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ENERGETICS OF GAS PHASE PROTON SOLVATION BY NH_3

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ABSTRACT

The absolute proton affinity of NH_3 (203.6 ± 1.3 kcal/mol at 298K) and the proton solvation energies by more than one NH_3 have been determined by the molecular beam-photoionization method. In addition, the $\text{NH}_3^+-\text{NH}_3$ interaction energy (0.79 ± 0.05 eV) has been measured by photoionization of the neutral van der Waals dimer. These experiments have shown that photoionization of van der Waals clusters is a very powerful method for determining the energetics of gas phase proton solvation.

INTRODUCTION

Proton transfer represents a very important class of reactions in both chemistry and biology. Understanding these reactions requires knowledge of the heats of formation of the protonated species as well as the effects of solvent interactions. Both the high pressure ion source mass spectrometric technique¹⁻⁴ and ion cyclotron resonance⁵ have been employed to determine relative proton affinities and the energy released upon solvation of an ionic species. The relative proton affinity is readily obtained by measurements of the equilibrium constant of the reaction $M_1H^+ + M_2 \rightleftharpoons M_2H^+ + M_1$. The equilibrium constant and hence ΔG^0 is measured as a function of temperature to determine the ion solvation energies of a reaction $(M_1H^+)M_2 \rightleftharpoons M_1H^+ + M_2$. Absolute values of the proton affinity are usually obtained from appearance potential measurements of a protonated species produced by electron impact.^{6,7} The drawback of this method is that the protonated species of many interesting molecules do not occur as fragment ions. It has recently been shown⁸ in a molecular beam photoionization mass spectrometry experiment that dimer molecules produced in a supersonic expansion are excellent parent molecules for the investigation of the ion-molecule interaction potential and the photoionization production of MH^+ . The finer control of ionizing radiation possible in a photoionization measurement of appearance potentials affords a more accurate means of determining thermochemical quantities such as absolute proton affinities directly from a measurement of a microscopic quantity such as a threshold energy. For instance, the stability of the ion-molecule cluster $H_2O^+ \cdot H_2O$ has been determined from the threshold energy of formation since the photoionization of the

van der Waals polymer is viewed as ionization of one of the species in the parent cluster. Further excitation of the ion cluster allows the vibrational energy induced ion-molecule reaction at zero kinetic energy to proceed yielding the threshold energy of formation of H_3O^+ . In this study, this technique is used to determine the proton affinity of NH_3 . It is further extended to investigate the protonated species formed by decomposition of higher polymers to yield solvation energies of an ammonium ion by ammonia solvent molecules.

EXPERIMENTAL

The apparatus and procedures have been described previously.^{9,10} The ammonia polymer beam was produced by expansion of the neat gas through a 0.003" dia. Monel nozzle. Seeding of the NH_3 in Ar at various mixing ratios, maintaining the same total pressure, did not improve the dimer production. Using the monochromator grating at zero order the intensity of the fragments was monitored as a function of stagnation pressure and is shown in Fig. 1. The behaviors of the protonated ammonia signal compared to the dimer ion signal and of the protonated dimer ion compared to the trimer ion signal are very similar, indicating the dominant parent species.

RESULTS

The photoionization efficiency curves of the ammonia dimer ion and of the protonated ammonia species are shown in Figs. 2 and 3. The standard deviation of the signal intensity at the threshold is about 10% for $(\text{NH}_3)_2^+$ and about 5% for the protonated ammonia species. Points are

measured at much lower energies than the threshold values so that an average background ion intensity can be measured. The threshold values are labeled as such when the photoionization efficiency values increase uniformly above this background ion intensity. The threshold uncertainties are taken as the difference in values obtained in two separate scans.

DISCUSSION

In high pressure mass spectrometry experiments, the $\text{NH}_3^+ + \text{NH}_3 \longrightarrow \text{NH}_4^+ + \text{NH}_2$ reaction, exothermic by 0.74 eV, occurs too rapidly for the $(\text{NH}_3^+)\text{NH}_3$ intermediate to be observed by stabilization from the gas bath molecules. In our investigation, the $(\text{NH}_3^+)\text{NH}_3$ intermediate is produced directly from photoionization of the neutral dimer. In addition, its stability can be determined from the threshold energy of formation. Figure 4 shows the energetics of this system. The well depth of the neutral ammonia-ammonia interaction is taken to be 0.35 kcal/mol from fitting the temperature dependence of second virial coefficient data.¹¹ Combination of the neutral well depth, the ionization potential of NH_3 ¹² and the threshold of $(\text{NH}_3)^+_2$ formation yields the $(\text{NH}_3^+)\text{NH}_3$ binding energy as 0.79 ± 0.05 eV or 18.1 ± 1.1 kcal/mole.

When the internal energy of the ammonia dimer ion is increased to 0.052 eV, the onset of the NH_4^+ fragment is observed. The appearance potential of NH_4^+ , the ionization potential¹² of H, the $\text{H}_2\text{N-H}$ bond energy¹³ and the neutral well depth are employed to calculate the proton affinity of NH_3 as 8.76 ± 0.06 eV or 202.1 ± 1.3 kcal/mol at 0 K as shown in Fig. 5. Assuming that all rotational degrees of freedom are excited

and that no vibrational degrees of freedom are excited at 298 K, the proton affinity becomes 203.6 ± 1.3 kcal/mol at 298 K. This value is in good agreement with a recent proton affinity measurement of 202.3 kcal/mol obtained in ion cyclotron resonance thermal equilibrium experiments at 298 K.⁵ The previously accepted value for the proton affinity of ammonia was 207 ± 3 kcal/mole.^{6,7} Recent theoretically calculated values for the proton affinity of NH_3 are 205.3¹⁴ and 208¹⁵ kcal/mole.

The appearance potentials of the higher protonated polymers, $(\text{NH}_4^+)\text{NH}_3$, a fragment from excited $(\text{NH}_3)_3^+$, and $(\text{NH}_4^+)(\text{NH}_3)_2$, a fragment from excited $(\text{NH}_3)_4^+$, allow the solvation energy of an ammonium ion by one or two ammonia molecules to be calculated via the cycles shown in Fig. 5. These values are listed in Table I along with literature values for the solvation energies.

It is clear from Table I that the agreement between the solvation energies measured in this study and the literature values is not good. The theoretical values from ab initio SCF calculations are too large probably due to the limited basis set employed. The experimental values are obtained by high pressure ion source mass spectrometry. One very common criticism of the photoionization technique for measuring appearance potentials is that the threshold may not correspond to the ground vibrational state of the ion but rather to some upper vibrational ionic state.²¹ This is true when large changes in geometry of the molecule occur upon ionization. Vibrationally excited ions would lead to higher thresholds and thus lower absolute values of the

solvation energies. In our case, however, the process that is essentially occurring is the unimolecular decomposition of the vibrationally excited parent clusters $(\text{NH}_3)_2^+$, $(\text{NH}_3)_3^+$ and $(\text{NH}_3)_4^+$. Franck-Condon factors will not play an important role in this case. If there is no barrier for proton transfer the threshold should correspond to the threshold of decomposition. Nevertheless, let us assume that the difference in energies between the two most recent high pressure mass spectrometry values^{2,4} and the photoionization value is due to vibrational excitation of the resulting ion in the photoionization experiments and that the kinetic energy of the electron is zero. Thus, the $(\text{NH}_4^+)(\text{NH}_3)_2$ produced will have $(42.3-20.2) = 22.1 \text{ kcal/mol}^2$ or $(37.7-20.2) = 17.5 \text{ kcal/mol}^4$ of excitation energy. Both these values are larger than the corresponding dissociation energies of 17.5^2 or 16.2 kcal/mol^4 for $(\text{NH}_4^+)(\text{NH}_3)_2$. Clearly, the notion that the ions $(\text{NH}_4^+)(\text{NH}_3)_2$ formed by photoionization of clusters are vibrationally excited is inconsistent with the equilibrium solvation energies.

The onset of the decomposition of the higher polymers to yield NH_4^+ serves as a check on the threshold measurements. The energy required to produce NH_4^+ from $(\text{NH}_3)_3$ can be calculated from the data in Fig. 5; one obtains that the threshold for the reaction $(\text{NH}_3)_3 \rightarrow \text{NH}_4^+ + \text{NH}_3 + \text{NH}_2 + e$ should occur at 9.75 eV or 127.2 nm. A plot of the log of the photoionization efficiency minus the background ion count versus $\log (E-E_T)$ where E_T is the threshold of NH_4^+ is shown in Fig. 6. The least squares line fit to the two slopes intersects at exactly 127.2 nm, corresponding to a new channel for NH_4^+ formation. The decomposition of the tetramer to NH_4^+ should occur at 125.0 nm.

In the photoionization efficiency curve of NH_4^+ in Fig. 3, a change of slope is distinct at 125.0 nm. Similarly, there are distinct changes in slope of the photoionization efficiency curves of $(\text{NH}_4^+)\text{NH}_3$ and $(\text{NH}_4^+)(\text{NH}_3)_2$ shown in Figs. 7 and 8. The fact that fragmentation of higher polymers into smaller ions (involving loss of NH_2 and one or more NH_3 molecules) is predicted correctly by the appearance potentials of NH_4^+ and $(\text{NH}_3)_2\text{H}^+$ indicates that the observed thresholds are self consistent and suggest that they do not correspond to vibrationally excited ions.

In summary, the proton affinity of NH_3 has been determined by measuring the appearance potential of NH_4^+ formed to be 202.1 ± 1.3 kcal/mol at 0 K from decomposition of the ammonia dimer ion. The proton solvation energies by more than one ammonia have been determined by measuring the appearance potential of fragments from larger cluster ions. The appearance potential of the dimer ions formed from the neutral van der Waals dimer yields the binding energy of $\text{NH}_3^+-\text{NH}_3$ to be 18.1 ± 1.1 kcal/mole.

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TABLE I Energetics of proton solvation by NH_3

$$\text{NH}_4^+(\text{NH}_3)_n \rightleftharpoons \text{NH}_4^+(\text{NH}_3)_{n-1} + \text{NH}_3$$

<u>n,n-1</u>	THIS WORK	LITERATURE		THEORETICAL
	<u>ΔH° kcal mol⁻¹</u>	<u>ΔH°</u>	<u>ΔG°_{298}</u>	<u>ΔH°</u>
1,0	13.8 ± 1.4	18.4 ^a	6.3 ^a	28.1 ^e
		21.5 ^b	15.5 ^b	36.0 ^f
		24.8 ^c	17.1 ^c	27.6 ^g
		27.0 ^d	17.5 ^d	
			10.7 ^h	
2,1	6.4 ± 1.6		5.5 ^a	
		16.2 ^b	9.4 ^b	
		17.5 ^c	9.0 ^c	
		17.0 ^d	8.9 ^d	
			9.7 ^h	

a) Ref. 17

e) Ref. 18

b) Ref. 4

f) Ref. 19

c) Ref. 2

g) Ref. 16

d) Ref. 20

h) Ref. 3

FIGURE CAPTIONS

Fig. 1. Intensity of ions measured with the monochromator adjusted at zero order versus stagnation pressure: Δ $(\text{NH}_3)_3^+$, $\blacktriangle$ $(\text{NH}_3)_2\text{H}^+$, $\circ$ $(\text{NH}_3)_2^+$, $\bullet$ NH_4^+

Fig. 2. Photoionization efficiency of $(\text{NH}_3)_2^+$ normalized at 116.0 nm.

Fig. 3. Photoionization efficiency of NH_4^+ , $(\text{NH}_3)_2\text{H}^+$ and $(\text{NH}_3)_3\text{H}^+$ normalized at 116.0 nm.

Fig. 4. Energetics of the $(\text{NH}_3)_2^+$ system.

Fig. 5. Energetics of the protonated ammonia system.

Fig. 6. $\log(\sigma - \sigma_0)$ where σ = photoionization efficiency, σ_0 = background ion count versus $\log(E - E_T)$ where E_T = threshold energy of NH_4^+ .

Fig. 7. Log-log plot of the photoionization efficiency of $(\text{NH}_4^+)\text{NH}_3$ in the threshold region. E_T is the threshold energy of $(\text{NH}_4^+)\text{NH}_3$. Two limiting lines are drawn through the low energy points, establishing maximum errors for the $(\text{NH}_3)_n$ dissociation energy.

Fig. 8. Log-log plot of the photoionization efficiency of $(\text{NH}_4^+)(\text{NH}_3)_2$ in the threshold region. E_T is the threshold energy of $(\text{NH}_4^+)(\text{NH}_3)_2$. Two limiting lines are drawn through the low energy points, establishing maximum errors for the $(\text{NH}_3)_n$ dissociation energy.

Fig. 1

XBL 7712-10926

Fig. 2

XBL 7712-10928

Fig. 3

XBL 7712-10939

XBL 7712-10936

Fig. 4

XBL 7712-10940

Fig. 5

XBL 7712-10924

Fig. 6

Fig. 7

XBL 786-5242

Fig. 8

XBL 786-5243

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