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Gas-phase ion chemistry of silane with ethane and ethyne

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Abstract

Silane–ethane and silane–ethyne systems have been studied by ion trap mass spectrometry and the variation of the abundances, with reaction time, of the ions containing silicon and carbon together in 5:1, 1:1 and 1:5 mixtures, have been reported. The best ion yield, which increases with the total pressure, is observed for 1:1 silane–ethyne mixture. Reaction mechanisms and rate constants of the first nucleation processes have been determined. In SiH_4–C_2H_2 systems, the formation of ions containing new Si–C bonds occurs starting mainly from $Si_mH_n^+$ ions in the first steps, whereas the $Si_mC_nH_p^+$ cluster species further reacts with high efficiency in processes with ethyne. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ion chemistry; Gas-phase; Silane; Ethane; Ethyne; Mass spectrometry

1. Introduction

The interaction and reactivity of ions and molecules in gaseous systems containing silane and small saturated and unsaturated hydrocarbon molecules have been investigated by both experimental and theoretical methods [1–7]. This research allows the mechanisms of formation of chemical bonds between silicon and carbon in species identified in interstellar clouds [8,9] to be simulated, and in general, provides information on the intrinsic reactivity of ions in the absence of perturbations due to solvents or counterions [10–15]. Moreover, knowledge of the mechanisms and rate constants of ion–molecule reactions for the formation of hydrogenated clusters containing silicon and carbon is interesting from an applicative point of view. In fact, these ion species can be considered the charged precursors of amorphous silicon carbides. These are semiconducting materials with properties depending on the composition, and can be prepared by deposition from appropriate mixtures suitably activated [16,17].

In this paper we report results on: (i) the trends of abundances of ions containing new Si–C bonds, as a function of the partial pressures of the reagents, the total pressure and reaction time; (ii) the mechanisms of chain propagation in silane–ethane and silane–ethyne systems, obtained by ion trap mass spectrometry. The rate constants of the main ion–molecule reactions are determined as well and compared with the collisional rate constants calculated by the Langevin theory [18]. A number of ion–molecule reactions observed in these systems have been studied previously in experiments carried out under rather different conditions [2,3].

2. Results and discussion

2.1. Silane–ethane mixtures

Variations of the total abundances of all the ions containing both silicon and carbon (mixed ions) for three SiH_4–C_2H_6 mixtures (5:1, 1:1 and 1:5 ratios of partial pressure of the reagents) are reported at the total pressure of 1.0×10^{-6} Torr, as a function of reaction time (Fig. 1). The best yield of all the mixed ions is given by the mixture with equal partial pressures, whilst an excess of C_2H_6 slightly lowers their relative abundances and an excess of SiH_4 strongly decreases them.

The reaction mechanisms have been studied through isolation steps of single ion species and identification of

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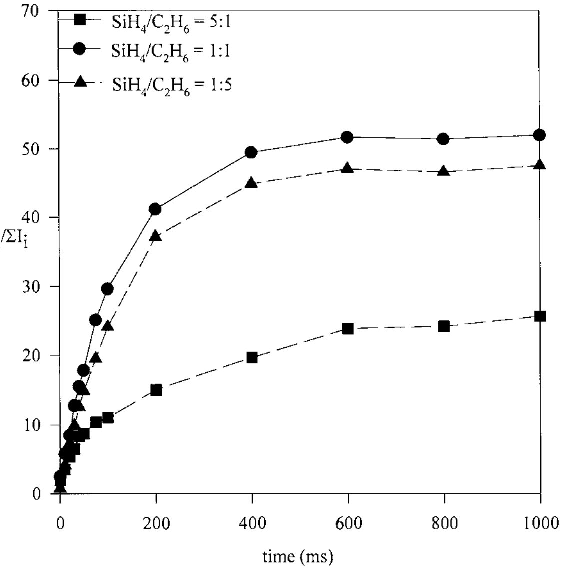


Fig. 1. Variation of total abundances with reaction time for silicon and carbon containing ions in SiH_4–C_2H_6 mixtures at 1.0×10^{-6} Torr total pressure.

their charged products. In some cases, ionization of the two reagents gives isobaric primary ions, such as Si^+ and $C_2H_4^+$ at m/z 28; SiH^+ and $C_2H_5^+$ at m/z 29; SiH_2^+ and $C_2H_6^+$ at m/z 30. The reaction mechanisms starting from these species have been elucidated by experiments with the pulse valve and, therefore, with just one reagent in the trap during the ionization step.

The SiH_n^+ ($n = 0$–3) primary ions of SiH_4 react with C_2H_6 to give the $SiC_2H_n^+$ ($n = 6$, 7) ions. These products are formed by reaction of C_2H_6 with SiH_2^+ and SiH_3^+, respectively, with ejection of a hydrogen molecule, while a small contribution to the abundance of $SiC_2H_6^+$and $SiC_2H_7^+$ is also given by addition of a molecule of ethane to Si^+ and SiH^+, without elimination of a neutral moiety. Moreover, Si^+ gives $SiCH_3^+$ and a methyl group, and SiH_3^+ forms $SiC_2H_5^+$ with elimination of two hydrogen molecules.

The $Si_2H_n^+$ ions, originated by self-condensation of SiH_4, react with ethane too, yielding ions containing silicon and carbon together. In particular, $Si_2H_4^+$ and $Si_2H_5^+$ give $Si_2C_2H_6^+$ and $Si_2C_2H_7^+$, respectively, and eliminate two hydrogen molecules. Peaks observed at m/z 84 and 85 are likely due to $Si_2C_2H_4^+$ and $Si_2C_2H_5^+$, respectively, which can originate in similar pathways, such as:

$$Si_2H_n^+ + C_2H_6 \rightarrow Si_2C_2H_{n+2}^+ + 2H_2 \qquad (n = 2, 3) \qquad (1)$$

or from the isobaric $SiC_2H_n^+$ ($n = 6$, 7) ions, according to the following reaction:

$$SiC_2H_n^+ + SiH_4 \rightarrow Si_2C_2H_{n-2}^+ + 3H_2 \qquad (n = 6, 7) \qquad (2)$$

However, the latter path is unlikely, as it involves the elimination of three neutral fragments. Moreover, a contribution from the $SiC_4H_8^+$ and $SiC_4H_9^+$ ions to the peaks at m/z 84 and 85 through the reaction:

$$SiC_2H_n^+ + C_2H_6 \rightarrow SiC_4H_{n+2}^+ + 2H_2 \qquad (n = 6, 7) \qquad (3)$$

cannot be ruled out by experimental evidence, as both reactant and product ions of the reactions (1)–(3) have the same m/z value. Experiments using pulse valve or double isolation steps are not useful, as $Si_2H_2^+$ and $SiC_2H_6^+$ are both formed from Si^+, just as $Si_2H_3^+$ and $SiC_2H_7^+$ are given by SiH^+.

The primary $C_2H_n^+$ ($n = 1$–6) ions of C_2H_6 react with SiH_4 to give the SiH_n^+ ($n = 0$–3) ion family and alkyl radicals or hydrocarbon molecules. A parallel reaction path forms the $SiC_2H_n^+$ ($n = 3$–7) ions with elimination of one or two hydrogen molecules. In Table 1, the rate constants of the ion–molecule reactions of $C_2H_n^+$ ($n =$ 2, 3) with SiH_4 and of $Si_2H_4^+$ with C_2H_6 are reported. The rate constants of other processes observed in this system could not be determined, either because they are too low to give reproducible results, or because the pressure is not constant in the experiments carried out with the pulse valve.

Table 1 also reports the reaction enthalpies, or their limits, of ion–molecule reactions involving species whose formation enthalpies are known from the literature [3,21–23]. The data show that all the processes observed are thermodynamically favoured.

Table 1
Rate constants for reactions of $C_2H_2^+$ and $C_2H_3^+$ ions with SiH_4 and of the $Si_2H_4^+$ ions with C_2H_6 in SiH_4–C_2H_6 systems [a]

Reaction		k_{exp}	Σk_{exp}	k_L [b]	Efficiency [c]	ΔH°_{298} [d]
$C_2H_2^+ + SiH_4$	$\rightarrow SiH_2^+ + C_2H_4$	2.6				−36.8
	$\rightarrow SiH_3^+ + C_2H_3$	1.3				−24.9
	$\rightarrow SiC_2H_4^+ + H_2$	1.1	5.0	12.85	0.39	< -50.4
$C_2H_3^+ + SiH_4$	$\rightarrow SiH_3^+ + C_2H_4$	3.2				−24.3
	$\rightarrow SiC_2H_5^+ + H_2$	2.1	5.3	12.72	0.42	−43.6
$Si_2H_4^+ + C_2H_6$	$\rightarrow Si_2C_2H_6^+ + 2H_2$	2.6	2.6	11.05	0.24	

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

[b] Rate constants have been calculated according to the Langevin theory [18] taking the polarizability of SiH_4 from [19] and of C_2H_6 from [20].

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

[d] Enthalpies are expressed in kcal mol^{-1} and have been calculated with heats of formation taken from [3,21–23].

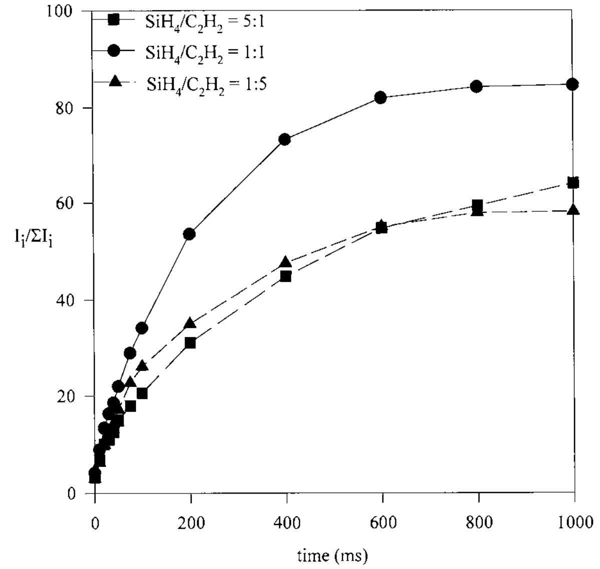


Fig. 2. Variation of total abundances with reaction time for silicon and carbon containing ions in SiH_4–C_2H_2 mixtures at 8.0×10^{-7} Torr total pressure.

2.2. Silane–ethyne mixtures

In Figs. 2 and 3 the variations of the abundances of all the ions containing both silicon and carbon are reported, as a function of reaction time, for three SiH_4–C_2H_2 systems (5:1, 1:1 and 1:5 ratios of partial pressure of the two reagents) at total pressures of 8.0×10^{-7} and $2.4x10^{-6}$ Torr, respectively. The increase of total pressure raises the yield of the $Si_mC_nH_p^+$ ions at any ratio of reagent partial pressures. At 2.4×10^{-6} Torr, the highest ion abundances are exhibited by the 1:1 mixture and the lowest ones by the mixture with an excess of ethyne.

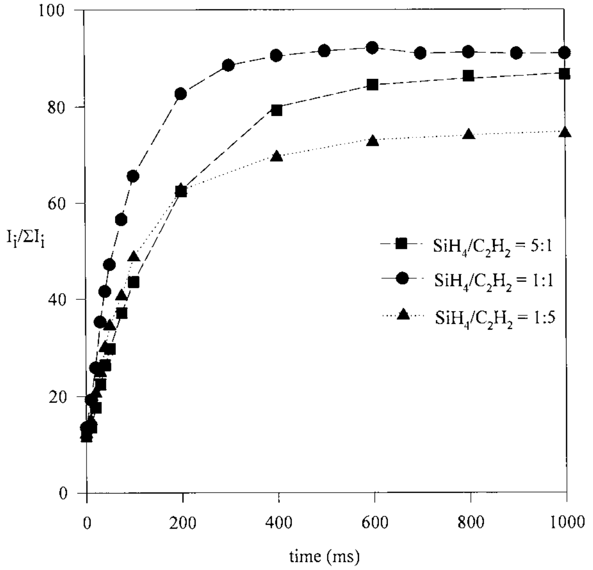


Fig. 3. Variation of total abundances with reaction time for silicon and carbon containing ions in SiH_4–C_2H_2 mixtures at 2.4×10^{-6} Torr total pressure.

A comparison of the trends of total ion abundances reported in Fig. 1 (silane–ethane) and Fig. 2 (silane–ethyne) shows a higher reactivity of ethyne with respect to ethane. This behaviour is not surprising basing on the presence of π electrons in ethyne, which enhance its reactivity with respect to ethane [10]. Moreover, in both systems the best yield of mixed ions is obtained in the 1:1 mixture, but an excess of ethyne reduces the abundances of mixed ions in the SiH_4–C_2H_2 mixture by a larger extent than an excess of ethane does in the SiH_4–C_2H_6 one.

The primary ions of silane SiH_n^+ ($n = 0$–3) react with C_2H_2 to originate the $SiC_2H_n^+$ ($n = 1, 3$) ions and with SiH_4 to give the usual $Si_2H_n^+$ ($n = 2$–5) ion species in self-condensation processes. Formation of $SiC_2H_n^+$ ($n = 1, 3$) occurs with good efficiencies from SiH^+ and SiH_2^+, respectively, as it can be seen from Table 2, where the rate constants of the main ion–molecule reactions of SiH_n^+, $Si_2H_n^+$ and $Si_3H_5^+$ ions with C_2H_2 are shown. Moreover, formation of $SiCH_3^+$ is also observed in the reaction of SiH^+ with ethyne. The values of the self-condensation rate constants of SiH_4, obtained in these experiments, are also reported in Table 2 and are in good agreement with the data published in the literature [11,15,27]. The secondary $Si_2H_n^+$ ($n = 2$–5) ions are involved in self-condensation reactions to give the $Si_3H_n^+$ ($n = 4$–7) species and react with ethyne to form the $Si_2CH_n^+$ ($n = 1$–3) and $Si_2C_2H_n^+$ ($n = 2, 3, 5$) ion families. As shown in Scheme 1, where the reaction pathways of SiH^+ are reported as an example, the third reaction step starting from $Si_3H_5^+$ and neutral C_2H_2 leads to the Si_2CH^+ ions, also formed from $Si_2H_3^+$, and to the most abundant $Si_3C_2H_3^+$ ions with elimination of two hydrogen molecules. These reactions show rather high rate constants. All the $Si_3H_n^+$ ($n = 4$–7) species exhibit a similar behaviour and the $Si_3C_2H_n^+$ ($n = 2$–5) ions are important charged products containing silicon and carbon together. Reaction of $Si_3H_5^+$ with C_2H_2 also gives $Si_2C_2H_3^+$, from which $Si_2C_2H^+$ is formed in a successive step. This is an example of a general process encountered in this system, in which ethyne extracts two hydrogen atoms from a charged species to give a molecule of ethene.

The chain propagation proceeds further, mainly from ions containing only silicon and hydrogen. The $Si_4H_7^+$ species, formed in self-condensation of $Si_3H_5^+$, react in two successive steps leading to $Si_4C_2H_5^+$ and $Si_5C_2H_7^+$, respectively. The former product is obtained in the reaction with C_2H_2 and subsequent elimination of two H_2 molecules, and the latter in a second reaction with SiH_4 followed by elimination of one H_2 molecule. Furthermore, $Si_4C_2H_5^+$ is involved in two parallel addition processes with both SiH_4 and C_2H_2, to give $Si_5C_2H_9^+$ and $Si_4C_4H_7^+$, respectively, without elimination of neu-

Table 2
Rate constants for reactions of SiH_n^+, $Si_2H_n^+$ and $Si_3H_5^+$ ions with C_2H_2 and SiH_4 in SiH_4–C_2H_2 systems [a]

Reaction	k_{exp}	Σk_{exp}	k_L [b]	Efficiency [c]	ΔH°_{298} [d]
$Si^+ + C_2H_2 \rightarrow SiC_2H^+ + H$	3.2	3.2	11.61	0.28	< -11.5
$+ SiH_4 \rightarrow Si_2H_2^+ + H_2$	6.5	6.5	12.59	0.52	-19.1
$SiH^+ + C_2H_2 \rightarrow SiC_2H^+ + H_2$	8.4	8.4	11.51	0.73	< -40
$+ SiH_4 \rightarrow Si_2H_3^+ + H_2$	7.8	7.8	12.47	0.63	-15.5
$SiH_2^+ + C_2H_2 \rightarrow Si^+ + C_2H_4$	2.0				-21
$\rightarrow SiC_2H_3^+ + H$	7.5	9.5	11.41	0.83	-26.5
$+ SiH_4 \rightarrow SiH_3^+ + SiH_3$	5.5				1.5
$\rightarrow Si_2H_4^+ + H_2$	7.3	12.8	12.36	1.04	-16.1
$SiH_3^+ + C_2H_2 \rightarrow SiH^+ + C_2H_4$	2.3				-5.6
$\rightarrow SiC_2H_3^+ + H_2$	0.83	3.1	11.32	0.28	-39.5
$+ SiH_4 \rightarrow Si_2H_5^+ + H_2$	0.5	0.50	12.26	0.04	-16.1
$Si_2H_2^+ + C_2H_2 \rightarrow Si_2CH^+ + CH_3$	6.0				
$\rightarrow Si_2C_2H_2^+ + H_2$	0.42				
$\rightarrow Si_2C_2H_3^+ + H$	0.79	7.2	10.05	0.72	
$+ SiH_4 \rightarrow Si_3H_4^+ + H_2$	0.35	0.35	10.71	0.03	< -29
$Si_2H_3^+ + C_2H_2 \rightarrow Si_2CH^+ + CH_4$	0.86				
$\rightarrow Si_2CH_2^+ + CH_3$	1.2				$+13.3$
$\rightarrow Si_2C_2H_3^+ + H_2$	2.4	4.5	10.03	0.45	
$+ SiH_4 \rightarrow Si_3H_5^+ + H_2$	3.4	3.4	10.68	0.32	< -34
$Si_2H_4^+ + C_2H_2 \rightarrow SiC_2H_3^+ + SiH_3$	0.43				-22
$\rightarrow Si_2H_2^+ + C_2H_4$	3.9				-24
$\rightarrow Si_2CH_3^+ + CH_3$	0.91				-29.7
$\rightarrow Si_2C_2H_4^+ + H_2$	1.4				
$\rightarrow Si_2C_2H_5^+ + H$	1.3	7.9	10.01	0.79	$< +5.6$
$+ SiH_4 \rightarrow Si_3H_6^+ + H_2$	0.2	0.20	10.65	0.02	$< +3$
$Si_2H_5^+ + C_2H_2 \rightarrow SiC_2H_3^+ + SiH_4$	0.24				-23.5
$\rightarrow Si_2H_3^+ + C_2H_4$	2.9				-5
$\rightarrow Si_2C_2H_5^+ + H_2$	5.1	8.2	9.98	0.83	
$+ SiH_4 \rightarrow Si_3H_7^+ + H_2$	0.62	0.62	10.62	0.06	
$Si_3H_5^+ + C_2H_2 \rightarrow Si_2CH^+ + SiCH_6$	2.5				
$\rightarrow Si_3H_3^+ + C_2H_4$	1.0				
$\rightarrow Si_3C_2H_3^+ + 2H_2$	4.0				
$\rightarrow Si_2C_2H_3^+ + SiH_4$	0.53	8.0	8.12	0.99	
$+ SiH_4 \rightarrow Si_4H_7^+ + H_2$	4.0	4.0	10.03	0.40	

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

[b] Rate constants have been calculated according to the Langevin theory [18] taking polarizability of C_2H_2 from [20] and of SiH_4 from [19].

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

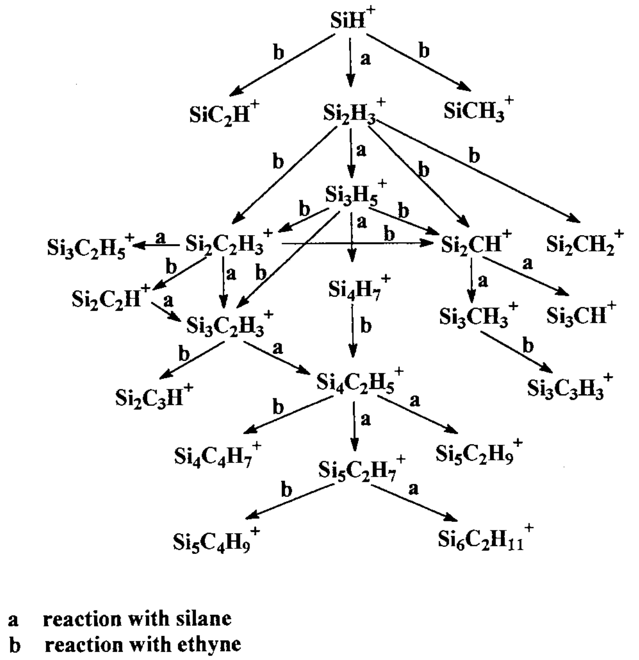
[d] Enthalpies are expressed in kcal mol^{-1} and have been calculated with heats of formation taken from [3,21–26].

tral species. A similar reaction pattern is displayed by $Si_5C_2H_7^+$, which gives $Si_6C_2H_{11}^+$ and $Si_5C_4H_9^+$. Again no neutral species are eliminated in these processes.

The primary ions of C_2H_2, $C_2H_n^+$ ($n = 0$–2), react with silane, leading to the SiH_n^+ ($n = 0$–3) and $SiC_2H_n^+$ ($n = 3$–5) ion families. Both C_2H^+ and $C_2H_2^+$ ions show high total efficiencies and relatively high rate constants for the reaction channels leading to silicon and carbon containing ions (see Table 3). Self-condensation of ethyne gives the $C_4H_2^+$ and $C_4H_3^+$ species, which also lead to ions containing new Si–C bonds, with formula $SiC_2H_n^+$ ($n = 1$–5) and $SiC_4H_5^+$. Very high efficiencies are obtained for reactions starting from $C_4H_2^+$ ions. The formation of $SiCH_3^+$ is observed too, which occurs either from reaction of SiH_4 with $C_2H_2^+$ and subsequent elimination of a methyl group, or with $C_4H_3^+$, followed by elimination of C_3H_4.

Formation of clusters of increasing size takes place also through reaction channels involving ion species containing silicon and carbon reacting with both the neutral reagents, as can be observed in Scheme 1 for the species originated by SiH^+. In particular, the $Si_2CH_n^+$ ($n = 1$–3) ions react with SiH_4 and, after elimination of H_2, give the $Si_3CH_n^+$ ($n = 1, 3$–5) family, which further reacts with C_2H_2 leading to $Si_3C_3H_n^+$ ($n = 3$–5). The $SiC_2H_n^+$ ($n = 3$–5) ions react with both silane and ethyne to give the $Si_2C_2H_n^+$ ($n = 5$–7) and $Si_2C_4H_n^+$ ($n = 5, 7$) products, respectively. By contrast, under the experimental conditions used, SiC_2H^+ does not react any further with appreciable rate constant. Finally, parallel reactions of $Si_3C_2H_n^+$ ($n = 3$–5) with silane and ethyne take place, and the $Si_4C_2H_n^+$ ($n = 5, 7$) and $Si_2C_3H_n^+$ ($n = 1, 3$) families are formed.

A comparison of the collisional rate constants, calculated on the basis of the Langevin theory, with the



Scheme 1. Reaction pathways of SiH^+ in SiH_4–C_2H_2 mixtures.

experimental rate constants of reaction of $SiC_2H_n^+$, $Si_2C_2H_n^+$, and $SiC_4H_5^+$ ions with C_2H_2 and SiH_4, reported in Table 4, indicates rather high efficiencies for reactions in which C_2H_2 is the neutral reagent, whilst efficiencies are very low when a SiH_4 molecule is involved in the processes. In Tables 2–4 the reaction enthalpies for all the ion–molecule reactions of species whose formation enthalpies are known from the literature are also reported [3,21–28]. The negative ΔH°_{298} values for most of them confirm that these processes are thermodynamically favoured.

3. Conclusions

The dependence of the yield of ions containing both silicon and carbon on the ratio of the partial pressures of reagents in silane–ethyne mixtures (Figs. 2 and 3) suggests an involvement, to a similar extent, of both silane and ethyne in their formation. In particular, the first steps of the chain propagation consist mainly of reactions of $Si_mH_n^+$ ions, given by self-condensation of SiH_4, with ethyne. This is in agreement with the increase of the abundances of $Si_mC_nH_p^+$ species with the partial pressure of SiH_4. A similarly high contribution to the abundances of mixed ions is to be ascribed to ethyne, because the $Si_mC_nH_p^+$ ions are involved in the chain propagation with high efficiency when the neutral molecule is ethyne. A further influence of ethyne on the yield of mixed ions is evident from Table 3, where processes of formation of the SiH_n^+ family from both $C_2H_n^+$ and $C_4H_2^+$ ions with SiH_4 show high efficiencies.

Table 3
Rate constants for reactions of $C_2H_n^+$ and $C_4H_n^+$ ions with SiH_4 in SiH_4–C_2H_2 systems [a]

Reaction	k_{exp}	Σk_{exp}	k_L [b]	Efficiency [c]	ΔH°_{298} [d]
$C_2H^+ + SiH_4 \rightarrow Si^+ + C_2H_5$	2.4				−87.9
$\rightarrow SiH^+ + C_2H_4$	0.68				−127
$\rightarrow SiH_2^+ + C_2H_3$	1.3				−73.5
$\rightarrow SiH_3^+ + C_2H_2$	1.2				−121.4
$\rightarrow SiC_2H_3^+ + H_2$	5.7	11.3	12.99	0.87	−161
$C_2H_2^+ + SiH_4 \rightarrow Si^+ + C_2H_6$	1.9				−48.4
$\rightarrow SiH_2^+ + C_2H_4$	2.9				−36.8
$\rightarrow SiH_3^+ + C_2H_3$	1.1				−24.9
$\rightarrow SiCH_3^+ + CH_3$	1.7				−55.6
$\rightarrow SiC_2H_3^+ + H + H_2$	2.7				−21.3
$\rightarrow SiC_2H_4^+ + H_2$	1.0				< -48.4
$\rightarrow SiC_2H_5^+ + H$	3.1	14.4	12.85	1.12	−43
$C_4H_2^+ + SiH_4 \rightarrow SiC_2H^+ + C_2H_5$	0.36				< -32
$\rightarrow SiC_2H_2^+ + C_2H_4$	2.1				$< +14.5$
$\rightarrow SiC_2H_3^+ + C_2H_3$	0.76				−32.6
$\rightarrow SiC_2H_4^+ + C_2H_2$	1.8				< -16.5
$\rightarrow SiC_3H_3^+ + CH_3$	3.7				−33.2
$\rightarrow SiC_4H_5^+ + H$	2.0	10.7	11.02	0.97	< -19.9
$C_4H_3^+ + SiH_4 \rightarrow SiCH_3^+ + C_3H_4$	0.45				−19.4
$\rightarrow SiC_2H_3^+ + C_2H_4$	0.72				−34.5
$\rightarrow SiC_2H_5^+ + C_2H_2$	1.9	3.1	10.97	0.28	−14.2

[a] Rate constants are expressed as 10^{-10} cm^3 $molecule^{-1}$ s^{-1}; experiments were run at 333 K.
[b] Rate constants have been calculated according to the Langevin theory [18] taking polarizability of SiH_4 from [19].
[c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_L$.
[d] Enthalpies are expressed in kcal mol^{-1} and have been calculated with heats of formation taken from [3,21–23,28].

Table 4
Rate constants of reactions of $SiC_2H_n^+$, $Si_2C_2H_n^+$ and $SiC_4H_5^+$ ions with SiH_4 and C_2H_2 in SiH_4–C_2H_2 systems [a]

Reaction	k_{exp}	Σk_{exp}	k_L [b]	Efficiency [c]	ΔH°_{298} [d]
$SiC_2H_3^+ + C_2H_2 \rightarrow SiC_2H^+ + C_2H_4$	3.1	3.1	10.15	0.31	<-6
$+ SiH_4 \rightarrow Si_2C_2H_5^+ + H_2$	0.23	0.23	10.81	0.02	
$SiC_2H_4^+ + C_2H_2 \rightarrow SiC_2H_2^+ + C_2H_4$	3.5				
$\rightarrow SiC_3H_3^+ + CH_3$	1.1				>-14.7
$\rightarrow SiC_4H_5^+ + H$	0.40	5.0	10.12	0.49	
$+ SiH_4 \rightarrow Si_2H_4^+ + C_2H_4$	0.57				>-2.5
$\rightarrow Si_2C_2H_6^+ + H_2$	0.56	1.1	10.78	0.10	
$SiC_2H_5^+ + C_2H_2 \rightarrow SiC_2H_3^+ + C_2H_4$	2.9				-2.3
$\rightarrow SiC_4H_5^+ + H_2$	2.5	5.4	10.09	0.54	<-8.8
$+ SiH_4 \rightarrow Si_2C_2H_7^+ + H_2$	0.20	0.20	10.75	0.02	
$SiC_4H_5^+ + C_2H_2 \rightarrow SiC_6H_5^+ + H_2$	1.6				
$\rightarrow SiC_6H_7^+$	0.37	2.0	9.61	0.21	
$+ SiH_4 \rightarrow Si_2C_2H_5^+ + C_2H_4$	0.56				
$\rightarrow Si_2C_4H_7^+ + H_2$	0.41				
$\rightarrow Si_2C_4H_9^+$	1.0	2.0	10.16	0.20	
$Si_2C_2H_3^+ + C_2H_2 \rightarrow Si_2CH^+ + C_3H_4$	0.23				
$\rightarrow Si_2C_2H^+ + C_2H_4$	1.6	1.8	9.59	0.19	
$+ SiH_4 \rightarrow Si_3C_2H_5^+ + H_2$	0.27	0.27	10.12	0.03	
$Si_2C_2H_4^+ + C_2H_2 \rightarrow Si_2C_2H_2^+ + C_2H_4$	1.3				
$\rightarrow Si_2C_3H_5^+ + CH$	1.7				
$\rightarrow Si_2C_4H_5^+ + H$	1.3	4.3	9.57	0.45	
$+ SiH_4 \rightarrow Si_3C_2H_6^+ + H_2$	0.41	0.41	10.10	0.04	
$Si_2C_2H_5^+ + C_2H_2 \rightarrow Si_2C_2H_3^+ + C_2H_4$	1.1				
$\rightarrow Si_2C_3H_4^+ + CH_3$	0.10				
$\rightarrow Si_2C_4H_5^+ + H_2$	0.78	2.0	9.56	0.21	
$+ SiH_4 \rightarrow Si_3C_2H_7^+ + H_2$	0.49	0.49	10.09	0.05	

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

[b] Rate constants have been calculated according to the Langevin theory [18] taking the polarizability of SiH_4 from [19] and of C_2H_2 from [20].

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

[d] Enthalpies are expressed in kcal mol^{-1} and have been calculated with heats of formation taken from [3,23–25].

4. Experimental

All the experiments were run on an ITMS Finnigan mass spectrometer. Silane, ethane and ethyne were obtained commercially in high purity. Each of them was introduced into a flask, containing anhydrous sodium sulfate as drier, which was connected to one line of the gas inlet system of the instrument. Helium, used as buffer gas, was supplied at an extra-high purity and used without further purification. A Bayard Alpert ionization gauge was used to measure pressure. All read pressures were corrected for the relative sensitivity of the ion gauge with respect to different gases, 1.70 for SiH_4 [29], 2.39 for C_2H_6 [29] and 1.53 for C_2H_2 [29], and for a calibration factor, calculated as reported previously [11], to obtain the real pressure in the trap. Helium was admitted to the trap at a pressure of about 4×10^{-4} Torr. The temperature of the trap was maintained at 333 K, at which other related systems have been investigated. In order to prevent side reactions with the water background, the manifold and the lines for the introduction of reagent gases and helium were frequently baked-up. In all the experiments, ions were detected in the 10–300 u mass range. In these experiments, the scan modes used both to study the overall ion reactivity, as a function of reaction time, and to determine reaction mechanisms and rate constants have been described in detail previously, as well as the procedures for calculations [11,12].

In kinetic experiments, isolation of ions at a specific *m*/*z* value was obtained by use of d.c. voltages and by resonance ejection. In the latter isolation method, no field is directly applied on the selected ion species and, therefore, the ions should contain a lower excitation energy. The rate constants obtained by these two different isolation procedures are very similar and have an uncertainty that falls within 20%. This is in agreement with the hypothesis that the reactant ions undergo a number of collisions sufficient to eliminate most of their excitation energy. The single-exponential decays observed in the kinetic experiments are in agreement with this hypothesis. As an example, Fig. 4 reports the logarithmic plot of the decrease in relative abundance of the SiH^+ species with reaction time in a silane–ethyne mixture. The correlation coefficient shows a high curve fitting of the experimental points, which is similar to those obtained for all the other ions considered.

In all the experiments, ionization was obtained by electrons at about 35 eV for times in the range 1–10

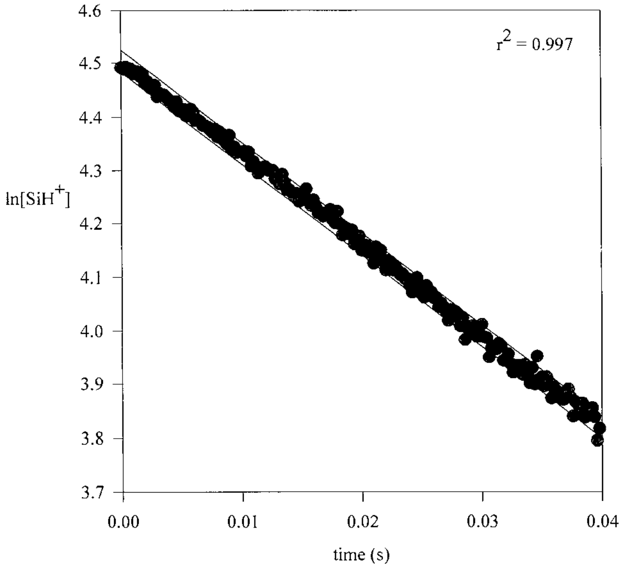


Fig. 4. Plot of ln[SiH$^+$] versus reaction time for a SiH_4 (3.9×10^{-7} Torr)–C_2H_2 (3.6×10^{-7} Torr) mixture.

ms. In experiments without selective storage of ions, ionization is followed by a reaction time that ranges from 0 to 1 s, without application of any potential to the trap. Acquisition of ion signals closes the experiment. When isolation of an ion species is performed, after the ionization event, a reaction time can follow in order to maximize the abundances of the ions under examination. Isolation of the selected ions, storage in the trap for convenient reaction times and acquisition are the successive events.

In some cases, when signals are due to two isobaric species, such as Si^+ and $C_2H_4^+$ (*m*/*z* 28) in the silane–ethane mixture, experiments were performed by pulsing one of the reagent gases. In this way, one gas is always present in the trap and the other reagent is pulsed into the trap only after the ionization step. Ion–molecule reactions occur between a single ion species (Si^+ or $C_2H_4^+$) and both neutrals and the reaction mechanisms of each of the isobaric ions can be determined. A General Valve Corporation Iota One pulsed valve was used [30]. The pressure of the pulsed gas behind the valve is previously set at 5.0×10^{-7} Torr by means of a by-pass channel and the valve opening time is 0.200 ms.

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References

[1] D.K. Bohme, Int. J. Mass Spectrom. Ion Proc. 100 (1990) 719.
[2] T.M. Mayer, F.W. Lampe, J. Phys. Chem. 78 (1974) 2645.
[3] S. Wlodek, A. Fox, D.K. Bohme, J. Am. Chem. Soc. 13 (1991) 4461.
[4] K.P. Lim, F.W. Lampe, J. Chem. Phys. 96 (1992) 2819.
[5] A.E. Ketvirtis, D.K. Bohme, A.C. Hopkinson, J. Phys. Chem. 98 (1994) 13225.
[6] A.E. Ketvirtis, D.K. Bohme, A.C. Hopkinson, J. Molec. Struct. (Teochem) 313 (1994) 1.
[7] P. Antoniotti, L. Operti, R. Rabezzana, G.A. Vaglio, P. Volpe, Int. J. Mass Spectrom. (1999) in press.
[8] S. Petrie, D.K. Bohme, Astrophys. J. 436 (1994) 411.
[9] S. Petrie, H. Becker, V. Baranov, D.K. Bohme, Astrophys. J. 476 (1997) 191.
[10] P. Benzi, L. Operti, G.A. Vaglio, P. Volpe, M. Speranza, R. Gabrielli, Int. J. Mass Spectrom. Ion Processes 100 (1990) 647.
[11] L. Operti, M. Splendore, G.A. Vaglio, A.M. Franklin, J.F.J. Todd, Int. J. Mass Spectrom. Ion Processes 136 (1994) 25.
[12] P. Antoniotti, L. Operti, R. Rabezzana, G.A. Vaglio, P. Volpe, J.F. Gal, R. Grover, P.C. Maria, J. Phys. Chem. 100 (1996) 155.
[13] F. Cacace, M. Speranza, Science 265 (1994) 208.
[14] M.T. Bowers, A.G. Marshall, F.W. McLafferty, J.Phys. Chem. 100 (1996) 12897.
[15] W.D. Reents Jr., M.L. Mandich, J. Chem. Phys. 96 (1992) 4429 and references therein.
[16] C.D. Stinespring, J.C. Wormhoudt, J. Cryst. Growth 87 (1988) 481.
[17] M.D. Allendorf, R.J. Kee, J. Electrochem. Soc. 138 (1991) 841.
[18] M.T. Bowers, Gas Phase Ion Chemistry, vol. 1, Academic Press, New York, 1979.
[19] E.R. Lippincott, J.M. Stutman, J. Phys. Chem. 78 (1974) 2422.
[20] J.O. Hirschfelder, C.F. Curtis, R.B. Bird, Molecular Theory of Gases and Liquids, John Wiley, New York, 1954, p. 950.
[21] B.H. Boo, P.B. Armentrout, J. Am. Chem. Soc. 109 (1987) 3549.
[22] S.G. Lias, J.E. Bartmess, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data Suppl. 1 (1988) 17.
[23] B.H. Boo, P.B. Armentrout, J. Am. Chem. Soc. 113 (1991) 6401.
[24] B.L. Kickel, E.R. Fisher, P.B. Armentrout, J. Phys. Chem. 96 (1992) 2603.
[25] P. Potzinger, F.W. Lampe, J. Phys. Chem. 73 (1969) 3912.
[26] T.M.T. Cheng, T.Y. Yu, F.W. Lampe, J. Phys. Chem. 78 (1974) 1184.
[27] J.F. Gal, R. Grover, P.C. Maria, L. Operti, R. Rabezzana, G.A. Vaglio, P. Volpe, J. Phys. Chem. 98 (1994) 11978.
[28] R. Bakhtiar, C.M. Holznagel, D.B. Jacobson, J. Phys. Chem. 97 (1993) 12710.
[29] M. Decouzon, J.F. Gal, P.C. Maria, A.S. Tchinianga, Personal communication.
[30] J. Carlin, B.S. Freiser, Anal. Chem. 55 (1983) 571.