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Gas phase ion-molecule reactions of monogermane with carbon oxides and ethylene: formation of germanium–carbon bonds

Paola Benzi, Lorenza Operti, Gian Angelo Vaglio *, Paolo Volpe,

Dipartimento di Chimica Generale e Organica Applicata, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

Maurizio Speranza *

Dipartimento di Agrochimica e Agrobiologia, Università della Tuscia, Viterbo (Italy)

and Roberto Gabrielli

Servizio FTMS, Area della Ricerca CNR di Roma, 00016 Monterotondo Stazione, Roma (Italy)

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Abstract

The gas phase ion-molecule reactions of GeH_4 with some carbon-containing compounds (CO, CO_2, and C_2H_4) have been studied by high pressure mass spectrometry and Fourier transform mass spectrometry. The effects of the total pressure and of the relative concentrations of the reagent gases on the ion pattern are reported. In the presence of CO and CO_2, GeH_nCO^+ or $GeH_nCO_2{}^+$, GeH_nO^+, and GeH_nC^+ ions are observed, all of which show very low abundances. In contrast, condensation processes of GeH_4 with C_2H_4 give $GeC_nH_m{}^+$ ($n = 1$–4) species, in very high yield for $n = 1, 2$ but lower for $n = 3, 4$. For all three systems, reaction mechanisms are suggested and are discussed in relation to the preparation of amorphous materials containing germanium carbides for photovoltaic applications.

Introduction

The recent discovery that amorphous silicon can be doped has opened up important possibilities, both economic and technical, for photovoltaic cell industry. Amorphous silicon can be obtained in very high purity degree by simple procedures since it is prepared from gaseous reactants from which impurities are easily removed. Even though the amorphous silicon has a higher optical gap than the crystalline one (1.55 eV vs. 1.1 eV) [1], a great deal of the current research in photovoltaic technology is devoted to the amorphous form [2], because of its lower cost. Amorphous layers are generally prepared by deposition methods such as chemical vapour deposition (CVD) [1–5] and glow discharge (GD) [6], which give good results.

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In previous studies [7], it was observed that the solid product obtained from volatile hydrides (SiH_4, GeH_4) by radiolytic fragmentation shows a similar composition to that of the analogous materials prepared by GD. The main advantage of the radiolytic method compared with both CVD and GD is that the radical reaction mechanisms in the gas phase can be interpreted. Moreover, the ionic reactions involved in these processes can be studied by chemical ionization mass spectrometry (CIMS) and Fourier transform mass spectrometry (FTMS) in self-condensation experiments [8]. The understanding of these mechanisms can lead to an a priori design of the structural characteristics of the desired solid with obvious economic and technical advantages.

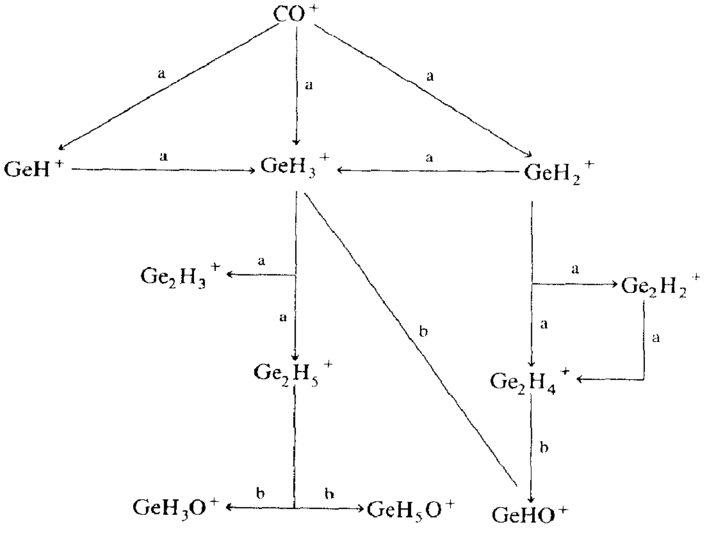
We focused our attention mainly on a study of the preparation and the properties of amorphous germanium, since amorphous silicon had already been well studied by many research groups [9] and also because use of germanium in the photovoltaic industry has very interesting possibilities. Germanium thin layers do not seem suitable to be used in solar cell productions because of their relatively low photoconductivity, but theoretical considerations indicate that germanium carbides (Ge_xC_{1-x}) have good photovoltaic properties since they show high conversion efficiency [10].

In this paper we report the results of a study of the gas phase ion-molecule reactions of GeH_4 in the presence of carbon-containing compounds as monitored by Fourier transform mass spectrometry (FTMS) and high pressure mass spectrometry (CIMS). The reactions of GeH_4 with different carbon-containing molecules, CO, CO_2 and C_2H_4, together with the reaction mechanisms, are described and discussed with the ultimate aim of identifying the experimental conditions leading to amorphous germanium carbides of the desired composition.

Results and discussion

Ion-molecule reactions in GeH_4/CO mixtures

A 20 eV electron beam on GeH_4/CO mixture (1/25) at the pressure of 5×10^{-7}



Scheme 1

torr in the FTMS cell produces essentially the CO^+ ion together with appreciable amounts of the primary germane ion family $GeH_n{}^+$ ($n = 0 - 3$). The main reactions, as revealed by double resonance experiments, are described in Scheme 1. Only ionic reagents/products are reported, the neutral reagent molecules being GeH_4 (a) or CO (b). Owing to the higher ionization potential of carbon monoxide, 14.013 ± 0.004 eV [11], compared with that of monogermane, 10.5 eV [12], collisions between CO^+ and GeH_4 lead to disappearance of CO^+ in less than 100 ms, with predominant formation of $GeH_3{}^+$ (ca. 65%), $GeH_2{}^+$ (ca. 20%), and GeH^+ (ca. 15%) ions (reaction 1).

$$CO^+ + GeH_4 \longrightarrow GeH_n{}^+ + \text{neutrals} \qquad (n = 1\text{–}3) \tag{1}$$

The $GeH_3{}^+$ ion, which shows the highest abundance, is also formed by reactions of neutral GeH_4 with $GeH_2{}^+$, by hydride abstraction, and with GeH^+ within the same reaction time. Moreover, reaction 1 is the most favoured when $n = 3$, as it is exothermic by more than 100 kcal/mol (HCO, neutral fragment) compared with ca. 90 kcal/mol and 50 kcal/mol when $n = 1$ (HCO and H_2, neutral fragments), and $n = 2$ (H_2CO, neutral fragment), respectively.

The $GeH_3{}^+$ species react with GeH_4 in accord with the normal ion pattern described previously [8], yielding essentially $Ge_2H_5{}^+$ and $Ge_2H_3{}^+$ (> 82%), while $GeH_2{}^+$ gives minor amounts of $Ge_2H_4{}^+$ and $Ge_2H_2{}^+$ (< 18%). These ions lose progressively their hydrogens by collisions with CO, leading eventually to $Ge_2{}^+$. Alternatively, $Ge_2H_5{}^+$ reacts with a CO molecule to yield GeH_5O^+, together with minor quantities of GeH_3O^+, in 200–500 ms reaction time. In addition, the $GeHO^+$ ion is observed, which is formed by comparatively slow condensation reactions of $Ge_2H_4{}^+$ or $GeH_3{}^+$ and CO. It should be pointed out that formation of the GeH_nO^+ ($n = 1, 3, 5$) ions, which may be regarded as the germanium-containing counterpart of protonated carbon monoxide ($n = 1$), formaldehyde ($n = 3$), and methanol ($n = 5$), respectively, proceeds via complex mechanisms which necessarily involve formation of a Ge–O covalent bond between the germane ions and CO and extensive rearrangement of the hydrogen atoms in the resulting adducts.

It is noteworthy that $Ge_2H_5{}^+$ reacts with neutral CO to give only GeH_nO^+ ions when n is an odd number ($n = 3, 5$), and neither GeH_4O^+ nor GeH_2O^+ species are ever observed in FTMS experiments. The lack of these latter ions is likely to be due to the energetics of their formation reactions, but insufficient thermochemical data are available for calculating the enthalpies of such reactions. However, reaction 2, which has been observed, and reaction 3, which does not occur, in which GeH_3O^+ and GeH_4O^+ are formed, respectively, differ by only one neutral fragment.

$$Ge_2H_5{}^+ + CO \longrightarrow GeH_3O^+ + GeC + H_2 \tag{2}$$

$$Ge_2H_5{}^+ + CO \longrightarrow GeH_4O^+ + GeC + H \tag{3}$$

A hydrogen molecule is a neutral fragment in reaction 2, while a hydrogen atom would be lost in reaction 3, and this increases the reaction enthalpy by more than 50 kcal/mol. Thus, the absence of GeH_nO^+ ($n = 2, 4$) ions does not imply that they have an higher heat of formation than the corresponding species with $n = 3, 5$, but could be due only to the different neutral fragments lost in their formation reactions.

Table 1

Relative abundances of significant ions in the mass spectra of GeH_4(9.83%)/CO mixtures at various pressures [a]

Ions	Pressures (torr)		
	0.3	0.1	0.03
$Ge_2H_5^+$	0.1	–	–
$Ge_2H_4^+$	0.3	0.2	0.1
$Ge_2H_3^+$	0.2	0.1	0.05
$Ge_2H_2^+$	0.4	0.2	0.1
Ge_2H^+	0.02	0.01	–
GeH_3CO^+	0.1	–	–
$GeHCO^+$	0.2	0.2	0.2
$GeCO^+$	0.6	0.8	0.6
GeH_5O^+	0.2	0.1	–
GeH_3O^+	0.3	0.4	0.2
GeH_2O^+	0.7	0.6	0.6
$GeHO^+$	0.1	0.1	0.2
GeH_3C^+	0.4	0.2	–
GeH_2C^+	0.5	0.4	0.2
$GeHC^+$	0.3	0.2	0.2
GeH_3^+	100	100	100
GeH_2^+	25	42	64
GeH^+	12	17	63
Ge^+	14	22	88

[a] Abundances refer to ^{76}Ge isotope.

In high pressure mass spectrometry the same primary steps occur as in FTMS experiments: formation of CO^+ and GeH_n^+ ($n = 1$–3) ions and charge exchange at each collision between CO^+ and GeH_4 to give secondary GeH_n^+ ($n = 0$–3) fragments. The relative abundances of the ions in the mass spectra of a GeH_4(9.83%)/CO mixture are reported in Table 1. The GeH_n^+ ($n = 0$–3) ions are the most abundant species and are involved in self-condensation reactions to give the $Ge_2H_n^+$ ($n = 1$–5) dimers. Germanium-containing ions take part in ion-molecule reactions with CO and form three different ionic families: (i) GeH_nCO^+ ($n = 0$–3) ions in which the entire molecule of the reagent gas is retained; (ii) GeH_nO^+ ($n = 1$–3, 5) and (iii) GeH_nC^+ ($n = 0$–3) ions in which one of the atoms of the reagent gas is lost in the neutral fragment. From the ion abundances it can be seen that the gas phase reactivity of GeH_n^+ ($n = 0$–3) and $Ge_2H_n^+$ ($n = 1$–5) with carbon monoxide is very low, being 97.1 and 99.2% of the total current transported by GeH_n^+ ($n = 0$–3) in the GeH_4(9.83%)/CO mixture at 0.3 and 0.03 torr, respectively. As the total pressure is decreased the relative abundances of oxygen- and carbon-containing ions also gradually decrease.

In the GeH_4(4.0%)/CO mixture (Table 2) the same ions are observed. The $Ge_2H_n^+$ ($n = 1$–5) dimers are weaker, whilst the GeH_nCO^+, GeH_nO^+, and GeH_nC^+ ions become gradually stronger. These changes are due to the different relative concentrations of the reagents. A lower number of collisions between germanium-containing ionic and neutral species and a higher number of collisions with CO occur when the concentration of monogermane is decreased with respect to that of carbon monoxide. Under drastic experimental conditions, such as total pressure > 1

Table 2

Relative abundances of significant ions in the mass spectra of GeH_4(4.0%)/CO mixtures at various pressures [a]

Ions	Pressures (torr)			
	0.3	0.1	0.03	0.01
$Ge_2H_5^+$	0.02	0.02	–	–
$Ge_2H_4^+$	0.4	0.3	0.1	0.04
$Ge_2H_3^+$	0.1	0.1	0.1	0.1
$Ge_2H_2^+$	0.3	0.2	–	–
Ge_2H^+	0.1	–	–	–
GeH_3CO^+	0.2	0.04	–	–
GeH_2CO^+	0.2	0.1	0.2	–
$GeHCO^+$	0.5	0.5	0.3	0.1
$GeCO^+$	1.3	1.4	1.2	0.8
GeH_5O^+	0.1	0.02	–	–
GeH_3O^+	0.4	0.6	0.4	0.4
GeH_2O^+	0.6	1.1	0.9	0.9
$GeHO^+$	0.05	0.1	–	–
GeH_3C^+	0.2	0.1	0.2	–
GeH_2C^+	0.9	0.5	0.3	0.2
$GeHC^+$	0.6	0.4	0.2	–
GeC^+	0.05	0.03	0.1	–
GeH_3^+	100	100	100	100
GeH_2^+	39	53	69	93
GeH^+	18	20	23	29
Ge^+	20	26	33	44

[a] Abundances refer to ^{76}Ge isotope.

torr and with GeH_4/CO ratio of about 1/10, the relative abundance of the GeH_nC^+ ($n = 0$–3) ionic family strongly increases, and about 5% of the total ion current is transported by these carbon-containing ions.

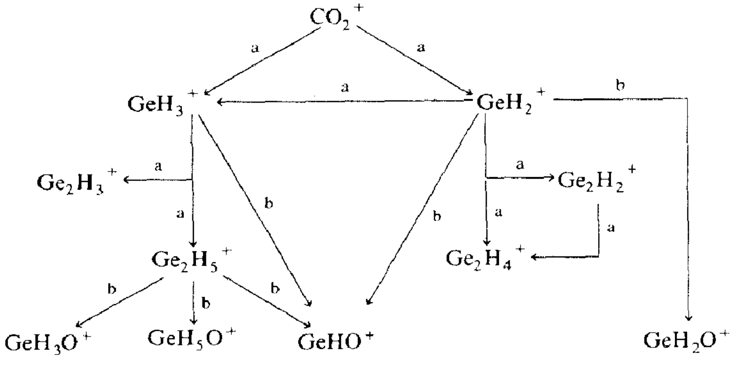
The overall behaviour of the GeH_4/CO mixtures is similar to that of the GeH_4/O_2 mixtures under similar conditions [8]. In the presence of molecular oxygen, formation is observed of $GeH_nO_2^+$ and GeH_nO^+ ions containing the entire molecule of the reagent gas and one of its atoms, respectively. The corresponding GeH_nCO^+, GeH_nO^+, and GeH_nC^+ ions originate in ion-molecule reactions with carbon monoxide. The main difference between the two systems consists in the much lower abundance of the oxygen- and carbon-containing species of the GeH_4/CO mixtures.

Of all these last ionic families only the GeH_nO^+ species are detected by FTMS, similarly to what has been reported for the GeH_4/O_2 mixtures [8]. As has been already pointed out, results from FTMS and CIMS experiments can be compared as far as bimolecular reactions are concerned [13]. Thus, the total number of collisions is about the same in the FTMS operating at 10^{-7} torr and 1 s delay time and in the CIMS experiments at 10^{-2} torr and 10^{-5} delay time. In contrast, thermalization of ionic species which have an excess of internal energy takes place through two different processes depending on the collision frequency, and so it is likely that ionic species observed in the low pressure system (FTMS) after a delay of ca. 0.4 s are formed by unimolecular decomposition of excited ions, which in a high pressure instrument (CIMS) are stabilized by unreactive collisions with the neutrals present in the ion chamber.

The data obtained in the high pressure experiments seem to be of interest mainly in respect of the presence of the GeH_nC^+ ($n = 1$–3) ions. By analogy with the hypothesis advanced previously [8] for the formation of $GeHO^+$ from $Ge_2H_2^+$ with O_2, it can be suggested that the GeH_nC^+ species are formed by a multistep process in which a cyclic four-membered transition state involving carbon, oxygen, and two germanium atoms is involved, and, indeed, GeH_nCO^+ ($n = 0$, 1, 3) ions are observed. The successive cleavage of the carbon–oxygen and germanium–germanium bonds, with distribution of the charge between the two fragments, each containing an oxygen or a carbon atom, leads to GeH_nO^+ ($n = 1$–3) and GeH_nC^+ ($n = 1$–3) in parallel pathways.

Ion-molecule reactions in GeH_4/CO_2 mixtures

An ion pattern similar to that operating in GeH_4/CO mixtures is generated by 20 eV electron impact on GeH_4/CO_2 (1/25) mixture at 5×10^{-7} torr total pressure under FTMS conditions. The main reactions, as monitored by double resonance experiments, are depicted in Scheme 2. Only ionic reagent/products are reported, the neutral reagent molecules being GeH_4 (a) or CO_2 (b). In addition to very minor abundances of the primary germane ions, GeH_n^+ ($n = 0$–3), electron bombardment produces essentially the CO_2^+ (IP(CO_2) 13.769 ± 0.03 eV) [11] ions, which rapidly react with GeH_4 to give predominantly GeH_3^+ (ca. 75%) and GeH_2^+ (ca. 25%), GeH_3^+ being formed also by GeH_2^+ as previously described. The primary and secondary GeH_n^+ ($n = 0$–3) fragments add to GeH_4 yielding the normal digermane ion pattern. As in the case of CO, progressive loss of hydrogen from $Ge_2H_n^+$ ($n = 2$–5) by collisions with CO_2 is observed. The correspondence between the GeH_4/CO and the GeH_4/CO_2 ion-molecule reaction networks also extends to the mechanism of formation of the GeH_nO^+ ($n = 1, 3, 5$) ion family. $Ge_2H_5^+$ is found to react with CO_2 in about 100 ms to give GeH_5O^+ (ca. 35%), GeH_3O^+ (ca. 15%), and $GeHO^+$ (ca. 50%). Further contribution to the $GeHO^+$ ion abundance arises from comparatively slow condensation of GeH_n^+ ($n = 2$, 3) ions with a CO_2 molecule. Moreover, attack of GeH_2^+ on CO_2 yields minor amounts of GeH_2O^+. By analogy with the conclusion reached for the GeH_4/CO mixtures, addition of $Ge_2H_5^+$ to CO_2 to yield GeH_nO^+ ($n = 1, 3, 5$) follows a complex reaction pathway



Scheme 2

involving formation of a Ge–O bond and extensive reshuffling of the hydrogen atoms in the addition complex.

Under chemical ionization conditions also the GeH_4/CO_2 mixtures show a very similar behaviour to that displayed by the GeH_4/CO system. Most of the charge is transported by GeH_n^+ ($n = 0$–3) ions, which are mainly originated by charge-exchange processes between CO_2^+ and GeH_4. In addition to the dimer species, the three ionic families of formula $GeH_nCO_2^+$ ($n = 0$, 1), GeH_nO^+ ($n = 0$–3, 5), and GeH_nC^+ ($n = 1$–3) are observed, as shown in Tables 3 and 4 for the $GeH_4(10.5\%)/CO_2$ and the $GeH_4(1.78\%)/CO_2$ mixtures, respectively. As it does towards CO, GeH_4 displays a very low reactivity towards CO_2 and, in the $GeH_4(10.5\%)/CO_2$ mixture, the GeH_nC^+ ions are barely detectable. Moreover, the changes of the ionic abundances with the variation of the total pressure follow the same trend with both CO and CO_2, and depend on the probability of collisions between germanium-containing ions and the reagent gas molecules. Once again, differences in relative abundances of ionic species under FTMS conditions compared with those under CIMS conditions can be ascribed to the more extensive decomposition processes which occur in the FTMS cell, and which lead, for example, to more abundant $GeHO^+$ ions in FTMS experiments than in the high pressure mass spectra.

Ion-molecule reactions in GeH_4/C_2H_4 mixtures

Both $C_2H_4^+$ and the germane ion family are observed after 12 eV electron bombardment of a GeH_4/C_2H_4 mixture (1/10) at a pressure of 5×10^{-7} torr in the FTMS cell. The main reactions, as monitored by double resonance experiments, are shown in Scheme 3. Only ionic reagents/products are reported, the neutral reagent molecules being GeH_4 (a) or C_2H_4 (b). Reactive collisions between $C_2H_4^+$ and the neutrals present lead to its rapid disappearance with formation of $C_3H_5^+$

Table 3

Relative abundances of significant ions in the mass spectra of $GeH_4(10.5\%)/CO_2$ mixtures at various pressures [a]

Ions	Pressures (torr)			
	0.4	0.1	0.03	0.01
$Ge_2H_5^+$	0.1	–	–	–
$Ge_2H_4^+$	0.2	0.1	0.1	0.01
$Ge_2H_3^+$	0.1	0.05	0.02	0.01
$Ge_2H_2^+$	0.2	0.1	0.1	0.1
Ge_2H^+	0.01	–	–	–
$GeCO_2^+$	0.1	0.1	0.1	0.1
GeH_5O^+	0.2	–	0.1	0.3
GeH_3O^+	1.6	1.1	0.9	0.7
GeH_2O^+	0.9	0.8	0.7	0.5
$GeHO^+$	1.2	0.9	0.6	0.5
GeH_3C^+	–	0.1	0.1	–
GeH_2C^+	0.1	0.1	–	–
GeH_3^+	100	100	100	100
GeH_2^+	59	74	88	95
GeH^+	12	17	22	22
Ge^+	21	28	36	36

[a] Abundances refer to ^{76}Ge isotope.

Table 4

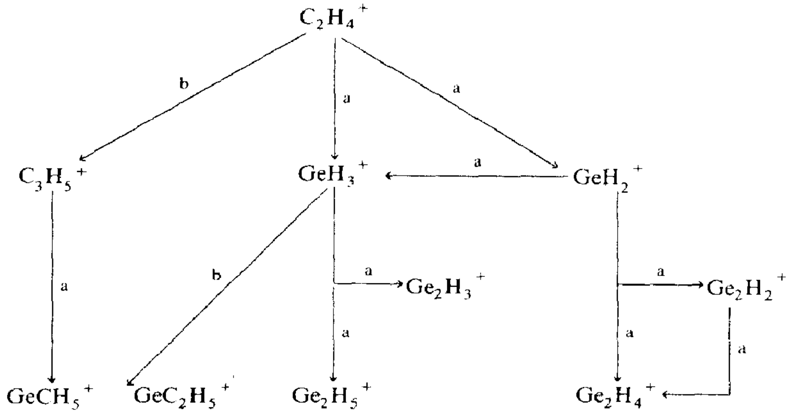
Relative abundances of significant ions in the mass spectra of GeH_4(1.78%)/CO_2 mixtures at various pressures [a]

Ions	Pressures (torr)		
	0.4	0.1	0.03
$Ge_2H_5^+$	–	0.2	–
$Ge_2H_4^+$	0.4	0.2	0.1
$Ge_2H_3^+$	0.1	0.1	–
$Ge_2H_2^+$	0.3	0.3	0.2
$GeHCO_2^+$	0.2	0.3	0.3
$GeCO_2^+$	1.1	1.4	1.1
GeH_5O^+	0.6	0.5	0.3
GeH_3O^+	0.5	1.2	1.0
GeH_2O^+	1.4	0.4	–
$GeHO^+$	–	0.1	–
GeO^+	1.0	1.5	1.3
GeH_3C^+	1.4	0.4	–
GeH_2C^+	0.2	–	0.3
$GeHC^+$	0.2	0.4	0.6
GeH_3^+	100	100	100
GeH_2^+	48	70	88
GeH^+	8	12	21
Ge^+	15	18	31

[a] Abundances refer to ^{76}Ge isotope.

from C_2H_4 and of GeH_3^+ (with very minor yield of GeH_2^+) from GeH_4. The GeH_n^+ ($n = 0$–3) fragments react with GeH_4 to produce the digermane daughter species, $Ge_2H_n^+$ ($n = 2$–5). The neutral C_2H_4 effectively competes with GeH_4 for GeH_3^+, yielding $GeC_2H_5^+$. Similarly effective is the attack of $C_3H_5^+$ on GeH_4 to give $GeCH_5^+$. Under the conditions prevailing in the FTMS experiments, the $Ge_2H_n^+$ ($n = 2$–5) ion family is found not to react with C_2H_4 even at relatively long reaction times (i.e. 400 ms). It is noteworthy that in this system germanium-containing analogues of the well known carbocations $C_2H_5^+$ (i.e. $GeCH_5^+$) and $C_3H_5^+$ (i.e. $GeC_2H_5^+$) are observed.

Under high pressure conditions, abundant ions containing germanium–carbon bonds are observed in the mass spectra of the GeH_4(10.1%)/C_2H_4 mixture, and the



Scheme 3

Table 5

Relative abundances of significant ions in the mass spectra of GeH_4(10.1%)/C_2H_4 mixtures at various pressures [a]

Ions	Pressures (torr)			
	0.5	0.2	0.05	0.01
$GeC_4H_{11}^+$	4.8	2.0	–	–
$GeC_4H_{10}^+$	1.0	0.4	–	–
$GeC_4H_9^+$	1.0	0.3	–	–
$GeC_4H_8^+$	0.3	0.3	–	–
$GeC_4H_7^+$	0.3	0.5	–	–
$GeC_3H_9^+$	9.9	6.2	0.5	–
$GeC_3H_8^+$	2.1	1.0	–	–
$GeC_3H_5^+$	0.3	0.2	–	–
$GeC_2H_7^+$	16	11	3.2	0.7
$GeC_2H_6^+$	3.0	2.3	–	–
$GeC_2H_5^+$	55	47	15	8.0
$GeC_2H_4^+$	10	8.4	5.3	3.3
$GeC_2H_3^+$	3.2	3.1	2.4	1.5
$GeCH_5^+$	22	22	12	5.0
$GeCH_4^+$	3.2	2.8	3.0	2.4
$GeCH_3^+$	5.2	3.2	2.1	1.1
$GeCH_2^+$	3.6	0.8	–	0.2
GeH_3^+	100	100	100	100
GeH_2^+	11	14	31	59
GeH^+	10	16	32	23
Ge^+	60	65	67	65

[a] Abundances refer to ^{76}Ge isotope.

Table 6

Relative abundances of significant ions in the mass spectra of GeH_4(1.0%)/C_2H_4 mixtures at various pressures [a]

Ions	Pressures (torr)			
	0.5	0.2	0.05	0.01
$GeC_4H_{11}^+$	0.7	0.4	–	–
$GeC_4H_{10}^+$	0.1	–	–	–
$GeC_4H_9^+$	0.3	0.3	–	–
$GeC_4H_8^+$	0.1	–	–	–
$GeC_3H_9^+$	2.0	1.4	0.3	–
$GeC_3H_8^+$	0.5	0.2	–	–
$GeC_3H_5^+$	0.1	–	–	–
$GeC_2H_7^+$	2.6	2.1	1.3	–
$GeC_2H_6^+$	0.8	0.6	–	–
$GeC_2H_5^+$	10	11	12	6.5
$GeC_2H_4^+$	2.5	2.1	2.0	–
$GeC_2H_3^+$	1.1	0.8	0.9	1.5
$GeCH_5^+$	4.3	5.0	2.5	1.0
$GeCH_4^+$	1.7	1.6	1.4	0.7
$GeCH_3^+$	1.7	1.4	1.4	1.5
$GeCH_2^+$	2.1	1.3	0.7	0.9
GeH_3^+	100	100	100	100
GeH_2^+	7.8	9.5	22	48
GeH^+	9.0	9.8	14	23
Ge^+	16	20	46	84

[a] Abundances refer to ^{76}Ge isotope.

monogermanium ones are reported in Table 5. The highest mass ions are $GeC_4H_n{}^+$ ($n = 7$–11), but species containing three, two, or one carbon atoms are also formed at 0.5, 0.2 and 0.05 torr total pressure. The base peak is again $GeH_3{}^+$ in this system at all pressures investigated, but at 0.5 torr only 56% of the total charge is carried by $GeH_n{}^+$ ($n = 0$–3), while 27.2 and 10.7% of the total charge is carried by $GeC_2H_n{}^+$ ($n = 3$–7) and by $GeCH_n{}^+$ ($n = 2$–5), respectively.

When ethylene alone is introduced into the ion source at about 0.5 torr, $C_2H_4{}^+$ is the base peak and abundant ions such as $C_2H_5{}^+$, $C_3H_3{}^+$, $C_3H_5{}^+$ (second most abundant ion), $C_4H_5{}^+$, $C_4H_7{}^+$, $C_5H_7{}^+$, and $C_5H_9{}^+$ are formed by ion-molecule reactions. Moreover, a decreasing total pressure corresponds to a gradual disappearance of the highest mass ions, which parallels the disappearance of the hydrocarbon ions containing five and four carbon atoms, and a decrease of the abundances of the lightest ionic species, Therefore, it is likely that formation of most of the ions observed in the mass spectra of GeH_4/C_2H_4 mixtures at high pressure occurs by reactions between neutral GeH_4 and carbon-containing ions originated from C_2H_4. This formation process is also in agreement with data of Table 6, where the abundances of monogermanium ions observed in the $GeH_4(1.0\%)/C_2H_4$ mixture are reported. There is a strong decrease in the abundances of the $GeC_nH_m{}^+$ ($n = 1$–4) ionic species when the concentration of GeH_4 is reduced. The number of collisions between neutral GeH_4 and carbon-containing ions from C_2H_4, whose abundances are about the same at the same pressure in the two different mixtures, is lower in the $GeH_4(1.0\%)/C_2H_4$ mixture with respect to the $GeH_4(10.1\%)/C_2H_4$ one, causing a reduced abundance of the reaction ionic products.

It is noteworthy that in both mixtures and at the highest pressures used, $Ge_2H_n{}^+$ ($n = 2$–5), $Ge_2C_2H_5{}^+$, and $Ge_2C_4H_8{}^+$ ions are also observed, though they are generally much weaker than the corresponding monogermanium species.

Conclusions

From these results interesting insights on the germanium chemistry can be obtained in respect of fundamental chemistry and the possibility of applications. The formation in the GeH_4/CO and GeH_4/CO_2 systems of ions such as GeH_nO^+, previously observed in the presence of molecular oxygen, and GeH_nC^+ is indicative of new reactions of GeH_4. Furthermore, the production of germanium-containing analogues of $C_2H_5{}^+$ and $C_3H_5{}^+$, i.e. $GeCH_5{}^+$ and $GeC_2H_5{}^+$, respectively, in the GeH_4/C_2H_4 systems provides valuable information on the reactivity of germanium-hydrogen compounds in relation to that of hydrocarbons. The study of the structures and stability of all these ionics species will be further explored.

Carbon monoxide and carbon dioxide show a low reactivity towards monogermane. Moreover, reactions of GeH_4 with CO and CO_2 under any experimental conditions give oxygen-containing ionic species, whose presence is undesirable in amorphous solids to be used in photovoltaic devices. In contrast, the high abundances of the $GeC_nH_m{}^+$ species (i.e. 44% of the total ion current in the $GeH_4(10.1\%)/C_2H_4$ mixture at 0.5 torr total pressure), observed in the mixtures of GeH_4 with C_2H_4, suggest that ethylene is a good reagent for the preparation of germanium carbides by decomposition of volatile hydrides. The photovoltaic properties of these carbides depend on the value of x in Ge_xC_{1-x}, and the results presented in this paper show that it can be adjusted by changing the total pressure, the relative concentrations of the reagent gases, and the nature of the carbon-containing substrate.

Experimental

GeH_4 was prepared by reduction of GeO_2 with KBH_4 and purified as described previously [7c].

Chemical ionization experiments were carried out with a double focussing Kratos MS80 mass spectrometer connected to a DS55 data system. Typical operating conditions were as follows: primary ionization electron energy 60 eV, emission current 500 μA, acceleration voltage 4 kV, ion repeller voltage zero, resolution 1000 (10% valley definition), scan rate 3 s/dec. The reaction mixtures containing various 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 appropriate amounts of the two gases to a total pressure of about 850 torr and connected to a valve of the multiple reagent gas inlet system of the mass spectrometer. The gaseous mixture was then introduced into the ion source, which was maintained at room temperature. Ion source pressures were evaluated from the relative concentrations of ions in CH_4 as a function of the pressure [14], and corrected by use of the relative sensitivities of the ion gauge for different gases [15]. However, small differences in pressure do not cause drastic variations in the nature and abundance of ions.

All FTMS experiments were performed with 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. Typical operating conditions were as follows: nominal electron beam energy 12–20 ev, emission current 400 nA, electron beam pulse 3–5 ms, total pressure 5×10^{-7} torr, resolution 1000 fwhh (full width half height) at mass 100. Sample pressures (uncorrected) were measured with a Granville–Phyllips 280 Bayard–Alpert Ion Gauge. 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 volt. The ionic sequences taking place in the reaction cell were examined by double resonance experiments by choosing suitable time sequences to maximize the abundance of a given precursor and suitable frequency windows to remove all the undesired ions from the cell. Detection of the daughter ion pattern after an appropriate delay time provides direct information about the reaction sequence concerning the precursor under investigation.

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