

Proton Affinities of Some Sulfur-Oxygen Compounds

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Abstract: The relative proton affinities of some simple sulfur-oxygen compounds have been determined by the bracketing technique of ion/molecule reactions: $153 \text{ kcal/mol} = \text{PA}(\text{CH}_3\text{F}) < \text{PA}(\text{SO}_2\text{F}_2) < \text{PA}(\text{SO}_2) < \text{PA}(\text{HSO}_3\text{F}) < \text{PA}(\text{C}_2\text{H}_4) = 159 \text{ kcal/mol}$; and $169 \text{ kcal/mol} = \text{PA}(\text{H}_2\text{O}) < \text{PA}(\text{H}_2\text{SO}_4) \approx \text{PA}(\text{CF}_3\text{SO}_3\text{H}) < \text{PA}(\text{H}_2\text{S}) = 172 \text{ kcal/mol}$. The proton affinities of these compounds fit reasonably well to a correlation curve of ionization potential vs. proton affinity and to a correlation curve of core binding energy, $O(1s)$, vs. proton affinity. A comparison of solution data with gas-phase data indicates that compounds whose gaseous proton affinities are less than the proton affinity of HSO_3F are not predominantly protonated in solution in HSO_3F . Compounds whose proton affinities are larger than the proton affinity of HSO_3F are predominantly protonated in HSO_3F .

Introduction

During the past two decades, much work has been done on the kinetics and thermochemistry of gaseous ions.¹⁻³ One of the thermochemical properties on which interest has focused during the past decade is the proton affinity of the molecule,⁴⁻⁸ defined according to the equation

$$\text{PA}(X) \equiv D(X-H^+) = \Delta H_f(H^+) + \Delta H_f(X) - \Delta H_f(XH^+) \quad (1)$$

The proton affinity is a direct measure of the basicity of a molecule without the complicating effects of solvation and is the property which should be correlated with molecular structure or molecular properties rather than a measure of basicity obtained from solution processes.

Comparisons have been made between solution basicities and proton affinities. The proton affinities of the methylamines follow the order predicted by a simple inductive effect, although the pK_s in solution follow another order. The inverted order in solution is explained by different solvation of the ammonium and methylammonium ions.^{4,9,10}

Correlations have been reported between gas-phase proton affinities and gas-phase ionization potentials for some time with the general trend that an increase in ionization potential corresponds to a decrease in proton affinity.¹⁰⁻¹² Recently an excellent correlation has been noted between the oxygen 1s ionization potentials and the proton affinities of an extensive series of oxygenated hydrocarbons.¹³⁻¹⁶

Proton affinities are now available for a very large number of organic compounds, predominantly nitrogen- and oxygen-containing compounds, although a few sulfur compounds have been studied.^{5-7,17,18} Although the proton affinities of several inorganic compounds have been determined, the proton affinities of many simple inorganic compounds have not yet been determined. We wish to report the proton affinities of some simple sulfur-oxygen compounds. These data will be helpful in correlations between gas-phase and solution behavior in solutions of strong acids.

Experimental Section

The majority of the experiments were performed with a CEC (Du Pont) 21-110B mass spectrometer which has been modified for high-pressure operation.¹⁹ Some experiments were performed with an ion cyclotron resonance (ICR) mass spectrometer which has also been described elsewhere.²⁰ The proton affinities which are reported here have been obtained by the bracketing technique from the occurrence or nonoccurrence of proton transfer reactions. This technique has been frequently used and is based on the observation that endothermic ion-molecule reactions are slow and not generally detected under the conditions of most mass spectrometric experiments.⁴ In the high-pressure mass spectrometric experiments, the reactions were

studied by noting the dependence of ionic composition on pressure, either the total pressure of a mixture of constant composition or the partial pressure of one component.

Several of the compounds reported in this study were particularly difficult to handle and to introduce into the mass spectrometer with minimal impurities. Sulfuric acid is not sufficiently volatile to be introduced from a heated oven or from an external glass bulb at room temperature. Consequently, H_2SO_4 was introduced from glass capillaries in the direct insertion probe. Small glass capillaries were dried in an oven, filled with fuming sulfuric acid (30% SO_3), and sealed with break-off tips at right angles to the tubes themselves. The tip of the capillary was broken in the vacuum chamber as the probe entered the source of the mass spectrometer. The SO_3 reacted with any water remaining in the system, and excess SO_3 was rapidly pumped away. The pressure of H_2SO_4 could not be measured directly in these experiments, but it was easily changed by varying the temperature of the probe. Sulfuric acid was easily obtained in the ICR by introducing fuming sulfuric acid into the inlet system. The SO_3 reacted with water in the ICR cell to produce the low pressure of H_2SO_4 needed for the experiments.

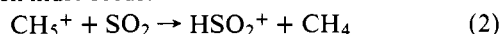
Fluorosulfuric acid, HSO_3F , was introduced from capillaries in the direct insertion probe or from an external glass bulb attached through a tapered joint to a hollow tube which was inserted through the vacuum lock directly into the source of the mass spectrometer. With the bulb, there was difficulty in introducing an intermediate pressure of HSO_3F . With the capillary, there was an initial surge in pressure which decreased rapidly with time as the sample of HSO_3F evaporated. Both the hollow glass probe and the glass capillaries were used for the introduction of $\text{CF}_3\text{SO}_3\text{H}$. For both of these acids, a small amount of fuming sulfuric acid was added to the capillaries to react with traces of water that were present. Sulfuric acid did not interfere because of its much lower volatility. Precise control and measurement of the pressures of these acids could not be achieved.

The experiments done with the ICR were standard double resonance experiments to show that a proton transfer reaction did or did not occur in the direction indicated.²⁰

The reagent gases of these experiments were obtained from Matheson and were 99.9% pure or higher. Fisher fuming sulfuric acid, 30% SO_3 , was used immediately after opening. SO_2 and SO_2F_2 were obtained from Matheson. HSO_3F and $\text{CF}_3\text{SO}_3\text{H}$ were obtained from Cationics, Inc.

Results

SO_2 . Typical data for proton transfer reactions indicated by pressure plots for mixtures of constant composition are shown in Figure 1 for a 2% (by volume) mixture of SO_2 in CH_4 . The major product ions in this mixture are CH_5^+ , C_2H_5^+ , and HSO_2^+ . For clarity, the primary ions of methane, CH_3^+ and CH_4^+ , are not shown. From this figure it is apparent that CH_5^+ is formed and reacts. CH_5^+ is nonreactive in CH_4 and HSO_2^+ is the only significant product ion which can account for the loss of CH_5^+ at high pressures. Consequently, the following reaction must occur:



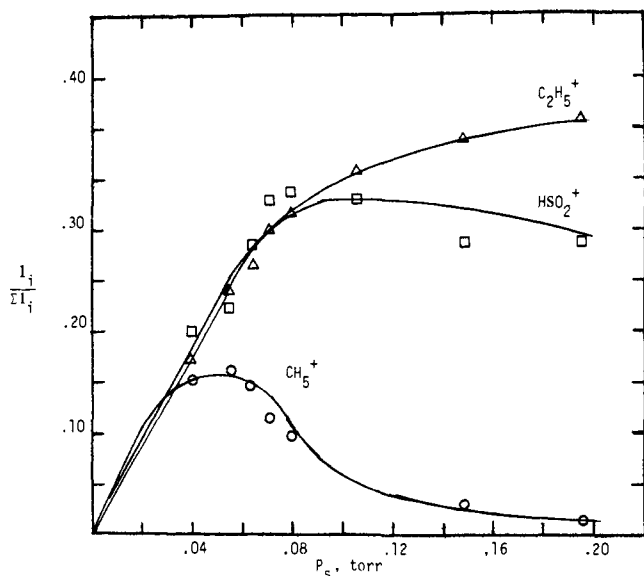
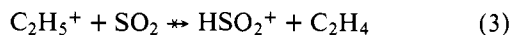


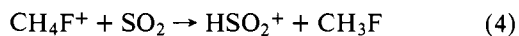
Figure 1. Fractional ionic abundance vs. pressure for 2% SO₂ in CH₄.

The thermochemical conclusion from the observation of this reaction is that PA (SO₂) > PA (CH₄). The invariance of the fractional abundance of C₂H₅⁺ at higher pressures indicates that the proton transfer reaction, eq 3, does *not* occur:



Exothermic proton transfer reactions are normally fast unless competing processes occur. Since C₂H₅⁺ does not react with SO₂ to a significant extent by any process, we infer that the reaction is endothermic and that PA (SO₂) < PA (C₂H₄).

High-pressure mass spectrometric experiments on mixtures of CH₃F and SO₂ were inconclusive, but ICR double resonance experiments showed that the proton transfer reaction, eq 4, does occur:



Similar double resonance experiments gave no indication of the occurrence of the reverse of reaction 4. Hence,

$$153 \text{ kcal/mol} = \text{PA} (\text{CH}_3\text{F}) < \text{PA} (\text{SO}_2) < \text{PA} (\text{C}_2\text{H}_4) = 159 \text{ kcal/mol}$$

The value for PA (CH₃F) is taken from earlier work indicating that PA (CH₃F) ≅ PA (C₂H₂),²¹ corrected for changes in the heats of formation of the reference compounds.¹² The value for PA (C₂H₄) is obtained from ΔH_f (C₂H₅⁺) = 219 kcal/mol,²² ΔH_f (C₂H₄) = 12.5 kcal/mol, and ΔH_f (H⁺) = 365.²³

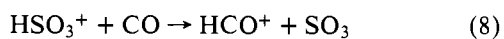
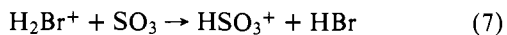
SO₂F₂. Similar high-pressure mass spectrometric and ICR double resonance studies were performed on mixtures containing SO₂F₂. The following reactions establish the narrowest limits for the proton affinity of SO₂F₂:



Hence,

$$153 \text{ kcal/mol} = \text{PA} (\text{CH}_3\text{F}) < \text{PA} (\text{SO}_2\text{F}_2) < \text{PA} (\text{SO}_2) < \text{PA} (\text{C}_2\text{H}_4) = 159 \text{ kcal/mol}$$

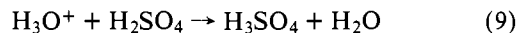
SO₃. Recently, we have reported reactions which establish limits for the proton affinity of SO₃:



and, therefore, PA (SO₃) = 142 ± 1 kcal/mol.²⁴

H₂SO₄. Small amounts of H₂SO₄ (<0.05 Torr) were added to a high pressure of CH₄ (0.7 Torr) and abundant H₃SO₄⁺ ions were observed. An increase in the pressure of H₂SO₄ from an increase in the temperature of the probe caused an increase in the relative abundance of H₃SO₄⁺ and a decrease in the abundances of CH₅⁺ and C₂H₅⁺. Addition of comparable amounts of sulfuric acid to similar pressures of propane or of hydrogen sulfide produced essentially no H₃SO₄⁺ and produced virtually no decreases in the dominant ions of the two gases, C₃H₇⁺ or H₃S⁺.

High-pressure experiments on CH₄/H₂O/H₂SO₄ mixtures gave ambiguous results because of the large abundances of cluster ions: H(H₂O)_x⁺, H(H₂SO₄)_y⁺, and H(H₂O)_x(H₂SO₄)_y⁺. However, the ICR double resonance experiments showed that reaction 9 occurs:



The absence of H₃SO₄⁺ in the H₂S/H₂SO₄ mixtures together with the nonreactivity of H₃S⁺ in these mixtures shows that reaction 10 does *not* occur:



Therefore,

$$169 \text{ kcal/mol} = \text{PA} (\text{H}_2\text{O}) < \text{PA} (\text{H}_2\text{SO}_4) < \text{PA} (\text{H}_2\text{S}) = 172 \text{ kcal/mol}$$

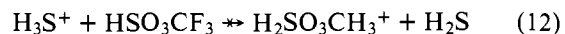
Several values have been reported for PA (H₂O) and PA (H₂S) which are in reasonable agreement. The above values are taken, however, from recently reported equilibrium values which are experimentally related to PA (*i*-C₄H₈) = 193.0 kcal/mol and which give an experimental difference for PA (H₂S) – PA (H₂O) = 3.0 kcal/mol.¹⁸

HSO₃CF₃. Additions of small amounts (~0.05 Torr) of HSO₃CF₃ to high pressures (~0.5 Torr) of methane produced abundant H₂SO₃CF₃⁺ ions and comparable decreases in the relative abundances of CH₅⁺ and C₂H₅⁺ ions. Similar additions of trifluoromethylsulfuric acid to comparable pressures of propane or of hydrogen sulfide produced essentially no H₂SO₃CF₃⁺ ions and no decreases in the abundances of the dominant ions of the two gases, C₃H₇⁺ or H₃S⁺.

High-pressure mass spectrometric experiments on CH₄/H₂O/HSO₃CF₃ mixtures gave inconclusive results because of cluster ions. However, ICR double resonance experiments showed that reaction 11 occurs:

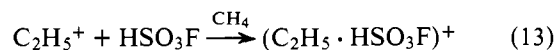


The absence of H₂SO₃CF₃⁺ ions in the H₂S/HSO₃CF₃ mixtures and the nonreactivity of H₃S⁺ in these mixtures indicate that reaction 12 does *not* occur:



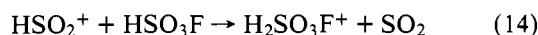
It was not possible to make a direct comparison of the proton affinities of trifluoromethylsulfuric acid and sulfuric acid.

HSO₃F. The addition of small amounts of fluorosulfuric acid to high pressures of methane caused the formation of H₂SO₃F⁺ with significant decreases in the relative abundances of CH₅⁺ and C₂H₅⁺. An additional abundant ionic species was observed in this mixture which establishes a new reaction:



No significant quantities of analogous addition ions were observed in any of the other mixtures with CH₄. This addition reaction of C₂H₅⁺ to fluorosulfuric acid is the dominant reaction of C₂H₅⁺ rather than proton transfer because the sum of relative abundances of C₂H₅⁺, (C₂H₅·HSO₃F)⁺, and (C₂H₅·2HSO₃F)⁺ is independent of the composition of the mixture. Fluorosulfuric acid was added to a mixture of 2% SO₂

in CH₄ from a glass capillary in the probe. The pressure of fluorosulfuric acid could not be controlled or measured accurately and decreased to essentially zero in about 10 min. During this period of monotonic decrease in concentration of fluorosulfuric acid, the relative abundance of H₂SO₃F⁺ continuously decreased and the relative abundance of HSO₂⁺ continuously increased. No addition of HSO₂⁺ to HSO₃F was noted; consequently, proton transfer is indicated.



From reactions 13 and 14 we conclude that PA (SO₂) < PA (HSO₃F) < PA (C₂H₄).

Discussion

The results of these experiments indicate the following order for the proton affinities of the compounds studied: 153 kcal/mol = PA (CH₃F) < PA (SO₂F₂) < PA (SO₂) < PA (HSO₃F) < PA (C₂H₄) = 159 kcal/mol and 169 kcal/mol = PA (H₂O) < PA (H₂SO₄) ≈ PA (HSO₃F) < PA (H₂S) = 172 kcal/mol. Experience indicates that we are able to observe rapid proton transfer reactions which are at least 2 kcal/mol exothermic. Consequently, we assign the following values to the proton affinities of the compounds: PA (SO₂F₂) = 155 ± 2 kcal/mol; PA (SO₂) = 157 ± 2 kcal/mol; PA (HSO₃F) = 158 ± 2 kcal/mol; and PA (H₂SO₄) ≈ PA (CF₃SO₃H) = 170 ± 2 kcal/mol.

Figure 2 shows a correlation plot of proton affinity vs. first ionization potential for a series of oxygenated compounds. The present data fit the general trend obtained from the oxygenated compounds, but the simple oxygenated compounds exhibit appreciable scatter. The correlation is not sufficiently good to allow the *accurate* prediction of proton affinities from ionization potentials or ionization potentials from proton affinities, but reasonable estimates may be made. From these values of proton affinities, we estimate that the ionization potentials of the substituted sulfuric acids will be 11.5 ± 0.5 eV; IP (H₂SO₄) ≈ IP (HSO₃CF₃) ≈ 11.2 eV and IP (HSO₃F) ≈ 11.7 eV. From the general trend of Figure 2 and the ionization potentials of SO₂Cl₂ (12.4 eV^{25,26}) and of SO₂ClF (12.6 eV²⁵), we estimate that their proton affinities should be 150 ± 10 kcal/mol.

Excellent correlations have been noted for oxygenated hydrocarbon derivatives between proton affinities and O(1s) core-binding energies.¹³⁻¹⁶ Different correlation lines were obtained for compounds with singly bonded oxygens and for compounds with doubly bonded oxygens and these correlations were used to assign the site of protonation in esters as the carbonyl oxygen.¹⁴⁻¹⁶ The point for SO₂ fits reasonably well to the correlation curves for oxygenated compounds (slightly below the line for doubly bonded oxygenated compounds) and the point for SO₂ does not fit with the correlation curve for proton affinities and S (2p) core-binding energies of H₂S, CH₃SH, C₂H₅SH, and CS₂. Consequently, we feel that these data support the intuitive picture that HSO₂⁺ is an O-protonated species.

Core-binding energies, O(1s), are not available for the other compounds of this study. However, from the proton affinities reported here, we estimate core-binding energies relative to O₂ as about -2.5 eV for SO₃, almost -3 eV for SO₂F₂ and HSO₃F, and almost -4 eV for H₂SO₄ and HSO₃CF₃.

The proton affinities of HOSO₂OH and HOSO₂CF₃ are significantly larger than the proton affinities of SO₂ and SO₃ and are approximately the same as the proton affinities of other hydroxy compounds, H₂O, CH₃OH, and HONO₂. Consequently, it appears reasonable to consider that the site of protonation in these acids is also the hydroxyl oxygen. By analogy, we feel that H₂SO₃F⁺ is also hydroxy protonated.

To the extent that we are able to check, our data for these

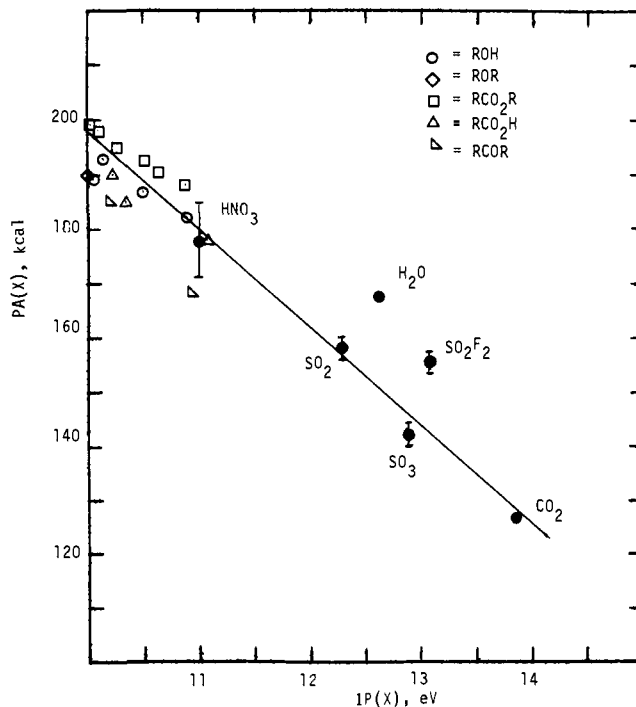


Figure 2. Correlation curve: proton affinity vs. ionization potential. Data from ref 6-8, 17, 18, 23-27.

compounds are self-consistent. Only very small amounts of HSO₃⁺ are present in the distribution of product ions of mixtures of methane either with sulfuric acid or with fluorosulfuric acid. That is, the following dissociative proton transfer reactions are slow:

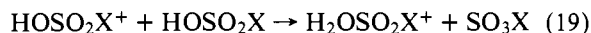


The following abstraction reactions also do not occur to any significant extent:



With the value of PA (SO₃) obtained in this work and other thermochemical data, reactions 15-18 are endothermic and therefore are expected to be slow.

Self-protonation reactions were observed when these acids were introduced into the source of the mass spectrometer at pressures of 0.01-0.1 Torr. Therefore, reactions of the type



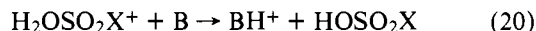
in which X = OH, F, and CF₃ are all rapid and probably exothermic. No thermochemical observations about the individual species may be obtained because of the absence of thermochemical data on the neutral species.

These acids are all good solvating agents for the proton, since cluster ions, H(HOSO₂X)_i⁺, are readily formed at relatively low pressures of the acids and in mixtures containing small amounts of these acids, X = OH, F, CF₃. The extent of solvation of protons by these acids is roughly comparable to the solvation of other hydroxy compounds like H₂O and CH₃OH.

At first glance, the high proton affinities of these strong acids may appear surprising. However, these values are in reasonable agreement with the proton affinities of other hydroxy compounds, including nitric acid for which PA (HNO₃) = 176 ± 7 kcal/mol.²⁷ Autoprotolysis in solution requires that the molecules accept as well as donate a proton. It appears

worthwhile to compare these gaseous data with observations in solution.

There are no data available for the anions of these acids; therefore, we cannot discuss relative autoprotolysis constants or ionization constants, only proton transfer reactions of the type



Gaseous proton transfer reactions, (20), will occur rapidly with all compounds, B, whose proton affinities are greater than the proton affinities of the acids, HOSO_2X . If $\text{PA}(\text{B}) < \text{PA}(\text{HOSO}_2\text{X})$, then the reaction as written in eq 20 is endothermic and will be slow. If we ignore differential solvation effects as a zeroth approximation, we would expect that those compounds whose proton affinities are greater than the proton affinity of fluorosulfuric acid will be extensively protonated in solution. Those compounds whose proton affinities are less than the proton affinity of fluorosulfuric acid should *not* be extensively protonated in solution.

It has been reported that nitrogen, oxygen, neon, xenon, hydrogen, nitrogen trifluoride, and carbon monoxide all have low solubilities in $\text{HSO}_3\text{F}/\text{SbF}_5/\text{SO}_3$ systems and do not appear to be protonated to any significant extent.²⁸ The proton affinities of all of the compounds are less than the proton affinity of fluorosulfuric acid.^{6,8} Similarly CO_2 , SO_2 , and SO_3 are not significantly protonated by $\text{HSO}_3\text{F}/\text{SbF}_5$ ²⁸ and the proton affinities of these compounds are less than the proton affinity of HSO_3F . Experiments have been reported which indicate that "HF probably behaves as a weak base" in fluorosulfuric acid.²⁹ Similarly, HCl is a nonelectrolyte in fluorosulfuric acid, although it was reported that HCl was a "fairly strong base" in $\text{HSO}_3\text{F}/\text{SbF}_5$.³⁰ Both of these halogen acids have lower proton affinities than fluorosulfuric acid.⁶

Acetic acid is a strong base in fluorosulfuric acid²⁸ as are water,³¹ hydrogen cyanide,³² acetaldehyde,³³ and acetone.³⁴ All of these compounds have proton affinities greater than the proton affinity of fluorosulfuric acid.⁶ Large negative heats of ionization have been reported for an extensive series of compounds whose proton affinities are greater than 165 kcal/mol, an observation which indicates extensive protonation in solution.³⁵

All of these observations of solution protonation are consistent with our predictions from gaseous proton transfer reactions except possibly SO_2 , HCl, and HF. The proton affinity of SO_2 is only slightly less than the proton affinity of HSO_3F ; hence, we would expect some protonation of SO_2 in solutions containing HSO_3F . The proton affinities of HF (114 kcal/mol)³⁶ and HCl (135 kcal/mol)¹² are sufficiently below the proton affinity of fluorosulfuric acid that we would expect no significant protonation in solution.

Some evidence has been reported for the existence of protonated forms of very weak bases in solution, although no spectroscopic evidence was obtained. Exchange reactions were observed between $\text{DSO}_3\text{F}/\text{SbF}_5$ and CH_4 ³⁷ and $\text{DSO}_3\text{F}/\text{SbF}_5$ and H_2 .³⁸ The proton affinity of H_2 is about 100 kcal/mol and the proton affinity of methane is about 127 kcal/mol.⁶ Since these compounds are much weaker gaseous bases than fluorosulfuric acid, we consider it most unlikely that significant concentrations of H_3^+ or CH_5^+ exist in solutions of $\text{HSO}_3\text{F}/\text{SbF}_5$.

Fluorosulfuric acid acts as a weak acid in sulfuric acid and sulfuric acid is a proton acceptor in fluorosulfuric acid.³⁹ These observations are in agreement with our rankings of the proton affinities of the two acids: $\text{PA}(\text{H}_2\text{SO}_4) > \text{PA}(\text{HSO}_3\text{F})$.

Although the data which are reported here are enthalpies and not free energies of protonation, the qualitative agreement between solution behavior and gas phase behavior appears reasonable. It is our hope that subsequent work will allow the more accurate determination of the proton affinities of these compounds and allow more precise comparisons between solution and gas phase properties.

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