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Gas Phase Ion–Molecule Reactions of Methylsilane and Methylgermane by Ion Trap Mass Spectrometry[†]

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Self-condensation processes of CH_3SiH_3 have been examined by ion trap mass spectrometry at 60 °C and 7.0×10^{-5} Torr helium pressure. Different reaction pathways have been identified, which occur with elimination of SiH_4, SiH_2, H_2, or SiH_3 or without elimination of neutral fragments. Ionic relative abundances in typical self-condensation experiments and their variations with reaction time are reported for CH_3SiH_3, SiH_4, CH_3GeH_3, and GeH_4. The results are discussed and compared also with respect to the relevance of these compounds in the preparation of materials interesting for their photovoltaic properties.

Introduction

Ion trap mass spectrometry has been shown to be a very powerful technique for investigating gas phase ion–molecule reactions and their mechanisms.[1–4] Selected ions are stored in the ion trap by the application of dc voltages on rf fields, and their reaction products are observed. Variation of ion abundaces versus time gives the reaction sequences, and thus the overall behavior of gaseous systems under different experimental conditions can be elucidated by this method.

Gaseous ionic species play a fundamental role in the deposition processes of amorphous hydrogenated solids by radiolysis of gaseous phases.[5–8] The reactivity of systems containing GeH_4 or CH_3GeH_3 with different simple hydrocarbons has been previously studied by chemical ionization mass spectrometry (CIMS) and Fourier transform mass spectrometry (FTMS).[9–11] Information has been obtained on the behavior of these mixtures in the radiolytic preparation of amorphous and solid germanium carbides of interest in photovoltaic technology.

Recently, results have also been reported on the preparation of Si–Ge:H layers, which are narrow band gap photoconductors.[12,13] Therefore, we have started a research on the reactivity of mixtures containing volatile hydrides of germanium and silicon by ion trap mass spectrometry. Results on the GeH_4/SiH_4 system have been reported previously,[14] and here we report the self-condensation processes of CH_3SiH_3 and also data on the variations with reaction time of the ionic abundances of SiH_4, CH_3GeH_3, and GeH_4, which have to be known to investigate mixtures in which these methyl hydrides are present.

Experimental Section

Germane[7] and methylgermane[15] were prepared as described in the literature. Silane and methylsilane were obtained commercially in high purity and were used as supplied.

All experiments were run on a Finnigan Mat ion trap mass spectrometer. A Bayard Alpert ionization gauge was used to measure the pressures, which were corrected on the basis of the relative sensitivities of the ion gauge response with respect to nitrogen.[16,17] Helium buffer gas was generally admitted to the vacuum chamber at a pressure of 7.0×10^{-5} Torr. The temperature was maintained at 60 °C in order to avoid thermal decomposition. Ions were detected in the m/z 20–400 mass range.

The scan mode for ion–molecule reaction experiments is reported in Figure 1. In period A, electrons enter the ion trap, resulting in the ionization of reagent molecules. The rf level was previously set so that all ions above m/z 20 had stable trajectories. The electron energy was about 70 eV, and the ionization time was typically 1 ms. In period B, primary ions react with neutrals present in the ion trap for times raised continuously from 0 to 100 ms. Acquisition is obtained by increasing linearly the ring rf voltage from low to high masses so that ions are sequentially ejected from the trap and detected (period C). At the end of each scan, the rf voltage is lowered to clean the trap from all ions (period D).

Figure 2 shows the schematic diagram of the scan function relative to ion–molecule reactions with mass selective storage. After ionization (period A), a first reaction time (period B) was chosen to maximize the abundance of ions to be stored. Isolation of the selected ion (period C) is achieved by increasing the rf voltage to an appropriate voltage and by applying a negative dc voltage. In period D the isolated ion is allowed to react with neutrals in the trap for convenient reaction times to observe formation of the product ions. Acquisition (period E) and

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(1) Todd, J. F. J. *Mass Spectrom. Rev.* **1991,** *10,* 3.
(2) Cooks, R. G.; Glish, G. L.; McLuckey, S. A.; Kaiser, R. E. *Chem. Eng. News* **1991,** 26.
(3) Nourse, B. D.; Cooks, R. G. *Anal. Chim. Acta* **1990,** *228,* 1.
(4) March, R. E. *Int. J. Mass Spectrom. Ion Processes* **1992,** *118/119,* 71.
(5) Castiglioni, M.; Tuninetti, M.; Volpe, P. *Gazz. Chim. Ital.* **1983,** *113,* 457.
(6) Belluati, R.; Castiglioni, M.; Volpe, P.; Gennaro, M. C. *Polyhedron* **1987,** *6,* 441.
(7) Benzi, P.; Castiglioni, M.; Volpe, P.; Battezzati, L.; Venturi, M. *Polyhedron* **1988,** *7,* 597.
(8) Antoniotti, P.; Benzi, P.; Castiglioni, M.; Operti, L.; Volpe, P. *Chem. Mater.* **1992,** *4,* 717.
(9) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *J. Organomet. Chem.* **1989,** *373,* 289.
(10) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *Int. J. Mass Spectrom. Ion Processes* **1990.** *100,* 647.
(11) Operti, L.; Splendore, M.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Occhiucci, G. *J. Organomet. Chem.* **1992,** *433,* 35.
(12) Wakagi, M.; Chigasaki, M.; Ohno, T.; Narose, M.; Hanazonoo, M.; Maruyama, E. *J. Non-Cryst. Solids* **1985,** *77/78,* 889.
(13) Racanelli, M.; Greve, D. W. *JOM* **1991,** *43,* 32.
(14) Operti, L.; Splendore, M.; Vaglio, G. A.; Volpe, P. *Spectrochim. Acta* **1993,** *49A,* 1213.
(15) Rustad, D. S.; Birchall, T.; Jolly, W. L. *Inorg. Synth.* **1968,** *11,* 128.
(16) Decouzon, M.; Gal, J. F.; Maria, P. C.; Tchinianga, A. S. Personal communication.
(17) Decouzon, M.; Gal, J. F.; Gayraud, J.; Maria, P. C.; Vaglio, G. A.; Volpe, P. *J. Am. Soc. Mass Spectrom.* **1993,** *4,* 54.

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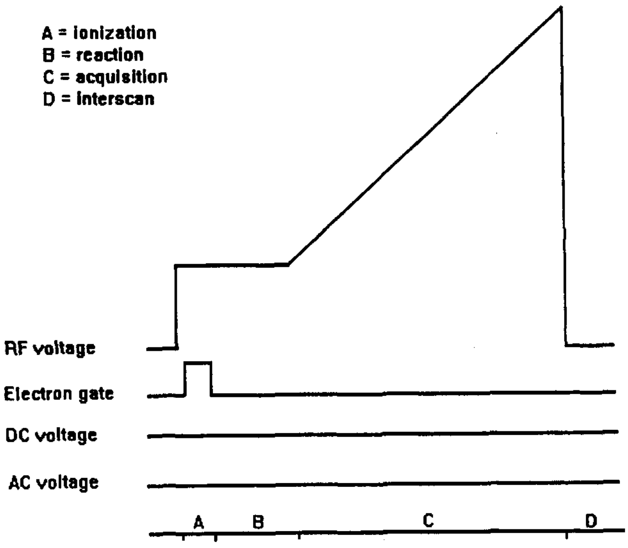

Figure 1. Scan mode for ion–molecule reactions.

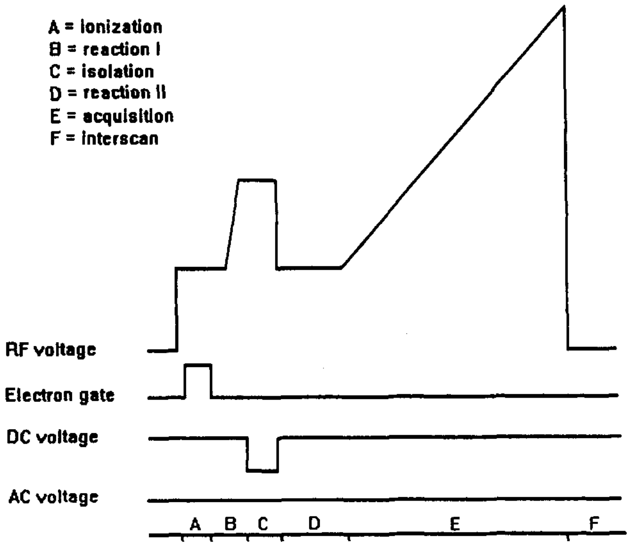

Figure 2. Scan mode for isolation and reaction of selected ions.

interscan (period F) follow as described above. Even if not shown in Figures 1 and 2, after the application of both rf and dc voltages, a settling time is required and also a 4 ms time is necessary for the stabilization of the multiplier. Therefore, when the reaction time is set to zero, some time has passed from the formation of ions (ionization event) and it cannot be ruled out that ion–molecule reactions have already occurred to some extent.

A third kind of experiment involves collision induced dissociation (CID) of selected ions, and its timing diagram is reported in Figure 3. The only difference with respect to Figure 2 is step D, in which dissociation takes place instead of reaction. The ion is excited by an ac voltage applied between the end caps of the ion trap during 10 ms. It dissociates by collision with the buffer gas, and the daughter ions are then detected in period E.

Results

The self-condensation reaction schemes of CH_3SiH_3 and its ionic relative abundances in typical self-condensation experiments are reported in this paper. For comparison purposes, the ionic abundances and their variations with reaction time are also displayed for the self-condensation of SiH_4, CH_3GeH_3, and GeH_4, as obtained by ion trap mass spectrometry under similar experimental conditions.

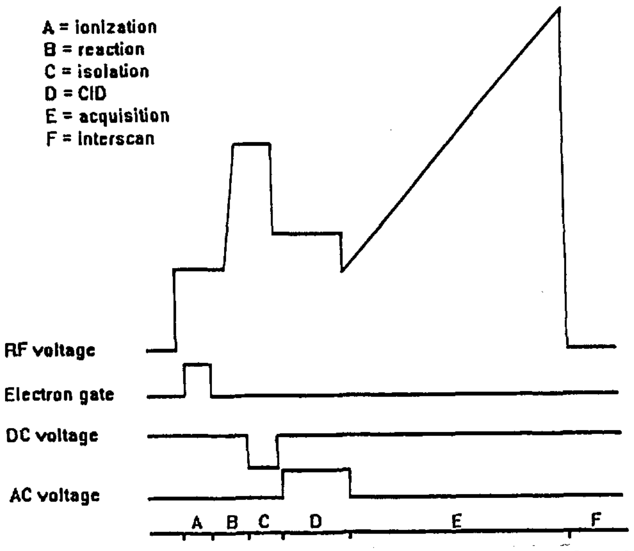

Figure 3. Scan mode for isolation and collision induced dissociation of selected ions.

Some results concerning GeH_4[18] and SiH_4[19] have already been published, as well as reaction schemes of CH_3GeH_3 obtained by Fourier transform mass spectrometry.[11]

Self-Condensation of CH_3SiH_3. Table I reports the relative abundances of the most significant ions in the ion trap (IT) mass spectra of CH_3SiH_3 at 5.4×10^{-7} Torr at reaction times ranging from 0 to 100 ms. All ionic abundances refer to the most abundant ion at any time here studied, which is $SiCH_5^+$ at zero reaction time. $SiCH_5^+$ can be reformulated as $CH_3SiH_2^+$, because it has been suggested that in the first breakdown steps only the hydrogen atoms linked to Si are lost.[20] Several ionic families are formed both by direct ionization and in ion–molecule processes: SiH_n^+ (n = 0–3), $SiCH_n^+$ (n = 2–5), $SiC_2H_n^+$ (n = 6, 7), $Si_2CH_n^+$ (n = 4–7), $Si_2C_2H_n^+$ (n = 6–9, 11), $Si_2C_3H_n^+$ (n = 8–13), $Si_3C_2H_n^+$ (n = 8–11, 13), $Si_3C_3H_n^+$ (n = 10–13), $Si_3C_4H_n^+$ (n = 12–15, 17), $Si_4C_3H_n^+$ (n = 14, 15, 17), and $Si_4C_4H_n^+$ (n = 16, 17). The highest mass ion reported in Table I is $Si_4C_4H_{17}^+$, whose abundance reaches 23.4% at 100-ms reaction time. At such reaction times (100 ms or more) also $Si_4C_5H_n^+$ ions were present in traces.

In some cases, more than one ion has the same nominal mass, i.e. m/z 59 can be $SiC_2H_7^+$ and $Si_2H_3^+$. Therefore, the formulas displayed in Table I, as well as in the following tables, have been assigned on the basis of the reaction mechanisms and on isotopic pattern calculations. For some ions collision induced dissociation (CID) experiments have also been performed.

At zero reaction time the SiH_n^+ (n = 0–3) and $SiCH_n^+$ (n = 2–5) ionic species together transport 57.8% of the total ion current. When reactions proceed, the SiH_n^+ (n = 0–3) and $SiCH_2^+$ ions disappear, and the $SiCH_n^+$ (n = 3–5) ionic abundances decrease. The other ionic species, which are produced in ion–molecule reactions and which, in turn, participate in ion–molecule reactions as reagent ions, show different behaviors which are evident only for ions displaying a rather good abundance.

However, three types of behavior can be detected. First, a continuous decrease of the ionic abundances with reaction

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[18] Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *J. Organomet. Chem.* **1988**, *354*, 39.

[19] Yu, T. Y.; Cheng, T. M. H.; Kempter, V.; Lampe, F. W. *J. Phys. Chem.* **1972**, *76*, 3321.

[20] Mayer, T. M.; Lampe, F. W. *J. Phys. Chem.* **1974**, *78*, 2422.

Table I. Relative Abundances of Significant Ions in the IT Mass Spectra of CH_3SiH_3[a] as a Function of the Reaction Time[b]

		reaction time (ms)							
m/z[c]	ions	0	10	20	30	40	50	75	100
28	Si^+	22.9	3.6	0.6					
29	SiH^+	7.6	0.7	0.3					
30	SiH_2^+	3.4	0.7	0.2					
31	SiH_3^+	2.0	0.4						
42	$SiCH_2^+$	17.6	4.9	1.9	0.6	0.3			
43	$SiCH_3^+$	73.3	51.0	29.0	18.2	10.0	5.6	1.5	0.7
44	$SiCH_4^+$	28.4	9.0	5.4	3.3	2.4	1.8	1.1	0.6
45	$SiCH_5^+$	100	88.5	71.5	55.6	41.5	34.1	17.5	9.0
58	$SiC_2H_6^+$	4.6	5.7	2.6	4.0	4.1	3.3	3.1	3.1
59	$SiC_2H_7^+$	42.4	65.5	74.8	81.1	82.1	83.7	91.5	83.9
72	$Si_2CH_4^+$	8.7	5.8	2.7	1.2	0.8	0.7	0.6	0.4
73	$Si_2CH_5^+$	7.4	7.2	6.5	5.4	4.4	4.8	5.2	5.3
74	$Si_2CH_6^+$	1.6	1.6	1.6	1.5	1.9	1.8	0.8	1.1
75	$Si_2CH_7^+$	1.2	1.3	1.3	1.0	1.3	1.1	1.3	1.1
86	$Si_2C_2H_6^+$	12.6	10.3	6.6	3.4	2.3	2.2	2.4	1.8
87	$Si_2C_2H_7^+$	8.5	12.3	11.4	9.9	6.5	6.6	4.4	6.2
88	$Si_2C_2H_8^+$	11.5	16.9	18.9	20.2	23.1	21.9	20.2	20.8
89	$Si_2C_2H_9^+$	8.8	29.0	40.7	41.5	46.0	46.8	46.0	42.8
91	$Si_2C_2H_{11}^+$	3.8	6.9	8.8	12.6	15.4	16.9	16.9	18.0
100	$Si_2C_3H_8^+$	3.2	4.7	4.6	3.8	2.1	3.1	1.9	2.2
101	$Si_2C_3H_9^+$	4.8	8.1	9.5	10.5	10.6	10.6	10.9	9.6
102	$Si_2C_3H_{10}^+$	0.7	1.0	1.4	1.8	1.4	2.4	4.8	3.7
103	$Si_2C_3H_{11}^+$	1.1	2.6	3.9	4.4	6.1	3.6	4.7	10.1
104	$Si_2C_3H_{12}^+$	0.8	1.6	1.9	4.2	3.7	4.6	6.4	7.4
105	$Si_2C_3H_{13}^+$	2.0	4.2	7.8	9.2	13.6	15.3	19.3	26.4
116	$Si_3C_2H_8^+$	4.2	7.2	7.3	6.9	5.6	4.8	6.0	4.9
117	$Si_3C_2H_9^+$	5.4	9.3	10.5	7.1	8.9	6.6	6.5	6.7
118	$Si_3C_2H_{10}^+$	1.6	3.9	4.1	4.6	4.1	5.3	4.3	2.5
119	$Si_3C_2H_{11}^+$	3.0	4.8	6.4	6.9	4.8	4.8	9.1	9.8
121	$Si_3C_2H_{13}^+$			0.2	0.3	0.9	1.3	1.8	2.1
130	$Si_3C_3H_{10}^+$	10.5	19.6	19.8	23.0	21.3	19.1	20.5	16.6
131	$Si_3C_3H_{11}^+$	10.4	19.7	25.3	28.2	27.6	26.3	24.3	18.0
132	$Si_3C_3H_{12}^+$	10.6	24.4	30.8	33.4	35.0	34.3	26.9	31.4
133	$Si_3C_3H_{13}^+$	6.2	16.4	25.6	32.6	33.9	34.5	37.1	26.4
144	$Si_3C_4H_{12}^+$	1.0	2.2	3.3	4.2	5.1	4.6	5.3	5.6
145	$Si_3C_4H_{13}^+$	0.4	0.9	1.6	1.7	2.1	3.0	2.5	3.0
146	$Si_3C_4H_{14}^+$	0.9	1.6	3.1	4.7	4.8	5.4	5.7	4.4
147	$Si_3C_4H_{15}^+$	0.9	2.6	3.7	5.0	6.2	6.8	8.8	9.1
149	$Si_3C_4H_{17}^+$	0.5	0.6	1.6	3.4	4.9	5.4	6.0	4.1
162	$Si_4C_3H_{14}^+$	2.4	5.0	6.9	8.5	7.8	10.3	10.1	10.6
163	$Si_4C_3H_{15}^+$	1.0	1.1	2.5	3.6	5.0	5.4	7.2	7.3
165	$Si_4C_3H_{17}^+$			1.1	0.7	0.6	1.8	1.2	1.9
176	$Si_4C_4H_{16}^+$	2.3	6.3	8.0	9.7	12.3	11.5	9.7	10.4
177	$Si_4C_4H_{17}^+$	1.5	3.8	6.2	9.0	12.4	12.9	19.8	23.4

[a] The pressure of CH_3SiH_3 is 5.4×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Si. [c] Masses are calculated on ^1H, ^{12}C, and ^{28}Si.

time, which sometimes is preceded by a small increase in the first 10 ms, is shown by $SiC_2H_6^+$, $Si_2CH_n^+$ (n = 4–7), and $Si_2C_2H_n^+$ (n = 6,7) ions. Secondly, an initial increase of ion abundances is followed by a decrease after at least 40–50-ms reaction time ($Si_2C_2H_n^+$ (n = 8, 9), $Si_2C_3H_n^+$ (n = 8–10), $Si_3C_2H_n^+$ (n = 8–10), and $Si_3C_3H_n^+$ (n = 10–13)). Finally, the ionic abundances of $SiC_2H_7^+$, $Si_2C_2H_{11}^+$, $Si_2C_3H_n^+$ (n = 12, 13), $Si_3C_2H_{11}^+$, $Si_3C_4H_n^+$ (n = 15, 17), $Si_4C_3H_n^+$ (n = 14, 15, 17), and $Si_4C_4H_{17}^+$ increase up to 75–100-ms reaction time. It is worth noting that, in the large ionic families $SiC_nH_x^+$ (n = 0–2), $Si_2C_nH_x^+$ (n = 1–3), $Si_3C_nH_x^+$ (n = 2–4), and $Si_4C_nH_x^+$ (n = 3–5), n is always equal to the silicon coefficient plus or minus one. Moreover, within the same family the ionic species having the same number of carbon and silicon atoms are the most abundant ones at any time considered. The only exception is the $SiC_2H_7^+$ ion, which after 20-ms reaction time becomes the most abundant ion, its abundance being higher than those of the $SiCH_n^+$ (n = 2–5) ions.

Scheme I. Reaction Mechanisms of Si^+ and $SiCH_2^+$ Ions in CH_3SiH_3

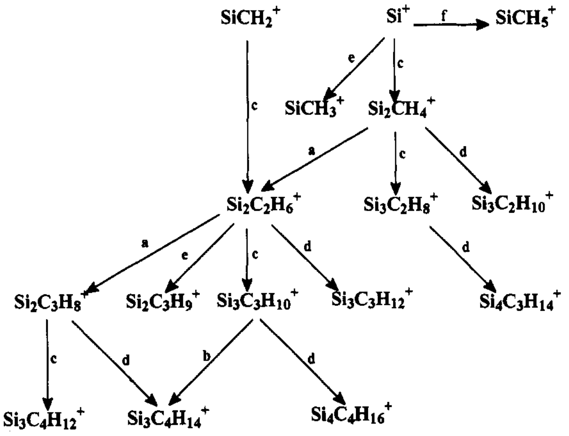


Table II. Labels on the Main Reaction Pathways As Reported in Schemes I–IV

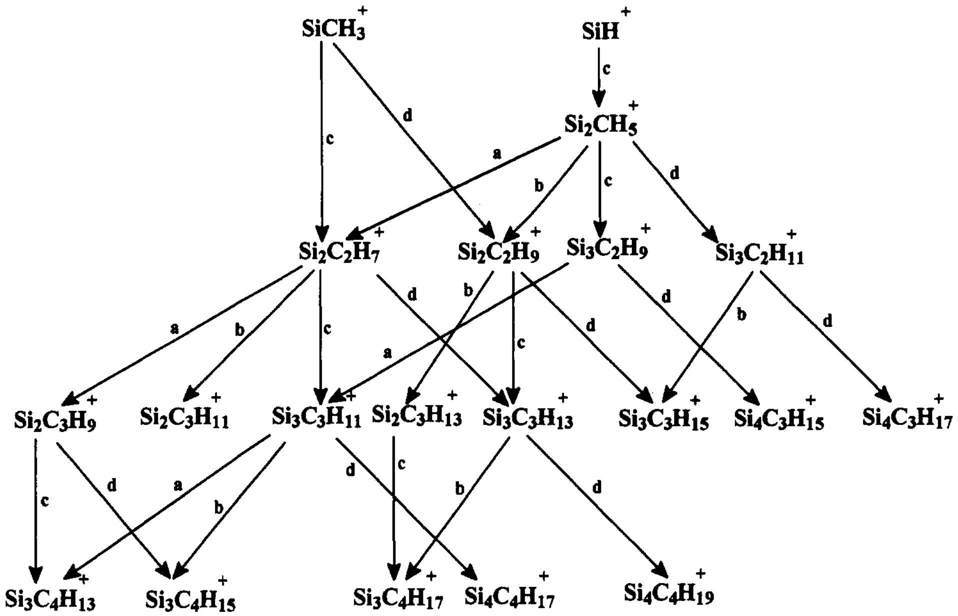
labels	neutral loss	labels	neutral loss
a	SiH_4	d	
b	SiH_2	e	SiH_3
c	H_2	f	SiH

The reaction pathways of the primary ions formed from CH_3SiH_3 are reported in four different schemes: Si^+ and $SiCH_2^+$ (Scheme I), SiH^+ and $SiCH_3^+$ (Scheme II), SiH_2^+ and $SiCH_4^+$ (Scheme III), SiH_3^+ and $SiCH_5^+$ (Scheme IV). The reaction sequences of the SiH_n^+ and $SiCH_{n+2}^+$ ions (n = 0–3) are reported in the same scheme when n is the same because the products of their ion–molecule reactions are mostly common. Moreover, $SiCH_4^+$ and $SiCH_5^+$ are also partially originated from SiH_2^+ and SiH_3^+, respectively. All schemes are built by isolating and storing the reactant ions for reaction times up to at least 100 ms. The reaction ionic products are identified and, again, isolated and stored for variable reaction times. This procedure is repeated until the instrumental sensitivity limits prevent reproducible results. The limitation in sensitivity is also the reason why not all the ions reported in Table I are present in the reaction sequences of Schemes I–IV.

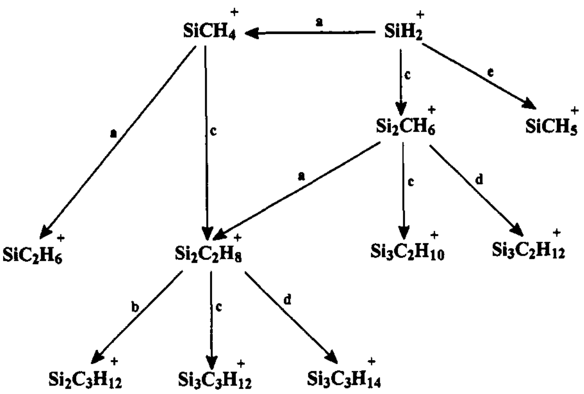
These schemes show that self-condensation processes of methylsilane take place through the four main reaction pathways, indicated as **a**–**d** (Table II). In pathway **a** the loss of a SiH_4 molecule is observed, while in pathway **b** a SiH_2 species is lost. In reaction **c** a hydrogen molecule is eliminated, and in **d** no neutral loss is displayed. In all cases, the isotopic pattern of the product ion was checked with respect to the precursor ion in order to determine if carbon or silicon atoms were added. The schemes show that primary ions having an odd number of hydrogen atoms (SiH^+ and $SiCH_3^+$, Scheme II; SiH_3^+ and $SiCH_5^+$, Scheme IV) form a higher number of product ions than primary ions without hydrogens or with even hydrogen atoms (Si^+ and $SiCH_2^+$, Scheme I; SiH_2^+ and $SiCH_4^+$, Scheme III). Moreover, SiH^+ ions decrease very quickly.

Products at m/z 191 and 193, formed in up to seven reaction steps, have been observed after times of 100 ms. However, these ions have not been reported in Scheme II, as they are so weak that it is impossible to univocally assign a formula. A different reaction pathway is present in Schemes I and III, in which Si^+ and SiH_2^+ reacting with CH_3SiH_3 give $SiCH_3^+$ and $SiCH_5^+$, respectively, eliminating the radical species SiH_3 (pathway **e**). Also $Si_2C_2H_6^+$ forms $Si_2C_3H_9^+$ through the same path **e**. Moreover, Si^+

Scheme II. Reaction Mechanisms of SiH^+ and $SiCH_3^+$ Ions in CH_3SiH_3



Scheme III. Reaction Mechanisms of SiH_2^+ and $SiCH_4^+$ Ions in CH_3SiH_3



Scheme IV. Reaction Mechanisms of SiH_3^+ and $SiCH_5^+$ Ions in CH_3SiH_3

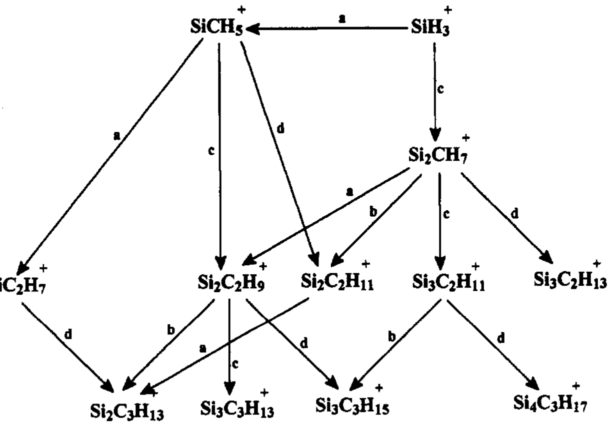


Table III. Relative Abundances of Significant Ions in the IT Mass Spectra of SiH_4[a] as a Function of the Reaction Time[b]

		reaction time (ms)							
m/z[c]	ions	0	10	20	30	40	50	75	100
28	Si^+	20.0	15.8	12.3	9.9	8.0	6.3	3.5	1.8
29	SiH^+	19.1	14.4	12.2	10.0	8.2	7.0	4.4	2.4
30	SiH_2^+	61.6	47.4	35.6	27.0	20.2	14.2	7.5	3.8
31	SiH_3^+	76.1	83.8	82.9	91.8	96.2	100	98.7	91.8
58	$Si_2H_2^+$	4.2	8.0	11.4	13.3	15.8	17.1	18.2	18.5
59	$Si_2H_3^+$	2.5	4.3	6.6	7.9	7.9	9.0	8.7	7.1
60	$Si_2H_4^+$	6.8	14.7	21.3	26.6	30.4	33.3	35.8	37.9
61	$Si_2H_5^+$	0.3	0.9	0.9	2.5	3.0	3.3	4.4	5.3
88	$Si_3H_4^+$		0.4	0.6	0.8	1.1	1.2	1.7	1.9
89	$Si_3H_5^+$		0.8	1.5	2.3	2.7	3.3	4.8	5.8
90	$Si_3H_6^+$			0.3	0.3	0.4	0.5		
91	$Si_3H_7^+$					0.3	0.3	0.4	
118	$Si_4H_6^+$							0.5	0.8
119	$Si_4H_7^+$					0.6	1.1	2.0	3.5

[a] The pressure of SiH_4 is 5.4×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Si. [c] Masses are calculated on ^1H and ^{28}Si.

reacts with CH_3SiH_3 to give $SiCH_5^+$ by eliminating a SiH radical species (pathway f).

Self-Condensation of SiH_4. Table III reports the relative abundance of the most significant ions in the ion trap mass spectra of SiH_4 at 5.4×10^{-7} Torr at different reaction times, from 0 to 100 ms. The most abundant ion at any time here examined is SiH_3^+ at 50-ms reaction time, and it is used as reference for the ionic abundances of all ions. Four ionic families are formed: SiH_n^+ (n = 0–3), $Si_2H_n^+$ (n = 2–5), $Si_3H_n^+$ (n = 4–7), and $Si_4H_n^+$ (n = 6, 7).

At zero reaction time the SiH_n^+ (n = 0–3) ionic species are the most abundant ones and transport 92.8% of the total ion current. After 100-ms reaction time, they transport only 55.2% of the total ion current, as the abundances of the SiH_n^+ (n = 0–2) ions sharply decrease. The SiH_3^+ ion does not follow the same trend, as its abundance is quite high all over the time range and reaches a maximum after 50-ms reaction time. All other ions behave in the same way, their abundances increasing continuously in the reaction time here considered. However, ions containing two silicon atoms are always more abundant than those with three Si, which, in turn, are more abundant than ions containing four Si.

Self-Condensation of CH_3GeH_3. In Table IV the relative abundances of the most significant ions in the ion trap mass spectra of CH_3GeH_3 at 4.0×10^{-7} Torr at reaction times ranging from 0 to 100 ms are reported. The most abundant ion at any time studied is $GeCH_5^+$ at 50-ms reaction time, and all ionic abundances refer to it. The most important ions are GeH_n^+ (n = 0–3), $GeCH_n^+$ (n =

Table IV. Relative Abundances of Significant Ions in the IT Mass Spectra of CH_3GeH_3[a] as a Function of the Reaction Time[b]

		reaction time (ms)							
m/z[c]	ions	0	10	20	30	40	50	75	100
70	Ge^+	35.7	29.4	25.1	16.5	13.2	11.9	6.5	3.4
71	GeH^+	21.7	16.1	13.0	10.7	9.8	8.0	5.0	4.4
72	GeH_2^+	34.4	21.0	12.3	11.0	9.5	9.1		
73	GeH_3^+	11.2	8.4	7.3	6.2	4.6	4.2		
83	$GeCH^+$	7.0	6.8	5.5	5.1	4.4	5.4	4.8	4.7
84	$GeCH_2^+$	10.4	9.4	9.8	8.3	7.6	6.1	5.6	3.5
85	$GeCH_3^+$	53.2	57.3	57.8	62.4	66.0	62.6	69.2	65.6
86	$GeCH_4^+$	39.4	36.8	36.5	33.0	29.6	24.9	15.4	10.7
87	$GeCH_5^+$	79.1	88.4	90.5	93.2	94.4	100	90.7	87.4
100	$GeC_2H_6^+$	2.1	2.9	3.3	3.6	6.7	5.9	8.1	8.6
101	$GeC_2H_7^+$	6.1	9.2	13.0	9.9	19.1	23.1	27.4	30.9
156	$Ge_2CH_4^+$	10.5	15.6	18.2	19.4	17.4	21.5	22.4	19.6
157	$Ge_2CH_5^+$	8.5	12.2	14.7	16.7	17.9	15.3	17.1	14.5
170	$Ge_2C_2H_6^+$	5.1	8.8	10.5	22.0	24.7	31.7	29.9	35.2
171	$Ge_2C_2H_7^+$		1.5	2.9	8.9	11.3	10.8	6.5	5.3
255	$Ge_3C_3H_9^+$		1.8	2.9	2.9	3.3	4.5	6.2	6.5
258	$Ge_3C_3H_{12}^+$		2.5	4.6	6.6	8.4	9.7	22.0	25.7

[a] The pressure of CH_3GeH_3 is 4.0×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Ge. [c] Masses are calculated on ^1H, ^{12}C, and ^{70}Ge.

1–5), $GeC_2H_n^+$ (n = 6, 7), $Ge_2CH_n^+$ (n = 4, 5), $Ge_2C_2H_n^+$ (n = 6, 7), and $Ge_3C_3H_n^+$ (n = 9, 12).

At zero reaction time, the most abundant ions are GeH_n^+ (n = 0–3) and $GeCH_n^+$ (n = 1–5), which transport the main fraction of the total ion current (90.0%). As the self-condensation processes take place from 0- to 100-ms reaction time, the abundances of the GeH_n^+ (n = 0–3) ions decrease from 31.7% to 2.4% of the total ion current, while those of the $GeCH_n^+$ (n = 1–5) ionic family decrease only from 58.3% to 52.7%. This different behavior is mainly due to the abundant $GeCH_3^+$ and $GeCH_5^+$ ions, whose abundances are rather constant during the time considered (16.4% and 20.1% of the total ion current for $GeCH_3^+$, 24.4% and 26.8% for $GeCH_5^+$).

As in the case of methylsilane, three different behaviors can be identified. The abundances of some ions continuously decrease from 0- to 100-ms reaction time, i.e. GeH_n^+ (n = 0–3) and $GeCH_n^+$ (n = 1, 2, 4). Other ionic abundances are almost constant during all the reaction times considered ($GeCH_n^+$ (n = 3, 5) and $Ge_2CH_n^+$ (n = 4, 5)), while the remaining ions show abundances which increase up to reaction times of 100 ms ($GeC_2H_n^+$ (n = 6, 7), $Ge_2C_2H_6^+$, $Ge_3C_3H_n^+$ (n = 9, 12)). Moreover, within the ionic families $GeC_nH_x^+$ (n = 0–2), $Ge_2C_nH_x^+$ (n = 1, 2), and $Ge_3C_nH_x^+$ (n = 2–4), the most abundant ions, at any time here studied, have the same number of carbon and germanium atoms.

The self-condensation reaction mechanisms of CH_3GeH_3 have been reported previously,[11] and it is worth mentioning the most significant pathways. The primary GeH_n^+ ions react with neutral CH_3GeH_3 to give $GeCH_x^+$ ions. Also the $Ge_2CH_x^+$ ionic species are formed with elimination of one or more hydrogen molecules. The $GeCH_n^+$ ions, which are formed in both primary and secondary processes, in turn react with CH_3GeH_3, yielding $Ge_2C_2H_6^+$ (n = 3), $GeC_2H_7^+$, and $GeC_3H_9^+$.

Self-Condensation of GeH_4. In Table V the relative abundances of the most significant ions in the ion trap mass spectra of GeH_4 at 4.0×10^{-7} Torr at reaction times ranging from 0 to 100 ms are reported. All ionic abundances refer to the most abundant ion at any time here considered, which is GeH_3^+ at 100-ms reaction time.

Table V. Relative Abundances of Significant Ions in the IT Mass Spectra of GeH_4[a] as a Function of the Reaction Time[b]

		reaction time (ms)							
m/z[c]	ions	0	10	20	30	40	50	75	100
70	Ge^+	26.8	24.7	23.7	21.8	21.3	20.4	14.4	11.3
71	GeH^+	14.1	14.1	13.7	13.4	11.8	10.5	8.1	6.4
72	GeH_2^+	47.8	45.0	37.8	34.9	30.2	26.4	17.9	14.2
73	GeH_3^+	67.7	76.2	84.7	85.1	94.3	95.3	97.6	100
142	$Ge_2H_2^+$	10.5	17.5	21.5	24.5	29.9	34.9	43.8	50.7
143	$Ge_2H_3^+$	1.9	3.5	7.6	7.9	11.4	13.5	14.8	16.4
144	$Ge_2H_4^+$	6.1	7.8	10.4	14.5	14.2	19.7	24.0	29.3

[a] The pressure of GeH_4 is 4.0×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the species containing all the isotopes of Ge. [c] Masses are calculated on ^1H and ^{70}Ge.

Only two ionic families are present, GeH_n^+ (n = 0–3) and $Ge_2H_n^+$ (n = 2–4), their abundances following the same trend described above for the self-condensation of SiH_4. In fact, in the reaction time from 0 to 100 ms, the abundances of the GeH_n^+ (n = 0–2) ions strongly decrease; that of GeH_3^+ is generally high, reaching a maximum after 100 ms and decreasing at longer reaction times; and those of the $Ge_2H_n^+$ (n = 2–4) ionic species continuously increase. The $Ge_2H_5^+$ ion is never observed up to 100-ms reaction time, but is formed in small amounts at longer times.

Discussion

Four main reaction pathways can be identified in self-condensation processes of CH_3SiH_3. In reaction sequence **a**, an increase of 14 mass units is observed between the reacting and the product ions, which can be assigned to CH_2:

$$Si_nC_mH_x^+ + CH_3SiH_3 \rightarrow Si_nC_{m+1}H_{x+2}^+ + SiH_4 \qquad (1)$$

In reaction 1, the neutral loss consists of a stable SiH_4 molecule. Due to the lack of thermochemical data, such as heats of formation, of the ionic species containing carbon and silicon atoms together, it is not possible to make calculations on the energetics of processes involving these types of ions. However, some general considerations can be drawn. In fact, the heats of formation of CH_3SiH_3 and SiH_4 in the gas phase are known to be −7 ± 1 and +8 kcal/mol,[21] respectively. Therefore, this reaction pathway is exothermic when the enthalpy of formation of the product ion is at least 15 kcal/mol lower than that of the reacting ion. The heats of formation of the ionic species SiH_n^+ and $SiCH_{n+2}^+$ (n = 1–3) are reported in the literature,[22,23] and the enthalpies of the reactions

$$SiH_n^+ + CH_3SiH_3 \rightarrow SiCH_{n+2}^+ + SiH_4 \qquad (2)$$

can be calculated: for $n = 1$, $\Delta H^0_r = +15 \pm 5$ kcal/mol; for $n = 2$, $\Delta H^0_r = +2 \pm 5$ kcal/mol; for $n = 3$; $\Delta H^0_r = +4 \pm 5$ kcal/mol.

When n = 2 or 3, the a process takes place, while it does not occur when n = 1, in agreement with thermodynamic results reported above.

Reaction pathway **b** is more intriguing to understand. In fact, the mass increase is of 16 units and it means that the neutral fragment should weigh 30 units, the reacting

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(21) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl.* **1988**, 17.

(22) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruscic, B. *J. Chem. Phys.* **1987**, *86*, 1235.

(23) Potzinger, P.; Lampe, F. W. *J. Phys. Chem.* **1970**, *74*, 587.

molecule being CH_3SiH_3 (MW = 46). In this case, two reactions are possible:

$$\mathrm{Si}_n\mathrm{C}_m\mathrm{H}_x^+ + \mathrm{CH_3SiH_3} \rightarrow \mathrm{Si}_n\mathrm{C}_{m+1}\mathrm{H}_{x+4}^+ + \mathrm{SiH_2} \qquad (3)$$

$$\mathrm{Si}_n\mathrm{C}_m\mathrm{H}_x^+ + \mathrm{CH_3SiH_3} \rightarrow \mathrm{Si}_{n+1}\mathrm{C}_{m-1}\mathrm{H}_x^+ + \mathrm{C_2H_6} \qquad (4)$$

Even if the heats of formation of all the species involved in these pathways are not known, it is evident that the relative enthalpy of the two reactions (3) and (4) only depends on the heat of formation of the products, the reagent species being the same. The difference between the neutral species is about 85 kcal/mol, as the heat of formation of SiH_2 is 65.6 ± 0.7 kcal/mol[22] and that of C_2H_6 is −20.1 ± 0.05 kcal/mol.[21] In the hypothesis that the enthalpies of formation of the two ionic species, $Si_nC_{m+1}H_{x+4}^+$ and $Si_{n+1}C_{m-1}H_x^+$, do not differ as much as 85 kcal/mol, reaction pathway 4 should be energetically favored with respect to pathway 3. Actually, it has been experimentally shown that the reaction proceeds through sequence 3. In fact, by isolation of the reacting ion and consideration of the isotopic pattern of the product ion, it has been observed that the number of silicon atoms does not change. Moreover, also ions which do not contain any carbon atoms give this reaction, which makes sequence 4 impossible. A tempting explanation of this behavior concerns the reaction intermediates. In reaction 3 it can be hypothesized that the carbon atom of methylsilane interacts with a carbon or silicon atom of the reacting ion, forming a linear intermediate. In pathway 4, elimination of C_2H_6 implies formation of an intermediate by interaction of the carbon atom of methylsilane with a terminal carbon atom of the $Si_nC_mH_x^+$ ion and simultaneous interaction of the silicon atom of methylsilane with a carbon or silicon atom of the reacting ion.

The **c** pathway takes place by elimination of an H_2 molecule:

$$\mathrm{Si}_n\mathrm{C}_m\mathrm{H}_x^+ + \mathrm{CH_3SiH_3} \rightarrow \mathrm{Si}_{n+1}\mathrm{C}_{m+1}\mathrm{H}_{x+4}^+ + \mathrm{H_2} \qquad (5)$$

It is impossible to rationalize thermodynamically this process, as the heats of formation of the product ions are not available in the literature even when $n = 1$ and $m = 0$. However, pathway 5 seems to be the most favored one being given by almost all ions present in the self-condensation processes of CH_3SiH_3. As suggested previously,[20] the ejected hydrogen comes from the breakdown of silicon–hydrogen bonds.

The formation of adduct ions (pathway **d**), in which a CH_3SiH_3 molecule is added to an ion without elimination of any neutral species, often takes place:

$$\mathrm{Si}_n\mathrm{C}_m\mathrm{H}_x^+ + \mathrm{CH_3SiH_3} \rightarrow \mathrm{Si}_{n+1}\mathrm{C}_{m+1}\mathrm{H}_{x+6}^+ \qquad (6)$$

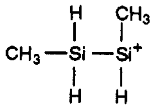
Similar association processes have already been observed in tandem mass spectrometry at 1.0×10^{-3} Torr[20] and in Fourier transform mass spectrometric studies[24-27] on sequential clustering reactions of SiH_n^+ and SiD_n^+ (n = 0–3) with SiH_4 and SiD_4, respectively. In these last cases, it has been hypothesized that the association intermediate complex is stabilized by collision with a third body (SiH_4 or SiD_4 at (1–4) × 10^{-7} Torr), instead of by elimination of a neutral fragment. Therefore, this mechanism is even more probable at 7.0×10^{-5} Torr total pressure, used in this study.

It is noteworthy that ions with the same formulas are sometimes originated through pathways **d** and **b** from different precursors. For example, in Scheme II $Si_2C_2H_9^+$ is shown to be given by both $SiCH_3^+$, path **d**, and $Si_2CH_5^+$, path **b**. We suggest that in both reactions 7 and 8 the neutral CH_3SiH_3 molecule is linked as a whole moiety and that the SiH_2 species lost in pathway **b** (8) comes from the reacting ion.

$$\mathrm{SiCH_3^+} + \mathrm{CH_3SiH_3} \rightarrow \mathrm{SiCH_3{\cdot}CH_3SiH_3^+} \qquad (7)$$

$$\mathrm{Si_2CH_5^+} + \mathrm{CH_3SiH_3} \rightarrow \mathrm{H_2Si{-}SiCH_3{\cdot}CH_3SiH_3^+} \rightarrow \mathrm{SiH_2} + \mathrm{SiCH_3{\cdot}CH_3SiH_3^+} \qquad (8)$$

Moreover, it may occur that ions with the same formulas have different structures. As reported above, $Si_2C_2H_9^+$ in Scheme II is an adduct ion which can be reformulated as $SiCH_3{\cdot}CH_3SiH_3^+$, while $Si_2C_2H_9^+$ from $SiCH_5^+$ through pathway **c** (Scheme IV) is likely to have the structure reported in (9), according to previously reported data[20] which localize the positive charge of the ion on a silicon atom.



$$\mathrm{CH_3{-}SiH_2{-}Si^+H(CH_3)} \qquad (9)$$

Collision induced dissociation experiments have been performed on a variety of ions with *m/z* 59, 87, 89, 105, 121, and 133, which have been chosen as their composition was doubtful, and our hypotheses have been confirmed. In all these experiments ejection of one or more hydrogen molecules from the ion under exam, followed by loss of diagnostic fragments, is observed. In particular, under different excitation conditions, $Si_2C_2H_9^+$ (*m/z* 89) gives rise to a very abundant signal at *m/z* 43, CH_3Si^+, with an easy elimination of CH_3SiH_3, or to a rather weak signal at *m/z* 59, $(CH_3)_2SiH^+$, which can derive from the species (9) by transfer of a methyl group and a breakdown of the Si–Si bond. On the contrary, $Si_3C_2H_{13}^+$, originated only by a **d** process from $Si_2CH_7^+$ (Scheme IV), gives only one collision induced decomposition process to form again its precursor $Si_2CH_7^+$ by an easy elimination of CH_3SiH_3.

The self-condensation processes of SiH_4 have been already published.[19,24-27] The Si^+, SiH^+, SiH_2^+, and SiH_3^+ primary ions react with neutral silane by elimination of a hydrogen molecule to give, respectively, the ions $Si_2H_2^+$, $Si_2H_3^+$, $Si_2H_4^+$, and $Si_2H_5^+$, containing two silicon atoms. Subsequent condensation steps lead to the formation of clusters containing three and four silicon atoms and always occur with ejection of H_2. It is worth noting that the largest ionic clusters detected in both SiH_4 and CH_3SiH_3 systems never contain more than four silicon atoms, under the experimental conditions here used. The same behavior has been previously observed in the self-condensation reactions of SiH_4 and SiD_4,[24-27] where the $Si_4H_n^+$ (n = 6–9) ions are considered bottleneck structures. They react only very slowly, and it has been calculated that further aggregation of the $Si_4D_6^+$ ion, formed in three sequential clustering reactions of Si^+ with SiD_4,[24] takes place at a rate which is 3 orders of magnitude slower than the first three reaction steps.

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(24) Mandich, M. L.; Reents, W. D., Jr.; Jarrold, M. F. *J. Chem. Phys.* **1988**, *88*, 1703.

(25) Reents, W. D., Jr.; Mandich, M. L. *J. Chem. Phys.* **1992**, *96*, 4429.

(26) Mandich, M. L.; Reents, W. D., Jr.; Kolebrander, K. D. *J. Chem. Phys.* **1990**, *92*, 437.

(27) Mandich, M. L.; Reents, W. D., Jr. *J. Chem. Phys.* **1991**, *95*, 7360.

Considering CH_3SiH_3 and SiH_4, the trend of the variations with reaction time of the relative abundances indicates a higher reactivity of the methyl hydride with respect to the hydride in gas phase ion–molecule reactions. In fact, under the same experimental conditions, the abundances of the primary ions decrease more rapidly and the secondary ions are more abundant in the CH_3SiH_3 system than in the SiH_4 one. Moreover, at zero reaction time, ions containing three silicon atoms are already formed by the self-condensation of methylsilane, while they are very weak in silane.

A very similar trend is observed by comparing the ionic abundances and their variation with reaction time for CH_3GeH_3 and GeH_4. Primary ions of methylgermane decrease faster than the corresponding ones of germane, and more abundant product ions are formed in the former system. In particular, ions containing three germanium atoms are observed only in CH_3GeH_3, under the experimental conditions here used. Again, this behavior suggests that CH_3GeH_3 is more reactive than GeH_4.

Moreover, comparing the silicon containing systems with the corresponding germanium containing ones, it is evident that a much higher number of ionic species is formed in self-condensation reactions of both CH_3SiH_3 and SiH_4 with respect to CH_3GeH_3 and GeH_4. This can be the reason ions containing only up to three germanium atoms with respect to ions containing four silicon atoms are observed in similar experimental conditions. However, in a previous mass spectrometric study on self-condensation reactions of monogermane,[18] at a GeH_4 pressure of 0.1 Torr, ions were formed containing up to four germanium atoms.

Results concerning only the two methyl hydrides, which can be used in the radiolytical preparation of amorphous materials, containing C and Si or C and Ge, important in photovoltaic technology, are of great interest. It can be seen that CH_3SiH_3 polymerizes more readily than CH_3GeH_3, showing a higher tendency to form cluster ions with increasing dimensions, which represent the precursors of the solid material deposited in radiolytical processes.

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