

Gas-phase ion–molecule reactions in ammonia–methylsilane mixtures studied by ion trapping

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Abstract

The gas-phase reactivity of ammonia–methylsilane mixtures has been studied by ion trap mass spectrometry. The mechanisms of ion–molecule reactions have been determined, and their rate constants measured and compared with the corresponding collisional rate constants calculated according to the average dipole orientation theory. The SiCH_n^+ ($n = 2-5$) and SiH_n^+ ($n = 0-3$) primary ions react with methylsilane according to the previously reported self-condensation processes. These ions also give the SiNH_n^+ ($n = 2-4$) and SiCNH_n^+ ($n = 5, 6$) ionic species in different reactions with NH_3 . Among them, SiNH_4^+ and SiCNH_6^+ , which are the most abundant N–Si-containing ions, react further with ammonia to form SiN_2H_n^+ ($n = 5, 6$) and $\text{SiCN}_2\text{H}_9^+$ respectively. The most frequent pathways of silicon-containing ions reacting with ammonia correspond to elimination of H_2 , or H, or adduct formation. Chain propagation proceeds mainly through ions of general formula $\text{Si}_x\text{C}_y\text{H}_n^+$ in reactions with NH_3 , while ions containing only silicon, nitrogen and hydrogen give species, such as NH_4^+ and SiN_2H_n^+ ($n = 5, 6$), which do not react further.

Keywords: Ammonia; Kinetics; Mass spectrometry; Mechanism; Methylsilane

1. Introduction

In the last two decades, the chemistry of silicon has become more and more important because of increasing interest in technological applications [1,2]. In particular, attention has been drawn to its gaseous compounds, from which high purity products can be obtained. The hydrides are the most frequently used derivatives in the deposition processes leading to silicon-containing solids, even if they have the drawback of burning in the presence of dioxygen and therefore must be handled with care [3]. Alkylsilanes exhibit a higher stability to dioxygen, as the presence of one or more alkyl groups prevents combustion in air [3]. However the methyl groups could make these compounds unsuitable for the synthesis of products free of carbon. The study of ion–molecule reactions which occur in a mixture containing alkylsilanes, interesting from a fundamental point of view, can also give information on the nature and mechanism of formation of the ionic species involved in processes such as thermal- or photon-assisted metal–organic chemical vapor deposition (MOCVD) [4,5].

Different mass spectrometry methods, as well as ab initio quantum-chemical calculations, have been applied to gas-phase ion–molecule reactions in methylsilane [6,7] and to the mechanisms and energetics of reactions of Si^+ with methylsilane to form small silicon ion clusters [8–12]. In this paper we describe studies of the ammonia–methylsilane system by ion trap mass spectrometry with the aim of investigating the influence of the methyl group bound to silicon on the growth of ion clusters and their effect on the mechanism and the kinetics of the observed ion–molecule reactions. In particular, reaction mechanisms, variations in ionic abundances with reaction time, and rate constants for reactions of the most significant ionic species in the $\text{NH}_3\text{--CH}_3\text{SiH}_3$ system are reported. A comparison is drawn with the behaviour of methylsilane alone [13], for which the reaction rate constants are given in this paper, and with the results of an analogous study on ammonia–silane systems [14].

2. Experimental section

Ammonia was commercially supplied at a high degree of purity. Methylsilane was prepared and purified

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as described in the literature [15]. Prior to use, each reagent gas was introduced in a separate flask containing anhydrous sodium sulphate as a drying agent, connected to the gas inlet system of the instrument. Helium was obtained commercially in extra-high purity and was used without further purification. The manifold and the lines were baked out quite frequently in order to reduce the water background in the trap.

A Finnigan Mat ITMS 70 ion trap mass spectrometer was used for all experiments, which were run at 333 K to avoid thermal decomposition. The gas inlet system was modified in order to introduce simultaneously three

gases (methylsilane, ammonia and helium buffer gas) into the trap through three different lines. The pressures were measured by a Bayard–Alpert ionization gauge. Methylsilane and ammonia were admitted to the trap at pressures in the range $(2-4) \times 10^{-7}$ Torr and helium buffer gas was added up to a pressure of about 5.0×10^{-4} Torr.

The scan modes for ion–molecule reactions experiments both without and with mass-selective storage have been previously described in detail [13,14,16–18].

In these systems, ions with different composition can have the same nominal mass, as the nominal mass of

Table 1
Rate constants for reactions of SiH_n^+ ($n = 0-3$), SiCH_n^+ ($n = 2-5$) and Si_2CH_n^+ ($n = 4-7$) in self-condensation of CH_3SiH_3 ^a

Reaction	k_{exp} ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	Σk_{exp} ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	k_{ADO} ^b ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	Efficiency ^c
$\text{Si}^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiCH}_3^+ + \text{SiH}_3$	6.3			
→ $\text{SiCH}_5^+ + \text{SiH}$	0.39			
→ $\text{Si}_2\text{CH}_4^+ + \text{H}_2$	11	18	18.9	0.95
$\text{SiH}^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiCH}_3^+ + \text{SiH}_4$	2.8			
→ $\text{SiCH}_5^+ + \text{SiH}_2$	0.86			
→ $\text{Si}_2\text{CH}_5^+ + \text{H}_2$	15	19	18.7	1.02
$\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiCH}_4^+ + \text{SiH}_4$	3.3			
→ $\text{SiCH}_5^+ + \text{SiH}_3$	1.3			
→ $\text{Si}_2\text{CH}_6^+ + \text{H}_2$	2.3	19	18.4	1.03
$\text{SiH}_3^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiCH}_5^+ + \text{SiH}_4$	17			
→ $\text{Si}_2\text{CH}_7^+ + \text{H}_2$	0.78	18	18.3	0.98
$\text{SiCH}_2^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_6^+ + \text{H}_2$	12	12	16.8	0.71
$\text{SiCH}_3^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_7^+ + \text{H}_2$	2.8			
→ $\text{Si}_2\text{C}_2\text{H}_9^+$	0.66	3.5	16.6	0.21
$\text{SiCH}_4^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiCH}_5^+ + \text{SiCH}_5$	2.0			
→ $\text{SiC}_2\text{H}_6^+ + \text{SiH}_4$	1.1			
→ $\text{SiC}_2\text{H}_7^+ + \text{SiH}_3$	8.0			
→ $\text{Si}_2\text{C}_2\text{H}_8^+ + \text{H}_2$	1.9	13.0	16.6	0.78
$\text{SiCH}_5^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{SiC}_2\text{H}_7^+ + \text{SiH}_4$	2.0			
→ $\text{Si}_2\text{C}_2\text{H}_{11}^+$	0.16	2.2	16.5	0.13
$\text{Si}_2\text{CH}_4^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_6^+ + \text{SiH}_4$	8.5			
→ $\text{Si}_2\text{C}_2\text{H}_8^+ + \text{SiH}_2$	2.0			
→ $\text{Si}_3\text{C}_2\text{H}_8^+ + \text{H}_2$	4.0	14.5	14.9	0.97
$\text{Si}_2\text{CH}_5^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_7^+ + \text{SiH}_4$	2.0			
→ $\text{Si}_2\text{C}_2\text{H}_9^+ + \text{SiH}_2$	2.0			
→ $\text{Si}_3\text{C}_2\text{H}_9^+ + \text{H}_2$	5.8	9.8	14.8	0.66
$\text{Si}_2\text{CH}_6^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_8^+ + \text{SiH}_4$	1.1			
→ $\text{Si}_2\text{C}_2\text{H}_{10}^+ + \text{SiH}_2$	0.96			
→ $\text{Si}_3\text{C}_2\text{H}_{10}^+ + \text{H}_2$	4.0	6.1	14.7	0.41
$\text{Si}_2\text{CH}_7^+ + \text{CH}_3\text{SiH}_3$				
→ $\text{Si}_2\text{C}_2\text{H}_{11}^+ + \text{SiH}_2$	0.54			
→ $\text{Si}_3\text{C}_2\text{H}_{11}^+ + \text{H}_2$	4.7	5.2	14.7	0.36

^a Experiments were run at 333 K; uncertainty is within 20%.

^b Rate constants have been calculated according to the average dipole orientation (ADO) theory [19] calculating polarizability of methylsilane [20] and taking dipole moment of methylsilane [21] as reported in the literature.

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

the most abundant isotope of silicon (^{28}Si) is twice the nominal mass of the most abundant isotope of nitrogen (^{14}N), which in turn has the same nominal mass of the $^{12}\text{CH}_2$ group. Therefore, to assign unequivocally a formula to an m/z value it has been necessary to identify the precursor of the ion and its formation mechanism by multiple ion isolation steps. As an example, to investigate the reaction pathways of SiNH_2^+ , $m/z = 44$, it is not possible simply to isolate ions at $m/z = 44$, as they mainly consist of SiCH_4^+ . It is necessary to isolate the ionic species at $m/z = 28$, Si^+ , or $m/z = 29$, SiH^+ (Table 1) both of which react with ammonia to form, among others, SiNH_2^+ as only ionic species at $m/z = 44$, which is in turn selectively stored for different reaction times, allowing us to study its products. The scan function relative to these experiments has also been described previously [14].

In all experiments, ionization was obtained by bombardment with an electron beam at ionization time in the range 1–10 ms. In the experiments without isolation of an ionic species, the ionization was followed by reaction (time ranging from zero to 300 ms) and acquisition in the 10–250 u mass range. When single isolation step of ions was performed, both with or without application of a d.c. voltage, after the ionization event, reactions took place during a time suitable to maximize the abundance of ions to be collected. Isolation of the selected ions, their reactions with neutral species present in the trap for convenient reaction times, and acquisition were the successive steps. In multiple-isolation-step experiments, reaction of the isolated ions with the neutral gases was followed by isolation of one of the secondary ionic products, which in turn was allowed to react for suitable reaction times. Acquisition and inter-scan periods closed the experiment.

Moreover, the presence of nitrogen in product ions has been confirmed by comparing their abundances in different mass spectra of the same experiments in which the partial pressure of NH_3 was reduced to zero and increased again to the original value by manually closing the entrance to the trap of the ammonia line.

The rate constants were determined by isolation of precursors by applying a suitable d.c. voltage in experiments as described above. For some ions they have been confirmed also using conditions under which the amount of excitation energy of the reacting ions is certainly negligible. In fact, a scan function was applied with isolation of the selected ion by resonance ejection without any d.c. voltage, which could add energy to the ions under examination [17,18].

Every time that an r.f. or a d.c. voltage is applied a settling time is necessary to stabilize the trap. Therefore, even if the reaction time is set to zero, some delay (1–2 ms) elapses from the ionization event and ion–molecule reactions have already occurred to some extent. This is the reason for the presence of very weak secondary ions

at zero reaction time, but it does not affect the calculations of rate constants.

In the kinetic experiments, accurate pressure measurements were necessary. For this purpose, the ion gauge was calibrated by determining the rate constant of formation of CH_5^+ from CH_4^+ in methane and comparing it with the rate constant reported in the literature [19]. The pressure was further corrected on the basis of the relative sensitivity of the ion gauge response with different gases [22,23]. The procedures for data acquisition and calculation of rate constants have been reported in previous papers [14,24]. Moreover, it had been previously established that the presence of helium buffer gas at different pressures does not affect these measurements [24]. Every value reported is the average of at least three different experiments and uncertainties of measurements are less than 20%.

The single-exponential behaviour of plots is consistent with thermalization of reactant ions due to collisional cooling which removes the majority of the internal energy for the high pressure (5.0×10^{-4} Torr) in the trap. Thermalization of ions in self-condensation of SiH_4 has been previously demonstrated by obtaining the same rate constants in experiments in which a large excess of argon was added to SiH_4 and helium as cooling gas [14]. In the present study similar results have been obtained by isolation with or without application of a d.c. voltage, again indicating that collisions in the trap are efficient in removing excitation energy from the reacting ions. A further proof of the ion thermalization is the absence of product ions formed with loss of two hydrogen molecules, which is typical of hot reactions in gas-phase reactions involving silane [25].

3. Results

3.1. Self-condensation of CH_3SiH_3

The complex reaction mechanisms of the primary ions of methylsilane, SiCH_n^+ ($n = 2-5$) and SiH_n^+ ($n = 0-3$), have been reported previously [13]. The rate constants of the first parallel reaction steps of these ions and of their products, Si_2CH_n^+ ($n = 4-7$) are reported in Table 1. In the same table the rate constants calculated according to the ADO theory [19] and the efficiencies of reaction are also shown. The evaluation of rate constants gives supplementary information on the reaction mechanisms, as previously shown [13]. It is possible to indicate which path is the most rapid from a unique precursor giving parallel reactions, or which is the fastest reaction leading to the formation of a particular ionic species and, as a consequence, which is its most efficient precursor.

The SiH_n^+ ($n = 0-3$) ions generally react faster than the other ionic species reported in the table and show

very similar total rate constants ranging from 18×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Si^+ and SiH_3^+) to 19×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (SiH^+ and SiH_2^+). For Si^+ and SiH^+ the fastest reaction occurs by elimination of a hydrogen molecule and formation of Si_2CH_4^+ and Si_2CH_5^+ respectively. In contrast, reactions of SiH_2^+ and SiH_3^+ lead with the highest rate constants to the formation of the same ion, SiCH_5^+ , and elimination of SiH_3 and SiH_4 respectively. The ions SiCH_n^+ ($n = 2-5$) react in a similar way as their fastest reaction is formation of $\text{Si}_2\text{C}_2\text{H}_{n+4}^+$ and elimination of molecular hydrogen for $n = 2$ or 3 and formation of SiC_2H_7^+ with

elimination of SiH_3 and SiH_4 respectively when $n = 4$ or 5. Among the SiCH_n^+ ($n = 2-5$) ionic species, only SiCH_2^+ and SiCH_4^+ show high total rate constants (12×10^{-10} and 13×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively), the others being of the 10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ order of magnitude. The secondary ions Si_2CH_n^+ ($n = 4-7$) display rather high total rate constants ranging from 5.2×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to 14.5×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reactions taking place with loss of an SiH_4 molecule or an SiH_2 fragment occur at rates which decrease with increasing number of hydrogen atoms on the reacting ion. In

Table 2
Rate constants for reactions of SiH_n^+ ($n = 0-3$), SiCH_n^+ ($n = 2-5$) and Si_2CH_n^+ ($n = 4-7$) with ammonia in an $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture ^a

Reaction	k_{exp} ($\times 10^{-10}$ cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	Σk_{exp} ($\times 10^{-10}$ cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	k_{ADO}^b ($\times 10^{-10}$ cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	Efficiency ^c
$\text{Si}^+ + \text{NH}_3 \rightarrow \text{SiNH}_2^+ + \text{H}$	8.2	8.2	20.3	0.40
$\text{SiH}^+ + \text{NH}_3 \rightarrow \text{SiNH}_2^+ + \text{H}_2$	9.1	9.5	20.2	0.47
$\text{SiH}^+ + \text{NH}_3 \rightarrow \text{SiNH}_3^+ + \text{H}$	0.39			
$\text{SiH}_2^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{SiH}$	2.2	15.5	20.1	0.77
$\text{SiH}_2^+ + \text{NH}_3 \rightarrow \text{SiNH}_3^+ + \text{H}_2$	6.7			
$\text{SiH}_2^+ + \text{NH}_3 \rightarrow \text{SiNH}_4^+ + \text{H}$	6.6			
$\text{SiH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{SiH}_2$	0.81	6.2	19.9	0.31
$\text{SiH}_3^+ + \text{NH}_3 \rightarrow \text{SiNH}_4^+ + \text{H}_2$	5.4			
$\text{SiCH}_2^+ + \text{NH}_3 \rightarrow \text{SiNH}_2^+ + \text{CH}_3$	3.8	5.2	18.7	0.28
$\text{SiCH}_2^+ + \text{NH}_3 \rightarrow \text{SiCNH}_5^+$	1.4			
$\text{SiCH}_4^+ + \text{NH}_3 \rightarrow \text{SiCNH}_6^+ + \text{H}$	13	13	18.6	0.70
$\text{SiCH}_5^+ + \text{NH}_3 \rightarrow \text{SiNH}_4^+ + \text{CH}_4$	1.7	8.7	18.5	0.47
$\text{SiCH}_5^+ + \text{NH}_3 \rightarrow \text{SiCNH}_6^+ + \text{H}_2$	7.0			
$\text{Si}_2\text{CH}_4^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Si}_2\text{CH}_3$	3.0	11.3	17.5	0.65
$\text{Si}_2\text{CH}_4^+ + \text{NH}_3 \rightarrow \text{SiNH}_2^+ + \text{SiCH}_5$	4.7			
$\text{Si}_2\text{CH}_4^+ + \text{NH}_3 \rightarrow \text{Si}_2\text{CNH}_5^+ + \text{H}_2$	3.6			
$\text{Si}_2\text{CH}_5^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Si}_2\text{CH}_4$	2.2	14	17.5	0.81
$\text{Si}_2\text{CH}_5^+ + \text{NH}_3 \rightarrow \text{SiNH}_3^+ + \text{SiCH}_5$	0.91			
$\text{Si}_2\text{CH}_5^+ + \text{NH}_3 \rightarrow \text{Si}_2\text{CNH}_6^+ + \text{H}_2$	11			
$\text{Si}_2\text{CH}_6^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Si}_2\text{CH}_5$	3.4	9.1	17.5	0.52
$\text{Si}_2\text{CH}_6^+ + \text{NH}_3 \rightarrow \text{SiCNH}_6^+ + \text{SiH}_3$	1.1			
$\text{Si}_2\text{CH}_6^+ + \text{NH}_3 \rightarrow \text{SiCNH}_8^+ + \text{SiH}$	1.1			
$\text{Si}_2\text{CH}_6^+ + \text{NH}_3 \rightarrow \text{Si}_2\text{CNH}_7^+ + \text{H}_2$	1.6			
$\text{Si}_2\text{CH}_6^+ + \text{NH}_3 \rightarrow \text{Si}_2\text{CNH}_8^+ + \text{H}$	1.9			
$\text{Si}_2\text{CH}_7^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Si}_2\text{CH}_6$	4.0	11.7	17.4	0.67
$\text{Si}_2\text{CH}_7^+ + \text{NH}_3 \rightarrow \text{SiNH}_3^+ + \text{SiCH}_5 + \text{H}_2$	3.5			
$\text{Si}_2\text{CH}_7^+ + \text{NH}_3 \rightarrow \text{Si}_2\text{CNH}_8^+ + \text{H}_2$	4.2			

^a Experiments were run at 333 K; uncertainty is within 20%.

^b Rate constants have been calculated according to the ADO theory [19] taking polarizability [26] and dipole moment of ammonia [21] as in the literature.

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

Table 3

Rate constants for reactions of NH_n^+ ($n = 2$ or 3) ions with ammonia and of SiNH_4^+ with both ammonia and methylsilane in an $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture ^a

Reaction	k_{exp} ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	Σk_{exp} ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	k_{ADO}^b ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)	Efficiency ^c
$\text{NH}_2^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{NH}_3^+ + \text{SiCH}_5$	3.0			
$\rightarrow \text{SiCH}_4^+ + \text{NH}_4$	2.4			
$\rightarrow \text{SiCH}_5^+ + \text{NH}_3$	5.2			
$\rightarrow \text{SiNH}_4^+ + \text{CH}_4$	2.2	12.8	22.8	0.57
$\text{NH}_3^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{NH}_4^+ + \text{SiCH}_5$	2.0	2.0	22.3	0.09
$\text{SiNH}_4^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{SiNH}_3$	1.6			
$\rightarrow \text{SiN}_2\text{H}_5^+ + \text{H}_2$	1.6			
$\rightarrow \text{SiN}_2\text{H}_6^+ + \text{H}$	0.88	4.1	18.2	0.22
$\text{SiNH}_4^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{SiCH}_5^+ + \text{SiH}_2 + \text{NH}_3$	2.9			
$\rightarrow \text{SiCNH}_6^+ + \text{SiH}_4$	4.7	7.6	16.4	0.46

^a Experiments were run at 333 K; uncertainty is within 20%.

^b Rate constants have been calculated according to the ADO theory [19] calculating polarizability of methylsilane [20], taking polarizability of ammonia [26] and dipole moment of both reagents [21] as in the literature.

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

contrast, when an H_2 molecule is lost, all the ions Si_2CH_n^+ ($n = 4\text{--}7$) react at very similar rates and without any particular trend related to the reacting species.

3.2. Ion-molecule reactions in $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixtures

Table 2 displays ion-molecule reactions of the same ionic species as in Table 1 (SiH_n^+ , $n = 0\text{--}3$; SiCH_n^+ , $n = 2\text{--}5$; Si_2CH_n^+ , $n = 4\text{--}7$) with ammonia and their rate constants in an $\text{NH}_3\text{-CH}_3\text{SiH}_3$ system. In Table 3 the data for reactions of NH_n^+ ($n = 2, 3$) with methylsilane and of SiNH_4^+ with both ammonia and methylsilane in an $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture are reported. The collisional rate constants have also been calculated according to the ADO theory [19] and are shown in Tables 2 and 3 together with reaction efficiencies.

The $\text{NH}_3\text{-CH}_3\text{SiH}_3$ system is very complex as it also involves consecutive reactions as well as parallel processes. Moreover, some ionic products are common to both parallel and consecutive reactions, making calculations of rate constants difficult. Therefore the determination of such rate constants requires quite complex calculations, which have been previously described [14]. Moreover, further experiments are involved with isolation of every product ion, followed by study of its reactions in the same mixture and time variation to provide evidence for its contribution to the formation of ionic species common to different precursors. Some ions have the same nominal mass and are formed from the same precursor, such as SiCH_5^+ and SiNH_3^+ at $m/z = 45$ originating in the $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture from SiH^+ reacting with methylsilane and ammonia respectively. In this case, the rate constant of formation of each ion is derived from different systems, i.e. for

SiCH_5^+ from reaction of SiH^+ and CH_3SiH_3 in methylsilane alone, and for SiNH_3^+ from reaction of SiH^+ and NH_3 in an $\text{NH}_3\text{-SiH}_4$ mixture [14], and it has been used alternatively to calculate the rate constant of formation of the other product ion in the mixture.

The rate constants for reactions of SiNH_2^+ and SiNH_3^+ could not be determined as they have the same nominal masses as SiCH_4^+ and SiCH_5^+ respectively, and there was no experiment which permitted their isolation in sufficient abundance to perform a kinetic measurement without the carbon-containing isobaric ion. Protonated ammonia NH_4^+ , which is produced at rather high rates from many ionic species, is not reactive under the experimental conditions used here. The rate constant for formation of NH_3^+ from reaction of NH_2^+ with CH_3SiH_3 has been calculated to be 3×10^{-10} cm³ molecule⁻¹ s⁻¹ by comparing the rate constant for formation of NH_3^+ in the $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture (19×10^{-10} cm³ molecule⁻¹ s⁻¹) and in ammonia alone [14] (16×10^{-10} cm³ molecule⁻¹ s⁻¹). In the same way the rate constant for reaction of NH_3^+ to form NH_4^+ , 24×10^{-10} cm³ molecule⁻¹ s⁻¹ in an $\text{NH}_3\text{-CH}_3\text{SiH}_3$ mixture, has been obtained. Compared with the rate constant of formation of NH_4^+ from NH_3^+ in ammonia alone (22×10^{-10} cm³ molecule⁻¹ s⁻¹ [14]) it gives 2×10^{-10} cm³ molecule⁻¹ s⁻¹ as the rate constant of formation of NH_4^+ from reaction of NH_3^+ with methylsilane.

The ions SiH_n^+ ($n = 0\text{--}3$) react with ammonia yielding the SiNH_n^+ ($n = 2\text{--}4$) family with elimination of a hydrogen molecule or a hydrogen atom at rather high reaction rates. The ions SiH_2^+ and SiH_3^+ also transfer a proton to neutral ammonia to form the very stable ammonium ion NH_4^+ .

In reactions with ammonia, SiCH_2^+ leads to forma-

Table 4

Relative abundances of significant ions in the mass spectra of a 1 : 1 NH₃ : CH₃SiH₃ mixture^a as a function of the reaction time

<i>m/z</i> ^b	Ion	Relative abundance for the following reaction times							
		0 ms	10 ms	20 ms	30 ms	40 ms	50 ms	75 ms	100 ms
16	NH ₂ ⁺	20.0	15.5	10.1	6.5	4.7	3.3	1.2	
17	NH ₃ ⁺	25.1	23.7	19.9	17.1	14.1	11.6	6.3	3.1
18	NH ₄ ⁺	8.5	22.1	34.4	48.3	61.6	72.3	86.5	100.0
28	Si ⁺	12.4	10.9	10.2	7.6	6.0	5.1	2.6	1.3
29	SiH ⁺	7.8	8.0	6.9	6.1	5.3	4.3	2.4	1.4
30	SiH ₂ ⁺	6.9	6.6	5.6	4.3	3.6	3.1	1.8	1.7
31	SiH ₃ ⁺	6.4	6.5	5.1	4.2	3.6	2.8	2.0	1.0
42	SiCH ₂ ⁺	12.2	10.9	9.5	8.2	7.0	6.1	3.4	2.2
43	SiCH ₃ ⁺	28.9	30.9	31.0	32.1	32.7	29.7	25.2	21.7
44	SiCH ₄ ⁺	52.6	36.2	31.6	27.8	22.7	14.2	8.9	6.9
45	SiCH ₅ ⁺	48.7	47.5	46.9	45.4	43.1	41.7	34.5	32.1
43	SiNH ⁺	1.0	2.5	4.0	4.6	4.7	3.8	3.2	3.0
44	SiNH ₂ ⁺	0.6	2.8	3.1	3.6	4.2	4.8	5.0	5.6
45	SiNH ₃ ⁺		1.0	1.9	2.5	2.9	2.6	3.1	3.3
46	SiNH ₄ ⁺	0.6	6.2	7.8	9.7	11.6	11.5	12.5	13.9
59	SiC ₂ H ₇ ⁺	1.9	9.8	11.6	14.9	17.5	19.3	22.8	23.7
60	SiCNH ₆ ⁺		8.3	13.7	18.6	24.8	27.8	34.8	41.7
62	SiN ₂ H ₆ ⁺				0.5	0.7	1.0	1.2	2.1
72	Si ₂ CH ₄ ⁺	0.9	1.3	1.9	2.9	3.1	3.4	2.7	2.2
73	Si ₂ CH ₅ ⁺	0.7	1.5	1.9	2.5	2.8	2.6	2.5	2.1
74	Si ₂ CH ₆ ⁺		0.5	0.6	0.8	1.5	1.7	1.8	2.3
75	Si ₂ CH ₇ ⁺				0.3	0.4	0.4	0.5	0.6
74	SiC ₂ NH ₈ ⁺					0.3	0.5	0.9	1.6
76	SiC ₂ NH ₁₀ ⁺				0.4	0.7	1.1	1.8	2.6
77	SiCN ₂ H ₉ ⁺						0.3	0.6	0.9
86	Si ₂ C ₂ H ₆ ⁺	0.6	1.5	2.2	2.8	3.0	3.9	3.7	3.3
87	Si ₂ C ₂ H ₇ ⁺		0.8	1.6	1.7	2.7	3.3	4.2	5.5
88	Si ₂ C ₂ H ₈ ⁺	0.7	1.5	2.3	3.2	3.5	3.6	4.5	5.0
89	Si ₂ C ₂ H ₉ ⁺		0.3	0.4	0.6	0.9	1.2	1.9	2.2
87	Si ₂ CNH ₅ ⁺					0.4	0.5	0.7	1.0
88	Si ₂ CNH ₆ ⁺						0.4	0.5	0.7
90	Si ₂ CNH ₈ ⁺							0.4	0.6
100	Si ₂ C ₃ H ₈ ⁺							0.7	0.9
101	Si ₂ C ₃ H ₉ ⁺					0.5	0.6	0.7	1.2
103	Si ₂ C ₃ H ₁₁ ⁺				0.3	0.5	0.5	0.8	1.0
104	Si ₂ C ₃ H ₁₂ ⁺						0.4	0.6	1.0
105	Si ₂ C ₃ H ₁₃ ⁺				0.4	0.4	0.5	0.6	0.7
102	Si ₂ C ₂ NH ₈ ⁺				0.6	0.7	1.0	1.4	1.5
103	Si ₂ C ₂ NH ₉ ⁺						0.3	0.4	0.6
105	Si ₂ C ₂ NH ₁₁ ⁺							0.5	0.6
106	Si ₂ C ₂ NH ₁₂ ⁺						0.5	0.8	1.0
116	Si ₃ C ₂ H ₈ ⁺				0.3	0.4	0.6	0.9	1.0
117	Si ₃ C ₂ H ₉ ⁺				0.3	0.4	0.6	1.0	0.8
118	Si ₃ C ₂ H ₁₀ ⁺							0.5	0.7
119	Si ₃ C ₂ H ₁₁ ⁺							0.5	0.6
130	Si ₃ C ₃ H ₁₀ ⁺					0.6	0.7	1.0	1.2
131	Si ₃ C ₃ H ₁₁ ⁺				0.4	0.5	0.7	1.2	1.9

Table 4 (continued)

m/z^b	Ion	Relative abundance for the following reaction times							
		0 ms	10 ms	20 ms	30 ms	40 ms	50 ms	75 ms	100 ms
132	$\text{Si}_3\text{C}_3\text{H}_{12}^+$					0.4	0.5	0.7	1.1
133	$\text{Si}_3\text{C}_3\text{H}_{13}^+$							0.5	0.9

^a The pressure of both NH_3 and CH_3SiH_3 is 3.4×10^{-7} Torr, the total pressure is 5.0×10^{-4} Torr, and the temperature is 333 K.

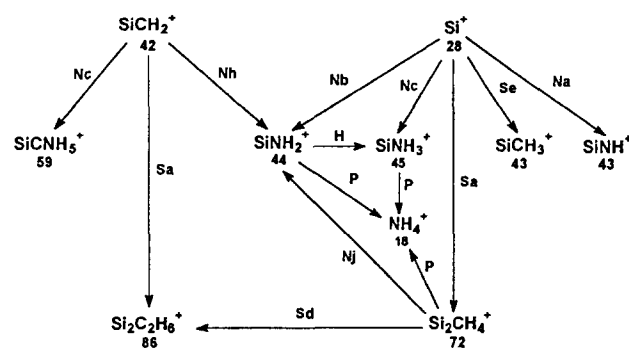
^b Masses are calculated on the basis of ^1H , ^{12}C , ^{14}N and ^{28}Si .

tion of the adduct ion SiCNH_5^+ , while SiCH_3^+ does not react with ammonia during the reaction times considered here. The ions SiCH_n^+ ($n = 4, 5$) give the same product SiCNH_6^+ , which is the second most abundant ion after 100 ms reaction time in a 1 : 1 NH_3 : CH_3SiH_3 mixture (Table 4). This SiCNH_6^+ species is obtained with elimination of H from SiCH_4^+ and with elimination of H_2 from SiCH_5^+ . Moreover, SiCH_2^+ reacts with NH_3 yielding SiNH_2^+ by elimination of a CH_3 neutral fragment and SiCH_5^+ gives SiNH_4^+ by loss of CH_4 .

All the secondary ions Si_2CH_n^+ ($n = 4-7$) protonate ammonia to give NH_4^+ with very similar rate constants, ranging from $2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for Si_2CH_5^+ to $4.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for Si_2CH_7^+ . Another common pathway is addition of NH and elimination of a hydrogen molecule, yielding the $\text{Si}_2\text{CNH}_n^+$ ($n = 5-8$) family. Alternatively, reactions of ammonia with the ions Si_2CH_n^+ eliminate fragments containing silicon and hydrogen ($n = 6$) or silicon, carbon and hydrogen ($n = 4, 5, 7$).

The results in Table 3 show that the ions NH_n^+ ($n = 2, 3$) form mainly NH_{n+1}^+ by reaction with methylsilane, whereas SiNH_4^+ reacts with ammonia to form the two-nitrogen-atom-containing ions SiN_2H_5^+ and SiN_2H_6^+ at appreciable rates.

It has been possible to identify successive reaction product ions by isolating and storing primary and secondary ions for reaction times up to 300 ms in mixtures with different reagent ratios, chosen to increase the abundances of the products. However, their very low abundances, even after long reaction times, prevented us from measuring their rate constants of formation with any reliability. The ions SiNH_n^+ ($n = 2, 3$) react in the NH_3 - CH_3SiH_3 mixture, mainly by hydrogen transfer, to form the SiNH_{n+1}^+ species. The very abundant SiCNH_6^+ further reacts with both NH_3 and CH_3SiH_3 without any loss of neutral molecules give $\text{SiCN}_2\text{H}_9^+$



Scheme 1.

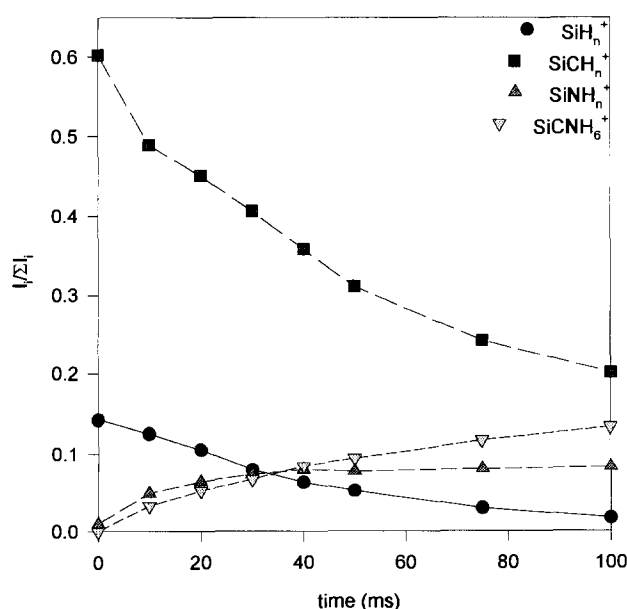
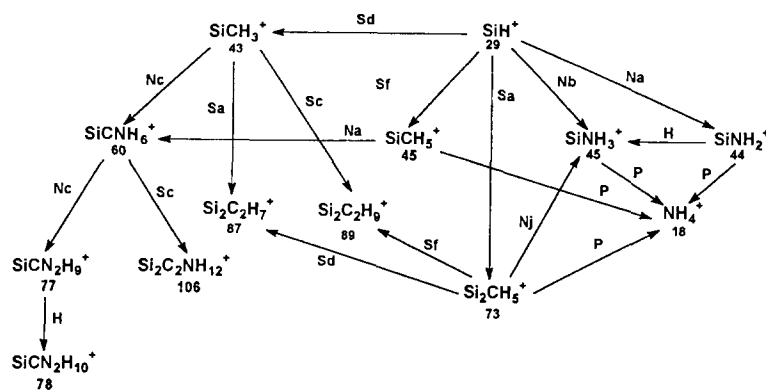
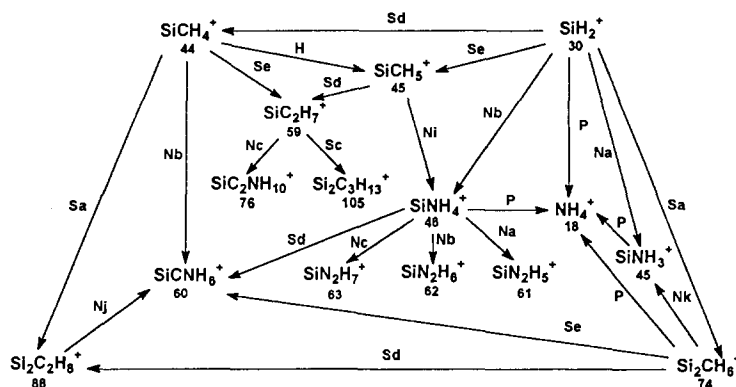


Fig. 1. Variations in ion abundances with time for an $\text{NH}_3(3.4 \times 10^{-7} \text{ Torr})$ - $\text{CH}_3\text{SiH}_3(3.4 \times 10^{-7} \text{ Torr})$ mixture.

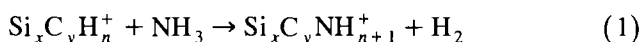


Scheme 2.



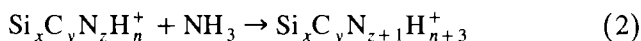
Scheme 3.

and $\text{Si}_2\text{C}_2\text{NH}_{12}^+$ respectively. The secondary ions which do not contain nitrogen react with ammonia with elimination of H_2 , as follows:



where $x = 2, y = 2, n = 7-8$; $x = 3, y = 2, n = 8$; $x = 2, y = 3, n = 13$.

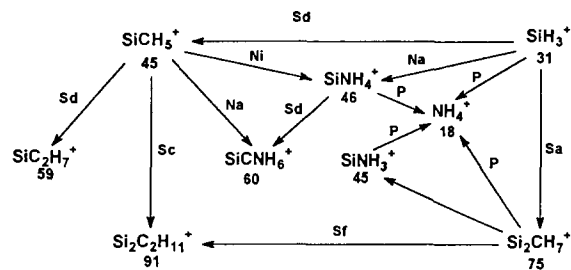
The most common pathway occurs with no neutral loss, as follows:



where $x = 2, y = 2, z = 0, n = 6-9$; $x = 3, y = 2, z = 1, n = 8$; $x = 2, y = 2, z = 1, n = 8-11$.

In Table 4, the relative abundances of the ionic species in the mixture NH_3 (3.4×10^{-7} Torr)– CH_3SiH_3 (3.4×10^{-7} Torr) are reported at reaction times up to 100 ms. All ionic abundances refer to the most abundant ion at any considered time. After 100 ms reaction time this is NH_4^+ . In this table, some pairs of ions, such as SiNH^+ and SiCH_3^+ at $m/z = 43$, have the same nominal masses. Therefore, the formulae and the relative abundances reported have been assigned on the basis of experiments of selective storage of ions and of the variation in relative abundances in the presence or absence of NH_3 .

At zero reaction time the most abundant species are



Scheme 4.

NH_n^+ ($n = 2-4$) which carry 22.7% of the total ion current and the silicon-containing ions, SiH_n^+ ($n = 0-3$) and SiCH_n^+ ($n = 2-5$), which carry 74.4% of the total ion current. The abundances of these silicon-containing ions decrease very sharply and, in fact, they transport 21.9% of the total ion current after reaction for 100 ms. Two different trends are shown by secondary ions as their abundances can increase continuously up to a 100 ms reaction time, or increase, reach a maximum and then decrease again. The variation in the abundances of the ionic families SiH_n^+ ($n = 0-3$), SiCH_n^+ ($n = 2-5$), SiNH_n^+ ($n = 1-4$), and SiCNH_6^+ , with reaction time are also shown in Fig. 1. In this Figure the behaviours of the primary and secondary ions are more evident. The abundances of primary ions SiCH_n^+ ($n = 2-5$) and SiH_n^+

($n = 0-3$) decrease throughout the reaction time considered here. The secondary ions behave in a different way, the SiNH_n^+ ($n = 2-4$) species showing a maximum abundance after 40 ms, the SiCNH_6^+ ion continuously increasing up to 100 ms.

4. Discussion

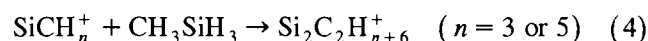
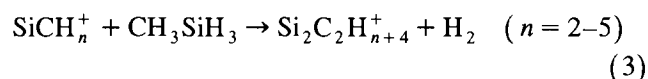
The study of the reactions of Si^+ with methylsilane [7–12] by different mass spectrometry methods and by ab-initio chemical calculations are in general agreement with data reported in this paper. For example, we observe that SiCH_3^+ and Si_2CH_4^+ are formed with high rate constants and these ions are reported to be the only exothermic products of Si^+ and CH_3SiH_3 [8–12]. Mayer and Lampe [6,7] also observed the SiCH_5^+ species which is formed with a very low rate constant from Si^+ ($3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) in our system.

The most favoured reaction, proposed by Raghavachari [11] and Gordon and coworkers [12] for the $\text{Si}^+ - \text{CH}_3\text{SiH}_3$ system, involves a first intermediate formed by insertion of Si^+ into an Si–H bond. This species can give a transition state with an H–H bridge linked to the terminal Si, which eliminates H_2 leading to Si_2CH_4^+ . The first intermediate also follows a parallel pathway involving the migration of two hydrogen atoms to the terminal silicon and loss of SiH_3 to give CH_3Si^+ . The methyl group never participates in the reaction, remaining a spectator. The same reaction mechanism with loss of H_2 has been previously reported for the consecutive reactions of all the SiH_n^+ ($n = 0-3$) ions to give $\text{Si}_2\text{H}_{n+2}^+$ in SiH_4 [27]. Therefore, even without ab-initio calculations on which to base the description of the ionic products, it is reasonable to hypothesize that this kind of mechanism operates for the analogous reactions of CH_3SiH_3 with the SiH_n^+ ($n = 0-3$) species to give the ions $\text{Si}_2\text{CH}_{n+4}^+$. The other main ionic products are

SiCH_4^+ from SiH_2^+ , and SiCH_5^+ from both SiH_2^+ and SiH_3^+ . All these ions can originate from the intermediate described above by breaking of the Si–Si bond and loss of SiH_3 or SiH_4 .

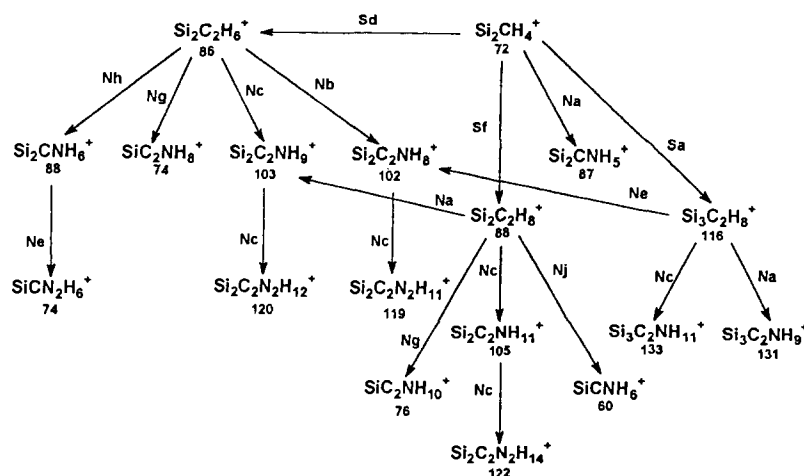
The efficiencies of reaction of the SiH_n^+ ($n = 0-3$) family with CH_3SiH_3 is greater than in SiH_4 [24]. This can be ascribed to the inductive effect of the methyl group, which increases the electron density on the hydrogen atoms of the silyl moiety. Therefore, the attack of the positive ions on a hydrogen atom linked to silicon of CH_3SiH_3 is favoured compared with SiH_4 [11,12,27].

This kind of reaction mechanism could also explain the formation of the $\text{Si}_2\text{C}_2\text{H}_{n+4}^+$ ($n = 2-5$) or $\text{Si}_2\text{C}_2\text{H}_{n+6}^+$ ($n = 3, 5$) ions from the SiCH_n^+ family:



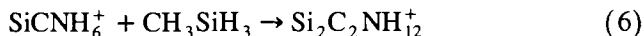
It has been previously determined that the SiCH_5^+ ion gives isotopic exchange [6,7] by hydride abstraction with a reaction rate constant of $2.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the systems studied here, both with methylsilane alone and with the $\text{NH}_3 - \text{CH}_3\text{SiH}_3$ mixture, this process was not detected, probably because of the low abundance of the ^{29}Si isotope with respect to ^{28}Si .

In the $\text{NH}_3 - \text{CH}_3\text{SiH}_3$ mixture, ion–molecule reactions involving methylsilane molecules as neutrals generally take place with ions which do not contain nitrogen, following reaction pathways which have been previously described in the self-condensation processes of methylsilane [13]. The ions SiNH_4^+ and SiCNH_6^+ are the only nitrogen-containing species reacting with CH_3SiH_3 to form SiCNH_6^+ according to



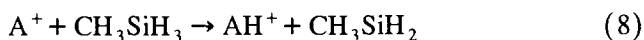
Scheme 5.

and to form $\text{Si}_2\text{C}_2\text{NH}_{12}^+$ according to



When the reacting molecule is ammonia, several reaction pathways can be identified, the most frequent involving elimination of H_2 or H , or no elimination. The first pathway is followed by many ions and this seems to indicate that it is thermodynamically favoured. Owing to the lack of thermochemical data on species containing silicon, carbon and nitrogen it is not possible to make calculations on the energetics of processes involving this kind of ion. However, the heats of formation of NH_3 and H_2 in the gas phase are -11.0 and 0 kcal mol^{-1} [28] respectively, and therefore this reaction is exothermic when the enthalpy of formation of the product ions is at least 11 kcal mol^{-1} lower than that of the reacting ions. As the enthalpy of formation of H is 52.10 kcal mol^{-1} [28], it follows that, for a pathway involving loss of H , the heats of formation of the product ions should be at least 63 kcal mol^{-1} lower than those of the reacting ionic species. These two reaction pathways generally take place from ions which do not contain any nitrogen atoms. In contrast, the formation of adduct ions, in which an ammonia molecule is added to an ion without any loss of neutral species is also a frequent process for ions which already contain a nitrogen atom. Protonation of neutral ammonia to yield the ammonium ion NH_4^+ takes place starting from a great number of different ionic species. It is likely that this reaction occurs because of the great stability of NH_4^+ , which lowers the enthalpy content of the product, making the process exothermic.

In hydrogen-transfer reactions, it is impossible to identify the neutral molecule involved, NH_3 or CH_3SiH_3 , as both lead to the formation of the same ionic product from the same reactant ion:



However, comparison of the differences of the heats of formation of the product and reagent neutral species of Eq. (7) (56 kcal mol^{-1}) and Eq. (8) (45 kcal mol^{-1}) indicates that hydrogen transfer is more thermodynamically favoured from CH_3SiH_3 than from NH_3 by about 11 kcal mol^{-1} .

Reactivity with NH_3 of the primary and secondary ions of methylsilane, SiH_n^+ ($n = 0-3$), SiCH_n^+ ($n = 2-5$) and Si_2CH_n^+ ($n = 4-7$), and of silane, SiH_n^+ ($n = 0-3$) and Si_2H_n^+ ($n = 2-5$) [14], can be compared with respect to the nature of the ion products and to the nature of the ejected neutral species.

SiNH_n^+ ($n = 2-4$) product ions can be formed from SiH_n^+ reagent ions, which are present in the spectra of both SiH_4 and CH_3SiH_3 , and from SiCH_n^+ ($n = 2$ or 5) reagent ions in processes where an $\text{Si}-\text{C}$ bond must also

be broken. Their formation occurs from all ions SiH_n^+ ($n = 0-3$) with rather high rate constants, and from SiCH_2^+ and SiCH_5^+ with low rate constants.

In contrast, comparison of analogous processes such as the reactions of SiH_2^+ to give SiNH_4^+ and of CH_3SiH^+ to give SiCNH_6^+ with elimination of H , indicates an activating effect of the methyl group. Similar evidence is displayed by the different rate constants for the reactions of SiH_3^+ to form SiNH_4^+ and of $\text{CH}_3\text{SiH}_2^+$ to give SiCNH_6^+ , in which H_2 is eliminated. Processes of the secondary ion families also taking place with ejection of H_2 or H to give Si_2NH_n^+ ($n = 3-6$) from Si_2H_n^+ ($n = 2-5$) [14] and $\text{Si}_2\text{CNH}_n^+$ ($n = 5-8$) from Si_2CH_n^+ ($n = 4-7$) (Table 2) respectively are always favoured by the presence of methyl groups, mainly when Si_2CH_5^+ is the reagent ion.

A further reaction pathway, observed for $\text{NH}_3-\text{CH}_3\text{SiH}_3$ and NH_3-SiH_4 systems, involves the substitution of a silicon atom by a nitrogen atom. Through this process, the secondary ions of silane, Si_2H_n^+ ($n = 2-5$), lead to formation of SiNH_n^+ ($n = 2-4$) with high rate constants [14]. In secondary ions of methylsilane, Si_2CH_n^+ ($n = 4-7$), only Si_2CH_6^+ reacts slowly, leading to SiCNH_6^+ .

Therefore in $\text{NH}_3-\text{CH}_3\text{SiH}_3$ systems the chain propagation proceeds mainly through the $\text{Si}_x\text{C}_y\text{H}_n^+$ ions, which are activated by the presence of methyl groups when they react with NH_3 to give $\text{Si}_x\text{C}_y\text{NH}_{n+1}^+$ or $\text{Si}_x\text{C}_y\text{NH}_{n+2}^+$ containing a nitrogen atom besides silicon, carbon and hydrogen. These reactions display rate constants of about 10^{-10} cm^3 molecule^{-1} s^{-1} . Some of these ions in turn react further with ammonia, yielding product ions such as $\text{Si}_2\text{C}_2\text{N}_2\text{H}_n^+$ ($n = 11$ or 12), after such a long reaction time that rate constants are difficult to measure. The ions containing only nitrogen, silicon and hydrogen, SiNH_n^+ ($n = 2-4$) and SiN_2H_n^+ ($n = 5$ or 6), originate from the same $\text{Si}_x\text{C}_y\text{H}_n^+$ ions, the required rupture of the silicon-carbon bond making these processes very slow, and by SiH_n^+ reagent ions which are rather weak in $\text{NH}_3-\text{CH}_3\text{SiH}_3$ mixtures. These trends indicate that ions containing only silicon, nitrogen and hydrogen do not play a significant role in chain propagation, or in NH_3-SiH_4 [14]. As a consequence, the ammonia-methylsilane mixtures seem unsuitable, at least for the contribution of ionic species, to prepare materials such as silicon nitrides, in which carbon must be absent, by radiolytic methods.

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