Intracluster rearrangement of protonated nitric acid: Infrared spectroscopic studies of $H^+(HNO_3)(H_2O)_n$

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Infrared spectra of clusters of protonated nitric acid and water exhibit a marked change with cluster size, indicating that an intracluster reaction occurs with sufficient solvation. In small clusters, H_2O binds to a nitronium ion core, but at a critical cluster size the NO_2^+ reacts. A lower bound of 174 kcal/mol is found for the proton affinity of HNO_3.

INTRODUCTION

The large differences between gas phase and solution phase basicities highlight the dramatic effects of solvation on ion chemistry. Strong aqueous acids such as HNO_3 can possess a proton affinity in the gas phase that is higher than that of H_2O. By clustering water molecules sequentially to a protonated nitric acid, the structure and properties of the ion will evolve towards the solvated form. Investigations of these hydrated cluster ions can provide insights into microscopic aspects of solvation.

Protonation of nitric acid occurs in the liquid phase under nearly anhydrous conditions, e.g., in neat nitric acid and in concentrated sulfuric acid, by the reaction $H^+ + HNO_3 \rightarrow NO_2^+ + H_2O$.[1] Upon addition of water, the nitronium ion (NO_2^+) rapidly undergoes the reverse reaction and is therefore not present in aqueous solution.

Experimental[2,3] and theoretical[4,5] studies have concluded that gas phase protonated nitric acid $H_2NO_3^+$ possesses several isomers. The most stable form is a weakly bound complex of NO_2^+ and H_2O and, as in nonaqueous liquids, the most basic site is on the OH group. Cacace et al.[3] found evidence for a second isomer, $(HO)_2NO^+$, which lies 10–20 kcal/mol higher and is formed by the protonation of a terminal oxygen atom of HNO_3. Ab initio calculations[5] by Lee and Rice confirmed the structures and relative stability of the two isomers, but the computed proton affinity for nitric acid is 182 ± 4 kcal/mol, in disagreement with Cacace's ICR bracketing measurement of 168 ± 3 kcal/mol and closer to an earlier measurement[2] of 176 ± 7 kcal/mol. These values lead to large differences in the binding energy of the $NO_2^+(H_2O)$ complex (5–19 kcal/mol).

The existence of hydrated $H_2NO_3^+$ was inferred by Fehsenfeld et al., who studied the ion chemistry of HNO_3 in a flowing afterglow apparatus.[2] They observed rapid proton transfer from H_3O^+ to HNO_3, and attributed the decay of $H_2NO_3^+$ to its association with H_2O. However, they were unable to detect hydrated clusters of protonated nitric acid, and postulated a fast reaction $H^+(HNO_3)(H_2O) + H_2O \rightarrow H_3O^+(H_2O) + HNO_3$ that would destroy the association products and convert NO_2^+ to HNO_3. In an ab initio calculation, Grandinetti et al.[6] predicted that the lowest energy structure of

$H^+(HNO_3)(H_2O)$ is $NO_2^+(H_2O)_2$. Kay et al. formed the clusters $H^+(HNO_3)(H_2O)_n$ ($n = 1$–12) by ionization of neutral clusters in a beam[7] and attributed a minimum in the size distribution at $n = 4$ to the formation of solvated ion pairs in the neutral complexes, but made no conclusions regarding the ionic clusters.

We have investigated the clusters $H^+(HNO_3)(H_2O)_n$ for $n = 0$ to 4 by infrared vibrational predissociation spectroscopy. In this Communication, we present evidence for solvent-induced changes in the structure of protonated nitric acid.

EXPERIMENT

The apparatus has been described elsewhere,[8] and is briefly described here. UHP helium was seeded with HNO_3/H_2O vapor by passage over the surface of concentrated (70%) nitric acid at 0 °C. The $HNO_3/H_2O/He$ mixture at a total stagnation pressure of 1000 Torr was then pulsed into a small channel where a high voltage pulse was applied between two electrodes to initiate a glow discharge. The resulting ions underwent many thermal collisions as the gas flowed through the channel and expanded into the vacuum, promoting cooling and clustering. The ion chemistry in our source was similar to that of high pressure discharges, producing the most stable ions. The ions were mass analyzed by a time-of-flight (TOF) mass spectrometer. A pulsed tunable infrared laser, a LiNbO3 optical parametric oscillator[9] with 1.5 cm^{-1} resolution, was timed to excite clusters of a selected mass. Upon photon absorption, clusters could vibrationally predissociate. The resulting fragment ions were mass analyzed by a reflectron mass spectrometer. Infrared spectra were obtained by measuring the photofragment intensity as a function of the laser wavelength.

We typically generated $H^+(HNO_3)(H_2O)_n$ clusters with n ranging from 0 to 7, as well as $H_3O^+(H_2O)_n$ and small amounts of $NO^+(H_2O)_n$. We obtained the vibrational predissociation spectra of $H^+(HNO_3)(H_2O)_n$ clusters, with $n = 0$ to 4, in the range 2650–3850 cm^{-1}.

RESULTS

The infrared spectrum of protonated nitric acid ($n = 0$) had two distinct bands, one centered at 3626 cm^{-1}

TABLE I. Vibrational predissociation band centers for $H^+(HNO_3)(H_2O)_n$ in cm^{-1}.

|	H_3O^+ H bonded	HNO_3, ν_1 NO–H	H_2O, ν_1 Symmetric	H_2O, ν_3 Antisymmetric
$H^+(HNO_3)$			3626	3708,3716
$H^+(HNO_3)(H_2O)$			3635	3715
$H^+(HNO_3)(H_2O)_2$			3636	3716
$H^+(HNO_3)(H_2O)_3$	~2600, ~3000	3519,3550	3644	3717
$H^+(HNO_3)(H_2O)_4$	~2700, ~3000	3523,3550	3644	3717,3733
H_2O monomer			3657	3756
HNO_3 monomer		3551		

and the other a doublet with maxima at 3708 and 3716 cm^{-1} (Table I). These were redshifted by less than 50 cm^{-1} from the symmetric and antisymmetric stretching bands of the water monomer. The only predissociation process observed was

$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O. \tag{1}$$

The dissociation signal was very weak and exhibited a nonlinear dependence on laser intensity, indicating that the photodissociation arose from a multiphoton process.

Clusters of protonated nitric acid solvated by one or two water molecules, $H^+(HNO_3)(H_2O)_n$ ($n=1,2$), behaved like the unsolvated $H_2NO_3^+$, with a single water molecule evaporating upon vibrational excitation:

$$H^+(HNO_3)(H_2O)_n \rightarrow H^+(HNO_3)(H_2O)_{n-1} + H_2O. \tag{2a}$$
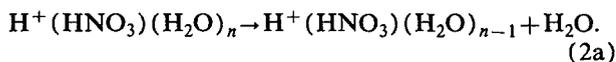
In both clusters, only two bands were observed in the OH stretch region, slightly redshifted from the water symmetric and antisymmetric stretches, respectively (Table I). The dissociation signal was much stronger than for $n=0$ and depended linearly on laser intensity. For $n=3$, two small features appeared in the 3550 cm^{-1} region.

For clusters $H^+(HNO_3)(H_2O)_n$ with $n \geqslant 2$, we observed the onset of a new photodissociation channel, loss of a nitric acid molecule,

$$H^+(HNO_3)(H_2O)_n \rightarrow H^+(H_2O)_n + HNO_3 \tag{2b}$$
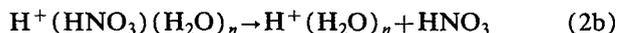
in competition with the water loss channel (2a). Although evaporation of nitric acid was a minor channel for $n=2$ predissociation, it was a major channel for $n=3$ and the dominant channel for $n=4$. The ratio of the nitric acid channel (2b) yield to the water channel (2a) yield was 1:8 for $n=2$, and 9:1 for $n=4$. In $n=3$, the yield depended on the band excited: it was 7:1 upon excitation in the 3550 cm^{-1} region and 2:1 in the 3600–3800 cm^{-1} region.

Three new bands were observed for the clusters $H^+(HNO_3)(H_2O)_3$ and $H^+(HNO_3)(H_2O)_4$ in addition to the two H_2O bands (Fig. 1). Two were close to 3550 cm^{-1}, the OH stretching frequency of the HNO_3 monomer. The third was a broad band at 2600–2700 cm^{-1}. A similar band at 2670 cm^{-1} was observed by Lee and co-workers in their studies of $H_3O^+(H_2O)_n$ clusters and assigned to the hydrogen-bonded OH stretches of the H_3O^+ ion.[10]

DISCUSSION

We can derive qualitative structural information about these clusters from their infrared spectra and photodissociation behavior. Protonated nitric acid, $H^+(HNO_3)$, has two redshifted H_2O stretch bands and dissociates directly into NO_2^+ and H_2O. Coupled with the absence of bands near 3550 cm^{-1}, we conclude that protonated nitric acid is a weakly bound complex $NO_2^+(H_2O)$, in agreement with earlier studies. The structure calculated by Lee and Rice[5] is a highly asymmetric top for which the symmetric H_2O stretching mode would be an a type band and the antisymmetric mode a b type band. This is consistent with the observed rotational contours, a single maximum at 3626 cm^{-1} and two closely spaced maxima at 3712 cm^{-1}.

The similarity in the spectra and the photoproducts of $H^+(HNO_3)$ and its hydrated clusters ($n=1,2$) indicates that the smaller hydrates are also complexes of an NO_2^+ ion core and H_2O ligands (Fig. 2). With additional ligands, the binding energy should be lower and the H_2O stretching modes less perturbed. This inference is confirmed by the stronger photodissociation signal and its linear power dependence, as well as the smaller redshift of the H_2O bands.

There is a striking difference in the properties of the larger clusters ($n=3,4$). The appearance of nitric-acidlike bands near 3550 cm^{-1} and the onset of dissociation releasing HNO_3 indicate that neutral HNO_3 exists intact in the clusters. The ~2650 cm^{-1} band and the bands in the 3600–3800 cm^{-1} region are evidence of H_3O^+ and H_2O,
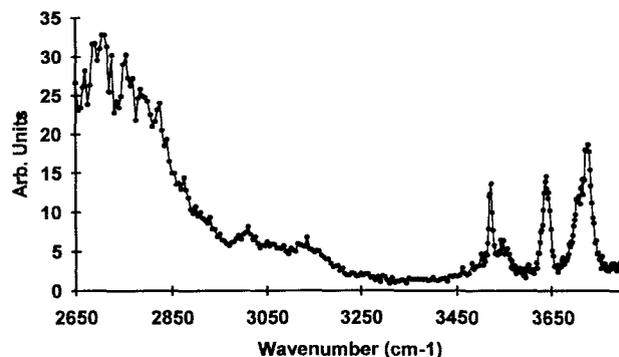

FIG. 1. Vibrational predissociation spectrum of $H^+(HNO_3)(H_2O)_4$. The ordinate is the $H_3O^+(H_2O)_3$ photofragment signal, with laser-independent background subtracted and normalized for laser intensity.

n = 1:

n = 4:

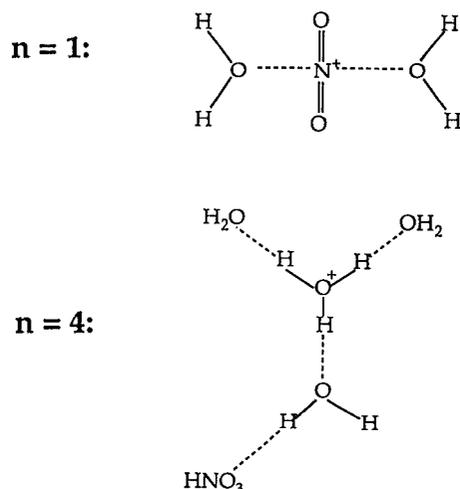FIG. 2. The proposed structures for $H^+(HNO_3)(H_2O)$ and $H^+(HNO_3)(H_2O)_4$.

respectively. We therefore conclude that the larger clusters are complexes of an H_3O^+ core surrounded by water ligands and a neutral HNO_3.

H_2O is more strongly bound than HNO_3 due to its more favorable hydrogen bonding,[2] suggesting that the first solvation shell in the $n=4$ cluster is occupied by water ligands with HNO_3 in the second shell, as depicted in Fig. 2. In both $n=3$ and $n=4$ clusters, channel (2b) dominates because the HNO_3 ligand is more likely to predissociate.

The wavelength dependence of the branching ratio in the $n=3$ cluster is surprising. HNO_3 evaporation is approximately three times more likely upon excitation of the HNO_3 band relative to excitation of the H_2O bands. This behavior suggests that the predissociation process is mode selective. However, it is more likely that two nearly isoenergetic isomers are present, one with a hydronium ion core, $H_3O^+(H_2O)_2(HNO_3)$, and the other with a nitronium ion, $NO_2^+(H_2O)_4$. The latter would absorb only at 3600–3800 cm^{-1} and would produce only H_2O fragments. The $H_3O^+(H_2O)_2(HNO_3)$ isomer would absorb at 3550 cm^{-1} as well, but would dissociate primarily by loss of HNO_3. A mixture of the two isomers would thus appear to have wavelength-dependent branching ratios.

Our results provide a lower limit on the proton affinity of nitric acid. From the nonlinear power dependence of the predissociation, we infer that dissociation requires at least two photons, and that the binding energy of $NO_2^+(H_2O)$ is >10.6 kcal/mol. Using known thermodynamic quantities[11,12] and a revised $\Delta \dot{H}_f$ for NO_2^+,[13] we can compute $\Delta \dot{H}_f$ for $H_2NO_3^+$ and hence the proton affinity of HNO_3. We find a lower limit on the proton affinity of 174 kcal/mol, which disagrees with the currently accepted value[3] of

168 kcal/mol, but agrees well with the earlier measurement of 176 kcal/mol by Fehsenfeld et al.[2] and the ab initio value of 182 kcal/mol.[5]

We found no evidence for the formation of the higher energy isomer $(HO)_2NO^+$ or its hydrates in our source. While this ion is covalently bound and may not predissociate upon photon absorption, the hydrates should. Møller–Plesset (MP2) calculations[5] predict that the (scaled) NO–H stretching frequencies lie near 3450 cm^{-1}, but no such bands were observed in any clusters.

In conclusion, we have observed the intracluster reaction $NO_2^+ + 2H_2O \rightarrow HNO_3 + H_3O^+$ upon sufficient solvation. The driving force for overcoming the intrinsic stability of gas phase NO_2^+ is the solvent stabilization of H_3O^+. This stabilization effect has also been observed in other studies.[14,15] Our technique provides a direct spectroscopic probe of solvent-induced phenomena in clusters; other systems are currently under investigation.

Note added in proof. The binding energy of $NO_2^+(H_2O)$ was recently measured directly and found to be 14.8 kcal/mol.[16]

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