Gas phase ion/molecule reactions in phosphine/methylsilane mixtures

Giuseppe Cetini, Lorenza Operti, Roberto Rabezzana, Gian Angelo Vaglio *, Paolo Volpe

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

Abstract

Phosphine/methylsilane mixtures investigated by ion trap mass spectrometry and reaction pathways together with the rate constants of the main reactions are reported. Mechanisms of ion/molecule reactions have been elucidated by single and multiple isolation steps. The SiH_n^+ ($n = 0$–3) ions react with phosphine to give mainly the $SiPH_n^+$ ($n = 1$–4) ion family. These ions further react with phosphine or methylsilane to yield $SiP_2H_n^+$ ($n = 2$, 4) and $Si_2CPH_n^+$ ($n = 5$–8) ions respectively. Mixed $SiPH_n^+$ ($n = 3$, 4) ions also originate from the PH_n^+ ($n = 1$, 2) phosphine primary ions. Hydride abstraction from methylsilane is a very common process, which takes place from a great number of ionic precursors, including the PH_n^+ ($n = 0$–2) ions, yielding the $SiCH_5^+$ species. Trends in relative abundance, respectively summed for the $SiCPH_n^+$ ($n = 5$, 6), $Si_2CPH_n^+$ ($n = 5$–8) and $Si_2C_2PH_n^+$ ($n = 7$–12) families of ions as a function of reaction time for different PH_3/CH_3SiH_3 pressure ratios, show that the nucleation of mixed Si–P ions proceeds to a lower extent with excess phosphine and is not substantially influenced by excess methylsilane.

Keywords: Gas-phase; Reaction mechanisms; Kinetics; Phosphine; Methylsilane; Mass spectrometry

1. Introduction

Recently, mechanisms and kinetic rate constants of ion/molecule reactions in gaseous systems containing volatile hydrides of elements of Groups 14 and 15 or their mixtures have been determined by Fourier transform and ion trap mass spectrometry [1–6]. These studies give valuable information from a theoretical point of view on the chemistry of these systems in the absence of perturbation due to the environment. Moreover, they allow interesting insights into the role of ion species in the deposition of amorphous solids containing elements of Groups 14 and 15 from appropriate gaseous systems by radiolytical and plasma methods [7,8].

As part of a study on the gas phase reactivity of systems containing hydrides such as GeH_4, SiH_4 or their methyl derivatives with ammonia and phosphine, in this paper we report the gas phase ion/molecule reactions of the PH_3/CH_3SiH_3 system. The reaction mechanisms have been elucidated by isolation of the main ion species and the rate constants of the first and second reaction steps have been determined by ion trap mass spectrometry. They have been compared with collisional rate constants calculated according to the average dipole orientation (ADO) theory [9]. The results have been discussed with respect to those of the related NH_3/SiH_4, NH_3/CH_3SiH_3 and PH_3/SiH_4 systems [5,6,10].

2. Experimental section

Methylsilane was prepared and purified as described in the literature [11]. Phosphine, helium and argon were obtained commercially in extra-high purity and were used without further purification. Experiments were run on a Finnigan Mat ITMS 70 ion trap mass spectrometer, at a temperature of 333 K, in order to obtain data comparable with previous results [5,6,10,12]. The pressures were measured and corrected as reported in previous papers [3,4]. Phosphine and methylsilane were admitted into the trap at pressures in the range $(1–4) \times 10^{-7}$ Torr and helium or helium/argon $(4:1)$ mixture buffer gases were added to a pressure of about 5.0×10^{-4} Torr.

Four different kinds of scan mode for ion/molecule reaction experiments were used. Each of them has been previously described in detail [3–5,10]. In the first kind of experiment [3], all the ions were stored for times

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* Corresponding author.

Table 1

Rate constants for reactions of SiH_n^+ ($n = 0-3$), $SiCH_4^+$, and $Si_2CH_n^+$ ($n = 4-6$) ions with PH_3 in a PH_3/CH_3SiH_3 mixture [a]

Reaction	k_{exp}	Σk_{exp}	k_{ADO} [b]	Efficiency [c]
$Si^+ + PH_3 \rightarrow SiPH^+ + H_2$	5.1	5.1	15.06	0.34
$SiH^+ + PH_3 \rightarrow SiPH_2^+ + H_2$	5.4	5.4	14.91	0.36
$SiH_2^+ + PH_3 \rightarrow SiH_3^+ + PH_2$	5.8			
$\rightarrow PH_4^+ + SiH$	0.6			
$\rightarrow SiPH_3^+ + H_2$	2.9	9.3	14.78	0.63
$SiH_3^+ + PH_3 \rightarrow SiPH_4^+ + H_2$	1.7	1.7	14.65	0.12
$SiCH_4^+ + PH_3 \rightarrow SiCH_5^+ + PH_2$	14	14	13.47	1.04
$Si_2CH_4^+ + PH_3 \rightarrow Si_2CPH_5^+ + H_2$	4.2	4.2	12.28	0.34
$Si_2CH_5^+ + PH_3 \rightarrow Si_2CPH_6^+ + H_2$	3.1	3.1	12.25	0.25
$Si_2CH_6^+ + PH_3 \rightarrow SiCH_5^+ + SiPH_4$	1.5	1.5	12.22	0.12

[a] Rate constants are expressed as 10^{-10} cm^3 mol^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%. [b] Rate constants have been calculated according to the ADO theory [9] taking the dipole moment of phosphine from Ref. [16] and the polarizability of phosphine from Ref. [17]. [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{ADO}$.

ranging from 0 to 500 ms to study the variations of ion abundance as a function of reaction time. The other three experiments all consisted of the isolation of selected ion species in order to determine ion/molecule reaction pathways and rate constants. Isolation was performed in a single step applying suitable r.f. voltages [10,13,14], the so-called resonance ejection isolation, or a superimposition of r.f. and d.c. voltages to the trap [3,4]. This last procedure was used in multiple isolation steps [5] for those ions having the same nominal mass but different composition. Moreover, the presence of some ions, such as $SiPH_n^+$ ($n = 3, 4$), at the same nominal mass as P_2^+ (m/z 62) and P_2H^+ (m/z 63) respectively has been confirmed by comparing their abundances in experiments in which the partial pressure of CH_3SiH_3 has been reduced to zero and increased again to the original value by a manual closing and opening of the entrance of the lines to the trap.

In all experiments, ionization was effected by electron beam bombardment for ionization times in the range 1–10 ms, at starting mass 10 u. In the experi-

ments without ion isolation, the ionization event was followed only by reaction (time ranging from 0 to 500 ms) and acquisition in the 10–250 u mass range. When a single ion isolation step was performed, either with or without application of a d.c. voltage, ionization was followed by a reaction time suitable to maximize the abundance of the ions to be stored. Isolation of the selected ions, their reactions with neutrals present in the trap for convenient reaction times, and acquisition were carried out successively. In multiple isolation steps experiments, reaction of the isolated ions with neutral gases was followed by isolation of one of the secondary ion products which, in turn, was reacted for suitable reaction times. Acquisition and interscan periods completed the experiment.

Rate constants were determined for reactions, different from self-condensation processes, of SiH_n^+ ($n = 0-3$), $SiCH_4^+$, $Si_2CH_n^+$ ($n = 4-6$), PH_n^+ ($n = 0-3$), $P_2H_n^+$ ($n = 0-3$), and $SiPH_n^+$ ($n = 1-4$), in a phosphine/methylsilane mixture. The presence of helium or helium/argon mixture buffer gases at different pressures

Table 2

Rate constants for reactions of PH_n^+ ($n = 0-3$) and $P_2H_n^+$ ($n = 0-3$) ions with CH_3SiH_3 in a PH_3/CH_3SiH_3 mixture [a]

Reaction		k_{exp}	Σk_{exp}	k_{ADO} [b]	Efficiency [c]
$P^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + PH$	9.5	9.5	15.95	0.60
$PH^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + PH_2$	11.6			
	$\rightarrow SiPH_3^+ + CH_4$	0.58	12.2	15.79	0.77
$PH_2^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + PH_3$	14			
	$\rightarrow SiPH_4^+ + CH_4$	0.54	14.5	15.65	0.93
$PH_3^+ + CH_3SiH_3$	$\rightarrow PH_4^+ + SiCH_5$	15	15	15.52	0.97
$P_2^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + P_2H$	7.3	7.3	13.35	0.55
$P_2H^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + P_2H_2$	6.4	6.4	13.30	0.48
$P_2H_2^+ + CH_3SiH_3$	$\rightarrow P_2H_3^+ + SiCH_5$	5.3			
	$\rightarrow SiCPH_5^+ + PH_3$	1.7	7.0	13.26	0.53
$P_2H_3^+ + CH_3SiH_3$	$\rightarrow SiCH_5^+ + P_2H_4$	0.74			
	$\rightarrow SiCPH_6^+ + PH_3$	2.1			
	$\rightarrow SiCP_2H_9^+$	1.4	4.2	13.22	0.32

[a] Rate constants are expressed as 10^{-10} cm^3 mol^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%. [b] Rate constants have been calculated according to the ADO theory [9] taking the dipole moment of methylsilane from Ref. [18] and calculating the polarizability of methylsilane as in Ref. [19]. [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{ADO}$.

does not affect these measurements. Every value reported is the average of at least three different experiments and the uncertainties of the measurements fall within 20%.

As both parallel and consecutive ion/molecule reactions have been observed, which in some cases give the same ion product, the determination of rate constants requires complex calculations which have been described previously [4,5]. Further experiments were also performed with isolation of every product ion, the successive reaction of each isolated ion species revealing its contribution to the formation of ion species common to different ionic precursors. Moreover, in some reactions a unique ion precursor yields a unique product ion by reaction with both neutral reactants. In such cases, as the reaction of $SiCH_4^+$ with both CH_3SiH_3 and PH_3 to give $SiCH_5^+$ or the reaction of PH_3^+ with both neutral reagents to give PH_4^+, the rate constants of formation of $SiCH_5^+$ [6] and PH_4^+ [15] measured in self-condensation have been subtracted from the rate constants determined in the PH_3/CH_3SiH_3 mixture. The results are the rate constants for formation of $SiCH_5^+$ from $SiCH_4^+$ and PH_3 (Table 1) and of PH_4^+ from PH_3^+ and CH_3SiH_3 (Table 2).

Thermalization of reactant ions was obtained in a short time by unreactive collisions with helium or helium/argon mixture buffer gases which are present in the trap at a pressure of 5.0×10^{-4} Torr. The efficiency of ion cooling was indicated by the single exponential behaviour of plots and by the similarity of results obtained in experiments involving isolation with or without application of a d.c. voltage.

3. Results

Fig. 1 reports the logarithmic plots of the decrease in relative abundance of the P^+, PH^+ and PH_2^+ ions with reaction time. The correlation coefficients show an appreciable curve fitting of the experimental points. Very similar coefficients have been obtained for all the other plots of the reacting ions.

Fig. 2 shows the variation of the relative abundances summed for the SiH_n^+ ($n = 0-3$), $SiCH_n^+$ ($n = 2-5$), PH_n^+ ($n = 0-3$) ion families, and of PH_4^+ as a function of time for the PH_3 (1.6×10^{-7} Torr)/CH_3SiH_3 (1.6×10^{-7} Torr) mixture. The abundances of the ion families PH_n^+, SiH_n^+, and $SiCH_n^+$ decrease with reaction time, the PH_n^+ ions showing a sharper decrease than the corresponding silicon-containing ions. In contrast, PH_4^+ displays an increase in abundance during the time range considered here. For the same mixture and in the same time range, Fig. 3 reports the relative abundances of the primary ions of CH_3SiH_3. The abundances of all ions decrease with reaction time, as expected, the only exception being the $SiCH_5^+$ ion species. In fact, its abun-
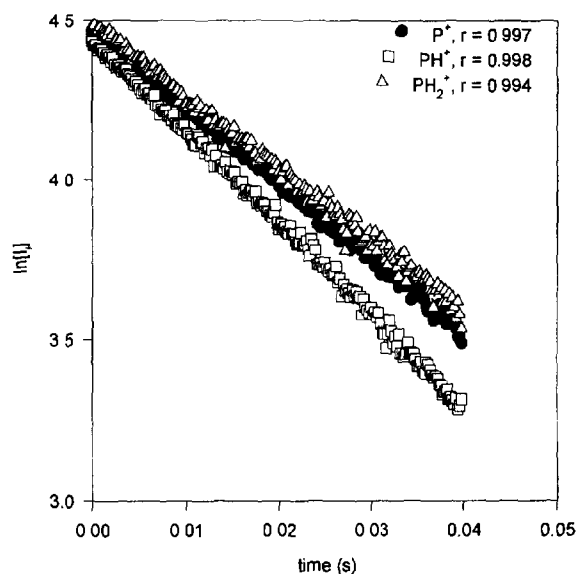

Fig. 1. Plot of $\ln[P^+]$, $\ln[PH^+]$, and $\ln[PH_2^+]$ versus reaction time for the reactions of P^+, PH^+, and PH_2^+ in the PH_3/CH_3SiH_3 mixture.

dance increases, reaches a maximum and decreases only after 100 ms of reaction. This trend indicates that the primary ion $SiCH_5^+$ is also produced in ion/molecule processes and is responsible for the slower decrease of the $SiCH_n^+$ ($n = 2-5$) ion family compared with the PH_n^+ ($n = 0-3$) ions of Fig. 2.

In Fig. 4, the relative abundances summed for the secondary $SiPH_n^+$ ($n = 1-4$) and $SiCPH_n^+$ ($n = 5, 6$) families of ions are reported as a function of reaction time for mixtures containing PH_3 and CH_3SiH_3 at 1:1 partial pressure ratio. The abundances of both ion fami-
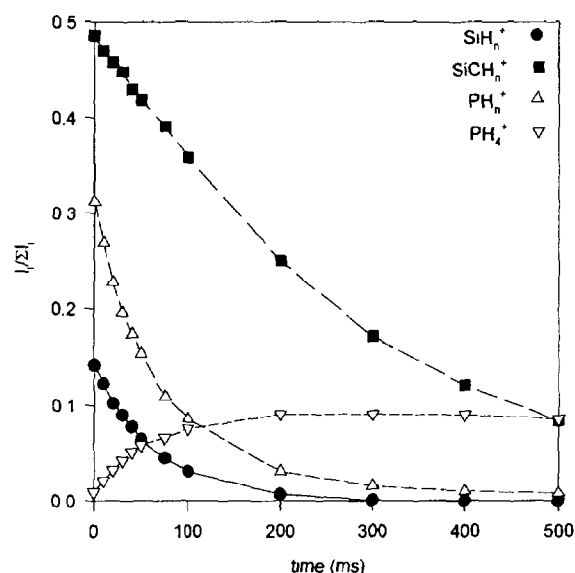

Fig. 2. Variation of relative abundances with time for SiH_n^+, $SiCH_n^+$, PH_n^+, and PH_4^+ ions in a PH_3 (1.6×10^{-7} Torr)/CH_3SiH_3 (1.6×10^{-7} Torr) mixture.
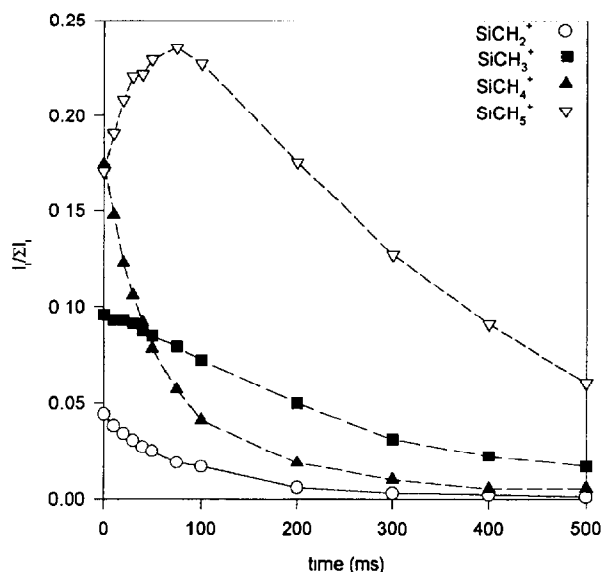
Fig. 3. Variation of relative abundances with time for $SiCH_2^+$, $SiCH_3^+$, $SiCH_4^+$, and $SiCH_5^+$ ions in a PH_3 $(1.6 \times 10^{-7}$ Torr)$/CH_3SiH_3$ $(1.6 \times 10^{-7}$ Torr) mixture.
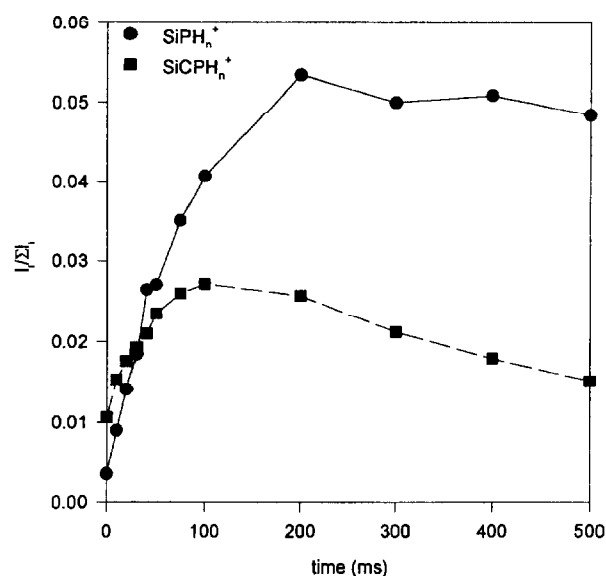

Fig. 4. Variation of relative abundances summed for the $SiPH_n^+$ and $SiCPH_n^+$ ion families with time in a PH_3 $(1.6 \times 10^{-7}$ Torr$)/CH_3SiH_3$ $(1.6 \times 10^{-7}$ Torr) mixture.

lies show the same trend, that of $SiPH_n^+$ $(n = 1-4)$ reaching a higher value.

Fig. 5 shows the variation of the combined relative abundances of $SiCPH_n^+$ $(n = 5, 6)$, $Si_2CPH_n^+$ $(n = 5-8)$, and $Si_2C_2PH_n^+$ $(n = 7-12)$ ions with time in PH_3/CH_3SiH_3 mixtures with 1:1, 1:5, and 5:1 partial pressure ratios. It is evident that Si–P clustering proceeds to a lower extent with increasing PH_3 content in the reacting mixture. It is also worth noting that an excess of methylsilane is not more efficient than a 1:1 mixture in clustering reactions.

In the tables the ion/molecule reactions occurring in PH_3/CH_3SiH_3 mixtures are reported, together with the experimental rate constants for formation of ionic products. The collisional rate constants are calculated according to the ADO theory [9] and the reaction efficiencies are reported as the ratio of experimental to collisional rate constants. The known self-condensation processes of both methylsilane [6] and phosphine [15] occur as parallel reactions of the reported pathways, but are not shown for reasons of clarity.

Tables 1 and 2 report the ion/molecule reactions of the main ions containing only silicon, carbon, and hy-

Table 3

Rate constants for reactions of $SiPH_n^+$ $(n = 1-4)$ ions with CH_3SiH_3 and PH_3 in a PH_3/CH_3SiH_3 mixture [a]

Reaction	k_{exp}	Σk_{exp}	k_{ADO} [b]	Efficiency [c]
$SiPH^+ + CH_3SiH_3 \rightarrow SiCH_5^+ + SiPH_2$	0.68			
$\rightarrow Si_2CH_4^+ + PH_3$	1.9			
$\rightarrow Si_2CPH_5^+ + H_2$	2.9	5.5	13.44	0.41
$SiPH^+ + PH_3 \rightarrow SiP_2H_2^+ + H_2$	2.9			
$\rightarrow SiPH_2^+ + SiCH_5$	0.51	3.41	12.66	0.27
$SiPH_2^+ + CH_3SiH_3 \rightarrow SiCH_5^+ + SiPH_3$	0.45			
$\rightarrow Si_2CPH_6^+ + H_2$	1.8			
$\rightarrow Si_2CPH_8^+$	0.65	2.9	13.40	0.22
$SiPH_3^+ + CH_3SiH_3 \rightarrow SiCPH_5^+ + SiH_4$	1.5			
$\rightarrow Si_2CH_6^+ + PH_3$	5.4			
$\rightarrow SiCPH_6^+ + SiH_3$	2.3			
$\rightarrow Si_2CPH_7^+ + H_2$	1.1	10.3	13.35	0.77
$SiPH_3^+ + PH_3 \rightarrow SiP_2H_4^+ + H_2$	0.73			
$\rightarrow SiPH_4^+ + PH_2$	4.6	5.3	12.59	0.42
$SiPH_4^+ + CH_3SiH_3 \rightarrow Si_2CH_7^+ + PH_3$	3.0			
$\rightarrow SiCPH_6^+ + SiH_4$	4.2	7.2	13.30	0.54

[a] Rate constants are expressed as 10^{-10} cm^3 mol^{-1} s^{-1}; experiments were run at 333 K; uncertainty is within 20%. [b] Rate constants have been calculated according to the ADO theory [9] taking the dipole moment of phosphine from Ref. [16], the polarizability of phosphine from Ref. [17], the dipole moment of methylsilane from Ref. [18] and calculating the polarizability of methylsilane as in Ref. [19]. [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_{ADO}$.

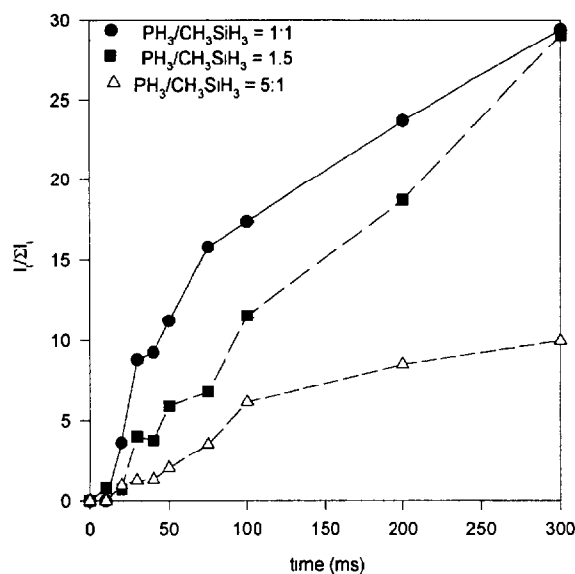Fig. 5. Variation of relative abundances with time for the combined $SiCPH_n^+$, $Si_2CPH_n^+$, and $Si_2C_2PH_n^+$ ion families in PH_3/CH_3SiH_3 mixtures with 1:1, 1:5, and 5:1 partial pressure ratios.

drogen with PH_3, and of the main ions containing only phosphorus and hydrogen with CH_3SiH_3 respectively. Table 3 shows the reaction pathways of the $SiPH_n^+$ ($n = 1$–4) ion family with both CH_3SiH_3 and PH_3. The PH_4^+ ion species is not shown in these tables as it is unreactive under the experimental conditions used here.

The most frequent reaction pathway displayed by the SiH_n^+ ($n = 0$–3) primary ions reacting with PH_3 (Table 1) involves elimination of a hydrogen molecule to form the $SiPH_n^+$ ($n = 1$–4) ion family. SiH_2^+ is also involved in a hydrogen transfer from PH_3 to give SiH_3^+, characterised by a rather high rate constant, and in a slow protonation of PH_3 to PH_4^+. Among the $SiCH_n^+$ ($n = 2$–5) primary ions of methylsilane, only $SiCH_4^+$ is observed to react with phosphine by a very fast hydrogen transfer to form $SiCH_5^+$. The secondary $Si_2CH_n^+$ ($n = 4$, 5) ions react with PH_3 to give the $Si_2CPH_n^+$ ($n = 5$, 6) ions with elimination of H_2, the associated rate constants being rather high. Moreover, the $Si_2CH_6^+$ ion species forms $SiCH_5^+$ at an appreciable rate by loss of an $SiPH_4$ neutral fragment. The $Si_2C_2H_n^+$ ($n = 6$–9) ions, originated from the $Si_2CH_n^+$ ($n = 4$–7) family in self-condensation processes, react with PH_3 to yield the $Si_2C_2PH_n^+$ ($n = 7$–12) species.

The PH_n^+ ($n = 0$–3) ions show a good reactivity towards CH_3SiH_3 (Table 2), but only when $n = 1$, 2 are they precursors of mixed $SiPH_n^+$ ($n = 3$, 4) species with elimination of a hydrogen molecule in a very slow process. The fastest reaction of P^+, PH^+, and PH_2^+ with methylsilane is hydride abstraction giving $SiCH_5^+$, while PH_3^+ abstracts a H atom to give PH_4^+ as the sole product. Also, some phosphine secondary ions exhibit ion/molecule processes with methylsilane to give ion
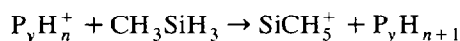
products containing new Si–P bonds. In fact, $P_2H_2^+$ and $P_2H_3^+$ give the $SiCPH_n^+$ ($n = 5$, 6) ions by elimination of a phosphine molecule. Again, a common pathway is hydride abstraction from CH_3SiH_3 and formation of the $SiCH_5^+$ ion with high efficiency for P_2^+ and P_2H^+ and low efficiency for $P_2H_3^+$. An addition reaction is also displayed by $P_2H_3^+$ and methylsilane leading to the formation of $SiCP_2H_9^+$.

The $SiPH_n^+$ ($n = 1$, 3) species react with both CH_3SiH_3 and PH_3 (Table 3) and eliminate a variety of neutral fragments to form, among others, $SiCPH_n^+$ ($n = 5$, 6), $Si_2CPH_n^+$ ($n = 5$, 7) and $SiP_2H_n^+$ ($n = 2$, 4) ions containing new Si–P bonds. In contrast, the $SiPH_2^+$ and $SiPH_4^+$ ions react only with methylsilane at a rather good efficiency.
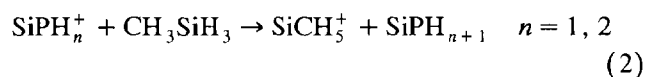
In some cases, further steps of ion nucleation take place, yielding ions containing three silicon and one phosphorus atoms or two silicon and two phosphorus atoms. However, all the ions produced in these reactions were of such low abundance that their rate constants of formation could not be determined with good precision.

4. Discussion

When methylsilane is the neutral reagent, hydride abstraction is one of the most common reaction pathways, occurring from several ions. This reaction mechanism has already been observed in the self-condensation of methylsilane [3,6]. Most phosphine primary and secondary ions, as well as some $SiPH_n^+$ ion species, give the $SiCH_5^+$ ion following reactions (1) and (2):

$$P_yH_n^+ + CH_3SiH_3 \rightarrow SiCH_5^+ + P_yH_{n+1}$$

$$y = 1, \ n = 0\text{–}2; \ y = 2, \ n = 0, 1, 3 \tag{1}$$

$$SiPH_n^+ + CH_3SiH_3 \rightarrow SiCH_5^+ + SiPH_{n+1} \quad n = 1, 2 \tag{2}$$

Owing to the lack of thermochemical data regarding ions containing Si, C, P and H together, it is not possible to calculate the enthalpy of the reactions reported above. However, the frequent occurrence of this kind of reaction suggests that it is thermodynamically favoured, due to the high stability of $SiCH_5^+$ [20]. In the NH_3/CH_3SiH_3 system previously studied [6], the $SiCH_5^+$ ion is mainly formed in self-condensation processes of methylsilane. In fact, nitrogen-containing ions show a very low reactivity towards methylsilane, the NH_n^+ ($n = 2$, 3) and $SiNH_4^+$ ions being the sole species which react with CH_3SiH_3 at appreciable rate constants. Among these ionic species, only the NH_3^+ ion does not give $SiCH_5^+$; it reacts only with methylsilane by extraction of a hydrogen atom.

Alternative reaction pathways consist of addition of a CH_3SiH_3 molecule, followed by loss of a neutral

molecule. In most cases, substitution of a PH_3 by a CH_3SiH_3 molecule takes place (reaction (3)):

$$Si_xP_yH_n^+ + CH_3SiH_3 \rightarrow Si_{x+1}CP_{y-1}H_{n+3}^+ + PH_3 \quad (3)$$
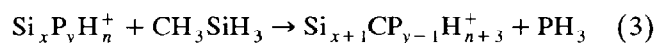
$x = 0$, $y = 2$, $n = 2, 3$; $x = 1$, $y = 1$, $n = 1, 3, 4$

but elimination of neutrals such as CH_4, H_2, SiH_4 and SiH_3 is also observed through many different pathways. This trend has already been observed, both in methylsilane alone and in the NH_3/CH_3SiH_3 mixture. In the first system, loss of a hydrogen molecule is the most frequent pathway, but formation of an SiH_n ($n = 1-4$) neutral fragment takes place in almost all cases. In the other system, substitution of an NH_3 by a CH_3SiH_3 molecule is observed, as well as loss of several kinds of neutral species.

Finally, formation of two adduct ions also occurs, according to reactions (4) and (5):
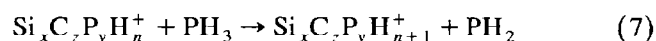
$$P_2H_3^+ + CH_3SiH_3 \rightarrow SiCP_2H_9^+ \quad (4)$$

$$SiPH_2^+ + CH_3SiH_3 \rightarrow Si_2CPH_8^+ \quad (5)$$
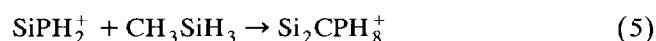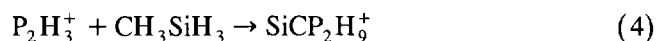
When the reacting molecule is phosphine, the most common pathway consists of the addition of a PH_3 molecule and loss of H_2:

$$Si_xC_zP_yH_n^+ + PH_3 \rightarrow Si_xC_zP_{y+1}H_{n+1}^+ + H_2 \quad (6)$$
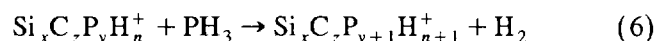
$x = 1$, $z = 0$, $y = 0$, $n = 0-3$; $x = 2$, $z = 1$, $y = 0$,

$n = 4, 5$; $x = 1$, $z = 0$, $y = 1$, $n = 1, 3$

Sometimes, addition of a PH_3 molecule leads to loss of a PH_2 fragment:

$$Si_xC_zP_yH_n^+ + PH_3 \rightarrow Si_xC_zP_yH_{n+1}^+ + PH_2 \quad (7)$$

$x = 1$, $z = 0$, $y = 0$, $n = 2$; $x = 1$, $z = 1$, $y = 0$,

$n = 4$; $x = 1$, $z = 0$, $y = 1$, $n = 3$

Comparison with the previously studied systems PH_3/SiH_4 [10] and PH_3/GeH_4 [12] confirms that elimination of a H_2 molecule is the most frequent pathway when phosphine is the neutral reagent. A reaction pathway involving addition of a PH_3 followed by loss of a PH_2 moiety takes place in a few cases in the PH_3/SiH_4 mixture, while it has not been observed in the PH_3/GeH_4 mixture.

Thermochemical data are available [21] only for the reaction of SiH_2^+ with PH_3 to give SiH_3^+ and PH_2, which is exothermic ($\Delta H = -29.3$ kJ mol^{-1}).

Protonation of phosphine occurs starting from SiH_2^+ only, leading to the formation of PH_4^+ and the neutral fragment SiH. This is a thermodynamically favoured process, as previously reported [10].

When a hydrogen transfer reaction occurs, the reacting molecule can be either phosphine or methylsilane. In fact, in both cases the formula of the product ion is the same. In order to determine the neutral reagent,

formation enthalpies [21,22] of the neutral species have to be considered, the ion species being the same:

$$A^+ + PH_3 \rightarrow AH^+ + PH_2 \quad (8)$$

$$A^+ + CH_3SiH_3 \rightarrow AH^+ + CH_3SiH_2 \quad (9)$$
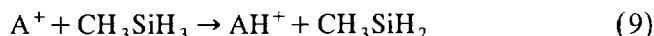
Reaction (8) is more favoured with respect to reaction (9) by about 54.4 kJ mol^{-1}. Hence it turns out that the main hydrogenating species is phosphine.

Clustering reactions proceed faster starting from methylsilane primary ions than from phosphine ones. The same behaviour is observed among the secondary ions of the two reagents. Ions containing Si-P bonds mainly react with CH_3SiH_3 to give, among others, the $Si_2CPH_n^+$ ($n = 5-8$) and $SiCPH_n^+$ ($n = 5, 6$) ions with rather good rate constants, whilst reactions with PH_3 are less frequent and proceed more slowly.

The behaviour of the PH_3/CH_3SiH_3 system has been compared with that of the NH_3/CH_3SiH_3 system [6]. Methylsilane primary and secondary ions generally react faster with ammonia than with phosphine. Most of these ions react with NH_3 in several parallel processes, while the reaction with phosphine occurs, in almost all the cases, to form just one product for each reacting ion. However, phosphine ions give a greater contribution to the growth of clusters with respect to the corresponding ions of ammonia. In fact, both primary and secondary ions of phosphine react with methylsilane to yield species containing new Si-P bonds, even if the rate constants are not very high. In contrast, among the NH_3 primary ions only NH_2^+ reacts to give a species containing an Si-N bond, while the ammonia secondary ions are absent in the NH_3/CH_3SiH_3 system.

Ion species containing only Si, N and H atoms do not play a significant role in chain propagation, neither in the NH_3/CH_3SiH_3 nor in the NH_3/SiH_4 system [5]. In contrast, the $SiPH_n^+$ ($n = 1-4$) ions show a good reactivity towards CH_3SiH_3 and PH_3, as they form clusters with appreciable rate constants. It turns out that, even if the first reaction step is faster in the NH_3/CH_3SiH_3 system with respect to the PH_3/CH_3SiH_3 mixture, the chain propagation starting from the secondary ions becomes more favoured in the PH_3/CH_3SiH_3 system.

Comparison of the results reported here can also be drawn with those obtained for the PH_3/SiH_4 system [10]. Phosphine primary ions react faster with methylsilane than with silane, but the highest rate constants are those of the reactions of hydride abstraction from CH_3SiH_3, whilst the reactions which lead to the formation of an Si-P bond are faster in the PH_3/SiH_4 system. In a similar way, the phosphine secondary ions P_2^+ and P_2H^+ give only hydride abstraction with methylsilane, and formation of species containing Si-P bonds with silane. The $P_2H_n^+$ ($n = 2, 3$) ions show an intermediate behaviour as they react with methylsilane to give

mixed clusters, with a rate constant with respect to SiH_4 lower for $P_2H_2^+$ and higher for $P_2H_3^+$.

The $SiPH_n^+$ ($n = 1-3$) ions generally react faster with CH_3SiH_3 than with SiH_4. Moreover, the $SiPH_4^+$ ion is unreactive in the PH_3/SiH_4 system and reacts with methylsilane through two different pathways with a high overall rate constant.

Previous studies [10,23] indicate that the attack on the CH_3SiH_3 and SiH_4 molecules occurs through insertion of the ion into an Si–H bond of the neutral reagent. The presence of a methyl group favours this process due to its inductive effect, which increases the electron density on the H atoms linked to silicon. This hypothesis is confirmed by the data obtained, which display efficiencies in the reactions with CH_3SiH_3 higher than with SiH_4. Comparison between the NH_3/SiH_4 [5] and the NH_3/CH_3SiH_3 systems revealed that the methyl group in the reacting ion favours the reactions with ammonia with loss of a hydrogen atom or molecule. This effect was not observed in this study, as rate constants of the same reactions with phosphine of the $Si_2H_n^+$ ($n = 2, 3$) and $Si_2CH_n^+$ ($n = 4, 5$) ions are very similar.

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