Reactions of Mixed Pb_M^+/Methanol Clusters

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Observations on the mass spectra of mixed lead/methanol cluster ions, $Pb_M(CH_3OH)_N^+$, for $M \leq 4$ and $N \leq 10$, show evidence of a bimolecular dehydration reaction which is promoted when $N \geq 3$. The experimental results are interpreted in terms of a metal atom insertion reaction, and the dehydration step is confirmed through the use of isotopes. An analogy is drawn between this reaction and those observed for solution phase plumboxanes.

Introduction

The isolation afforded a gas phase cluster ion provides an environment from which the effect of solvent molecules on metal ions may be studied. Ranging from elucidation of the charge distribution within a given solvated metal atom[1] to the catalysis of intracluster reactions,[2] work in this area has done much to clarify ideas about solution chemistry which, due to the complexity of interactions in the bulk phase, have not hitherto been examined in detail. Intracluster dehydration reactions have been observed in clusters of pure methanol[3] and in clusters consisting of methanol in association with a range of metal ions (M^+).[4,5] The latter reactions follow the general scheme

$$M^+(CH_3OH)_N \rightarrow M^+(CH_3OH)_{N-2}(H_2O) + CH_3OCH_3 \quad (1)$$

The onset of this reaction (in terms of a critical value for N) has been shown to vary depending on M^+. For M = Li, Na, and K, $N \geq 8$ and for M = Rb and Cs, $N \geq 9$. To verify that the observed reaction products are not simply due to water that has been picked up from the cluster source, the reaction has also been observed with CH_3OD and CD_3OD. When CH_3OH and CD_3OH clusters are attached to the metal the only observable dehydration products are H_2O and CH_3OCH_3. However, when CH_3OD and CD_3OD are used to form the solvating cluster, the observed products are D_2O and the complementary symmetric ether (i.e., CH_3OCH_3 from CH_3OD and CD_3OCD_3 from CD_3OD).

Solvation and subsequent dehydration mechanisms involving solvated main group metal atoms or metal clusters have been less studied than those with the alkali metal atoms detailed above. The presence of many unfilled orbitals in such species (for example Pb_2^+) implies that they should be more reactive in the solvent environment than the relatively stable, closed shell alkali metal cations. In the present study the gas phase reactions of lead clusters Pb_M^+ for $1 \leq M \leq 8$ with methanol are examined, and deuterated methanol has been used to establish the reaction pathways. These results demonstrate that a dehydration reaction occurs in small lead clusters, $Pb_M^+(CH_3OH)_N$, when $N \geq 3$.

Experimental Section

The combined lead/methanol clusters are generated using a pulsed arc cluster source (PACS)[6] and detected using a commercial reflectron time-of-flight mass spectrometer (Jordan). The lead cathode was obtained from Sigma-Aldrich and the anode was composed of either copper or stainless steel. The application of a high current pulse (∼11 ms duration) across the two electrodes positioned some small distance apart, resulted in the ablation of material from the cathode. A sputtering process, specifically brought about by the pulsed nature of the arc, is thought to be responsible for the removal of material, since the consumption of the cathode is in contrast to the behavior of a continuous arc where the anode is consumed. Both electrodes are 6 mm in diameter and are held in a vertical position with a typical separation of 1 mm within a machined ceramic block (Macor) of external dimensions 100 × 25 × 25 mm. The block was crossed by a 1.8 mm diameter channel which passes through the gap between the electrodes. Helium (at a purity of > 99%) at a pressure of ∼70 psi was injected into the channel from a pulsed fuel injector type nozzle (Bosch), such that the ablated material was entrained in the carrier gas. The delay between triggering the nozzle and the pulsed arc was of the order of 1300 μs; at delays less than 900 μs the arc became unstable.

Methanol was introduced into the expansion by placing a reservoir in the helium carrier gas line prior to the nozzle. For these experiments, spectroscopic grade methanol (Sigma-Aldrich) was used and dried in-house until it contained less than 0.005% water; the deuterated methanol (Goss Scientific) was of a similar purity. The beam emerging from the PACS source was expanded through a brass extender cone (15°) which was cooled to a temperature of approximately −100 °C with liquid nitrogen. Cooling the system to such an extent increased the shot-to-shot signal stability and suppressed thermal degradation of the ceramic block.

The ensuing cluster beam was skimmed before passing between the acceleration plates of the reflectron time-of-flight mass spectrometer; the cluster ions were extracted into the spectrometer using high voltage switches (Behlke Electronic GmbH). By varying the time at which the ions formed in the pulsed arc are extracted it was possible to obtain a range of different product ions. For short delays (<200 μs) between firing the arc and extraction into the reflectron, a mass spectrum containing exclusively ionic methanol clusters is obtained. As this time is increased (>450 μs) charged methanol clusters are no longer observed, but instead ionic lead clusters Pb_N^+ are

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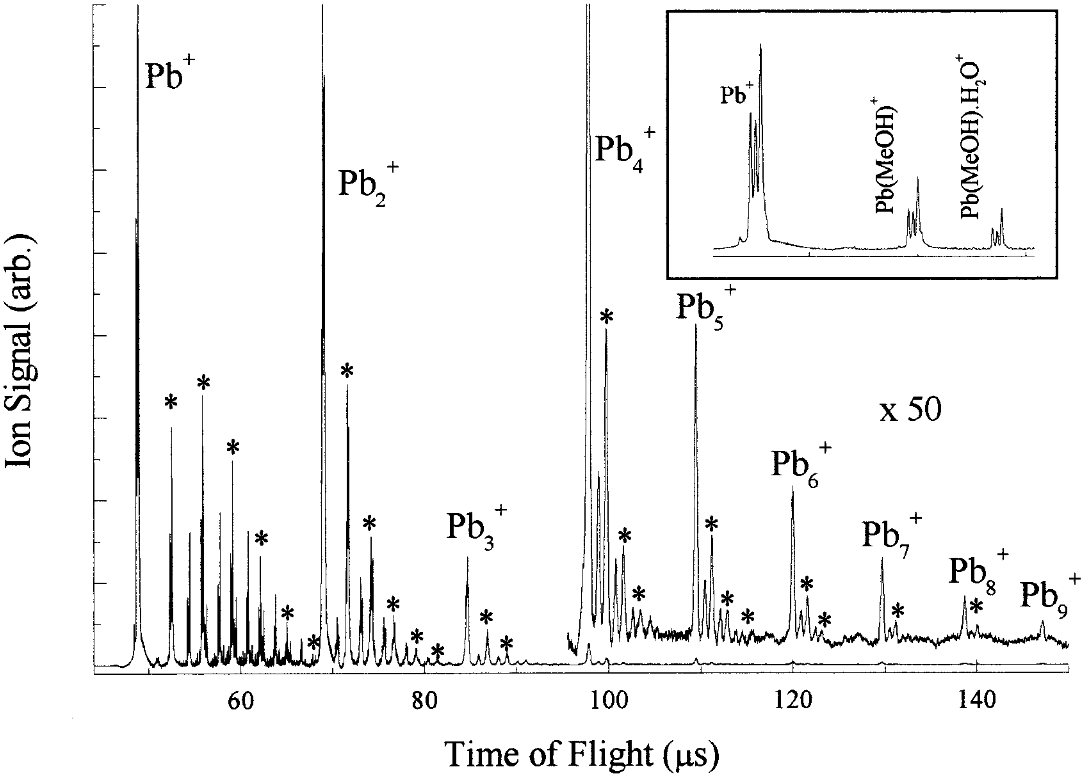

Figure 1. Typical time-of-flight mass spectrum of lead/methanol mixed cluster ions of the form $Pb_M(CH_3OH)_N^+$ where $1 \leq M \leq 9$ and $0 \leq N \leq 6$. The inset in the figure shows the isotope pattern of the Pb^+ ion. The peaks labeled with an asterisk (*) correspond to clusters of the form $Pb_M(CH_3OH)_N^+$.

detected. For delay times longer than 550 μs mixed lead methanol clusters are observed. It is probable that the methanol clusters are formed just after the exit from the nozzle and prior to entry between the electrodes of the PACS; in contrast, the production of bare metal clusters from the PACS takes a longer time since it relies on the discharge actually ablating atoms from the surface of the electrodes and for these excited atoms to then cluster in the supersonic expansion. In addition, flight times from the PACS to the extraction zone may depend on mass, which would also account for the range of delay times given above. Other experiments using the PACS with metals where the co-clustering process is much less marked, for example with copper, have shown, via photoionization, that there are neutral homogeneous methanol clusters in the beam at these longer delay times.[7] Therefore, a possible mechanism for the formation of the mixed ions is that neutral methanol clusters are "picked-up" by the metal cluster ions formed in the arc. This mechanism, at least for the single metal ion case, is not too dissimilar to that proposed by Lisy and co-workers for the formation of $Cs^+(CH_3OH)_n$ cluster ions.[4] However, the fact that the first ionization energy for Pb (7.4 eV) is significantly lower than that of methanol (10.9 eV) means that even if neutral lead atoms (or clusters) are picked up by charged methanol clusters, the charge would still transfer to the metal.

Spectra were accumulated using a fast digital oscilloscope (LeCroy 9310M) averaged over 2000 arc pulses. To obtain an optimized cluster mass spectrum, adjustments are made to the helium backing pressure, the time delay between pulsing the nozzle and striking the arc, and also to the time of extraction of ions into the mass spectrometer. Figure 1 shows a typical mass spectrum obtained with a delay time of 600 μs between firing the arc discharge pulse and extraction into the mass spectrometer. Clusters of the form $Pb_M(CH_3OH)_N^+$ are indicated by an asterisk (*).

To identify unambiguously a dehydration reaction in the mixed lead/methanol cluster ions, it is necessary to eliminate background water from the source; otherwise, there is no way of determining whether a given $Pb(CH_3OH)_N(H_2O)^+$ peak is due to a reaction, or simply the attachment of water in the source to the metal or the methanol cluster, or both. Therefore, extreme care was taken to clean and dry both the electrodes and the ceramic source block. The electrodes were placed in the source block, and both were baked in an oven for 12 h before being transferred to the vacuum chamber. When deuterated species are used in a typical cluster beam system, a major problem is the exchange of labile deuterium for hydrogen, which is adsorbed on the mainly stainless steel walls of the nozzle assembly. To reduce the probability of exchange, the reservoir and nozzle housing were "washed" with CD_3OD in order to displace any adsorbed hydrogen. In addition, the nozzle was pulsed with a mixture of helium and CD_3OD for 2 h prior to the arc being struck. Finally, the peak for CH_3OH^+ in the mass spectrum was monitored as it reduced in intensity to a point where it was no longer observable.

Results

A mass spectrum of lead and methanol clusters (Figure 1) shows clear evidence of peaks from mixed methanol and lead $Pb(CH_3OH)_N^+$ clusters which also contain water for each N. These peaks would appear to correspond to an intracluster reaction and the implication is that the reaction is initiated at $N + 2$ with lead, i.e.,

$$Pb(CH_3OH)_{N+2}^+ \rightarrow Pb(CH_3OH)_N(H_2O)^+ + (CH_3)_2O \quad (2)$$

At least one methanol attaches to all the metal clusters shown, and in the case of Pb^+ and Pb_2^+, up to eight methanol molecules

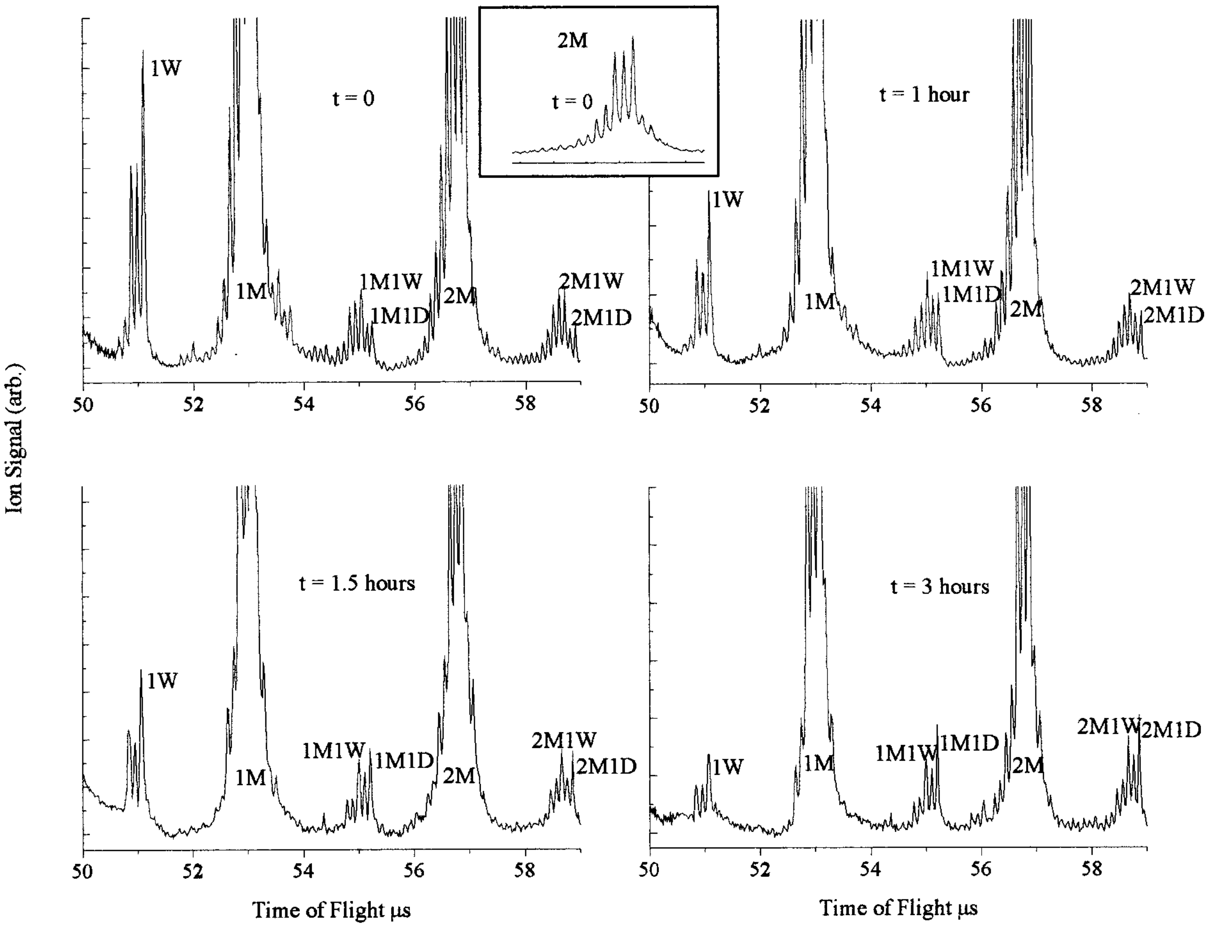

Figure 2. Series of mass spectra consisting of mixed lead and deuterated methanol cluster ions. Note the reduction in intensities of the associated H_2O peaks compared with those of the associated D_2O peaks. The notation 1M1W etc. implies a cluster consisting of one lead atom in association with one methanol molecule and one water molecule.

are seen to solvate the metal ($N = 7$ and 8 have not been labeled in Figure 1 for reasons of clarity). For Pb^+ there appears to be some increased structural stability at $N = 2$ as is indicated by $Pb(CH_3OH)_2{}^+$ being stronger than $Pb(CH_3OH)_1{}^+$, after which the intensity decreases with increasing N. For the series $Pb_2(CH_3OH)_N{}^+$, the peak intensities decrease with increasing N and a similar pattern of behavior is seen at larger values of M for the series $Pb_M(CH_3OH)_N{}^+$. Due to the low intensities of the precursor bare metal clusters, it is unclear from the mass spectrum shown whether the larger ($M > 4$) lead clusters are solvated by methanol to the same extent as those for which $M \leq 4$. However, by altering the extraction conditions into the reflectron, the shape of the observed mass distribution can be shifted to display higher mass clusters, and in this way it is possible to show that the larger lead clusters can be found in association with to up to six methanol molecules.

Spectra similar to that shown in Figure 1 were obtained with lead and deuterated methanol. However, the enhanced intensity of $Pb(CH_3OH)_2{}^+$ over its neighbors was not reproduced in the $Pb_M(CD_3OD)_N{}^+$ system, and it is therefore probable that there is only some slight structural stability of $N = 2$ over $N = 1$ and 3 in the undeuterated system. The intensities of $Pb_M(CD_3OD)_N{}^+$ clusters were observed to decrease with N, for all values of M which, taken together with the majority of $Pb_M(CH_3OH)_N{}^+$ results, is in contrast to solution phase PbR_N systems where a coordination number of four is strongly favored over other stoichiometries.[8,9] The gas phase results may be understood in terms of a statistical evaporative loss of methanol units prior to detection. It is also likely, considering the size of the lead ion (covalent radius = 1.47 Å), that the first solvation shell of a $Pb_N{}^+$ cluster would contain larger numbers of methanol molecules than are achieved here. This assumption would be in line with the findings of Kaya et al.[10] for indium with methanol, where they observe no appreciable intensity drop off for $N > 2$. In contrast, theirs and other evidence from studies on smaller transition metal ions show a pronounced solvation shell occurring with just two solvating methanol molecules. The experiments made here indicate that it is unlikely that any solvation shell is present for $N = 2$ (although of course it is impossible to infer accurate structural information from mass distribution) which implies that any acceptable mechanism for the proposed dehydration reaction within the solvating methanol molecules, should also involve the metal ion.

Figure 2 shows a series of mass spectra obtained when deuterated methanol is expanded thought the discharge with a lead cathode. Each spectrum covers the same mass range, which has been chosen to show peaks corresponding to $Pb(CD_3OD)_N{\cdot}(D_2O)^+$ for $N = 1$ and 2. The label 1M1D is placed on the peak due to $^{208}Pb(CD_3OD){\cdot}(D_2O)^+$, and likewise for the case of two methanol molecules (2M1D). The label 1M1W refers to the peak due to $^{208}Pb(CD_3OD){\cdot}(H_2O)^+$ and also, as a consequence of mass coincidence, to $^{206}Pb(CD_3OD){\cdot}(D_2O)^+$. While the appearance of peaks identified as $Pb(CD_3OD)_N{\cdot}(D_2O)^+$ should go some way toward confirming the presence of a dehydration reaction, it proved impossible to eliminate peaks assigned to $Pb_M(CD_3OD)_N{\cdot}(H_2O)^+$. On first inspection it would then appear that H_2O is merely associated with the methanol as an impurity from the carrier gas system. However,

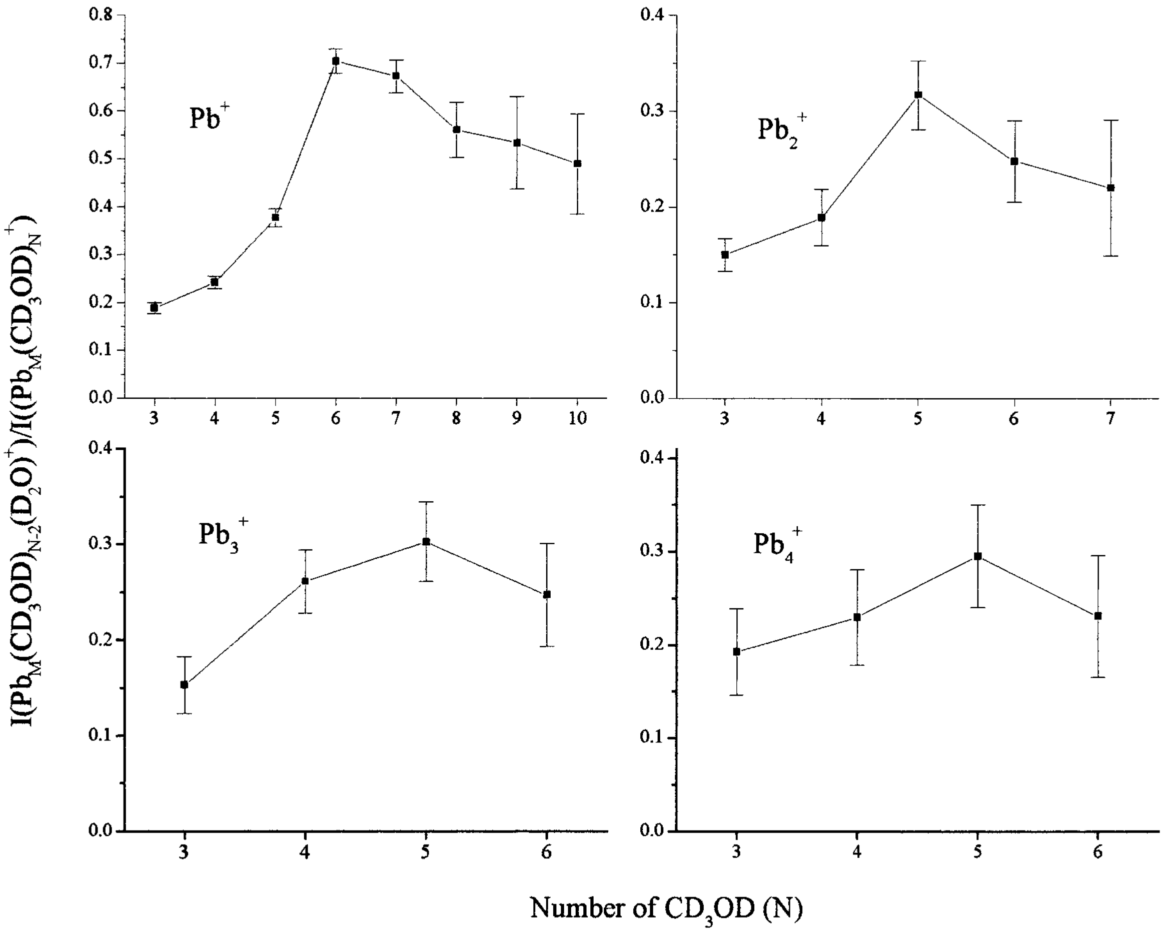

Figure 3. Ratios of the product ($Pb_M(CD_3OD)_{N-2}\cdot(D_2O)^+$) peaks to the (assumed) parent ($Pb_M(CD_3OD)_N^+$) peaks for $1 \leq M \leq 4$.

by taking a series of mass spectra over time (Figure 2), the intensities of the $Pb_M(CD_3OD)_N\cdot(D_2O)^+$ peaks were observed to increase relative to those of the $Pb_M(CD_3OD)_N\cdot(H_2O)^+$ system.

Two further features of this series of spectra are worthy of note. In each spectrum there is a series of peaks corresponding to $Pb(H_2O)^+$, labeled here as 1W. This signal is seen to decrease in intensity with time, but what is interesting is the complete absence of a comparable set of peaks for $Pb(D_2O)^+$. It seems plausible that the $Pb(H_2O)^+$ peaks are due to water which has been picked up from the source, possibly from the ceramic block. The decline in intensity of this signal with time implies a decrease in the absorbed water content. The inference from this observation is that the peaks due to $Pb(CD_3OD)_N\cdot(H_2O)^+$ are also a result of water pickup on the methanol clusters, which would explain the decline in signal intensity as a function of time. The absence of any peak due to $Pb(D_2O)^+$ strongly suggests that the presence of D_2O in $Pb(CD_3OD)_N\cdot(D_2O)^+$ clusters is due to an intracluster reaction and not simply pickup by the $Pb(CD_3OD)_N^+$ ions (see above). In addition, the inset in Figure 2 shows that the intensities of the $Pb(CD_3OD)_N^+$ ions do not follow the isotope pattern of lead, as can be seen by a comparison with intensities recorded for $Pb(CH_3OH)_N^+$ ions (inset in Figure 1). The reason for this is that isotope exchange (D for H) and D loss occurs, and hence lower mass peaks, corresponding to $Pb(CD_3OD)_{N-X}(CD_3OH)_X^+$ and $Pb(CD_3OD)_{N-X}(CD_3O)_X^+$ (where $X \geq 1$), are observed with increasingly probability at higher values of N. With time this isotope exchange on the $Pb_M(CD_3OD)_N^+$ decreases as hydrogen in the system is replaced with deuterium. The observed variation in signal with time, allows for three possible explanations for the production of peaks attributed to $Pb(CD_3OD)_N\cdot(H_2O)^+$: first, the proposed dehydration reaction could occur from the precursor cluster ion $Pb(CD_3OD)_{N-2}(CD_3OH)_2^+$; second, the peaks could be due to the pickup of H_2O or D_2O by lead + methanol clusters; or, finally, a combination of these could mean that the peaks are due to deuterium loss resulting in $Pb(CD_3OD)_N\cdot(OD)^+$. The difficulty in eliminating peaks corresponding to $Pb_M(CD_3OD)_N\cdot(H_2O)^+$ implies D/H exchange is occurring at some point in the experiment, either prior to the expansion or within the discharge. While it could also mean that residual water is being picked up by the deuterated methanol/metal clusters, the decrease in intensity of the $Pb_M(CD_3OD)_N\cdot H_2O)^+$ peaks, and especially of the $Pb_M(H_2O)^+$ peak with prolonged exposure to the deuterated solvent, points to D/H exchange as being a more probable cause. Despite this qualitative observation, however, the possibility that residual water is involved, renders the mass spectra obtained for the $Pb_M(CH_3OH)_N^+$ systems unreliable for an analysis of the product to reactant intensity ratios.

Before postulating a mechanism for the observed dehydration reaction, it is instructive to consider the behavior of the $Pb_M(CD_3OD)_N^+$ systems with respect to N and M. Figure 3 shows the ratios of the product ($Pb_M(CD_3OD)_{N-2}\cdot(D_2O)^+$) peaks to the (assumed) parent ($Pb_M(CD_3OD)_N^+$) peaks for $1 \leq M \leq 4$. For $M = 1$ the 208 isotope has been used, for $M = 2$ the peak corresponding to $Pb_2^+ = 414$ was used. For $M = 3$ and 4 the isotopic resolution was no longer clear, instead the centroid of the Pb_M^+ signal was used as a mass marker, and from this was calculated the flight times for the reactant and product ions. What is immediately evident is the increase in intensity of the $Pb_M(CD_3OD)_{N-2}(D_2O)^+$ peak relative to the corresponding

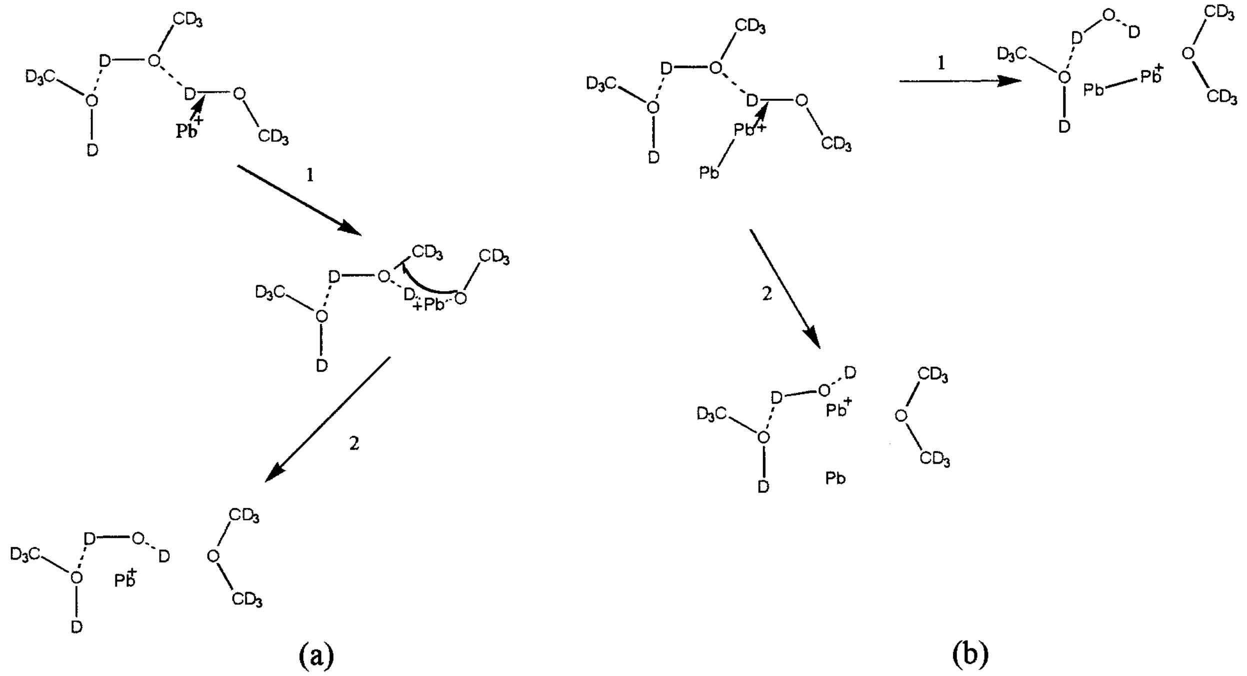

Figure 4. Schematics showing a proposed mechanism for the dehydration reaction (a) for a single lead atom cluster and (b) for the lead dimer.

$Pb_M(CD_3OD)_N^+$ ion as a function of N. The error bars increase for $M = 3$ and 4 due to the low intensities of these peaks in the recorded mass spectra.

Inspection of the plots in Figure 3 shows that the Pb^+ system behaves somewhat differently from those of higher M. For Pb^+, the reaction reaches a peak at $N = 6$, and for $N > 6$ the product-to-reactant ratio decreases; this could imply a partial solvation shell at $N = 6$ which then hinders the dehydration reaction. For $M = 2$, 3, and 4 the peak of the reaction in terms of the measured ratios occurs for $N = 5$, after which the relative intensities of the reaction products decline slightly.

Discussion

There is a possibility that the dehydration reactions occur in neutral methanol clusters for $N > 9$ prior to metal ion pick up, and that the subsequent evaporation of single methanol molecules leaves the resultant $Pb(CD_3OD)_{N-2}(D_2O)^+$ series for $(N - 2) < 8$. However, this likelihood can be ruled out on the grounds that the product-to-reactant ratios are much greater for the metal + methanol cluster ion systems than in bare methanol cluster ions (which have also been examined).[7] Figure 4 (a) shows a proposed mechanism for the reaction

$$Pb(CD_3OD)_3^+ \rightarrow Pb(CD_3OD)(D_2O)^+ + O(CD_3)_2$$

It is proposed that the reaction begins with the lead ion inserting into the O−D bond of a solvating methanol molecule, which then promotes the migration of CD_3 from a second methanol molecule hydrogen bonded to the first. The ether, $O(CD_3)_2$, is then lost from the charged complex to leave D_2O hydrogen bonded to the remaining methanol molecule, which is therefore of paramount importance to the proposed dehydration process. This mechanism contrasts with that presented by Huang et al.,[11] who accounted for dehydration in metal ion−single molecule complexes by proposing that the metal ion inserts into the C−O bond of the alcohol. However, for the case of a single methanol molecule in association with a metal ion, dehydrogenation rather than dehydration is observed, and to account for this both Huang et al.[11] and Fialko et al.[12] proposed metal ion insertion into the O−H bond.

A key component to the reaction mechanism discussed here is believed to be the presence of a third methanol. The higher polarizability of $O(CD_3)_2$ (6.0 Å^3) compared to that of D_2O (1.59 Å^3)) would imply that water would be the more favorable leaving group and that ether would remain with the charged metal cluster. For the case of H^+, competitive solvation between dimethyl ether, methanol and water has been studied, and under those circumstances, enthalpy changes follow the trend predicted by polarizability.[13] Since there is no evidence of products of the form $Pb(CD_3OD)_{N-2}O(CD_3)_2^+$ and, furthermore, $Pb(D_2O)^+$ is never observed as a reaction product (corresponding to a reaction involving only two methanol ligands), the third methanol molecule is considered to be essential to this dehydration route. A solution phase parallel to this reaction is the Williamson synthesis of ethers[14] which is used to produce unsymmetrical ethers and involves an S_N2 reaction of a sodium alkoxide with, for example, an alkyl sulfonate.

The decline in the ratio of product to reactant after $N = 6$ (shown in Figure 3) may be reconciled in terms of a partial solvation shell occurring with seven methanol molecules. The effect of the shell stabilizes the cluster, and hence the reaction probability is reduced; it is also possible that monomer methanol evaporation acts as a competing reaction (to ether loss) for $N \geq 7$. The rise in the product-to-reactant ratio on going from $N = 3$ to $N = 7$ may be due, in part, to the increased probability of bond insertion presented by the larger numbers of methanol molecules; these will also provide the product water molecule with more opportunities for stabilization.

In analyzing the data recorded on the dehydration reaction, it is noted that for lead clusters of sizes $M = 2$, 3, and 4, the reaction products reach a maximum when the cluster ion is solvated by five methanol molecules. This result was found to be reproducible for many different expansion conditions, and the plots shown in Figure 3 are the average of five different data sets. This is in contrast to the single ion case where the peak occurs at $N = 6$. For the case of $M \geq 2$ the dehydration reaction leads to identical products to those seen for the single atomic ion, i.e., $Pb_M(CD_3OD)_N{\cdot}D_2O^+$. Hence it would appear likely that the mechanism for dehydration is very similar to the single ion case; the only significant differences being the value of N (the number of solvating methanol molecules) at which the reaction peaks and the overall reduced intensities of the reaction products. One interpretation of this latter observation would be that the presence of more than one lead atom provides a steric hindrance to the insertion of a single lead atom into a O−D bond. Alternatively, the larger radius of the metal cluster compared to the single ion could result in larger distances between the methanol molecules. Finally, the distribution of positive charge throughout the metal cluster would decrease the effectiveness of any one metal ion to insert into a O−D bond. Although these points could be used to explain the reduction in the product-to-reactant ratios for $M \geq 2$ which is apparent when $N > 5$ as seen in Figure 3, they do not give a satisfactory explanation for the shift in peak intensity as a function of M.

A possible explanation of this latter observation is provided by a consideration of the pickup of the methanol by the metal cluster. It would seem likely that the charged metal cluster forms and then picks up a neutral methanol cluster; this being the case then it is quite possible that the methanol cluster is sited on just a single metal atom. The work of Kirkwood et al.[15] revealed the following infrared photoinduced dissociation of a chromium dimer associated with two ethanol molecules:

$$[Cr_2(EtOH)_2]^+ + nh\nu \rightarrow [Cr(EtOH)_2]^+ + Cr \qquad (3)$$

The explanation given for this observation is that both ethanol molecules are positioned on one of the chromium atoms. If there is a similar pattern of behavior here, then it could be inferred that six methanol molecules and another metal atom will fulfill the same partial solvation shell criteria seen for seven methanol molecules in the case of a single metal ion. This then raises the possibility that the larger product-to-reactant ratio observed for the single metal ion methanol clusters is artificially enhanced by metal−metal bond breaking in the larger metal clusters. A possible reaction mechanism for metal−metal bond breaking accompanying dehydration on the lead dimer is shown in Figure 4b. This mechanism is essentially the same as that shown in 4a and can either proceed such that the metal dimer remains intact in the product, or via the elimination of a neutral lead atom along with the ether. Since the structures of Pb_N^+ clusters for $N > 2$ are not known, even a schematic diagram of a suitable mechanism for the dehydration reaction could be very inaccurate. However, the implication from product-to-reactant ratios is that for larger metal clusters, the methanol molecules remain associated with just a single metal atom. If methanol molecules were positioned uniformly around the metal cluster, then, in the case of Pb_4^+, the spatial separation between molecules would lead to a considerable reduction in reaction probability: this is clearly not observed.

Organolead compounds have many industrial uses,[16−18] which stem in part from the wide range of structural forms they can adopt. The variety of coordination numbers that may be accessed means that such compounds are not limited to the tetravalent state, although this state is dominant. Unlike transition metal elements, where for a ground-state ion possessing an electronic configuration of X d^n, the promotion of one or more electrons to an s or p orbital may be necessary for the metal to be reactive,[15] lead cations have ground state electronic configurations with electrons in s and p orbitals, rendering them more reactive. With regard to the dehydration reaction observed here, there is an interesting analogy with organometal hydroxides[6] which undergo a condensation reaction to form plumboxanes of the general form $(R_3Pb)_2O$. In the presence of an alcohol, these oxanes exhibit solvolytic cleavage to form organometallic alkoxides. This reaction could be affected as a result of bulk solvent stabilization by the alcohol in a similar way to that observed in the work presented here, whereby the presents of at least one extra solvating methanol is necessary for the reaction to lead to a stable product. The solution phase reaction involves the elimination of water according to

$$(R_3Pb)_2O \xrightarrow{-H_2O\ R'OH} 2R_3PbOR' \qquad (4)$$

The oxide formed in this reaction will then readily pick up water from the atmosphere. This analogy underlines the importance of performing gas phase studies on such systems in order to better establish the behavior of both the immediate and more distant solvent environment.

Conclusion

The interaction of simple solvent molecular clusters with metal ions in the gas phase, and the interaction of single solvent molecules with metal clusters has been extensively studied. The work presented here has combined these two approaches and provides the first quantitative study of the behavior of small metal cluster ions with solvent clusters. Bare methanol cluster ions $(CH_3OH)_NH^+$ produced in the PACS[7] exhibit a dehydration reaction for $N \geq 7$, and the presence of a transition or alkali metal ion in a methanol cluster causing the formation of a more tightly bound complex in which the methanol molecules are held further apart from one another effectively delays the onset of this reaction until $N \geq 9$[3,4] In contrast, Pb^+ appears to promote the reaction since the reaction onset shifts downward to $N \geq 3$. The work of Castleman and Guo[19] states that the bonding interaction between Pb^+ and CH_3OH is of the same order as that between Na^+ and CH_3OH, which implies that the ligand to metal ion distance is small in lead + methanol complexes. This strengthens the argument that the lead ion is directly involved in the dehydration process.

The mechanism proposed for this insertion reaction is speculative but is analogous to similar process reported both in solution and in the gas phase. Although quantitative data is available only for small lead clusters, the mass spectra imply that the dehydration reaction also occurs for higher mass metal + methanol clusters. Due to the possibility of water absorption leading to ambiguity in assigning the intensity of the product peaks in the methanol + lead cluster systems, no quantitative data analysis was possible, but it appears that the product peaks are larger than for the deuterated methanol + metal cluster systems. This observation is consistent with the findings of Lu et al.[20] with reference to deuterium substitution in the iron + methanol cluster system. They state that the stronger hydrogen bonds formed after deuterium substitution in the cluster system result in a stronger barrier to the dehydration reaction. Further work must be performed to confirm this effect for the lead + methanol cluster systems investigated here. A time-of-flight mass spectrometric investigation of cluster ions cannot provide direct structural information about the clusters observed, although the trends in the occurrence of the reaction peak with M for Pb_M^+ imply that the methanol is grouped around just a single lead ion in the cluster.

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