that it was *endo*-**4c** (Figure 2), resulting exclusively from a mechanism analogous to that in path b (Scheme I); no adducts derived from the alternative mode of addition [cf. path c (Scheme I)] were observed. The normal [3 + 2] cycloadducts **3b,c** were also obtained in yields of 9% and 2%, respectively. Under similar conditions, keto aldehydes **2e,f** afforded the corresponding ozonides **3e** (39%) and **3f** (22%) as the major peroxidic products. Treatment of **3f** with trifluoroacetic acid at room temperature gave the rearrangement product **4f** (21%). Substantial quantities of the starting keto aldehydes **2b–f** were also recovered in each case.

Supplementary Material Available: Physical properties, including melting points and NMR, IR, and analyical data, of compounds **3a–c,e,f**, **4a,b**, *exo-* and *endo*-**4c,d**, **4f**, **5a**, and **6a** and crystal data, bond lengths and angles, fractional coordinates, and anisotropic vibration parameters for compounds *endo*-**4c** and **5a** (15 pages); listing of observed and calculated structure factors for compounds *endo*-**4c** and **5a** (21 pages). Ordering information is given on any current masthead page.

Production of Protonated Methanol Ions via "Intermolecular" Reactions within van der Waals Clusters of Dimethyl Ether

M. Todd Coolbaugh, William R. Peifer, and
James F. Garvey*

Department of Chemistry, Acheson Hall
State University of New York at Buffalo
Buffalo, New York 14214

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Mass spectrometric studies of van der Waals clusters have proliferated during the last decade, and much has been learned concerning the formation and physical properties of many cluster systems.[1] The study of chemical reactions within clusters has also attracted considerable attention driven by the desire to create a conceptual bridge between the two seemingly disparate fields of gas-phase and condensed-phase chemistry.

Various groups have recently observed the generation of new cluster ions that are not observed in typical gas-phase bimolecular reactions (i.e., chemistry that can only occur within a cluster). These new processes include the generation of $(NH_3)_nN_2H_8^+$ ions from ammonia clusters,[2] $(CH_3OCH_3)_nH_3O^+$ ions from dimethyl ether clusters,[3] $(CH_3F)_nCH_3CH_3^+$ ions from methyl fluoride clusters,[4] and most recently, $(C_2H_4F_2)_{n\geq4}H^+$ from clusters of 1,1-difluoroethane.[5] We feel this body of work has revealed a new class of chemical reactions within clusters and hope to employ these systems to further study the role played by ion solvation in the reaction dynamics within cluster ions. To that end, we have reinvestigated neat clusters of dimethyl ether (DME) and have observed a new cluster ion of the formula $(DME)_nCH_3OH_2^+$.

Our molecular beam apparatus consists of a Campargue-type beam source[6] and has been described previously.[7] The cluster beam is generated from neat DME (Linde, minimum purity[8] 99.0%) expanded at 1.5 atm through a 250-μm orifice. The mass spectrometer is an Extrel C-50 instrument (200 W, 3/8-in-diameter rods, open-design ionizer) capable of unit mass resolution and uniform sensitivity up to m/z = 1400. The electron emission current for these experiments was kept at 0.65 mA. During beam operation, the pressure in the mass spectrometer chamber was kept below 5 × 10^{-7} Torr.

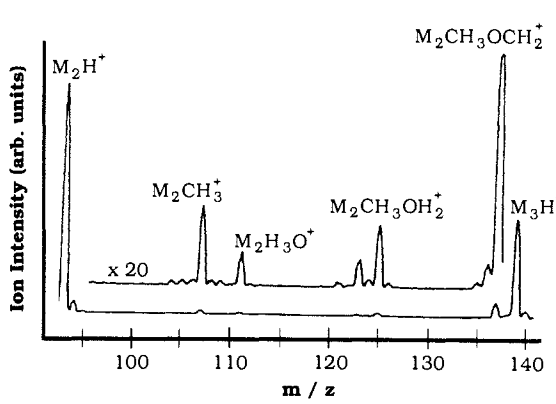

Figure 1. Raw mass spectrum of neat dimethyl ether clusters at 70 eV from 80 to 140 amu. Major ion peaks are identified by their empirical formulas (M = $(CH_3)_2O$).

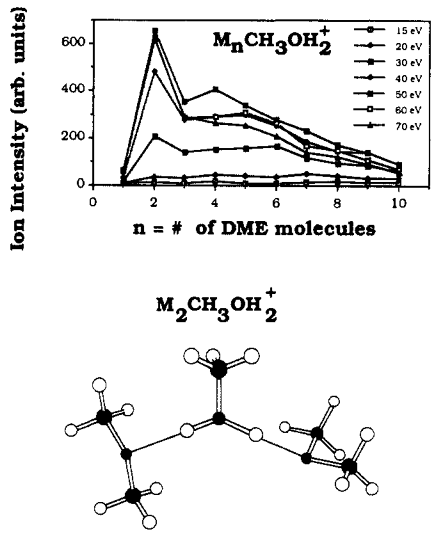

Figure 2. Top: Plot of $[((CH_3)_2O)_n\text{–}CH_3OH_2^+]$ ion intensity as a function of n for a variety of electron energies (15–70 eV). Note prominent magic number for n = 2. Bottom: Proposed structure for the $((CH_3)_2O)_2\text{–}CH_3OH_2^+$ cluster ion. This species is the most prevalent of all cluster ions in the series $[((CH_3)_2O)_n\text{–}CH_3OH_2^+]$ and is believed to be a protonated methanol molecule with two DME molecules hydrogen bonded to it. The dark circles correspond to carbon atoms and the shaded circles to oxygen atoms, while the open circles are hydrogen atoms.

Figure 1 shows a typical 70-eV electron impact mass spectrum of DME clusters extending from the dimer to the trimer. In addition to the expected peaks, there are two additional peaks corresponding to the hydronium ion (which has been reported before[3]) and protonated methanol ions, both solvated by two DME molecules. This sequence of peaks is observed throughout the entire cluster mass spectrum to the limit of our sensitivity.

We have based our identification of the $(DME)_nCH_3OH_2^+$ ions not only on mass assignment of that particular sequence of peaks but also on the observation of strong "magic" numbers in the DME cluster mass spectrum (i.e., cluster size values at which variations in an otherwise smoothly varying ion distribution occur). Magic numbers provide important clues as to the structure of the cluster ion and the identity of the central ionic moiety.[9] The top of Figure

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2 represents a plot of ion intensity of $(\mathrm{DME})_n\mathrm{CH_3OH_2}^+$ as a function of n for a variety of electron energies. For energies above 20 eV, a prominant magic number at $n = 2$ is exhibited. As shown at the bottom of Figure 2, we believe this is due to hydrogen bonding of two DME molecules directly to the hydroxy hydrogens of the protonated methanol. This type of "magic number" stability within hydrogen-bonded ion clusters has previously been demonstrated by Stace and Moore.[10]

It is interesting to now note that while the $\mathrm{CH_3OCH_2}^+$ cation is extremely intense in the monomer mass spectrum of DME (~34% of all ion intensity), the same *cluster* cation $(\mathrm{DME})_n\mathrm{CH_3OCH_2}^+$ is now substantially reduced in intensity (Figure 1). We postulate that this lowered intensity of the fragment cation is due to the $\mathrm{CH_3OCH_2}^+$ being consumed in an ion–molecule reaction within the cluster. One likely candidate is the ion–molecule reaction of the $\mathrm{CH_3OCH_2}^+$ cation with a neutral DME (within the bulk cluster) to form a trimethyloxonium cation intermediate by loss of formaldehyde.

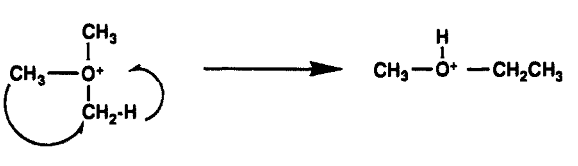
$$\mathrm{CH_3OCH_2}^+ + (\mathrm{CH_3})_2\mathrm{O} \rightarrow (\mathrm{CH_3})_3\mathrm{O}^+ + \mathrm{CH_2O} \qquad (1a)$$

This type of ion–molecule reaction has been previously observed by Harrison and Young through the use of a tandem mass spectrometer.[11] This newly formed trimethyloxonium cation may then undergo a rearrangement to form a protonated methanol cation and ethylene.

$$(\mathrm{CH_3})_3\mathrm{O}^+ \rightarrow \mathrm{CH_3OH_2}^+ + \mathrm{C_2H_4} \qquad (1b)$$

This mechanism is similar to that observed for the decomposition of $(\mathrm{CH_3})_2\mathrm{O}$ over zeolite catalysts. The most commonly accepted mechanism for such a decomposition involves just such a trimethyloxonium intermediate.[12] This intermediate is believed to undergo, within the zeolite, a Stevens-type rearrangement giving methyl ethyl ether (methoxyethane), which then generates the olefin products via elimination. van Hooff et al.[13] also observed that conversion of DME over a zeolite catalyst gave comparable amounts of ethylene and propene as primary olefins, and once again, methoxyethane was believed to play a role as an intermediate.

We speculate that the DME cluster reactions leading to the formation of protonated methanol involve an intermediate similar to that found to occur on the zeolite catalysts. That is, following formation of the trimethyloxonium ion within the DME cluster (reaction 1a), excess energy derived from the ionization/reaction processes can drive a simple rearrangement reaction (reaction 1b) to form the products of protonated methanol and ethylene. For the case of DME clusters, we postulate that the internally generated trimethyloxonium ion internally isomerizes to protonated methoxyethane (reaction 2), where it then forms protonated methanol via elimination of ethylene. This analogous process has previously been reported for the collisional activation of the monomer $(\mathrm{CH_3})_3\mathrm{O}^+$ ion.[14] However, recent additional work appears to be at variance with that original result.[15] This variance could be due to the thermodynamic instability of the bare $(\mathrm{CH_3})_3\mathrm{O}^+$, in that unimolecular dissociation can now effectively compete with the rearrangement reaction (2). However, within the solvating environs of a cluster, this unstable intermediate may be stabilized on a long enough time scale to now allow it to undergo this rearrangement reaction.



$$\mathrm{CH_3{-}\underset{CH_2{\cdot}H}{\overset{CH_3}{O^+}}} \longrightarrow \mathrm{CH_3{-}\overset{H}{O^+}{-}CH_2CH_3} \qquad (2)$$

To gain insight into this mechanism, we have measured the appearance potentials of the relevant cluster ions observed in this experiment. We observe that the $(\mathrm{CH_3})_3\mathrm{O}^+$ cation and the $\mathrm{M}_n(\mathrm{CH_3OH_2})^+$ cations all have the same appearance potential (12.5–12.7 eV).[16] This result is consistent with the conjecture that the $\mathrm{M}_n(\mathrm{CH_3OH_2})^+$ ions are produced via a $(\mathrm{CH_3})_3\mathrm{O}^+$ intermediate.

As a further probe, we generated mixed clusters of DME–$\mathrm{H_2O}$, via bubbling gas through a reservoir containing water at room temperature, and observed that the ions corresponding to the formula $(\mathrm{DME})_n\mathrm{CH_3OH_2}^+$ decreased by a factor of 3 in intensity, compared to a pure DME expansion.[17] This effect is consistent with the proposed mechanism (2) in that a water molecule would presumably strongly hydrogen bond directly to the oxygen end of the trimethyloxonium cation. This additional water molecule then sterically hinders any possible rearrangement, thereby quenching the reaction. Just such a mechanism has recently been suggested by Tzeng et al.[18] to explain the quenching of an acetone dehydration reaction in mixed clusters of acetone and water.

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Total Synthesis of the Tumor-Associated $\mathrm{Le^X}$ Family of Glycosphingolipids[†]

K. C. Nicolaou,* T. J. Caulfield, H. Kataoka,[‡] and
N. A. Stylianides

Department of Chemistry
Research Institute of Scripps Clinic
10666 North Torrey Pines Road
La Jolla, California 92037
Department of Chemistry
University of California at San Diego
La Jolla, California 92037

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Glycosphingolipids carrying the Lewis antigen X ($\mathrm{Le^X}$) determinant [Gal-β-1→4-(Fuc-α-1→3)-GlcNAc] are known to accumulate in a wide variety of human cancers[1] and have been

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[*] Address correspondence to this author at the Research Institute of Scripps Clinic.

[†] This work was partially carried out at the University of Pennsylvania.

[‡] Visiting Scientist from Nippon Zeon Co., Japan, 1987–1989.

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