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Influence of Solvation on Dehydration Reactions of Alkali Metal–Methanol Cluster Ions

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Abstract: Alkali metal–methanol cluster ions $A^+(CH_3OH)_n$ (A = Li, Na, K, Rb, Cs; n up to 20) are produced at low temperature, and their reactions are investigated using a fast flow reactor operated under thermal conditions. Surprisingly, dehydration reactions of methanol clusters are observed to occur beyond certain critical cluster sizes. The critical size is found to be dependent on the specific alkali metal ion in the clusters, with the observed product ions being $A^+(CH_3OH)_n(H_2O)$, where $n \geq 8$ for Li, Na, and K and $n \geq 9$ for Rb and Cs. The size-dependent dehydration reactions are interpreted as effects of charge and solvation on the reaction energetics.

Introduction

Investigations of cluster ions provide information essential to the further understanding of the changing properties and reactivity of matter as it undergoes transition from the gas phase to the condensed phase.[1] The dynamics of cluster-ion reactions are known to be oftentimes greatly influenced by the degree of aggregation as well as the nature of the solvent.[2] For example, the size-dependent intracluster reactions of ether, acetone, and methanol clusters have been observed under different experimental conditions.[3-8] In the gas phase, the reaction of $CH_3OH_2^+$ with CH_3OH is known to proceed through the following nucleophilic displacement.[7-10]

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad \Delta H^\circ = -15.5 \text{ kcal/mol} \quad (\text{ref } 11) \quad (1)$$

Earlier studies[7,9,12] show that when $CH_3OH_2^+$ is solvated by a few methanol molecules, the exothermic reaction is quenched,[7] an effect which has been attributed[12] to the difficulty of transferring the solvent from the reactant ion to the product ion within the reaction intermediate. Interetingly, studies of large protonated methanol clusters formed through multiphoton ionization (MPI) reveal that further solvation of $CH_3OH_2^+$ by methanol molecules promotes the following intracluster reactions:[7]

$$(CH_3OH)_{n+3}H^+ \rightarrow (CH_3OH)_n(H_2O)H^+ + CH_3OCH_3 + CH_3OH \quad n \geq 7 \quad (2)$$

In order to determine whether analogous intracluster reactions can proceed under thermal conditions, the reaction patterns of protonated methanol clusters $H^+(CH_3OH)_n$ (n up to 24) were recently investigated in a flow tube reactor.[3] The results showed that reaction 2 takes place even under conditions in which no additional energy is imparted due to the ionization step. An especially important finding is that the reaction commences only beyond a critical cluster size. The product ions $H^+(CH_3OH)_n(H_2O)$ ($n \geq 7$) were seen, in agreement with the previous MPI studies.

Particularly surprising were findings that analogous intracluster reactions of methanol clusters are also induced by the alkali metal ion Cs^+, despite the weak interaction between Cs^+ and methanol molecules. In the recent beam study of $Cs(CH_3OH)_n^+$ by Draves and Lisy,[8] the following reactions were observed:

$$Cs^+(CH_3OH)_n \rightarrow Cs^+(CH_3OH)_{n-2}(H_2O) + CH_3OCH_3 \quad (3)$$

with the onset for this reaction determined to be at $n = 10$.

In the present work, a systematic study is carried out to investigate whether these reactions can be induced by either Cs^+ or other alkali metal ions under thermal conditions, i.e., in the absence of high-energy collisions which might possibly accompany reactions taking place in the vicinity of the nozzle expansion and filament region where ion attachment is accomplished. Mixed-cluster ions $A^+(CH_3OH)_n$ (A = Li, Na, K, Rb, Cs; n up to 20) are produced at low temperature, and their reaction patterns are studied in a fast-flow reactor. Particularly revealing are observations made in the present study which show that the dehydration reactions have different critical sizes which are dependent on the specific alkali metal ion in the cluster.

Experimental Section

The experiments are conducted in a fast-flow reactor with a "poor-man's" high-pressure ion source. The details of the apparatus and the operation have been given in a previous publication,[13] and only those aspects pertinent to the present experiments are described here. Briefly, alkali metal ions are generated by thermionic emission from a Pt filament coated with a 2:1:2 ANO_3:Al_2O_3:SiO_2 mixture, A = Li, Na, K, Rb, and Cs, respectively. Methanol vapor introduced into the source becomes attached to the ions, thereby producing mixed alkali metal–methanol clusters $A^+(CH_3OH)_n$ at a source pressure of about 20 Torr. The cluster ions exit the source and are thereafter carried down the flow tube by He at a typical flow rate of 8000 cm^3(STP) min^{-1}, where they become rapidly thermalized by multiple collisions. The pressure in the flow tube is about 0.3 Torr in these experiments. In order to generate large clusters, the temperature of the source and flow tube has to be maintained far below room temperature. Temperatures as low as 130 K can be achieved by circulating liquid nitrogen through a copper coil wrapped along the flow tube. A small portion of the ion products are sampled, scanned by a quadrupole mass spectrometer, and detected by a channeltron electron multiplier.

Results

1. $Cs^+(CH_3OH)_n$. Only small cluster ions corresponding to $Cs^+(CH_3OH)_{0-2}$ are observed at room temperature. A typical

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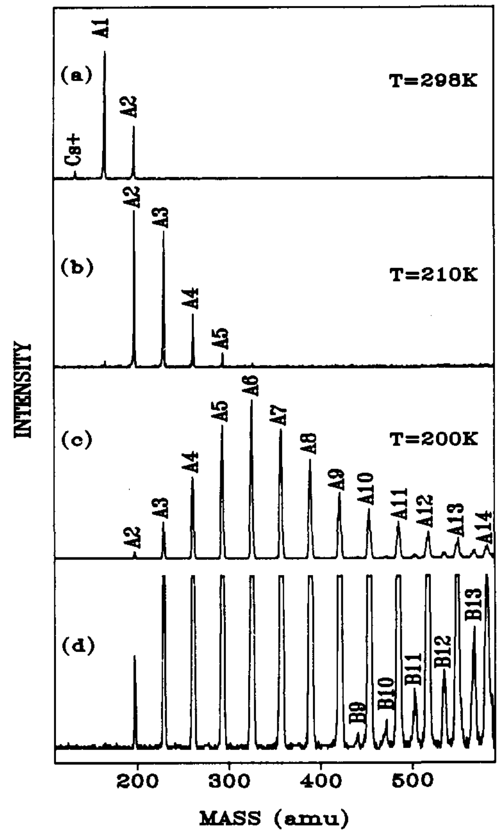

Figure 1. Mass spectra at T = (a) 298 K, (b) 210 K, and (c) 200 K and (d) an expanded mass spectrum of part c: An = $Cs^+(CH_3OH)_n$; Bn = $Cs^+(CH_3OH)_n(H_2O)$.

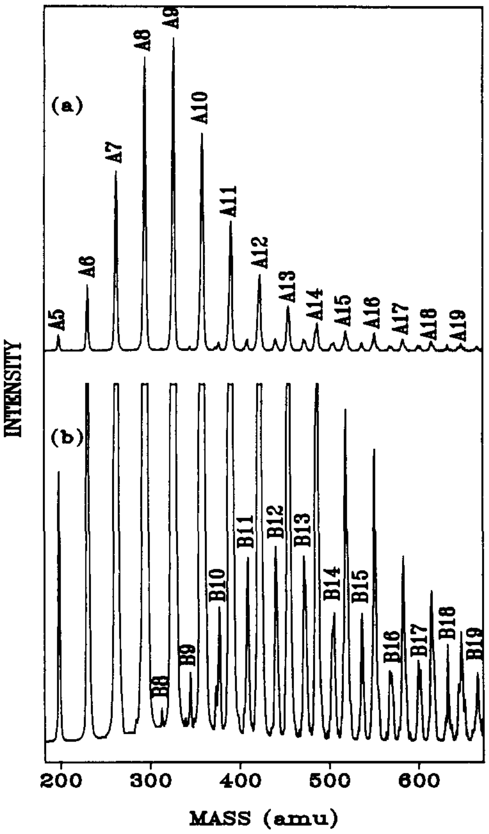

Figure 2. (a) Mass spectrum at T = 150 K and (b) expanded mass spectrum of part a: An = $Li^+(CH_3OH)_n$; Bn = $Li^+(CH_3OH)_n(H_2O)$.

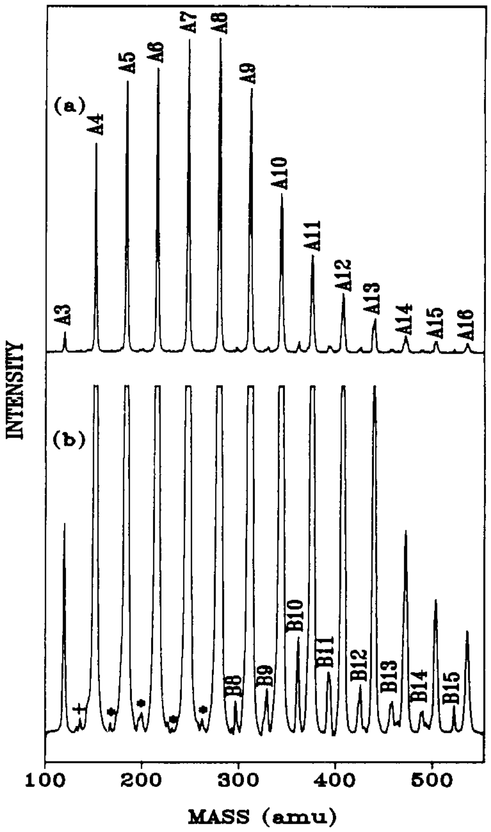

Figure 3. (a) Mass spectrum at T = 130 K and (b) expanded mass spectrum of part a: An = $Na^+(CH_3OH)_n$; Bn = $Na^+(CH_3OH)_n(H_2O)$.

spectrum of $Cs^+(CH_3OH)_n$ (labeled as An) is shown in Figure 1a. It is evident that no dehydration reactions take place in this size range, nor do any others in which water is retained and ether is lost. Indeed, no cluster ions corresponding to either $Cs^+(CH_3OH)_n(H_2O)$ or $Cs^+(CH_3OH)_n(CH_3OCH_3)$ are detected. When the temperature of the flow tube is lowered, clusters aggregate in a stepwise fashion and the distribution shifts to larger sizes. As shown in Figure 1b, cluster ions $Cs^+(CH_3OH)_n$, n up to 6, are formed at T = 210 K, but still no dehydration reactions (with accompanying ether or water loss) are detectable.

As the temperature is decreased further, even larger cluster ions are formed. A typical spectrum of $Cs^+(CH_3OH)_n$ at T = 200 K is presented in Figure 1c,d. At this point, it is obvious that a new cluster series $Cs^+(CH_3OH)_n(H_2O)$ (denoted as Bn, $n \geq 9$) appears in the spectrum. There are two possible origins for this new cluster series: either from a water impurity or from dehydration reactions. Extensive experiments with a wide range of high-purity methanol, carefully transferred under an inert atmosphere, and others with varying isotopic composition were made to answer this crucial question. All of the results tended to exclude water impurity as the source of the new cluster series. Moreover, the possibility of a water impurity can be excluded, since the water cluster series does not exist in the small-cluster range (see Figure 1a,b) and the series (Bn) only starts at critical cluster sizes, i.e., $n \geq 9$ in this case. Importantly, when trace water is intentionally added, it is observed in clusters of all sizes.

The critical cluster size $n \geq 9$ for the dehydration reactions observed in the present work is in good agreement with the recent beam studies by Draves and Lisy.[8] In their work, the intensity ratio of $Cs^+(CH_3OH)_{n-2}(H_2O)$ over $Cs^+(CH_3OH)_n$ was plotted as a function of cluster size, n. The ratio remained flat until cluster size n = 10, at which point a sharp increase in the curve was observed; therefore, n = 10 was taken as the critical size for the reaction.

2. $A^+(CH_3OH)_n$, A = Li, Na, K, and Rb. To find out whether other alkali metal ions have the same "catalytic effect", studies of other alkali metal ions were carried out in our laboratory at both room temperature and low temperatures. At room temperature, the following cluster ions are observed: $Li^+(CH_3OH)_{2-4}$, $Na^+(CH_3OH)_{1-4}$, $K^+(CH_3OH)_{1-3}$, and $Rb^+(CH_3OH)_{0-2}$. The fact that no cluster ions are detectable corresponding either to

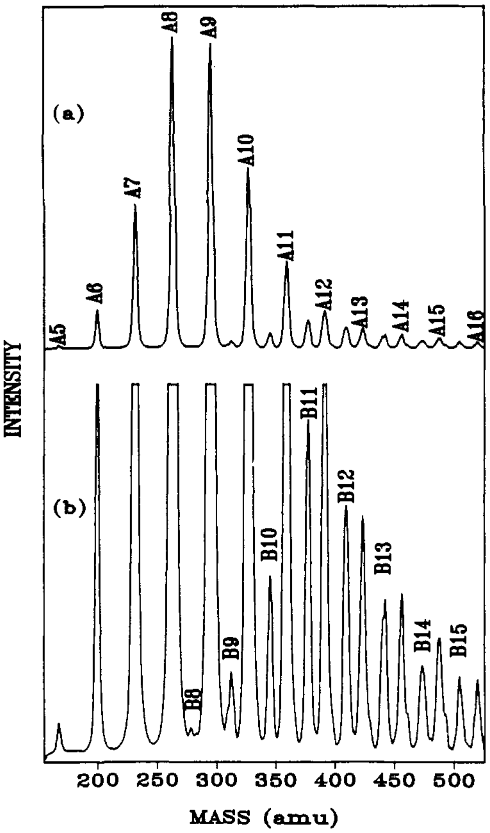

Figure 4. (a) Mass spectrum at T = 140 K and (b) expanded mass spectrum of part a: An = $K^+(CH_3OH)_n$; Bn = $K^+(CH_3OH)_n(H_2O)$.

$A^+(CH_3OH)_n(H_2O)$ or $A^+(CH_3OH)_n(CH_3OCH_3)$, indicates that the dehydration reactions do not take place in this cluster size range. As in the case of Cs^+, at low temperatures, large clusters $A^+(CH_3OH)_n$, with n up to 20, are formed. Typical mass spectra are shown in Figures 2–5 with A = Li, Na, K, and Rb, respectively. It is clear that two cluster series are present in the spectra, one corresponding to the parent ion distribution and the other to the intracluster reaction products. The dominant one is the alkali metal–methanol cluster ions $A^+(CH_3OH)_n$ (labeled as An). The ion intensity distribution of this cluster series depends on the temperature of the flow tube, and the most intense peak shifts to larger cluster sizes as the temperature is gradually decreased. No magic numbers are observed in these studies. Another cluster series corresponding to $A^+(CH_3OH)_n(H_2O)$ (labeled as Bn; $n \geq 8$ for Li, Na, and K and $n \geq 9$ for Rb) is also clearly visible in the spectra. Water impurity cannot account for its presence for the same reasons stated above. Instead, this new series arises from the following dehydration reactions, but where the water molecule is retained in the solvation shell and ether is ejected to accomodate the energy of reaction.

$$A^+(CH_3OH)_nCH_3OH + CH_3OH \rightarrow A^+(CH_3OH)_n(H_2O) + CH_3OCH_3 \quad (4)$$

Interestingly, it is seen from the spectra that the critical cluster size for the water cluster series is $n \geq 8$ for Li, Na, and K while $n \geq 9$ for Rb and Cs. Importantly, beyond the critical size, the reactions proceed for the full range of clusters investigated, namely to at least n = 20.

The critical sizes reported here are based on several measurements and are reproducible under different conditions. The mass assignment was carefully calibrated using high-resolution settings and was confirmed by isotope-labeled alcohol. The weak features marked by + and ✱ in Figure 3b resulted from oxide contamination. They were seen at room temperature, and they do not belong to Bn.

3. Tests to Ascertain the Lack of Reaction below the Critical Size. Since clusters of the form $A^+(CH_3OH)_{n-2}(H_2O)(CH_3OCH_3)$ have the same mass-to-charge ratio as $A^+(CH_3OH)_n$, a series of experiments were carried out to determine whether cluster ions of the form $A^+(CH_3OH)_{n-2}(H_2O)(CH_3OCH_3)$ might exist at small cluster sizes but retain both water and ether in the solvation shell. The idea behind the experiments was that switching reactions can be effected between species of the same chemical composition but with different isotopic content. If species of mixed composition were present in a cluster, these could be revealed by adding a great excess of one into the flow tube reactor, with isotopes different from those possibly retained in a cluster as a result of an intracluster reaction; its presence would be signaled by a mass change equivalent to the isotope difference.

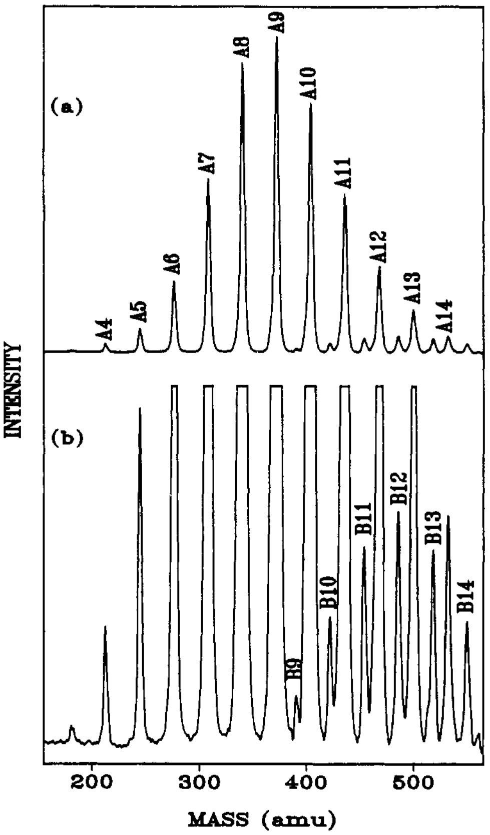

Figure 5. (a) Mass spectrum at T = 150 K and (b) expanded mass spectrum of part a: An = $Rb^+(CH_3OH)_n$; Bn = $Rb^+(CH_3OH)_n(H_2O)$.

The studies were performed in two ways, one in which reactions were effected for CD_3OD clustered to the ions and an excess of CH_3OCH_3 was added through the reactant gas inlet. The second series corresponded to the converse experiment with reactions between light alcohols, followed by addition of deuterated ether molecules. Should ether be solvated in small clusters, partial replacement would be easily detected. The experiments failed to reveal any reaction products in clusters below the assigned critical sizes. For example, when CH_3OCH_3 is introduced from the reactant gas inlet to react with $A^+(CD_3OD)_n$, only association of dimethyl ether with the alkali metal–methanol mixed clusters is observed. There are no clusters of the form $A^+(CD_3OD)_{n-2}(D_2O)(CH_3OCH_3)$ detected. Therefore we conclude that no cluster ions of the form $A^+(CH_3OH)_{n-2}(H_2O)(CH_3OCH_3)$ exist in the system and the dehydration reactions only proceed beyond a critical size.

Discussion and Conclusions

The present work clearly reveals that the dehydration of methanol is effected under thermal reaction conditions even by very inert alkali metal ions. The studies of possible switching reactions with ether established that the reactions do not commence at low degrees of solvation but require a specific degree of aggregation. A similar conclusion that reactions have not proceeded in very small clusters was also inferred from attempts to photodissociate the complexes,[8] and hence the conclusions of our study and the earlier one on the Cs^+ system, made under beam conditions, are consistent.

The results of the present studies also show that there is a small dependence of the ion type on the critical size where the reaction is initiated, the required degree of solvation being slightly smaller for ions of smaller radius and hence stronger bonding.[15] Clearly, the fact that the dehydration reactions lead to the retention of water in the clusters, but with ether loss, indicates preferential bonding and solvation of the water in the mixed cluster–ion complex.

It is worth noting that intracluster reactions have been observed[6,7] in protonated methanol clusters and the product cluster ions $H^+(CH_3OH)_n(H_2O)$ found at $n \geq 7$. Nevertheless, it is surprising that reactions occur for the alkali metal ions that are similar to those that occur for the proton, since the bonding properties are so much different. The proton affinity of methanol is 184.9 kcal/mol,[14] while the binding energies of alkali metal ions with one methanol are 38.1 kcal/mol[15] for Li^+, 26.6 kcal/mol[16] for Na^+, 21.9 kcal/mol[17] for K^+, and 13 kcal/mol[18] for Cs^+. There are no thermal energy data available in the case of Rb. In the protonated case, the dehydration reaction of $CH_3OH_2^+$ with CH_3OH to produce $(CH_3)_2OH^+$ and H_2O (reaction 1) is exoergic[11] ($\Delta G° = -13.26$ kcal/mol) but has a considerable activation barrier of 26.5 kcal/mol.[9] The gas-phase dehydration reaction of two methanol neutral molecules to form dimethyl ether and water is also slightly exoergic[8] ($\Delta G° = -4.56$ kcal/mol) but has an activation barrier that should be comparable if not larger than the protonated case.

The fact that identical dehydration reactions are observed in both the protonated methanol clusters and the mixed methanol–alkali metal ion clusters is strong evidence that solvation plays an important role in overcoming (or reducing) the energy barrier to reaction. For small cluster ions, the dehydration reactions are evidently not observed due to a high reaction barrier, despite the exothermicity of reaction 4. As the degree of solvation increases, the exothermicity of the overall reaction (reaction 4) should increase accordingly due to the large ion–dipole interaction of the product ion ($\mu = 1.85$ D for H_2O; $\mu = 1.30$ D for CH_3OCH_3).[19] At the same time, the reaction barrier may also be reduced due to the solvation. As a result, the dehydration reactions become accessible beyond a critical cluster size. In fact, different critical cluster sizes are observed for different charge centers, in accordance with expected trends in their binding energies.

Finally, it should be noted that the critical size for the protonated methanol cluster is only slightly different from that for the mixed methanol–alkali metal ion clusters. This may indicate that the dehydration reactions leading to ether loss beyond a critical size take place away from the charge center (not in the first solvation shell) in both cases. For reactions directly involving the charge center (such as reaction 1), the reaction barrier is evidently raised (not reduced) as the solvation degree increases due to the difficulty of transferring the solvent from the reactant ion to the product ion within the intermediate. However, this difficulty may not be a major factor when the reactions take place away from the charge center, as evidenced by the observation that the dehydration reactions occur in all of these systems at sufficiently large degrees of solvation.

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