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Gas-phase ion chemistry of the propyne/ammonia and silane/propyne/ammonia systems

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Abstract

Ion/molecule reactions in the C_3H_4/NH_3 and $SiH_4/C_3H_4/NH_3$ gaseous mixtures were investigated by ion trap mass spectrometry, with the aim of finding the best experimental conditions for formation and growth of ion clusters containing silicon, carbon and nitrogen. These species may play an important role in the deposition of silicon carbides doped with nitrogen by X-ray assisted chemical vapour deposition methods from suitable systems. In the study of the C_3H_4/NH_3 mixture the main reaction pathways leading to formation of C/N-containing species were identified. Few mixed C/N ions are formed, with low formation rates, and their overall abundance reaches only 7% of the total ion current after 1 s reaction time. In the ternary mixture, mixed Si-containing ions were found to be the most efficient precursors of ternary ion species. The $SiC_nH_q^+$ ($n = 1$–3; $q = 2$–5, 7) ions efficiently react with ammonia, but only in few cases these reactions lead to formation of ternary mixed ions as hydrocarbon loss mostly occurs with formation of binary $SiNH_q^+$ ($q = 2, 4$) ions. On the other hand, propyne was found to be very reactive and several ternary mixed ions were formed from its reactions with $SiNH_q^+$ ($q = 2, 4$) and $SiCNH_q^+$ ($q = 6, 8$) ions. The total abundance of ternary mixed ions reaches 20% of the total ion current after 1 s reaction time.

Keywords: Silane; Propyne; Ammonia; Ion trap mass spectrometry

1. Introduction

In recent years, the study of gas-phase ion chemistry has stimulated increasing interest from both fundamental and application points of view. The subject of earlier studies was the intrinsic reactivity of ions in the absence of perturbative effects, such as solvents or counterions [1–8]. Moreover, theoretical methods provided valuable data regarding the reaction mechanisms and thermochemistry [9–11]. Recently, experimental studies were performed on mixtures of volatile hydrides of Group 14 elements because of their possible applications in the semiconductor field [4,8,12–18]. Gas mixtures containing SiH_4 and hydrocarbons have been used to prepare silicon amorphous carbides by radiolytic activation [19]. In the course of the irradiation process several ion species are formed and it was observed that the amount of Si and C in the solid is a function of the composition of the gaseous system, but without a direct or predictable correlation. The study of the first steps of nucleation and clustering reactions leading to the precursors of the final solid is very useful in order to find the relationship between the partial pressures of the reagent gases and the abundance of Si in the amorphous polymers. The activity of semiconductor materials may be improved by doping them with phosphorus or nitrogen, and this is the reason why the SiH_4/PH_3 and SiH_4/NH_3 mixtures have been previously investigated [8,12].

This paper reports on the reactivity of the silane/propyne/ammonia ternary system, studied with the aim of checking the possibility of synthesizing a material containing silicon carbide doped with nitrogen in a single reaction step. The investigation of a ternary mixture requires the preliminary knowledge of the reaction mechanisms in all related binary mixtures. Silane/ammonia and silane/propyne mixtures have been investigated previously [12,17], while the study of the propyne/ammonia system is reported in this paper.

2. Experimental

All the experiments were performed with an ITMS Finnigan instrument. Silane, propyne and ammonia were

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commercially purchased at a high purity grade and directly connected to the inlet system. Helium buffer gas was supplied at an extra-high purity grade and used with no further purification. In all experiments the total sample pressure ranged between 1.2×10^{-6} and 1.8×10^{-6} Torr (1 Torr = 133.3 Pa). The overall working pressure was approximately 8.0×10^{-5} Torr after helium introduction. Pressure was measured by a Bayard-Alpert ion gauge; the corrected pressure was obtained by dividing the ion gauge readings by the relative sensitivity factor of the ion gauge with respect to different gases (1.7 for silane, 2.16 for propyne, 1.11 for ammonia and 0.20 for helium, M. Decouzon, J.-F. Gal, P.-C. Maria, A.S. Tchinianga, personal communication), and for a calibration factor which depends on the geometry of the instrument, as reported previously [2]. The temperature was set at 333 K in order to avoid thermal decomposition of the reactants. Positive ions were formed by electron ionization at about 35 eV for times in the 10–50 ms range. Ions were detected in the 14–300 u mass range. The scan functions used to investigate the reactivity of the ions (no isolation step) and to determine the reaction mechanisms and the kinetic constants (selective isolation steps) are described elsewhere, as well as the calculation procedures [7,8,10,12]. The first step of investigation consists of reaction of the ionized gaseous mixture for a suitable reaction time (usually ranging from 0 to 1 s) in order to detect the main ion species formed and to follow the variation of their abundances with reaction time. In successive experiments, all the ions formed with enough abundance (ca. 2%) are isolated by superimposition of rf and dc voltages and reacted with the neutral molecules in order to identify the ion products and to measure the rate constants of the main processes observed. This procedure was followed for the study of both propyne/ammonia and silane/propyne/ammonia systems. In many cases, several signals were observed which could be attributed to different isobaric species, e.g., at *m/z* 60 ($Si_2H_4^+$, $SiN_2H_4^+$ and $SiCNH_6^+$). When two or more isobaric ion species can be hypothesized, the double isolation method could permit to selectively isolate each of them. This method consists of selecting a precursor ion which reacts to give only one among two or more isobaric ions. If the suitable precursor is available, its selection and reaction yield the desired ion which may in turn be isolated and reacted. This multiple-stage isolation method may be extended up to the second step only, as the abundances of the ions decrease with increasing number of isolation steps.

3. Results and discussion

3.1. Propyne/ammonia

Ionization of propyne/ammonia mixtures with 35 eV electrons gives the primary $C_3H_n^+$ ($n = 1$–4) and NH_n^+ ($n = 1$–3) ions and fragment $C_2H_n^+$ ($n = 3, 4$) ion species, which react with neutral species to produce several charged species of higher mass. Three different C_3H_4/NH_3 mixtures with pressure ratios of 1:1, 1:5 and 5:1 and total pressure of about 1.2×10^{-6} Torr were reacted up to 1 s, in order to determine which pressure ratio gave the best yield of mixed ion species. The variation of the total abundances of ions containing both C and N atoms versus time is reported in Fig. 1 for the three mixtures. Due to the presence of many isobaric ion species, only the mixed ions which were unambiguously

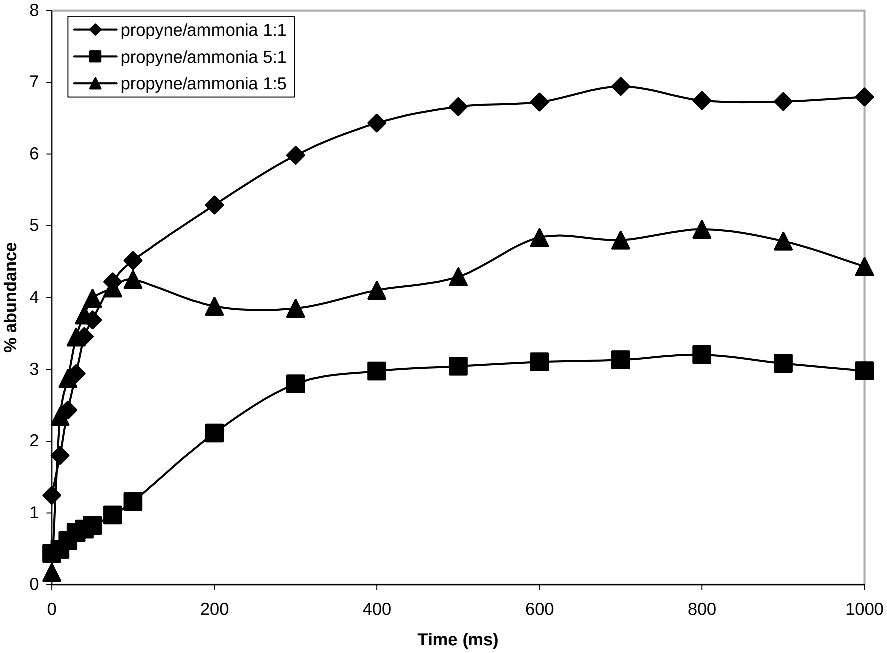


Fig. 1. Trends of the abundances of C- and N-containing ions in three different C_3H_4/NH_3 mixtures, with partial pressure ratios of 1:1, 1:5 and 5:1, respectively.

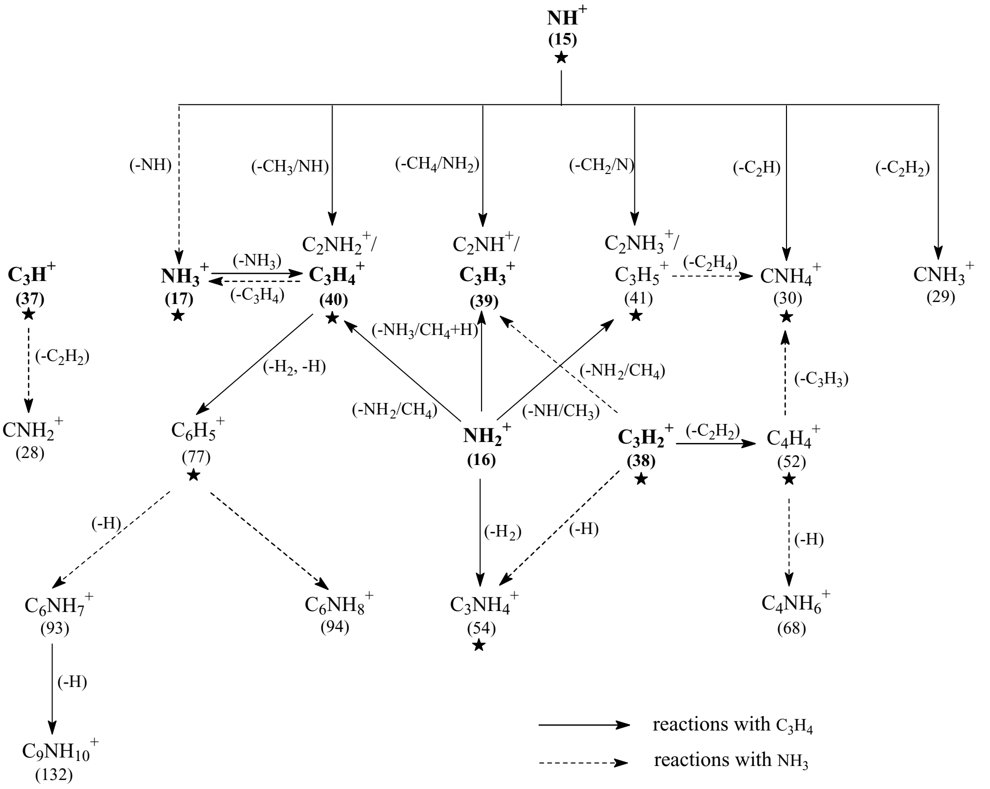
Table 1
Relative abundances of the main ion species observed in a C_3H_4/NH_3 1:1 mixture at different reaction times[a]

Ion	Reaction time (ms)												
	0	20	50	100	200	300	400	500	600	700	800	900	1000
NH^+	1.04	0.28	0.18	0.23	0.27	0.23	0.24	0.19	0.14	0.20	0.14	0.19	0.19
NH_2^+	4.31	2.73	2.66	3.19	3.53	3.60	3.66	3.61	3.52	3.56	3.59	3.54	3.54
NH_3^+	8.96	8.27	6.17	2.32	2.47	2.47	2.49	2.50	2.43	1.65	0.86	0.84	0.84
NH_4^+	5.62	13.70	23.45	33.71	39.14	40.98	41.79	42.07	42.18	42.61	43.26	43.49	43.49
$C_2H_3^+$	0.68	0.63	0.38	0.10	–	–	–	–	–	–	–	–	–
$C_2H_4^+$, $\mathbf{CNH_2}^+$	1.47	1.09	0.82	0.44	–	–	–	–	–	–	–	–	–
$\mathbf{CNH_3}^+$	0.35	0.24	0.23	0.14	–	–	–	–	–	–	–	–	–
$\mathbf{CNH_4}^+$	0.14	0.08	0.15	0.27	0.39	0.40	0.39	0.39	0.40	0.39	0.34	0.31	0.31
C_3H^+	5.58	2.90	1.09	0.19	–	–	–	–	–	–	–	–	–
$C_3H_2^+$	9.21	5.38	2.81	0.87	0.17	0.27	0.12	0.17	0.21	0.18	0.20	0.14	0.14
$C_3H_3^+$	28.82	28.44	26.31	24.76	24.44	24.69	25.13	25.43	25.76	26.11	26.37	26.61	26.61
$C_3H_4^+$	23.46	15.19	6.84	2.20	0.81	0.71	0.73	0.74	0.70	0.75	0.75	0.77	0.77
$C_3H_5^+$	2.80	3.87	3.44	2.21	0.69	0.20	–	–	–	–	–	–	–
$C_4H_3^+$	0.98	1.58	1.33	0.58	–	–	–	–	–	–	–	–	–
$C_4H_4^+$	1.07	1.93	2.20	1.53	0.55	0.26	0.18	0.13	0.16	0.10	0.06	–	–
$C_4H_5^+$	0.58	1.05	1.29	1.14	0.76	0.60	0.55	0.56	0.57	0.58	0.50	0.54	0.54
$\mathbf{C_3NH_4}^+$, $C_4H_6^+$	0.80	2.18	3.14	3.53	3.35	3.29	3.28	3.32	3.34	3.41	3.36	3.43	3.43
$C_5H_3^+$	0.18	0.46	0.55	0.54	0.48	0.46	0.44	0.49	0.47	0.50	0.50	0.50	0.50
$C_5H_5^+$	0.30	0.56	1.13	1.48	1.50	1.43	1.38	1.38	1.37	1.39	1.40	1.36	1.36
$\mathbf{C_4NH_6}^+$	–	–	–	–	–	0.02	0.04	0.07	0.08	0.08	0.09	0.10	0.10
$C_6H_5^+$	1.14	3.18	5.44	5.94	3.36	1.60	0.89	0.65	0.59	0.58	0.56	0.55	0.55
$C_6H_7^+$	2.06	5.84	8.38	9.55	8.19	6.44	5.19	4.40	3.96	3.83	3.64		
$C_7H_7^+$	0.14	0.26	1.29	2.92	5.12	5.44	4.88	4.12	3.48	2.85	2.53		
$\mathbf{C_6NH_7}^+$	0.02	0.00	0.12	0.31	0.70	0.95	1.12	1.17	1.18	1.23	1.20		
$\mathbf{C_6NH_8}^+$	–	0.05	0.17	0.35	0.87	1.35	1.64	1.77	1.77	1.87	1.85		
$C_9H_7^+$	0.10	0.12	0.44	1.51	3.17	3.89	3.62	3.16	2.78	2.34	2.03		
$C_{10}H_{11}^+$	–	–	–	–	0.05	0.54	1.53	2.36	3.10	3.65	4.27		
$C_{12}H_{11}^+$	–	–	–	–	–	0.22	0.74	1.26	1.74	2.12	2.52	2.71	2.88

[a] Mixed ions are reported in bold.

detected are considered here. The highest yield is reached in the C_3H_4/NH_3 1:1 system, and hence this pressure ratio was adopted in the following experiments. Table 1 reports the abundances normalized with respect to the total ion current of the main ions observed in the C_3H_4/NH_3 1:1 mixture at different reaction times ranging from 0 to 1 s. For isobaric ions, the total relative intensity of the signal is reported. The primary ion $C_3H_3^+$ is poorly reactive, as it remains very abundant up to 1 s, while the abundance of the NH_4^+ ion grows rapidly and it becomes the most abundant ion after 75 ms reaction time. These two ions together carry more than 55% of the total ion current after 75 ms. All the other ion species are little abundant; in particular, as evidenced from Fig. 1, the mixed ion species barely reach 7% as their maximum abundance. Scheme 1 reports the reaction mechanisms derived from experiments of ion isolation and reaction; primary ions are in bold characters, solid arrows are referred to reactions in which the neutral species is propyne, and dashed arrows to reactions where ammonia is the neutral reagent. Most of the self-condensation pathways, already published [12,17], are not reported for sake of clarity. Moreover, all the ions that form the ammonium ion are simply indicated with a star, without reporting the complete reaction. The ion species which only give self-condensation reactions and/or the NH_4^+ ion, i.e., $C_2H_3^+$, $C_4H_3^+$, $C_4H_5^+$, $C_5H_5^+$, $C_6H_7^+$, $C_7H_7^+$, $C_9H_7^+$ and $C_{10}H_{11}^+$, are not reported in the Scheme. The ammonium ion is very stable and it is unreactive in the experimental conditions used here. It is worth noting that in reactions of NH^+ and NH_2^+, three ions at *m/z* 39–41 are formed. Two formulas are possible for each product ion, as reported in the Scheme. The abundance of the $C_2NH_q^+$ ($q = 1$–3, *m/z* 39–41) ions in the overall C_3H_4/NH_3 mixture is negligible, and therefore they are not reported in Table 1. However, even if it was not possible to identify the reaction paths which generate them, their formation starting from NH^+ and NH_2^+ cannot be ruled out.

Experimental and collisional rate constants, and reaction efficiencies of the main reactions taking place after ionization of propyne/ammonia mixture are reported in Tables 2 and 3. Table 2 displays the reaction rate constants of ions from propyne with ammonia, and Table 3 reports the reaction rate constants of ions from ammonia with both propyne and ammonia. In this Table the reaction rate constants of ammonia self-condensation are also reported even if they were already published [12], because in this paper collisional rate constants are calculated according to the more recent Parameterized Trajectory Theory [20], while in the preceding paper the Average Dipole Orientation (ADO) Theory [24] was used. Table 3 also reports reactions of the only mixed ion (CNH_4^+) which yields a product ion (NH_4^+)



Scheme 1.

with enough abundance to determine the reaction rate constant. Ions from ammonia react with propyne with efficiency of about 40%, the self-condensation pathways generally being the most favourite with efficiencies which can reach 80%. The efficiency of the only reaction taking place from a mixed ion is lower of about an order of magnitude, accordingly to what is generally observed for secondary ion species. In reactions of propyne ions with neutral ammonia (Table 2), the reaction efficiencies are appreciable for primary ions and decrease for secondary and tertiary ions.

Table 2
Ion/molecule reactions of ions from propyne with ammonia[a,b]

Reaction	k_{exp}	Σk_{exp}	k_{cap}[c]	Efficiency[d]
(27) $C_2H_3^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_2H_2$	14	14	24.27	0.58
(38) $C_3H_2^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_3H$	1.4			
(38) $C_3H_2^+ + NH_3 \rightarrow$ (39) $C_3H_3^+ + NH_2$	1.5			
(38) $C_3H_2^+ + NH_3 \rightarrow$ **(54)** $\mathbf{C_3NH_4}^+ + H$	7.7	11	22.87	0.46
(40) $C_3H_4^+ + NH_3 \rightarrow$ (17) $NH_3^+ + C_3H_4$	2.1			
(40) $C_3H_4^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_3H_3$	13	15	22.69	0.65
(41) $C_3H_5^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_3H_4$	9.0	9.0	22.61	0.40
(51) $C_4H_3^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_4H_2$	9.9	9.9	21.95	0.45
(52) $C_4H_4^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_4H_3$	3.2			
(52) $C_4H_4^+ + NH_3 \rightarrow$ **(30)** $\mathbf{CNH_4}^+ + C_3H_3$	0.44	3.6	21.9	0.16
(53) $C_4H_5^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_4H_4$	4.7	4.7	21.84	0.21
(65) $C_5H_5^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_5H_4$	0.35	0.35	21.35	0.016
(77) $C_6H_5^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_6H_4$	0.74			
(77) $C_6H_5^+ + NH_3 \rightarrow$ **(93)** $\mathbf{C_6NH_7}^+ + H$	0.48			
(77) $C_6H_5^+ + NH_3 \rightarrow$ **(94)** $\mathbf{C_6NH_8}^+$	0.86	2.1	21	0.10
(79) $C_6H_7^+ + NH_3 \rightarrow$ (18) $NH_4^+ + C_6H_6$	2.2	2.2	20.95	0.10

[a] Mixed ions are reported in bold.

[b] Rate constants are expressed as 10^{-10} cm^3 $molecule^{-1}$ s^{-1}; uncertainty is within 20%.

[c] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarizability and the dipole moment of ammonia from Refs. [21,22], respectively.

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

Table 3
Ion/molecule reactions of ions from ammonia and of CNH_4^+ in a C_3H_4/NH_3 mixture[a,b]

Reaction	k_{exp}	Σk_{exp}	k_{cap}[c]	Efficiency[d]
(15) $NH^+ + C_3H_4 \rightarrow$ **(29)** $\mathbf{CNH_3}^+ + C_2H_2$	1.1			
(15) $NH^+ + C_3H_4 \rightarrow$ **(30)** $\mathbf{CNH_4}^+ + C_2H$	0.87			
(15) $NH^+ + C_3H_4 \rightarrow$ (39) $C_3H_3^+/\mathbf{C_2NH}^+ + NH_2/CH_4$	3.2			
(15) $NH^+ + C_3H_4 \rightarrow$ (40) $C_3H_4^+/\mathbf{C_2NH_2}^+ + NH/CH_3$	2.6			
(15) $NH^+ + C_3H_4 \rightarrow$ (41) $C_3H_5^+/\mathbf{C_2NH_3}^+ + N/CH_2$	1.3	9.1	21.18	0.43
(15) $NH^+ + NH_3 \rightarrow$ (17) $NH_3^+ + NH$	9.1			
(15) $NH^+ + NH_3 \rightarrow$ (18) $NH_4^+ + N$	1.8	10.9	27.77	0.39
(16) $NH_2^+ + C_3H_4 \rightarrow$ (40) $C_3H_4^+/\mathbf{C_2NH_2}^+ + NH_2/CH_4$	2.9			
(16) $NH_2^+ + C_3H_4 \rightarrow$ (41) $C_3H_5^+/\mathbf{C_2NH_3}^+ + NH/CH_4 + H$	2.9			
(16) $NH_2^+ + C_3H_4 \rightarrow$ **(54)** $\mathbf{C_3NH_4}^+ + H_2$	2.0	7.8	20.69	0.38
(16) $NH_2^+ + NH_3 \rightarrow$ (17) $NH_3^+ + NH_2$	18	18	27.30	0.66
(17) $NH_3^+ + NH_3 \rightarrow$ (18) $NH_4^+ + NH_2$	22	22	26.88	0.82
(30) $\mathbf{CNH_4}^+ + NH_3 \rightarrow$ (18) $NH_4^+ + CNH_3$	1.1	1.1	23.79	0.045

[a] Mixed ions are reported in bold.

[b] Rate constants are expressed as 10^{-10} cm^3 molecule^{-1} s^{-1}; uncertainty is within 20%.

[c] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarizability and the dipole moment of ammonia from Refs. [21,22], respectively, and the polarizability and the dipole moment of propyne from Refs. [22,23], respectively.

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

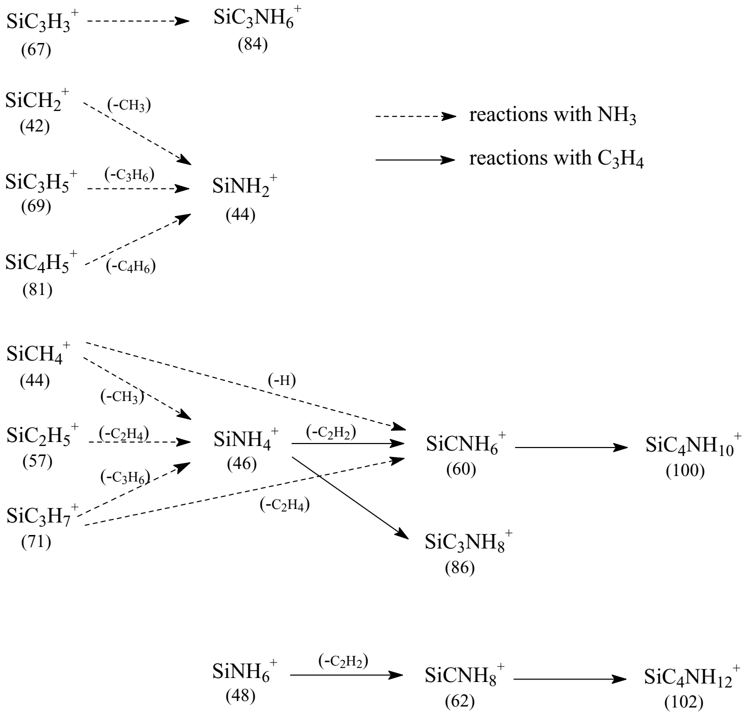
In these reactions, high experimental rate constants are frequently observed when NH_4^+ is the product ion. This is due to the high proton affinity of ammonia [25], which is higher than those of most of the neutral hydrocarbons [25] eliminated in NH_3 protonation reactions. For some species (C_3H, C_4H_3, C_4H_4 and C_5H_4) the proton affinity is not available in the literature. Moreover, heats of formation of C_3H and C_4H_3 are not available too; therefore, no indications about the exothermicity of NH_3 protonation reactions forming these two neutrals can be drawn from thermochemical data. On the other hand, the enthalpies of reactions (a) $C_4H_5^+ + NH_3 \rightarrow NH_4^+ + C_4H_4$ and (b) $C_5H_5^+ + NH_3 \rightarrow NH_4^+ + C_5H_4$ were calculated, considering the most stable isomer for each ion and molecule [26]. Reaction (a) is exothermic by 48.1 kJ mol^{-1}, while reaction (b) is endothermic by 88.9 kJ mol^{-1}. This latter value may be surprising, as we assume that reactant ions in the ion trap are thermalized and hence only exothermic reactions should be observed. However, it should be noted that the reaction enthalpy is calculated considering the most stable isomer for the reactant $C_5H_5^+$ ion, i.e., a vinyl-cyclopropenyl structure. If the $HC{\equiv}CCHCH{=}CH_2^+$ isomer is considered, reaction (b) becomes exothermic by about 31 kJ mol^{-1}. Besides being the most stable isomer, the cyclic structure of $C_5H_5^+$ necessitates more rearrangements to be formed than the open-chain structure, which may not take place in the time scale of an ITMS experiment. Therefore, the pent-1-en-4-yn-3-yl isomer ion is likely the reactant ion in reaction (b). Reaction pathways leading to mixed ion species are not very favored. The only exception is the reaction yielding $C_3NH_4^+$ from $C_3H_2^+$, with $k_{exp} = 7.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Due to mass overlapping, the reactivity of some ion species, such as CNH_2^+ and $C_2H_4^+$ (*m/z* 28), was not studied. In fact, the double isolation experiment cannot be performed for the primary $C_2H_4^+$ ion and, in the case of the mixed CNH_2^+ ion species, the signal-to-noise ratio was too low. This is the reason why these ions do not appear neither in Scheme 1 nor in the Tables.

Experimental rate constants were compared to those available in the literature. In the present work, ammonia protonation reaction by $C_2H_3^+$ (Table 2) proceeds at a much lower rate with respect to that previously reported, i.e., $k = 14 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} versus the 24.8×10^{-10} cm^3 molecule^{-1} s^{-1} value by Huntress (W.T. Huntress, unpublished results). This latter value may be overestimated as it slightly exceeds the collisional constant ($k_{cap} = 24.27 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). However, it is likely that incomplete thermalization of the reactant ion in the present experiments is responsible for reaction efficiencies lower than unity. This is also the case for reactions of NH^+ and NH_2^+ with ammonia, where our rate constant values are lower than those reported by Adams et al. [27], while an excellent agreement is found for reaction of NH_3^+ and NH_3 [27].

3.2. Silane/propyne/ammonia

Formation of ion species containing Si, C and N together takes place through reaction of binary mixed ions, i.e., ions containing two among the three elements mentioned, with the neutral reagent containing the third element. Therefore, isolation and reaction of binary mixed ions in the ternary mixture, and comparison of the mass spectra with those recorded in the binary mixtures after the same reaction time, allows to identify the ions formed through reaction with the third molecule. In the ternary mixture, mass overlapping among different ion species is observed even more frequently than in the secondary one. Propyne results to be very reactive, and several ion species are formed when C_3H_4 is the neutral reagent. Moreover, the nominal masses of the C_2H_4 and N_2 moieties and of the most abundant silicon isotope are the same (*m/z* 28). As a consequence, almost every



Scheme 2.

mixed ion detected in the binary mixtures shows one or more isobaric ion species in the ternary mixture. In order to isolate and react the mixed ions, the double isolation procedure was employed in almost all the cases. This procedure was not always successful, as sometimes isobaric products are given by isobaric parent ions. In many other cases, this kind of experiment generates low and poorly reproducible ion currents. Therefore, it was possible to isolate only few mixed ion species and no rate constants could be determined. Scheme 2 reports the reaction mechanisms observed in the ternary mixture. The reactant Si/C ions are formed through different ion/molecule processes occurring in the silane/propyne mixture, as already reported [17], while the $SiNH_6^+$ ion is a product of a series of ion/molecule reactions taking place in the silane/ammonia system [12]. Solid arrows are referred to reactions where C_3H_4 is the neutral reagent, while dashed arrows to reactions where ammonia is the neutral. Most of these reactions imply the loss of a hydrocarbon fragment, thus yielding a binary Si/N ion and not a ternary ion species. However, the subsequent reaction of a Si/N ion with C_3H_4 frequently leads to the formation of a ternary ion. No mixed C/N ions could be isolated in the ternary mixture, and no Si/C/N ion reacts with silane to give higher mass ternary ions. For this reason silane does not appear in the Scheme as neutral reagent.

In order to evaluate the overall abundance of ternary ions in the ternary mixture, mass spectra were recorded for the ternary mixture and subsequently for each binary mixture at several different reaction times. Comparison of the ion currents at each *m*/*z* value between ternary and binary systems allows to find out the ion species only formed in the ternary system, which are necessarily ternary ions or, at least, ions formed in reactions involving all three reagents. Table 4 reports the ion abundances recorded at the longest reaction time examined (1 s), where the mixed ion abundances resulted to be the highest. In the first column, *m*/*z* values are given of all ions detected in the mass spectrum of the ternary mixture at 1000 ms reaction time. For each *m*/*z* ratio, the second column displays the possible composition of ions, as previously observed in the three binary mixtures at any reaction time. Finally, the following four columns report ion currents of ions present in the ternary mixture and in the three binary mixtures at 1000 ms reaction time, recorded in sequential experiments. The ion currents have been chosen, rather than the percentage abundances, to permit direct comparison of experimental data. When a species is present only in the ternary mixture, or displays a remarkably higher abundance in this system (values in bold character in Table 4) with respect to the binary ones, it can be deduced that it is formed in reaction paths involving all three reagent gases. In these cases, an ion composition is suggested in the first column. In some cases, a formula was assigned to a particular ternary ion on the basis of the results of ion isolations reported in Scheme 2, and these are the cases of *m*/*z* 60 ($SiCNH_6^+$), *m*/*z* 100 ($SiC_4NH_{10}^+$) and *m*/*z* 101 ($SiC_4NH_{11}^+$). In all the other cases, where more than one formula could match an *m*/*z* ratio, a generic formula is reported. However, it was possible to evaluate the overall abundance of mixed ions, which roughly exceeds 20% of the total ion current after 1 s reaction time.

Table 4
Ion abundances in the ternary $SiH_4/C_3H_4/NH_3$ and in the binary SiH_4/C_3H_4, C_3H_4/NH_3, and SiH_4/NH_3 mixtures after 1000 ms reaction time[a,b]

(*m/z*) Ion	Ternary	$SiH_4 + C_3H_4$	$C_3H_4 + NH_3$	$SiH_4 + NH_3$
(14) N^+	16050	–	16300	16500
(16) $NH_2{}^+$	56450	–	46800	56300
(17) $NH_3{}^+$	46100	–	16750	16900
(18) $NH_4{}^+$	956000	–	726550	876050
(38) $C_3H_2{}^+$	26450	36100	–	–
(39) $C_3H_3{}^+$	326200	206700	476450	–
(40) $C_3H_4{}^+$	56450	76600	16500	–
(48) $SiNH_6{}^+$	950	–	–	56350
(54) $C_4H_6{}^+/SiC_2H_2{}^+/NC_3H_4{}^+$	26350	–	66750	–
(59) $SiC_2H_7{}^+/Si_2H_3{}^+$	950	450	–	–
(60) $Si_2H_4{}^+/\mathbf{SiCNH_6}{}^+$	**86700**	–	–	–
(61) $Si_2H_5{}^+/SiN_2H_5{}^+$	26300	–	–	46400
(67) $C_5H_7{}^+/SiC_3H_3{}^+$	26450	86550	–	–
(73) $Si_2CH_5{}^+/SiC_3H_9{}^+/Si_2NH_3{}^+$	76350	406750	–	–
(74) $Si_2CH_6{}^+/Si_2NH_4{}^+$	56150	146050	–	–
(75) $Si_2CH_7{}^+/Si_2NH_5{}^+$	16600	66100	–	–
(76) $Si_2CH_8{}^+/Si_2NH_6{}^+$	16600	16400	–	–
(77) $C_6H_5{}^+$	16900	16050	750	–
(78) $C_6H_6{}^+/SiN_3H_8{}^+/\mathbf{SiC}_{\boldsymbol{n}}\mathbf{N}_{\boldsymbol{p}}\mathbf{H}_{\boldsymbol{q}}{}^+$	**16000**	900	–	–
(79) $C_6H_7{}^+$	26100	66400	–	–
(90) $Si_3H_6{}^+/\mathbf{Si}_{\boldsymbol{m}}\mathbf{C}_{\boldsymbol{n}}\mathbf{N}_{\boldsymbol{p}}\mathbf{H}_{\boldsymbol{q}}{}^+$	**146400**	26050	–	–
(91) $C_7H_7{}^+/Si_2N_2H_7{}^+$	26650	46700	16100	–
(93) $C_7H_9{}^+/SiC_5H_6{}^+/C_6NH_7{}^+$	66400	136900	26000	–
(94) $SiC_5H_6{}^+/C_6NH_8{}^+$	16200	36600	26550	–
(100) $\mathbf{SiC_4NH_{10}}{}^+$	**96850**	–	–	–
(101) $\mathbf{SiC_4NH_{11}}{}^+$	**16200**	–	–	–
(107) $SiC_6H_7{}^+$	26450	56850	–	–
(117) $\mathbf{Si}_{\boldsymbol{m}}\mathbf{C}_{\boldsymbol{n}}\mathbf{N}_{\boldsymbol{p}}\mathbf{H}_{\boldsymbol{q}}{}^+$	**56000**	–	–	–
(118) $\mathbf{Si}_{\boldsymbol{m}}\mathbf{C}_{\boldsymbol{n}}\mathbf{N}_{\boldsymbol{p}}\mathbf{H}_{\boldsymbol{q}}{}^+$	**16650**	–	–	–
(131) $C_{10}H_{11}{}^+$	26350	106150	46000	–
(155) $C_{12}H_{11}{}^+$	950	26650	–	–

[a] Ion species present in the ternary mixture only are reported in bold. Their formulas are assigned on the basis of reactions of isolated binary ions with the third gas.

[b] Ion abundances are reported in arbitrary units.

3.2.1. Comparison with systems previously studied

3.2.1.1. Silane/propyne/ammonia versus silane/propene/ammonia. This comparison is not straightforward because of the low number of mixed ion species that could be isolated in the $SiH_4/C_3H_4/NH_3$ mixture. In the silane/propene/ammonia system [16], several mixed ions were selected and reacted, and numerous rate constants were reported. When the reactivity of ions with the same formula in the two ternary systems is compared, it often looks quite different. As an example, ions with formula $SiC_2H_5{}^+$ were isolated and reacted with NH_3 in both systems: in the mixture containing propene, a high number of products is obtained, and quite high rate constants were calculated, while in the present mixture the $SiC_2H_5{}^+$ ion only yields $SiNH_4{}^+$, and the reaction rate constant could not be calculated due to the low product yield. Many other similar cases turn out by comparing the two mixtures. The apparent lower reactivity of the present system could be ascribed to the frequent mass overlapping observed, leading to very unfavorable conditions, such as isolation of a mixed ion starting from a very low-abundance parent ion, which necessarily yields low signal-to-noise ratios. Therefore, mass overlapping hindered ion isolation and determination of rate constants in the system with propyne. Moreover, it is also very likely that ions with the same formula correspond to different isomers in the two systems, and hence their reactivity may be quite different, as for $SiC_2H_5{}^+$ ions. A comparison of the reactivity of the two systems may be drawn from the percentage abundances of mixed ions: in the mixture with propene, mixed ions reach 20% abundance after 500 ms reaction time, while they represent only 12% of the total ion current in the present system after the same reaction time.

3.2.1.2. Silane/propyne/ammonia versus silane/propyne/phosphine. The present mixture shows an higher yield of mixed ions with respect to the analogous silane/propyne/phosphine system [18], where the abundance of mixed ions after 500 ms is about 7%. When the silane/propene/phosphine [15] and the silane/propene/ammonia [16] were compared, the latter showed a higher yield of mixed ions and the present results confirm the higher reactivity of ammonia with respect to phosphine towards silane and propene.

3.2.1.3. Further remarks. If analogous systems with the two different hydrocarbons considered here (propyne and propene) are compared, a slight discrepancy is revealed. While, as noted in Section 3.2.1.1, propene gives an higher abundance of mixed ions with respect to propyne in mixtures with silane and ammonia, the reactivity of the silane/propyne/phosphine system is slightly higher than that of the silane/propene/phosphine, as previously outlined [18]. However, the different reactivity between the last two systems is not as evident as the one between the analogous systems containing ammonia.

4. Conclusions

Ion/molecule reactions in the propyne/ammonia and silane/propyne/ammonia mixtures have been studied by ion trap mass spectrometry and experimental rate constants for the main processes of the binary mixture were calculated. The high reactivity of propyne toward positive ions, due to the presence of two π-electron pairs, leads to the formation of several ion products with high efficiencies, even if each rate constant is generally rather low. In the binary propyne/ammonia mixture, the NH_4^+ ion rapidly becomes the most abundant species as it is extremely stable and not reactive in the experimental conditions used here, whereas only few processes lead to formation of mixed ions, and this is not encouraging in view of the synthesis of silicon carbides doped with nitrogen from appropriate gaseous mixtures. The 1:1 pressure ratio among propyne and ammonia gives the highest yield of mixed ions, with $C_3NH_4^+$ as the most abundant species. The presence of many isobaric ion species allowed to perform only few ion isolations in the ternary mixture. However, an appreciable number of pathways leading to ternary ion species was identified, in particular reactions of $SiC_nH_q^+$ ($n = 1$–3; $q = 2$–5, 7) ions with ammonia and of $SiNH_q^+$ ($q = 2$, 4) and $SiCNH_q^+$ ($q = 6$, 8) with propyne. Comparison of ion abundances between the ternary and the three possible binary mixtures revealed that the maximum abundance of mixed species in the ternary system reaches the appreciable value of 20% after 1 s reaction time. Therefore, even if the propyne/ammonia system was not very promising, the ternary silane/propyne/ammonia mixture resulted to be quite interesting in view of the synthesis of silicon carbide doped with nitrogen in the gas phase.

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