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Gas phase ion-molecule reactions in methylgermane/ oxygen, /ammonia, and /unsaturated hydrocarbon systems

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Abstract

Gas phase ion-molecule reactions in systems containing CH_3GeH_3 and oxygen, or ammonia, or unsaturated hydrocarbons (C_2H_4, C_3H_6, C_3H_4) have been studied by Fourier-transform mass spectrometry and high-pressure mass spectrometry. The self-condensation processes of CH_3GeH_3 as well as the effects of the nature and the concentration of the reagent, and of the total pressure of the system on the formation of new Ge–O, Ge–N and Ge–C bonds are investigated. For each system the reaction pattern is presented and the gas phase reactivity of CH_3GeH_3 compared with that of GeH_4 towards the same reagents. The formation of ionic species containing new Ge–C bonds observed in the CH_3GeH_3/unsaturated hydrocarbons systems is discussed in relation to the preparation of amorphous germanium carbides, which are promising materials for photovoltaic applications.

Introduction

The chemistry of plasma is fundamental to the formation of materials such as amorphous semiconductors or ceramics, which are produced through vapour deposition assisted by glow discharge, laser or ionizing radiations [1–5]. Likely models of the ion reaction mechanisms involved in these processes can be simu-

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lated both in the cell of a Fourier-transform mass spectrometer and in the ionization chamber of a conventional mass spectrometer operating under chemical ionization conditions [6]. By these methods valuable information has been obtained for the γ-radiolytic deposition of solid products from GeH_4 or SiH_4 [7] and for the preparation of analogous materials by glow discharge [8,9]. Fourier-transform mass spectrometry has also been used to investigate ion-molecule reactions in SiH_4/NH_3 systems, to elucidate the processes involved in silicon nitride deposition from silane-ammonia plasmas [10].

In order to study the X-ray-assisted deposition of the amorphous material a-GeC:H, we have previously examined the GeH_4/hydrocarbons systems [11,12], and we have recognized the difficulty of obtaining products with a controlled content of germanium and carbon from these mixtures. It has also been reported [13] that a-GeC:H can be produced by chemical vapour deposition starting from gaseous compounds which already contain germanium and carbon bonded together and in 1:1 ratio.

With the aim of finding out the most convenient systems to obtain a-GeC:H by radiolytic procedures, we have examined the self-condensation reactions of methylgermane and have studied CH_3GeH_3/unsaturated hydrocarbon mixtures to investigate the chain propagation involving addition of carbon atoms by Fourier-transform mass spectrometry (FTMS) and chemical ionization mass spectrometry (CIMS). We have also extended our studies to CH_3GeH_3/O_2 mixtures, in order to evaluate the formation of oxygenated species, undesirable in the final product; and CH_3GeH_3/NH_3 mixtures to know the extent to which doping with nitrogen is possible.

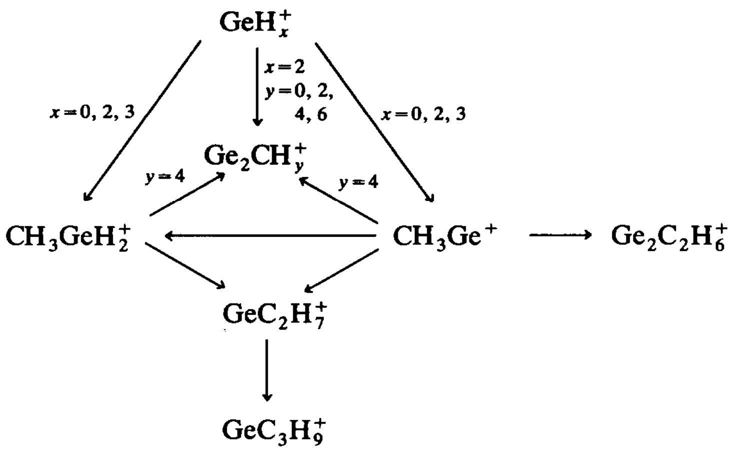
Apart from the practical applications of these investigations, the information drawn from the present research has an intrinsic interest in a comparison of the gas-phase ion-molecule reactions of CH_3GeH_3 with those of GeH_4 in the presence of small inorganic and organic molecules, and in particular in determining the influence of a preformed Ge–C bond in primary ions.

Results and discussion

Self-condensation ion-molecule reactions in pure methylgermane

Interaction of 20 eV electrons with CH_3GeH_3 ($p = 2.3 \times 10^{-7}$ torr) yields two different families of primary ions, *viz.*, $CH_3GeH_y^+$ ($y = 0$, 14%; $y = 1$, 22%; $y = 2$, 64%) and GeH_x^+ ($x = 0$, 13%; $x = 2$, 65%; $x = 3$, 22%) in the overall ratio 2:1. The members of the $CH_3GeH_y^+$ family, like those of the more general $GeC_nH_m^+$ ($n = 1$–3; $m = 3$–9) family, are thought to arise from Ge–H bond cleavages, rather than from C–H bond fragmentations, in view of: (i) the substantially higher average C–H bond energy (99 Kcal mol^{-1}) [14] compared with that of the Ge–H bond (69 Kcal mol^{-1}) [14]; (ii) the much higher stability of Ge-centred cations over the C-centred cations [15]; and (iii) the low stability of multiple bonds between C and Ge atoms [14]. However, structures different from those proposed in this work, although rather unlikely, cannot be *a priori* excluded.

As shown in Scheme 1, the GeH_x^+ ($x = 0$, 2, 3) ions react with neutral CH_3GeH_3 to yield secondary $CH_3GeH_y^+$ ($y = 0$, 55%; $y = 2$, 45%) at approximately every collision. Thus, after a few tens of milliseconds of reaction time, only the $CH_3GeH_y^+$ ($y = 0$–2) ions are present in the FTMS cell. The detailed



Scheme 1.

mechanism for the formation of secondary $CH_3GeH_y{}^+$ ions from their $GeH_x{}^+$ parents, whether proceeding via electrophilic attack at the carbon or hydrogen centres of CH_3GeH_3, is still under investigation and will be discussed in a later publication.

Minor reaction pathways involving $GeH_x{}^+$ ($x = 2$) are those yielding digermanium ions, such as Ge_2C^+, $Ge_2CH_2{}^+$, $Ge_2CH_4{}^+$, and $Ge_2CH_6{}^+$, with an overall rate of 7×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

Primary and secondary CH_3Ge^+ ions react with CH_3GeH_3 to generate $CH_3GeH_2{}^+$ ($k = 4 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}), $GeC_2H_7{}^+$ ($k = 1.5 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}), and, with lower rates, $Ge_2CH_4{}^+$ and $Ge_2C_2H_6{}^+$. Assuming that the first two daughter ions are formed by electrophilic attack of CH_3Ge^+ on the H and C centres of CH_3GeH_3, respectively, the structure $(CH_3)_2GeH^+$ is proposed for the $GeC_2H_7{}^+$ ions.

Primary and higher order $CH_3GeH_2{}^+$ ions, in turn, attack CH_3GeH_3 to produce $(CH_3)_2GeH^+$ ($k = 3.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) and $Ge_2CH_4{}^+$. The observation that the efficiency of formation of $Ge_2CH_4{}^+$ from this latter path is significantly lower than that for the formation of the same daughter species from CH_3Ge^+ suggests the dual origin of $Ge_2CH_4{}^+$ from both precursors through essentially independent and parallel pathways.

The $(CH_3)_2GeH^+$ ion reacts with CH_3GeH_3 yielding eventually an apparently unreactive $GeC_3H_9{}^+$ daughter species, with a $(CH_3)_3Ge^+$ structure being likely.

Ion-molecule reaction in methylgermane / oxygen mixtures

The impact of a 15 eV electron beam on a CH_3GeH_3/O_2 (2:1) mixture at a total pressure of about 2.3×10^{-7} torr in a FTMS source cell produces the same ionic families as detected in pure methylgermane. No reactions are observed leading to the formation of ionic species containing oxygen atoms, even after rather long reaction times (*ca.* 500 ms).

On the other hand, in high-pressure conditions typical of the chemical ionization mass spectrometry some oxygenated ions are formed. Table 1 shows the variation in the abundances of the most significant ions containing only one

Table 1

Relative abundances of significant ions in the mass spectra of CH_3GeH_3(11.4%)/O_2 mixture at various pressures [a,b]

Ions	Pressure (torr)		
	0.3	0.1	0.05
Ge^+	28	38	42
GeH^+	13	16	18
GeH_2^+	38	48	58
GeH_3^+	15	16	18
GeC^+	0.5	1.0	1.1
$GeCH^+$	4.3	6.4	7.8
$GeCH_2^+$	8.8	12	14
$GeCH_3^+$	45	44	43
$GeCH_4^+$	53	64	67
$GeCH_5^+$, $GeOH^+$	100	100	100
$GeC_2H_6^+$, $GeCOH_2^+$	1.4	0.7	
$GeC_2H_7^+$, $GeCOH_3^+$	6.2	3.2	1.1
$GeCOH_4^+$	0.7	0.5	
$GeCOH_5^+$	1.7	0.8	

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.

germanium atom in the mass spectra of the CH_3GeH_3(11.4%)/O_2 mixture at 0.3, 0.1, 0.05 torr total pressure.

Most of the ion current is carried by the families of primary ions GeH_n (n = 0–3) and $GeCH_n^+$ (n = 0–4). The base peak is assigned to two different ionic species, $GeCH_5^+$ and $GeOH^+$, having the same nominal mass. The mass spectra of the gaseous mixtures containing methylgermane here studied always display $GeCH_5^+$ as a very abundant ion, which is often the base peak. On the other hand, $GeOH^+$ has been reported [6] to be the most abundant oxygen-containing ion in the mass spectra of GeH_4/O_2 systems. It reaches a value of 15% of the base peak (GeH_3^+) in the GeH_4(10.0%)/O_2 mixture at 0.5 torr total pressure. With reference to ions containing the ^{76}Ge isotope, it is therefore likely that $GeOH^+$ also contributes to the peak at $m/z = 93$. Similarly, ions at nominal mass $m/z = 106$, corresponding to $(CH_3)_2Ge^+$ and $GeCOH_2^+$, and at nominal mass $m/z = 107$, corresponding to $(CH_3)_2GeH^+$ and $GeCOH_3^+$, cannot be assigned unequivocally.

The oxygenated species $GeCOH_n^+$ (n = 4–5), formed in ion-molecule reactions, show low abundances at the highest total pressure used for this mixture, 0.3 torr, and decrease with decreasing total pressure, while the abundances of the primary ions increase. This behaviour is predictable on the basis of the lower extent to which ion-molecule reactions leading to secondary ions take place in systems at lower total pressure.

The relative abundances of the ions in the mass spectra of the CH_3GeH_3(2.3%)/O_2 system at total pressure in the range 0.3–0.05 torr are shown in Table 2. The overall behaviour is very similar to that described in Table 1, the only difference being the slightly higher relative abundances of oxygen-containing ions ($GeCOH_4^+$ and $GeCOH_5^+$) in the 2.3% mixture compared with the 11.4% mixture. In fact, a higher oxygen partial pressure increases the probability of collision of germanium-containing species with oxygen. The disappearance of

Table 2

Relative abundances of significant ions in the mass spectra of CH_3GeH_3(2.3%)/O_2 mixture at various pressures [a,b]

Ions	Pressure (torr)			
	0.3	0.2	0.1	0.05
Ge^+	34	36	42	47
GeH^+	14	16	18	19
$GeH_2{}^+$	45	60	63	83
$GeH_3{}^+$	15	18	20	22
GeC^+	0.4	0.8	0.8	1.2
$GeCH^+$	4.8	5.7	6.8	8.2
$GeCH_2{}^+$	9.5	10	13	16
$GeCH_3{}^+$	35	37	42	46
$GeCH_4{}^+$	63	60	69	78
$GeCH_5{}^+$, $GeOH^+$	100	100	100	100
$GeC_2H_7{}^+$, $GeCOH_3{}^+$	1.8	1.0	0.7	
$GeCOH_4{}^+$	1.3	0.8	0.6	
$GeCOH_5{}^+$	2.9	2.2	1.9	0.6

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.

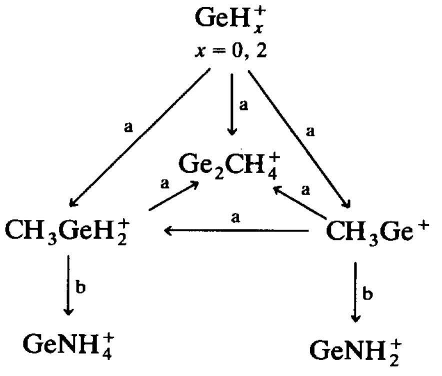
the ions at $m/z = 106$ and the decrease in abundance of species at $m/z = 107$ seem to indicate that these ions are constituted mainly by $GeC_2H_6{}^+$ and $GeC_2H_7{}^+$, respectively.

The results of both FTMS and CIMS suggest a very low reactivity of CH_3GeH_3 toward oxygen. Comparison with the mass spectra of GeH_4/O_2 mixtures at different pressures [16] indicates that methylgermane is less reactive than germane.

Ion-molecule reactions in methylgermane / ammonia mixtures

Interaction of 20 eV electrons on CH_3GeH_3/NH_3 (2 : 3) mixtures at 2.8×10^{-7} torr in the FTMS cell produces the ionic families typical of both CH_3GeH_3 and NH_3. $NH_3{}^+$ reacts very rapidly with neutral NH_3 to give $NH_4{}^+$ ions, which are inert towards the components of the gaseous mixture.

The $GeH_x{}^+$ ($x = 0$, 2) ions, especially $GeH_2{}^+$, react with CH_3GeH_3 producing CH_3Ge^+, $CH_3GeH_2{}^+$, and $Ge_2CH_4{}^+$ (Scheme 2). Both CH_3Ge^+ (22%) and



Scheme 2. Neutral reagent molecules: (a) CH_3GeH_3; (b) ammonia.

Table 3

Relative abundances of significant ions in the mass spectra of CH_3GeH_3(11.5%)/NH_3 mixture at various pressures [a,b]

Ions	Pressure (torr)			
	0.5	0.3	0.1	0.05
Ge^+	41	44	44	52
GeH^+	17	20	20	22
$GeH_2{}^+$	27	23	35	64
$GeH_3{}^+$	6.9	13	16	25
$GeCH^+$	4.9	0.8	0.8	1.2
$GeCH_2{}^+$	14	14	14	19
$GeCH_3{}^+$	96	63	56	56
$GeCH_4{}^+$	42	39	44	72
$GeCH_5{}^+$	100	100	100	100
$GeNH_4{}^+$	90	30	18	8.0
$GeNH_5{}^+$	5.3	2.8		
$GeCNH_4{}^+$	0.9			
$GeCNH_5{}^+$	5.1	3.0	1.5	
$GeCNH_6{}^+$, $GeN_2H_4{}^+$	20	8.5	4.0	
$GeCNH_7{}^+$, $GeN_2H_5{}^+$	1.4	0.8	0.8	
$GeN_2H_6{}^+$	10	4.2	1.8	
$GeN_2H_7{}^+$	1.1			
$GeCN_2H_8{}^+$	1.4			
$GeCN_2H_9{}^+$	0.7			

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.

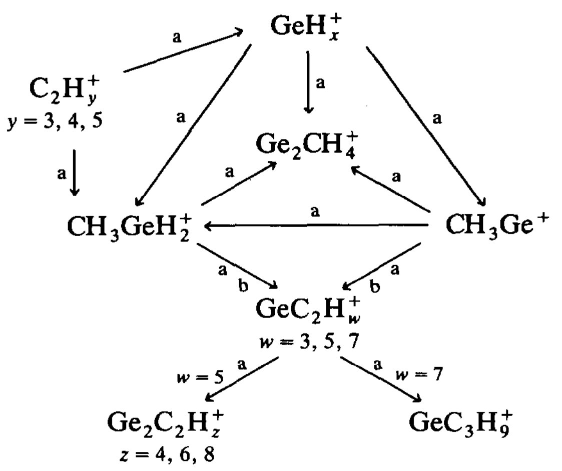
$CH_3GeH_2{}^+$ (78%) attack NH_3 yielding $GeNH_2{}^+$ ($k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and $GeNH_4{}^+$ ($k = 2.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}), respectively.

Table 3 shows the relative abundances of the significant ions in the mass spectra of a CH_3GeH_3(11.5%)/NH_3 mixture at different total pressures (from 0.5 to 0.05 torr). The number of nitrogen-containing ions is rather high, the most abundant being $GeNH_4{}^+$, which is 90% of the base peak at 0.5 torr total pressure. Under these chemical ionization conditions, ions of general formula $GeC_wN_yH_z{}^+$ (with $w = 0, 1$; $y = 1$–3; $z = 4$–9) are also observed. Their abundances dramatically decrease with the total pressure, the $GeNH_4{}^+$ ion being the only one detectable in the mass spectra of the mixture at 0.05 torr of total pressure. This pressure dependence, coupled with the FTMS evidence, points to $GeNH_4{}^+$ as the major precursor of $GeC_wN_yH_z{}^+$ ions, whose actual formulae are then represented by $GeN_yH_z{}^+$, with $y = 2$ or 3 and $z = 2$–7, although some minor contribution from isobaric species containing a C atom ($GeCN_{y-1}H_{z+2}{}^+$) cannot be *a priori* excluded.

However, precise evaluation of the relative abundances of the two isobaric ion families is beyond the specific purposes of the present study, since, in all cases, a strong affinity of the methylgermane ions for the N atom of ammonia is observed.

Ion-molecule reactions in methylgermane / ethene mixtures

The impact of 20 eV electrons on a CH_3GeH_3/C_2H_4 (1:2) mixture at 1.5×10^{-7} torr in the FTMS cell yields both the CH_3GeH_3 and C_2H_4 ion



Scheme 3. Neutral reagent molecules: (a) CH_3GeH_3; (b) ethene.

families. The $C_2H_y{}^+$ ($y = 3$ or 4) primary ions from C_2H_4 rapidly attack their neutral precursor, eventually yielding $C_2H_5{}^+$ and $C_3H_5{}^+$.

Whereas $C_3H_5{}^+$ is inert, the $C_2H_y{}^+$ ($y = 3$–5) ion family, especially $C_2H_4{}^+$, reacts with CH_3GeH_3 at approximately the collision rate yielding $GeH_x{}^+$ ($x = 0$, 9%; $x = 2$, 6%) and $CH_3GeH_2{}^+$ (85%). These ions attack CH_3GeH_3, starting the normal reaction network already shown in Scheme 1. Besides these reactions, both CH_3Ge^+ and $CH_3GeH_2{}^+$ ions react very rapidly with C_2H_4 producing the $GeC_2H_w{}^+$ ($w = 3$, 5, or 7) ion family, which, in turn, produces the $Ge_2C_2H_z{}^+$ ($z = 4$, 6, or 8) ions by interaction with CH_3GeH_3 (Scheme 3).

Table 4 reports the variations of ion abundance in the mass spectra of a CH_3GeH_3(9.9%)/C_2H_4 mixture at different total pressures (0.5, 0.1, and 0.02 torr). Under these high-pressure conditions, a great number of very abundant ions containing new Ge–C bonds is formed. The highest mass ions have up to five carbon atoms and have the $GeC_5H_n{}^+$ ($n = 12$ or 13) general formula with abundances as high as 0.7% of the total ion current transported by monogermane ions at 0.5 torr total pressure. The other ions containing new carbon atoms in the mass spectrum of the mixture at 0.5 torr are $GeC_4H_n{}^+$ ($n = 9$ or 11), $GeC_3H_n{}^+$ ($n = 7$–9), and $GeC_2H_n{}^+$ ($n = 3$–7), and their abundances are 0.4%, 8.7%, and 7.6%, respectively.

The $GeCH_n{}^+$ ($n = 1$–5) ions are considered primary species formed directly in the ionization event or in self-condensation reactions. This Ge–C bond is therefore suggested to exist in the reacting molecule, and not to be formed in ion-molecule processes involving ethene. This hypothesis is in good agreement with both the FTMS results and the behaviour of the system at decreasing total pressure. In fact, it is generally observed that the abundances of the primary ions increase and those of the secondary species decrease at lower total pressure. This trend is also shown by the methylgermane/ethene mixture studied here, in which the abundance of the $GeC_nH_m{}^+$ ions increases from 0.5 to 0.02 torr total pressure when $n = 0$ or 1, and decreases when $n = 2$–5.

Table 4

Relative abundances of significant ions in the mass spectra of $CH_3GeH_3(9.9\%)/C_2H_4$ mixture at various pressures [a,b]

Ions	Pressure (torr)		
	0.5	0.1	0.02
Ge^+	33.3	46.6	73.6
GeH^+	7.8	15.9	23.2
GeH_2^+	6.1	24.8	38.1
GeH_3^+	5.9	14.1	22.6
$GeCH^+$	1.4	4.5	8.2
$GeCH_2^+$	4.1	10.2	19.0
$GeCH_3^+$	43.3	40.5	55.3
$GeCH_4^+$	19.8	33.4	66.5
$GeCH_5^+$	100	100	100
$GeC_2H_3^+$	2.5	2.3	1.9
$GeC_2H_4^+$	2.1	1.8	1.9
$GeC_2H_5^+$	10.4	5.0	2.2
$GeC_2H_7^+$	5.3	1.3	2.1
$GeC_3H_7^+$	1.2	1.1	0.4
$GeC_3H_8^+$	0.8	0.2	
$GeC_3H_9^+$	21.4	1.8	0.5
$GeC_4H_9^+$	0.6		
$GeC_4H_{11}^+$	0.5		
$GeC_5H_{12}^+$	0.3		
$GeC_5H_{13}^+$	1.6		

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.

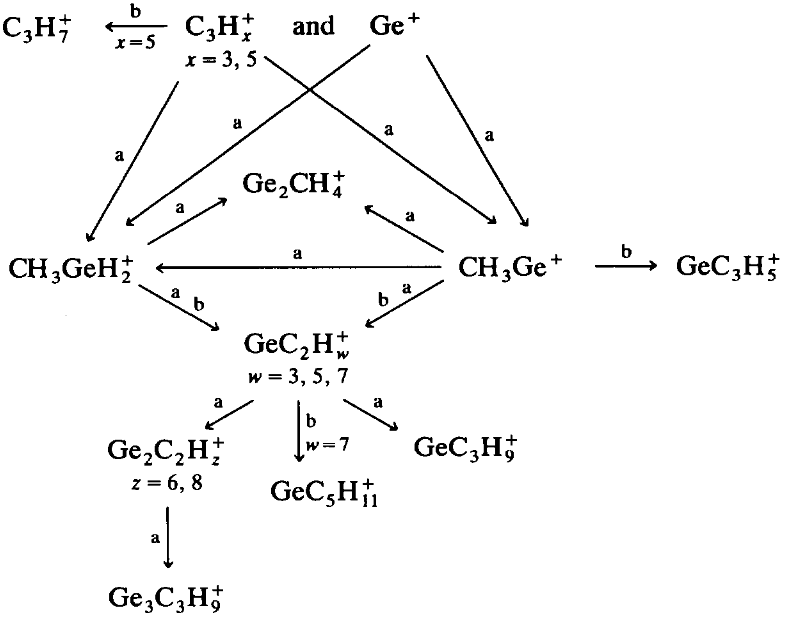
Ion-molecule reactions in methylgermane / propene mixtures

Interaction of 20 eV electrons with a CH_3GeH_3/C_3H_6 (1:7) mixture at 4.0×10^{-7} torr in the FTMS cell gives both the CH_3GeH_3 and the C_3H_6 ion families.

The $C_3H_x^+$ ($x = 3$–5) primary ions from C_3H_6 rapidly attack both their neutral precursors, eventually yielding the unreactive $C_3H_7^+$ ion, and CH_3GeH_3, forming the daughter $CH_3GeH_y^+$ ($y = 0$ or 2) ions. A further precursor of these latter species is the primary Ge^+ ion.

As shown in Scheme 4, both Ge^+ and $CH_3GeH_y^+$ ($y = 0$ or 2) ions interact with CH_3GeH_3 *via* the reaction sequences displayed in Scheme 1. $CH_3GeH_y^+$ ($y = 0$ or 2) attack CH_3GeH_3 and C_3H_6 yielding $GeC_2H_w^+$ ($w = 3$, 5, or 7) ions which, in turn, generate $Ge_2C_2H_z^+$ ($z = 6$ or 8) ions by collision with CH_3GeH_3. This family may slowly interact with CH_3GeH_3, eventually producing $Ge_3C_3H_9^+$. Furthermore, CH_3Ge^+ attacks C_3H_6 yielding $GeC_3H_5^+$. After long reaction times (> 300 ms), a $GeC_5H_{11}^+$ ion, probably $(CH_3)_2GeC_3H_5^+$, is observed from $(CH_3)_2GeH^+$ attack on C_3H_6.

The mass spectra of the $CH_3GeH_3(10.3\%)/C_3H_6$ mixture have been studied at different total pressures, ranging from 0.01 to 0.5 torr, and the results are reported in Table 5. The overall behaviour is very similar to that displayed by the CH_3GeH_3/C_2H_4 system, the only difference being the higher relative abundance of the ions containing new Ge–C bonds. Again, in this CH_3GeH_3/C_3H_6 mixture, the highest mass ions contain five carbon atoms, $GeC_5H_n^+$ ($n = 12$ or 13).



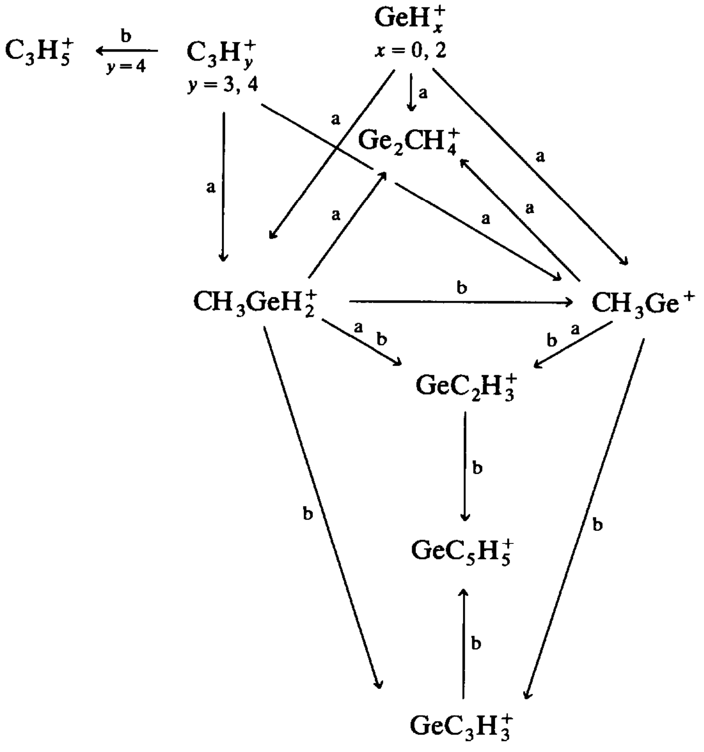
Scheme 4. Neutral reagent molecules: (a) CH_3GeH_3; (b) propene.

Table 5

Relative abundances of significant ions in the mass spectra of CH_3GeH_3(10.3%)/propene mixture at various pressures [a,b]

Ions	Pressure (torr)		
	0.5	0.05	0.01
Ge^+	19.8	38.5	59.4
GeH^+	3.9	13.1	21.0
$GeH_2{}^+$	7.0	27.8	45.7
$GeH_3{}^+$	4.6	11.2	19.9
$GeCH^+$	0.9		
$GeCH_2{}^+$	3.4	9.3	15.3
$GeCH_3{}^+$	51.9	53.2	70.2
$GeCH_4{}^+$	25.5	51.0	57.4
$GeCH_5{}^+$	100	100	100
$GeC_2H_4{}^+$	0.4		
$GeC_2H_5{}^+$	1.8		
$GeC_2H_6{}^+$	8.1	1.9	1.2
$GeC_2H_7{}^+$	40.9	9.9	5.2
$GeC_3H_5{}^+$	2.4		
$GeC_3H_6{}^+$	21.9	6.7	3.1
$GeC_3H_7{}^+$	5.7	4.5	2.6
$GeC_4H_9{}^+$	5.1		
$GeC_4H_{10}{}^+$	4.2		
$GeC_4H_{11}{}^+$	13.3		
$GeC_5H_{12}{}^+$	0.75		
$GeC_5H_{13}{}^+$	10.7		

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.



Scheme 5. Neutral reagent molecules: (a) CH_3GeH_3; (b) allene.

However, their abundance is 3.4% of the total ion current transported by monogermane ions at 0.5 torr total pressure, compared with 0.7% of the CH_3GeH_3/C_2H_4 mixture under very similar experimental conditions. Also the other ionic species containing new carbon atoms in the propene system are more abundant than the corresponding ions in the ethene mixture. In fact, $GeC_4H_n^+$ ($n = 9$–11) is 6.7% (*vs.* 0.4%), $GeC_3H_n^+$ ($n = 5$–7) is 9.8% (*vs.* 8.7%), and $GeC_2H_n^+$ ($n = 4$–7) is 15.3% (*vs.* 7.6%). As in the previous system, an increase of abundance of the primary ions $GeC_nH_m^+$ ($n = 0$ or 1) is observed on decreasing the total pressure. At the same time, ionic products of ion-molecule reactions between species deriving from CH_3GeH_3 and C_3H_6 decrease in abundance ($n = 2$ or 3) or disappear ($n = 4$ or 5).

Ion-molecule reactions in methylgermane / allene mixtures

The impact of 20 eV electrons on a CH_3GeH_3/allene (1:2) mixture at 3.0×10^{-7} torr produces the ion family derived from CH_3GeH_3, in addition to that from C_3H_4, *i.e.* $C_3H_y^+$ ($y = 3$ or 4). Both these ions and GeH_x^+ ($x = 0$ or 2) react at collision rates with CH_3GeH_3 to give $CH_3GeH_2^+$, which rapidly transfers a hydrogen molecule to allene, eventually yielding CH_3Ge^+ (Scheme 5). It is well established that $C_3H_3^+$ from the bombardment of allene is present in the cell as a mixture of two isomers. One is the very stable cyclopropenyl ion, $C_3H_3^+$, and the other is the more reactive propargylic isomer, $HCCCH_2^+$. It is noteworthy that, as distinct from their very different reactivities towards hydride-ion donors, including GeH_4 [12], they both can abstract a hydride ion from CH_3GeH_3 at rates approaching the collision limit. Production of $CH_3GeH_2^+$ and CH_3Ge^+ from $C_3H_y^+$ ($y = 3$ or 4) is accompanied by formation of the inert $C_3H_5^+$ ion by attack of $C_3H_4^+$ on C_3H_4. Apart from their well-established reaction network with CH_3GeH_3 (Scheme 1), CH_3Ge^+ and, especially, $CH_3GeH_2^+$ are able to react with C_3H_4 generating $GeC_3H_3^+$ (70%) and $GeC_2H_3^+$ (30%), at the overall rate of 4.3×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. These last two species add further to C_3H_4, eventually yielding $GeC_5H_5^+$.

The mass spectra of the CH_3GeH_3(10.0%)/C_3H_4 (allene) mixture have been studied at 0.01, 0.05, 0.2, and 0.6 torr total pressures, and the results are reported in Table 6. The overall behaviour is very similar to that displayed by the previous systems containing ethene and propene, the main difference being the lower content of hydrogen of all the ionic species. Compared with the CH_3GeH_3/C_2H_4 mixture, a higher relative abundance of the ions containing new Ge–C bonds is observed, almost the same as in the CH_3GeH_3/C_3H_6 mixture. In this CH_3GeH_3/C_3H_4 system, the highest mass ion contains six carbon atoms, $GeC_6H_7^+$, and is of relatively high abundance, (2.8% of the total ion current transported by monogermane ions at 0.6 torr total pressure). Again, the abundances of the primary ions, $GeC_nH_m^+$ ($n = 0$ or 1) increase with decreasing total pressure, as observed in the previous systems. At the same time, the abundances of

Table 6

Relative abundances of significant ions in the mass spectra of CH_3GeH_3(10.0%)/allene mixture at various pressures [a,b]

Ions	Pressure (torr)			
	0.6	0.2	0.05	0.01
Ge^+	11.1	20.3	49.0	71.9
GeH^+	4.1	6.8	20.2	31.0
GeH_2^+	5.5	8.8	31.8	62.0
GeH_3^+	3.6	5.0	14.4	24.0
$GeCH^+$	1.0	1.1	7.2	14.0
$GeCH_2^+$	4.0	5.6	18.7	25.0
$GeCH_3^+$	100	100	100	77.0
$GeCH_4^+$	7.5	16.9	49.6	74.0
$GeCH_5^+$	23.3	31.6	74.9	100
GeC_2H^+	0.9	0.9	0.5	
$GeC_2H_2^+$	2.0	1.8	1.4	
$GeC_2H_3^+$	5.7	5.5	6.0	4.0
GeC_3H^+	0.8			
$GeC_3H_2^+$	1.4	1.5		
$GeC_3H_3^+$	11.8	11.3	11.5	5.5
$GeC_3H_4^+$	7.1	5.6	5.7	
$GeC_3H_5^+$	24.3	17.5	20.5	9.3
$GeC_4H_5^+$	1.1	1.0	0.6	
$GeC_4H_7^+$	10.2	5.2	1.6	
$GeC_5H_5^+$	3.0	2.1		
$GeC_5H_7^+$	0.8			
$GeC_6H_7^+$	2.8	1.0		

[a] Abundances refer to the ^{76}Ge isotope. [b] Ions containing two Ge atoms are not reported.

secondary ions formed in ion-molecule reactions between species deriving from CH_3GeH_3 and C_3H_4, decrease when $n = 2$, 3, or 4 or disappear when $n = 5$ or 6.

Ion-molecule reactions in methylgermane / propyne mixtures

The impact of a 20 eV electron beam on a CH_3GeH_3/propyne (1:2.5) mixture at 2.8×10^{-7} torr in the FTMS cell produces the ion families deriving from CH_3GeH_3 and C_3H_4, *i.e.* $C_3H_y^+$ ($y = 3$ or 4) (Scheme 6). Whereas $C_3H_4^+$ produces the unreactive $C_3H_5^+$ daughter by collision with C_3H_4, both $C_3H_y^+$ ($y = 3$ or 4) and GeH_x^+ ($x = 0$ or 2) react rapidly with CH_3GeH_3 to give $CH_3GeH_2^+$ (80%) and CH_3Ge^+ (20%). Apart from the well-established reaction sequence involving CH_3GeH_3 (Scheme 1), the $CH_3GeH_2^+$ and CH_3Ge^+ ions attack C_3H_4 forming $GeC_2H_7^+$ ($k = 2.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) and, at a lower rate, $GeC_3H_3^+$ ($k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Whereas $GeC_2H_7^+$ produces $GeC_3H_9^+$ by collision with CH_3GeH_3 and, perhaps C_3H_4, the $GeC_3H_3^+$ ion generates $GeC_5H_5^+$ by collision with C_3H_4. The $GeC_3H_9^+$ ion, in turn, collides with C_3H_4 eventually yielding $GeC_5H_{11}^+$.

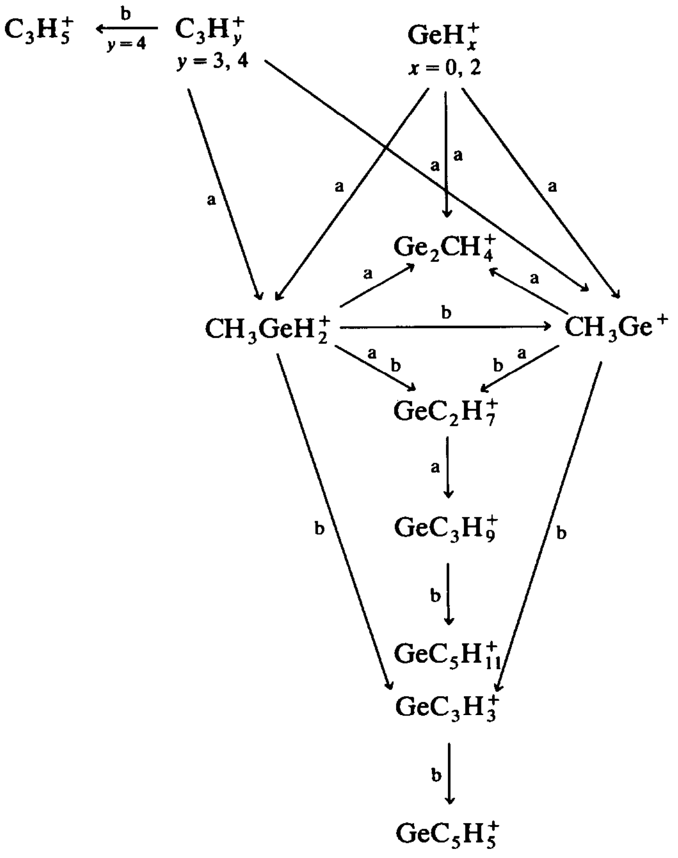
Conclusions

These results complete our previous studies on the chemistry of germanium hydrides, which are of interest from both fundamental and applicational points of view. CH_3GeH_3 is less reactive than GeH_4 in the gas phase. Under similar experimental conditions, oxygenated species are not observed in FTMS and are weaker in the presence of CH_3GeH_3 than in the presence of GeH_4 in CIMS. Analogous results are observed for the relative abundance of nitrogen-containing ions in methylgermane/ammonia compared with germane/ammonia systems. Moreover, germanium ions containing carbon atoms added by ion-molecule reactions with unsaturated hydrocarbons are in higher abundance in GeH_4 systems than in CH_3GeH_3. For example, $GeC_nH_m^+$ ions, ($n = 1$–4 for GeH_4; $n = 2$–5 for CH_3GeH_3) formed in ion-molecule reactions with ethene under very similar experimental conditions, are 43.8% and 17.4% of the total ion current transported by monogermanium ions with GeH_4 and CH_3GeH_3, respectively. Using allene as reagent molecule the percentage of $GeC_nH_m^+$ ($n = 1$–5 for GeH_4; $n = 2$–6 for CH_3GeH_3) is 73.2% for GeH_4 compared with 31.0% for CH_3GeH_3. This behaviour may be due, in part, to the lower electrophilicity of the $CH_3GeH_x^+$ species compared with GeH_x^+ ions, because of the presence of the methyl group.

In distinction, if the radiolytical formation of germanium carbides, Ge_xC_{1-x}, is considered, the total ion current transported by all ions containing a Ge–C bond is higher in methylgermane/hydrocarbon systems than in the germane systems. 80.2% of the total ion current is carried by monogermanium ions in the presence of ethene (43.8% for germane) and 89.5% in the presence of allene (73.2% for germane). To evaluate the best reagent (GeH_4 or CH_3GeH_3) for radiolytical deposition of amorphous germanium carbides, it becomes important to take into account that CH_3GeH_3 is synthesized from GeH_4.

Experimental

CH_3GeH_3 was prepared from GeH_4 according to the published method [17]. High-pressure mass-spectrometric experiments were carried out with a double



Scheme 6. Neutral reagent molecules: (a) CH_3GeH_3; (b) propyne.

focusing Kratos MS 80 spectrometer connected to a DS 55 data system. Typical operating conditions were as follows: primary ionization electron energy 60–70 eV, emission current 500 μA, ion repeller voltage zero, acceleration voltage 4 kV, resolution 1000 (10% valley) and scan rate 3 s/decade. CH_3GeH_3 and reagent gas were introduced into a vial (1.5 l) connected to a vacuum line. The vial, filled with the appropriate amounts of the two gases to a total pressure of about 800 torr, was then connected to a valve of the multiple reagent gas inlet system of the mass spectrometer. The mixture was introduced into the ion source at room temperature at variable pressures. The ion source pressures were evaluated from the relative concentrations of ions in CH_4 as a function of the pressure [18], and corrected using the relative sensitivities of the ion gauge for different gases [19]. However, small differences in pressure did not give significant variations in the ionic abundances.

The FTMS experiments were run on a Nicolet FTMS 1000 equipped with a 2.54 cm cubic trapping cell situated between the poles of a superconducting magnet operated at 2.0 T. Typical experimental conditions were as follows: nominal electron energy 15–20 eV, electron beam pulse 3–5 ms, emission current 400 nA, total pressure 1.5×10^{-7}–4.0×10^{-7} torr, resolution 1000 fwhh (full width at half height) at mass 100. Sample pressures (uncorrected) were measured with a Granville–Phyllips 280 Bayard-Alpert ion gauge. The inlet system and trapping cell were kept at room temperature. The ion sequences in the reaction cell were investigated by multiple resonance experiments, choosing suitable time sequences to maximize the abundance of a given precursor and appropriate frequency windows to remove all the undesired ions from the cell. Detection of daughter ions after suitable delay times gives direct information about the reaction sequence of the precursor and the rate of formation of its daughter species.

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