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Reactions of NO^+ in Heterogeneous Water Clusters

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In the D-region of the lower ionosphere, the reaction $NO^+(H_2O)_3 + H_2O \rightarrow (H_2O)_3H^+ + HONO$ is considered to be an important source of proton hydrates. In an earlier publication (Stace et al. *J. Phys. Chem.* **1994**, *98*, 2012), it was shown that ionic clusters of the form $NO^+(H_2O)_n$ could be used as half-collision intermediates in order to demonstrate how effective the above reaction step is at promoting the formation of proton hydrates. Reported here are the results of a new series of complementary experiments, which have studied the reactions of heterogeneous ionic clusters of the form $NO^+\cdot(H_2O)_n\cdot X$, where X is one of either NH_3, C_2H_5OH, CH_3CN, or $(CH_3)_2CO$. These experiments have been undertaken in order to explore the influence trace atmospheric species may have on the reaction sequence leading from NO^+ to proton hydrates (PHs) and nonproton hydrates (NPHs). It is shown that most of the above molecules enhance the formation of both NPHs and PHs and that under certain circumstances their presence can introduce new reaction channels.

Introduction

In the D-region of the ionosphere proton hydrates (PHs) of the form $H^+(H_2O)_2$, $H^+(H_2O)_3$, and $H^+(H_2O)_4$ have been observed to replace NO^+ and O_2^+, which are dominant in the E-region.[1,2] The origin of proton hydrates has been explained in terms of the successive hydration of NO^+ followed by the reaction

$$NO^+(H_2O)_3 + H_2O \rightarrow H^+(H_2O)_3 + HNO_2 \qquad (1)$$

However, this reaction sequence is considered too slow to allow the complete conversion of NO^+ hydrates to hydronium ions,[3] and a sequence of switching reactions, where N_2 and CO_2 are initially involved, is understood to promote more rapid PH formation.[3] Composition measurements of the ionosphere and stratosphere have also detected nonproton hydrates (NPHs), and these take the form $H^+[X\cdot(H_2O)_n]$, where H^+X is the inner core ion of the cluster and is a species (X) with a higher proton affinity (PA) than that of water. Tentative identification of possible candidate molecules for X has included the following: CH_3CN, $(CH_3)_2CO$, NH_3, CH_3OH, and C_2H_5OH.[4−7] In this paper we examine the influence these chemical species have on the $NO^+\cdot(H_2O)_n$ system via their effect on reaction 1 and the subsequent loss of HNO_2 from each type of cluster. In an earlier publication on the $NO^+\cdot(H_2O)_n$ system,[8] it was shown how cluster ions could be used to establish reaction pathways for bimolecular ion−molecule reactions that are thought to proceed via a stable intermediate. Preliminary results have also been presented for the reactions of $NO^+\cdot(H_2O)_nCH_3OH$ clusters,[9] and these results are discussed again in the context of proton hydrate formation.

Experiment

Neutral clusters of the form $NO\cdot(H_2O)_n\cdot X$, where X is either CH_3CN, $(CH_3)_2CO$, NH_3, or C_2H_5OH, were prepared using a "pick-up" technique on an apparatus that consists of a pulsed supersonic nozzle coupled to a modified high-resolution, double-focusing VG ZAB-E mass spectrometer. Argon, at a pressure of approximately 40 psi, was directed through a reservoir containing a mixture of room-temperature water vapor together with a small fraction of one of the above compounds. The concentration of X was adjusted in order to maximize the signal intensities of the required ions. The resulting pressurized gas was then expanded through a 200 μm diameter conical nozzle into a vacuum chamber to form $Ar_m\cdot(H_2O)_n\cdot X$ clusters. Following collimation through a 1 mm diameter skimmer, the mixed clusters then passed through a region containing 10^{-5} mbar of NO, where collisions resulted in the formation of $NO\cdot(H_2O)_n\cdot X$. The clusters then entered the ion source of the mass spectrometer and were ionized by electron impact at an energy of 70 eV. To study fragmentation patterns, $NO^+\cdot(H_2O)_n\cdot X$ clusters for specific values of n were mass-selected using a magnet and allowed to travel a further 1.5 m through a field-free region before entering an electrostatic analyzer, which directed fragments to a scintillation detector, where their intensities could be monitored. The time spent travelling between the magnet and the electrostatic analyzer is approximately 5×10^{-5} s, which is sufficient for cluster ions to undergo a range of unimolecular and internal bimolecular chemical reactions.

Results and Discussion

$NO^+\cdot(H_2O)_n$. To place the results that follow into perspective, a short discussion on the fragmentation pattern of the $NO^+\cdot(H_2O)_n$ system[8] is presented first, and this is based on the results reproduced in Figure 1. The data show measurements recorded by monitoring the following competitive decay channels,

$$NO^+(H_2O)_n \rightarrow H^+(H_2O)_{n-1} + HNO_2$$

$$NO^+(H_2O)_n \rightarrow NO^+(H_2O)_{n-1} + H_2O$$

as a function of n. The results show that water loss is the major fragmentation route for clusters with $n = 2$ and 3. At $n = 4$ there is a switch to HNO_2 loss, which then becomes dominant

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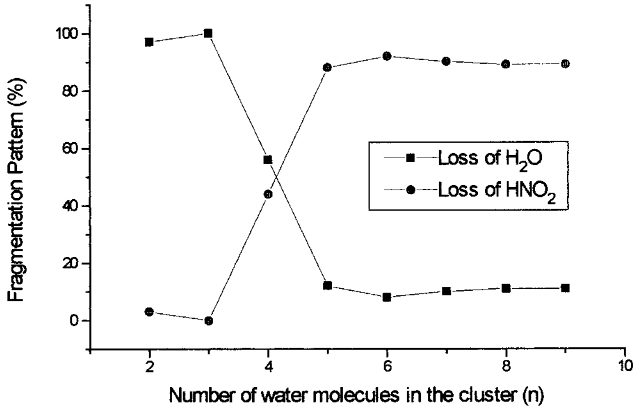


Figure 1. Fragmentation pattern of $NO^+{\cdot}(H_2O)_n$ cluster ions plotted as a function of the number of water molecules, *n*. These results verify work previously presented in ref 8 and are repeated here because of their relevance to the discussion.

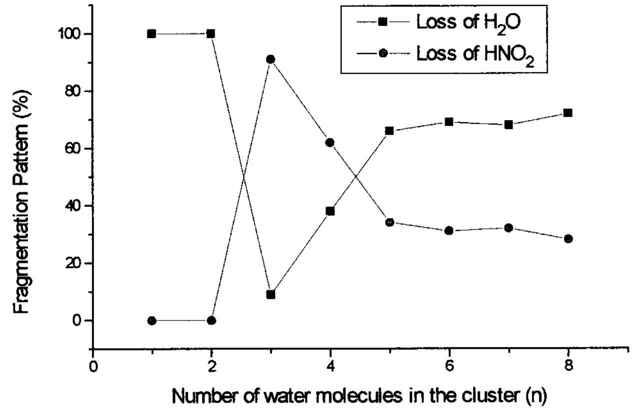


Figure 2. Fragmentation pattern of $NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ cluster ions plotted as a function of the number of water molecules, *n*.

in the range $n = 5-9$. The $NO^+{\cdot}(H_2O)_4$ cluster can be considered the half-collision intermediate of reaction 1, but as Figure 1 shows, less than 50% of fragmentation follows that route. Only for clusters in the range $n = 5-9$ is the formation of PHs approaching 100% efficiency or could be said to have the equivalent of a gas kinetic reaction cross section (i.e., reaction occurs at every collision). Similar results were recorded in work by Choi et al.[10] and Poth et al.[11]

$NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$. The fragmentation pattern of $NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ clusters shown in Figure 2 can be seen in the initial stages as being very similar to that found for the $NO^+{\cdot}(H_2O)_n$ system. At $n = 1$ and 2 the only loss channel is that of H_2O; however, at $n = 3$, HNO_2 loss "switches on" and immediately accounts for ~90% of the fragmentation pattern. The loss of HNO_2 from the cluster at $n = 3$ leaves a protonated ion of the form $H^+CH_3CN{\cdot}(H_2O)_2$ ion, which could be considered as equivalent to reaction 1, but with one of the water molecules being replaced by an acetonitrile molecule.

$$NO^+{\cdot}(H_2O)_2{\cdot}CH_3CN + H_2O \rightarrow H^+[CH_3CN{\cdot}(H_2O)_2] + HNO_2 \quad (2)$$

As Table 1 shows, acetonitrile has a larger proton affinity than water, which may account for the higher degree of reactivity from the $NO^+{\cdot}(H_2O)_3{\cdot}CH_3CN$ cluster when compared with that recorded for the $NO^+{\cdot}(H_2O)_4$ cluster. For an ionic reaction product of the type shown in reaction 2 above, a high proton affinity would help to stabilize the positive charge. In this system the result would be a CH_3CNH^+ ion core with hydration by two H_2O molecules being the most stable NPH product. However, once the chemical pathway has been "switched on", Figure 2 shows that further hydration of the $NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ system beyond $n = 4$ favors the loss of H_2O over HNO_2 loss. This pattern of behavior is quite similar to that seen previously in $NO_2^+{\cdot}(H_2O)_n$ and $NO_2^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ clusters[12] and where it was accounted for as follows. The initial "switching on" of the reaction, when $n = 3$, reveals the minimum number of water molecules needed in the $NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ clusters to produce nitrous acid. For clusters where $n \geq 4$ the reaction is postulated to still take place, but the greater number of solvent molecules can now accommodate HNO_2, and the preferred loss channel reverts to involving the more abundant water molecules. The behavior of $NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN$ clusters of size $n = 4-8$ is therefore best represented by the following equation:

$$NO^+{\cdot}(H_2O)_n{\cdot}CH_3CN + H_2O \rightarrow H^+[HNO_2{\cdot}(H_2O)_{n-1}{\cdot}CH_3CN] + H_2O \quad (3)$$

The ionic cluster produced has the general form $H^+[HNO_2{\cdot}X{\cdot}(H_2O)_n]$ and is quite different from that of the PHs and NPHs discussed previously. However, whether the growth of the parent cluster ion reaches a point where reaction 3 can proceed very much depends on the magnitude of the rate constant for the bimolecular equivalent of reaction 2.

$NO^+{\cdot}(H_2O)_n{\cdot}(CH_3)_2CO$. The fragmentation pattern of $NO^+{\cdot}(H_2O)_n{\cdot}(CH_3)_2CO$ clusters shown in Figure 3 is very similar to that seen for both the $NO^+{\cdot}(H_2O)_n$ and $NO^+{\cdot}(H_2O)_n{\cdot}$

TABLE 1: Proton Affinities of Selected Species

species	proton affinity kJ mol^{-1}
H_2O	697[a]
$(H_2O)_2$	848[b]
$(H_2O)_3$	941[b]
HNO_2	787[c]
HNO_3	764[d]
CH_3ONO	782[c]
CH_3ONO_2	740[d]
CH_3CN	788[a]
$(CH_3)_2CO$	823[a]
C_2H_5OH	788[a]
CH_3OH	761[a]
NH_3	854[a]

[a] Proton affinities taken from Lias, S. G.; Liebman J. F.; Levin, R. D.*J. Phys. Chem. Ref. Data,* **1984**, *13*, 695. [b] Kebarle, P.; Searles, S. K.; Zolla, A.; Scarborough, J.; Arshadi, J. *J. Am. Chem. Soc.* **1967**, *89*, 6393. [c] Aschi, M.; Grandinetti, F. *Chem. Phys. Lett.* **1996**, *258*, 123. [d] Lee, T. J.; Rice, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 8247.

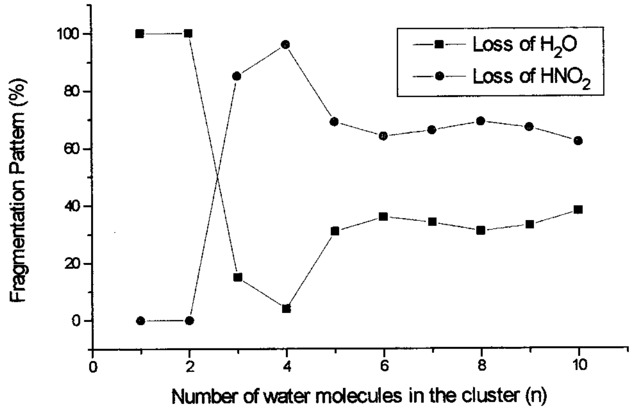


Figure 3. Fragmentation pattern of $NO^+{\cdot}(H_2O)_n{\cdot}(CH_3)_2CO$ cluster ions plotted as a function of the number of water molecules, *n*.

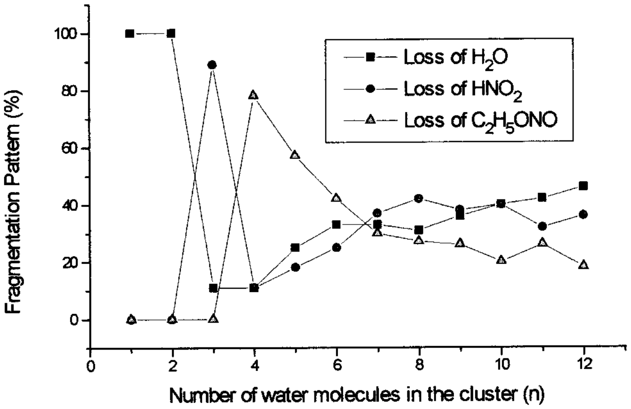


Figure 4. Fragmentation pattern of $NO^+\cdot(H_2O)_n\cdot C_2H_5OH$ cluster ions plotted as a function of the number of water molecules, *n*.

CH_3CN systems. As observed before, the larger proton affinity (Table 1) of acetone when compared with water leads to a greater degree of fragmentation in favor of HNO_2 at $n = 3$. The overall reaction at this point is given by

$$NO^+\cdot(H_2O)_2\cdot(CH_3)_2CO + H_2O \rightarrow H^+[(CH_3)_2CO\cdot(H_2O)_2] + HNO_2 \quad (4)$$

In the acetone-containing system there is a further increase in relative HNO_2 loss from the $NO^+\cdot(H_2O)_n\cdot(CH_3)_2CO$ cluster at $n = 4$. This is the same pattern shown by the $NO^+\cdot(H_2O)_n$ system and has also been identified in $NO_2^+\cdot(H_2O)_n\cdot(CH_3)_2CO$ clusters.[12] This behavior suggests that the $H^+[(CH_3)_2CO\cdot(H_2O)_3]$ cluster has greater structural stability than the smaller $H^+[(CH_3)_2CO\cdot(H_2O)_2]$, and stable configurations that might account for this observation have been identified earlier.[13] In these experiments,[13] Stace and Moore presented experimental data that showed that ion clusters consisting of certain combinations of acetone with water were far more stable than others. At higher levels of hydration there is a relative decrease in HNO_2 loss and, hence, the formation of $H^+(CH_3)_2CO\cdot(H_2O)_n$ NPHs; however, it still remains the dominant fragmentation channel.

$NO^+\cdot(H_2O)_n\cdot C_2H_5OH$. The fragmentation pattern recorded for $NO^+\cdot(H_2O)_n.C_2H_5OH$ clusters is shown in Figure 4, where the initial pattern is seen to be very similar to that for previous examples. At $n = 3$ there is a sharp switch to a reaction that leads to the formation of HNO_2, but more remarkable is the behavior at $n = 4$, where the dominant fragmentation route corresponds to a loss of C_2H_5ONO. Equally unexpected is the rapid decline in loss of HNO_2 at $n = 4$ and beyond. As seen for the other three systems discussed so far, HNO_2 loss is first detected in a cluster comprising four ligands and NO^+. This is represented by the following reaction and is equivalent to reactions 1, 2, and 4.

$$NO^+\cdot(H_2O)_2\cdot C_2H_5OH + H_2O \rightarrow H^+[C_2H_5OH\cdot(H_2O)_2] + HNO_2 \quad (5)$$

The resulting NPH, $H^+[C_2H_5OH\cdot(H_2O)_2]$, is again detected with a higher relative yield than the PH, $H^+(H_2O)_3$, which may also be due to the increased proton affinity of ethanol compared with water (Table 1). At $n = 4$, NO^+ would appear to favor a reaction with ethanol to leave the symmetric and very stable $H^+(H_2O)_4$ cluster ion.

$$NO^+\cdot(H_2O)_4\cdot C_2H_5OH \rightarrow H^+(H_2O)_4 + C_2H_5ONO \quad (6)$$

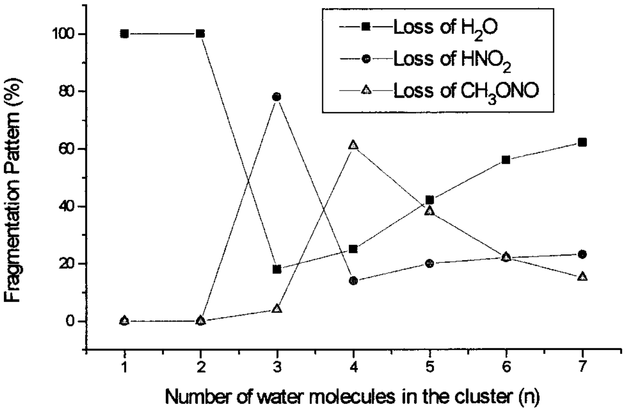


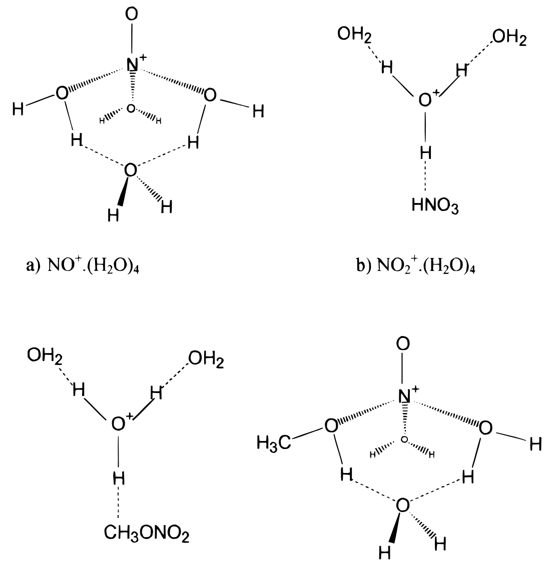
Figure 5. Fragmentation pattern of $NO^+\cdot(H_2O)_n\cdot CH_3OH$ cluster ions plotted as a function of the number of water molecules, *n*. These results have been adapted from ref 9.

Ethyl nitrite loss continues to be the dominant reaction channel from each cluster until $n = 7$, when all three loss channels become approximately equal.

The fragmentation pattern is very similar to that seen previously in the system $NO^+\cdot(H_2O)_n\cdot CH_3OH$,[9] and because of their direct relevance to this discussion, these results have been reproduced in Figure 5. Water loss is the dominant process for $n = 1$ and 2, loss of HNO_2 switches in at $n = 3$, and loss of CH_3ONO is the largest single process at $n = 4$.[9] In both the methanol and ethanol systems, the prime consequence of their presence appears to be that of facilitating HNO_2 formation and loss from the cluster at $n = 3$. The reaction proceeds at a ~90% efficiency when normalized with the alternative loss channels of water and/or the alkyl nitrite. The dominance of HNO_2 loss at this stage is significant because it could stop further hydration and so $NO^+\cdot(H_2O)_n\cdot CH_3CH_2OH$ clusters of size $n > 3$ would not necessarily be expected.

These results are in marked contrast to earlier work published by us on the $NO_2^+\cdot(H_2O)_n\cdot CH_3OH$ and C_2H_5OH systems,[12] and at this stage some comparison of the two systems would be quite instructive. The ethanol/NO_2^+ system exhibited dominant H_2O loss throughout the hydration sequence $n = 1-8$ with very little evidence of any reactions involving the ethanol molecule. In contrast, the analogous methanol system showed dominant loss of CH_3ONO_2 at both $n = 3$ and 4. This pattern of behavior could be rationalized in terms of the binding energies of water and methanol to NO_2^+ and the proton affinities of the various reactants and products.[14-16] However, the behavior seen in Figures 4 and 5 for the formation and loss of HNO_2 at $n = 3$ and CH_3CH_2ONO or CH_3ONO loss at $n = 4$ suggests that the driving force for these competitive loss channels may be determined by different factors, such as the relative stability of the products and/or the structure of the parent cluster. The distinction between the NO^+ and NO_2^+ systems is an important one. In clusters containing the former ion, nitrous acid loss precedes CH_3ONO formation as a function of cluster size, but for clusters containing NO_2^+, CH_3ONO_2 is lost and there is no evidence of nitric acid formation.[12] Thus, the reaction leading to the formation of CH_3ONO_2 has an opportunity to compete effectively with other possible decay channels.

Okumura and co-workers[10,17] have proposed certain cluster structures for both $NO^+\cdot(H_2O)_n$ and $NO_2^+\cdot(H_2O)_n$ clusters. Their work suggests that the first three water ligands bind directly to the NO^+ or NO_2^+ cation, forming the first solvation shell. The analysis of clusters with four H_2O ligands brought evidence of differences in structure between the two main cluster types. The analysis of the $NO^+\cdot(H_2O)_4$ cluster provided evidence that in



a) $NO^{+}.(H_2O)_4$ b) $NO_2^{+}.(H_2O)_4$

c) $NO_2^{+}.(H_2O)_3.CH_3OH$ d) $NO^{+}.(H_2O)_3.CH_3OH$

Figure 6. Proposed structures for the cluster ions: (a) $NO^{+}\cdot(H_2O)_4$, (b) $NO_2^{+}\cdot(H_2O)_4$, (c) $NO^{+}\cdot(H_2O)_3\cdot CH_3OH$, and (d) $NO_2^{+}\cdot(H_2O)_3\cdot CH_3OH$. These structures have been adapted from work presented in refs 10 and 18.

the dominant cluster structure the fourth H_2O molecule formed hydrogen bonds with two of the first shell water ligands, beginning a second solvation shell. In this structure (Figure 6a) the water bridges two adjacent ligands to form a six-atom ring. These findings differed from the $NO_2^{+}\cdot(H_2O)_4$ system, which showed evidence of a structure that had a HNO_3 molecule already formed and present in the first solvation shell of the cluster surrounding a H_3O^{+} ion core (Figure 6b). Extrapolating these results to the CH_3OH systems suggests that a $NO_2^{+}\cdot(H_2O)_3\cdot CH_3OH$ cluster may consist of an H_3O^{+} ion core with a first solvation shell containing two H_2O molecules and a CH_3ONO_2 molecule (Figure 6c). This would explain the dominant loss of CH_3ONO_2 from the cluster by the process of simple bond fission. In contrast, the structure of the $NO^{+}\cdot(H_2O)_3\cdot CH_3OH$ cluster will probably follow the pattern for $NO^{+}\cdot(H_2O)_4$ and consist of an NO^{+} ion core and a first solvation shell containing two H_2O molecules and a CH_3OH molecule, with a single H_2O molecule in the second solvation shell hydrogen bonded to a water and methanol molecule from the first shell (Figure 6d). The products from fragmentation of this cluster will come from solvent rearrangement and a redistribution of charge from NO^{+} to a proton, which because of a higher proton affinity will be preferentially taken up by the methanol molecule rather than water. This pattern of behavior would explain the formation of the NPH $H^{+}[CH_3OH\cdot(H_2O)_2]$ and loss of HNO_2 from the cluster. At $n = 4$, the switch to loss of CH_3ONO can be accounted for because the $NO^{+}\cdot(H_2O)_4\cdot CH_3OH$ cluster now reverts to an H_3O^{+} ion core,[10] which results in the formation of a very stable $H^{+}(H_2O)_4$ product ion. A similar driving force will also be responsible for the formation and loss of CH_3CH_2ONO from $NO^{+}\cdot(H_2O)_4\cdot CH_3CH_2OH$ clusters.

$NO^{+}\cdot(H_2O)_n\cdot NH_3$. The fragmentation pattern recorded for $NO^{+}\cdot(H_2O)_n\cdot NH_3$ clusters and shown in Figure 7 is unique among the systems studied thus far. Although HNO_2 loss is seen as the dominant loss channel at $n = 1$, for larger clusters that process is rapidly overtaken by the loss of water. The pattern of behavior in the smaller clusters is quite interesting, because for $n = 1$, the ionic fragment is either the very stable species NH_4^{+} or, when H_2O is lost, the complex $NO^{+}\cdot NH_3$. With clusters of size $n \geq 2$ and water being the dominant loss channel, there remain two possibilities for the types of cluster ion being generated; these are either $NO^{+}\cdot NH_3\cdot(H_2O)_n$ or $NH_4^{+}\cdot HNO_2\cdot(H_2O)_{n-1}$. The latter cluster has the potential for forming a stable $NH_4^{+}\cdot(H_2O)_n$ unit, which at $n = 5$ would be expected to exhibit increased loss of HNO_2. Such behavior was observed for the $NO_2^{+}\cdot NH_3\cdot(H_2O)_5$ ion and can also be seen to some degree in Figure 7, although HNO_2 loss does continue to increase after $n = 5$. The absence of an appropriate fragmentation route does not preclude the formation of $NH_4^{+}\cdot HNO_2\cdot(H_2O)_{n-1}$, because it is quite possible that NH_4^{+} is more strongly bound to nitrous acid than water. In the $NO_2^{+}\cdot NH_3\cdot(H_2O)_n$ system, the dominant loss of H_2O right across the cluster range was attributed to the formation of a stable $NH_4^{+}\cdot HNO_3$ unit.[12] However, the results shown in Figure 7 would suggest that $NH_4^{+}\cdot HNO_2\cdot(H_2O)_{n-1}$ clusters may not be the only species present in the $NO^{+}\cdot NH_3\cdot(H_2O)_n$ system.

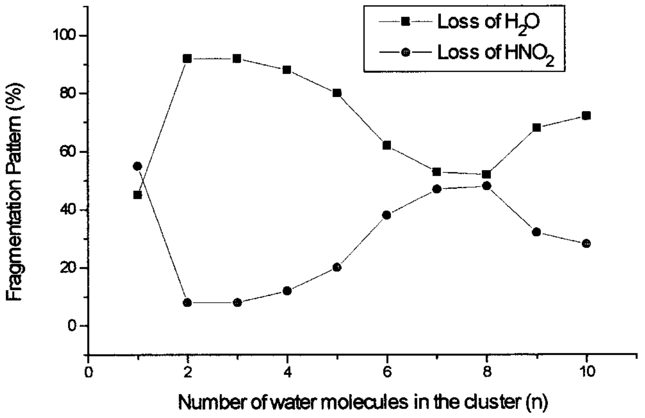


Figure 7. Fragmentation pattern of $NO^{+}\cdot(H_2O)_n\cdot NH_3$ cluster ions plotted as a function of the number of water molecules, n.

Conclusions

The behavior exhibited by mixed cluster ions of the form $NO^{+}\cdot X\cdot(H_2O)_n$, where X is either methanol, ethanol, acetone, or acetonitrile, shows that NPHs of the form $H^{+}[X\cdot(H_2O)_2]$ are more favorably produced than PHs of the form $H^{+}(H_2O)_3$. All four molecules can be understood to act as catalysts for reactions that ultimately lead to the formation of HNO_2, and there is good evidence to conclude that chemical processes in $NO^{+}\cdot(H_2O)_3\cdot X$ clusters are facilitated by the presence of a trace component with a high proton affinity. The experiment shows evidence of steps leading to the formation of a series of cluster ions of the form $H^{+}(H_2O)_n$, $H^{+}[X\cdot(H_2O)_n]$, and $H^{+}[Y\cdot X\cdot(H_2O)_n]$, all of which fall within the size distribution observed in mass spectrometric measurements undertaken in the stratosphere and ionosphere.[2,7] Interestingly, the methanol and ethanol systems are observed to generate and lose methyl and ethyl nitrite, respectively, thus contributing to the formation of PHs specifically of the form $H^{+}(H_2O)_4$. However, for these reactions to be significant, the reactive steps at clusters of a smaller size would have to be at a rate slow enough to enable further hydration to proceed.

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