

Gas phase ion-molecule reactions of monogermane with oxygen and ammonia *

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Abstract

High pressure and Fourier transform mass spectrometry have been used to study the ion-molecule reactions of germanium-containing ions with oxygen, ammonia, and GeH_4 itself. The effects of the total pressure and of the ratio between GeH_4 and oxygen or ammonia are reported. In self-condensation reactions the most reactive species are Ge^+ and GeH_2^+ , which give dimer ions containing an even number of hydrogen atoms. Formation of GeH_nO_2^+ ($n = 0, 1$) and GeH_nO^+ ($n = 0-3$) ions is observed in the GeH_4/O_2 mixture. The most abundant species is GeHO^+ , which originates in the reaction of Ge_2H_2^+ with one O_2 molecule, as demonstrated by FTMS. High pressure experiments suggest that oxygen-containing ions are also formed by pathways involving monogermanium ions. Analogous behaviour is observed in the GeH_4/NH_3 mixtures, where GeNH_n^+ ($n = 2, 3, 4, 6$) ions are formed in higher abundances than GeHO^+ ($n = 0-3$) ions under similar conditions.

Introduction

In the last few years great efforts have been made to produce more efficient and cheaper photovoltaic cells using amorphous instead of crystalline materials [1].

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Glow discharge processes and chemical vapour deposition of volatile hydrides give quite good results [2–4], but the operating conditions used to give solar cells with the higher conversion efficiency generally have an empirical basis. Knowledge of the gaseous reactant decomposition mechanism and of the deposition of solid could thus be useful in indicating the way towards improved conditions for the process.

The radiolytic process provides an alternative method of decomposing the volatile hydrides but is not yet considered for industrial use. When the solid material is produced at room temperature, it consists of a partially cross-linked mixture of polymers, which becomes amorphous upon thermal treatment [5]. The final material is very similar to that obtained by glow discharge under the same conditions. Moreover, the radiolytic method allows formulation of some hypotheses about the mechanism of formation of the solid polymeric product.

Studies on the mechanism of polymerization of SiH_4 and GeH_4 by γ -radiolysis have been described previously [6,7], and some suggestions made about the decomposition pathways, but the quantitative contributions of the various species, such as ions and radicals, to the final product have not been evaluated.

Low and high pressure mass spectrometric methods provide valuable tools for investigating gas phase ion-molecule reactions and the intermediates involved. Many papers have been published on the reactions of SiH_4 [8], and one investigation of self-condensation reactions of GeH_4 , examined by high pressure mass spectrometry, has been reported previously [9].

In this paper we describe and discuss the gas phase reactions of GeH_4 in the self-condensation processes and in the presence of oxygen, ammonia and dimethylamine as monitored by Fourier transform mass spectrometry (FTMS) and high pressure mass spectrometry. These two methods give complementary results on the behaviour of gaseous systems under the respective operating conditions and provide valuable information for developing the study of the production of amorphous germanium containing added doping agents.

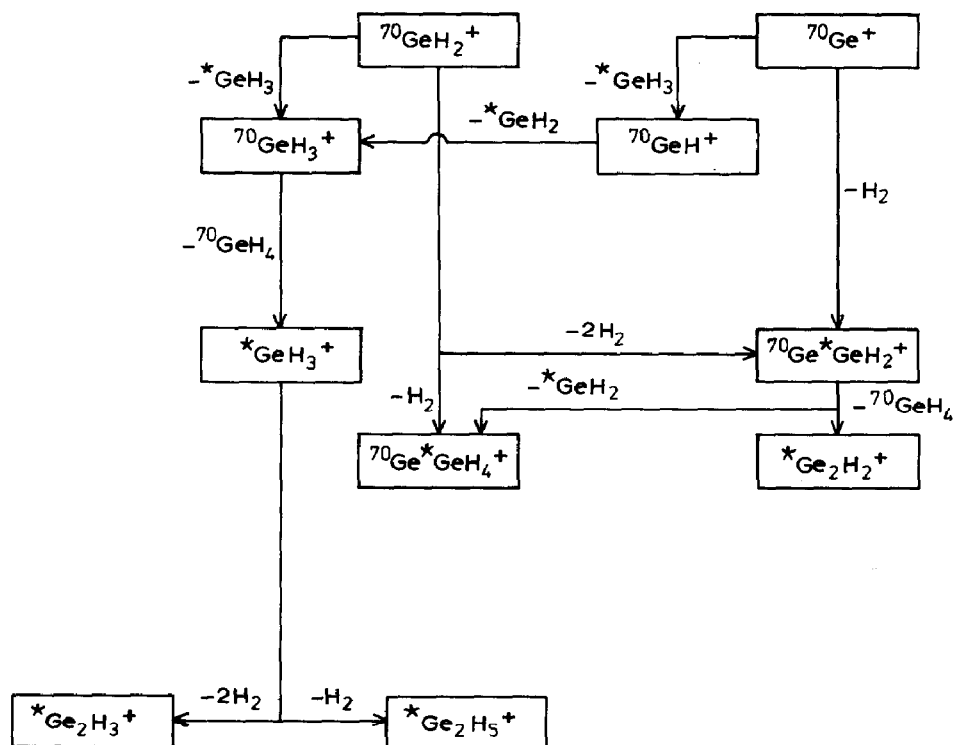
Results and discussion

Self-condensation reactions

When GeH_4 is introduced into the ion source under a pressure of about 0.1 torr ion-molecule reactions lead to the formation of dimers, trimers, and tetramers, which transport 26, 0.6 and 0.4% of the total ion current respectively, while 73% is transported by the monomer ions.

As the pressure of GeH_4 is decreased a general decrease in the proportion of oligomers is observed, as expected. In particular, the proportion of trimer ions decreases faster than that of the tetramer ions, indicating that there may be a dimerization of the dimers Ge_2H_n^+ ($n = 0-5$) to give the tetramers. Moreover the multiplet due to the GeH_n^+ ($n = 0-3$) ions changes as the ratio of the relative abundances of $\text{GeH}_3^+/\text{GeH}_2^+$ is progressively decreased.

A direct investigation of the individual reaction pathways in reactions of GeH_4 has been carried out by use of FTMS. A major difficulty is that of discriminating between the contributions of the various ionic species with different Ge isotopes (^{70}Ge : 20.52%; ^{72}Ge : 27.43%; ^{73}Ge : 7.76%; ^{74}Ge : 36.54%; ^{76}Ge : 7.76%) to the same nominal ion mass. However, when advantage is taken of the very different reactivities toward GeH_4 itself of Ge^+ , GeH^+ , GeH_2^+ , and GeH_3^+ ions from 20 eV



Scheme 1.

electron impact on GeH_4 it is possible to isolate each of them after a suitable lapse of time from their generation. For instance, $^{70}\text{Ge}^+$ (m/z 70) and $^{70}\text{GeH}^+$ (m/z 71) ions can be easily isolated from the accompanying fragments by multiple resonance experiments, and allowed to react with $^*\text{GeH}_4$ (the asterisk denotes all the natural isotopic family of germanium). After a relatively short reaction time (< 10 ms), all the $^{70}\text{Ge}^+$ and $^{70}\text{GeH}^+$ ions have been consumed to give their daughter species. Therefore, after this delay following the electron pulse, peaks at m/z 72 and 73 are observed, which represent exclusively the $^{70}\text{GeH}_2^+$ and $^{70}\text{GeH}_3^+$ fragments, with no significant contribution from $^{72}\text{Ge}^+$, $^{72}\text{GeH}^+$, and $^{73}\text{Ge}^+$ ions. Multiple resonance experiments on the $^{70}\text{Ge}^+$, $^{70}\text{GeH}^+$, $^{70}\text{GeH}_2^+$, and $^{70}\text{GeH}_3^+$ fragments, carried out at $^*\text{GeH}_4$ pressures ranging from 0.4 to 1.0×10^{-7} torr, enabled us to establish the reaction network shown in Scheme 1, where the neutral reactant is always $^*\text{GeH}_4$ and the species in the boxes are the ionic reactants. Analysis of Scheme 1 reveals a dramatically different behaviour of germane ions with no ($^{70}\text{Ge}^+$) or even hydrogen atoms ($^{70}\text{GeH}_2^+$) compared with those with an odd number of hydrogens ($^{70}\text{GeH}^+$ and $^{70}\text{GeH}_3^+$). In fact, both $^{70}\text{Ge}^+$ and $^{70}\text{GeH}_2^+$ follow a similar reaction pattern involving; (i) a very fast hydrogen-atom abstraction from $^*\text{GeH}_4$ yielding $^{70}\text{GeH}^+$ and $^{70}\text{GeH}_3^+$, respectively, and (ii), a slower addition reaction with $^*\text{GeH}_4$ with elimination of one ($^{70}\text{Ge}^+ \rightarrow ^{70}\text{Ge}^*\text{GeH}_2^+$; $^{70}\text{GeH}_2^+ \rightarrow ^{70}\text{Ge}^*\text{GeH}_4^+$) or two H_2 molecules ($^{70}\text{GeH}_2^+ \rightarrow ^{70}\text{Ge}^*\text{GeH}_2^+$). The secondary $^{70}\text{Ge}^*\text{GeH}_2^+$ ion slowly reacts further with $^*\text{GeH}_4$, promoting both Ge isotope scrambling ($^{70}\text{Ge}^*\text{GeH}_2^+ \rightarrow ^*\text{Ge}_2\text{H}_2^+$) and a H_2 -molecule transfer ($^{70}\text{Ge}^*\text{GeH}_2^+ \rightarrow ^{70}\text{Ge}^*\text{GeH}_4^+$). Under

the conditions prevailing in the FTMS experiments, the above digermene ions are found not react further with $^{\star}\text{GeH}_4$ even after 200 ms.

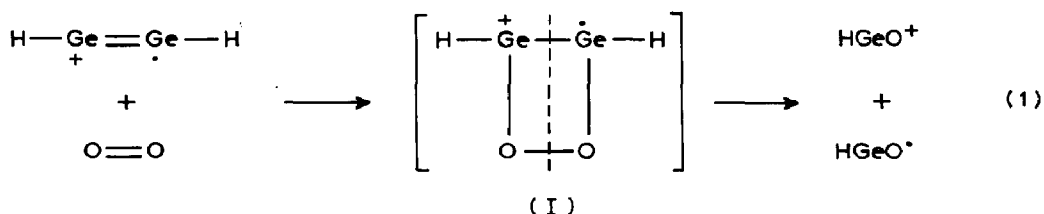
Primary and secondary germane ions with odd hydrogen atoms, i.e. $^{70}\text{GeH}^+$ and $^{70}\text{GeH}_3^+$, are found to follow a similar reaction pattern but this is very different from that found for $^{70}\text{Ge}^+$ and $^{70}\text{GeH}_2^+$. Thus $^{70}\text{GeH}^+$ rapidly abstracts a H_2 molecule from $^{\star}\text{GeH}_4$ to give $^{70}\text{GeH}_3^+$ and this, in turn, undergoes germanium isotope scrambling by collision with $^{\star}\text{GeH}_4$. The ensuing $^{\star}\text{GeH}_3^+$ appears to be rather inert toward $^{\star}\text{GeH}_4$, since it undergoes many unreactive collisions with the parent gas before condensing to yield both $^{\star}\text{Ge}_2\text{H}_3^+$ and $^{\star}\text{Ge}_2\text{H}_5^+$ species, which do not react further with germane.

It is clear that Ge^+ , GeH_2^+ , and GeH_3^+ ions are the main precursors of digermene ionic species, i.e. Ge_2H_2^+ , Ge_2H_4^+ , Ge_2H_3^+ , and Ge_2H_5^+ . The Ge_2H_2^+ and Ge_2H_4^+ ions with an even number of hydrogen atoms are efficiently produced by addition of GeH_4 to Ge^+ and GeH_2^+ . The rather unreactive GeH_3^+ is the only precursor of the Ge_2H_3^+ and Ge_2H_5^+ dimeric ions.

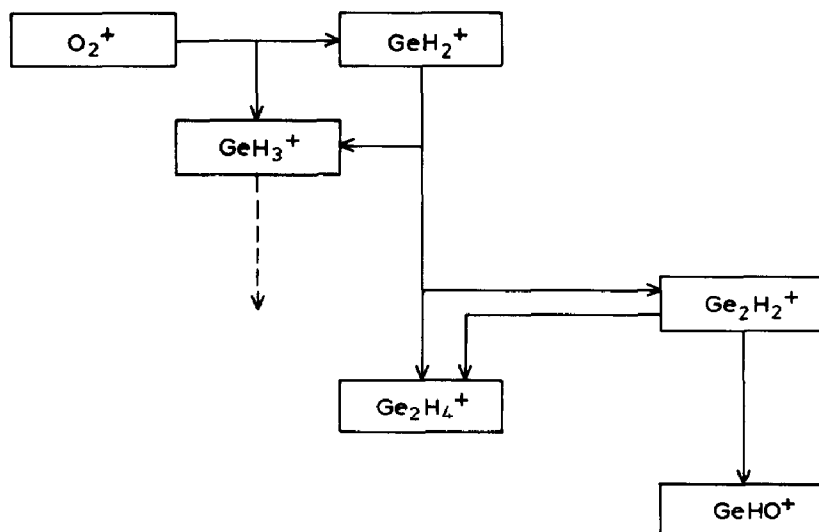
In γ -radiolysis experiments, both ionic and radical species are involved in formation of the amorphous material. Only the contribution by radicals could be evaluated by the radiolytic method (i.e. by use of scavengers), and no information was obtained on the nature and contribution of the ionic species [7]. It was suggested that GeH_2 is the main precursor, with GeH_3 playing no significant role in the formation of the solid material. The results presented above are in good agreement with those findings, as they show that GeH_2^+ is very reactive, and that GeH_3^+ , which is formed as a secondary product, is rather unreactive. Moreover, the Ge/H ratio in the radiolysis product is substantially < 2 [7], and this is likely to be due to the all-important contribution of the Ge^+ ion as polymerization precursor.

Ion-molecule reactions in GeH_4/O_2 mixtures

Both O_2^+ and the germane ion family are observed after 20 eV bombardment of a GeH_4/O_2 mixture (1/5) at the pressure of 0.5×10^{-7} torr in the FTMS cell. Owing to the higher ionization potential of oxygen (12.075 eV) [10] compared with that of germane (10.5 eV) [8a], collision between O_2^+ and GeH_4 leads to rapid disappearance of O_2^+ with predominant formation of GeH_3^+ and GeH_2^+ (Scheme 2). Both ions react with GeH_4 in accord with the normal ion pattern described in the previous section, yielding inter alia Ge_2H_4^+ and Ge_2H_2^+ . This latter ion, however, reacts with an O_2 molecule to yield GeHO^+ as predominant product. It is tempting to propose a reaction mechanism for GeHO^+ formation involving addition of the O_2 molecule to the Ge_2H_2^+ to give adduct I, which breaks apart symmetrically to form a GeHO^+ ion and a GeHO radical (eq. 1):



In high pressure experiments it is likely that a fraction of germanium containing ions are formed by electron ionization of the monogermene, mainly when it is present at the highest concentrations.



Scheme 2.

Table 1 shows the variation in the abundances of the most significant mono-germanium ions in the mass spectra of the GeH_4 (10.0%)/ O_2 system as a function of the total pressure. Ions containing more than one germanium atom are not shown, and this is also the case in the subsequent tables. The most remarkable feature is the presence of oxygenated ions, containing up to two oxygen atoms. The GeHO^+ species, which is the only oxygenated ion detected by FTMS, is the most abundant product ion in the ion-molecule reactions involving oxygen observed in high pressure mass spectra. In addition, GeO^+ , GeH_2O^+ , GeH_3O^+ , GeO_2^+ and GeHO_2^+ are formed to smaller extents. However, the oxygen-containing ions are much weaker than the GeH_n^+ ($n = 0-3$) species, and this could account for the poor ability of O_2 as a radical scavenger [7].

Table 1

Relative abundances of significant ions in the mass spectra of GeH_4 (10.0%)/ O_2 mixture at various pressures ^{a,b}

Ions	Pressures (torr)			
	0.5	0.1	0.05	0.02
GeHO_2^+	2.6	1.0	0.7	0.1
GeO_2^+	2.6	1.6	1.5	0.1
GeH_3O^+	1.4	0.6	0.9	0.5
GeH_2O^+	0.9	0.9	1.1	0.4
GeHO^+	15	6.6	5.6	1.1
GeO^+	2.2	1.8	1.8	0.7
GeH_3^+	100	100	99	88
GeH_2^+	66	99	100	100
GeH^+	16	30	34	24
Ge^+	22	36	38	37

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms, observed at all pressures used, are not shown.

Table 2

Relative abundances of significant ions in the mass spectra of $\text{GeH}_4(2.0\%)/\text{O}_2$ mixture at various pressures ^{a,b}

Ions	Pressures (torr)			
	0.5	0.3	0.1	0.05
GeHO_2^+	8.1	3.5	0.5	0.3
GeO_2^+	3.6	3.1	0.9	0.3
GeH_3O^+	1.7	1.6	0.7	0.8
GeH_2O^+	0.9	1.7	1.2	0.8
GeHO^+	30	13	4.1	1.8
GeO^+	5.2	4.1	1.7	1.5
GeH_3^+	100	100	93	86
GeH_2^+	76	98	100	100
GeH^+	18	27	25	30
Ge^+	21	35	37	43

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms, observed at 0.5, 0.3, and 0.1 torr, are not shown.

As the total pressure is decreased the abundances of GeH_nO_2^+ ($n=0, 1$), GeHO^+ and GeO^+ also gradually decrease; for GeH_3O^+ and GeH_2O^+ this effect is not so evident, since these ions are very weak at all the pressures used. Ge_2H_n^+ ($n=0-5$) dimer ions are observed in all experiments from 0.5 to 0.02 torr of total pressure, and their oxygenated derivatives $\text{Ge}_2\text{H}_n\text{O}^+$ ($n=0, 1$) are present at 0.5 and 0.1 torr total pressure. At the pressures reported in Table 1, the abundances of GeH_nO^+ ($n=0-3$) and GeH_nO_2^+ ($n=0, 1$) display a similar trend to those of the Ge_2H_n^+ ($n=0-5$) ions, and, in fact, they decrease almost proportionally. Thus it is likely that under these experimental conditions the formation of oxygenated ionic species involves dimeric germanium ions, as observed in FTMS experiments.

However, when the partial pressure of GeH_4 is decreased, so that the dimers are not detected, and that of O_2 increased above 1 torr, the GeH_nO_2^+ ($n=0, 1$) and GeH_nO^+ ($n=0-3$) ions are still observed. This indicates that oxygenated ions can also be formed from precursor ions containing the same number of germanium atoms under high pressures of oxygen. The formation of $\text{Ge}_2\text{H}_n\text{O}^+$ ($n=0, 1$) in the absence of Ge_3H_n^+ supports this suggestion.

The $\text{GeH}_4(2.0\%)/\text{O}_2$ system shows the same trend as the $\text{GeH}_4(10.0\%)/\text{O}_2$ mixture when studied at different total pressures, as can be seen from Table 2. The higher relative abundance of the oxygenated ions at 0.5 torr and the presence of the dimer ions only to 0.1 torr total pressure in the 2.0% mixture compared with the 10.0% one, are both due to the different ratio between the two reagent gases. A lower concentration of GeH_4 reduces the probability of collision between germanium-containing species and, at the same time, the relatively higher concentration of O_2 increases the contribution of bimolecular reactions leading to oxygenated ions.

The same monogermanium species are formed when the $\text{GeH}_4(0.17\%)/\text{O}_2$ mixture is used. The ion currents transported by the oxygenated species are, as shown in Table 3, much weaker than those observed with the mixtures considered above, and are not detected below 0.3 torr total pressure. The dimer ions are not observed even at 0.5 torr.

Table 3

Relative abundances of significant ions in the mass spectra of $\text{GeH}_4(0.17\%)/\text{O}_2$ mixture at various pressures ^{a,b}

Ions	Pressures (torr)	
	0.5	0.3
GeHO_2^+	4.0	3.5
GeO_2^+	2.8	2.7
GeH_3O^+	2.3	2.0
GeH_2O^+	2.6	2.3
GeHO^+	16	14
GeO^+	8.6	8.2
GeH_3^+	94	95
GeH_2^+	100	100
GeH^+	24	24
Ge^+	31	32

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms were not observed.

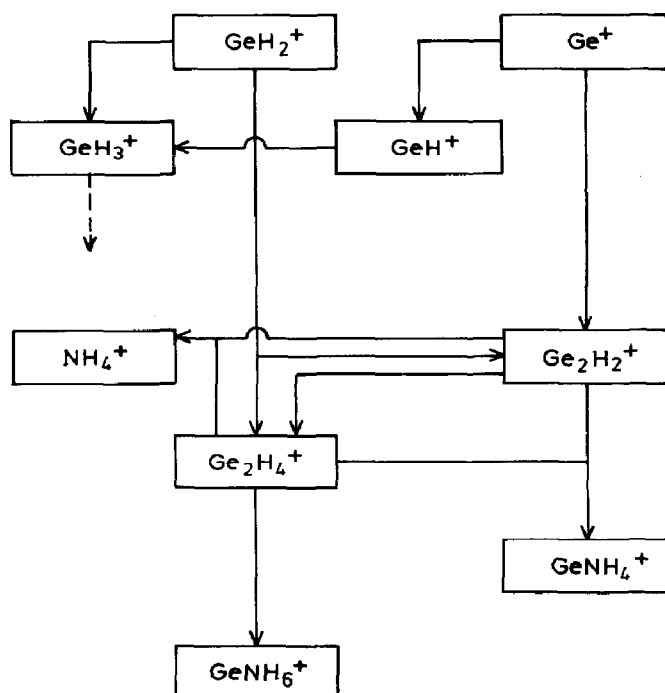
A GeH_4/O_2 mixture containing 0.03% of GeH_4 was also studied. No data are reported for the ions formed in this system, because very weak multiplets due to the GeH_n^+ ($n = 0-3$) ions were the only species detected even at 0.5 torr total pressure.

The relative abundances of GeH_2^+ in Tables 1 and 2 increase relative to those of GeH_3^+ as the total pressure is decreased, and this can be ascribed to the higher reactivity of GeH_2^+ , which gives dimers and possibly also oxygenated ions.

The results obtained from FTMS experiments on GeHO^+ and the observations reported above suggest that the formation of the oxygenated species involves ion-molecule reactions between dimer or monomer germanium-containing ions and molecules of oxygen. Primary oxygenated ions are formed in parallel pathways involving elimination of radicals or molecules, such as H_2 , which dissipate the excitation energy. However, fragmentation of these ions also occurs, as can be confirmed by B/E linked scan measurements. In particular, GeHO_2^+ loses an oxygen atom to give GeHO^+ , which then forms GeH^+ by ejection of the second oxygen atom. The corresponding reaction sequence involving the steps $\text{GeO}_2^+ \rightarrow \text{GeO}^+ \rightarrow \text{Ge}^+$ has also been observed.

Ion-molecule reactions in GeH_4/NH_3 mixtures

An ion pattern, similar to that operating in GeH_4/O_2 mixtures, is generated by 15 eV electron impact on GeH_4 -containing variable amounts of NH_3 (10–20%) under FTMS conditions ($p \approx 1.0 \times 10^{-7}$ torr). In addition to germane and digermane ions, the spectra are characterized by the presence of both GeNH_4^+ and GeNH_6^+ as well as NH_4^+ . Their relative yields are found to depend primarily upon the total pressure of the system, the relative concentration of NH_3 , and the reaction time. Multiple resonance experiments indicate that all the germane ions, including Ge_2H_2^+ and Ge_2H_4^+ , are precursors, and lose a proton to the very basic NH_3 to give NH_4^+ (Scheme 3). The Ge_2H_2^+ and Ge_2H_4^+ ions can, however, undergo substitution by NH_3 to yield GeNH_4^+ . At longer reaction times, Ge_2H_4^+ also can attack NH_3 to give GeNH_6^+ in low yield. Plausible intermediates for such reactions are adducts (II) (eq. 2), (III) (eq. 3), and (IV) (eq. 4).



Scheme 3.

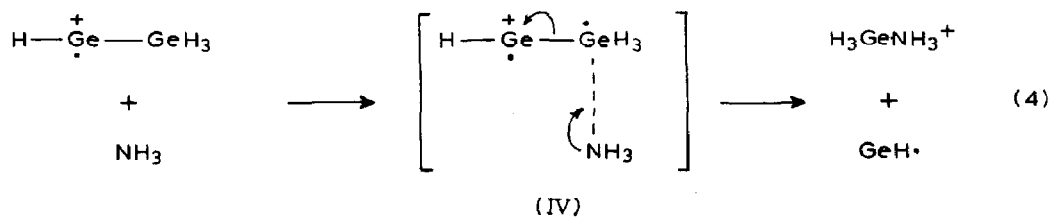
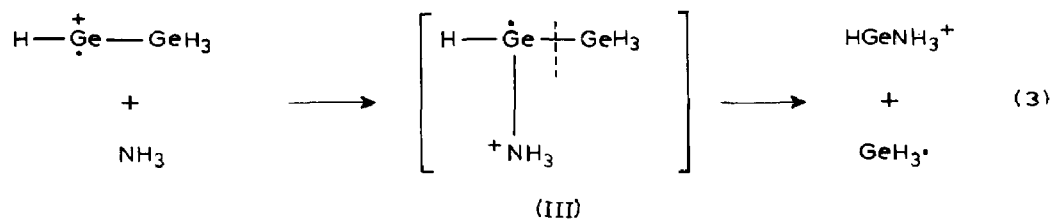
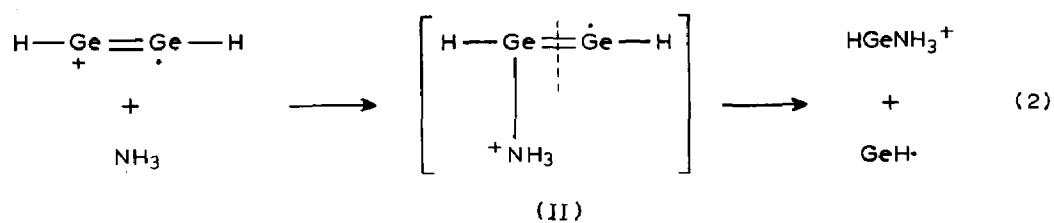


Table 4

Relative abundances of significant ions in the mass spectra of $\text{GeH}_4(10.1\%)/\text{NH}_3$ mixture at various pressures ^{a,b}

Ions	Pressures (torr)			
	0.5	0.2	0.08	0.02
GeN_2H_7^+		0.3		
GeN_2H_6^+		0.2		
GeN_2H_5^+	8.5	0.7	0.2	
GeN_2H_4^+	4.5	0.7	0.2	
GeNH_6^+	13	14	1.6	0.8
GeNH_5^+	1.6	2.4	0.4	0.5
GeNH_4^+	82	30	18	8.0
GeNH_3^+	66	35	13	6.9
GeNH_2^+	46	31	5.1	2.6
GeH_3^+	95	100	100	100
GeH_2^+	57	94	87	99
GeH^+	66	42	33	32
Ge^+	100	52	47	40

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms, observed at all pressures examined, are not shown.

At high pressures, neither GeH_5^+ nor adduct ions with NH_4^+ were observed. This is consistent with the fact that the proton affinity of GeH_4 [11] is lower than that of NH_3 [12], and with the absence of a site suitable for NH_4^+ addition to GeH_4 [13].

Under chemical ionization conditions, GeH_4 is likely to be ionized by charge-exchange processes, but because of the lower ionization potential of NH_3 , 10.154 eV [10], than of GeH_4 , 10.5 eV [8a], it is plausible that ionization occurs by collisions with NH_2^+ and NH^+ species, whose ionization potentials are 11.4 and 13.1 eV [14], respectively. Moreover, the possibility cannot be ruled out that a small population of ions of GeH_4 is formed by electron ionization as the fraction of ionic current transported by germanium-containing ions decreases with decreasing concentration of GeH_4 in different mixtures.

Tables 4, 5, and 6 show the most significant ions in the mass spectra of monogermanc/ammonia systems containing 10.1, 1.85, and 0.17% of GeH_4 , respectively, at different pressures. As in the case of GeH_4/O_2 mixtures, the dimer ions are not shown; their formation depends on both the concentration of GeH_4 and the total pressure. Dimers are always observed in the $\text{GeH}_4(10.1\%)/\text{NH}_3$ mixture, and never in the $\text{GeH}_4(0.17\%)/\text{NH}_3$ one. Ge_2H_n^+ ($n = 0-5$) ions are formed till 0.08 torr total pressure and weak Ge_2NH_n^+ ($n = 2-4$) at 0.5 torr total pressure in the $\text{GeH}_4(1.85\%)/\text{NH}_3$ system.

The overall behaviour is similar to that in the presence of O_2 . However, the ratios $\text{GeNH}_n^+/\text{GeH}_n^+$ are generally higher than the ratios of the corresponding oxygenated ions $\text{GeH}_n\text{O}^+/\text{GeH}_n^+$ measured at a similar concentration of reagents and the same total pressure. For example, at 0.08 torr total pressure the $\text{GeNH}_n^+/\text{GeH}_n^+$ ratios are 0.143 and 0.226 in the GeH_4/NH_3 10.1 and 1.85% mixtures, respectively, compared with the $\text{GeH}_n\text{O}^+/\text{GeH}_n^+$ ratios at 0.1 torr total pressure, of 0.037 and 0.030 in the GeH_4/O_2 10.0% and 2.0% mixtures, respectively.

Table 5

Relative abundances of significant ions in the mass spectra of $\text{GeH}_4(1.85\%)/\text{NH}_3$ mixture at various pressures ^{a,b}

Ions	Pressures (torr)		
	0.5	0.08	0.02
GeN_2H_7^+	5.1		
GeN_2H_6^+	3.3		
GeN_2H_5^+	14	1.1	
GeN_2H_4^+	7.2	1.0	
GeNH_6^+	8.7	4.4	
GeNH_5^+	1.2	0.2	
GeNH_4^+	69	15	6.1
GeNH_3^+	58	22	4.8
GeNH_2^+	81	12	3.3
GeH_3^+	36	100	93
GeH_2^+	23	87	100
GeH^+	59	42	34
Ge^+	100	68	55

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms, observed at 0.5 and 0.08 torr, are not shown.

The ions GeNH_6^+ and GeNH_4^+ are the only nitrogen-containing species also detected by FTMS. At high pressures GeNH_6^+ is observed only when dimer ions are present, in good agreement with the mechanism of their formation established by FTMS. In contrast GeNH_n^+ ($n = 2-4$) ions are detected at such low pressures that dimers are not formed. Therefore, it is likely that ions containing one germanium atom can also react with ammonia to give GeNH_n^+ ($n = 2-4$) species, as it was observed for the GeH_4/O_2 mixtures. Moreover, under high pressures, ions containing two nitrogen atoms, GeN_2H_n^+ ($n = 4-7$), are detected, and are likely to be formed by reaction of GeNH_n^+ species with a second NH_3 molecule with ejection of hydrogen radicals or molecules.

The ions formed from GeH_4 react with dimethylamine at 0.5 torr to give $\text{Ge}(\text{CH}_3)_2\text{NH}_4^+$, $\text{Ge}(\text{CH}_3)_2\text{NH}_2^+$, and $\text{Ge}(\text{CH}_3)_2\text{NH}^+$ as the main products. These species correspond to the ions observed in the presence of NH_3 at high

Table 6

Relative abundances of significant ions in the mass spectra of $\text{GeH}_4(0.17\%)/\text{NH}_3$ mixture at various pressures ^{a,b}

Ions	Pressures (torr)			
	0.5	0.2	0.08	0.02
GeNH_4^+	75	39	8.4	traces
GeNH_3^+	49	35	13	13
GeNH_2^+	56	22	9.5	14
GeH_3^+	46	100	96	81
GeH_2^+	44	84	100	100
GeH^+	60	53	39	41
Ge^+	100	79	61	62

^a Abundances refer to the ^{76}Ge isotope. ^b Ions containing two Ge atoms were not observed.

pressure, but $\text{Ge}(\text{CH}_3)_2\text{NH}_4^+$ has the highest abundance, with the $\text{Ge}(\text{CH}_3)_2\text{NH}_2^+$ and $\text{Ge}(\text{CH}_3)_2\text{NH}^+$ ions less abundant.

Conclusions

These results give valuable information about the mechanism of the reactions in which ionic species are involved during the first steps of the polymerization of GeH_4 initiated by γ -radiolysis. The observation of oxygenated and nitrogenated ions, whose nature and abundance depend on the pressure of the system and the ratio between GeH_4 and oxygen, ammonia or dimethylamine, is also important. In fact, the presence of elements other than germanium can substantially affect the properties of the solid product obtained by γ -radiolysis, as has been observed upon irradiating GeH_4/O_2 mixtures [5].

Experimental

GeH_4 was prepared by reduction of GeO_2 with KBH_4 and purified as described previously [5].

High pressure experiments were run on a double focussing Kratos MS 80 mass spectrometer connected to a DS 55 data system. Operating conditions were as follows: primary ionization electron energy 60 eV, emission current 500 μA , acceleration voltage 4 keV, ion repeller voltage zero, resolution 1000 (10% valley definition), scan rate 3 s/dec. The reaction mixtures containing different ratios of GeH_4 and reagent gas were prepared in a vial (1.50 l) connected to a vacuum line. It was filled with the relative appropriate amounts of the two gases to a pressure of about 1.10 atm then connected to a valve of the multiple reagent gas inlet system of the mass spectrometer, and the gaseous mixture was introduced into the ion source which was maintained at room temperature. Ion source pressures were evaluated by the relative concentrations of ions in CH_4 as a function of pressure [15], and corrected by use of the relative sensitivities ion gauge for different gases [16]. However, small differences in pressure do not cause drastic variations in the nature and abundance of ions.

All FTMS experiments were performed on a Nicolet FTMS 1000 spectrometer equipped with a 2.54 cm cubic trapping cell situated between the poles of a superconducting magnet operated at 2.0 T. Sample pressures (uncorrected) were measured with a Granville-Phillips 280 Bayard-Alpert Ion Gauge. Resolution was typically 1000 fwhh (full width half height) at mass 100. Inlet system and trapping cell were kept at room temperature. Ions were trapped in the cell by a differential trapping voltage of about 1.0 V. Typical operating conditions were as follows: nominal electron beam energy: 15–20 eV, electron beam pulse: 3–5 ms, emission current: 400 nA, total pressure: $0.4\text{--}1.0 \times 10^{-7}$ torr. The ionic sequences taking place in the reaction cell were examined by ion ejection experiments by choosing suitable time sequences to maximize the abundance of a given precursor and frequency windows to remove all the accompanying undesired ions from the cell. Detection of the daughter ion pattern after a suitable reaction time provides direct information about the reaction sequence concerning the precursor in question.

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