International Journal of Mass Spectrometry 179/180 (1998) 277–283

Gas phase ion chemistry in methylgermane and methylgermane/silane

M. Castiglioni, L. Operti, R. Rabezzana, G.A. Vaglio*, P. Volpe

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

Received 4 May 1998; accepted 13 July 1998

Abstract

The rate constants of the gas phase ion/molecule reactions in CH_3GeH_3 alone and in CH_3GeH_3/SiH_4 mixture have been determined by ion trap mass spectrometry and compared with those obtained in GeH_4 and CH_3SiH_3 alone, and in GeH_4/SiH_4 mixture. Collision rate constants have been calculated and efficiencies determined. Chain propagation of ions containing Ge, Si, and, possibly C, important in the radiolytical preparation of materials of interest in photovoltaic technology, occurs through ions such as $GeSiCH_n^+$ ($n = 4, 6$) from $Si_2H_n^+$ ($n = 2, 4$) reacting with methylgermane and $GeSi_2CH_n^+$ ($n = 6, 7$) from $Si_3H_n^+$ ($n = 4, 5$) reacting with methylgermane at rather high rates. The experimental conditions to increase yield of formation of ions with silicon and germanium are discussed. (Int J Mass Spectrom 179/180 (1998) 277–283) © 1998 Elsevier Science B.V.

Keywords: Methylgermane; Silane; Ion/molecule reactions; Kinetics; Ion trap mass spectrometry

---

1. Introduction

In the last few years, hydrogenated amorphous compounds of elements of the group 14 of the periodic table have been extensively studied for their possible applications in electronic and optoelectronic devices [1]. Ternary amorphous semiconductors, i.e. *a*-CGeSi:H, have been considered recently [2] in order to obtain wide range light collectors.

These materials are generally prepared by laser assisted, x-ray assisted, or other way assisted chemical vapour deposition (CVD) techniques, starting from suitable gaseous mixtures of volatile hydrides containing carbon, germanium, and silicon. The amount of each element in the final solid depends on the molar composition of the gaseous system, but not in a direct or predictable way. Therefore, it is very important to find the relationship between the partial pressure of the gaseous reactants and the abundance of the corresponding elements in the solid material. In previous studies, the mechanisms of ionic reactions involved in radiolytically assisted CVD of several mixtures have been determined by mass spectrometric methods [3–7].

In this article we continue the investigation of systems based on methylgermane, in which a Ge–C bond already exists, by ion trap mass spectrometry. In fact, it has been observed that the radiolytical production of a-CGe:H materials has a higher yield when the reactant is CH_3GeH_3, rather than a GeH_4/CH_4 mixture [8]. In particular, the rate constants of the first steps of

---

* Corresponding author.

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

1387-3806/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved
PII S1387-3806(98)14101-5

the chain propagation in CH_3GeH_3, and CH_3GeH_3/SiH_4 systems are reported. The rate constants for reactions of some secondary and tertiary ions of silane with GeH_4 have also been calculated and are reported in this paper.

The reaction pathways of methylgermane and of methylgermane/silane mixtures have been already published, as determined by ion trap mass spectrometry [3,4]. Moreover, ion/molecule self-condensation reactions of CH_3GeH_3 have been investigated by Fourier transform mass spectrometry and conventional mass spectrometry under chemical ionization conditions [9].

Finally, comparison of the results of the present study on CH_3GeH_3 with those concerning GeH_4 in corresponding systems (GeH_4 and GeH_4/SiH_4) [5] can give information on the effect of a methyl group on the ionic reactivity of germanium hydrides. In the same way, a comparison can be drawn on the gas phase behaviour of CH_3GeH_3 with respect to CH_3SiH_3 [3,10].

2. Experimental

Methylgermane was prepared as described in the literature [11]. Silane was commercially supplied at a high purity degree. Prior to use, these gases were introduced into different flasks which contained anhydrous sodium sulfate as drier. The flasks were then connected to the gas inlet system of the instrument. Helium was commercially obtained with extra high purity and used without further purification.

All experiments were performed on a Finnigan ITMS ion trap mass spectrometer, maintained at 333 K to obtain results comparable with previously published data on similar systems. The gas inlet system was modified in order to permit the introduction of three gases simoultaneously through different lines. The reagents were admitted into the trap at pressures in the range $(1–5) \times 10^{-7}$ Torr (1 Torr = 133 Pa) and helium buffer gas at about 5×10^{-4} Torr. A Bayard Alpert ion gauge was used to measure the pressures. As for determination of rate constants it is necessary to perform accurate pressure measurements, the ion gauge was calibrated [5] and the pressure reading was further corrected on the basis of the relative sensitivity of the ion gauge response (CH_3GeH_3, 2,67; SiH_4, 1,70; GeH_4, 1,94; He, 0,20) to different gases [12,13].

The scan modes for the determination of reaction pathways and rate constants, as well as the procedures for absolute rate constants calculations, have been previously described in detail [5,7,14]. The experiments consist of single or multiple isolation steps of selected ion species, which are then reacted with the neutral molecules present in the trap for variable reaction times, up to a maximum of 80 ms. Isolations have been achieved both by the resonance ejection method, which causes low excitation of the selected ions, and by the apex method which involves a superimposition of dc and rf voltages. Species containing the ^{28}Si isotope have been isolated from silane; the Ge^+, GeH^+, CH_3Ge^+, and CH_3GeH^+ selected ions contained the ^{70}Ge isotope, while GeH_2^+, GeH_3^+, and $CH_3GeCH_2^+$ the ^{76}Ge one.

Ions were formed by electron ionization with electrons at an average energy of 35 eV and with ionization times ranging from 1 to 20 ms. Ions were detected in the 14–300 mass range.

All ion/molecule reactions observed in these systems follow a pseudo-first-order kinetic law. Thermalization of reactant ions by unreactive collisions with helium buffer gas is consistent with the single exponential decay of their abundances. The values of rate constants reported are the average of the data obtained from at least three different experiments, and uncertainities of measurements fall within ±20%. Such uncertainities are calculated as the ratio between the difference of the average value minus one limit value and the average value and, therefore, are the consequence of combinations of errors.

3. Results and discussion

3.1. Self-condensation of CH_3GeH_3

The impact of a 35 eV electron beam on CH_3GeH_3 gives two families of primary ions, GeH_n^+ ($n = 0–3$) and $CH_3GeH_n^+$ ($n = 0–2$), which react with their

Table 1
Rate constants for reactions of GeH_n^+ ($n = 0$–3) and $CH_3GeH_n^+$ ($n = 1, 2$) ions in CH_3GeH_3[a]

Reaction	k_{exp}	Σk_{exp}	k_{ADO}[b]	Efficiency[c]
$Ge^+ + CH_3GeH_3 \rightarrow CH_3Ge^+ + GeH_3$	3.5			
$\rightarrow Ge_2CH_4^+ + H_2$	6.9	10.4	10.88	0.96
$GeH^+ + CH_3GeH_3 \rightarrow CH_3Ge^+ + GeH_4$	0.98			
$\rightarrow Ge_2CH_5^+ + H_2$	10.0	11.0	10.84	1.01
$GeH_2^+ + CH_3GeH_3 \rightarrow CH_3GeH^+ + GeH_4$	2.7			
$\rightarrow CH_3GeH_2^+ + GeH_3$	7.3			
$\rightarrow Ge_2CH_6^+ + H_2$	0.96	11.0	10.80	1.02
$GeH_3^+ + CH_3GeH_3 \rightarrow CH_3GeH_2^+ + GeH_4$	12	12	10.77	1.11
$CH_3GeH^+ + CH_3GeH_3 \rightarrow GeC_2H_7^+ + GeH_3$	2.2			
$\rightarrow Ge_2CH_6^+ + CH_4$	1.0			
$\rightarrow Ge_2C_2H_8^+ + H_2$	2.5	5.7	10.33	0.55
$CH_3GeH_2^+ + CH_3GeH_3 \rightarrow$ isotopic scrambling	4.1	4.1	10.29	0.40

[a] Rate constants are expressed as 10^{-10} cm^3 $molecule^{-1}$ s^{-1}; experiments were run at 333 K; uncertainty is within 20%.

[b] Rate constants have been calculated according to the ADO theory [15] taking the dipole moment of methylgermane ($\mu_D = 0.644 \times 10^{-18}$ esu cm) from [16] and calculating its polarizability ($\alpha = 6.735 \times 10^{-24}$ cm^3) as in [17] starting from polarizability of GeH_4 [18].

[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{ADO}$.

neutral precursor in different condensation processes. Table 1 reports the rate constants for reactions of GeH_n^+ ($n = 0$–3) and $CH_3GeH_n^+$ ($n = 1, 2$) ions with methylgermane, together with the collisional rate constants calculated according to the ADO theory [15]. The CH_3Ge^+ ion species is not shown as it does not react further under the experimental conditions examined.

The most common condensation pathways take place with elimination of a GeH_3 group, a GeH_4 molecule, or a hydrogen molecule. A methane molecule is also lost when CH_3GeH^+ reacts with CH_3GeH_3. All the GeH_n^+ ($n = 0$–3) ions react quite quickly, the overall rate constants being in the 10^{-9} cm^3 $molecule^{-1}$ s^{-1} order of magnitude and with efficiences of reaction close to unit. However, among these ions, Ge^+ and GeH^+ show a higher rate in the condensation process which takes place with loss of a hydrogen molecule. To the contrary, for the GeH_2^+ and GeH_3^+ ion species the fastest reaction is hydride abstraction from methylgermane leading to the formation of the $CH_3GeH_2^+$ ion, which gives only isotopic scrambling. The CH_3GeH^+ ion species displays a lower reactivity than the GeH_n^+ ($n = 0$–3) ions, forming three different products with similar rate constants which range from 1.0 to 2.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

Elimination of a H_2 molecule is a common process from GeH_n^+ ($n = 0$–2) also observed in the self-condensation of GeH_4 [5]. The primary GeH_n^+ ($n = 0$, 1) ions, formed by GeH_4, give only this process yielding the $Ge_2H_n^+$ ($n = 2, 3$) ions in slower reactions than the corresponding species from methylgermane. GeH_2^+ is also involved in hydride abstraction to give GeH_3^+ or $CH_3GeH_2^+$ in GeH_4 or CH_3GeH_3, respectively, which is the fastest process. GeH_3^+ reacts with GeH_4 [5] only in an isotopic scrambling process, the same behaviour being shown by the corresponding $CH_3GeH_2^+$ ion in methylgermane, occuring with comparable rate constants. A comparison of the rate constants of the same ions present in the two systems shows an overall reactivity in CH_3GeH_3 higher than in GeH_4 [5], the reaction efficiencies being close to unit in the first system (Table 1).

The effect of a germanium with respect to a silicon atom can be evaluated by comparing the present system with the self-condensation of CH_3SiH_3 [10]. As far as the XH_n^+ (X = Ge, Si; $n = 0$–3) ions are concerned, the general behaviour is very similar for both reaction mechanisms and reaction efficiencies. To the contrary, XCH_n^+ (X = Ge, Si; $n = 2$–5) ions display very different reaction pathways and, when $n = 2$, the ion species does not exist in methylgermane. Moreover, CH_3Ge^+ does not react at all and

Table 2
Rate constants for reactions of GeH_n^+ ($n = 0$–3) and $CH_3GeH_n^+$ ($n = 1, 2$) ions with CH_3GeH_3 and SiH_4 in a CH_3GeH_3/SiH_4 mixture[a]

Reaction	k_{exp}	Σk_{exp}	k_L or k_{ADO}[b]	Efficiency[c]
$Ge^+ + CH_3GeH_3 \rightarrow CH_3Ge^+ + GeH_3$	3.3			
$\rightarrow Ge_2CH_4^+ + H_2$	6.3	9.6	10.88	0.88
$GeH^+ + CH_3GeH_3 \rightarrow CH_3Ge^+ + GeH_4$	0.96			
$\rightarrow Ge_2CH_5^+ + H_2$	8.4	9.4	10.84	0.87
$GeH^+ + SiH_4 \rightarrow GeSiH_3^+ + H_2$	1.6	1.6	10.38	0.15
$GeH_2^+ + CH_3GeH_3 \rightarrow CH_3GeH^+ + GeH_4$	3.5			
$\rightarrow CH_3GeH_2^+ + GeH_3$	7.5	11.0	10.80	1.01
$GeH_2^+ + SiH_4 \rightarrow GeSiH_4^+ + H_2$	1.8	1.8	10.23	0.18
$GeH_3^+ + CH_3GeH_3 \rightarrow CH_3GeH_2^+ + GeH_4$	12	12	10.77	1.11
$CH_3GeH^+ + CH_3GeH_3 \rightarrow GeC_2H_7^+ + GeH_3$	2.2			
$\rightarrow Ge_2CH_6^+ + CH_4$	1.2			
$\rightarrow Ge_2C_2H_8^+ + H_2$	2.0	5.4	10.33	0.52
$CH_3GeH^+ + SiH_4 \rightarrow GeSiCH_6^+ + H_2$	0.67	0.67	10.09	0.066
$CH_3GeH_2^+ + CH_3GeH_3 \rightarrow$ Isotopic scrambling	4.7	4.7	10.29	0.46

[a] Rate constants are expressed as 10^{-10} cm^3 molecule^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%.

[b] Rate constants have been calculated according to the Langevin theory [15] for SiH_4, taking its polarizability ($\alpha = 4.339 \times 10^{-24}$ cm^3) from [18], and according to the ADO theory [15] for CH_3GeH_3 taking its dipole moment ($\mu_D = 0.644 \times 10^{-18}$ esu cm) from [16] and calculating its polarizability ($\alpha = 6.735 \times 10^{-24}$ cm^3) as in [17] starting from polarizability of GeH_4 [18].

[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{Langevin}$ or $\Sigma k_{exp}/k_{ADO}$.

$CH_3GeH_2^+$ gives only isotopic scrambling, while the corresponding silicon containing ions are involved in two different processes, although with rather low efficiency. CH_3GeH^+ and CH_3SiH^+, which are the species showing the highest similarity, have two corresponding products, $XC_2H_7^+$ and $X_2C_2H_3^+$ (X = Ge, Si) ions, which are formed with rather different rate constants.

3.2. CH_3GeH_3/SiH_4 mixture

The same primary ions of methylgermane, GeH_n^+ ($n = 0$–3) and $CH_3GeH_n^+$ ($n = 1, 2$), have been reacted in a CH_3GeH_3/SiH_4 mixture and the ionic products together with their rates of formation are reported in Table 2. When the neutral reactant is methylgermane, the same processes are observed as in self-condensation of CH_3GeH_3 alone, the corresponding rate constants generally showing a good agreement. If the reacting molecule is silane, only a few ions (GeH^+, GeH_2^+, and CH_3GeH^+) react leading to species containing a new Ge–Si bond by loss of a hydrogen molecule. Moreover, these three reactions occur with very low efficiences, which range from 0.066 to 0.18. The same behaviour was previously observed, limited to GeH^+ and GeH_2^+ ions, in GeH_4/SiH_4 mixtures [5].

Table 3 shows the rate constants for reactions of primary ions of silane, SiH_n^+ ($n = 0$–3), and Table 4 of secondary and tertiary ions containing silicon, $Si_2H_n^+$ ($n = 2$–5), $CH_3SiH_2^+$, $Si_3H_4^+$ and $Si_3H_5^+$. Again, when these ion species react with silane, self-condensation species are observed. They occur with rate constants in good agreement with previously reported data for SiH_4 alone [5,19,22], or SiH_4/GeH_4 [5] and SiH_4/NH_3 [6] mixtures. Reactions of SiH_n^+ ($n = 0$–3) ions with methylgermane lead to a variety of products, which never contain silicon and germanium together. In particular, when $n = 1$–3, three kinds of processes are observed: (i) formation of the $CH_3SiH_2^+$ ion with elimination of GeH_n ($n = 2$–4) neutral fragments, respectively, occurring with very similar rate constants (1.9, 2.7, 2.7 × 10^{-10} cm^3 molecule^{-1} s^{-1}); (ii) formation of $CH_3GeH_2^+$ with loss of SiH_n ($n = 2$–4) groups, which is always the fastest reaction of the considered ions and shows increasing rate constants from SiH^+ to SiH_3^+ (3.2, 7.8, 9.9 × 10^{-10} cm^3 molecule^{-1} s^{-1}); (iii) elimination of SiH_4 molecule yielding to the formation of $CH_3GeH_n^+$ ($n = 0$–2) ion species, which takes place at the

Table 3
Rate constants for reactions of SiH_n^+ ($n = 0$–3) ions with CH_3GeH_3 and SiH_4 in a CH_3GeH_3/SiH_4 mixture[a]

Reaction	k_{exp}	Σk_{exp}	k_L or k_{ADO}[b]	Efficiency[c]
$Si^+ + CH_3GeH_3 \rightarrow GeH^+ + CH_3SiH_2$	0.95			
$\rightarrow CH_3Ge^+ + SiH_3$	6.2	7.2	14.95	0.48
$Si^+ + SiH_4 \rightarrow Si_2H_2^+ + H_2$	7.6	7.6	12.58	0.60
$SiH^+ + CH_3GeH_3 \rightarrow CH_3SiH_2^+ + GeH_2$	1.9			
$\rightarrow GeH^+ + CH_3SiH_3$	1.6			
$\rightarrow CH_3Ge^+ + SiH_4$	2.8			
$\rightarrow CH_3GeH_2^+ + SiH_2$	3.2	9.5	14.76	0.64
$SiH^+ + SiH_4 \rightarrow SiH_3^+ + SiH_2$	0.66			
$\rightarrow Si_2H_3^+ + H_2$	6.2	6.9	12.46	0.55
$SiH_2^+ + CH_3GeH_3 \rightarrow CH_3SiH_2^+ + GeH_3$	2.7			
$\rightarrow CH_3GeH^+ + SiH_4$	3.2			
$\rightarrow CH_3GeH_2^+ + SiH_3$	7.8	13.7	14.56	0.94
$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3$	5.1			
$\rightarrow Si_2H_4^+ + H_2$	5.7	10.8	12.35	0.87
$SiH_3^+ + CH_3GeH_3 \rightarrow CH_3SiH_2^+ + GeH_4$	2.7			
$\rightarrow CH_3GeH_2^+ + SiH_4$	9.9	12.6	14.39	0.88
$SiH_3^+ + SiH_4 \rightarrow Si_2H_5^+ + H_2$	0.48	0.48	12.25	0.039

[a] Rate constants are expressed as 10^{-10} cm^3 $molecule^{-1}$ s^{-1}; experiments were run at 333 K; uncertainty is within 20%.

[b] Rate constants have been calculated according to the Langevin theory [15] for SiH_4, taking its polarizability ($\alpha = 4.339 \times 10^{-24}$ cm^3) from [18], and according to the ADO theory [15] for CH_3GeH_3 taking its dipole moment ($\mu_D = 0.644 \times 10^{-18}$ esu cm) from [16] and calculating its polarizability ($\alpha = 6.735 \times 10^{-24}$ cm^3) as in [17] starting from polarizability of GeH_4 [18].

[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{Langevin}$ or $\Sigma k_{exp}/k_{ADO}$.

maximum rate when $CH_3GeH_2^+$ is formed (9.9×10^{-10} cm^3 $molecule^{-1}$ s^{-1}). Processes (ii) and (iii) are coincident for reaction of SiH_3^+. The comparison of the reactions of SiH_n^+ ($n = 0$–3) ions and methylgermane with reactions in the presence of germane shows that, in this case, the methyl group strongly affects the reactivity of the germanium hydride [5]. In fact, in the SiH_n^+/CH_3GeH_3 system, the absence of new Ge–Si bonds is particularly evident, while the formation of C–Si bonds is observed in both ionic and neutral species. To the contrary, Si^+, SiH^+, and SiH_2^+ react with GeH_4 forming, among others, the $GeSiH_n^+$ ($n = 2$–4) ions. Moreover, efficiencies of reaction are higher for all the SiH_n^+ ($n = 0$–3) ions reacting with germane than with methylgermane.

Secondary ions of silane containing two silicon atoms, $Si_2H_n^+$ ($n = 2$–5), give ion species containing Si and Ge together when $n = 2$, 3 and Si, Ge, and C when $n = 2$–4, with loss of CH_3SiH_3 or SiH_4, respectively. When both processes are possible, the fastest is the formation of the carbon containing ions $GeSiCH_n^+$ ($n = 4, 5$). However, $Si_2H_3^+$ ions display an efficiency much lower than those of the $Si_2H_2^+$ and $Si_2H_4^+$ species. $Si_2H_5^+$ is involved in different processes, which are hydride abstraction from CH_3GeH_3 and formation of $Si_2CH_7^+$, with an intermediate overall efficiency.

Reactions of $CH_3SiH_2^+$, a secondary ion species containing a Si–C bond, with silane lead to very slow substitution of the carbon by a silicon atom to form $Si_2H_3^+$ and with methylgermane give again hydride abstraction to yield $CH_3GeH_2^+$. In any case no ion product with Si and Ge is observed. To the contrary, from reactions of the tertiary $Si_3H_4^+$ and $Si_3H_5^+$ ions with methylgermane, substitution of a silicon by a germanium atom and by a $GeCH_2$ group occurs forming $GeSi_2H_n^+$ ($n = 4, 5$) and $GeSi_2CH_n^+$ ($n = 6, 7$) with rather high reaction rate constants.

For comparative purposes, Table 5 reports the rate constants for reactions of $Si_2H_2^+$, $Si_2H_4^+$, $Si_3H_4^+$, and $Si_3H_5^+$ with germane, as only their mechanisms have been published previously [23]. No strong difference is observed in the rate constants of formation of Ge–Si containing ions from $Si_2H_2^+$, $Si_3H_4^+$, and $Si_3H_5^+$ in reactions with GeH_4 or CH_3GeH_3 and elimination of SiH_4 or CH_3SiH_3 neutral molecules, respectively

Table 4
Rate constants for reactions of $Si_2H_n^+$ ($n = 2$–5), $CH_3SiH_2^+$, $Si_3H_4^+$, and $Si_3H_5^+$ ions with CH_3GeH_3 and SiH_4 in a CH_3GeH_3/SiH_4 mixture

Reaction	k_{exp}	Σk_{exp}	k_L or k_{ADO}[b]	Efficiency[c]
$Si_2H_2^+ + CH_3GeH_3 \rightarrow GeSiH_2^+ + CH_3SiH_3$	1.2			
$\rightarrow GeSiCH_4^+ + SiH_4$	6.9	8.1	11.62	0.70
$Si_2H_2^+ + SiH_4 \rightarrow Si_3H_4^+ + H_2$	0.47	0.47	10.70	0.044
$Si_2H_3^+ + CH_3GeH_3 \rightarrow GeSiH_3^+ + CH_3SiH_3$	0.53			
$\rightarrow GeSiCH_5^+ + SiH_4$	1.2	1.7	11.57	0.15
$Si_2H_3^+ + SiH_4 \rightarrow Si_3H_5^+ + H_2$	1.1	1.1	10.67	0.10
$Si_2H_4^+ + CH_3GeH_3 \rightarrow GeSiCH_6^+ + SiH_4$	6.6	6.6	11.50	0.57
$Si_2H_4^+ + SiH_4 \rightarrow Si_3H_6^+ + H_2$	0.32	0.32	10.64	0.030
$Si_2H_5^+ + CH_3GeH_3 \rightarrow Si_2CH_7^+ + GeH_4$	2.0			
$\rightarrow CH_3GeH_2^+ + Si_2H_6$	3.0	5.0	11.44	0.44
$Si_2H_5^+ + SiH_4 \rightarrow Si_3H_7^+ + H_2$	0.24	0.24	10.61	0.023
$CH_3SiH_2^+ + CH_3GeH_3 \rightarrow CH_3GeH_2^+ + CH_3SiH_3$	4.6	4.6	12.61	0.36
$CH_3SiH_2^+ + SiH_4 \rightarrow Si_2H_3^+ + CH_4 + H_2$	0.30	0.30	11.24	0.027
$Si_3H_4^+ + CH_3GeH_3 \rightarrow GeSi_2H_4^+ + CH_3SiH_3$	2.2			
$\rightarrow GeSi_2CH_6^+ + SiH_4$	3.8	6.0	10.34	0.58
$Si_3H_4^+ + SiH_4 \rightarrow Si_4H_6^+ + H_2$	2.1	2.1	10.04	0.21
$Si_3H_5^+ + CH_3GeH_3 \rightarrow GeSi_2H_5^+ + CH_3SiH_3$	2.3			
$\rightarrow GeSi_2CH_7^+ + SiH_4$	5.4	7.7	10.32	0.75
$Si_3H_5^+ + SiH_4 \rightarrow Si_4H_7^+ + H_2$	3.5	3.5	10.02	0.35

[a] Rate constants are expressed as 10^{-10} cm^3 molecule^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%.

[b] Rate constants have been calculated according to the Langevin theory [15] for SiH_4, taking its polarizability ($\alpha = 4.339 \times 10^{-24}$ cm^3) from [18], and according to the ADO theory [15] for CH_3GeH_3 taking its dipole moment ($\mu_D = 0.644 \times 10^{-18}$ esu cm) from [16] and calculating its polarizability ($\alpha = 6.735 \times 10^{-24}$ cm^3) as in [17] starting from polarizability of GeH_4 [18].

[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{Langevin}$ or $\Sigma k_{exp}/k_{ADO}$.

($GeSiH_4^+$ is observed only in the mixture with GeH_4). A different behaviour is shown comparing the reactions of the $Si_2H_2^+$, $Si_2H_4^+$, $Si_3H_4^+$, and $Si_3H_5^+$ ions, which take place with elimination of a molecule of silane and give $GeSi_nH_m^+$ ($n = 1$, $m = 2,4$; $n = 2$, $m = 4$, 5) when the neutral reactant is GeH_4, and $GeSi_nCH_m^+$ ($n = 1$, $m = 4,6$; $n = 2$, $m = 6,7$) when the neutral reactant is CH_3GeH_3. In fact, the rate constants of these reactions are always higher in the presence of methylgermane than with germane, their ratios ranging from a minimum of 1.9 to a maximum of 4.1. Similar values (from 2.2 to 3.7) are obtained as ratios of efficiencies of the reactions of the $Si_2H_2^+$, $Si_2H_4^+$, $Si_3H_4^+$, and $Si_3H_5^+$ ions with CH_3GeH_3 with respect to GeH_4, suggesting a higher reactivity of the methylhydride.

Table 5
Rate constants for reactions of $Si_2H_n^+$ ($n = 2$–5), $Si_3H_4^+$, and $Si_3H_5^+$ ions with GeH_4 and SiH_4 in a GeH_4/SiH_4 mixture[a]

Reaction	k_{exp}	k_L^b	Efficiency[c]
$Si_2H_2^+ + GeH_4 \rightarrow GeSiH_2^+ + SiH_4$	1.7	9.06	0.19
$Si_2H_4^+ + GeH_4 \rightarrow GeSiH_4^+ + SiH_4$	2.2	8.97	0.24
$Si_3H_4^+ + GeH_4 \rightarrow GeSi_2H_4^+ + SiH_4$	1.8	8.13	0.22
$Si_3H_5^+ + GeH_4 \rightarrow GeSi_2H_5^+ + SiH_4$	2.8	8.11	0.34

[a] Rate constants are expressed as 10^{-10} cm^3 molecule^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%.

[b] Rate constants have been calculated according to the Langevin theory [15] taking polarizabilities of SiH_4 ($\alpha = 4.339 \times 10^{-24}$ cm^3) and of GeH_4 ($\alpha = 4.966 \times 10^{-24}$ cm^3) from [18].

[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{Langevin}$.

4. Conclusions

The study of ion/molecule reactions occurring in the CH_3GeH_3/SiH_4 mixture allows to find which are the most favourable conditions leading to the formation of clusters of growing size in which germanium, silicon, and, possibly, carbon are present together. The results show that ions containing germanium and silicon, $GeSiH_n^+$ ($n = 2–4$), are formed only from GeH^+ and GeH_2^+ reacting with silane or $Si_2H_2^+$ and $Si_2H_3^+$ reacting with methylgermane, all these processes having low rate constants (the maximum value is $k = 1.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Reactions of CH_3GeH^+ with silane and of the $Si_2H_n^+$ ($n = 2–4$) ion species with methylgermane lead to the ions $GeSiCH_n^+$ ($n = 4–6$), formed in the case of $n = 4$ and 6, quite rapidly from $Si_2H_2^+$ (k = 6.9×10^{-10} cm^3 molecule^{-1} s^{-1}) and $Si_2H_4^+$ (k = 6.6×10^{-10} cm^3 molecule^{-1} s^{-1}), respectively. A very similar trend is shown by the two tertiary ions examined, $Si_3H_n^+$ ($n =$ 4,5), which, reacting with CH_3GeH_3, yield the ion families $GeSi_2H_n^+$ ($n =$ 4,5) and $GeSi_2CH_n^+$ ($n = 6, 7$) with rate constants ranging from 2.2 to 5.4×10^{-10} cm^3 molecule^{-1} s^{-1}.

Therefore, the experimental results indicate that the main contribution to the formation of ions containing Si and Ge or Si, Ge, and C, is due to secondary and tertiary ions containing only silicon and hydrogen atoms by substitutions of Si by Ge or $GeCH_2$ moieties and elimination of CH_3SiH_3 or SiH_4, respectively. This trend is also supported by the quite high rate at which these processes take place, the highest rate constants being observed in the formation of ions containing also a carbon atom. It follows that the best experimental conditions for the growth of these clusters are those favoring the formation of secondary and tertiary species containing silicon, that means a high partial pressure of silane with respect to methylgermane.

Acknowledgement

The authors thank Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support.

References

[1] J.G. Ekerdt, Y.-M. Sun, A. Szabo, G.J. Szulczewski, J.M. White, Chem. Rev. 96 (1996) 1499.

[2] P. Hess, Electron. Mat. Chem. 127 (1996) 169.

[3] L. Operti, M. Splendore, G.A. Vaglio, P. Volpe, Organometallics 12 (1993) 4509.

[4] L. Operti, M. Splendore, G.A. Vaglio, P. Volpe, Organometallics 12 (1993) 4516.

[5] L. Operti, M. Splendore, G.A. Vaglio, A.M. Franklin, J.F.J. Todd, Int. J. Mass Spectrom. Ion Processes 136 (1994) 25.

[6] J.-F. Gal, R. Grover, P.-C. Maria, L. Operti, R. Rabezzana, G.A. Vaglio, P. Volpe, J. Phys. Chem. 98 (1994) 11978.

[7] P. Antoniotti, L. Operti, R. Rabezzana, G.A. Vaglio, J.-F. Gal, R. Grover, P.-C. Maria, J. Phys. Chem. 100 (1996) 155.

[8] P. Benzi, M. Castiglioni, P. Volpe, unpublished results.

[9] L. Operti, M. Splendore, G.A. Vaglio, P. Volpe, M. Speranza, G. Occhiucci, J. Organomet. Chem. 433 (1992) 35.

[10] L. Operti, R. Rabezzana, G.A. Vaglio, P. Volpe, J. Organomet. Chem. 509 (1996) 151.

[11] D.S. Rustard, T. Birchall, W.L. Jolly, Inorg. Synth. 11 (1968) 128.

[12] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.

[13] M. Decouzon, J-F. Gal, J. Gayraud, P.-C. Maria, G.A. Vaglio, P. Volpe, J. Am. Soc. Mass Spectrom. 4 (1993) 54.

[14] P. Benzi, L. Operti, R. Rabezzana, M. Splendore, P. Volpe, Int. J. Mass Spectrom. Ion Processes 152 (1996) 61.

[15] M.T. Bowers, Gas Phase Ion Chemistry, Academic, New York, 1979, Vol. 1.

[16] A.L. McClellan, Tables of Experimental Dipole Moments, Freeman, San Francisco, 1963.

[17] K.J. Miller, J. Am. Chem. Soc. 912 (1990) 8533.

[18] E.R. Lippincot, J.A. Stutman, J. Phys. Chem 68 (1964) 296.

[19] M.L. Mandich, W.D. Reents Jr., M.F. Jarrold, J. Chem. Phys. 88 (1988) 1703.

[20] M.L. Mandich, W.D. Reents Jr., K.T. Kolenbrander, J. Chem. Phys. 92 (1990) 487.

[21] M.L. Mandich, W.D. Reents Jr., J. Chem. Phys. 95 (1991) 7360.

[22] W.D. Reents Jr., M.L. Mandich, J. Chem. Phys. 96 (1992) 4429.

[23] L. Operti, M. Splendore, G.A. Vaglio, P. Volpe, Spectrochim. Acta 49A (1993) 1213.