

through a 6-ft column of 25% Carbowax 20M on 60-80 Chromosorb W.

Mass Spectral Analysis. Mass spectral analysis of the isotopically labeled compounds was done with 70-V electrons with a Consolidated Model 21-103C spectrometer. Source and inlet temperatures were both 250°.

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Weak Bases in Strong Acids. III.¹ Heats of Ionization of Amines in Fluorosulfuric and Sulfuric Acids. A New General Basicity Scale²

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Abstract: Some inherent difficulties in determining the pK_a 's of weak organic bases by acidity function methods are examined. The heat of protonation in an appropriate strong acid is proposed as an alternative criterion of base strength. As a test of this proposition, enthalpies of protonation for 35 amines, both aliphatic and aromatic, have been measured calorimetrically at 25° in pure fluorosulfuric acid and concentrated sulfuric acid. A good linear correlation between these enthalpies and the pK_a values of the corresponding conjugate acids in water is found spanning a range of 40 kcal/mole in enthalpy and 22 pK_a units. The correlation coefficient is 0.992. The significance of enthalpy-free energy correlations is discussed. Such diverse types of compounds as primary, secondary, and tertiary aromatic and aliphatic amines, pyridines, cyclopropanones, nitroaromatics, phosphine oxides, and acid chlorides fit the ΔH - pK_a correlation and it is used to estimate the pK_a 's (± 0.7) of alcohols, ethers, water, and triphenylamine.

The transfer of protons from Bronsted acids to basic molecules in solution is probably the most important and general reaction in chemistry.⁴ All organic compounds are acids or bases (or both) and their ability to undergo proton transfer is an important criterion of their reactivity. Accurate measurements of proton transfer thermodynamics are, therefore, of fundamental chemical interest. They are also essential for the detailed kinetic interpretation of acid- and base-catalyzed reactions which, in turn, comprise the largest single class of reaction mechanisms in organic and biological chemistry.⁵

The aqueous pH scale is the traditional standard of reference for determination of pK_a 's of acid-base equilibria.⁶ However, less than a half-dozen of the hundred-odd functional groups commonly encountered in organic chemistry ordinarily give measurable protolysis in the pH range of proton activity, although it has

been known for years that most of them are completely protonated in concentrated sulfuric acid.⁷ Hammett's suggestion⁸ that the pH range be extended to strong aqueous sulfuric acid solutions through an indicator-based acidity function was, therefore, a reasonable approach to the quantitative comparison of weak bases. Despite three decades of effort by many ingenious experimenters, the strengths of most classes of weak organic bases are poorly defined. The refined acidity function developed by Jorgenson and Hartter⁹ for primary aniline indicators has not proven to be generally applicable to other families of bases in concentrated aqueous acid solutions. Its failure has been demonstrated for tertiary aromatic amines,¹⁰ pyrroles,¹¹ indoles,¹² azulenes,¹³ esters,¹⁴ amides,¹⁵ ketones,¹⁶ alde-

(1) Previous paper in this series: E. M. Arnett and J. J. Burke, *J. Am. Chem. Soc.*, **88**, 4308 (1966).

(2) Supported by N. S. F. Grant GP-6550X and NIH Grant GM-10872.

(3) Taken in part from the thesis of J. J. Burke, University of Pittsburgh, 1966.

(4) Although approximately 1000 papers dealing with the strengths of weak bases have been published, we have cited only recent or very relevant papers and reviews.

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(13) F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964).

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hydres,^{16b,d} phosphine oxides,¹⁷ pyridine 1-oxides,¹⁸ phosphinates,¹⁹ uraciles,²⁰ phloroglucinol and its methyl ethers,²¹ sulfonamides,²² carboxylic acids,^{16a,d,23} thiohydantoin,²⁴ diarylolefins,²⁵ and arylmethanols.²⁶ Special acidity functions have been generated for some of these classes. The acidity function behavior of numerous other important classes of organic compounds has still not even been approached.

Since the Hammett indicator approach has failed to produce an acidity function which is applicable to all classes of weak bases in aqueous sulfuric acid, workers in the field have sought other solvent-acid combinations in which the activity coefficient postulate^{7g,27} might be more generally valid. This has met with only limited success. Acidity function scales have been defined recently²⁸ for HCl-ethanol,²⁹ HBr-aqueous acetic acid,³⁰ H₂SO₄-aqueous ethanol,³¹ H₂SO₄-aqueous 2-butoxyethanol,³² HClO₄-aqueous ethanol,³³ various acids in sulfolane,³⁴ and aqueous *p*-toluenesulfonic acid.³⁵

Another approach to the problem is that suggested by Bunnett and Olsen,³⁶ who have developed a linear free energy relationship to determine the thermodynamic pK_a of a base from indicator ratios by means of the equation

$$\log [BH^+]/[B] + H_0 = \phi(H_0 + \log [H^+]) + pK_{BH^+}$$

where ϕ is the slope of the linear plot characterizing the response of the indicator ratio $[BH^+]/[B]$ to changing acid concentration. Yates^{14a} has used an expression of similar form to estimate the pK_a 's of non-Hammett

$$\log [BH^+]/[B] = -mH_0 + pK_a$$

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bases and Johnson^{16b} has shown that the two expressions give good agreement for carbonyl bases.

The failure of the Hammett activity coefficient assumption, with consequent proliferation of acidity functions specific to various classes of compounds, is now widely recognized. What is not realized so generally is the experimental difficulty of determining a reliable value for the indicator ratio referring unequivocally to a simple Brønsted equilibrium. *Indeed, it may be said that although the pK_a 's of strong bases in weak acid are clearly defined by a variety of methods which agree well, the pK_a 's of most weak bases in strong acids are badly defined operationally.*

A major limitation on the determination of accurate indicator ratio values in aqueous sulfuric acid through absorption spectra is the problem of correcting for medium effects. These can cause variation in both the intensity and position of absorption bands as the acid concentration is varied, even though there is no evidence that the base is suffering protonation.^{16b} This is not a serious problem for aniline indicators for which the disappearance of free base is followed by observing the decreasing intensity of the ($n \rightarrow \pi^*$) band as the nonbonding electrons on nitrogen are coordinated with protons. For other types of spectral transitions the problem can be serious. Several methods of interpretation have been developed to correct for these medium effects; however, the calculated pK_a values are sensitive to the correction technique employed and the choice between them is often rather subjective.

A case in point is the wide disagreement between many groups on the best treatment of absorption spectra for conjugated aldehydes and ketones in strong aqueous acid of varying strength.^{16b,d}

Not all of the problems encountered in determining the strengths of weak bases can be ascribed to the limitations of the Hammett acidity function or to the difficulties of correcting for medium effects in the region of protonation. For many important types of compounds, the region of protonation cannot even be defined *operationally* with consistency. Different analytical methods lead to different indicator ratios at a given acid concentration, and thus, different pK_a 's at the standard state of dilute aqueous acid. Table I contains a summary of available pK_a values for some important compounds and the methods used in their determination. Their failure to agree does not necessarily reflect any lack of ingenuity or care on the part of the experimenters whose conflicting values are juxtaposed. Rather, it reflects the uncertainties of interpreting apparent solute concentration variations as the acidity changes.

The range of these pK_a estimates obtained with a variety of probes suggests that processes other than complete proton transfer are affecting the results. A number of authors^{7g,37} have suggested that these effects are due to varying degrees of solvent-solute interaction (e.g., hydrogen bonding) as a function of acid concentration. These results were anticipated by the early solubility work of Hammett,³⁸ which showed drastic

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Table I. Literature Values for pK_a 's of Several Weak Bases

Compound	pK_a	Analytical method
Acetone	-0.24	Calorimetric ^a
	-0.3	Electrical conductivity ^b
	-0.46	Competitive indicator (uv) ^c
	-1.6	Indicator (uv) ^d
	-3.0	Solvent extraction ^{e,f}
	<-4.5	Competitive indicator (uv) ^g
	-7.2	Indicator (uv) ^h
	-7.2	Raman ⁱ
	-7.2	Nmr ^j
	Diethyl ether	-0.30
-0.47		Electrical conductivity ^l
-3.53		Vapor pressure ^m
-3.59		Solvent extraction ⁿ
-4.14		Solvent extraction ^o
-5.7		Titration ^p
-6.2		Nmr ^q
Ethanol	-0.33	Calorimetric ^a
	-0.33	Electrical conductivity ^r
	-2.3	Kinetics ^s
Methanol	-4.8	Nmr ^t
	-0.34	Electrical conductivity ^r
	-1.05	Competitive indicator (uv) ^r
	-2.2	Raman ^u
2-Propanol	-4.9	Raman ^v
	-0.35	Electrical conductivity ^r
	-0.47	Competitive indicator (uv) ^r
	-2.5	Solvent extraction ^{e,f}
	-3.2	Kinetics ^t
	-3.8	Kinetics ^u
	<-4.5	Kinetics ^v
-4.7	Raman ^w	
-5.2	Raman ^x	

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acidity dependence for the solubilities of nitrobenzene and benzoic acid in a series of aqueous sulfuric acid media which were too weak to give any measurable degree of protonation of these bases.

We believe that the ambiguity associated with free energy measurements of weak bases in continually changing strong acid media is a fundamental problem which will only be more exhaustively documented rather than "solved" by further use of the acidity function approach. This belief has stimulated us to seek other criteria for discussing base strengths.

Heats of interaction have been measured for many strong bases with strong protonic³⁹ and Lewis acids.⁴⁰

(38) L. P. Hammett and R. P. Chapman, *J. Am. Chem. Soc.*, **56**, 1282 (1934).

(39) (a) H. C. Brown, D. H. McDaniel, and O. Häffiger, "Determination of Organic Structures by Physical Methods," E. A. Braude and

The complexing of a number of weak bases with Lewis acids has also been measured calorimetrically.⁴¹ However, this technique has not been systematically applied to the study of weak bases with strong protonic acids, the field of our present inquiry. This paper and the one following it in this series report such an investigation and the establishment through it of an independent basicity scale based on enthalpies of protonation for most types of weak bases in a single acid medium, fluorosulfuric acid. For comparison, some results for concentrated sulfuric acid are also presented.

Experimental Section

Chemicals. Most of the compounds used in this study were available commercially. Liquids were generally dried, using an appropriate agent, and then distilled. Solids were recrystallized and dried. Some were purified by vacuum sublimation. All melting points, boiling points, and refractive indices were in good agreement with literature values. Carbon tetrachloride (Baker reagent grade) was stored over Linde Type 4A molecular sieves. *sym*-Tetrachlorethane (Eastman White Label) was passed through a column of neutral alumina before use. Concentrated sulfuric acid (Baker and Adamson C. P. grade) was used as received. Fluorosulfuric acid (Baker and Adamson Technical Grade) was flushed with dry nitrogen and distilled, bp 163°. Further details regarding the purification and physical constants of many of the compounds investigated may be found in the Ph.D. thesis of J. J. Burke.

Calorimetric Methods. The calorimetric equipment and procedures are basically as described previously.⁴² Stainless steel-coated, 2090-ohm thermistors (Keystone Carbon Co., St. Marys, Pa.) were used in fluorosulfuric acid. All of the heat measurements were calibrated electrically. Solid samples were introduced into fluorosulfuric acid (contained in a 200-ml dewar flask) by means of a modified plastic 1-cc syringe (Pharmaseal Laboratories, Glendale, Calif.) with a Teflon tape-covered plunger and a solid Teflon plug to protect the sample from the acid solution during thermal equilibration. Liquid samples were introduced by means of Hamilton syringes (509 μ l, gas tight with Chaney adapter) using calibrated stainless steel stops to deliver accurately and reproducibly ca. 100 μ l of solute. Sample sizes ranged from 50 to 150 \pm 0.2 mg, depending on the magnitude of the observed heats so as to give optimum displacement of the recorder pen.

Results

Systematic errors were detected and avoided by frequent checks of the calorimeters against well-accepted values for the heats of solution of solutes in the systems under investigation. The accuracy and precision of our calorimetric methods can be evaluated by comparison of our data with literature values as listed in Table II. The error limits represent standard deviations mostly from the mean of seven dependent measurements. Incidentally, these results and many others gathered in this laboratory over the past 5 years attest to the accuracy as well as convenience of our unorthodox procedure of introducing samples *via* syringes in-

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Table II. Comparison of Observed Heats of Solution with Literature Values for Various Solutes and Solvents

Solute	Solvent	$-\Delta\bar{H}_{\text{obsd}}$ at 25°, kcal/mole	$-\Delta\bar{H}_{\text{lit.}}$ at 25°, kcal/mole
KCl ^a	H ₂ O	-4.10 ± 0.06	-4.115 ± 0.01^b
		-4.12 ± 0.05	
		-4.15 ± 0.03	
		-4.11 ± 0.06	
NH ₄ Cl	H ₂ O	-0.94 ± 0.01	-0.975 ± 0.025^b
Pyridine	H ₂ O	2.28 ± 0.08	2.32 ± 0.010^c
Ethanol	H ₂ O	2.43 ± 0.04	2.39 ± 0.02^d
H ₂ O	39.94% H ₂ SO ₄	0.336 ± 0.012	0.348^e
H ₂ O	50.09% H ₂ SO ₄	0.672 ± 0.009	0.666^e
H ₂ O	59.54% H ₂ SO ₄	1.113 ± 0.021	1.098^e
H ₂ O	69.63% H ₂ SO ₄	1.870 ± 0.029	1.866^e
H ₂ O	80.53% H ₂ SO ₄	3.591 ± 0.045	3.574^e
H ₂ O	89.73% H ₂ SO ₄	6.307 ± 0.043	6.360^e
Nitrobenzene	FSO ₃ H	5.63 ± 0.09	5.55 ± 0.2^f
Benzoic acid	FSO ₃ H	6.20 ± 0.2	8.80 ± 0.25^f
H ₂ O	FSO ₃ H	12.2 ± 0.1	11.95 ± 0.04^f
Acetic acid	FSO ₃ H	13.1 ± 0.2	13.26 ± 0.1^f

^a Four different calorimeters were used during the course of this investigation. ^b V. B. Parker, "Thermal Properties of Aqueous Univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards, 2, Washington, D. C., 1965. ^c L. Sacconi, P. Paoletti, and M. Ciampolina, *J. Am. Chem. Soc.*, **82**, 3828 (1960). ^d R. Aveyard and A. S. C. Lawrence, *Trans. Faraday Soc.*, **60**, 2265 (1964). ^e W. F. Giaque, E. W. Hornung, J. E. Kuzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960). ^f G. W. Richards and A. A. Woolf, *J. Chem. Soc., A*, 470 (1968).

stead of the conventional technique of breaking glass ampoules.

The agreement of our results with literature values is excellent except for the heat of solution of benzoic acid in fluorosulfuric acid. We have made several measurements with samples of benzoic acid which had been recrystallized, sublimed, or zone refined and have still failed to obtain agreement with Woolf's value. We are unable to explain the discrepancy.

The heats of solution at 25° in carbon tetrachloride, *sym*-tetrachloroethane, 96.48% sulfuric acid, and fluorosulfuric acid are listed in Table III. The heats of protonation of several oxygen bases are listed in Table IV using both the gas phase and carbon tetrachloride as standard states. Of necessity heats of solution at infinite dilution in these inert solvents (*sym*-tetrachloroethane or carbon tetrachloride) rather than the gas phase have been used to correct the heats of solution in acids for the energy associated with separating the solute molecules. This procedure has been justified previously by the observation that the relative differences in heats of formation of carbonium ions were the same using either the gas phase or dilute carbon tetrachloride solutions as the reference state for the unprotonated precursor.^{43,44} Furthermore, the heats of solution of approximately 100 unassociated liquid solutes measured here⁴⁵ in carbon tetrachloride are in the range 0.0 ± 1.0 kcal/mole, indicating (by this criterion) the usual formation of nearly perfect solutions in this medium. *sym*-Tetrachloroethane was used as a reference solvent for several nitroaniline bases because they were insoluble in carbon tetrachloride. We have avoided its use whenever possible, however, because of its potential ability as a C-H hydrogen bond donor to basic solutes

with consequent errors from the enthalpy of hydrogen bonding.⁴⁶

Discussion

Basicity Scales. We propose the enthalpies of protonation listed in Table III as a useful criterion of base strength. The responsiveness of this property to structural variations is demonstrated through comparison of the heats of protonation of triethylamine (-49.1 kcal/mole) and trinitroaniline (-13.2 kcal/mole) in FSO₃H while the heat of solution of a typical nonbase, carbon tetrachloride, in FSO₃H is (+) (*sic.*) 1.8 kcal/mole. In Figure 1 our calorimetrically determined heats of protonation are plotted *vs.* the corresponding

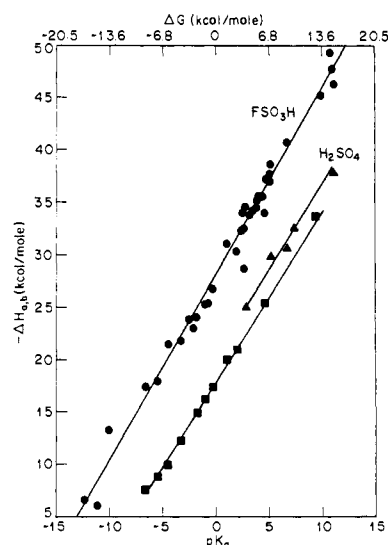


Figure 1. Heats of protonation of amines in strong acids *vs.* pK_a values of their conjugate acids in water: ●, amines in FSO₃H; ▲, pyridines and piperidine in 96.48% H₂SO₄; ■, anilines and benzylamine in 96.48% H₂SO₄.

(43) E. M. Arnett and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 1438 (1969).
 (44) For comparison of adduct formation in the gas phase and in solution see (a) L. J. Sacks, R. S. Drago, and D. P. Eymann, *Inorg. Chem.*, **7**, 1484 (1968); (b) W. Partenheimer, T. D. Epley, and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 3886 (1968); (c) J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965); (d) F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965).

(45) Unpublished data of J. V. Carter, E. Mitchell, T.S.S.R. Murty, J. W. Larsen, and R. P. Quirk in this laboratory.

(46) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

Table III. Thermodynamic Quantities for the Protonation of Bases in FSO₃H and 96.4% H₂SO₄ at 25° from CCl₄ or *sym*-Tetrachloroethane Reference State

Compound	$-\Delta H_{\text{FSO}_3\text{H}}^a$	$-\Delta H_{\text{H}_2\text{SO}_4}^b$	$-\Delta H_{\text{CCl}_4}^c$	$-\Delta H_{\text{sym}}^d$	$\Delta H_{a,b}^e$	$\Delta H_{a,b}^f$	pK_a
Triethylamine	49.8 ± 0.03		+0.64 ± 0.08		49.2 ± 0.3		10.75 ^h
Diethylamine	48.1 ± 0.3		+0.42 ± 0.06		47.7 ± 0.3		10.98 ^h
Piperidine		39.9 ± 0.3		2.08 ± 0.06		37.8 ± 0.4	11.12 ^h
Di- <i>n</i> -butylamine	46.7 ± 0.5		+0.3 ± 0.05		46.4 ± 0.5		11.25 ^h
Tri- <i>n</i> -butylamine	45.0 ± 0.3		-0.21 ± 0.08		45.2 ± 0.3		9.93 ^h
Benzylamine		35.5 ± 0.6		1.82 ± 0.01		33.7 ± 0.6	9.35 ^h
2,4,6-Trimethylpyridine		35.2 ± 0.5		2.61 ± 0.01		32.6 ± 0.5	7.43 ^h
2,6-Lutidine	41.0 ± 0.2	32.9 ± 0.4	+0.27 ± 0.08	2.27 ± 0.08	41.3 ± 0.2	30.6 ± 0.5	6.72 ^h
Pyridine	38.2 ± 0.2	31.7 ± 0.3	-0.36 ± 0.02	1.84 ± 0.01	38.6 ± 0.2	29.9 ± 0.3	5.21 ^h
N,N-Dimethylaniline	37.6 ± 0.3		-0.12 ± 0.01		37.7 ± 0.3		5.07 ^h
4-Fluoroaniline	35.1 ± 0.09		-2.09 ± 0.04		37.2 ± 0.1		4.65 ^h
4-Methylaniline	31.4 ± 0.3		-5.54 ± 0.05		36.9 ± 0.3		5.08 ^h
4-Chloroaniline	28.9 ± 0.4		-6.73 ± 0.09		35.6 ± 0.4		3.98 ^h
2-Methylaniline	34.0 ± 0.2		-1.59 ± 0.05		35.6 ± 0.2		4.45 ^h
4-Bromoaniline	29.3 ± 0.4		-5.88 ± 0.02		35.2 ± 0.4		3.86 ^h
3-Bromopyridine	34.4 ± 0.4	26.3 ± 0.2	-0.23 ± 0.03	1.32 ± 0.07	34.6 ± 0.4	25.0 ± 0.3	2.84 ^h
4-Iodoaniline	28.0 ± 0.5		-6.5 ± 0.2		34.5 ± 0.5		3.78 ^h
3-Chloroaniline	32.2 ± 0.2		-2.02 ± 0.04		34.2 ± 0.2		3.52 ^h
3-Nitroaniline	29.0 ± 0.3			-5.0 ± 0.1	34.0 ± 0.3		2.47 ^h
Aniline	34.3 ± 0.4	25.8		0.31 ± 0.02	34.0 ± 0.4	25.5 ± 0.2	4.60 ^h
2-Fluoroaniline	32.2 ± 0.1		-1.72 ± 0.02		33.9 ± 0.1		3.20 ^h
2-Chloroaniline	30.5 ± 0.2		2.0		32.5 ± 0.2		2.65 ^h
4-Nitroaniline	27.0 ± 0.3 ^g	15.9 ± 0.2		-4.14 ± 0.04	31.1 ± 0.3	20.0 ± 0.2	1.00 ^h
2-Iodoaniline	26.0 ± 0.1		-6.4 ± 0.2		32.4 ± 0.2		2.55 ^h
2,4-Dichloroaniline	24.1 ± 0.2	15.9 ± 0.5	-6.2 ± 0.1	-5.06 ± 0.06	30.3 ± 0.2	21.0 ± 0.6	2.00 ^h
Triphenylphosphine ^q	24.9 ± 0.3		-3.83 ± 0.1		28.7 ± 0.3		2.73 ⁱ
2-Nitroaniline	22.8 ± 0.3	13.4 ± 0.2		-3.99 ± 0.02	26.8 ± 0.3	17.4 ± 0.2	-0.26 ^h
2,4,6-Tribromoaniline	18.5 ± 0.4		-6.8 ± 0.3		25.3 ± 0.5		0.8 ^j
4-Chloro-2-nitroaniline	20.9 ± 0.5	11.8 ± 0.2		-4.40 ± 0.05	25.3 ± 0.5	16.2 ± 0.3	-1.02 ^h
2,5-Dichloro-4-nitroaniline	19.0 ± 0.2	9.8 ± 0.3		-5.11 ± 0.16	24.1 ± 0.3	14.9 ± 0.5	-1.78 ^h
Diphenylcyclopropenone	18.7 ± 0.3		-5.2 ± 0.2		23.9 ± 0.4		-2.5 ⁱ
Triphenylphosphine oxide	18.8 ± 0.2		-4.2 ± 0.2		23.0 ± 0.3		-2.10 ^m
Benzene	18.6 ± 0.3						
2,6-Dichloro-4-nitroaniline	16.4 ± 0.2	6.8 ± 0.7		-5.41 ± 0.01	21.8 ± 0.2	12.2 ± 0.7	-3.27 ^h
2,4-Dinitroaniline	17.2 ± 0.2	5.6 ± 0.9		-4.29 ± 0.07	21.5 ± 0.2	9.9 ± 1.0	-4.53 ^h
Triphenylamine	15.3 ± 0.5		-3.8 ± 0.1		19.1 ± 0.5		
2,6-Dinitroaniline	14.5 ± 0.2	5.4 ± 0.2		-3.43 ± 0.04	17.9 ± 0.3	8.8 ± 0.2	-5.54 ^h
2-Bromo-4,6-dinitroaniline	13.1 ± 0.3	3.2 ± 0.4		-4.27 ± 0.01	17.4 ± 0.3	7.5 ± 0.4	-6.68 ^h
2,4,6-Trinitroaniline	9.0 ± 0.2	-1.2 ± 0.2		-4.17 ± 0.15	13.2 ± 0.3		-10.1 ^k
Nitrobenzene	5.63 ± 0.09		-1.25 ± 0.02	-1.0 ± 0.01	6.6 ± 0.1		-12.42 ⁿ
Benzoyl chloride	5.3 ± 0.5		-0.7 ± 0.1		6.0 ± 0.5		-11.15 ^o
Carbon tetrachloride	+1.79 ± 0.06						

^a Heat of solution of pure compound into FSO₃H in kcal/mole. ^b Heat of solution of pure compound into 96.48% H₂SO₄ in kcal/mole. ^c Heat of solution of pure compound into CCl₄ in kcal/mole. ^d Heat of solution of pure compound into *sym*-tetrachloroethane in kcal/mole. ^e Heat of transfer of pure compound from the inert solvent to FSO₃H in kcal/mole. ^f Heat of transfer of pure compound from inert solvent to 96.48% H₂SO₄ in kcal/mole. ^g A value of -28.0 ± 0.3 kcal/mole was obtained at 10 ± 2°. ^h See ref 61. ⁱ W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960). ^j E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1686 (1954). ^k See ref 9. ^l R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965). ^m C. Klofutar, F. Krasovec, and M. Kusar, *Croat. Chem. Acta*, **40**, 23 (1968). ⁿ See ref 51. ^o M. Liler, *J. Chem. Soc., B*, 205 (1966). ^p Unpublished results of E. Mitchell.

Table IV. Heats of Protonation of Several Oxygen Bases

Compound	$\Delta H_{\text{FSO}_3\text{H}}$, kcal/mole	ΔH_{CCl_4} , kcal/mole	ΔH_{vap} , kcal/mole	ΔH_1^a , kcal/mole	$\Delta H_{a,b}^b$, kcal/mole
Tetrahydrofuran	-20.2 ± 0.2	-0.60 ± 0.02	7.6 ^c	-27.8	-19.6
Diethyl ether	-19.5 ± 0.7	-0.42 ± 0.01	6.5 ^d	-26.0	-19.1
Ethanol	-15.3 ± 0.3	3.8	10.3 ^d	-25.6	-19.1
Acetone	-18.3 ± 0.1	0.79 ± 0.02	7.1 ^d	-25.4	-19.1
Water	-12.2 ± 0.1	4.2 ^e	10.5 ^d	-22.7	-16.4

^a Heat of transfer from the gas phase to FSO₃H. ^b Heat of transfer from CCl₄ to FSO₃H. ^c B. Watson, Ph.D. Thesis, University of Bradford, 1968. ^d A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, New York, N. Y., 1955. ^e Heat of solution of H₂O into *sym*-tetrachloroethane. Unpublished work of Dr. J. V. Carter.

pK_a values.⁴⁷ The reader should note that a good linear correlation between these two basicity properties holds over the enormous range of 40 kcal/mole for the enthalpies and 22 pK_a units (28 kcal/mole in

free energy) from the weakly basic benzoyl chloride and nitrobenzene to the strongly basic alkylamines. Least squares equations for these data are as follows.

$$-\Delta\bar{H}(\text{anilines, } 96.48\% \text{ H}_2\text{SO}_4) = (1.62 pK_a + 17.9) \text{ kcal/mole} \quad (1)$$

(47) The standard state for the heats of protonation is either dilute CCl₄ or *sym*-tetrachloroethane. The standard state for the pK_a 's is dilute aqueous solution.

$$-\Delta\bar{H} \text{ (pyridines, 96.48\% H}_2\text{SO}_4) = \\ (1.65 \text{ p}K_a + 20.3) \text{ kcal/mole} \quad (2)$$

$$-\Delta\bar{H} \text{ (amines, FSO}_3\text{H)} = \\ (1.78 \text{ p}K_a + 28.1) \text{ kcal/mole} \quad (3)$$

The standard deviations of the slope and intercept for eq 3 were 0.04 and 0.22, respectively. The average deviation of points from the correlation line was 1.2 kcal/mole and the correlation coefficient was 0.992. Consideration of these errors leads us to set error limits of ± 0.7 on $\text{p}K_a$'s predicted from this correlation. The correlation of our heats of protonation with the best available (see below) estimates of $\text{p}K_a$'s in dilute aqueous solutions provides justification for the use of these heats as an independent measure of basicity.

This enthalpimetric basicity scale provides a useful tool for examining the effects of small structural changes on basicity because of the expanded scale resulting from the use of very strong acids (see the slopes and intercepts of eq 1, 2, and 3).

The use of FSO_3H , however, limits the range of substituents to groups which will not themselves interact strongly with the acid. Thus, benzene gave a very high apparent heat of solution (-18.6 ± 0.3 kcal/mole) in FSO_3H (probably because of rapid exothermic sulfonation⁴⁸). This warns us of a possible source of error in the study of other aromatic bases.

Different families of bases apparently generate their own $\Delta H-\Delta G^\circ$ correlations in H_2SO_4 , while no such resolution into families could be detected in fluorosulfuric acid. Such diverse classes of bases as primary, secondary, and tertiary aromatic and aliphatic amines, pyridines, nitroaromatics, cyclopropanones, acid chlorides, phosphines, and phosphine oxides are displayed for the $\Delta H-\Delta G^\circ$ correlation in fluorosulfuric acid.

In addition to generating a larger range of enthalpy values, fluorosulfuric acid possesses several other characteristics which make it preferable to sulfuric acid. Fluorosulfuric acid has a much lower viscosity (1.56⁴⁹ vs. 24.5 cP for H_2SO_4 ^{7d}) and higher dielectric constant (ca. 120⁵⁰ vs. 100 units for H_2SO_4 ^{7d}) than concentrated sulfuric acid. Serious solubility and mixing problems were encountered in attempting to extend our $\Delta H-\Delta G^\circ$ scale in H_2SO_4 to aromatic carbonyl compounds, but we have never encountered any solubility problems or solute concentration dependence in fluorosulfuric acid. A further advantage of fluorosulfuric acid is its greater acidity, which probably accounts for larger heats measured in it. Gillespie and coworkers have assigned an H_0 acidity function value of -13.9 to FSO_3H compound with -12.1 for 100% H_2SO_4 .⁴⁹ Thus, nitrobenzene ($\text{p}K_a -12.4^{51}$), which is incompletely protonated in 99.5% H_2SO_4 , is completely ionized within the limits of measurement in FSO_3H .⁵⁰

The use of enthalpies of protonation as a measure of basicity possesses several distinct advantages over the free energy measurements obtained by acidity function techniques. The former are carried out in a single medium and so are free of ambiguous medium effects found in studying protonation equilibria. Furthermore, the

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(49) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968).

(50) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

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protonation process is complete and well defined for many anilinium and other onium ions in these strong acids shown by freezing point depressions, electrical conductivities, nmr observations, and ultraviolet spectroscopy.^{7d,49,50,52} Finally, our heat measurements are accurately and relatively easily obtained using a simple calorimeter.

It was not anticipated that the heats of protonation for aniline bases in FSO_3H or concentrated H_2SO_4 would correlate with aqueous $\text{p}K_a$ values. Many of these were determined by the Hammett overlap procedure^{5d,7g} which relies on a lengthy extrapolation to the standard state of infinite dilution in water. Previous justification for this overlap procedure was based on (a) the approximate parallelism of $\log [\text{BH}^+]/[\text{B}]$ vs. $[\text{H}^+]$ plots and (b) the constant $\Delta \text{p}K_a$ values for two indicators in different solvents. The correlation of $\text{p}K_a$ values determined by this procedure with heats of protonation in strong acids is a third justification for the overlap method of estimating $\text{p}K_a$ values.

$\Delta H^\circ-\Delta G^\circ$ Correlations. Although the question of whether enthalpy or free energy is a better measure of potential energy is debatable, most chemists prefer free energy measurements as a practical expression of chemical driving force. Enthalpy measurements can be expected to parallel free energy changes in another medium in those cases where linear free energy correlations^{7b,53} and isokinetic or isoentropic relationships^{7b,53a,c,54} exist simultaneously. This can be demonstrated readily as follows.

Using the operator formalism of Leffler and Grunwald,^{55d} the effect of a substituent change, R, on the basic thermodynamic quantities can be expressed as

$$\delta_R \Delta G_w^\circ = \delta_R \Delta H_w^\circ - T \delta_R \Delta S_w^\circ \quad (4)$$

in water and

$$\delta_R \Delta G_a^\circ = \delta_R \Delta H_a^\circ - T \delta_R \Delta S_a^\circ \quad (5)$$

in acid. If an isokinetic relationship exists in the acid solution, then

$$\delta_R \Delta H_a^\circ = \beta \delta_R \Delta S_a^\circ \quad (6)$$

and

$$\delta_R \Delta G_a^\circ = \delta_R \Delta H_a^\circ [1 - (T/\beta)]$$

If the effects of molecular structure variation on free energies in the two media are also proportional so that

$$\delta_R \Delta G_w^\circ = \rho_M \delta_R \Delta G_a^\circ \quad (8)$$

then by combination of eq 7 and 8, it follows that

$$\delta_R \Delta G_w^\circ = \rho_M \delta_R \Delta H_a^\circ [1 - (T/\beta)] \quad (9)$$

where δ_R represents the substituent operator and β and ρ_m are isokinetic and linear free energy proportionality constants, respectively.

(52) (a) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (b) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, **5**, 468 (1966); (c) T. Birchall, Ph.D. Thesis, McMaster University, 1963; (d) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

(53) (a) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964); (b) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (c) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (d) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.

(54) (a) J. E. Leffler, *J. Org. Chem.*, **31**, 533 (1966); (b) *ibid.*, **20**, 1202 (1955); (c) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).

Linear ΔH° - ΔG° correlations would also be expected for an isoentropic series. Thus, if the entropy in acid solution were constant

$$\delta_R \Delta S_a^\circ = 0 \quad (10)$$

and thus from eq 5

$$\delta_R \Delta G_a^\circ = \delta_R \Delta H_a^\circ \quad (11)$$

The combination of eq 8 and 11 leads again to a relationship between ΔG_w° and ΔH_a° , *i.e.*

$$\delta_R \Delta G_w^\circ = \rho_m \delta_R \Delta H_a^\circ \quad (12)$$

Equations 6, 8, and 10 are extrathermodynamic relationships in the sense that they are not demanded by the formal structure of thermodynamics, although they are frequently observed as empirical correlations.^{53d} The applicability of enthalpy-free energy correlations should be as general and as valid as linear free energy, isokinetic, or isoentropic ones since they may be derived from them.

Simple electrostatic theory for isoelectric reactions also predicts a linear relationship between ΔH° in acid solution and ΔG° in water.^{55a} However, the multiplicity of terms involved in considering these equilibria^{55b} precluded quantitative evaluation of this treatment.

Many of the isokinetic correlations reported so far cannot be accepted as heuristically significant. When both ΔH° and ΔS° are derived from the same experimental data through temperature coefficients of equilibrium or rate constants, errors in ΔH° are accompanied by corresponding errors in ΔS° . This can lead to a linear relationship between the errors in these quantities.^{54a,56} Less questionable ΔH° - ΔS° correlations are obtained using calorimetric enthalpies.⁵⁷ These do not include the first derivative errors common to van't Hoff-Arrhenius treatments. After critical examination of this field, Ritchie^{58a} has concluded that good linear free energy and isokinetic correlations are rarely found simultaneously.⁵⁸ Within this framework, it is reasonable to look for ΔH° - ΔG° correlations in cases where reliable calorimetric enthalpies and free energies may be compared and use them to estimate structural effects on free energy in systems where ΔG° cannot be measured directly, as in FSO_3H . We have previously reported examples of good linear ΔH° - ΔG° correlations for the calorimetric heats of protonation of polyalkylbenzenes in SbF_5 - FSO_3H *vs.* their free energies of protonation in HF^{59a} and also for the calorimetric heats of ionization of triarylcarbinols in 96% H_2SO_4 *vs.* their free energies of ionization in dilute aqueous acid.^{59b}

Although our correlations appear to be general, we anticipate that these ΔH° - ΔG° correlations will ultimately suffer from the same shortcomings as linear free energy correlations. The failure of the simple Ham-

mett $\sigma\rho$ treatment to fit all cases of substituent effects on free energy change has led to a bewildering array of substituent "constants" in order to cover so-called anomalous situations.^{53a,b} Medium effects on ΔH° - ΔG° correlations will probably fare even worse than linear free energy correlations of solvent effects such as the Hammett acidity function^{7b,g} and the Winstein-Grunwald equation.⁶⁰ These are well known to be poorer correlations than those for structural change.

pK_a Estimates. The ΔH° - ΔG° correlation in Figure 1 and eq 3 can be applied to the estimation of base strengths of classes of compounds whose basicities are controversial or which cannot be studied in aqueous sulfuric acid. For example, by using eq 3 and the observed heat of protonation of triphenylamine, a pK_a value of -5.0 can be estimated for this compound referred to dilute aqueous solution. No previous estimate of its basicity is known to us, presumably because of its limited solubility in conventional acid solutions. This estimate for triphenylamine appears reasonable in view of the effect of phenyl groups on amine basicities (pK_a 's) in the series NH_3 (9.24) aniline (4.60), and diphenylamine (0.79).⁶¹

Our correlation also provides information about the relative basicities of alcohols, ethers, and water. The heats of protonation of several of these compounds are listed in Table IV. The gas phase and *sym*-tetrachloroethane have been chosen as the reference state for water because of its low solubility in CCl_4 . By our criterion of basicity, these compounds fall in the order $\text{ROR} > \text{ROH} \gg \text{H}_2\text{O}$; the same order was found by Munson for the gas phase proton affinities of these compounds.⁶² Using eq 3 we obtain the relatively low estimate of -6.7 for the basicity of water, which agrees with the value of -6.66 reported by Deno and Taft in concentrated sulfuric acid.⁶³ The estimated pK_a values for ethanol (-5.1) and diethyl ether (-5.1) are in disagreement with the results of distribution studies but are very close to some of the Raman spectroscopy results for alcohols (see Table I). In view of the particular difficulty in defining the solvated free base and ionic species for water and the alcohols in aqueous strong acids, we think there is little profit in discussing agreement with these other estimates. As Table I shows, it would be remarkable if *any* number we obtained were not fortuitously close to some previously determined value.

This calorimetric basicity scale should be useful in evaluating the relative basicities of other important classes of compounds and for discriminating among widely varying estimates in aqueous acid. We have applied the treatment to the determination of the base strengths of carbonyl compounds and will report our results in the following paper.

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(63) N. C. Deno and R. W. Taft, *ibid.*, **76**, 244 (1954).

(55) (a) See ref 3, pp 147, 153, 210; (b) see ref 3, p 205.

(56) (a) R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961); (b) R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962).

(57) J. J. Christensen, J. L. Oscarson, and R. M. Izatt, *J. Am. Chem. Soc.*, **90**, 5949 (1968), and references cited therein.

(58) The ionization of anilinium ions in dilute aqueous acid is one reaction series which does apparently obey both of these relationships. See P. D. Bolton and F. M. Hall, *J. Chem. Soc., B*, 259 (1969), and A. I. Biggs and R. A. Robinson, *ibid.*, 388 (1961).