The Gas-Phase Basicity of Sulfuric Acid

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Abstract: A flowing afterglow-tandem mass spectrometer has been used to measure the 298 K gas-phase basicity (GB) of sulfuric acid. The kinetic method gives GB(H_2SO_4) = 683 ± 5 kJ/mol, which corresponds to a proton affinity of 714 kJ/mol. Reaction rate measurements give GB(H_2SO_4) ≥ 680 ± 3 kJ/mol, while high-level ab initio calculations give a proton affinity of 720 kJ/mol, in good agreement with the kinetic method results. These GB values are higher than the previously bracketed limits. The GB is higher than that for water and lower than that for nitric acid, the other two important components of polar stratospheric clouds.

Introduction

Sulfuric acid is important for several reasons. Natural and anthropogenic sulfuric acid (an incidental byproduct of fuel combustion) are primary components of both acid rain and stratospheric aerosols.[1] Sulfuric acid remains the chemical with the largest production in the United States, with an output of 95 billion pounds in 1995.[2] Furthermore, the oxidation of sulfur to H_2SO_4 is a complex topic of practical and fundamental interest.[3,4] Nevertheless, much of the thermochemistry of sulfuric acid is not precisely known. The compound itself is strongly corrosive and prone to react with many metals. The equilibrium of reaction 1,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O \quad (1)$$

which has a substantial barrier,[5−8] complicates most experiments on sulfuric acid. Among the numbers that are not precisely known is the basicity of H_2SO_4(g).[9]

In 1978, Smith and Munson[10] bracketed the gas-phase basicity of H_2SO_4 between GB(H_2O) = 660.0 kJ/mol[11] and GB(H_2S) = 673.8 kJ/mol.[11] (The gas-phase basicity, GB, is ΔG°_{298} for addition of a proton, while the proton affinity, PA, is ΔH for addition of a proton). The lower limit was based on observation of reaction 2 in an ion cyclotron resonance instrument.[10] The upper limit was based on the fact that H_3S^+ and not $H_3SO_4^+$ was observed emanating from a high-pressure ion source containing both H_2S and H_2SO_4, suggesting that reaction 3 does not occur.

$$H_3O^+ + H_2SO_4 \rightarrow H_2O{-}H^+{-}H_2SO_4 \rightarrow H_2O + H_3SO_4^+ \quad (2)$$

$$H_3S^+ + H_2SO_4 \rightarrow H_2S{-}H^+{-}H_2SO_4 \rightarrow H_2S + H_3SO_4^+ \quad (3)$$

Later, Viggiano and co-workers determined that the rate coefficient for reaction 2 was approximately 17% of the collision rate.[12] The fact that this reaction is substantially slower than the collision rate suggested that reaction 2 is nearly thermoneutral. However, measurement of the reverse reaction (reaction −2) was not attempted.

The basicity of a strong acid is of practical concern only under extremely acidic conditions, where the acid is predominantly undissociated. Clusters of sulfuric acid, nitric acid, and water present in the stratosphere provide such conditions.[1,13] The similar basicities of sulfuric acid and water make it unclear which of these molecules is the more favorable target for protonation. (The gas basicity of nitric acid is somewhat higher at 711 ± 10 kJ/mol.[14]) Therefore, the experiments and calculations described below were performed to determine a more precise basicity for sulfuric acid.

Experimental Section

The flowing afterglow tandem mass spectrometer (MS) used in these experiments consists of an ion source region, a flow reactor, and the tandem MS. A brief description of this instrument follows; a more detailed account has been published.[15]

The ion source used in these experiments is a DC discharge that typically operates at 1200 V with 1 mA of emission current. Protonated

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sulfuric acid was produced by attaching a flask of fuming (30% SO_3) sulfuric acid to a reagent inlet near the ion source. Only glass, a Teflon stopcock, and a rubber O-ring were in contact with the acid. For some experiments, concentrated sulfuric acid was used instead. It was necessary to heat the concentrated acid to nearly the boiling point (at the flow tube pressure) to obtain a sufficient flow of the acid, while the fuming sulfuric acid was used at room temperature. With concentrated sulfuric acid, it is possible to make varying amounts of $H_2O-H^+-SO_3$ in the flow tube; a comparison of these two isomers of $H_3SO_4^+$ is in progress.[16] The data discussed in this work were taken under conditions where $H_2O-H^+-SO_3$ did not influence the results.

The flow tube is a 92 cm × 7.3 cm i.d. stainless steel pipe with five neutral reagent inlets. When sulfuric acid was used as a neutral reagent, an inlet was fitted with a Teflon stopcock and a flask, as described above. The pressure in the flow tube at the middle gas inlet is measured by a capacitance manometer, and the helium flow is controlled by a mass flow controller. The typical pressure in the flow tube is 0.4 Torr, and the typical flow rate is 200 standard cm^3/s. The helium flows through a molecular sieve trap cooled by liquid nitrogen to remove condensable impurities.

The main chamber is a stainless steel box divided into five separate regions by stainless steel interior partitions to allow differential pumping by a roots blower and four diffusion pumps. The pressures after the first chamber are low enough that further collisions of the ions with the buffer gas are unlikely. Ions from the flow tube are extracted through an orifice and focused through four electrostatic lenses into the first quadrupole mass filter. The ions then pass through another set of four electrostatic lenses and enter the octopole ion guide.[17] The middle of the octopole is enclosed in a gas cell with two inlets, which are connected to a capacitance manometer and a leak valve for controlling the pressure of the collision gas. Collision-induced dissociation (CID) experiments are performed by adding the collision gas (Ar) to the gas cell and varying the collision energy by changing the DC offset voltage on the octopole rods. From the octopole, reactant and product ions are focused by four electrostatic lenses into a second quadrupole. The detector is an electron multiplier operating in pulse-counting mode.

For kinetics studies, the neutral reagent gas is introduced into the flow tube via a ring inlet. The position of the ring inlet can be adjusted through the length of the flow tube. The gas flow rate to the ring inlet[15] and bimolecular reaction rate coefficients[18] are determined as described previously. The typical uncertainty is ±20%.

For CID studies, the reactant ion beam energy zero is measured by using the octopole as a retarding field analyzer.[17,19] Collision energies are reported in the center-of-mass (CM) frame; $E_{CM} = E_{lab}m/(m + M)$, where m and M are the masses of the neutral and ionic reactants, respectively. The CRUNCH program written by Professor P. B. Armentrout and co-workers is used in the data analysis.[19,20] The data in these experiments are affected by broadening from the thermal motion of the collision gas (Doppler broadening) and from the kinetic energy distribution of the reactant ion. The effects of such broadening on the slowly varying product ratios seen in this work are not significant.

Calculations. The geometry of H_2SO_4 and $H_3SO_4^+$ was first optimized at the HF/6-31G* level, and analytic frequencies were used to confirm the nature of the structures. On the basis of these results, further optimization at the MP2/6-311+G* level was performed on H_2SO_4 with C_2 symmetry and $H_3SO_4^+$ with C_3 symmetry. The energies of both structures were then obtained at MP4SDTQ/6-311+G**//MP2/6-31+G**. The MP2 zero-point vibrational energies were scaled by 0.9646. All calculations were performed with GAUSSIAN-92.[21]

Results and Discussion

Reaction Rate Measurements. Several techniques utilizing a flowing afterglow-tandem MS can, in principle, be used to measure the gas-phase basicity of H_2SO_4. One is to measure the rate of reaction −2, combine this with the rate for reaction 2 to determine an equilibrium constant, and use this to calculate ΔG for the reaction. However, when the kinetics of reaction −2 were measured in the flowing afterglow, the signal for $H_3SO_4^+$ was not depleted by addition of H_2O except at very high neutral flow rates, where clustering to form $H_2SO_4-H^+-H_2O$ occurred. Due to the presence of protonated water and water clusters from the H_2SO_4 reservoir and background sources, it was impossible to determine if a small amount of reaction −2 occurred. Therefore, a conservative upper bound on the reaction rate coefficient is estimated to be 2×10^{-11} cm^3/s.

Analogous experiments were performed for reaction −3. When H_2S is added through the ring inlet, the abundance of $H_3SO_4^+$ shows a slow decay as a function of reaction distance, with $k_{-3} = (3.3 \pm 1.3) \times 10^{-11}$ cm^3/s. This should be considered an upper limit on the *proton transfer* rate because of the possibility of other reactions, such as clustering, contributing to the depletion of $H_3SO_4^+$.

Viggiano et al. previously succeeded in measuring reaction rates with sulfuric acid as a *neutral* reagent by flowing a carrier gas over heated sulfuric acid and admitting these vapors into a flow tube through a specially designed inlet.[12] Although it was not possible to directly measure the flow rate of sulfuric acid, relative rate constants were obtained, and absolute rate constants were calculated making reasonable assumptions on the rate of calibration reactions. Attempts in this laboratory to measure the rates for reactions 2 and 3 through similar techniques were only partially successful. It was necessary to use very high flows of either nitrogen or helium over the sulfuric acid in order to carry the acid into the flow tube. This gas flow changes the flow dynamics of the instrument, and thus the measured ion intensities, to a significant degree. Thus, the measured depletion rates were unreliable. Qualitatively, however, both H_3O^+ and H_3S^+ react with H_2SO_4, with the former reacting about twice as fast. Since k_2 was measured to be 7×10^{-10} cm^3/s,[12] a very rough estimate of $k_3 \approx 3.5 \times 10^{-10}$ cm^3/s can be made. This can be combined with the rate constants given above to derive $K_{eq}(2) \geq 35$ and $K_{eq}(3) \geq 10$, with error limits estimated as a factor of 3. These two equilibrium constants can be used to derive $GB(H_2SO_4) \geq GB(H_2O) + RT \ln(35)$ [$GB(H_2SO_4) \geq 669 \pm 3$ kJ/mol] and $GB(H_2SO_4) \geq RT \ln(10) + GB(H_2S)$ [$GB(H_2SO_4) \geq 680 \pm 3$ kJ/mol].

Kinetic Method. The kinetic method for determining relative affinities eliminates most of the complications that affect the reaction rate measurements described above. This technique, the subject of a recent in-depth review,[22] typically involves collision-induced dissociation of a proton-bound dimer in a tandem MS, as in reaction 4. The ratio of the two product intensities is taken to be the ratio of the rate coefficients for the two dissociation channels, and it is assumed that an effective temperature T_{eff} can be assigned to the decomposition. Given these assumptions, k_{4b}/k_{4a} is the equilibrium constant for reaction 5, and the thermodynamic relationship in eq 6 is true.[23]

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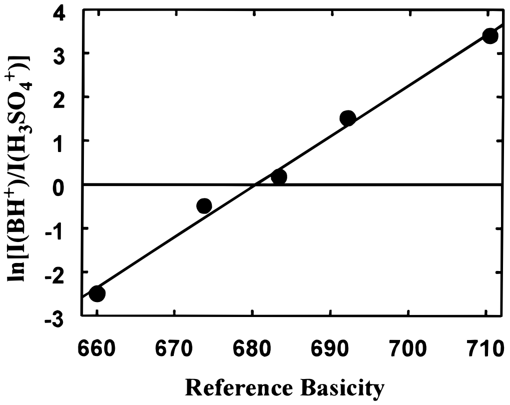
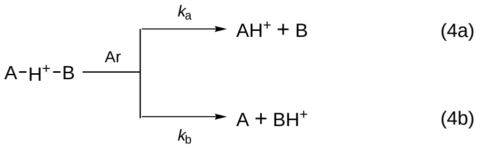


Figure 1. Kinetic method plot showing the natural log of the branching ratio for CID of $H_2SO_4-H^+-B$ versus the gas-phase basicity of B (in kJ/mol) at a collision energy of 3.0 eV. See Table 1 for the list of reference bases.



$$AH^+ + B \rightleftarrows A + BH^+ \tag{5}$$

$$\Delta G(5) = RT_{\mathrm{eff}} \ln(k_{4a}/k_{4b}) \tag{6}$$

Thus, CID of cluster ions containing sulfuric acid and reference bases can be used to determine the basicity of H_2SO_4. First, a consistent set of reference bases must be chosen. Recently, there has been controversy over the gas-phase basicity/proton affinity scale. The comprehensive 1984 compilation of Lias, Liebman, and Levin[24] is generally considered to be the standard reference. An updated version of this work has been developed at NIST.[11] Other recent experimental[25-27] and theoretical[28] studies are in generally good agreement in the region of present interest. The recent NIST table will be taken as the standard reference for this paper. Comparison of the recent scales suggests that the absolute uncertainty of kinetic method results due to uncertainty in the reference values in this region of the proton affinity scale is ±3 kJ/mol.

The standard data analysis for the kinetic method is to measure the branching ratio for CID of proton-bound dimers of reference bases with the molecule of interest. The logarithms of the branching ratios are then plotted against the basicities of the reference compounds, and the x-intercept of the data is taken to be the basicity of the molecule of interest. Such a plot is shown in Figure 1 for a collision energy of 3.0 eV. The reference bases are listed in Table 1. Very similar plots with collision energies of 1.5, 2.0, and 4.0 eV are given as Supporting Information. The x-intercepts vary from 681.6 kJ/mol at 1.5 eV to 678.7 kJ/mol at 4.0 eV, with an average value of 680 kJ/mol. The effective temperature ranges from 800 K at a collision energy of 1.5 eV to 1250 K at 4.0 eV.

Table 1. Reference Bases[a]

base	gas basicity (kJ/mol)
H_2O	660
H_2S	673.8
H_2CO	683.3
CF_3COCH_3	692
HCOOH	710.3

[a] Data from ref 11.

Temperature effects on the gas basicity can complicate analysis of data from the kinetic method. Three methods of correcting for these effects are discussed below. The first method is to use experimental or computational rotational and vibrational constants to calculate the partition functions of the dissociation transition states. This technique depends heavily on assumptions about the temperatures and the symmetries at the transition states. The calculated effects are minor (3 kJ/mol or less) except for CID of $H_2SO_4-H^+-H_2CO$. The $H_3CO^+/H_3SO_4^+$ product ratio varies from 0.8 at a collision energy of 1.5 eV to 1.5 at a collision energy of 4 eV. These ratios and the effective temperatures derived above suggest that H_2CO is a weaker base than H_2SO_4 by 1.5 kJ/mol at 800 K and a stronger base by 4.2 kJ/mol at 1250 K. The rotational symmetries of the ($H_3CO^+ + H_2SO_4$) products in their ground vibrational states are one and two, while those for ($H_2CO + H_3SO_4^+$) are two and three. This corresponds to a difference of a factor of 3 in the rotational partition function, and a difference of 4.1 kJ/mol between the relative free energies of proton transfer from H_2CO to H_2SO_4 at 800 and 1250 K. This value is consistent with the experimental difference of 5.7 kJ/mol, which suggests that rotational entropy differences do have an effect.

If the data are corrected for differences in the rotational partition functions, a new intercept of 682 kJ/mol is obtained. However, the fits to the data in corrected plots such as Figure 1 are noticeably worse, suggesting that this method is not optimal.

A second method is direct extrapolation of the intercepts to $T_{\mathrm{eff}} = 298$ K. This method gives a value of 684 kJ/mol for GB(H_2SO_4). While this method has no theoretical justification, it has the advantage of simplicity.

A more sophisticated approach has been developed by Fenselau and co-workers.[22,29] Since $\Delta G/T_{\mathrm{eff}} = \Delta H/T_{\mathrm{eff}} - \Delta S$, at $1/T_{\mathrm{eff}} = 0$, $\Delta G/T_{\mathrm{eff}} = \Delta S$. Extrapolating $\Delta G/T_{\mathrm{eff}}$ as a function of $1/T_{\mathrm{eff}}$ to $1/T_{\mathrm{eff}} = 0$ gives $\Delta S = 3.7$ J/(mol·K). Correcting for the entropy at each of the effective temperatures gives GB(H_2SO_4) values ranging from 683.4 to 684.6 kJ/mol, with an average value of 684 kJ/mol.

The difference between the uncorrected result and the three corrected results is not large. Averaging all four results gives a value of 683 ± 3 kJ/mol as the best value for the basicity of sulfuric acid. The average of the results from the rotational partition function correction and the Fenselau method, which are the most reasonable corrected values, is also 683 kJ/mol.

Discrimination against either heavy or light masses in the second quadrupole, the ion optics, or the detector can alter the ratio of products. The uncertainty due to possible discrimination is taken to be the variation in the product ratio as a function of focusing conditions. When the ion optics are focused on first one product and then the other, a variation of up to ±40% is seen, which corresponds to an uncertainty of ca. ±3 kJ/mol. The branching ratios reported are the average for a variety of focusing conditions.

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A possible complication is reaction 7, decomposition of the protonated sulfuric acid.

$$H_2SO_4{-}H^+{-}H_2O \xrightarrow{Ar} H_3O^+ + H_2O + SO_3 \qquad (7)$$

Even a small amount of this reaction would drastically affect the apparent CID product ratio. Indeed, the $H_3O^+/H_3SO_4^+$ ratio is roughly 1:1 at higher energies, suggesting that decomposition of the acid is occurring. However, there is no evidence in the kinetic data plots such as Figure 1 that this reaction is significant at collision energies of 4 eV or less.

In summary, the three primary sources of error are the uncertainties in the basicities of the reference bases, correcting from the effective temperatures to room temperature, and discrimination against certain products. Combining the uncertainties, the final estimate from the kinetic method is $GB(H_2SO_4) = 683 \pm 5$ kJ/mol. This is consistent with the result from reaction rate constant measurements, $GB(H_2SO_4) \geq 680 \pm 3$ kJ/mol.

Collision-Induced Dissociation. In principle, CID could also be used to determine the heat of formation of $H_3SO_4^+$, and thus its basicity. CID of $H_3SO_4^+$ leads to two ionic products, H_3O^+ and HSO_3^+. However, there is a barrier to the reaction, which makes this approach to determining the basicity unusable. The CID results will be discussed in a separate report.[16]

Thermochemical Conclusions. The proton affinity of sulfuric acid at 298 K can be derived by calculating the entropy of protonation with use of the rotational and vibrational constants from the ab initio calculations. The result is that the proton affinity of sulfuric acid is 31.0 kJ/mol higher than the gas basicity, or $PA(H_2SO_4) = 714 \pm 5$ kJ/mol. Subtracting $PA(H_2SO_4)$ from the sum of $\Delta_f H^\circ(H^+) = 1530.0 \pm 0.1$ kJ/mol[11] and $\Delta_f H^\circ(H_2SO_4) = -735.1 \pm 8.4$ kJ/mol[30] gives $\Delta_f H^\circ_{298}(H_3SO_4^+) = 81 \pm 10$ kJ/mol.

Computational Results. The 0 K proton affinity of H_2SO_4 is calculated to be 716.1 kJ/mol at the MP4/6-311+G**+ZPE level, where the geometry optimization is at the MP2 level. This can be adjusted to 720 kJ/mol at 298 K by using the heat capacities of the involved species, where the dominant effect is the $3kT/2$ change in the translational energy in going from one particle to two. The proton affinity derived is in good agreement with the experimental value. This agreement corroborates the kinetic method results, and suggests that calculations at this level are adequate for molecules of the complexity of sulfuric acid. For comparison, previous calculations[6] at a similar level of theory give values for the relative stability of H_2SO_4 compared to H_2O and SO_3 within 7 ± 8 kJ/mol of the experimental value.

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Supporting Information Available: Supporting Information Available: Computational parameters for H_2SO_4 and $H_3SO_4^+$ and kinetic method plots at collision energies of 1.5, 2.0, and 4.0 eV (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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