Fragmentation and Intracluster Reactions of Hydrated Aluminum Cations $Al^+(H_2O)_n$, $n = 3-50$

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Abstract: Hydrated aluminum cluster cations $Al^+(H_2O)_n$ with $n = 3-50$ were stored in a collision-free environment, and their unimolecular fragmentation induced by the room temperature "black body" infrared background was studied. An interesting size-dependent intracluster reaction resulting in oxidation of the aluminum cation and elimination of molecular hydrogen was observed. The results are discussed and compared with similar recent studies of hydrated magnesium clusters.

Introduction

Aluminum is one of the most abundant elements of the earth's crust, and by far the most abundant metal.[1] It is therefore not surprising that it is one of the major components of atmospheric aerosol particles from natural sources, i.e. volcanic activity and aeolian dust.[2] Recently, based on measurements between 1976 and 1984, a 10-fold increase in the abundance of large solid particles in the stratosphere has been reported by Zolensky et al.[3] This was attributed to solid rocket fuel exhaust and rocket and satellite debris.

Particulates from space travel sources are especially aluminum rich. Aluminum is common solid rocket fuel, and also in the process of reentrance of a spacecraft in the earth's atmosphere, a real evaporation of aluminum takes place, leading to very small aluminum and aluminum oxide particles. Even aluminum atoms or ions may be formed in this process. The amount and chemical impact of Al_2O_3 particulates originating from the space shuttle's and other solid fuel rockets' engine exhausts have been studied by Cofer et al.[4] Even though a considerable amount of bare aluminum atoms, ions, or clusters might be formed in the rapid combustion process of a space shuttle launch, their effects lie completely in the dark. Considering the lack of knowledge on that subject, the latest WMO Ozone report[5] consequently states that "particulates from solid-fuel rockets deserve careful attention, especially as their stratospheric abundance may increase in the near future."

In view of the potential importance of this topic, and the scarcity of available information, laboratory studies of aluminum atoms and clusters and their reactions and solvation are desirable. In a few previous investigations the solvation of Al^+ with various organic molecules, including methanol and acetone, has been studied.[6−9] Also the $Al^+(H_2O)_n$-clusters, $n \leq 10$, have been investigated by means of photoionization and photodissociation.[10] In our laboratory, we have for the last 6 months investigated in an FT-ICR mass spectrometer the reactions of solvated magnesium ions, $Mg^+(H_2O)_n$. These exhibit a series of interesting and puzzling size-dependent reactions, fragmentation, and other properties.[11] In the present study we extend these investigations of hydrated metal ions to aluminum. We are motivated on one hand by interest in aluminum atom reactions per se and on the other hand by the hope of gaining some additional insight into the Mg^+ ion system. We report here the observations of black body radiation induced fragmentation of $Al^+(H_2O)_n$, $n = 3-50$, ion clusters. We observe interesting intracluster reactions which are strongly size dependent and are accompanied by the elimination of molecular hydrogen, $Al^+(H_2O)_n \rightarrow Al(OH)_2{}^+(H_2O)_{n-3} + H_2O + H_2$.

Experimental Section

The experiments were performed on a modified FT-ICR mass spectrometer Spectrospin CMS47X[12] equipped with an external molecular ion beam source chamber, a 4.7-T superconducting magnet, and a 60 × 60 mm cylindrical "infinity cell".[13] Aluminum cations solvated with water were produced in a disk type laser vaporization source. Compressed granular aluminum (99+%, Aldrich) was vaporized with a focused 532-nm radiation of a Spectra Physics GCR3 Nd:YAG laser (spot size on target about 500 μm) operating at 25 Hz with 10 mJ per 5-ns pulse to produce the initial metal plasma. The laser vaporization was synchronized with pulses of water vapor seeded in helium, supplied by a home-built piezoelectric valve with a 50 μs opening time. Typical pressures of water and helium are 35 mbar (vapor pressure at 27 °C) and 7 bar, respectively. The metal plasma entrained in the helium−water pulse was subsequently cooled by

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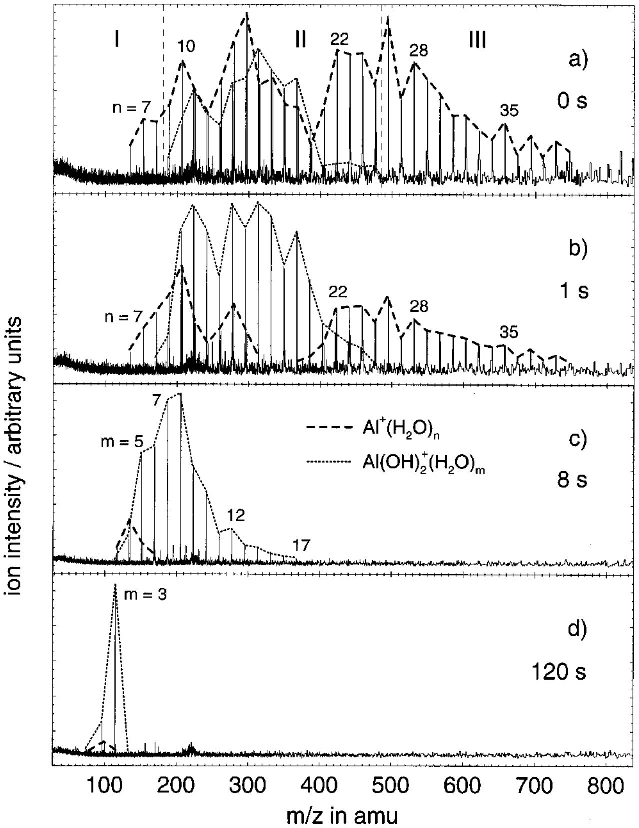

Figure 1. Mass spectra of a large cluster ion distribution $Al^+(H_2O)_n$, $n = 6-50$, taken with different delays, thus exposing the clusters to the black body infrared radiation within the cell for different times before detection: (a) 0, (b) 1, (c) 8, and (d) 120 s. The initial cluster distribution $Al^+(H_2O)_n$, $n = 6-50$, is observed after accumulating the cluster ions for 2 s in the cell (a). In regions I and III, corresponding to $n = 6-8$ and $n > 25$, a pure $Al^+(H_2O)_n$ progression is observed, while in region II, $n = 9-25$, each peak is accompanied by a nominally $AlO^+(H_2O)_{n-1}$ peak. Large clusters, $n > 25$, exclusively evaporate water (b). Clusters with $n < 25$ may also react to the dihydroxide species $Al(OH)_2{}^+(H_2O)_{n-2}$, which further evaporate water (c) until the fairly stable clusters $Al(OH)_2{}^+(H_2O)_3$ and $Al(OH)_2{}^+(H_2O)_2$ are reached (d).

flowing through a confining channel (50 mm, 2 mm i.d.) and by subsequent supersonic expansion into high vacuum, resulting in cluster formation. The cluster ions, produced without postionization, were accelerated downstream from a 400-μm skimmer, transferred into the high-field region of the superconducting magnet, decelerated, and stored inside the ICR cell at a pressure of $<6 \times 10^{-10}$ mbar. The pressure gauge indication was verified by examining reactions with well-known collisional cross sections. The low pressure used in the present study corresponds to one collision of a cluster ion with a residual gas molecule about every 100 s. To improve the cluster ion signals, up to 50 injection cycles were accumulated at the 25 Hz repetition rate of the Nd:YAG laser, prior to the reaction delay and detection. The temperature of the vacuum tube enclosing the ICR cell was kept at a constant value of $T = 291 \pm 5$ K by a water flow cooling jacket.

Results and Discussion

A typical initial hydrated cation distribution produced by our source is shown in Figure 1a). Even though the specific distribution depends somewhat upon the source conditions, the essential characteristics remain relatively constant. In general, under the conditions of the present experiments, mainly clusters containing a single Al atom and $\approx$1−50 water molecules are formed. In the total distribution, three different regions can be distinguished, and are readily observable in Figure 1a. In region I, $n = 6-8$, and region III, $n > 25$; only clusters with $Al^+(H_2O)_n$ composition are observed. In the intermediate region between $n = 9$ and 25, on the other hand, also clusters with masses 2 amu lower, that is with a nominal $AlO^+(H_2O)_{n-1}$ composition, are detected.

This observation raises the question whether these are two different distributions originating already in the expansion channel with the $AlO^+(H_2O)_{n-1}$ being formed by solvation of AlO^+ ions or if an interconversion between the two types of clusters occurs in the cell. A separate question involves the specific structure of the ions. Are they actually hydrated AlO^+ as written above, or should they be understood as hydrated hydroxides? It may be noted that $Al(OH)_2{}^+(H_2O)_4$ was reported to be the stable singly charged cation in solutions.[14] Similarly one might ask if the nominally $Al^+(H_2O)_n$ ions are actually hydrated Al^+, or could they be hydrated aluminum hydroxide hydride, $HAlOH^+(H_2O)_{n-1}$?

To address these questions, we stored the clusters in the ICR cell for different times, exposed them to the black body infrared radiation, and observed their fragmentation. Our previous studies with water and other solvated clusters have shown that in all cases an efficient fragmentation by the infrared background radiation takes place. A closer analysis of the process[15] has revealed that the cluster temperature is controlled by competition between evaporative cooling and heating by absorption of the black body radiation from the apparatus walls. The effect of such fragmentation process upon the hydrated aluminum clusters can be seen in panels b to d of Figure 1, showing the changes in the cluster distribution after 1, 8, and 120 s in the collision free environment. The first quite apparent effect is the rapid shift of the overall distribution to lower masses. At the same time, there is also a distinct shift in favor of the clusters of the "hydrated hydroxide type". While at $t = 0$ s the hydrated Al^+ represents about 75% of all clusters, already at $t = 1$ s the "hydrated hydroxide" species prevail, indicating clearly that interconversion between the two types takes place in the ICR cell. One might also note, that while in Figure 1a the distribution of the $Al(OH)_2{}^+(H_2O)_m$ clusters present in significant amount extends only to about $m = 19$, in Figure 1b, 1 s later, clusters up to $m = 23$ can be detected. One can actually observe a "hole" in the hydrated Al^+ distribution in Figure 1b. Although $Al^+(H_2O)_n$ with $n = 6-16$ and 21−41 are present, the clusters with $n = 17-20$ are almost completely depleted. In Figure 1c, after 8 s, a further shift to lower masses and in favor of the hydroxide ions has occurred. The higher mass distribution of the hydrated Al^+ clusters has completely disappeared, and only small, $n = 5-8$, $Al^+(H_2O)_n$ clusters remain. The "hydrated hydroxides" now represent more than 90% of all the ions, and their distribution has also shifted to lower masses, with only $Al(OH)_2{}^+(H_2O)_m$, $m = 4-17$, being present. Finally, in Figure 1d after 120 s the fragmentation process has come nearly to completion. About 85% of the "hydrated hydroxide" clusters now appear as $Al(OH)_2{}^+(H_2O)_3$, with only small amounts of $m = 2$ and 4 species. Similarly, among the hydrated Al^+ clusters $Al^+(H_2O)_4$ dominates, with only minor quantities of $n = 3$ and 5. There is almost no evidence of further shift in favor of the hydroxides, with the hydrated Al^+, which were dominant prior to fragmentation, representing in the final distribution only about 5−7% of the total ions.

The rapid shift in distribution toward smaller clusters in the collision-free, high-vacuum environment indicates that similar to pure water clusters, also the hydrated aluminum containing cluster ions efficiently absorb the infrared background radiation and fragment. The change in the relative abundance of

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$Al^+(H_2O)_n$ which represent some 70−80% of the initial cluster distribution and only about 5% of the terminal cluster ions (see Figure 1), shows conclusively, that not only a simple water ligand loss, but also more complex, efficient intracluster reactions, and a conversion of the “pure hydrated clusters” into “hydroxide clusters” takes place. Examination of the data suggests that the reaction may be written as:

$$Al^+(H_2O)_n \rightarrow Al(OH)_2{}^+(H_2O)_{n-m-2} + H_2 + mH_2O \qquad (1)$$

This indicates that not only water ligands are succesively evaporated, but also an H_2 molecule is lost in the process. Studies with size selected clusters show that the dominant process in reaction 1 is $m = 1$, that is elimination of one molecule of water simultaneously with the loss of H_2; we can not eliminate the presence of minor $m = 0$ or 2 parallel reaction channels. While the mass-spectroscopy data give no information about the outgoing neutral products, and we cannot distinguish against elimination of for instance water plus two hydrogen atoms, molecular hydrogen is on energetic grounds clearly the most likely product.

A more detailed examination of the data as presented in Figure 1 also shows that the intracluster reaction is strongly size dependent. While the initial cluster distributions depend somewhat on the vaporization laser focusing and power, carrier gas pressure, timing of the experiment, and other experimental factors, in no cases were “hydroxide clusters” larger than about $m = 23$ observed under the conditions of our experiment. Also, even though much larger pure “hydrated aluminum” clusters $Al^+(H_2O)_n$ (with n up to ≈50) are observed, these large clusters initially just evaporate water ligands and no conversion into the “hydroxide clusters” was detected. Only when the fragmentation reaches region II below about $n = 24$ does the intracluster hydrogen elimination reaction set in. The intracluster reaction also does not seem to occur for very small clusters, below about $n = 12$. This can be seen by comparing Figures 1c and 1d. Once the cluster sizes have dropped below about $n = 10-12$, no further intracluster reaction and H_2 elimination takes place. The clusters in this range lose further water ligands to form eventually the very small ($n = 3-5$) terminal clusters, but the relative abundances of the two types of clusters remain constant.

As a further check of this point we have carried out an experiment under slightly modified source conditions, where the seeding water pressure was lowered to 23 mbar, and the carrier gas stagnation pressure was held constant. Under these conditions only smaller clusters, mainly in the range $n = 6-10$, are formed. Although smaller amounts of clusters containing two or three atoms of Al can be detected, almost no “hydroxide clusters” are present in the initial distribution (Figure 2a). When clusters produced under these conditions are allowed to fragment, only water ligand loss, but no intracluster H_2 elimination, is observed. After a sufficiently long time (128 s, Figure 2c) most clusters have fragmented to form mainly $Al^+(H_2O)_4$, with only a very slow further fragmentation to $Al^+(H_2O)_3$. There is no evidence for the formation of $Al(OH)_2 + (H_2O)_3$ or other hydroxide clusters.

While we have not specifically attempted to study clusters containing more than one Al atom, some clusters with two or three Al can be detected in Figure 2. The most abundant clusters with two aluminum atoms can be written as $[Al_2(OH)_5]^+(H_2O)_n$, or alternatively as $[Al_2O(OH)_3]^+(H_2O)_{n+1}$, with $n = 2$ and 3 species dominating the final distribution. Perhaps they contain an $(Al-O-Al)^+$ entity with OH and H_2O ligands.

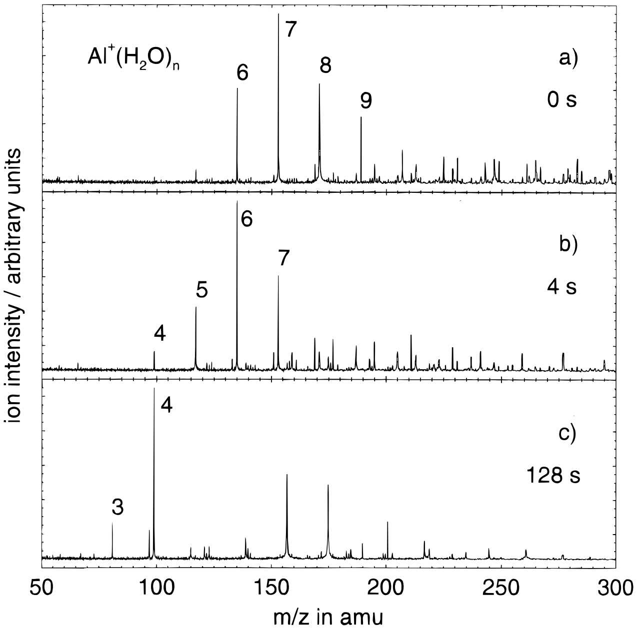

Figure 2. Mass spectra of a distribution of small cluster ions $Al^+(H_2O)_n$, $n = 5-9$, taken after a fragmentation times of (a) 0, (b) 4, and (c) 128 s. Only evaporation of H_2O is observed, forming fairly stable $Al^+(H_2O)_4$ and $Al^+(H_2O)_3$ clusters (c). The small peak with mass 97 amu is the fragmentation product of small amounts of larger clusters, and the other nonlabeled peaks are solvated $Al_2{}^+$ cations and their fragments.

In contrast with very small ($n < 12$) or very large ($n > 25$) clusters, the intracluster reaction and hydrogen loss occurs efficiently in the intermediate size range, about $12 < n < 24$, and apparently dominates for cluster sizes $n = 16-23$. The intracluster reaction may perhaps be compared with dissolving metals in acid solutions and elimination of hydrogen by more electropositive metals. Very interesting is the comparison of the present result with similar studies of hydrated magnesium.[11] In that case a size dependent intracluster reaction and hydrogen elimination also takes place. Unlike the present case, for the $Mg^+(H_2O)_n$ the boundaries between the various regions seem to be less fuzzy, with the elimination of hydrogen occurring between $n = 16$ and 21. Small $Mg^+(H_2O)_n$ clusters with $n = 2-5$ can be produced, but none are observed between $n = 6-15$. Even more interesting is the observation that while in the intracluster reaction of the hydrated $Al^+(H_2O)_n$ clusters molecular hydrogen, H_2, is eliminated, in the case of magnesium a single hydrogen atom is lost. A possible reason for this difference may lie in the fact that the $Mg^+(H_2O)_n$ clusters are open-shell species, and the loss of a hydrogen atom results in the formation of stabler, closed shell “hydrated hydroxide” $MgOH^+(H_2O)_n$ product clusters. The corresponding hydrated aluminum cations, $Al^+(H_2O)_n$, on the other hand, are closed shell. In this case elimination of molecular hydrogen is favored, since the products remain closed shell.

It is interesting to speculate on the reasons for the size dependence of the intracluster reactions. Several preliminary calculations we have carried out have shown clearly that reaction 1, oxidation of Al^+ to Al^{3+} with formation of hydroxide and elimination of molecular hydrogen, is strongly exothermic even for $n = 2$, yet the reaction proceeds only in a relatively narrow range of sizes. In considering the reasons for this size dependence, it is perhaps useful to consider the structure of the hydrated clusters. Aluminum III cations in aqueous solutions are believed to be hexacoordinate,[16] and as noted above, also the hydroxide forms stable hexacoordinated $Al(OH)_2{}^+(H_2O)_4$

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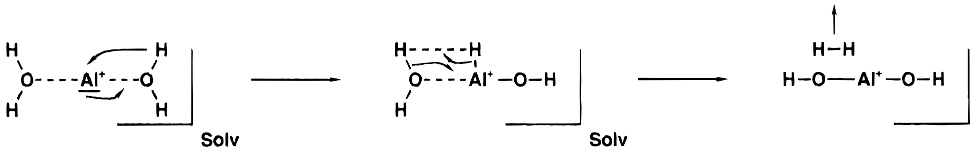
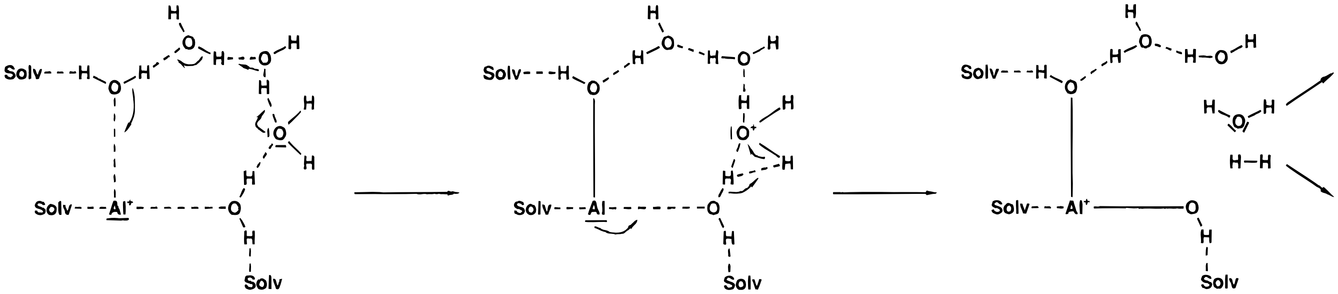
Scheme 1. OH Bond Insertion Mechanism



Scheme 2. Proton Transfer Mechanism



cations in solution. On the other hand, the results of the fragmentation experiment, with the very stable $Al^+(H_2O)_4$ “terminal” ions, would suggest that the Al^+ ion distinctly prefers tetracoordination. It is conceivable also that the singly ionized Al^+ forms in the larger clusters a relatively stable $Al^+(H_2O)_4$ entity. In a second solvation shell an additional eight water molecules would be bound to each of the hydrogens, and the entire structure further stabilized by the third and higher layers. The fact that the intracluster reactions start at about the point where the third coordination sphere will start to be incomplete might suggest that interactions of these third coordination sphere molecules are important. With the evaporation of ligand molecules the solvent stabilization decreases. Below some critical size, the solvation shell is sufficiently destabilized so that hydrogen of one of these weaker bound third shell molecules might come close to the tetracoordinated Al^+ central ion, so that insertion of Al^+ into the OH bond and formation of a hexacoordinated $H-Al^+-OH$ hydride−hydroxide can take place, as visualized in Scheme 1. The hydrogen atom of the relatively unstable AlH hydride may then further react with a second water ligand to form hydroxide, $HO-Al^+-OH$, and eliminate molecular hydrogen.

An alternative reaction mechanism is shown in Scheme 2, where this time oxygen of a third coordination sphere water molecule comes near one of the hydrogen atoms of the first coordination sphere inducing a proton transfer and the formation of a hydroxyl group on aluminum. A series of further proton transfers then results in the elimination of molecular hydrogen and the formation of the second aluminum hydroxyl group. One might thus speculate that since the reaction requires involvement of a weaker bound and mobile third sphere molecules, it does not occur for $Al^+(H_2O)_n$, $n \leq 10-12$, where no such molecules are present, even though it apparently on energetic grounds could take place. It also does not occur for $n > 24-25$, where enough molecules are present to complete and stabilize the third solvation shell.

Similar mechanisms could be advanced even if the clusters actually have the hydrated [H--Al−OH] structures. To establish the structures of the ions and their reactions unambiguously additional experimental studies, preferably supported by theoretical modeling, will be needed.

Summary

Fragmentation of ionized aluminum water clusters $Al^+(H_2O)_n$ induced by the background infrared radiation of a room temperature environment shows that for $n \approx 12-24$ the evaporation of water is accompanied by oxidation of the central Al^+ ion and by the loss of an H_2 molecule according to the intracluster reaction 1. A solvated $Al(OH)_2{}^+(H_2O)_{n-2}$ hydroxide ion cluster is formed, similar to the known $Al(OH)_2{}^+(H_2O)_4$ ions in solutions. Further investigation of the $Al^+(H_2O)_n$ system in the gas phase may lead to a deeper and more detailed understanding of the solvation process of aluminum and other metals in bulk liquids. Gas-phase chemical reaction studies, for instance with HCl, may be of relevance in the field of atmospheric chemistry.

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