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Formation of Nitric Acid from Gas-Phase Ionic Complexes of Ammonium Nitrate

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The sputtering of condensed-phase ammonium nitrate by high-energy xenon atoms (fast-atom bombardment[1]) results in the desorption of ionic ammonium nitrate complexes of the form $(NH_4NO_3)_nNH_4^+$ where $n = 1, 2, 3, ..., >25$. Mass spectra and MS/MS experiments[2] show that a completed solvent shell exists when the first member of the series $NH_4^+(NO_3^-)NH_4^+$ is fully solvated by the hydrogen-bonding of six NH_4NO_3 molecules to the six available hydrogen atoms of the two ammonium ions. The metastable loss of a nitric acid molecule occurs from complexes with less than six ligands and is shown to occur by the rearrangement of the cluster core.

Figure 1 shows a partial mass spectrum[3] of sputtered ammonium nitrate. The persistent series of cluster ions has the general formula $(NH_4NO_3)_nNH_4^+$. The series shows a roughly exponential decrease in ion abundance ending with a stair-step decrease between the $n = 7$ and the $n = 8$ ions, suggesting that a significant structural change occurs at this point. A minor series of ions has the general formula $(NH_4NO_3)_mNH_3NH_4^+$. The m series ions are formed by the loss of nitric acid (HNO_3) from n series ions via the reaction

$$(NH_4NO_3)_nNH_4^+ \rightarrow HNO_3 + (NH_4NO_3)_mNH_3NH_4^+ \quad (1)$$

where $n = 2$, 3, or 4 and $m = n - 1$.

This is confirmed by MS/MS of the series n ions. Figure 2a–c shows the metastable (unimolecular) dissociation spectra of the $n = 5$, 6, and 7 ions. The spectra show not only that reaction 1 occurs, but also that it is competitive with the loss of NH_4NO_3 via

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

where $n = 5$, 6, or 7 for both reactions 1 and 2. Spectra of $n = 5$ and $n = 6$ ions (Figure 2a and b) show the transition of the dominant reaction from reaction 1 to reaction 2 as the cluster size increases. Metastable spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 1$–20 show that ions with $n < 5$ dissociate almost exclusively by reaction 1 and ions with $n > 6$ dissociate almost exclusively by reaction 2.

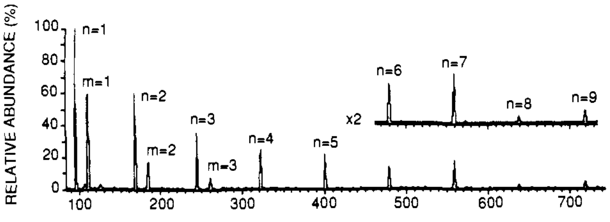

Figure 1. Partial mass spectrum of sputtered ammonium nitrate. $(NH_4NO_3)_nNH_4^+$ ions and $(NH_4NO_3)_mNH_3NH_4^+$ ions are indicated.

The MS/MS collision-induced dissociation (CID) spectra of the $n = 5$, 6, and 7 ions are shown in Figure 2d–f. It is seen that for $n = 5$ (Figure 2d), high-energy collisions[4] result in the dominance of reaction 2 over reaction 1, in contrast with the lower-energy metastable reactions where reaction 1 dominates (Figure 2a). For $n = 6$ (Figure 2e), the direct loss of HNO_3 through collisional activation represents a minor dissociation pathway compared to its greater relative abundance observed under metastable conditions (Figure 2b). At $n = 7$, both CID (Figure 2f) and metastable (Figure 2c) spectra show insignificant direct loss of HNO_3. CID spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 1$–20, in contrast with the metastable spectra, show that reaction 2 (direct loss of NH_4NO_3) is significant or dominant for all ammonium nitrate clusters under high-energy conditions.

CID spectra of $(NH_4NO_3)_nNH_4^+$ ions with $n = 1$–6 (Figure 2d, for instance) show that when nitric acid is lost directly from a reactant ion, only one HNO_3 molecule is lost. Consecutive loss of HNO_3 is not observed. CID spectra of those ions with $n = 7$–25 (Figure 2f, for example) show that when consecutive losses of NH_4NO_3 lead to the formation of a product ion with $n < 7$, loss of HNO_3 may occur once. Subsequent dissociative reactions of these CID products include further losses of NH_4NO_3 or the direct loss of NH_3 followed by further losses of NH_4NO_3.

The stair-step decrease in ion abundance in the mass spectrum (Figure 1) as n becomes greater than 7 was noted above. In addition, the $n = 7$ ion is produced in enhanced abundance by collisional activation, under multiple-collision conditions, of all ions with $n = 8$–20 (not shown). The later observation indicates that the enhanced abundance of the $n = 7$ ion is not a consequence of sputtering conditions but is a function of the inherent stability of the gas-phase ion with respect to all other ions in the distribution. Both observations strongly suggest that a filled solvent shell is achieved at $n = 7$. The simplest structure that fits this criterion is the fully solvated $n = 1$ ion $(NH_4NO_3)_nNH_4^+$ (**1**). The numbered hydrogens indicate sites available for hydrogen-bonding to six NH_4NO_3 molecules, all equivalent, for a total of seven units. Clearly, nitric acid cannot be lost from this structure without rearrangement. In fact, the observation that HNO_3 loss dominates in the metastable spectra and NH_4NO_3 loss dominates in the CID spectra of small clusters provides strong evidence that HNO_3 is lost by dissociative rearrangement. Rearrangements are low-energy processes[5] 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 where reactions with high rate constants such as simple bond cleavages dominate.[6]

Structure **2** is the proposed transition-state structure for the loss of HNO_3 from $(NH_4NO_3)_nNH_4^+$ ions with $n < 7$ (bonds

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[1] Barber, M.; Bordoli, R. S.; Elliot, G. J.; Sedgewick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *64*, 645A. Alexander, A. J.; Hogg, A. M. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *69*, 297–311. Ammonium nitrate samples were pressed into indium foil affixed to the tip of a FAB probe. Xenon atoms with an average kinetic energy of 6.5 keV were generated by a saddle-field gun operated at 8 kV with an ion current of 1.5 mA. The xenon neutral current equivalent was approximately 7 μA applied to a target area of 4 mm². Variation of the saddle-field gun potential over the allowable range of 6–9 keV resulted in no observable change in the ion-abundance distribution.

[2] McLafferty, F. W. *Tandem Mass Spectrometry*; Wiley: New York, 1983. Cooks, R. G. *Collision Spectroscopy*; Plenum: New York, 1978. Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: New York, 1973.

[3] Mass spectra, metastable spectra, and collision-induced dissociation[2] (CID) spectra were obtained using a ZAB-2F (VG Analytical Ltd.) reverse-geometry, double-focusing mass spectrometer operated with an accelerating potential of 8 kV. CID spectra were obtained under multiple-collision conditions with the collision gas (He) maintained at a pressure sufficient to reduce the reactant ion signal by 80%. Metastable spectra were obtained with helium evacuated from the collision cell. Experimental details can be found in: Doyle, R. J., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4120–4126. Doyle, R. J., Jr. *Org. Mass Spectrom.* **1993**, *28*, 83–91.

[4] The kinetic energy of the reactant ion is 8 keV. The collisional-energy-transfer distribution peaks at a few electronvolts and tails out to several tens of electronvolts. Examples derived by experiment are shown in: Wysocki, V. H.; Kenttämaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *75*, 181–208. A recent review may be found in: McLuckey, S. A. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 599–614.

[5] McLafferty, F. W. *Interpretation of Mass Spectra*; University Science: Mill Valley, CA, 1980.

[6] 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.

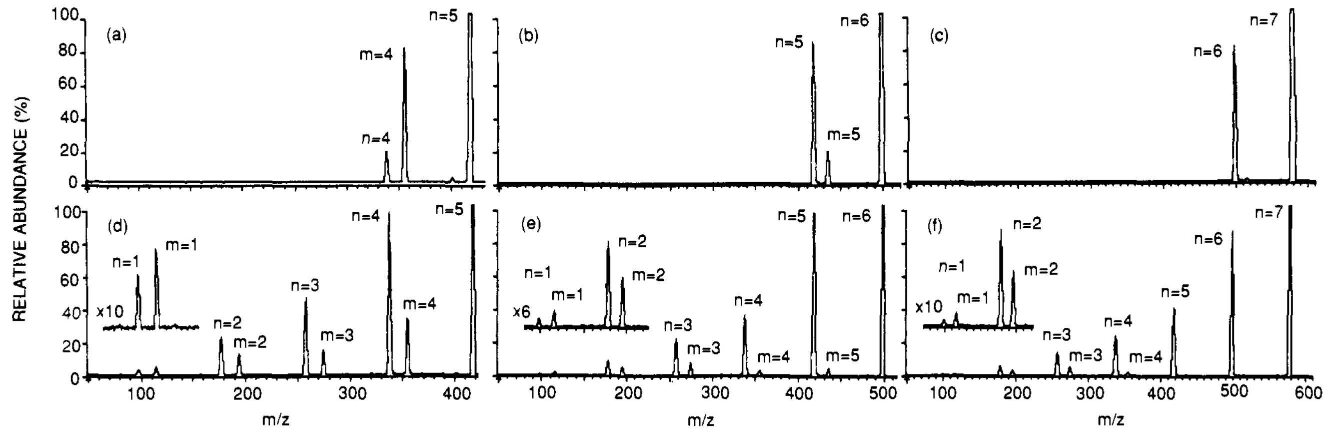
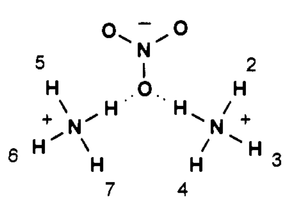


Figure 2. Metastable spectra of (a) $(NH_4NO_3)_5NH_4^+$, (b) $(NH_4NO_3)_6NH_4^+$, and (c) $(NH_4NO_3)_7NH_4^+$ and CID spectra of (d) $(NH_4NO_3)_5NH_4^+$, (e) $(NH_4NO_3)_6NH_4^+$, and (f) $(NH_4NO_3)_7NH_4^+$. The mass-selected, reactant ion signal is saturated in each spectrum.



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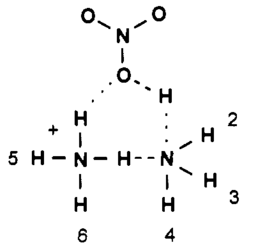

2

breaking = ···, bonds forming = - -). It is consistent with the observations that only one nitric acid molecule is lost from a reactant ion and that nitric acid is lost only from $(NH_4NO_3)_nNH_4^+$ ions with $n < 7$. The rearrangement of **1** through **2** requires that at least one hydrogen-bonding site be available to form a bond with nitrogen. This limits the number of NH_4NO_3 units to a total of 6, although fewer ligands increases the frequency factor for rearrangement, again in agreement with observations. Accordingly, the rearrangement cannot occur if $n > 6$. Finally, it is apparent that ions with $n > 7$ must undergo multiple losses of NH_4NO_3 units to strip the ion to its first solvation shell, $n = 7$, at which point the loss of additional units from **1** enables rearrangement and nitric acid may be lost.

While the experimental evidence presented here strongly supports a rearrangement similar to that shown in **1** and **2**, the actual atom connectivity between the ammonium ions and the nitrate ion is somewhat more speculative. The structure proposed for **1** is supported by work showing that the OH oxygen of HNO_3 is the most basic oxygen and is the most likely site for protonation of nitric acid.[7] In addition, 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 on the OH oxygen is significantly more negative than the charges on the other two oxygen atoms.[8] The analogy applied is that if protonation is most probable at the OH oxygen of HNO_3, then ammoniation is most probable at the O···H oxygen of NH_4NO_3, a situation similar to that seen in the condensed-phase structure.[9] Nevertheless, whether the ammonium ions are bonded to the same or to adjacent oxygen atoms of the nitrate ion, the important point remains that for large ammonium nitrate cationic complexes the loss of nitric acid occurs by a rearrangement that cannot take place until a sufficient number of solvent molecules have been removed from the core ion.

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[8] Latajka, Z.; Szczęsniak, M. M.; Ratajczak, H.; Orville-Thomas, W. J. *J. Comput. Chem.* **1980**, *1*, 417–419.

[9] Choi, C. S.; Prask, H. J.; Prince, E. *Appl. Crystallogr.* **1980**, *13*, 403–409. Lucas, B. W.; Ahtee, M.; Hewat, A. W. *Acta. Crystallogr.* **1979**, *B35*, 1038–1041. Choi, C. S.; Mapes, J. E.; Prince, E. *Acta Crystallogr.* **1972**, *B28*, 1357–1361.