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Formation of Nitric Acid by Structural Rearrangements of Gas-Phase Ionic Complexes of Ammonium Nitrate

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Abstract: A detailed study of nitric acid formation in gas-phase ionic aggregates of ammonium nitrate is reported. Fast-atom bombardment was used to sputter cationic ammonium nitrate complexes from neat ammonium nitrate crystals. The sputtered complexes are of the form $(NH_4NO_3)_nNH_4^+$ and have been detected in the range of $n = 1$–43. The formation of nitric acid from gas-phase cationic complexes of ammonium nitrate is shown to occur by a rearrangement of $NH_4^+(NO_3^-)NH_4^+$, the core ion of the first solvent shell. Metastable and collisional-activation dissociation spectra show that a completed first solvent shell exists when the core ion is solvated by the hydrogen bonding of six NH_4NO_3 molecules to the six available hydrogen atoms of the two ammonium ions, yielding $(NH_4NO_3)_7NH_4^+$. The metastable loss of HNO_3 occurs only from complexes with less than six ligands; a fully solvated core ion cannot rearrange. Collisional activation of larger complexes ($n > 7$), under multiple-collision conditions, induces sequential losses of NH_4NO_3 until an ion with $n < 7$ (incomplete first solvent shell) is formed, at which point rearrangement may occur and one nitric acid molecule may be lost.

Introduction

Nitric acid is formed in the earth's atmosphere by a number of important gas-phase reactions. Among these are the reaction of N_2O_5 with water on particle surfaces, the reaction of $ClONO_2$ with both water and HCl in polar stratospheric clouds,[1] and the oxidation of NO in photochemical fog.[2] The reaction of nitric acid with ammonia in the atmosphere produces ammonium nitrate, a significant component of atmospheric aerosols.[2] The reversible reaction

$$NH_3 + HNO_3 \rightleftarrows NH_4NO_3 \qquad (1)$$

has been studied under various simulated atmospheric conditions[3] in attempts to characterize the complex nature of ammonium nitrate aerosol formation and dissociation. Historically, the study of ammonium nitrate has been driven by its use in propellants and explosives. The scientific literature is rich with reports on all aspects of ammonium nitrate decomposition by combustion and dates back several centuries.[4]

The ability to generate large ionized aggregates of ammonium nitrate would enable the application of the powerful techniques available in multisector mass spectrometry to the study of ammonium nitrate decomposition. An early field-desorption study of inorganic ionic compounds showed that $(NH_4NO_3)NH_4^+$ could be directly desorbed from condensed-phase ammonium nitrate.[5] The laser-microprobe mass spectrum of ammonium nitrate aerosol also revealed the formation of the gas-phase $(NH_4NO_3)NH_4^+$ ion.[6] The study described herein made use of the simplicity of fast-atom bombardment[7] (FAB) of neat salts to directly sputter a wide range of gas-phase ionic ammonium nitrate complexes with the general formula $(NH_4NO_3)_nNH_4^+$, where $n = 1$–43. This technique greatly increases the number of ammonium nitrate units bound within each cluster ion.[8] Tandem mass spectrometry techniques such as mass spectrometry/mass spectrometry (MS/MS) and MS/MS/MS were then applied to study the dissociation of selected complexes under low-energy (metastable) and high-energy (collisional activation) conditions.

Unlike conventional FAB, where samples are dissolved in a solvent such as glycerol and sputtered as a matrix, this technique makes use of the fact that ionic compounds show a high yield of gas-phase ions when the neat crystals are sputtered by high-energy xenon atoms. Interferences from solvent ions and solvent/solute complexes are therefore avoided. It differs from secondary ion mass spectrometry (SIMS) only in the charge state of the impinging particle. The method has been used to study a number of inorganic compounds.[8–10]

The experimental results described here show that large ionic complexes of ammonium nitrate ($(NH_4NO_3)_nNH_4^+$, where $n \geq 7$) dissociate almost exclusively by losses of NH_4NO_3. Smaller complexes ($n < 7$), whether formed directly by sputtering or by the dissociation of large complexes, dissociate either by the loss of NH_4NO_3 or by a competitive reaction in which HNO_3 is lost through structural rearrangement. The loss of NH_3 is observed only after HNO_3 has been lost from an ion. In general, the evidence will show that large ammonium nitrate cluster ions dissociate in the following sequence: (1) loss of NH_4NO_3, (2) loss of HNO_3, and finally (3) loss of NH_3.

Experimental Section

Ammonium nitrate was evaporated from aqueous solution onto an aluminum plate affixed to the tip of a FAB probe. The solid sample was sputtered with high-energy xenon atoms generated by a saddle-field gun (Ion Tech, Ltd.) operated at 8 kV with an ion current of 1.5 mA. The Xe neutral current equivalent[11] was approximately 7 μA applied to a target area of 4 mm². The average kinetic energy of Xe atoms generated with this type of saddle-field gun is reported to be 6.6 keV.[11]

[●] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

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Mass spectra, metastable spectra, and collision-induced dissociation (CID) spectra[12] were obtained using a ZAB-2FQ (VG Analytical Ltd.) mass spectrometer. The ZAB-2FQ is a three-stage mass spectrometer with a magnetic sector, electric sector, and a collision-quadrupole/analyzer-quadrupole stage,[13] configured in that order. The first two sectors constitute a double-focusing, reverse-geometry instrument; the magnetic sector precedes the electric sector. MS/MS CID spectra were obtained by adjusting the magnetic field to transmit only the ion of interest. The mass-selected ion beam was focused on a collision cell located in the field-free region between the two sectors. The collision gas was helium and the helium pressure was adjusted to reduce the reactant-ion current by 70%. The electric sector was scanned to sequentially transmit CID fragment ions which were subsequently detected using an electron multiplier. MS/MS metastable spectra were obtained by the same method except that helium was evacuated from the collision cell. The product ions were formed by metastable reactions occurring during transit through the 1-m flight tube between the magnetic sector and electric sector.

MS/MS/MS spectra were obtained similarly to MS/MS spectra described above except that, after energy selection by the electric sector, a product ion of the first reaction was decelerated to a kinetic energy of 50 eV and focussed into the collision quadrupole. Xenon was used as the collision gas in the quadrupole; its pressure was adjusted to reduce the reactant-ion signal intensity by 50%. The analyzer quadrupole was scanned to sequentially transmit fragment ions produced by collision-induced dissociation. Ion detection was by electron multiplier.

The mass spectrometer was operated with an accelerating potential of 8 kV except when ions with a m/z ratio greater than 1750 were studied, in which case the instrument was operated at 5 kV. For CID and metastable spectra, the collector resolving slits were adjusted to achieve the minimum resolution to just resolve all fragment ions. All reported spectra are the result of cumulative signal addition of 50 to 200 scans, as required.

To determine if an MS/MS CID peak was coincident with a metastable peak, a potential was applied to the collision cell. The cell potential was varied until CID peaks were shifted and fully resolved from metastable peaks.[14] This technique was also used to identify consecutive reactions in MS/MS experiments.[10] MS/MS of $(NH_4NO_3)_nNH_4^+$ ions with $n > 19$ revealed interferences from metastable dissociations of larger cluster ions occurring in the first field-free region of the mass spectrometer (prior to the magnet).[15] These artifacts are typical for an extended cluster-ion series and they make qualitative measurements unreliable, although some general trends may still be confirmed with caution.

Results and Discussion

The Mass Spectrum of Sputtered Ammonium Nitrate. Figure 1, parts a and b, shows partial mass spectra of sputtered ammonium nitrate. Two series of ions are indicated. The first is a minor series with the general formula $(NH_4NO_3)_mNH_3NH_4^+$, where $m = 0, 1, 2,$ and 3 ($m = 0$, $NH_3NH_4^+$, is observed but not shown). The second, more persistent series of ions, has the general formula $(NH_4NO_3)_nNH_4^+$. This series exhibits a roughly exponential decrease in ion abundance ending with a stair-step decrease between the $n = 7$ and 8 ions. Additional stair-step decreases are seen between the $n = 12$ and 13 ions and the $n = 15$ and 16 ions. The series is observed to extend beyond the $n = 43$ species, inclusive (not shown). The ion abundance decreases nearly exponentially from $n = 18$ to 43 and there are no inflections in the ion abundance in this range. The distinctive steps in ion abundance between $n = 1$ and 18 suggest that structural changes occur at the points of inflection. Furthermore, the stair-step pattern observed as the number of NH_4NO_3 neutral units (n) increases suggests that solvent shells are being filled. It will be shown that when the ion size reaches $n = 7$, the first solvation shell is completed (closed).

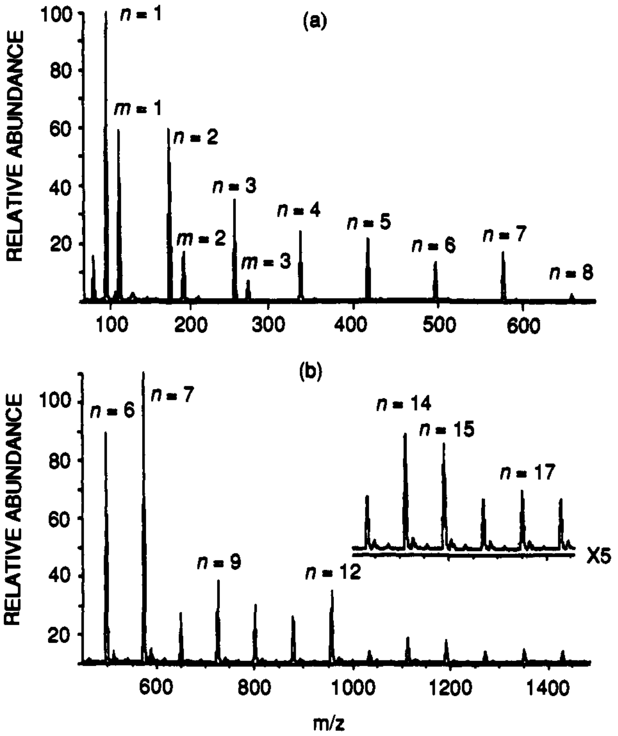

Figure 1. (a) Partial mass spectrum of sputtered ammonium nitrate. $(NH_4NO_3)_nNH_4^+$ ions and $(NH_4NO_3)_mNH_3NH_4^+$ ions are indicated. The peak to the left of the $n = 1$ peak is from $(NH_4NO_3)H^+$ which corresponds to the loss of NH_3 from $(NH_4NO_3)NH_4^+$. (b) High m/z region of the mass spectrum of sputtered ammonium nitrate showing sharp decreases in the average ion abundance at $n = 7$, 12, and 15.

Two dissociation pathways for $(NH_4NO_3)_nNH_4^+$ ions can be proposed based on the mass spectra shown in Figure 1. The first is loss of NH_4NO_3 via

$$(NH_4NO_3)_nNH_4^+ \rightarrow NH_4NO_3 + (NH_4NO_3)_{n-1}NH_4^+ \quad (2)$$

which is observed for all n-series ions. The second pathway involves the minor m-series aggregate ions in Figure 1a. The m-series ions may be formed by the loss of nitric acid (HNO_3) from n-series ions via the reaction

$$(NH_4NO_3)_nNH_4^+ \rightarrow HNO_3 + (NH_4NO_3)_mNH_3NH_4^+ \quad (3)$$

where $n = 1, 2, 3,$ or 4 and $m = n - 1$. Both reactions are integral to the overall decomposition mechanism of ammonium nitrate aggregates. Reaction 3 will be shown to be the dominant dissociation reaction for small ions and the primary source of nitric acid.

Unimolecular Dissociation and Collision-Induced Dissociation of Low-Molecular-Weight Aggregate Ions. Table 1 summarizes the metastable (unimolecular) dissociation spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 1$–10. The table shows that both reactions 2 and 3 are observed for each of the listed reactant ions. The loss of HNO_3 through reaction 3 is an important dissociation pathway for the $n = 1$–6 and 8 reactant ions. These reactions yield the $m = 0$–5 and 7 product ions, respectively. Collectively, the metastable dissociation spectra show a greater range of m-series ions than is seen in the mass spectrum (Figure 1a), where only the $m = 0$–3 ions are observed in significant abundance. For the metastable dissociation of the $n = 5$, 6, and 8 reactant ions, reactions 1 and 2 are competitive. Figure 2a shows the metastable dissociation spectrum of $(NH_4NO_3)_5NH_4^+$ as an example. Table 1 shows that as the cluster size increases from the $n = 5$ to the $n = 6$ ion (boldface) the dominant dissociation channel undergoes

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Table 1. Neutral Losses Observed from the Metastable Dissociation of Ammonium Nitrate Cluster Ions[a]

	reactant ion ($(NH_4NO_3)_nNH_4^+$)									
neutral loss	$n = 1$	$n = 2$	$n = 3$	$n = 4$	**$n = 5$**	**$n = 6$**	$n = 7$	$n = 8$	$n = 9$	$n = 10$
HNO_3	100	100	100	100	**100**	**23**	2	58	<1	<1
NH_4NO_3	<1	1	2	4	**23**	**100**	100	100	100	100

[a] Numbers indicate the abundance of the corresponding product ion as a percentage of the most abundant product ion.

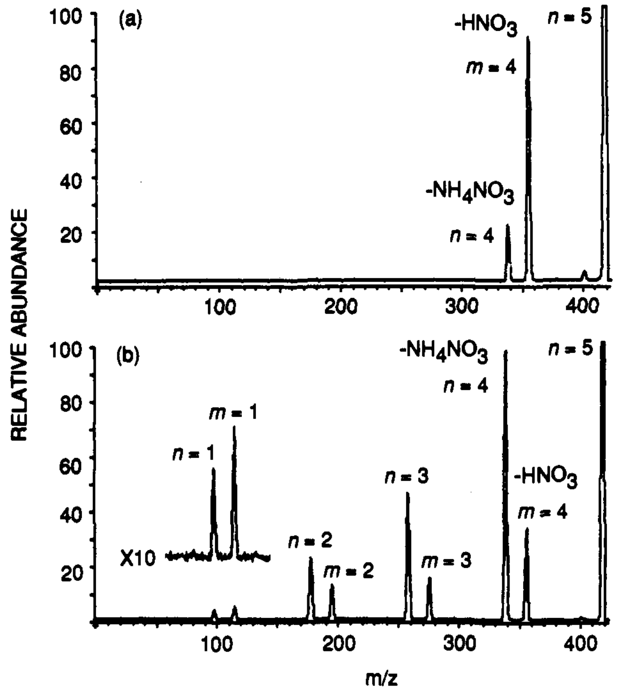
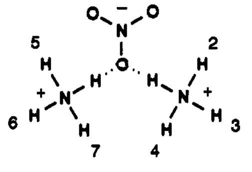


Figure 2. (a) Metastable spectra of $(NH_4NO_3)_5NH_4^+$ and (b) CID spectra of $(NH_4NO_3)_5NH_4^+$ under multiple-collision conditions. The $(NH_4NO_3)_nNH_4^+$ reactant ion and the $(NH_4NO_3)_nNH_4^+$ and $(NH_4NO_3)_mNH_3NH_4^+$ product ions are indicated. The mass-selected, reactant-ion signal is saturated in each spectrum.

a transition from loss of HNO_3 to loss of NH_4NO_3. Ions with $n \leq 5$ dissociate predominately by the loss of HNO_3, through reaction 3, and ions with $n \geq 6$ dissociate predominately by the loss of NH_4NO_3 through reaction 2. Ions with $n = 11$–20 (not shown) all dissociate predominantly by the metastable loss of NH_4NO_3 with the metastable loss of HNO_3 measured at less than 1% of that for NH_4NO_3. With the exception of the anomalous $n = 8$ ion, discussed later, the metastable loss of nitric acid is observed in significant abundance only from ions with $n < 7$.

The MS/MS, collision-induced dissociation (CID) spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 1$–10 are summarized in Table 2. Figure 2b shows an example for $(NH_4NO_3)_5NH_4^+$. Direct loss of HNO_3 is again an important reaction for the smaller cluster ions. The transition of the dominant reaction occurs as the cluster size increases from the $n = 3$ ion to the $n = 4$ ion. Ions with $n = 1$–4, in contrast to the metastable spectra, show an appreciable direct loss of NH_4NO_3 under high-energy conditions. In addition, the loss of NH_3 by the $n = 1$ ion is a purely collision-induced reaction and was not observed as a metastable dissociation product of that ion. Ions with $n = 11$–20 (not shown) all dissociate predominately by the loss of NH_4NO_3 with the direct loss of HNO_3 measured at less than 1% of that for NH_4NO_3. The $n = 8$ ion is again anomalous with respect to the trend of decreasing HNO_3 abundance with increasing reactant-ion size. As was observed for metastable reactions, with the same exception noted, a significant direct loss of nitric acid by CID reactions occurs only from $(NH_4NO_3)_nNH_4^+$ ions with $n < 7$.

Structures of Low-Molecular-Weight Ions. It is convenient to begin with the simplest member of the n-series ions, $n = 1$, $(NH_4NO_3)NH_4^+$. There are two reasonable structures for this ion. The first, **1**, has both ammonium cations bonded to one oxygen of the nitrate anion. This structure resembles the hydrogen-bonding network in room-temperature, condensed-phase ammonium nitrate.[16] In the second structure, **2**, each ammonium cation is bonded to a different oxygen of the nitrate anion. Both **1** and **2** can hydrogen bond to six NH_4NO_3 ligands, each structure forming an ion corresponding to $(NH_4NO_3)_7NH_4^+$, the proposed first solvent shell. The core ion (**1** or **2**) for this system must be



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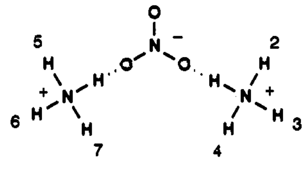

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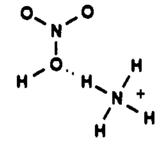
at the center of the first completed solvent shell. The MS/MS spectra of the $n = 1$ ion, summarized in Tables 1 and 2, do not provide sufficient information to distinguish between the two structures. Each can lose NH_3 and NH_4NO_3 by simple bond cleavage and each can lose HNO_3 only through a structural rearrangement (discussed in the next section). However, the loss of NH_3 from $(NH_4NO_3)NH_4^+$ (Table 2) results in the formation of $(NH_4NO_3)H^+$ which does undergo a structurally diagnostic dissociation.

Protonated ammonium nitrate, like its progenitor ion above, can exist as two structures, **3** and **4**. The difference, as above, is



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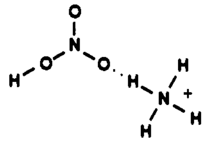

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that either one or two oxygen atoms of the nitrate anion are involved in external bonding. There are two experimental approaches to the problem and each involves the CID of $(NH_4NO_3)H^+$. In the first, protonated ammonium nitrate that has been directly extracted from the ion source is collisionally activated. The assumption is made that it is structurally identical with the ion formed by loss of NH_3 from $(NH_4NO_3)NH_4^+$ (**1** or **2**). The CID spectrum of $(NH_4NO_3)H^+$ is shown in Figure 3a. The dissociation products are NH_4^+, NO^+, NO_2^+, and a trace of $H_2NO_3^+$ at m/z 64. NH_4^+ can be formed from **3** or **4**. The floating-collision-cell technique (see the Experimental Section) shows that NO^+ is formed from NO_2^+ in a secondary reaction. NO_2^+ is a likely primary fragment only from **3**. The structurally diagnostic reaction is therefore

$$(NH_4NO_3)H^+ + He \rightarrow NO_2^+ + NH_4OH + He \quad (4)$$

because **4** cannot lose NH_4OH to form NO_2^+.

The second experimental approach reinforces this conclusion. This requires the MS/MS/MS spectrum of $(NH_4NO_3)NH_4^+$ and dispels any uncertainty concerning the origin of the secondary

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Table 2. Neutral Losses Observed from the Collisional Activation of Ammonium Nitrate Aggregate Ions under Multiple Collision Conditions[a]

	reactant ion ($(NH_4NO_3)_nNH_4^+$)									
neutral loss	$n = 1$	$n = 2$	n = 3	n = 4	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$
NH_3	100	<1	<1	<1	<1	<1	<1	<1	<1	<1
HNO_3	93	100	**100**	**93**	35	5	<1	13	<1	<1
NH_4NO_3	20	58	**74**	**100**	100	100	100	100	100	100
$HNO_3 + NH_4NO_3$			21	24	16	3	<1	<1	2	<1
$2NH_4NO_3$			20	48	48	33	48	24	94	22
$HNO_3 + 2NH_4NO_3$				15	13	7	4	<1	<1	1
$3NH_4NO_3$				10	23	21	32	21	43	65
$HNO_3 + 3NH_4NO_3$					5	5	8	1	<1	<1
$4NH_4NO_3$					3	9	20	11	32	27
$HNO_3 + 4NH_4NO_3$						2	4	3	3	<1
$5NH_4NO_3$						1	7	6	19	27
$HNO_3 + 5NH_4NO_3$							1	1	3	2
$6NH_4NO_3$							<1	1	8	10
$HNO_3 + 6NH_4NO_3$								<1	1	2
$7NH_4NO_3$								<1	2	4

[a] Numbers indicate the abundances of the corresponding product ions as a percentage of the most abundant product ion.

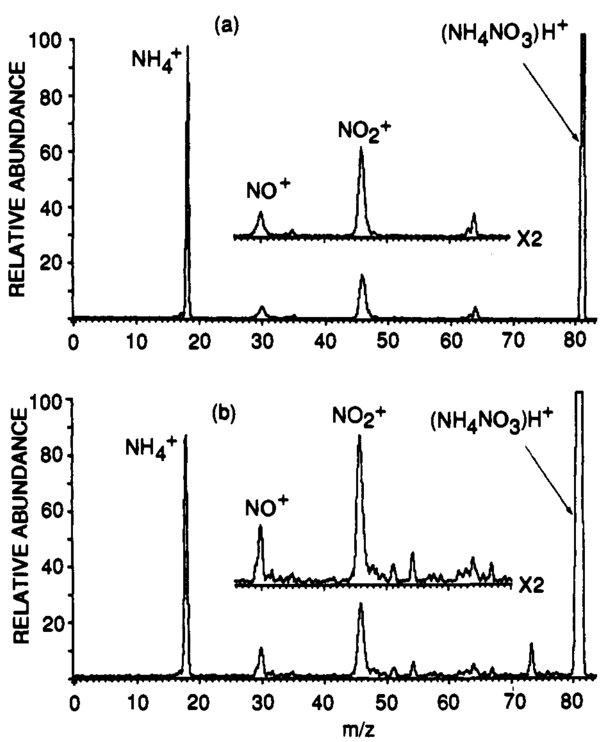

Figure 3. (a) MS/MS CID spectrum of protonated ammonium nitrate, $(NH_4NO_3)H^+$, that was extracted from the ion source. (b) MS/MS/MS CID spectrum of $(NH_4NO_3)H^+$ that was formed by the collision-induced loss of NH_3 from $(NH_4NO_3)NH_4^+$.

reactant ion. The first of two consecutive reactions produces $(NH_4NO_3)H^+$ by collisional activation of $(NH_4NO_3)NH_4^+$ via

$$(NH_4NO_3)NH_4^+ + He \rightarrow (NH_4NO_3)H^+ + NH_3 + He \quad (5)$$

The selected product ion, $(NH_4NO_3)H^+$, then undergoes CID in a second collision region. The resulting spectrum is shown in Figure 3b. The major product ions are seen to be identical with those observed in the MS/MS spectrum in Figure 3a and the structurally diagnostic reaction is again loss of NO_2 by reaction 4. From this evidence, it can be concluded that the structure of protonated ammonium nitrate, $(NH_4NO_3)H^+$, must correspond to structure 3. Finally, by extension, the structure of the $(NH_4NO_3)NH_4^+$ reactant ion that loses NH_3 to form 3 must be **1**.

In addition to the experimental evidence, the structures proposed are supported by studies showing that the OH oxygen of HNO_3 is the most basic oxygen and therefore is the most likely site for the protonation of nitric acid.[17] An *ab initio* study of the $O_2NOH{\cdots}NH_3$ hydrogen bond between HNO_3 and NH_3 has shown that the Mulliken charge density on the OH oxygen makes it significantly more negative than the other two oxygen atoms.[18] This also suggests that one of the hydrogen atoms in **1** may be effectively fully transferred to the oxygen of the nitrate anion. This would result in one of the strongest reported "nonionic" hydrogen-bonded complexes,[18] that of ammonia and nitric acid. The additional ammonium ion would be hydrogen bonded to the complex at the O–H oxygen. It is also necessary to consider that the complex may be a resonant hybrid with equivalent bonds between the ammonium ions and one oxygen of the nitrate anion. The atom connectivity is the same in all cases and structure **1** is arbitrarily shown with both NH_4^+ ions hydrogen bonded to one oxygen of the nitrate anion.

The Formation of Nitric Acid by the Rearrangement of Low-Molecular-Weight Ions. HNO_3 cannot be lost from **1**, whether it is fully or partially solvated, by simple bond breaking. Nevertheless, it is clear that ions with $n < 7$ do lose HNO_3 readily. Both metastable dissociation reactions (Table 1 and Figure 2a) and collision-induced dissociation reactions (Table 2 and Figure 2b) result in a direct loss of HNO_3 from these precursor ions. There is a significant difference, however, in the relative yields of HNO_3 and NH_4NO_3 from metastable reactions versus collision-induced reactions. That is, for ions with $n = 1$–6, the ratio of the product-ion abundance resulting from the direct loss of HNO_3 to the product-ion abundance resulting from the direct loss of NH_4NO_3 is much greater for metastable dissociation than it is for collision-induced dissociation. For example, Table 1 shows that the ratios $((n\text{-}HNO_3)/(n\text{-}NH_4NO_3))$ for metastable losses are >100/1, 100/1, 50/1, 25/1, 4.3/1, and 0.23/1 for reactant ions with $n = 1$–6, respectively. Table 2 shows that the product ion ratios for CID of the same ions are 4.6/1, 1.7/1, 1.4/1, 0.9/1, 0.35/1, and 0.05/1. In each case production of HNO_3 is considerably less favored for CID than for metastable dissociations. This strongly suggests that HNO_3 is lost by a dissociative rearrangement.

Molecular (or ionic) rearrangements are relatively low energy processes[19] and therefore tend to dominate metastable (low internal energy) spectra. On the other hand, rearrangements have low frequency factors and consequently low rate constants. They therefore tend to be less important in CID (high internal energy) spectra in which reactions with high rate constants such

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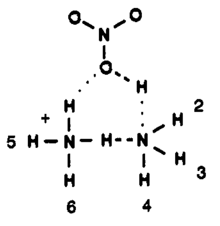
as simple bond cleavages (loss of NH_4NO_3) dominate.[20] The observations described above can be explained in terms of this argument. Structure **5** is a proposed transition-state structure



5

for the loss of HNO_3 by the rearrangement of $(NH_4NO_3)_nNH_4^+$ ions with $n < 7$ (bonds breaking, ···, bonds forming, --). This transition-state structure is consistent with the observations that nitric acid is lost in significant abundance only from $(NH_4NO_3)_nNH_4^+$ ions with $n < 7$. The rearrangement of **1** through a transition-state structure such as **5** requires that at least one hydrogen-bonding site be available to form a bond with the nitrogen atom of an ammonium ion. For this reaction to occur, the number of NH_4NO_3 *ligands* must be five or less. A smaller number of ligands will lead to an increased frequency factor for rearrangement, in agreement with the increase in the HNO_3/NH_4NO_3 ratio as n decreases in Table 1.

In further support of the proposed rearrangement is the observation that only one nitric acid molecule is lost by the collisional activation of n-series ions under multiple-collision conditions. Consecutive losses of HNO_3 are not observed from any $(NH_4NO_3)_nNH_4^+$ ion in Table 2. This would indicate that the loss of nitric acid takes place only through a rearrangement of the core ion, (NH_4NO_3), and does not involve (mechanistically) any ligands to which it is hydrogen bonded. That is, the ligands themselves do not rearrange.

It is instructive to examine the m-series ions, which arise from the loss of HNO_3 from n-series ions. This enables a closer look at the structure of the ion that is formed by the elimination of HNO_3 and confirms that no further loss of HNO_3 takes place. The experimental approach is the same as that used in the elucidation of structure **1**. The assumption is made that m-series ions ($(NH_4NO_3)_mNH_3NH_4^+$) extracted from the ion source are structurally the same as m-series ions formed by the loss of HNO_3 from n-series ions ($(NH_4NO_3)_nNH_4^+$). Figure 4a shows the MS/MS CID spectrum of mass-selected $(NH_4NO_3)_3NH_3NH_4^+$. The most abundant dissociation product is formed by the loss of NH_3 via

$$(NH_4NO_3)_3NH_3NH_4^+ + He \rightarrow NH_3 + (NH_4NO_3)_3NH_4^+ + He \quad (6)$$

to form the $n = 3$ ion. Additional products are formed by losses of NH_4NO_3 and $NH_4NO_3NH_3$. The other series m ions (m = 1–3), extracted from the ion source, show a similar pattern of neutral losses. All show the loss of a single ammonia molecule and none dissociate by the loss of nitric acid.

The use of MS/MS/MS eliminates any ambiguity associated with the above assumption concerning the origin of the reactant ion. Figure 4b shows the dissociation spectrum of collisionally activated $(NH_4NO_3)_3NH_3NH_4^+$ that was formed by the metastable dissociation of $(NH_4NO_3)_4NH_4^+$ in the second field-free region of the mass spectrometer. The overall reaction sequence is

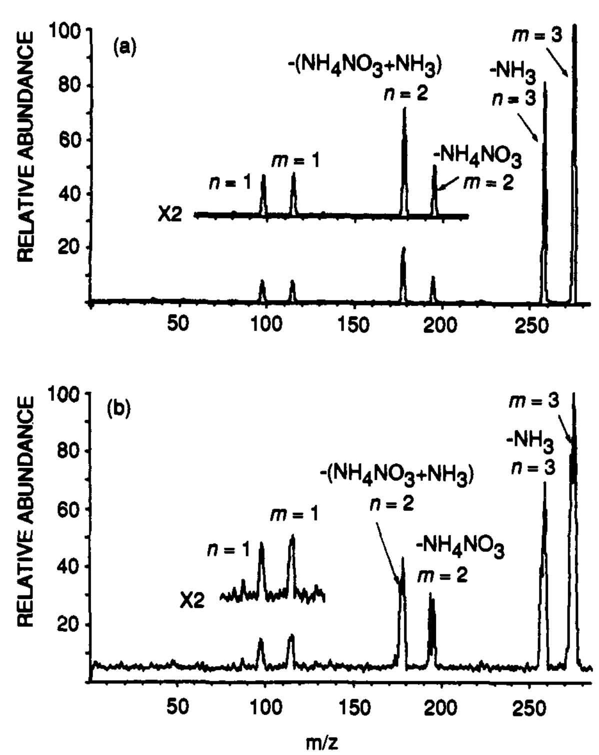


Figure 4. (a) The MS/MS CID spectrum of $(NH_4NO_3)_3NH_3NH_4^+$ that was extracted from the ion source. (b) The MS/MS/MS CID spectrum of $(NH_4NO_3)_3NH_3NH_4^+$ that was formed by the metastable loss of HNO_3 from $(NH_4NO_3)_4NH_4^+$.

$$(NH_4NO_3)_4NH_4^{+\bullet} \rightarrow HNO_3 + (NH_4NO_3)_3NH_3NH_4^+ \quad (7)$$

a metastable reaction occurring between the magnet and the electric sector, and followed by

$$(NH_4NO_3)_3NH_3NH_4^+ + Xe \rightarrow NH_3 + (NH_4NO_3)_3NH_4^+ + Xe \quad (8)$$

one of the subsequent reactions that take place by low-energy collisional activation in the collision quadrupole. All m-series ions formed from n-series ions by loss of HNO_3 show the subsequent loss of a single ammonia molecule and no detectable loss of HNO_3.

The bonds that are formed and broken in the transition state structure shown as **5** are bonds within the $NH_4^+NO_3^-NH_4^+$ core ion only. Bonds to or within the solvating NH_4NO_3 ligands are not involved in the rearrangement. The solvation of structure **1** is by NH_4NO_3 ligands that are strongly associated ion pairs. They likely play no role in the mechanism of the rearrangement process except to effect the frequency factor. Ligands are always lost as intact ion pairs and, as pointed out in Table 2, are sequentially lost through multiple collisions. The rearrangement of **1** through **5**, in addition to forming nitric acid, changes the core ion to $NH_3NH_4^+$, from which no further rearrangement is observed.

The Anomalous n = 8 Ion. As mentioned earlier the $n = 8$ ion is anomalous with respect to the trend of decreasing HNO_3 loss with increasing ion size in both metastable and CID spectra (Tables 1 and 2). One possible explanation stems from the likelihood that there are many isomers for the $n = 8$ species. While this is true for the other aggregate ions discussed here, its importance for this ion is magnified by the fact that most $n = 8$ ions dissociate rapidly to form the very stable $n = 7$ ion by the metastable loss of one NH_4NO_3 molecule. This is evident in the mass spectrum in Figure 1 where the abundance of the $n = 8$ ion is even less than that for the $n = 9$ ion.

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[20] Beynon, J. H.; Gilbert, J. R. *Application of Transition State Theory to Unimolecular Reactions*, Wiley: New York, 1984. Wagner, W.; Heimbach, H.; Levsen, K. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 125–142.

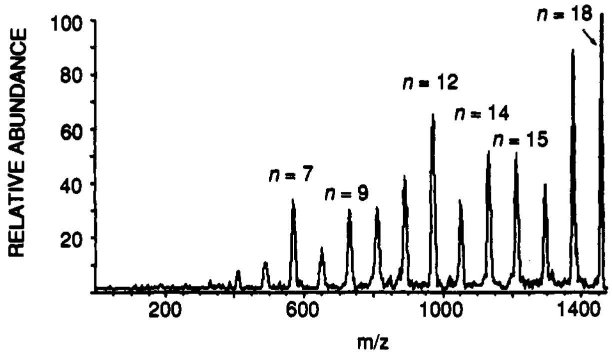

Figure 5. The CID spectrum of $(NH_4NO_3)_{18}NH_4^+$. The $(NH_4NO_3)_n$-NH_4^+ product ions are indicated. The $n = 7$ and 12 ions show enhanced abundances when compared to their $n + 1$ and $n - 1$ neighbor ions. The $n = 14$ and 15 ions may both show enhanced abundance.

It would be expected that one isomer of the $(NH_4NO_3)_8NH_4^+$ ion would have a structure based on the model proposed here. The model requires that the $n = 8$ species correspond to the beginning of a new solvent shell. It would be a fully solvated structure **1** with an additional NH_4NO_3 unit hydrogen bonded to another NH_4NO_3 at any one of the occupied sites from 2 to 7. This hydrogen bonded NH_4NO_3 unit, farthest from the charge center, is the most weakly bonded ligand and therefore the most readily lost. This is consistent with the low abundance of the $n = 8$ species in the MS/MS spectra and the MS/MS tables presented here.

What is proposed is that the $n = 8$ ions sampled directly in an MS/MS experiment have a relatively low population of ions in the structural configuration described above, because a large percentage of such ions will have undergone metastable dissociation in the approximately 13 μs of ion flight time between the ion source and the collision cell. If this reasoning is correct, the population of $n = 8$ ions that is sampled would contain an inordinately large percentage of ions in other isomeric configurations; these then are the ions that are observed to lose HNO_3. The latter may be a series of chain-like structures that would have vacant hydrogen-bonding sites or may be a series of ions formed by the hydrogen bonding of NH_4NO_3 ion pairs to one or both of the available oxygen atoms of the nitrate anion in structure **1**. It should also be noted that the more stable $n = 7$, 9, and 10 ions (Tables 1 and 2) each show *some* loss of HNO_3 (<1%) and therefore, according to the model proposed, must also exist as other isomers. The difference is that, for these ions, the population of ions conforming to the model of structure **1** is much greater than the population of those that do not.

Unimolecular Dissociation and Collision-Induced Dissociation of High-Molecular-Weight Ions. An examination of the CID spectra of larger $(NH_4NO_3)_nNH_4^+$ ions returns to a point suggested earlier: that the stair-step decreases in ion abundances observed in the mass spectrum are the consequences of structural changes that occur at those transitions. If this is true, then those structural changes should be reflected in the relative abundances of fragment ions produced by gas-phase collisional activation of $(NH_4NO_3)_nNH_4^+$ ions. For example, the mass spectrum of sputtered ammonium nitrate (Figure 1) shows ion-abundance decreases at $n = 7$, 12, and 15. If these breaks in the ion-abundance distribution represent transitions from more stable configurations to less stable configurations as the cluster size increases, then the CID spectrum of a large cluster ion, say $n = 18$, should show enhanced abundances (or step increases) for fragment ions with $n = 15$, 12, and 7 as fragment ion size decreases and transitions are made from less stable to more stable configurations.

This is precisely what is observed in the CID spectrum of $(NH_4NO_3)_{18}NH_4^+$ shown in Figure 5. Both the $n = 7$ and 12 fragment ions show significantly enhanced relative abundances with respect to their nearest-neighbor ions, $n + 1$ and $n - 1$. The $n = 15$ fragment ion shows minor enhanced abundance with respect to its $n + 1$ neighbor but it appears that the $n = 14$ fragment ion may also exhibit some anomalously high abundance. Table 3 summarizes the CID spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 7$–19. The $n - 1$ fragment ion is the most abundant product ion from all the reactant ions listed in Table 3; but it can be shown that in each case the reaction producing the $n - 1$ product ion by the loss of NH_4NO_3 has a large metastable component. All other product ions are formed by CID with no detectable metastable components. The relative abundances of the $n = 12$ and 7 product ions are shown in boldface. In every case, except when an $n - 1$ product ion is an adjacent ion, the $n = 12$ and 7 product ions demonstrate enhanced abundances over nearby ions.

Several conclusions can be drawn from the data in Table 3. First, $(NH_4NO_3)_nNH_4^+$ ions all undergo multiple losses of NH_4NO_3 to yield all possible $(NH_4NO_3)_nNH_4^+$ product ions. There are no missing product ions in this series and no product ions in this series are observed with a very low relative abundance. Second, and less obvious, there is no indication that the loss of a particular neutral ammonium nitrate cluster, $(NH_4NO_3)_n$, occurs preferentially.[21] This is only observed for the $n - 1$ product ions and these are formed by the loss of a single ammonium nitrate molecule. Third, as noted above, the $n = 7$ and 12 ions exhibit unusually high relative abundances when produced from any of the reactant ions in Table 3. This is consistent with the mass spectrum (Figure 1). Moreover, it demonstrates that the high relative abundances of these species are unequivocally the result of their gas-phase stabilities.

One further observation concerning the collisional activation of sputtered ammonium nitrate clusters consolidates the discussions of both the loss of HNO_3 from low-molecular-weight ions and the loss of NH_4NO_3 from high-molecular-weight ions. The CID spectra of high-molecular-weight $(NH_4NO_3)_nNH_4^+$ ions consistently show that the predominate reactions involve losses of NH_4NO_3 via

$$(NH_4NO_3)_nNH_4^+ + He \rightarrow (n-k)NH_4NO_3 + (NH_4NO_3)_kNH_4^+ + He \quad (9)$$

where $k = n - 1, n - 2, n - 3, ..., 0$. The products can arise from a single-step reaction or from multiple-step reactions. However, when k is less than 5, the loss of HNO_3 occurs as a subsequent reaction of the fragment ions and is competitive with further loss of NH_4NO_3 from those same fragment ions.

As an example, the CID spectrum of $(NH_4NO_3)_{10}NH_4^+$ is shown in Figure 6. Fragment ions with $n = 9$–2 are formed by losses of NH_4NO_3 under multiple collision conditions. But, with the appearance of smaller fragment ions ($n \leq 5$), m-series product ions, formed by the loss of HNO_3 from the n-series fragment ions, are detected. This pattern is observed for all $(NH_4NO_3)_nNH_4^+$ ions, including those with $n > 20$, given a sufficient number of collisions and an adequate signal-to-noise ratio. In Table 2 it was shown that direct loss of HNO_3 through collisional activation of ions with $n \leq 5$ was competitive with the direct loss of NH_4NO_3. In Figure 6 it is demonstrated that a high-molecular-weight reactant ion, in this case $(NH_4NO_3)_{10}NH_4^+$, upon losing a sufficient number of NH_4NO_3 molecules will form $(NH_4NO_3)_nNH_4^+$ ions with $n \leq 5$ that subsequently lose nitric acid.

Conclusions

This study focussed on the mechanism of the formation of nitric acid from ionic aggregates of ammonium nitrate. The experimental evidence established that (1) the first important structural transition occurs at the $(NH_4NO_3)_7NH_4^+$ ion, (2) only ions with $n < 7$ dissociate by the direct loss of nitric acid, (3) the

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[21] Doyle, R. J., Jr.; Campana, J. E. *J. Phys. Chem.* **1985**, *89*, 4251–4256. Campana J. E.; Doyle, R. J., Jr. *J. Chem. Soc. Chem. Commun.* **1985**, *2*, 45–46.

Table 3. Product Ions Formed by Collisional Activation of Sputtered Ammonium Nitrate Cluster Ions ($(\mathrm{(NH_4NO_3)_nNH_4^+})$) under Multiple Collision Conditions[a]

reactant	product ion ($\mathrm{(NH_4NO_3)_nNH_4^+}$)														
ion, n =	n = 19	n = 18	n = 17	n = 16	n = 15	n = 14	n = 13	**n = 12**	n = 11	n = 10	n = 9	n = 8	n = 7	n = 6	n = 5
7													**R**	100	48
8												R	**100**	24	21
9											R	100	**94**	43	32
10										R	100	22	**65**	27	27
11									R	100	41	23	**55**	14	17
12								**R**	100	36	36	23	**49**	19	14
13							R	**100**	20	19	22	12	**35**	16	11
14						R	100	**81**	48	47	53	27	**73**	31	19
15					R	100	24	**70**	49	43	33	22	**52**	16	9
16				R	100	37	20	**65**	39	39	36	18	**39**	15	10
17			R	100	46	41	20	**67**	37	34	28	13	**43**	10	6
18		R	100	42	58	58	39	**74**	47	37	33	19	**35**	11	8
19	R	100	61	47	73	81	32	**95**	55	55	48	26	**45**	23	18

[a] Numbers indicate the abundance of a product ion as a percentage of the most abundant product ion. The reactant ion is designated by R. Only ions formed by losses of $\mathrm{NH_4NO_3}$ are listed in this table.

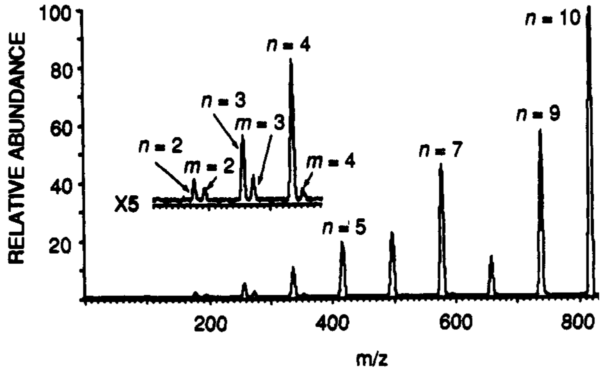

Figure 6. The CID spectrum of $\mathrm{(NH_4NO_3)_{10}NH_4^+}$. The $\mathrm{(NH_4NO_3)_n}$-$\mathrm{NH_4^+}$ and $\mathrm{(NH_4NO_3)_mNH_3NH_4^+}$ product ions are indicated. The loss of $\mathrm{HNO_3}$ is observed in significant abundance from product ions with $n \leq 5$ and results in the formation of the m-series ions.

loss of nitric acid is predominantly a metastable process, and (4) a nitric acid molecule is lost only once in the chain of dissociation steps. The first two observations indicate that the $n = 7$ ion is the first completely solvated shell and that the loss of nitric acid occurs only when at least one ligand is stripped from the first solvation shell. The final two observations indicate that nitric acid is formed by a rearrangement of the core ion.

The core ion is the first member of the n-series ions, $\mathrm{(NH_4NO_3)NH_4^+}$. Its structure is established as **1** (unsolvated) through the tandem MS experiments described in the preceding section. The metastable dissociation of $\mathrm{(NH_4NO_3)NH_4^+}$ occurs by the loss of $\mathrm{HNO_3}$; the metastable loss of $\mathrm{NH_4NO_3}$ is insignificant. Structure **1** has six hydrogen atoms available for hydrogen bonding to six $\mathrm{NH_4NO_3}$ ligands. A fully solvated structure **1** has the general formula $\mathrm{(NH_4NO_3)_7NH_4^+}$. Ligands are seen to be lost as $\mathrm{NH_4NO_3}$ ion pairs. The ionic mechanism for the formation of nitric acid by proton transfer is through a rearrangement of the core ion through the transition-state structure proposed as structure **5**.

The structural configurations of the larger $\mathrm{(NH_4NO_3)_nNH_4^+}$ ions ($n > 7$) are unlikely to be resolved satisfactorily from the types of experiments carried out in this study. High-molecular-weight ions ($n > 7$) dissociate predominantly by the consecutive losses of $\mathrm{NH_4NO_3}$. Direct loss of $\mathrm{HNO_3}$ is unimportant from large ions. The ion chemistry leading to the formation of $\mathrm{HNO_3}$ begins only when a sufficient number of $\mathrm{NH_4NO_3}$ units have been lost to form a fragment ion with $n \leq 5$. At this point the loss of nitric acid by core-ion rearrangement becomes competitive with the loss of $\mathrm{NH_4NO_3}$ that occurs by simple bond breaking. The sequence of consecutive dissociations of high-molecular-weight ions is (1) loss of $\mathrm{NH_4NO_3}$, (2) loss of $\mathrm{HNO_3}$, and (3) loss of $\mathrm{NH_3}$.

This is not the first time that the influence of a solvent on intracluster reactions has been noted. Solvent effects have been observed for the dissociation of protonated acetone cluster ions. The presence of water was found to inhibit the dehydration of the cluster ions by blocking a site required for hydrogen transfer.[22] The reaction rates of intramolecular ion–molecule reactions within methyl halide cluster ions were shown to be dependent on the number of methyl halide solvent molecules present.[23] In a study of protonated methanol clusters, it was observed that the unimolecular loss of methanol monomers occurred for all cluster sizes but that the unimolecular loss of $\mathrm{H_2O}$ occurred only from the protonated dimer, a situation somewhat similar to that reported here.[24]

Finally, the most important conclusion resulting from this study is the identification of the dissociative rearrangement responsible for the formation of nitric acid from small cationic clusters of ammonium nitrate. High-molecular-weight ions must dissociate to form an ion with $n \leq 5$ in the configuration of **1** before a loss of $\mathrm{HNO_3}$ becomes facile. Collisional activation of large complexes, under multiple-collision conditions, induces sequential losses of $\mathrm{NH_4NO_3}$ until an incomplete first solvent shell is formed; at which point rearrangement through structure **5** may occur and one nitric acid molecule may then be lost.

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(22) Tzeng, W. B.; Wei S.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6035–6040.

(23) Garvey, J. F.; Bernstein, R. B. *J. Phys. Chem.* **1986**, *90*, 3577–3583.

(24) Morgan, S.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2867–2870.