Gas-Phase Proton Transfer—a Breakthrough for Solution Chemistry

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Most reactions which take place in solution do not occur in the gas phase, and *vice versa.* The factors which account for the enormous discrepancies between these two different worlds of chemistry are operationally defined as "solvation." Clearly, a quantitative knowledge of solvation forces might lead to the understanding and manipulation of enormous new areas of solution chemistry.

We have chosen to attack the problem through proton-transfer processes, one of the few reactions which may be studied both in the gas and in condensed phases. Proton transfer is the most general and important of all chemical reactions, and so may be considered a prototype for studying the effects of structure on reactivity.

In this Account we describe how quantitative measurements of proton-transfer energies in the gas phase provide the information which is needed to exactly dissect classical acid–base thermodynamics into solvation terms and internal energy terms. Furthermore, we show how the application of this knowledge has led us to predict and discover enormous substituent effects in solution.

The Relation of Gas-Phase Proton Transfer to Solution Processes

The bridge between gas-phase protolysis and that in solution is provided by classical thermodynamics as shown in the following cycle[1] (Scheme I) where P represents any thermodynamic property ($G°$, $H°$, $S°$), g and l represent the gas and liquid phase, and subscripts i and s represent ionization and solution processes, respectively.

Scheme I

$$\begin{tikzcd}
\text{gas phase} & BH^+(g) \arrow[r, "1"] \arrow[d, "2"'] & H^+(g) \arrow[d, "3"'] & + & B(g) \arrow[d, "4"'] \\
\text{aqueous solution} & BH^+(l) \arrow[r, "5"] & H^+(l) & + & B(l)
\end{tikzcd}$$

$$BH^+(g) \longrightarrow H^+(g) + B(g) \qquad \Delta P_i(g) \qquad (1)$$

$$BH^+(g) \longrightarrow BH^+(l) \qquad \Delta P_s(BH^+) \qquad (2)$$

$$H^+(g) \longrightarrow H^+(l) \qquad \Delta P_s(H^+) \qquad (3)$$

$$B(g) \longrightarrow B(l) \qquad \Delta P_s(B) \qquad (4)$$

$$BH^+(l) \longrightarrow B(l) + H^+(l) \qquad \Delta P_i(l) \qquad (5)$$

$$\Delta P_i(g) = \Delta P_i(l) - \Delta P_s(B) - \Delta P_s(H^+) + \Delta P_s(BH^+) \qquad (6)$$

If the same proton-transfer process can be studied both in solution and in the gas phase, all that is needed for completion of the cycle is to determine the thermodynamic properties ($\Delta G°_s$, $\Delta H°_s$, $\Delta S°_s$) for transfer of the base B from the gas phase to solution. Combination of the terms on the right side of eq 6 leads at once to an *empirical* value for the corresponding property for transferring the onium ion, BH^+, from the gas phase to the solvent in question.

Two further comments are in order. Firstly, it should be clear that the cycle in Scheme I can apply equally well to the deprotonation of neutral acids (BH) to give the solvation thermodynamics of anions (B^-). Secondly, since we are concerned chiefly with comparing the solvation of related onium ions or anions we shall cancel the heat of solvation of the proton $\Delta H_S(H^+) = -261$ kcal/mol[2] by considering equilibria such as

$$BH^+ + B' \rightleftharpoons B + B'H \qquad (7)$$

We now consider briefly the methods used to obtain the data which are necessary for the application of the cycle in Scheme I.

Experimental Methods

Gas-Phase Protolysis. Ordinary mass spectrometers are designed to operate at low pressures in order to reduce ion–molecule collisions. Accordingly, gas-phase investigation of ion–molecule thermodynamics such as that shown in eq 7 are accessible if enough collisions occur to ensure that equilibrium is reached before the ions are monitored. This is now accomplished by several independent methods which give results in close agreement for gas-phase proton-transfer energies, thus dispelling some well-grounded, initial skepticism.

High-Pressure Mass Spectrometry. By operating at total pressures up to 10 Torr, Kebarle[3] has actually been able to observe the stepwise solvation of ions and the thermodynamics of equilibrium processes. Ions are generated in a gas mixture such as ammonia, methylamine, and an inert gas.[3] The intensities of peaks (corresponding in mass to different ions and their conjugate neutrals) are then monitored as a function of pressure. There is reason to believe that a Boltzmann distribution of energies is achieved.[4]

The "Flowing Afterglow," Kinetic Method. The

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(2) See P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967), and references cited therein.

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confusing misnomer for this technique has stuck with it since it was first used to simulate high-altitude phenomena. The reaction chamber is simply a long tube with an electron gun at one end and a mass analyzer at the other. A high-velocity pump sweeps the gases to be studied past the electron gun, where ionization occurs, and the products are analyzed at various points downstream. The rates of the gas-phase reactions are deduced from the flow rate of the gas and the concentration of the various species found at the monitor points. A recent article[5] from Kaufman's group refers to earlier literature and gives independent confirmation of results obtained by Kebarle. Bohme's group[6] has reported gas-phase acidities by this method which generally support ion cyclotron resonance results.

Ion Cyclotron Resonance (ICR).[7-9] A strong magnetic field causes free charged particles to go into a circular orbit. The exploitation of this fact makes it possible to hold ions in a cyclotron chamber for several hundred milliseconds, during which time many ion–molecule collisions can occur. A pulsing system with double irradiation helps to identify the actual partners in ion–molecule collisions.

In the three methods described above one seeks to determine directly the concentrations of the desired species at equilibria or to measure the rates of forward and reverse proton-transfer reactions in order to get an equilibrium constant. In this manner Aue[10,11] and Taft[1,12] and their colleagues have managed to obtain free energies of proton transfer to within ±0.3 kcal/mol in favorable cases. Ordinarily, the proton affinity, PA, the enthalpy change for the deprotonation reaction

$$BH^+ \longrightarrow B + H^+$$

is obtained to within ±2 kcal/mol by observing the mass spectrum as a function of pressure and electron energy.

For symmetrical reactions such as eq 7, there is every reason to believe that the only significant entropy factor is a small symmetry term depending on the number of ionizable protons in BH^+ compared to $B'H^+$.[13]

Thermodynamics for Proton Transfer in Solution. Although all organic compounds are Brønsted acids or bases or both, only a very few classes undergo observable protonation equilibria within the pH range of proton activities. The acid–base thermodynamics for amines, carboxylic acids, and phenols have served for many years as the most extensive and useful guide to structure–reactivity relationships. The data are of high precision, easily obtained, and well documented.[14-19] Most other functional types are too weakly basic or acidic to be studied directly with a pH meter.

The protonation of weak bases requires strong acids and the ionization of weak acids requires strong bases. The theoretical framework for relating ionization equilibria in these media to a standard state in dilute aqueous media was worked out 35 years ago by Hammett and his students.[20] During the ensuing years his method has been applied extensively and has been documented in a number of reviews.[20-25] Although serious experimental and interpretive obstacles often arise in the determination of the ionization constant of a weak acid or base by acidity function techniques,[23,26,27] progress is gradually being made in settling the pK_a's and acidity functions of many important simple compounds.

The Thermochemical Comparison of Acids and Bases. For a variety of reasons we do not at this time have quantitative comparison of many organic acids and bases in terms of their pK's. In order to provide immediately accessible information about the energetics of proton transfer in solution, we have chosen to avoid the direct determination of free energies entirely and instead to measure heats of proton transfer of acids in a standard superbase system[28] and of bases in a standard superacid,[27] using a relatively simple solution calorimeter.[29,30]

Weak Bases. In order to completely protonate all types of oxygen, sulfur, and phosphorus bases a very strong acid is required. We have chosen fluorosulfuric acid[31] as our superacid reference medium. Addition of antimony pentafluoride or other Lewis acid halides increases the acidity considerably. "Magic acid" systems such as these may be 10^6 times stronger than pure sulfuric acid as Brønsted acids;[32] also, they remain liquid below −100°.

Nmr spectroscopy may be used for authenticating these proton-transfer reactions[24] in superacids. Without these spectral techniques to validate pre-

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sumed protonation processes, the calorimetric results might be meaningless numbers!

The ordinary solution calorimeter is designed to handle noncorrosive systems close to ambient temperatures. Small amounts (a few millimoles) of solute are added to about 200 ml of solvent and the heat change is displayed immediately on a strip-chart recorder. Special techniques and equipment for measuring heats of protonation of solid or liquid bases in superacids at −50° have been described by Arnett and Larsen.[33] More recently, Arnett and Wolf[34] have adapted apparatus developed by Jones[35] for measuring heats of solution of gaseous solutes. This capability is very important since the best theoretical approach to protonation through quantum chemistry is presently limited to rather small molecules which are usually gases.

Weak Acids. The quantitative study of weak acids in strong bases is somewhat less fully developed than that for weak bases in strong acids, but it is clear that many problems are common to both areas of study. Study of the latter is subject to the further complication of ion pairing, as well as other problems.[3,36]

However, in spite of these difficulties, a number of workers have obtained reproducible pK_a values using metal amide and metal alcoholate systems. Ritchie has actually made direct potentiometric pK_a determinations of weak acids using a dimethyl sulfoxide (DMSO) solution of the cesium salt of DMSO (Cs^+DMSYL^--DMSO) with a reversible glass electrode.[37]

Because of its widespread use and the availability of good free energy of ionization data, we have adopted K^+DMSYL^- in DMSO as the reference superbase system for comparing weak and strong acids.

Results from the Thermochemical Comparison of Weak Bases and Weak Acids

We have determined heats of ionization (ΔH_i) in HSO_3F at 25° for over 100 compounds.

ΔH_i values are *bona fide* energies of ionization in a single solution for a wide variety of compounds under a single set of conditions. Although they are primarily of interest and value in their own right, it is natural to compare them with other proton-transfer properties. Of course, it would be best to compare them to standard free energies of ionization in HSO_3F. No such values are available. Accordingly, we have plotted ΔH_i *vs.* the best estimates of pK_a, referred to a standard state in water by acidity function methods.[27] For 50 compounds the linear equation $-\Delta H_i = (1.78 \pm 0.4)\mathrm{p}K_a + (28.1 \pm 0.22)$ is followed with a coefficient of correlation (r) of 0.992. The estimated standard error for pK_a's predicted from the correlation is ±0.7 pK_a unit.

The relationships between ΔH_i, ΔG_i, and pK_a at the same standard state are $\Delta H_i = \Delta G^\circ_i - T\Delta S^\circ_i$ and $\Delta G^\circ_i = 2.303RT\mathrm{p}K_a$. Although ΔH_i in HSO_3F and pK_a in water are two different properties measured in two different media, they respond in nearly the same way over a range of 50 kcal/mol to the same changes in molecular structure. However, the fact that the slope of the correlation line is 1.78 instead of 1.36 ($2.303RT$ at 25°) indicates that other factors, probably entropy terms, are significant.

The correlation between ΔH_i in HSO_3F and pK_a in water is mostly of value in showing that both properties are fundamentally controlled by the potential energy of ionization.[20] In some cases ΔH_i is useful for estimating pK_a's of weak bases in water, but departures from linearity make this risky for fine discrimination. In view of the notoriously large effects of entropy terms on aqueous processes, we are surprised that the correlation is as good as it is.

Striking evidence for this is found in our comparison of a variety of weak acids in K^+DMSYL^--DMSO.[28] Here we have measured the heat of deprotonation, ΔH_D, of the acid by measuring the molar heat of solution of successive increments into this superbase system. The heat of solution in the absence of ionization was measured by determining the heat of solution of the acidic solute into pure DMSO.

When such ΔH_D values are properly combined with the ΔG_i values from the pK_a's of Ritchie and Uschold,[37] it is found that within experimental error most neutral acids have a negligible entropy of ionization for deprotonation in this medium. Furthermore, particular advantage can be made of the pK_a's obtained by Stewart's group[38] for *deprotonation* of a series of nitroanilines and nitrodiphenylamines referred to a standard state in water by acidity function measurements. Correlation of their pK_a's with ΔH_D of these compounds in K^+DMSYL^--DMSO follows the equation $\Delta H_D = (1.85 \pm 0.17)\mathrm{p}K_a - 55.5 \pm 8.2$ with a coefficient of correlation of 0.96.

Nitroanilines and nitrodiphenylamines are the compounds which provide the most reliable pK_a values for protonation used for the correlation with ΔH_i in HSO_3F described above. It is highly significant that the slopes of these two correlation lines (1.78 and 1.85) are identical (within experimental error) for *protonation* in HSO_3F and *deprotonation* in K^+DMSYL^--DMSO, even though these two media differ by about 50 pK units in acid–base strength.

Thermodynamic Properties for Solution from the Gas Phase

All that is needed now to complete the cycle in Scheme I are the appropriate thermodynamic properties of $\Delta P_s(B)$ for solution of the neutral base or acid from the gas phase to the medium in question.

Standard Free Energies of Solution. The distribution of a compound between a state of high dilution in a solvent and the gas phase depends on its chemical potential in each phase. In the gas phase the partial pressure, p_2 (more exactly, fugacity), is the relevant concentration term and in solution it is usually the mole fraction, X_2. At high dilution the two are directly related through Henry's law

$$p_2 = kX_2$$

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Henry's law constants and distribution data are widely scattered through the literature and are of enormously varied quality. A much more serious obstacle to the use of such data lies in determining exactly what standard state conventions the author actually used in calculating and reporting his free energy terms.[39-41]

For solutes of low volatility, distribution between the crystalline state or a state of high dilution, in an inert solvent, may also be used.[42] In this case the standard free energy of transfer back to the vapor phase is determined from the vapor pressure through appropriate thermodynamic cycles. Although these measurements are conceptually simple, the experimental work behind them can be very demanding.

Enthalpies and Entropies of Solution. Heats of solution ($\Delta \bar{H}_s$) may be obtained by the van't Hoff method from the temperature coefficient of distribution constants, or, better, by solution calorimetry. For gases, $\Delta \bar{H}_s$ may be determined directly from the vapor phase to high dilution in the medium under consideration. If the solute is a liquid or solid its measured heat of solution is easily referred back to the gas phase if its heat of vaporization[43] is known. Again, reports of $\Delta \bar{H}_s$ measurements are few, scattered, and of varied quality. There are no general reviews of such data of which we are aware aside from that about the amines.[39] Fortunately, there is little ambiguity regarding standard-state descriptions of enthalpy measurements.[40,44,45]

Entropies of solution are readily derived from $\Delta G°_s$ and $\Delta H°_s$ through the familiar expression: $\Delta G°_s = \Delta H°_s - T\Delta S°_s$. However, all of the standard-state problems which can complicate $\Delta G°$ carry over to $\Delta S°$.

Dissection of the Anomalous Basicity Order of Amines: An Application of the Solvation Cycle

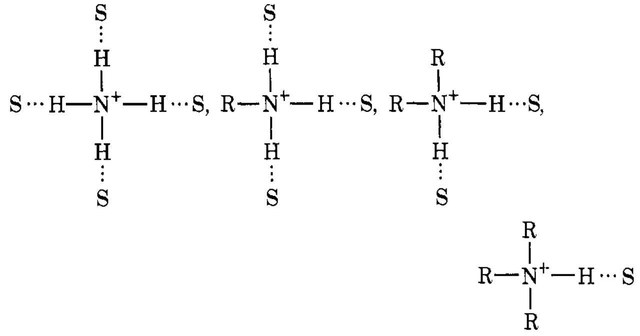
We shall demonstrate the use of gas-phase thermodynamics for the resolution of structure–reactivity problems in solution by considering a classical puzzle involving the amines.

For almost a century it has been known that the proton-acceptor abilities of the amines in aqueous solution, as expressed by pK_a's, are in the order $NH_3 < RNH_2 = R_2NH > R_3N$. This reversal in ranking is found for all the common alkyl groups and is not limited to 25° nor to aqueous media. We have discussed the background of the problem at some length elsewhere[1,35,39] and will not elaborate it here. It is obvious that the "anomalous" order might be understood in terms of two opposed influences if one is base strengthening and the other base weakening; these influences might operate on the neutral bases, on their conjugate onium ions, or on both. In the absence of reliable gas-phase data, the resolution of these questions was impossible and a variety of plausible explanations were advanced for the amine anomaly.

The cleavage of this Gordian knot was accomplished in 1965 when Munson[46] demonstrated by high-pressure mass spectrometry that the gas-phase order of basicity is a monotonic increase from ammonia to the tertiary amines: $NH_3 < RNH_2 < R_2NH < R_3N$. Since the expected monotonic basicity order is found for the amines in the gas phase, it is logically necessary that the anomalous inversion of basicities in solution be a solvation phenomenon.

Stabilization of the positive center by alkyl groups may be considered in terms of the inductive effect so long as that implies interaction polarization[47] and *does not* imply electron repulsion. It has been demonstrated[6,48] that alkyl groups stabilize both cations and anions in the gas phase.

A number of years ago Trotman-Dickenson[49] proposed that the anomaly could be explained if the factor which opposed stabilization of the ions by increasing alkylation was the reduction in their ability to enjoy stabilization through hydrogen bonding to the surrounding solvent (or counterion). Thus for the series



$$\begin{array}{ccc} & S & \\ & \vdots & \\ & H & \\ & | & \\ S\cdots H- & N^+ & -H\cdots S, \\ & | & \\ & H & \\ & \vdots & \\ & S & \end{array} \quad \begin{array}{ccc} & S & \\ & \vdots & \\ & H & \\ & | & \\ R- & N^+ & -H\cdots S, \\ & | & \\ & H & \\ & \vdots & \\ & S & \end{array} \quad \begin{array}{ccc} & R & \\ & | & \\ R- & N^+ & -H\cdots S, \\ & | & \\ & H & \\ & \vdots & \\ & S & \end{array} \quad \begin{array}{ccc} & R & \\ & | & \\ R- & N^+ & -H\cdots S \\ & | & \\ & R & \end{array}$$

the substitution of alkyl groups for acidic hydrogens in the ammonium ion reduces its ability to be stabilized by hydrogen bonding to solvent molecules S even as the alkyl groups help to stabilize it by dispersal of the positive charge through an inductive effect. This approach is reasonable and has proved to be mostly correct.[1]

The high-precision ICR measurements of Beauchamp[1] and Aue[11] allow a complete dissection of the thermodynamics for ionization in water when combined with Jones's[35,39] careful calculations and measurements of the heats, free energies, and entropies of the free bases into aqueous solution from the gas phase. Our dissection[1] of all four processes in Scheme I and eq 6 and 7 into all three thermodynamic properties ($\Delta G°$, $\Delta S°$, $\Delta H°$) for 12 amines is probably the most complete partitioning yet reported for the effect of structural change on a chemical process. The reader is referred to these articles for further discussion of the role which structural and solvation effects play on each property.[1,11,35,50]

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Other Bases

At this writing we do not have gas-phase free-energy data for other Brønsted bases of the same precision as that for the amines. We also do not have exact pK_a data in water for many other simple bases. However, gas-phase proton affinities (PA's) have been established for many compounds within ±3 kcal/mol and are equivalent to gas-phase heats of protonation, $\Delta H_i(g)$. Furthermore, we have measured heats of protonation in HSO_3F and other superacids for many simple bases for which PA's have been measured. We are therefore in a position, right now, to compare heats of protonation in the gas phase and in superacid solution for most types of nitrogen, oxygen, sulfur, and phosphorus bases. In considering the following results it is well to remember that for gas-phase proton transfers the relative proton affinity, heat of protonation, and standard free energy changes are equivalent within a kilocalorie per mole.

Oxygen Bases. One of the most interesting observations to come from gas-phase protonation studies is the remarkably low proton affinity of water compared to ammonia, hydrogen sulfide, or phosphine. Despite its very feeble inherent attraction for protons, water as a solvent has an ability to ionize even relatively weak protonic acids. Thus even though an ammonium ion (NH_4^+) is stabler by about 43 kcal/mol than is a hydronium ion (H_3O^+) in the gas phase, the NH_4^+ ion shows considerable ability to hydrolyze to H_3O^+ and NH_3 in aqueous medium. The ubiquity of H_3O^+ in aqueous systems is clear and dramatic evidence for the importance of hydrogen bonding in stabilizing protonated onium ions. It is the superior ability of H_3O^+ to donate hydrogen bonds and the superior ability of H_2O to receive them that accounts for the enormous discrepancy between the basicity of isolated H_2O molecules and bulk water. The ability of water to donate and accept hydrogen bonds accounts for many of its other properties including its high boiling point and heat of vaporization.[51] In contrast, ammonia is only weakly associated and intermolecular forces in H_2S and PH_3 are comparable to those in hydrocarbons and ethers.

Replacement of the hydrogen atoms of water by alkyl groups produces an enormous increase in the stability of the resulting oxonium ion in the gas phase, the differences between H_2O, CH_3OH, and $(CH_3)_2O$ being as large as or larger than in the amine series.

In HSO_3F the heats of protonation of water, the simple alcohols, and ethers are all very close to each other. This behavior is just like that for the amines in HSO_3F and water. The best available data for the pK_a's of ethanol[52] and diethyl ether[53] indicate that toward aqueous acid they are of comparable basicity to each other and also to water.

Thus, the oxygen bases show behavior closely analogous to the amines in that the abilities of alkyl groups to provide enormous stabilization of onium ions in the gas phase are almost completely leveled in aqueous solution. This is attributable to the equal and opposite trends of hydrogen bonding in the two series of ions.

Sulfur Bases. Hydrogen sulfide is slightly more basic to protons in the gas phase than is water. However, this hydride shows little if any ability to associate through hydrogen bonding if one uses heat of vaporization, boiling point,[54] or infrared S–H shifts[55] as criteria. Unlike water, it does not generate a strong tetrahedral crystal structure.[56] Sulfur bases are moderately good hydrogen-bond acceptors, but H_2S and mercaptans seem to be poor hydrogen-bond donors.

We expect that sulfonium ions from the protonation of H_2S, RSH, or R_2S will probably also be poor hydrogen-bond donors. Data in Table I show that the substitution of alkyl groups for hydrogens in H_2S leads to large increases in the gas-phase stability of the onium ion such as were seen for the oxygen and nitrogen bases. If these ions are unable to find comparable stabilization in aqueous solution through hydrogen bonding, then we might expect that the leveling of basicities which was observed for nitrogen and oxygen bases in solution would not be seen for the sulfur bases and large substituent effects which are observable for gas-phase stabilities would carry over, at least in part, into solution. This has in fact been observed[57] by Wolf, who has found the same increment of 14 kcal/mol between the heat of protonation of H_2S and MeSH in HSO_3F as found in the gas phase. At present we do not understand why a comparable increase in stability is not found for Me_2S. However, nmr spectra show that all of these compounds are completely protonated under these conditions. Several workers have found that mercaptans and sulfides have comparable basicities in aqueous acids but that their acidity functions suggest a drastically different ability to hydrogen bond to the solvent than was found for the comparable oxygen bases.[23,58,59]

Phosphorus Bases. For many years there have been speculations and indirect evidence that phosphine is dramatically less basic than the alkylphosphines.[23,24,60-66] The kinetic study of Weston and Bigeleisen,[60] when compared to the direct potentiometric measurements of Henderson and Streuli,[63,64] suggested that the pK_a for the conjugate acid of phosphine might be as low as −14 compared to about 0 for isobutylphosphine, 4.5 for diisobutylphosphine, and 8 for triisobutylphosphine. It is remark-

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Table I
Various Measures of Proton Basicity and the Solvation Energies of Ammonium Ions

Compound	Proton affinity[a,b,d]	$-\Delta H$,[a,c,d] HSO_3F	pK_a	$-\Delta H$,[d] H_2O	$\Delta H_s(BH^+)$[d]
Me_3P	230	44.6	8.65 (63)		
Pyridine	225	38.6 (27)	5.25	4.80	63.8
Aniline	216	34.0 (27)	4.63	7.7	76.2
Me_3N	226.6	47.5	9.80	8.82	65.2
Me_2NH	222.4	47.8	10.79	11.86	72.6
$MeNH_2$	216.3	46.3	10.65	13.09	77.8
NH_3	207	43.3	9.24	12.48	83.8
$(C_6H_{11})_2PH$		32.5	4.55 (63)		
$C_6H_{11}PH_2$		30.3	0.27 (63)		
Me_2S	197	18.1	−6.95 (59)		
Me_2O	186	18.2	−2.52 (53)		
MeSH	185	19.2	−6.4		
PH_3	185	14.4			
MeOH	180	17.1	−1.98 (53)		
H_2S	170	5.3	−9.6		
H_2O	164	16.5	*e*		

[a] All values in the first two columns are taken from ref 1, 27, 51, 57. [b] Values in this column have errors of *ca.* ± 3 kcal/mol if given to three figures and *ca.* ±0.2 kcal/mol if given to four figures. [c] Values in this column have errors of *ca.* ±0.5 kcal/mol. [d] Units for all values are kcal/mol at 25°. [e] See ref 23 for comments about the difficulty of defining this term. Note that Modena has recently found that methanol and dimethyl ether are half-protonated in about 70% sulfuric acid. This is also the concentration where H_2O is stoichiometrically converted to H_3O^+; thus, if water were considered to follow the same acidity function as MeOH and MeOMe, its pK_a should be around −2.

able that, in the search for large substituent effects which has occupied so many chemists during the past decades, this enormous stabilization factor has passed almost unnoticed.

To us it has seemed important to find some direct way of testing the claim and of setting quantitative limits on the base strengths of the phosphines. The possibility of doing this opened up when Olah and McFarland[65] observed that a number of phosphines, including PH_3, were cleanly protonated in HSO_3F. This meant that the pK_a of PH_3 was probably more positive than −14 and that, by using the gas–liquid calorimeter at low temperature, ΔH_i for this base and the alkylphosphines could be determined. Phosphine, like H_2S, decomposes rapidly in HSO_3F at room temperature. After several explosions, each of which demolished a calorimeter, we decided to operate at −50°.

As can be seen from Table I, the very low basicity of PH_3 compared to the alkylphosphines is confirmed completely by our results, and a pK_a close to −14 is supported. Henderson's and Streulis' work[63,64] had suggested that substituent effects for protonation of the phosphines are much larger than for the amines. Our results with HSO_3F support this conclusion. The phosphines, like the sulfur bases, appear to produce onium ions which are very weakly hydrogen bonded to the solvent so that the replacement of a hydrogen on the basic atom serves to stabilize the charge almost as much as would be expected in the gas phase without sacrificing stabilization through hydrogen bonds.

Factors Affecting "Basicity"

From what has been said it is apparent that the three factors which affect the protonation energy of a simple Brønsted base are: (a) the proton affinity of the parent hydride; (b) the number and types of alkyl groups substituting the central atom; and (c) the number and type of hydrogen bonds which the onium ion (BH^+) of the base can make with the medium if it is in solution.

With regard to (a), we know already that the proton affinities of the simple hydrides do not follow the periodic table in any simple way.[7] The proton affinity of a molecule is determined by the strength of the $B–H^+$ bond, which follows the periodic table quite well, and by the ionization potential of B, which does not. The low proton affinity of water reflects its abnormally high ionization potential.[7]

The facts so far suggest that (b) is determined rather simply by the number, size, and polarizability of the groups involved as long as we consider the gas phase. As the quantity and accuracy of proton affinity measurements increase, the simple patterns produced by these pioneering results will probably give way to more complex ones.

The pK_a of a base is determined by the difference in energy between the solvated base, the solvated onium ion, and the solvated proton. It is now clear that there is no simple relationship between the ability of a base to accept a hydrogen bond and its pK_a.[67-69] This discrepancy must lie primarily in the solvation energy of BH^+ which can now be determined in the manner shown above.

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