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# Gas-phase ion chemistry of $\text{Ge}(\text{OCH}_3)_4$

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## Abstract

The ion/molecule reactions of the main fragment ions of  $\text{Ge}(\text{OMe})_4$ , namely  $\text{HGe}(\text{OMe})_3^+$ ,  $\text{Ge}(\text{OMe})_3^+$ ,  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ ,  $\text{HGe}(\text{OMe})_2^+$ , and  $\text{GeOMe}^+$ , have been studied in a Fourier transform ion cyclotron resonance (FTICR) spectrometer in the presence of the neutral substrate. A series of distinct reactions leading to  $\text{Ge}_2(\text{OMe})_n^+$  ( $n = 3-7$ ) ions are essentially the only products observed besides reactions leading to protonated  $\text{Ge}(\text{OMe})_4$ . Infrared multiphoton photodissociation initiated with a  $\text{CO}_2$  laser has been used to help in the isolation of some of the primary ions and to investigate the lowest energy channels for dissociation of the product ions. While the actual structure of the product ions could not be unequivocally determined in the present experiments, it is likely that a number of the product ions are ions containing a germanium–germanium bond. (Int J Mass Spectrom 179/180 (1998) 223–230) © 1998 Elsevier Science B.V.

*Keywords:* Germanium tetramethoxide; Ion/molecule reactions; Infrared (IR) photodissociation of ions; Gas-phase Ge ions

## 1. Introduction

The gas-phase ion chemistry of organogermanes remains relatively unexplored in spite of the increasing interest in these compounds for organometallic synthesis and as precursors of new kinds of polymers, film formation, and synthesis of new ceramic materials by chemical vapor deposition methods [1–3]. The first report on ion/molecule reactions in monogermane [4] revealed that such simple ions as  $\text{GeH}_2^+$  and  $\text{GeH}_3^+$  undergo complex reactions with  $\text{GeH}_4$  leading to various  $\text{Ge}_2\text{H}_x^+$  ( $x = 2-5$ ) ions. Unlike  $\text{CH}_5^+$  and  $\text{SiH}_5^+$ ,  $\text{GeH}_5^+$  is not easily observed as a product of

ion/molecule reactions and the determination of an accurate value for the proton affinity of monogermane is still an experimental challenge [5]. Recent high quality ab initio calculations [6] predict the proton affinity of monogermane to be  $673.9 \text{ kJ mol}^{-1}$  at 298 K, which is just below the lower limit originally placed by ion beam scattering experiments [5]. A much more interesting and richer set of ion/molecule reactions has been reported for monogermane and methylgermane with oxygen, ammonia, unsaturated hydrocarbons, and silicon hydrides resulting in a variety of condensation products [7–12].

A somewhat different family of volatile organogermanes,  $\text{Ge}(\text{OR})_4$  ( $\text{R} = \text{alkyl}$ ), has recently received attention because of its potential advantages for deposition of germanium oxide [13,14]. The very interesting and diversified ion chemistry we reported [15–17] for the  $\text{Si}(\text{OR})_4$  ( $\text{R} = \text{Me, Et}$ ) analogs

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

provided the major impetus for the present investigation of the ion chemistry of  $\text{Ge}(\text{OMe})_4$ . This study is useful for establishing similarities and differences between the ion chemistry of silicon and germanium substrates. It also provides insight on the chemistry of germyl cations, a subject of considerable interest and speculation in condensed phases [18].

## 2. Experimental

Experiments were carried out with a homemade Fourier transform ion cyclotron resonance (FTICR) spectrometer interfaced with an IonSpec Omega Fourier Transform Data System. The general characteristics of the spectrometer and its application towards the elucidation of ion reaction sequences have been illustrated in recent publications from these laboratories [17,19,20]. The magnetic field (Varian 9 in. electromagnet) was usually set at 1 T but some experiments were carried out at fields of 1.1 and 1.25 T without any marked improvement in the performance of the spectrometer. The cell is a modified near-cubic 1 in. cell in which both transmitter plates are drilled with a center hole to allow for laser irradiation of the ion cloud. The bottom receiver plate also has a center hole outside of which a tungsten wire is permanently mounted to act as an in situ high temperature black-body source as previously described [21]. The temperature of the cell under normal operating conditions is typically in the range of  $333 \pm 5$  K as measured with a Pt wire thermometer located near one of the transmitter plates.

Positive ions were generated by electron bombardment at 20 eV in most experiments. Lower electron energies were used in a few experiments in order to determine qualitatively appearance energies and to verify the possibility of decreasing the number of overlapping fragment ions (see Results). The reactivity of different fragment ions (with all their isotopic components) was determined by ejecting all unwanted ions from the ICR cell with a combination of radio frequency pulses. Because the mass spectrum of  $\text{Ge}(\text{OMe})_4$  reveals fragment ions with overlapping

mass species arising from five different Ge isotopes ( $^{70}\text{Ge}$ , 20.5%;  $^{72}\text{Ge}$ , 27.4%;  $^{73}\text{Ge}$ , 7.7%;  $^{74}\text{Ge}$ , 36.5%;  $^{76}\text{Ge}$ , 7.7%), the specific isolation of  $\text{HGe}(\text{OMe})_3^+$ ,  $\text{Ge}(\text{OMe})_3^+$ ,  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ , and  $\text{HGe}(\text{OMe})_2^+$  was achieved with the help of selective multiphoton dissociation as discussed in the Results. Our early attempts to specifically isolate the  $^{70}\text{Ge}$  isotopic component of these ions (for which no overlap is possible) proved to be of very limited use because the resulting signal/noise (S/N) conditions for the isolated ions were very poor.

A grating tunable cw  $\text{CO}_2$  laser (SYNRAD, Model 48G-1-cation) was used for the infrared multiphoton dissociation of ions. The laser was operated on the  $P(20)$  line at  $1047\text{ cm}^{-1}$ , a frequency close to the center of a strong infrared absorption band of neutral  $\text{Ge}(\text{OMe})_4$  [22]. No attempt was made to look into the wavelength dependence of the dissociation processes. The power level of the laser was externally controlled by varying the width of a 10 kHz modulation pulse provided by a Hewlett-Packard pulse generator. The laser power measured at the exit window of the vacuum system of the spectrometer was typically 3 W. However, considerable fluctuation in power was observed unless the water cooling and room temperature were maintained well below  $20^\circ\text{C}$  [23]. The irradiation time (0.2 to 1 s depending on the experiment) was controlled by electronically varying the duration of the open-time of a Uniblitz shutter placed in front of the laser.

Ion/molecule reactions of  $\text{Ge}(\text{OMe})_4$  were studied typically at pressures in the range of  $5\text{--}9 \times 10^{-8}$  Torr (ion gauge reading), and at trapping voltages of 1 V. No attempt was made to determine the absolute rate constants due to the large uncertainties associated with measuring the absolute pressure of the highly hygroscopic  $\text{Ge}(\text{OMe})_4$ .

Fresh samples of tetramethoxygermane (germanium (IV) methoxide, 97%, Aldrich) were used in most experiments. These samples were repeatedly distilled under vacuum prior to introduction in the cell. This procedure was essential for minimizing the amount of methanol present in the sample due to facile hydrolysis of this compound.

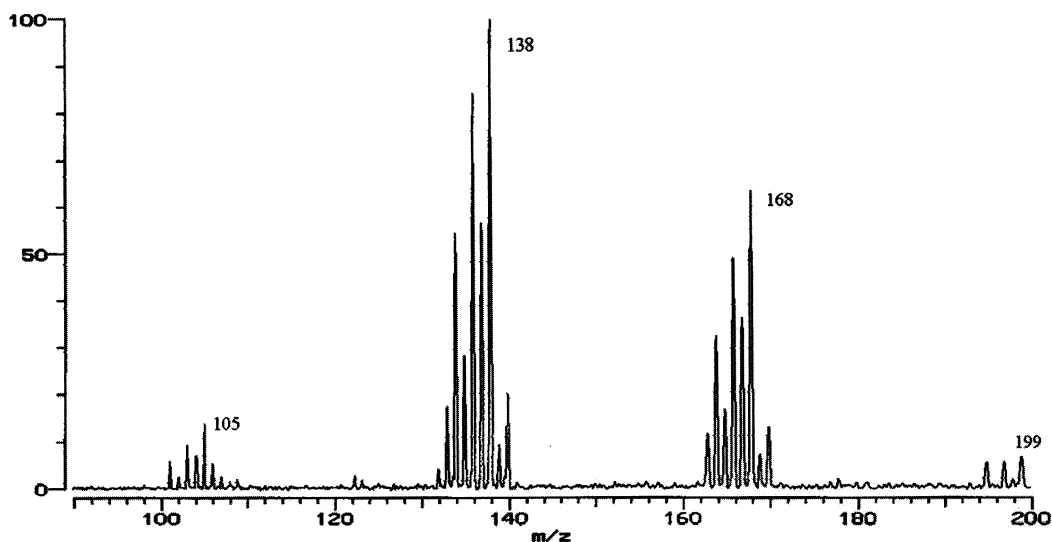


Fig. 1. Mass spectrum of  $\text{Ge}(\text{OMe})_4$  obtained in our FTICR spectrometer at 20 eV and short ion trapping time (40 ms).

### 3. Results and discussion

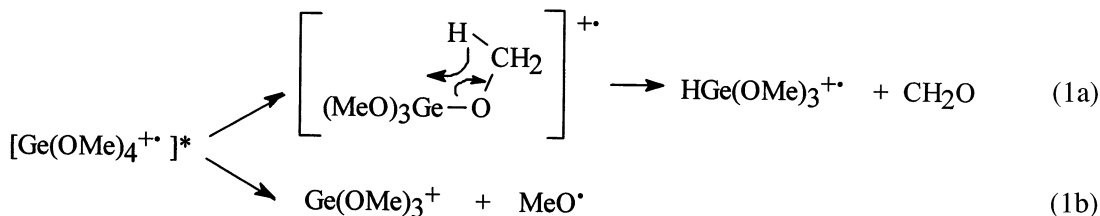
#### 3.1. Mass spectrum of $\text{Ge}(\text{OMe})_4$

An early study of the mass spectrum of  $\text{Ge}(\text{OMe})_4$  reported fragmentation patterns characterized by loss of  $\text{CH}_2\text{O}$  or  $\text{CH}_3\text{O}^\cdot$  [24]. The FTICR spectrum obtained in our spectrometer at 20 eV ionizing energy and 40 ms after the ionization pulse is shown in Fig. 1. The molecular ion is not observed in this spectrum even at low electron energies, but  $\text{HGe}(\text{OMe})_4^+$  is readily observed due to fast ion/molecule reactions occurring at these pressures during the 40 ms delay

time. At higher electron energies, a minor amount of  $\text{Ge}^+$  is also observed in the mass spectrum.

The main species observed at this electron energy can be identified as  $\text{HGe}(\text{OMe})_3^+$ ,  $\text{Ge}(\text{OMe})_3^+$ ,  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ ,  $\text{HGe}(\text{OMe})_2^+$ , and  $\text{GeOMe}^+$ . Spectra recorded at lower electron energies reveal that  $\text{HGe}(\text{OMe})_3^+$  is the fragment with the lowest appearance energy.

The fragmentation process resulting in the formation of  $\text{HGe}(\text{OMe})_3^+$  and  $\text{Ge}(\text{OMe})_3^+$  can be easily viewed as the result of elimination of formaldehyde coupled with a hydrogen shift, or methoxy radical loss from an unstable molecular ion.



Although the FTICR experiments do not provide any detailed information about these fragmentation processes, formation of the  $\text{H}_2\text{Ge}(\text{OMe})_2^+$  and  $\text{HGe}(\text{OMe})_2^+$  ions can be rationalized by similar

mechanisms as those shown in reaction (1). It is interesting to note that although the symmetric molecular ion  $\text{Ge}(\text{OMe})_4^+$  is not observed in the mass spectrum, its fragmentation gives rise to other

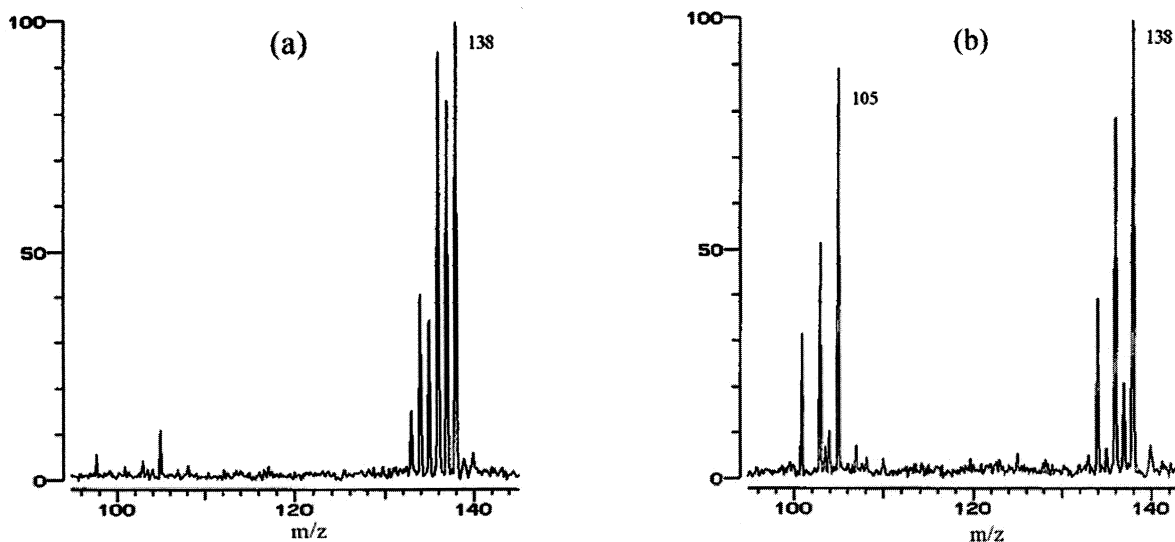
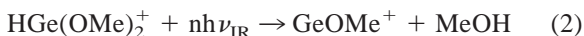


Fig. 2. (a) FTICR spectrum obtained after isolation of the different isotopic species of  $\text{H}_2\text{Ge}(\text{OMe})_2^+$  and  $\text{HGe}(\text{OMe})_2^+$ ; (b) FTICR spectrum obtained after irradiation of  $\text{H}_2\text{Ge}(\text{OMe})_2^+$  and  $\text{HGe}(\text{OMe})_2^+$  ions with the  $\text{CO}_2$  laser showing the selective dissociation of  $\text{HGe}(\text{OMe})_2^+$ . (Spectra recorded without full optimization for isotopic relative abundances.)

radical cations like  $\text{HGe}(\text{OMe})_3^+$  and  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ .

Neither  $\text{HGe}(\text{OMe})_3^+$  nor  $\text{Ge}(\text{OMe})_3^+$  undergo dissociation under irradiation with the  $\text{CO}_2$  laser. By comparison, a similar type of experiment, after isolating the cluster of isotopic species corresponding to  $\text{H}_2\text{Ge}(\text{OMe})_2^+$  and  $\text{HGe}(\text{OMe})_2^+$ , reveals that the  $\text{CO}_2$  laser can selectively dissociate the  $\text{HGe}(\text{OMe})_2^+$  ion (Fig. 2)



This type of experiment eventually allowed us to isolate  $\text{H}_2\text{Ge}(\text{OMe})_2^+$  ions ( $m/z$  140, 138, 137, 136, and 134) free of any interference from the  $\text{HGe}(\text{OMe})_2^+$  ions.

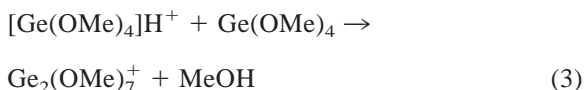
### 3.2. Ion/molecule reactions

A preliminary investigation of the ion/molecule reactions of  $\text{Ge}(\text{OMe})_4$  reveals that the primary fragment ions give rise to  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  and a progressive and characteristic sequence of  $\text{Ge}_2(\text{OMe})_n^+$  ( $n = 3-7$ ) ions. Although these ions are represented as

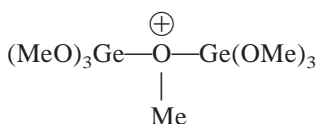
condensation-type species, there is no conclusive evidence to rule out structures obeying the empirical formula  $\text{Ge}_2(\text{OCH}_3)_n^+$  that do not necessarily maintain all the MeO moieties intact, however. The only exception to this general sequence is the observation of  $\text{Ge}_2\text{O}_3\text{C}_3\text{H}_8^+$ , a neighbouring species to the  $\text{Ge}_2(\text{OMe})_3^+$  ion. Because these ions are produced in minor quantities and the isotopic structure of spectra involving neighbouring ions with two germanium atoms is quite complex, a thorough investigation of these products proved difficult. A detailed analysis of the individual reactivity of the different ions is presented below.

#### 3.2.1. $[\text{Ge}(\text{OMe})_4]\text{H}^+$

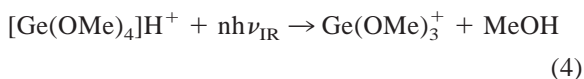
Reactions leading to protonated  $\text{Ge}(\text{OMe})_4$  are fast and arise primarily from proton transfer of  $\text{HGe}(\text{OMe})_3^+$  and  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ . A quantitative analysis of these reactions has not been pursued because protonation reactions also arise from background water and methanol that are common contaminants when using  $\text{Ge}(\text{OMe})_4$ . The  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  ions undergo readily secondary reaction with the neutral substrate as shown in reaction (3),



This reaction is reminiscent of the ion chemistry of  $\text{Si}(\text{OMe})_4$  [17] where a process similar to reaction (3) was viewed as a nucleophilic attack by an oxygen lone pair on a positively charged Ge with simultaneous displacement of methanol. This mechanism views  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  as a germal cation solvated with methanol,  $(\text{MeO})_3\text{Ge}^+(\text{MeOH})$ , and assumes that the reaction can be explained in terms of the “voracious appetite” for nucleophiles expected for Ge by analogy with Si [25]. A very likely structure for the product ion that is consistent with this view is an ion exhibiting a Ge–O–Ge central moiety.



Photodissociation of the protonated ion  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  with the  $\text{CO}_2$  laser yields exclusively the germal cation  $\text{Ge}(\text{OMe})_3^+$

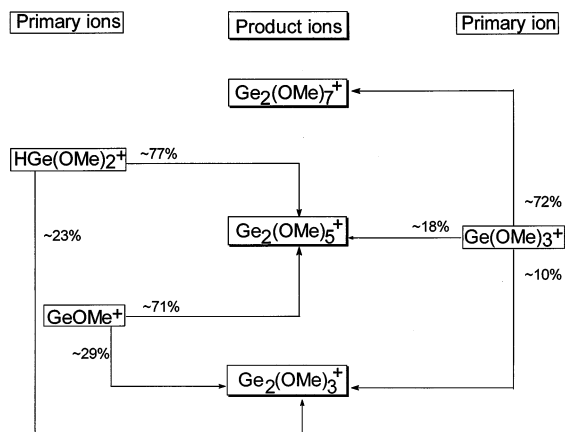


This experiment provides a unique and useful way to produce  $\text{Ge}(\text{OMe})_3^+$  ions free of any interference from the different isotopic species of  $\text{HGe}(\text{OMe})_3^+$ .

### 3.2.2. $\text{Ge}(\text{OMe})_3^+$ , $\text{HGe}(\text{OMe})_2^+$ , and $\text{GeOMe}^+$

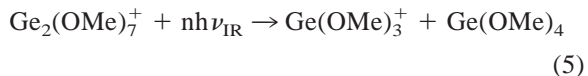
The even-electron primary ions undergo a series of related ion/molecule reactions that are displayed in Scheme 1 as a general reactivity map.

$\text{Ge}(\text{OMe})_3^+$  ions are observed to produce  $\text{Ge}_2(\text{OMe})_n^+$  ( $n = 3, 5, \text{ or } 7$ ) through a sequence of reactions that formally entail progressive elimination of  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$ . The main product ion,  $\text{Ge}_2(\text{OMe})_7^+$ , is assumed to be identical to that formed in reaction (3), resulting from the attachment of a nucleophile on the germal cation. This behavior is reminiscent of that previously encountered for the  $\text{Si}(\text{OMe})_3^+$  ion [17]. Photodissociation of  $\text{Ge}_2(\text{OMe})_7^+$  with the  $\text{CO}_2$  laser, regardless of whether the ion is



Scheme 1. Reactivity map and branching ratio of the even-electron primary ions,  $\text{Ge}(\text{OMe})_3^+$ ,  $\text{HGe}(\text{OMe})_2^+$ , and  $\text{GeOMe}^+$ , with the parent neutral  $\text{Ge}(\text{OMe})_4$ . The neutral products of these reactions are discussed in the text.

formed by ion/molecule reactions of  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  or  $\text{Ge}(\text{OMe})_3^+$ , yields almost exclusively the  $\text{Ge}(\text{OMe})_3^+$  ion



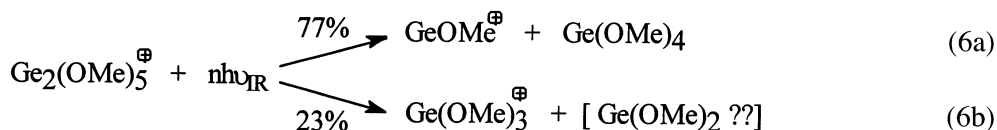
Complete dissociation is achieved with irradiation times of less than 400 ms. At long irradiation times that result in total dissociation ( $\sim 400$  ms), other two-germanium-containing ions also become noticeable in the photodissociation experiment. In decreasing order of importance, the base peaks of these ions correspond to  $m/z$  255 [ $^{74}\text{Ge}^{72}\text{Ge}(\text{O})(\text{OMe})_3^+$  (?)],  $m/z$  225 [ $^{74}\text{Ge}^{72}\text{Ge}(\text{OH})(\text{OMe})_2^+$  (?)], and  $m/z$  239 and  $m/z$  238 [ $^{74}\text{Ge}^{72}\text{Ge}(\text{OMe})_3^+$  and  $^{74}\text{Ge}^{72}\text{GeO}_3\text{C}_3\text{H}_8$ ]. A particularly important result of these experiments is the fact that  $\text{Ge}_2(\text{OMe})_5^+$  is noticeably absent as a product of photodissociation even at the longer irradiation times.

The  $\text{Ge}_2(\text{OMe})_5^+$  ion is a common product ion of all three primary ions considered in this section. The likely mechanisms leading to this ion and its structure require some discussion. For example, the reactivity of  $\text{Ge}(\text{OMe})_3^+$  differs in this case from that of  $\text{Si}(\text{OMe})_3^+$ . Although  $\text{Si}(\text{OMe})_3^+$  reacts with  $\text{Si}(\text{OMe})_4$  to yield  $\text{Si}_2(\text{OMe})_7^+$ , and presumably  $(\text{MeO})_3\text{SiOSi}(\text{OMe})_2^+$  as a result of  $\text{Me}_2\text{O}$  elimination

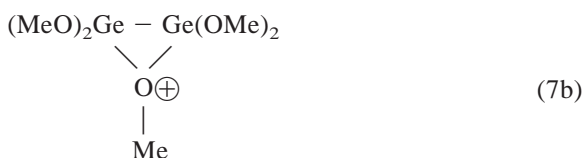
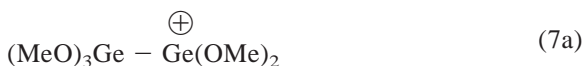
from energy rich  $\text{Si}_2(\text{OMe})_7^+$  ions [17], the reaction of  $\text{Ge}(\text{OMe})_3^+$  with  $\text{Ge}(\text{OMe})_4$  to yield  $\text{Ge}_2(\text{OMe})_5^+$  by elimination of MeOH and  $\text{CH}_2\text{O}$  can be rationalized by a variety of structures. The fact that  $\text{Ge}_2(\text{OMe})_5^+$  is not produced by the low power infrared photodissociation of  $\text{Ge}_2(\text{OMe})_7^+$  suggests that either these ions are produced through different intermediates, or elim-

ination of MeOH and  $\text{CH}_2\text{O}$  requires a higher energy threshold than dissociation back to the original reagents. Furthermore,  $\text{Ge}_2(\text{OMe})_5^+$  is the major reaction product from  $\text{HGe}(\text{OMe})_2^+$  (with elimination of neutral MeOH) and  $\text{GeOMe}^+$ .

Infrared photodissociation of the  $\text{Ge}_2(\text{OMe})_5^+$  ion yields



These results are not sufficient to establish the actual structure of  $\text{Ge}_2(\text{OMe})_5^+$  unequivocally. All three structures shown below must still be regarded as distinct possibilities



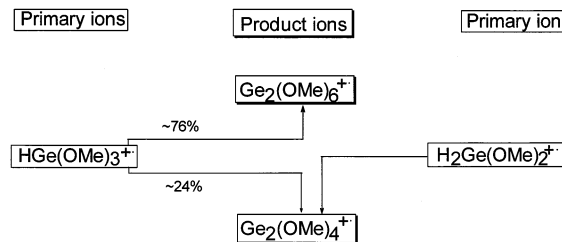
Structure (7b) would probably be expected to yield the more stable germyl cation (7a), even though a salt of a three-membered germyl cation has been isolated recently [26]. The fact that all three primary ions,  $\text{Ge}(\text{OMe})_3^+$ ,  $\text{HGe}(\text{OMe})_2^+$ , and  $\text{GeOMe}^+$  yield the ubiquitous  $\text{Ge}_2(\text{OMe})_3^+$  ion strongly suggests that formation of product ions with germanium–germanium bonds is likely for both  $\text{Ge}_2(\text{OMe})_5^+$  and  $\text{Ge}_2(\text{OMe})_3^+$ . This is particularly interesting in view of the increasing number of stable germenes that are presently known [27].

Further support for claiming ion structures that retain the methoxy moieties intact comes from pre-

liminary ab initio calculations on some of the primary fragment ions. For example, calculations using density functional methods at the B3LYP/6-31G (d) level with GAUSSIAN 94 [28] for  $\text{GeH}_3\text{CO}^+$  species show that the  $\text{GeOMe}^+$  structure is  $264 \text{ kJ mol}^{-1}$  more stable than  $\text{HGeOCH}_2^+$ , and at least  $293 \text{ kJ mol}^{-1}$  more stable than  $\text{MeGeO}^+$  and  $\text{H}_3\text{GeCO}^+$  [29].

### 3.2.3. $\text{HGe}(\text{OMe})_3^+$ and $\text{H}_2\text{Ge}(\text{OMe})_2^+$

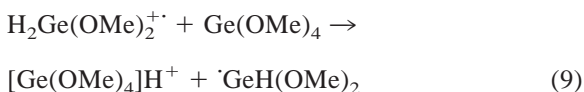
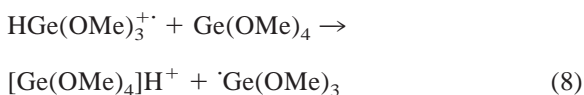
The reactivity of the radical cations formed in the primary fragmentation process is displayed in Scheme 2. The proton transfer reactions (8) and (9) have not been explicitly considered in Scheme 2 because reliable quantitative measurements proved difficult because of competing proton transfer reactions from



Scheme 2. Reactivity map and branching ratio of the primary radical ions,  $\text{HGe}(\text{OMe})_3^+$ , and  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ , with the parent neutral  $\text{Ge}(\text{OMe})_4$ . The proton transfer reactions leading to  $[\text{Ge}(\text{OMe})_4]\text{H}^+$  have not been included because of difficulties in assessing the relative contribution of each ion. The neutral products of these reactions are discussed in the text.



water and methanol, and because of the subsequent reaction of  $\text{HGe}(\text{OMe})_4^+$  with the parent substrate [reaction (3)]



Scheme 2 shows that both radical cations, interestingly enough, also give rise to radical ion products in their ion/molecule reactions with the parent neutral. Two very distinct possibilities exist for the structure of  $\text{Ge}_2(\text{OMe})_6^+$ ; (1) a 1, 2 elimination of MeOH to yield an ion containing a germanium–germanium bond,  $(\text{MeO})_3\text{Ge–Ge}(\text{OMe})_3^+$ ; (2) a nucleophilic type reaction similar to that advocated in reaction (3) with



For these smaller ions,  $\text{Ge}_2(\text{OMe})_4^+$ ,  $\text{Ge}_2(\text{O}_3\text{C}_3\text{H}_8)^+$ , and  $\text{Ge}_2(\text{OMe})_3^+$ , it is probably safe to assume gemene type structures in agreement with the growing number of neutral germenones that have been identified as stable species [27,31]. Alternative structures for this case are less likely as germenones structures are predicted to undergo favorable isomerization [32].

#### 4. Conclusions

The ion chemistry of  $\text{Ge}(\text{OMe})_4$  has been shown to give rise to a progressive number of secondary ions (even- and odd-electron species) corresponding to  $\text{Ge}_2(\text{OMe})_n^+$  ( $n = 3–7$ ) clusters. While secondary ion/molecule reactions were not thoroughly studied, the efficiency of these processes is very low compared to similar processes observed in the Si analogs. For the lowest members of the  $\text{Ge}_2(\text{OMe})_n^+$  ions there is strong indication that these ions contain germanium–germanium bonds. This situation parallels closely the trend observed earlier in the pioneering studies of the

elimination of methanol and a methyl migration to a germanium atom giving rise to  $[(\text{MeO})_3\text{Ge–O–Ge}(\text{Me})(\text{OMe})_2]^+$ . This latter type of structure has been taken into consideration repeatedly in this article because of the known stability of Ge–O–Ge systems that eventually lead to polymeric units [30]. Unfortunately, our experiments cannot distinguish between these two possibilities. Furthermore, photodissociation experiments were not feasible in this case since  $\text{Ge}_2(\text{OMe})_6^+$  is not an intense species in the overall spectrum.

The formation of  $\text{Ge}_2(\text{OMe})_4^+$  from both radical cations,  $\text{HGe}(\text{OMe})_3^+$  and  $\text{H}_2\text{Ge}(\text{OMe})_2^+$ , involves the familiar elimination of MeOH and  $\text{CH}_2\text{O}$  in analogous fashion to the reactions encountered for the even-electron primary ions. Photodissociation of  $\text{Ge}_2(\text{OMe})_4^+$  is unlike the previous cases because it does yield ions containing two germanium atoms,

ion chemistry of germanium hydrides [7–12] where  $\text{Ge}_n$  containing ions are also common products of ion/molecule reactions.

Further experimental and theoretical work is presently under way in order to determine possible thermochemical and structural information on these systems. In this respect, very little is still known even for the precursor neutral molecule  $\text{Ge}(\text{OMe})_4$  [33,34].

Preliminary experiments with mixtures of  $\text{Ge}(\text{OMe})_4$  and  $\text{Si}(\text{OMe})_4$  reveal that a very similar chemistry is observed resulting in ions containing a Si and Ge atom. The practical consequences of these experiments should be particularly useful in the analysis of processes that are initiated either by a plasma or glow discharge.

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