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Evidence of Delayed "Internal" Ion–Molecule Reactions Following the Multiphoton Ionization of Clusters: Variation in Reaction Channels in Methanol with Degree of Solvation

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Abstract: Reactions of methanol cluster ions produced by the multiphoton ionization of neutral methanol clusters are studied by using a reflecting electric field time-of-flight mass spectrometer (reflectron). Following the formation of protonated cluster ions via internal ion–molecule half-reactions, two reaction channels are observed: one involves the unimolecular (evaporative) loss of CH_3OH monomers, while the other leads to the production of protonated ether and loss of H_2O. While the first channel is observed for all cluster sizes, the second shows a distinct dependence on the degree of solvation and only occurs for the protonated dimer. The product ion resulting from loss of H_2O is not observed in the direct mass spectrum and is found to involve a metastable loss process; the rate is determined to be $(5.5 \pm 0.5) \times 10^5\ s^{-1}$. A correspondence with known bimolecular gas-phase ion–molecule reactions is discussed.

It is well-established that under certain conditions following the ionization of a cluster, reactions proceed between various moieties within the cluster ion that in terms of products parallel bimolecular gas-phase in molecule reactions. One of the first examples discussed in this context was the formation of protonated water clusters which Klots and Compton[1] attributed to an ion–molecule half-reaction taking place within a water cluster following its ionization. They also reported observing metastable components in such reactions, as well as in the formation of $C_3H_5^+$ following the ionization of the ethylene dimer. Numerous other authors, including ourselves, have made similar observations.[2-5] Further evidence for the importance of internal ion–molecule reactions in governing the product ions formed following the ionization of neutral clusters was derived from other studies conducted in our laboratory showing the first direct evidence for substantial dissociation (unimolecular decomposition) leading to the evporative loss of multiple monomer units from a cluster.[6] In particular, up to six ammonia molecules were lost from $NH_4^+(NH_3)_8$ by a combination of unimolecular and collisional-induced dissociation processes following production of the cluster ion from neutral clusters via multiphoton ionization. It is expected that trends as a function of the degree of cluster aggregation should provide evidence of the extent to which neighboring solvent molecules perturb the reactions of the ions.

Although metastable (unimolecular evaporative) dissociation has been the subject of numerous papers, in all cases the products of the ensuing reactions having bimolecular ion–molecule counterparts were the same as the prompt daughter products (i.e., those formed at times short compared to the observation time of the technique employed). Herein, we report what to the best of our knowledge is the first evidence of a delayed internal cluster reaction, namely, the metastable loss of H_2O following the ionization of methanol clusters via multiphoton ionization, which has a direct bimolecular ion–molecule counterpart. In contrast to earlier work where the product ions detected have always appeared as peaks in the direct ionization spectrum, in the present studies, no direct product is observed for the channel corresponding to the loss of water following ionization of methanol clusters.

Experimental Section

The apparatus used in these studies has been described in detail elsewhere.[6,7] Hence, only a brief description of the features relevant to the present study are given herein. Neutral methanol clusters are formed in an argon-seeded supersonic expansion of methanol vapor from a pulsed nozzle source. Experiments are performed by subjecting the cluster beam to multiphoton ionization and analyzing the resulting cluster ions in a time-of-flight mass spectrometer system equipped with a reflectron. The molecular beam is crossed by a Nd:Yag pumped dye laser and wavelength extension system providing frequency doubling and mixing capabilities. Typical photon fluxes of 10^{16} photons per pulse of duration approximately 6 ns are obtained. Ions formed by multiphoton absorption are accelerated in an electrostatic field to approximately 2 KeV, deflected by a few degrees in a transverse field to separate the ion and neutral beams, and subsequently detected by a particle multiplier. The time-of-flight spectra of the ions, equivalent to mass spectra, are digitized and signal averaged in a transient recorder with 10-ns resolution.

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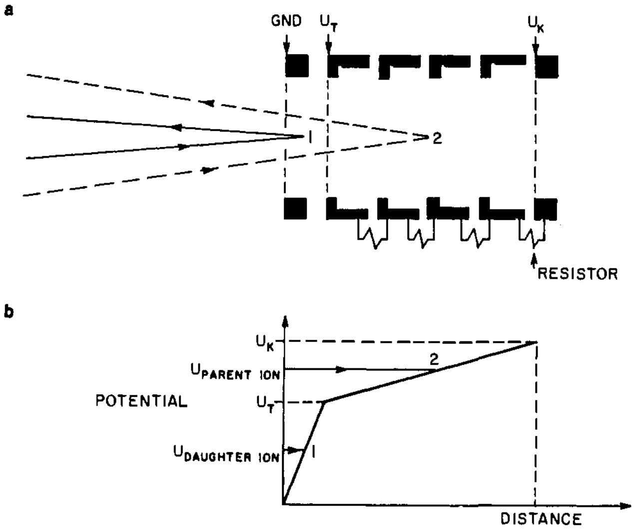

Figure 1. (a) The reflectron is comprised of two uniform electric fields. The potential across the first gap is U_T. The second homogeneous field is defined by the potentials U_T and U_K, as well as the guard rings in between. The four equal resistors serve as a voltage divider. (b) The potential along the TOF lens-reflectron axis is plotted. Points 1 and 2 indicate where the daughter and parent ions, respectively, are reflected.

In a conventional time-of-flight mass spectrometer without a reflectron, dissociation products formed in the field-free drift region show up at parent ion masses so that dissociation processes cannot be studied directly. A crucial feature of the present studies is the incorporation of a reflecting electric field following the drift region of the time-of-flight mass spectrometer system which does enable dissociation processes to be investigated. With an application of appropriate potentials at the reflectron grids, a time difference between daughter ions born in the drift region and undissociated parent ions (typically about 0.6 μs) enables their separate detection. A unique identification can be made on the basis of both time differences and energy analysis as discussed previously.[6] In the present study, the neutral clusters are ionized via nonresonant multiphoton absorption at the focus of a pulsed laser beam of 266-nm wavelength light. The newly formed cluster ions undergo a rapid proton-transfer reaction (eq 1) which has a well-known bimolecular counterpart that proceeds at near collision rate;[8] only protonated methanol cluster ions are observed.

$$(CH_3OH)_n^+ \rightarrow (CH_3OH)_{n-1}H^+ + CH_3O \qquad (1)$$

Figure 1 shows a schematic of the reflectron setup used in the present study and displays the nature of the reflecting fields which lead to a time difference between parent and daughter ions. Application to an energy analysis is also evident from Figure 1b. Parent ions can be removed from the overall spectrum by reducing the potential between U_T and U_K to a value which allows parent ions to penetrate through the reflectron. Successive changes of potentials enable separation of daughter ions of various kinetic energies to be performed as well.

Results and Discussion

A conventional time-of-flight mass spectrum of the ionized methanol clusters is shown in Figure 2. Only the product ions formed from a proton-transfer reaction (eq 1) are observable in the mass spectrum. Through appropriate use of the reflectron, however, evidence for metastable processes can be obtained. For example, Figure 3 shows data taken under conditions where the parent ions are reflected along with daughters giving rise to a small time separation between them. The daughter ions (shaded peaks designated $n - 1$) appear as resolved peaks at times just preceding those of the parents. These correspond to ions arising from the unimolecular (and partial contributions from collision induced dissociation) evaporation of monomer units of CH_3OH from the protonated cluster ions, in direct analogy to observations that we have made on the ammonia system.[6] The details of the unimolecular dissociation and collision-induced dissociation work will be reported elsewhere.[7]

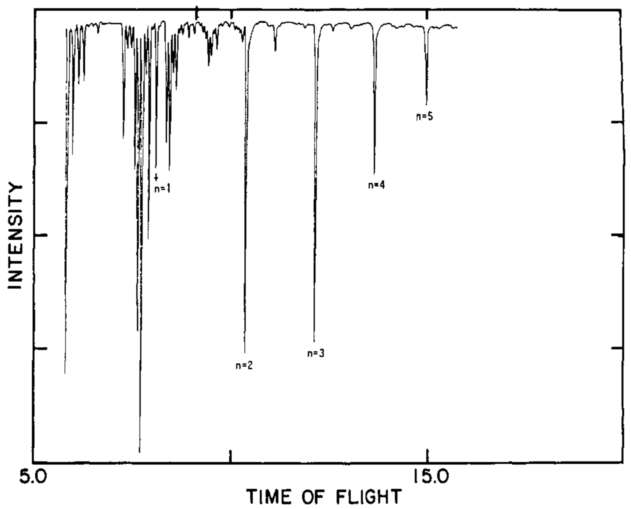

Figure 2. Time-of-flight mass spectrum of $(CH_3OH)_nH^+$ ($n < 6$) at $\lambda = 266$ nm. The arrow indicates the position of mass 47 amu. The large peak immediately to the right of 10 μs is $(CH_3OH)_2H^+$.

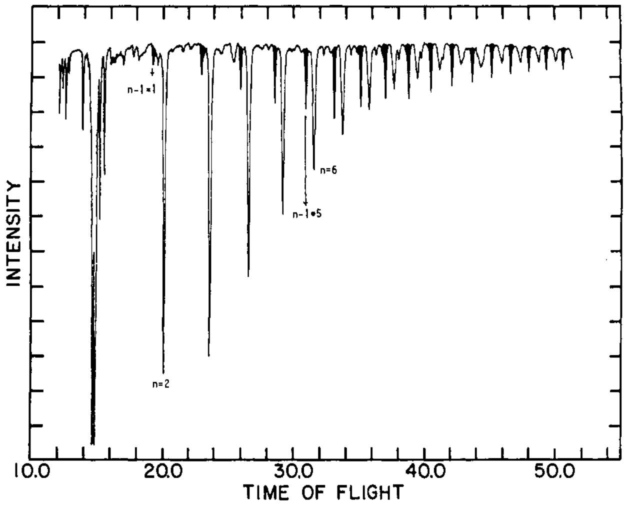

Figure 3. Time-of-flight mass spectrum at $\lambda = 266$ nm. The shaded peaks are the daughter ions resulting from a 32 amu mass loss, i.e., $(CH_3OH)_{n-1}H^+$. The large unshaded peak to the right of each daughter ion is the corresponding parent ion, $(CH_3OH)_nH^+$.

A very interesting observation was made in studies where the reflecting conditions were weakened, such that the parent ion was removed from the mass spectrum. Operation under such conditions enables the dissociation processes to be observed with better time and energy resolution. The results of this study are shown in Figure 4. Of particular significance in this study is the appearance of a peak preceding the metastable daughter (A, $n - 1 = 2$) of $(CH_3OH)_{n-1}H^+$ ($n = 3$). Through analysis of both the arrival time and the threshold energy for reflection, this peak is definitively attributed to the metastable loss of 18 amu from the (initially formed) protonated methanol dimer ion of mass 65 amu according to reaction 2. The protonated methanol dimer ion

$$(CH_3OH)_2H^+ \rightarrow \text{daughter}^+ \text{ (47 amu)} + \text{neutral (18 amu)} \qquad (2)$$

$(CH_3OH)_2H^+$ can rearrange as will be discussed below. The daughter ion of 47 amu is protonated dimethyl ether $(CH_3)_2OH^+$ formed by the loss of H_2O (18 amu) from $[C_2H_9O_2^+]$ the parent ion cluster[9,10] (eq 3).

$$(CH_3OH)_2H^+ \rightarrow (CH_3)_2OH^+ + H_2O \qquad (3)$$

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(8) Bowers, M. T.; Su, T.; Anicich, V. G. *J. Chem. Phys.* **1973**, *58*, 5175.

(9) The formation of protonated dimethyl ether from the gas-phase ion-molecule reaction has been verified by collision-induced decomposition studies of M. F. Jarrold and M. T. Bowers (see footnote 14 in ref 10).

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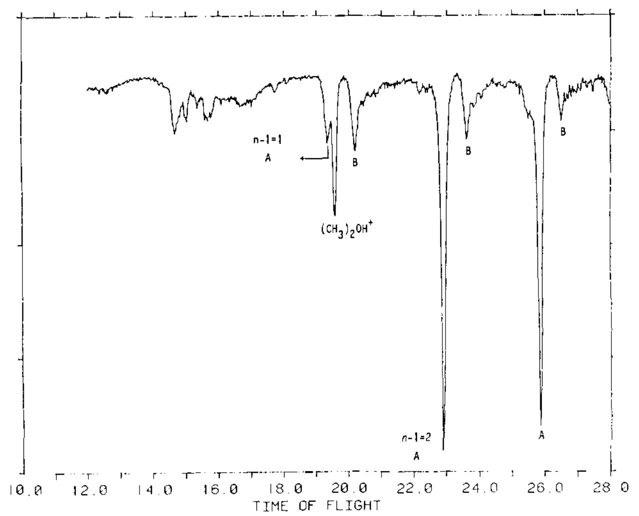

Figure 4. Time-of-flight mass spectrum at λ = 266 nm. Daughter ions of $(CH_3OH)_nH^+$ (n = 2–4) are shown. The peaks at 19.4 and 19.6 μs are the daughter ions formed by loss of CH_3OH and H_2O, respectively, from $(CH_3OH)_2H^+$. The peaks labeled A (n − 1) belong to the daughter ion series $(CH_3OH)_{n-1}H^+$. These ions are formed via loss of CH_3OH from parent ions $(CH_3OH)_nH^+$. The peaks labeled B correspond to residual parent ion intensity. The peaks located at time-of-flight less than 18 μs are background peaks.

It is worthy of note that this metastable peak only arises through an internal ion–molecule reaction associated only with the protonated dimer parent (eq 2), a fact which has been confirmed by our time and energy analyses. As seen from Figure 4, no channel corresponding to the loss of mass 18 amu is observed for the protonated trimer or tetramer (nor for other clusters of higher degrees of aggregation).

Peak A ($n - 1 = 1$) located just to the left of the $(CH_3)_2OH^+$ peak corresponds to the metastable loss of 32 amu (one monomer unit) from the protonated dimer ion (eq 4). [Under the conditions

$$(CH_3OH)_2H^+ \rightarrow (CH_3OH)H^+ + CH_3OH \qquad (4)$$

of the data shown in Figure 4, the daughter ions $(CH_3OH)H^+$ and $(CH_3)_2OH^+$ are formed in a 1:2 ratio.] By studying the ratio of daughter to parent under conditions of varying acceleration time in the region of ionization, we have been able to determine a rate constant for the reaction leading to the appearance of the protonated ether metastable peak (see Figure 5). A rate coefficient of (5.5 ± 0.5) × 10^5 s^{-1} was measured for reaction 3. This was deduced from the following considerations.

The rate of unimolecular loss of H_2O from $(CH_3OH)_2H^+$ is derived from eq 5, where the brackets designate concentration,

$$\frac{[(CH_3)_2OH^+]}{[(CH_3OH)_2H^+]_{t=0}} = 1 - e^{-kt} \qquad (5)$$

which is proportional to measured intensity. The dissociation time, t, for an ion is composed of the acceleration time (time in the ion lens) plus the drift time (time in the field free region). Evaluation of eq 5 at t_a (acceleration time) and $t_a + t_d$ (acceleration + drift time) followed by algebraic combination of the two expressions yields:

$$\frac{[(CH_3)_2OH^+]_{t_a} - [(CH_3)_2OH^+]_{t_a+t_d}}{[(CH_3OH)_2H^+]_{t=0}} = \frac{[(CH_3)_2OH^+]}{[(CH_3OH)_2H^+]_{t=0}} = e^{-kt_a}(1 - e^{-kt_d}) \qquad (6)$$

The average unimolecular rate coefficient is obtained from the slope of a plot of the natural logarithm of the ratio of the daughter ions to the daughter plus parent ion intensity at any time vs. acceleration time as shown in Figure 5. The time in the drift region (initial ion energy) is kept constant for all measurements as a function of the acceleration time.

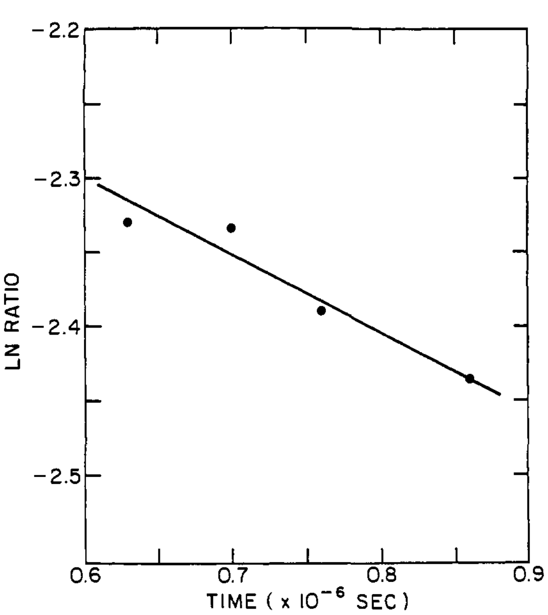

Figure 5. The natural logarithm of the integrated intensity ratio is plotted vs. the acceleration time. The ratio is given by $[(CH_3)_2OH^+]/[(CH_3OH)_2H^+]_{t=0}$ (see eq 6), where $[(CH_3OH)_2H^+]_{t=0}$ is the sum of $[(CH_3OH)_2H^+]$ and $[(CH_3)_2OH^+]$ at any time. The slope of the line yields k, the average unimolecular rate constant for the process $(CH_3OH)_2H^+ \xrightarrow{k} (CH_3)_2OH^+ + H_2O$.

Discussion

The gas-phase ion–molecule association reaction of protonated methanol ion with neutral methanol to form protonated dimethyl ether ion and water has been reported in the literature (eq 7).[12]

$$CH_3OHH^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad (7)$$

Henis[10] confirmed the identity of the m/e 47 amu product ion as the protonated dimethyl ether. Analogous reactions also have been reported from studies on other alcohols as well.[13-16]

It is interesting to consider the essentially negligible amount of intensity attributable to $(CH_3)_2OH^+$ in the prompt spectrum (i.e., mass 47 amu in Figure 2) compared to that expected if the production of the protonated ether did not involve an induction time. Under the experimental conditions employed for the data presented in Figure 2, the time spent by the parent of $(CH_3)_2OH^+$ in the acceleration region is 0.5 μs. Metastable dissociation is proceeding at 5.5 × 10^5 s^{-1}, from which it is estimated that the time of induction is at least 0.2 μs. The time over which we observe the reaction in the metastable experiments (Figure 4) is the drift time window corresponding to 0.91–7.1 μs following ionization which gives rise to a significant intensity of $(CH_3)_2OH^+$ observable in the metastable spectrum.

Bowers and co-workers[10] also have investigated reactions of protonated methanol with methanol in the second field free region of a reverse geometry mass spectrometer. They report lifetimes of 10^5–10^6 s^{-1} for the elimination of H_2O from metastable $(CH_3OH)_2H^+$. Interestingly, in the gas phase the protonated dimer reaction with methanol monomer only led to an association (isomerization) product.

By comparison with the gas-phase studies, an important finding of our work is that the reactions in clusters bear a direct analogy to the well-known gas-phase ion–molecule reactions. Of particular significance is the fact that the daughter ion corresponding to the loss of an H_2O molecule does not appear in the direct mass spectrum but only following some substantial time delay. Our measured unimolecular rate for H_2O loss of (5.5 ± 0.5) × 10^5

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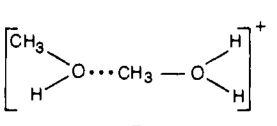
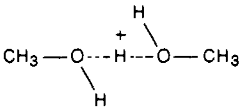
s^{-1} is in very good agreement with the range of values deduced by Bowers for the gas-phase analogue discussed above. Of equal significance is the observation that the reaction proceeds only for a specific cluster size and hence displays significant variation with the degree of ion solvation in the cluster as well as in the isolated ion–molecule reactions. These results establish further connection between changes in reaction processes proceeding in the gas compared to the condensed phase due to the effects of solvation.

It is interesting to speculate on reasons for the variation in reactivity. A number of structures have been proposed for the parent ion species of mass 65 amu that decays unimolecularly via loss of H_2O. Isotope-labeling work of Kleingeld and Nibbering[17] suggests an intermediate of structure I while Bowers' and coworkers'[10] interpretation of kinetic results suggests a structure II.



I



II

The studies of Morton and co-workers[15] indicate that, at least for the case of 2-butanol, reaction to form the meso isomer of the ether occurs by backside displacement. It is suggested that a vibrationally excited proton-bound dimer undergoes rearrangment to expel water. The work of Bowers and colleagues provides some evidence for structure II, although they admit to the possibility that internally excited ions may react via structure I as suggested by the findings of Kleingeld and Nibbering.

The fact that we observe metastable loss of H_2O and CH_3OH subsequent to the formation of the protonated dimer suggests the possibility of two distinct intermediates (structures I and II). Structure II might be the species initially formed following ionization with the possibility of isomerization to structure I occurring in the microsecond time frame observable by our reflectron technique. The energy acquired upon the rearrangement of the alcohol molecules about the newly formed charged center would undoubtedly provide considerable excess energy for structural interconversion. We estimate this excess energy to be 0.6, 1.1, and 1.3 eV for the unprotonated trimer, tetramer, and pentamer ions, respectively. This estimate is based on energetics of the proton transfer reaction, rearrangement energy, and hydrogen bond energy.[18,19] Structure I would seem to be appropriate for the facile loss of H_2O. Following the ionization of larger neutral clusters, structures involving protonated alcohol molecules corresponding to higher analogues of structure II may be an appropriate description. Perhaps at larger degrees of solvation (more analogous to the liquid phase) there is a hinderance to the necessary rearrangement to structure I, thus preventing the loss of H_2O as an important product channel in the reaction. It is also possible that another core ion exists in the case of the trimer[20] and higher clusters. However, our estimates suggest that reaction channels corresponding to the loss of H_2O should be energetically competitive with those leading to loss of CH_3OH, but we only observe the latter process.

Acknowledgment. We thank Dr. Robert G. Keesee for helpful discussions during the course of this work. Support by the U. S. Department of Energy, Grant No. DE-AC02-82ER60055, is gratefully acknowledged.

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He I Photoelectron Spectra of the Unstable Substituted Aminoboranes, Aminodifluoro-, Aminodichloro-, and Aminodibromoborane. An Experimental and Theoretical Study

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Abstract: He I photoelectron spectra are reported for the unstable aminodifluoro-, aminodichloro-, and aminodibromoborane molecules, H_2NBF_2, H_2NBCl_2, and H_2NBBr_2. High yield routes to these molecules have been demonstrated, and the identities and orbital assignments have been established by a comparison with other similar molecules, notably the more stable methyl-substituted analogues and the isoelectronic ethylenes. The HOMO in all cases is π. Electronic and geometric structures have been investigated theoretically at the semiempirical (MNDO) and ab initio (3-21G*) levels; these provide an investigation of the structures of the H_2NBCl_2 and H_2NBBr_2 molecules, the H_2NBF_2 cation, and the barriers to internal rotation for the molecules. In conjunction with results for the unsubstituted H_2NBH_2 molecule these experimental and theoretical studies provide an assessment of B-halogenation and hence π donating ability on the nature of the BN π bond.

Small alkyl-substituted aminohaloboranes are unstable as monomeric species, having a tendency to form dimers and trimers, with the result that they have not been well-characterized.[1-4] The dimethylamino derivatives are perhaps the most widely studied, but these also undergo self-association,[2,5] and the simplest aminoboranes, unsubstituted on nitrogen, exist only as transient in-

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