14. Dimethyl sulfite	158 ^{f,l}						
15. Diethyl carbonate					16.4		
16. Cyclopentanone	246 ^{f,i}					-7.5 ⁱ	202 ^m
17. Ethyl acetate	199 \pm 5	0.975	1.74	4.8	17.1	-4.47 ^{l,j,q}	202 ^m
18. Cyclohexanone	229					-6.8 ⁱ	204 ^m
19. Acetone	232 ^{f,i}	0.987	2.33	5.2	17.0	-7.2 ⁱ	190 ^k
20. Triphenylphosphine oxide	422 \pm 5					-2.10 ⁿ	
21. Di- <i>n</i> -butyl sulfide	261 ^{f,o}					-6.7 ^q	
22. <i>N,N</i> -Dimethyltrifluoroacetamide	190 ^{f,h}						
23. Diethyl ether	285	0.963	3.25	5.5	19.2	-2.42 ^{cc}	199 ^k
24. Diethyl sulfide	263 ^{f,o}	0.339	7.40	4.7 ^p		-6.8 ^q	197 ^k
25. Trimethyl phosphate	323 ^{o,r}				23.0		
26. Tetrahydrofuran	292	0.978	4.27	6.0	20.0	-2.02 ^{oo}	199 ^k
27. Tetrahydrothiophene	282 ^{f,o}	0.341	7.90	4.9 ^p		-7 ^q	
28. Phenyl methyl sulfoxide						-2.27 ^t	
29. Triethyl phosphate	341 ^{f,i}						
30. 1,4-Dioxane	252	1.09	2.38	5.6		-3.22 ⁱ	
31. Diethyl ethylphosphonate	389 ^{o,r}						
32. <i>N</i> -Methylformamide	271 \pm 10					-1.7 ^q	
33. 2,6-Dimethyl- γ -pyrone	400 ^{o,r}					-0.28 ^{dd}	
34. <i>N,N</i> -Dimethylchloroacetamide	280 ^{f,h}						
35. 3,5-Dichloropyridine	385 ^{f,i}					+0.75 ^u	
36. Dimethyl sulfoxide	367	1.34	2.85	6.9	29.8	-1.80 ^t	
37. Trimethylphosphine oxide	480 ^{o,r}					-0.5 ^q	
38. 1,2-Dimethoxyethane	248 ^{f,i}						
39. <i>N,N</i> -Dimethylbenzamide	279 ^{r,bb}					-1.4 ^{ss}	
40. <i>N,N</i> -Dimethylformamide	305 \pm 5	1.23	2.48	6.2	26.6	-1.5 ^{t,hh}	
41. Di- <i>n</i> -butyl sulfoxide	384 ^{o,r}					-1.47, ^z -1.7 ^q	
42. Tetramethylene sulfoxide	380 ^{f,l}	1.38	3.16	7.2			
43. Pyridine <i>N</i> -oxide	454 ^{f,l}	1.34	4.52	7.6		+0.69 ^{ee}	
44. 2-Bromopyridine	340 ^{bb}					+0.80 ^v	
45. 2-Chloropyridine	384 ^{f,i}					+0.60 ^v	
46. <i>N</i> -Methyl-2-pyrrolidone	339 ^{f,o}					-0.92 ^{dd}	
47. <i>N,N</i> -Dimethylacetamide	356 \pm 5	1.32	2.58	6.7	27.8	-0.36 ^{dd}	
48. 3-Bromopyridine	421					+2.84 ^v	
49. Quinoline	498 \pm 10					+4.81 ^v	
50. Pyridine	485 \pm 10	1.17	6.40	7.7 ^p	33.1	+5.21 ^v	226 ^e
51. 1,1,3,3-Tetramethylurea	350 ^{f,ooo}	1.20	3.10	6.4	29.6	+0.40 ^w	
52. 4-Methylpyridine	495 \pm 10					+6.03 ^v	231 ^e
53. 2,6-Dimethylpyridine	614 ^{f,r}					+6.65 ^v	
54. 2,4,6-Trimethylpyridine	644 ^{f,r}					+7.51 ^v	
55. Quinuclidine	814 ^{r,v}					+10.95 ^v	
56. Triethylamine	756 ^{f,r}	0.991	11.09	9.1 ^p		+10.75 ^v	230 ^k
58. Hexamethylphosphoramide	479 \pm 10	1.518 ^{bb}	3.548 ^{bb}	7.9	38.8		
59. Diphenyl sulfoxide	311 \pm 5						
60. Triphenyl phosphate	238 ^{f,i}						
62. 4-Dimethylaminopyridine	650 ^{f,r}						
63. 2-Butanone	221 \pm 5						
65. Cyclopropylamine	561						
66. Benzene	49	0.525 ^{bb}	0.681 ^{bb}	2.5			
67. Toluene	57						
68. Cyclohexyl iodide	95						
69. <i>n</i> -Butyl iodide	78						
70. Mesitylene	76	0.574	2.19	3.4			
71. <i>n</i> -Butyl bromide	71						
72. Diphenyl ether	132; 43 \pm 5						
73. <i>n</i> -Butyl chloride	62						
74. Cyclohexyl bromide	90						
75. Cyclohexyl chloride	71						
76. Anisole	169; 43 \pm 5						
77. <i>N,N</i> -Dimethylaniline	382 \pm 10; 83						
78. Dibenzyl ether	249; 38 \pm 5						

Footnotes to Table VIII

^a Unless otherwise noted, data taken from ref 24. ^b Reference 13. ^c Calculated using: $(-\Delta H_f = E_A E_B + C_A C_B)^b$ with $E_A = 4.17^b$ and $C_A = 0.446^b$ for *p*-fluorophenol. ^d V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, New York, N. Y., 1968, Chapter 2. ^e Proton affinity measured in the vapor phase. ^f Calculated from the value for phenol, using $\Delta\nu_{\text{phenol}}/\Delta\nu_{\text{PPP}} = 0.973$; P. v. R. Schleyer, private communication. ^g Reference 47. ^h M. D. Joesten and R. S. Drago, *J. Amer. Chem. Soc.*, **84**, 3817 (1962). ⁱ L. J. Bellamy and R. J. Pace, *Spectrochim. Acta, Part A*, **25**, 319 (1969). ^j E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963). The data from this source represent best estimates for the H_0 at half-protonation available in 1973. Since the Φ values for correcting the pK_a to water are not known, the listed pK_a may be seriously in error. ^k Reference 8. ^l T. Gramstad, *Spectrochim. Acta*, **19**, 829 (1963). ^m E. G. Melby, Ph.D. Thesis, University of Cincinnati, Cincinnati, Ohio, 1971. ⁿ C. Klofutar, F. Krasovec, and M. Kusar, *Croat. Chem. Acta*, **40**, 23 (1968). ^o G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970). ^p Drago recommends the use of hexane with these bases. ^q Personal communication of best estimate from Professor G. Scorrano. ^r Calculated from value for methanol using $\Delta\nu_{\text{PPP}}/\Delta\nu_{\text{MeOH}} = 1.846$; P. v. R. Schleyer, private communication, June 1971. ^s J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967. ^t D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, **91**, 6703 (1969). ^u C. D. Johnson, A. Katrizky, B. J. Ridgewell, N. Shaker, and A. M. White, *Tetrahedron*, **21**, 1055 (1965). ^v P. v. R. Schleyer, private communication, June 1971. ^w R. L. Adelman, *J. Org. Chem.*, **29**, 1837 (1964). ^x P. Olavie, I. Virtanen, and J. Korpella, *Suom. Kemistilehti B*, **41**, 326 (1968). ^y D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solutions," Butterworths, London, 1965. ^z M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972). ^{aa} T. Gramstad and J. Sandström, *Spectrochim. Acta, Part A*, **25**, 31 (1969). ^{ab} F. L. Slejko, R. S. Drago, and D. G. Brown, *J. Amer. Chem. Soc.*, **94**, 9210 (1972). ^{ac} P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *ibid.*, **95**, 5960 (1973). ^{ad} M. Liler, "Reaction Mechanisms in Sulfuric Acid and Other Strong Acid Solutions," Academic Press, London, 1971. ^{ae} C. Klofutar, S. Paljk, and D. Krenser, *Spectrochim. Acta, Part A*, **29**, 139 (1973). ^{af} C. A. Lane, *J. Amer. Chem. Soc.*, **86**, 2521 (1964). ^{ag} Calculated from data of D. G. Lee and R. Cameron, *Can. J. Chem.*, **50**, 445 (1967). ^{ah} P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967). ^{ai} K. Yates and J. B. Stevens, *Can. J. Chem.*, **43**, 529 (1965). ^{aj} There are many published pK_a estimates for the bases listed here. For reasons having to do with the acquisition and treatment of the experimental data, we consider that some of these published values are so seriously in error that they should not be used. Accordingly, we have cited only what we consider are "best" values and rejected all others even though they might be numerically close.

accurate prediction of ΔH_f values, there are many limitations on its use.⁷²

Figure 8 suggests that several lines, roughly parallel to each other are generated for several series of compounds (*e.g.*, amines, sulfoxides, phosphoroxy compounds). Others (*e.g.*, ethers and carbonyl bases) have lines with different slopes.

D. Theories of the Hydrogen Bond. The nature of the hydrogen bond has been a perennial challenge to theoreticians whose work has been summarized in a number of reviews.^{46,74-78} Following Pauling⁴² and Coulson^{74a} there is generally recognition of the importance of Coulombic contributions to the bond. In addition a variety of other factors (*e.g.*, charge transfer, exchange, dispersion, and charge delocalization) have been invoked.

Most theories are applied to only a few simple model systems and so can scarcely have predictive value for large molecules in solution. Nevertheless a few general results emerge from our study.

(a) Comparison of nitrogen and oxygen *vs.* phosphorus and sulfur bases indicates support for Pauling's original correlation of electronegativity of A and B in the strength of $A-H \cdots B$.

(b) Further, since the electronegativity of an atom is related to its hybridization,^{74b} the hydrogen bond acceptor ability of an atom should get smaller as the *s* character of the lone-pair electrons increases. Again, data from Table II show that for nitrogen compounds, tri-

(72) Overall comparison of measured ΔH_f values compared to those calculated using the Drago-Epley equation $(-\Delta H_f = 0.0103\Delta\nu + 3.08)^{72}$ shows that the calculated values differ from the experimental values by an average of ± 0.8 kcal/mol. Omitting the obvious two site bases, the remaining data show average agreement of about ± 0.6 kcal/mol between the two sets of values. For an extensive and detailed critique of the Badger-Bauer equation see the thesis of L. Joris, Princeton University, 1970.

(73) T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967); R. S. Drago and T. D. Epley, *ibid.*, **91**, 2883 (1969).

(74) (a) C. A. Coulson in ref 44, p 339; (b) "Valence," Clarendon Press, Oxford, 1952.

(75) Reference 43a, Chapter 8.

(76) S. Bratoz, *Advan. Quantum Chem.*, **3**, 309 (1967).

(77) S. H. Lin, "Physical Chemistry—An Advanced Treatise," H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N. Y., 1970, p 439.

(78) A. S. N. Murthy and C. N. R. Rao, *J. Mol. Struct.*, **6**, 253 (1970).

ethylamine ($\Delta H_f = -8.9$ kcal/mol) is a better acceptor than pyridine ($\Delta H_f = -7.1$ kcal/mol) which is superior to acetonitrile ($\Delta H_f = -4.2$ kcal/mol). Unfortunately, the data do not permit us to distinguish between diethyl ether ($\Delta H_f = -5.6$ kcal/mol) and acetone ($\Delta H_f = -5.6$ kcal/mol), but the results for the nitrogen bases bear out the prediction that increased *s* character in the lone-pair electrons of an atom results in decreased hydrogen bond acceptor ability.

(c) The superior acceptor ability of amides (compared to ketones), of sulfoxides and phosphine oxides, and of substituted pyridines indicates that delocalization and polarizability can be important in stabilizing a hydrogen bond. This conclusion is supported by several studies (Drago,⁷³ Styme,⁷⁰ etc.) using substituted phenols against single bases.

II. Proton Transfer—Brønsted Acidity. In several previous publications^{17,79,80} we have described the use of ΔH_i (heat of transfer from an inert solvent to fluorosulfuric acid at 25°) as a broadly applicable criterion of Brønsted basicity. ΔH_i measurements are readily obtained for the protonation of most bases in this single medium in which the protonation process is complete and well defined, as is shown by freezing point depressions, electrical conductivities, nmr observations, and ultraviolet spectroscopy.^{27,28,81}

Several years ago we noted that a surprisingly good linear correlation is found between ΔH_i and pK_a for many compounds including a variety of weak bases whose pK_a 's have been determined by acidity function methods. In view of the errors in many previous pK_a estimates¹⁷ and the availability of a number of new

(79) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970).

(80) E. M. Arnett, J. J. Burke, J. V. Carter, and C. F. Douty, *J. Amer. Chem. Soc.*, **94**, 7837 (1972).

(81) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, **93**, 5083 (1971); J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964); R. J. Gillespie and E. A. Robinson, "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965, pp 117-210; T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, **5**, 468 (1966); R. Birchall, Ph.D. Thesis, McMaster University, Toronto, Ontario, Canada, 1963; R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963); G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972), and previous papers in this series.

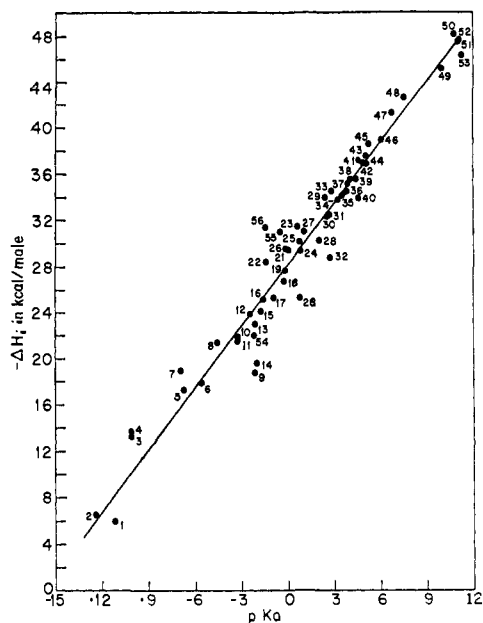


Figure 9. Plot of ΔH_i vs. pK_a for the following bases (data taken from ref 17 or Table VIII of this work): (1) benzoyl chloride, (2) nitrobenzene, (3) 2,4,6-trinitroaniline, (4) acetonitrile, (5) 2-bromo-4,6-dinitroaniline, (6) 2,6-dinitroaniline, (7) diethyl sulfide, (8) 2,4-dinitroaniline, (9) diethyl ether, (10) 2,6-dichloro-4-nitroaniline, (11) 1,4-dioxane, (12) diphenylcyclopropanone, (13) triphenylphosphine oxide, (14) tetrahydrofuran, (15) 2,5-dichloro-4-nitroaniline, (16) *N,N*-dimethylbenzamide, (17) 4-chloro-2-nitroaniline, (18) 2-nitroaniline, (19) *N,N*-dimethylacetamide, (20) *N*-methylformamide, (21) *N,N*-dimethylformamide, (22) dimethyl sulfoxide, (23) 2-chloropyridine, (24) pyridine *N*-oxide, (25) 2-bromopyridine, (26) 2,4,6-tribromoaniline, (27) 4-nitroaniline, (28) 2,4-dichloroaniline, (29) 3-nitroaniline, (30) 2-iodoaniline, (31) 2-chloroaniline, (32) triphenylphosphine, (33) 3-bromopyridine, (34) 2-fluoroaniline, (35) 3-chloroaniline, (36) 4-iodoaniline, (37) 4-bromoaniline, (38) 4-chloroaniline, (39) 2-methylaniline, (40) aniline, (41) 4-fluoroaniline, (42) quinoline, (43) *N,N*-dimethylaniline, (44) 4-methylaniline, (45) pyridine, (46) 4-methylpyridine, (47) 2,6-dimethylpyridine, (48) 2,4,6-trimethylpyridine, (49) tri-*n*-butylamine, (50) triethylamine, (51) quinolidine, (52) diethylamine, (53) di-*n*-butylamine, (54) phenyl methyl sulfoxide, (55) 2,6-dimethyl- γ -pyrone, (56) *N*-methyl-2-pyrrolidone.

improved values we have tabulated what we believe are the present best pK_a values in Table VIII.

In Figure 9, calorimetrically determined heats of protonation, ΔH_i , are plotted vs. the most reliable aqueous pK_a values available in the literature.⁸² A good linear correlation between these two measures of proton basicity holds over the range of 40 kcal/mol for the enthalpies and 22 pK_a units (29 kcal/mol in free energy). Data for such diverse classes of bases as primary, secondary, and tertiary aliphatic and aromatic, amines, pyridines, pyridine *N*-oxides, nitroaromatics, sulfoxides, amides, ketones, acid chlorides, sulfides, ethers, phosphines, nitriles, and phosphine oxides are all included on this plot. The least-squares equation for the data is

$$-\Delta H_i = (1.77 pK_a + 28.1) \text{ kcal/mol}$$

and the correlation coefficient is 0.986.

The standard deviation of points from the line is 1.3 kcal/mol or 1 pK_a unit so that in general ΔH_i —the heat of protonation in HSO_3F —provides a rough estimate of the pK_a (or standard free energy) for protonation in

(82) We appreciate the suggestions of Dr. Gianfranco Scorrano in choosing these data.

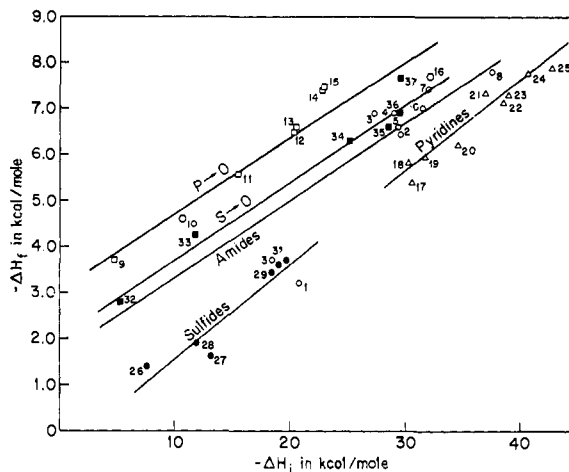


Figure 10. Plot of ΔH_i vs. ΔH_i for amides, phosphoroxy compounds, pyridines, sulfides, and sulfoxides. Data points in the figure refer to the following compounds: (1) *N,N*-dimethyltrifluoroacetamide, (2) *N*-methylformamide, (3) *N,N*-dimethylchloroacetamide, (4) *N,N*-dimethylbenzamide, (5) *N,N*-dimethylformamide, (6) *N*-methyl-2-pyrrolidone, (7) *N,N*-dimethylacetamide, (8) 1,1,3,3-tetramethylurea, (9) phosphoroychloride, (10) dichlorophenylphosphine oxide, (11) diethyl chlorophosphate, (12) trimethyl phosphate, (13) triethyl phosphate, (14) triphenylphosphine oxide, (15) diethyl ethylphosphonate, (16) trimethylphosphine oxide, (17) 3,5-dichloropyridine, (18) 2-bromopyridine, (19) 2-chloropyridine, (20) 3-bromopyridine, (21) quinoline, (22) pyridine, (23) 4-methylpyridine, (24) 2,6-dimethylpyridine, (25) 2,4,6-trimethylpyridine, (26) diphenyl sulfide, (27) phenyl methyl sulfide, (28) chloromethyl methyl sulfide, (29) di-*n*-butyl sulfide, (30) diethyl sulfide, (31) tetrahydrothiophene, (32) dimethyl sulfoxide, (36) di-*n*-butyl sulfoxide, (37) tetramethylene sulfoxide; (○) amides, (□) phosphoroxy compounds, (Δ) pyridines, (●) sulfides, (■) sulfoxides.

water. In view of the different entropy factors which might be expected in these two solvents it is surprising that the correlation is this good. We expect that it will eventually disperse into a series of different lines for different families as more precise pK_a 's become known.

Even a cursory comparison of Tables IV and VIII shows that there is little correlation between ΔH_i and the gas phase proton affinities of bases for which these properties are known. We shall return to this matter later.

III. Comparisons of Basicity Factors. A. ΔH_i vs. ΔH_i . In Figure 10 the enthalpies for hydrogen bonding and protonation which occasioned this study are displayed. For the 37 bases shown there, a general scatter diagram is the result and it is obvious that there is no single general correlation between ΔH_i and ΔH_i for these different types of bases. For example, although triphenylphosphine oxide and 4-methylpyridine have essentially the same heat of hydrogen bond formation to *p*-fluorophenol, -7.4 ± 0.1 kcal/mol vs. -7.3 ± 0.2 kcal/mol, the heat of protonation for the pyridine is some 16 kcal/mol more exothermic than ΔH_i for the phosphine oxide. This corresponds to a difference of more than 9 pK_a units. However, if a separate line is drawn for each family of compounds, a series of nearly parallel (within experimental error) lines result.⁸³

The various straight lines drawn in the figure are least-squares fits of the data for phosphoroxy compounds, sulfoxides, amines, sulfides, and substituted pyridines. For the sake of clarity, a number of points

(83) The slopes and intercepts of these lines can be found in Table XI of E. J. M. s thesis.

Table IX. Comparison of ΔH_f for Bases with Different Functional Group Donors

Functional group	$-\Delta H_f^a$ kcal/mol	Pauling's electronegativity ^b
Phosphine	1.3	2.1
Sulfide	5.1	2.5
Amine	5.2	3.0
Pyridine	5.3	
<i>N</i> -Oxide	6.7	
Ether	6.7	3.5
Nitrile	6.9	
Amide	7.0	
Carbonyl	7.1	
Sulfoxide	7.4	
Phosphine oxide	8.7	

^a Calculated at point where $\Delta H_i = -28.1$ kcal/mol. ^b Reference 42.

representing data for several ethers, ketones, esters, carbonates, amines, nitriles, and *N*-oxides have been deleted from Figure 10. Only a few members of each of these families of bases have been studied, so that no statistically valid comparison of ΔH_i with ΔH_f was possible for any of these series of compounds. However, in view of the behavior of those families of bases shown in Figure 10, it seems quite likely that each of these basic types—amines, ethers, etc.—would generate its own line correlating proton basicity with hydrogen bond basicity. Indeed, the few data which are available for these compounds do not appear to correlate well with any of the lines shown in Figure 10.

Taft^{25,84} has reported exactly the same type of dispersal of lines for different functional groups in an attempted correlation between the free energy of hydrogen bonding and the free energy of proton transfer for the same compounds. A plot of aqueous pK_a , measured at 25°, vs. $\log K_f$, the logarithm of the equilibrium constant for hydrogen bond formation to *p*-fluorophenol in CCl_4 at 25°, for primary amines, 3- and 4-substituted pyridines, and carbonyl bases showed three essentially parallel lines, each correlating pK_a with $\log K_f$ for bases of a common structural type. The slopes of the linear free energy relationships found by Taft are the same as the slopes of the linear enthalpy relationships shown in Figure 10. For both of these thermodynamic measurements, free energy and enthalpy, ionization *via* proton acceptance is about five times more sensitive to substituent effects than is the formation of a hydrogen bond.

Additional data which may aid in the interpretation of the results shown in Figure 10 are presented in Table IX. The ΔH_f values in the first column of this table represent the enthalpy of hydrogen bond formation to PFP for each functional group family, all calculated at the point where ΔH_i is equal to -28.1 kcal/mol, or a pK_a of about zero. In other words, these data are relative hydrogen bond acceptor abilities for different types of bases, all of which have equal proton acceptor abilities. Data for basic types other than those for which a correlation between ΔH_i and ΔH_f had been generated already were calculated from the data for the few compounds of that type which had been studied by assuming that ΔH_i and ΔH_f could be related by a line whose slope is 0.2, the same as that found for other families of bases (Figure 10). Table IX shows that, as suggested by

(84) H. B. Yang and R. W. Taft, *J. Amer. Chem. Soc.*, **93**, 1310 (1971).

Pauling⁴² some 30 years ago and reiterated by Taft in 1969,²⁵ the hydrogen bond acceptor ability of these basic types correlates roughly with the electronegativity of the acceptor atom. Phosphines are weaker hydrogen bond acceptors relative to proton acceptance than sulfides, which are weaker than amines, which are weaker than ethers.

We explain the discrepancy between the behavior of different classes of bases in terms of the most obvious difference between the proton transfer process eq 1 and hydrogen bonding eq 2. For a series of bases with the same acid, the principal component which is characteristic of proton transfer is the solvated onium ion $BH^+ \cdots S$. Taft²⁵ and Drago⁷³ have shown that there is a close parallel between the hydrogen bonding ability of different R-OH hydrogen bond donors to a given series of bases. We would thus expect that the hydrogen bonding energies of PFP and H_2O with the same series of bases would correlate in at least rough proportionality. At present very little is actually known about the relative hydrogen bonding donor ability of onium ions BH^+ .

Dr. James Wolf⁸⁵ in this laboratory has shown that the solvation energies of 25 ammonium ions in HSO_3F are closely proportional to the corresponding energies in water. As of this writing only the hydration energies of the ammonium ions in water are known; however, the order of solvation energies for a number of diverse types of onium ion in HSO_3F , relative to the gas phase, are drastically different from the hydrogen bonding energies of the corresponding free bases as hydrogen bond acceptors and in the order which can explain the difference between protonation behavior and hydrogen bonding in terms of differing solvation donors of BH^+ .⁸⁶ In the absence of any means for directly estimating the hydration energies of oxonium, sulfonium, or other onium ions than ammonium, it is not possible at present to give an exact quantitative accounting for pK_a 's in terms of relative solvation energies of B vs. BH^+ . However, this approach has already led to the prediction and discovery of some remarkably large pK_a differences.^{87,88} These results support, but of course do not prove our position that the principal cause for the large differences between proton transfer in solution and hydrogen bonding as reported by Taft²⁵ and shown in Figure 10 lies in the differing solvation energies of various families of onium ions.⁸⁹ Correspondingly, it is primarily the solvation energy of BH^+ which is responsible for the often striking difference between gas phase pK_a 's and those in solution.⁹¹⁻⁹⁴

(85) E. M. Arnett and J. Wolf, *J. Amer. Chem. Soc.*, in press.

(86) G. Scorrano and E. M. Arnett, to be submitted for publication.

(87) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973).

(88) E. M. Arnett, *Accounts Chem. Res.*, **6**, 404 (1973).

(89) In contrast, Satchell and Satchell⁹⁰ have attempted to account for Taft's results²⁵ in terms of varying numbers of hydrogen bonds donated by water to the free bases.

(90) D. P. N. Satchell and R. S. Satchell, *Quart. Rev., Chem. Soc.*, **25**, 171 (1971).

(91) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holty, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(92) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(93) W. G. Henderson, M. Taagepera, D. Holty, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).

(94) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).

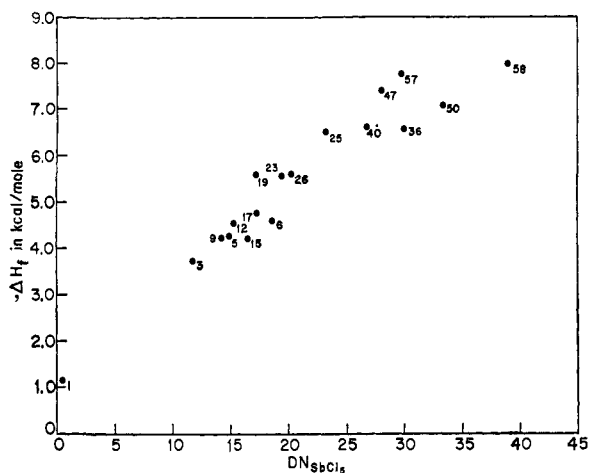


Figure 11. Plot of $-\Delta H_f$ of PFP with various bases vs. DN_{SbCl_5} of the bases. Numbers for data points correspond to numbers listed in Table VIII; e.g., data point 1 refers to thionyl chloride.

B. Donicity. As part of an effort to characterize and classify various solvent effects of chemical reaction, Gutmann⁹⁵ has developed an empirical treatment designed to correlate and predict the enthalpies of donor-acceptor interactions. He has proposed the use of so-called "donor numbers," DN, as the essential property needed to characterize the basic properties of solvents. The "donor number" of a base is simply the calorimetrically determined enthalpy of adduct formation between the base and antimony pentachloride ($SbCl_5$), measured at high dilution in 1,2-dichloroethane. Drago¹³ has called into question the data used by Gutmann to construct linear DN-enthalpy plots. In testing the relationship between donor number and enthalpy of hydrogen bonding to phenol, Gutmann used enthalpies calculated from temperature coefficients of equilibrium constants for the interactions of phenol with 12 different electron donors. The straight line relationship that he obtained corresponds to

$$-\Delta H_{(\text{phenol-donor})} = 0.24DN + 0.37$$

However, comparison of our calorimetric data with the ΔH_f values by Gutmann show poor agreement. This, of course, makes the reported linear correlation of ΔH_f and DN_{SbCl_5} suspect.

We have reexamined the relationship between hydrogen bonding enthalpies and donor numbers using calorimetric data for ΔH_f and also using a more extensive series of bases than was used by Gutmann. A plot of ΔH_f vs. DN_{SbCl_5} (see Table VIII) is shown in Figure 11. A least-squares fit yields the empirical equation

$$-\Delta H_f = 0.182DN_{SbCl_5} + 1.68$$

Using this equation and Gutmann's donor numbers with experimental ΔH_f values, we find that the average deviation of calculated ΔH_f values from experimental results is ± 0.4 kcal/mol. Since calorimetrically determined hydrogen bond strengths generally have error limits of ± 0.1 - 0.2 kcal/mol, we conclude that donor numbers may be good qualitative and reasonable quantitative indicators for assessing hydrogen bond acceptor abilities of bases.

(95) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, New York, N. Y., 1968, Chapter 2.

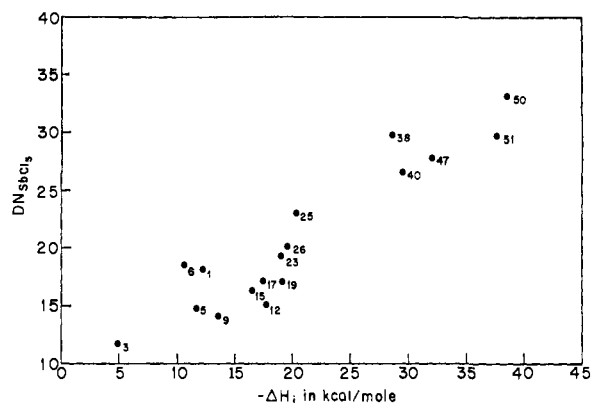


Figure 12. Plot of $-\Delta H_i$ of various bases vs. DN_{SbCl_5} of the bases. Numbers for data points correspond to numbers listed in Table VIII; e.g., data point 10 refers to water.

An attempted correlation of ΔH_i with donicity (Figure 12) shows that donor numbers are a less satisfactory measure for proton basicity than for hydrogen bond basicity. This is as expected. Since ΔH_f and ΔH_i do not show a general correlation with each other, any measure of basicity that shows a good general correlation with ΔH_f cannot correlate as well with ΔH_i . Unfortunately, there are not enough donor numbers to test whether a plot of DN_{SbCl_5} vs. ΔH_i would show the same dispersion into correlation lines for various families of bases as is shown by a plot of ΔH_f vs. ΔH_i .

Since the formation of a Lewis acid complex is formally more similar to hydrogen bonding than it is to formation of a solvated onium ion, we would expect a better correlation of DN with ΔH_f than with ΔH_i .

C. Drago's E and C Parameters. A number of authors have attempted to correlate acid-base behavior through multiparameter treatments.¹¹⁻¹⁵ Of these, the most extensive proposal for treating donor-acceptor interactions empirically is due to Drago.^{13,96} He has proposed that the following equation be used to predict the enthalpy of donor-acceptor interactions in the gas phase or in poorly solvating solvents. The

$$-\Delta H = E_A E_B + C_A C_B$$

parameters E_A and E_B are interpreted as the susceptibility of the acid and the base, respectively, to undergo electrostatic interaction; C_A and C_B are interpreted as the susceptibility of the acid and the base respectively to form a covalent bond. The E_A and C_A values for 31 electron acceptors, and C_B and E_B values for 43 electron donors have recently been tabulated.¹³ They have been used to correlate over 280 enthalpies of adduct formation and are said to be capable of predicting over 900 unmeasured enthalpies of interaction. Some of these enthalpies have now been measured as a part of the present study, thereby providing a test of Drago's four-parameter equation for predicting enthalpies in the systems to be studied here.

C_B and E_B values for a number of the bases that we have studied are listed in Table VIII. Also included in this table are the enthalpies of hydrogen bond formation that we have calculated using these values with the equation: $-\Delta H_f = E_A E_B + C_A C_B$. The average deviation, for 15 compounds (deleting those bases for

(96) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).

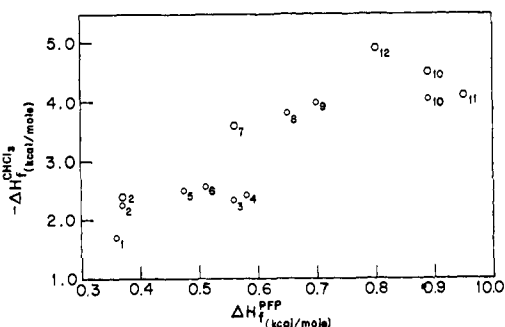


Figure 13. $-\Delta H_f^{\text{CHCl}_3}$ vs. $-\Delta H_f^{\text{PFP}}$ for the following bases: (1) diethyl sulfide, (2) tetrahydrothiophene, (3) acetone, (4) cyclohexanone, (5) ethyl acetate, (6) 1,4-dioxane, (7) tetrahydrofuran, (8) triethyl phosphate, (9) *N*-methyl-2-pyrrolidone, (10) triethylamine, (11) quinuclidine, (12) hexamethylphosphoramide; (○) data taken from ref 98; (◻) data taken from ref 97.

which Drago recommends the use of hexane as solvent), between the calculated and measured data (Table II) is ± 0.5 kcal/mol. These results indicate that the use of *E* and *C* parameters can give reasonable estimates of enthalpies of hydrogen bond formation but since deviations can be greater than 1 kcal/mol the use of Drago's equation is of limited predictive value.

D. Other Acid-Base Data. Finally we have plotted several different sets of acid-base data for similar processes against each other. Thus in Figure 13 our ΔH_f data using PFP as acid are plotted against the data of Drago, *et al.*,⁹⁷ and Wiley and Miller⁹⁸ for the same bases using chloroform as the acid. The correlation is poor compared to those usually observed for relating data for two ROH hydrogen bond donors.

In Figure 14 are plotted heats of interaction of the Lewis acids SbCl_5 ⁹⁵ and $\text{Al}(\text{Me})_3$ ⁹⁹ with a variety of bases. Again correlation is not very good.

A Concluding Viewpoint

We have seen that the energies for the variety of acid-base interactions do not correlate very well with each other, even when the processes are quite similar. It is not surprising then that there is no general correlation between hydrogen bonding energies and those for protonation.

In view of the failure of such two-parameter linear correlations there has been increasing use of four-

(97) F. L. Slejko, R. S. Drago, and D. G. Brown, *J. Amer. Chem. Soc.*, **94**, 9210 (1972).

(98) G. R. Wiley and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 3287 (1972).

(99) C. H. Henrikson, *et al.*, *Inorg. Chem.*, **6**, 1461 (1967); **7**, 1028, 1047 (1968).

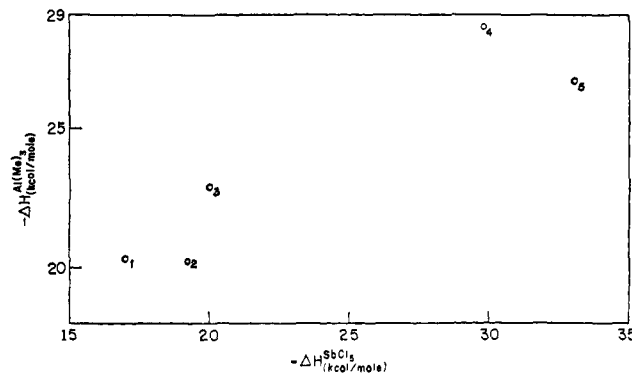


Figure 14. Enthalpy of interaction with $\text{Al}(\text{Me})_3$ vs. enthalpy of interaction with SbCl_5 : (1) acetone, (2) diethyl ether, (3) tetrahydrofuran, (4) dimethyl sulfoxide, (5) pyridine.

parameter equations which naturally improve the ability to fit old data and predict new ones. However, one may expect by analogy to recent experience with linear free energy relationships, that as our data base grows in size and quality, equations of increasing complexity with more special parameters will be needed to "explain" the data and accordingly the credibility of each *ad hoc* explanation will gradually erode.

What then is a suitable experimental reference point for discussing basicity? In view of the recent development of mass spectroscopic methods suitable for highly precise determination of proton affinities and even equilibrium constants in the gas phase we recommend that the gas phase proton affinity be the fundamental operational definition of basicity. No other acid at this time can be used to compare bases of so many types and strengths as the proton. Furthermore, starting from gas phase proton affinities it is now possible in favorable cases to analyze completely the solvation energies of all species involved.^{88,91}

Unfortunately, the proton affinity is itself a composite term involving ionization potential and bond energy⁸ and does not follow the periodic table in a simple way. It is not therefore surprising to find, as we have done in this article, that the acid-base properties of complex molecules in solution are not simple.

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