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Gas-phase ion chemistry in $GeH_4/C_2H_4/XH_3$ (X = P, N) systems

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Dedicated to Professor Helmut F. Schwarz on the occasion of his 60th birthday.

Abstract

The C_2H_4/PH_3, C_2H_4/NH_3, $GeH_4/C_2H_4/PH_3$ and $GeH_4/C_2H_4/NH_3$ gaseous mixtures were studied by ion trap mass spectrometry, with the aim of finding the best experimental conditions leading to the formation of Ge/C/P (or N) ion clusters. In fact, these species are possible precursors of semiconductor materials based on germanium carbides, doped with P and N, and prepared by chemical vapour deposition methods from suitable gaseous systems. For the binary mixtures the rate constants of the main processes were determined and compared with collisional rate constants in order to calculate reaction efficiencies. For the ternary mixtures the mechanisms of ion/molecule reactions yielding Ge, C and P (or N) ion clusters were studied. In the $GeH_4/C_2H_4/PH_3$ system, formation of $Ge_mC_nP_pH_s^+$ ions was observed only from C/P ions reacting with germane, the C/P ions being formed with good yields through ion/molecule reactions in the ethene/phosphine system. In the ammonia-containing mixtures, the yield of C/N ions is quite poor because most of the reactions observed lead to ammonium ion formation, which is unreactive under the experimental conditions used. Furthermore, the amounts of $Ge_mC_nH_s^+$ and $Ge_mN_nH_s^+$ ion products were found to be small and weakly reactive and no processes leading to Ge/C/N ions were detected in the $GeH_4/C_2H_4/NH_3$ mixture.

Keywords: Ammonia; Ethene; Germane; Phosphine; Ion trap mass spectrometry; Ion clusters

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1. Introduction

In recent years, the gas-phase ion chemistry of organogermanes has attracted a great deal of interest, both from experimental and theoretical points of view [1], among others for their potential use in the synthesis of amorphous solid germanium carbides which display semiconductor properties [2]. The preparation of these materials takes place through laser or X-ray-assisted chemical vapour deposition methods, and may involve the use of germane and small hydrocarbons as starting reagents [3,4]. Although no direct correlation can be drawn among the compositions of the gas phase and of the final solid, the study of the ion species involved in the first polymerisation steps may give an indication about the experimental conditions leading to amorphous solids of the desired composition [5]. This study may be easily performed by suitable mass spectrometric methods. Moreover, the investigation of the behaviour of gaseous mixtures provides information about the intrinsic reactivity of the systems under examination in the absence of the

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solvent or of counterions [6,7]. Again, mass spectrometry appears to be a very powerful tool for this kind of investigation, as it is successfully applied in the study of overall reactivity of gaseous systems and determination of reaction mechanisms and kinetics of selected ions [6–17].

Ion/molecule reactions in monogermane [14], experimental data on bond energies in GeH_4 and ionisation energies of the $GeH_n{}^+$ species [15] have already been reported. Moreover, studies are available on $Ge(OR)_4$ (R = alkyl) species [16] and on mixtures of germane with small molecules [17]. Recently, results have been published about germane cluster anions [18], and on germane activation by actinide ions [19].

In the present paper, ion/molecule reactions in the $GeH_4/C_2H_4/PH_3$ and $GeH_4/C_2H_4/NH_3$ gaseous mixtures are studied by ion trap mass spectrometry. This work is based on the preliminary study of all the possible binary mixtures of the neutral reagents involved. The GeH_4/PH_3 [17c], GeH_4/NH_3 [17d] and GeH_4/C_2H_4 [17e] systems have been previously investigated, while the C_2H_4/PH_3 and C_2H_4/NH_3 mixtures are also objects of the present study. The aim of this work consists of identifying the reaction paths leading to the formation of Ge/C/X (X = P, N) cluster ions, which may be possible precursors of germanium carbides doped with phosphorus or nitrogen atoms, directly prepared from the suitable ternary mixture (without requiring further doping process).

2. Experimental

Ethene, phosphine and ammonia were supplied by SIAD (Bergamo, Italy) in high purity. Germane was synthesised as described in the literature [5]. Before using, each reagent gas was dried by sodium sulphate. Helium buffer gas was supplied by SIAD at an extra-high purity grade and was used without further purification. All the experiments were run on a Finnigan (Austin, TX, USA) ITMS instrument maintained at 333 K in order to obtain results comparable to those from previous studies [17c–e]. Pressures were measured by a Bayard Alpert ion gauge and corrected for both the relative sensitivity of the ion gauge with respect to different gases (M. Decouzon, J.-F. Gal, P.-C. Maria and A.S. Tchinianga, personal communication) and a calibration factor, which depends on the geometry of the instrument, determined as reported previously [17c]. The manifold and the lines for introduction of gases were frequently baked out in order to avoid side reactions with water background. Pressures were typically 6.0×10^{-7} Torr for reagent gases and 7.0×10^{-5} Torr for helium (1 Torr = 133 Pa). At this buffer gas pressure, empirically set in order to maximise the abundance of signals, it is reasonable to suppose that most of the reactant ions are thermalised. The scan modes for ion/molecule reaction experiments used to determine reaction mechanisms and rate constants for reaction of selected ions, and the corresponding calculation procedures have been previously described in detail [17]. Ionisation was achieved by electron ionisation using an electron beam with an average energy of 35 eV. Selective isolation of ions was achieved by the apex method (superimposition of dc and rf voltages). In all experiments ions were detected in the 10–300 u mass range. Due to the presence of many isobaric ions, the double isolation procedure (MS/MS) [17] was often necessary. It consists of selection and reaction of the precursor ion of the desired species, in order to unambiguously yield it and maximise its abundance, followed by its isolation among the ion products. The method is successfully applied when there is at least an ion species that yields one of the isobaric ions observed.

Experiments for the determination of each rate constant were repeated two or three times and the results reported here are the means of the calculated values.

3. Results and discussion

3.1. Ethene/phosphine mixture

In a first kind of experiments, without isolation of selected ion species, the trend of all ions was determined for increasing reaction times. The variations

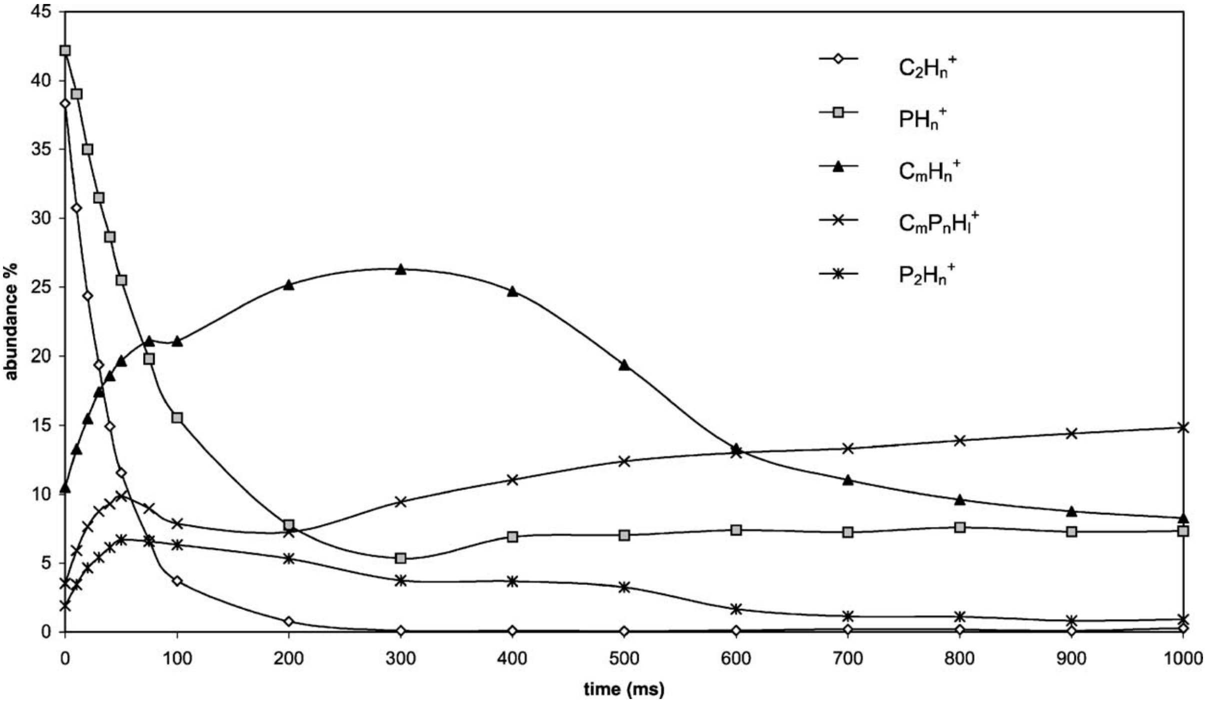

Fig. 1. Trends of the abundances of the main ion families in a C_2H_4/PH_3 mixture as a function of reaction time.

of the abundances of these ions, grouped in families, are shown in Fig. 1 for a C_2H_4/PH_3 1:1 mixture. The phosphonium ion is not reported in the figure, as its abundance is much higher with respect to the other ion species observed in this system. As expected, the abundances of primary ions of both reagents sharply decrease to zero for ethene and to about 7% for phosphine. Also self-condensation ion products of the gases behave similarly, as they initially increase, reach a maximum (higher for $C_mH_n^+$ species with respect to $P_2H_n^+$ ones), and then decrease. The abundance of the C/P ions increases quite regularly and they become the most abundant species after 600 ms reaction time, with a maximum yield of almost 15% at 1 s. Table 1 reports mechanisms and rate constants of the reactions of ions from ethene with phosphine, together with collisional rate constants (k_{coll}) and reaction efficiencies. Collisional rate constants are calculated according to the Parameterized Trajectory Theory [20]. The neutral products are determined from stoichiometric balance of reagents and products. In many cases, a reasonable formula of molecule or radical can be proposed (i.e., H_2, C_2H_4, CH_3), and is indicated in this way in the tables. In all other cases the formula reported only indicates a combination of atomic species, without information on their connectivity. Ethene primary ions ($C_2H_n^+$, $n = 1$–4) generally react with phosphine with good efficiencies. However, most of the reactions observed consist of charge or hydrogen transfer and phosphine protonation, hence not leading to the formation of C–P bonds. The C_2H^+ ions react with PH_3 to give the $C_2PH_2^+$ ion species, by loss of a hydrogen molecule. These $C_2PH_2^+$ ions are yielded by $C_2H_3^+$ as well, with rather low rate constant, in a process involving elimination of two hydrogen molecules. $C_2H_3^+$ species also originate the $C_2PH_4^+$ ions, with H_2 neutral loss. $C_2H_4^+$ and $C_2H_5^+$ give phosphine molecular ion and PH_4^+ as the only products, with high rate constants. All the ethene secondary ions react with PH_3 through several paths, and most of them lead to the formation of C/P ion species. However, the rate constants

Table 1
Ion/molecule reactions of $C_mH_n^+$ ions with phosphine[a]

Reaction	k_{exp}	$\sum k_{exp}$	k_{coll}[b]	Efficiency[c]
$C_2H^+ + PH_3 \rightarrow C_2H_2^+ + PH_2$	0.64			
$C_2H^+ + PH_3 \rightarrow C_2H_3^+ + PH$	2.4			
$C_2H^+ + PH_3 \rightarrow C_2H_4^+ + P$	2.6			
$C_2H^+ + PH_3 \rightarrow PH_3^+ + C_2H$	6.0			
$C_2H^+ + PH_3 \rightarrow C_2PH_2^+ + H_2$	2.8	14	15.64	0.92
$C_2H_2^{\bullet+} + PH_3 \rightarrow C_2H_3^+ + PH_2$	0.50			
$C_2H_2^{\bullet+} + PH_3 \rightarrow C_2H_4^+ + PH$	1.7			
$C_2H_2^{\bullet+} + PH_3 \rightarrow PH_3^+ + C_2H_2$	7.4	9.6	15.46	0.62
$C_2H_3^+ + PH_3 \rightarrow C_2H_5^+ + PH$	1.4			
$C_2H_3^+ + PH_3 \rightarrow PH_4^+ + C_2H_2$	3.0			
$C_2H_3^+ + PH_3 \rightarrow C_2PH_2^+ + 2H_2$	0.72			
$C_2H_3^+ + PH_3 \rightarrow C_2PH_4^+ + H_2$	1.9	7.0	15.30	0.46
$C_2H_4^{\bullet+} + PH_3 \rightarrow PH_3^+ + C_2H_4$	9.5			
$C_2H_4^{\bullet+} + PH_3 \rightarrow PH_4^+ + C_2H_3$	1.6	11	15.15	0.73
$C_2H_5^+ + PH_3 \rightarrow PH_4^+ + C_2H_4$	5.9	5.9	15.00	0.39
$C_3H_3^+ + PH_3 \rightarrow CPH_2^+ + C_2H_4$	0.44			
$C_3H_3^+ + PH_3 \rightarrow C_3PH_4^+ + H_2$	0.30	0.74	13.93	0.053
$C_3H_5^+ + PH_3 \rightarrow PH_4^+ + C_3H_4$	0.48			
$C_3H_5^+ + PH_3 \rightarrow CPH_4^+ + C_2H_4$	0.40			
$C_3H_5^+ + PH_3 \rightarrow C_3PH_6^+ + H_2$	0.70	1.6	13.77	0.11
$C_3H_6^+ + PH_3 \rightarrow PH_4^+ + C_3H_5$	0.51			
$C_3H_6^+ + PH_3 \rightarrow C_3H_5^+ + PH_2 + H_2$	6.8			
$C_3H_6^+ + PH_3 \rightarrow C_3H_7^+ + PH_2$	0.31			
$C_3H_6^+ + PH_3 \rightarrow CPH_4^+ + C_2H_5$	0.20			
$C_3H_6^+ + PH_3 \rightarrow CPH_5^+ + C_2H_4$	0.26	8.1	13.70	0.59
$C_4H_3^+ + PH_3 \rightarrow PH_4^+ + C_3H_2$	2.5			
$C_4H_3^+ + PH_3 \rightarrow C_2PH_2^+ + C_2H_4$	0.67			
$C_4H_3^+ + PH_3 \rightarrow C_4PH_4^+ + H_2$	0.71	3.9	13.14	0.30
$C_4H_4^+ + PH_3 \rightarrow C_4H_5^+ + PH_2$	0.36			
$C_4H_4^+ + PH_3 \rightarrow C_3PH_4^+ + CH_3$	0.54	0.90	13.09	0.069

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

[b] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarisability of PH_3 from ref. [21] and the dipole moment of PH_3 from ref. [22].

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

of these processes are quite low and never exceed 1.0×10^{-10} cm^3 molecule^{-1} s^{-1}, with consequent low reaction efficiencies. In the reactions of ions from ethene with PH_3, the most frequently observed neutral losses consist of combinations of carbon and hydrogen atoms, and it follows that formation of large clusters such as $C_3PH_4^+$ (m/z 71) and $C_4PH_4^+$ (m/z 83) is seldom observed, and is given when hydrogen is lost as neutral.

Table 2 displays mechanisms and rate constants of reactions of phosphine primary (PH_n^+, $n = 0$–3) and secondary ($P_2H_n^+$, $n = 0$–2) ions with ethene, together with collisional rate constants and reaction efficiencies. Among phosphine primary ions, PH_3^+ ions simply abstract a hydrogen atom to give the very stable phosphonium ion. On the other hand, the P^+, PH^+ and PH_2^+ ions react with high efficiencies with C_2H_4 to yield several mixed ions, i.e., ions containing both

Table 2
Ion/molecule reactions of $P_mH_n^+$ ions with ethene[a]

Reaction	k_{exp}	$\sum k_{exp}$	k_{coll}[b]	Efficiency[c]
$P^+ + C_2H_4 \rightarrow PH_3^+ + C_2H$	2.1			
$P^+ + C_2H_4 \rightarrow C_2PH_2^+ + H_2$	8.3	10	12.58	0.83
$PH^{\bullet+} + C_2H_4 \rightarrow PH_3^+ + C_2H_2$	3.0			
$PH^{\bullet+} + C_2H_4 \rightarrow CPH_2^+ + CH_3$	3.1			
$PH^{\bullet+} + C_2H_4 \rightarrow C_2PH_2^+ + H_2 + H$	0.92			
$PH^{\bullet+} + C_2H_4 \rightarrow C_2PH_3^+ + H_2$	4.4	11	12.48	0.92
$PH_2^+ + C_2H_4 \rightarrow C_2H_5^+ + PH$	1.6			
$PH_2^+ + C_2H_4 \rightarrow CPH_2^+ + CH_4$	0.60			
$PH_2^+ + C_2H_4 \rightarrow C_2PH_2^+ + 2H_2$	0.69			
$PH_2^+ + C_2H_4 \rightarrow C_2PH_4^+ + H_2$	6.9	9.8	12.39	0.79
$PH_3^{\bullet+} + C_2H_4 \rightarrow PH_4^+ + C_2H_3$	2.9	2.9	12.31	0.24
$P_2^+ + C_2H_4 \rightarrow C_2H_4^+ + P_2$	1.2			
$P_2^+ + C_2H_4 \rightarrow CP_2H^+ + CH_3$	7.1	8.3	10.98	0.76
$P_2H^+ + C_2H_4 \rightarrow C_2H_5^+ + P_2$	5.3	5.3	10.95	0.48
$P_2H_2^+ + C_2H_4 \rightarrow CPH_5^+ + CPH$	0.75	0.75	10.93	0.069

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

[b] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarisability of C_2H_4 from ref. [23].

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

C and P atoms. As far as phosphine secondary ions are regarded, reaction efficiencies decrease with increasing number of H atoms in the reactant ion, and the $P_2H_3^+$ ions do not react at all. The P_2^+ ions react quite fast with C_2H_4 to form the CP_2H^+ ions, by loss of a methyl radical. Moreover, the $P_2H_2^+$ ions yield the CPH_5^+ ion species in a process characterised by a low rate constant and by loss of a neutral moiety containing one carbon, one phosphorus and one hydrogen atom together.

Comparison of the present results with literature data reveals some remarkable discrepancies. SIFT experiments performed by Smith et al. [24] indicate that P^+ reacts with C_2H_4 to give $C_2PH_2^+$ as the only product, while the PH_3^+ product is not observed. For PH^+, Smith et al. report the CPH_2^+ and $C_2PH_3^+$ products only, whereas in the present experiments the PH_3^+ and $C_2PH_2^+$ ions were detected as well, the latter one with a quite low rate constant. The PH_2^+ ion reacts with ethene to give CPH_2^+ and $C_2PH_4^+$ according to Smith et al.; in addition, we also observe the $C_2H_5^+$ and $C_2PH_2^+$ product ions. Finally, Smith et al. do not report any reaction between PH_3^+ and ethene, while the phosphonium ion is observed in our experiments. Generally, formation rate constants for the products observed from both Smith et al. and us are quite different, but the overall rate constants of the reactant ions are in good agreement. It is worth noting that ion products derived from hydrogen transfer are not observed in the SIFT experiments, and this is probably the reason for the different branching ratios among the two series of results.

The most abundant mixed ions were in turn isolated and reacted, and the main reaction paths are reported in Table 3. They react with both phosphine and ethene with comparable efficiencies. In reactions with phosphine, substitution of a C_2H_4 by a PH_3 molecule is frequently observed, while growth of C/P ion clusters mainly takes place through molecular hydrogen neutral loss. Protonation of phosphine is again a frequent reaction path, and is displayed by mixed ions of lower mass. In the reaction of CPH_5^+ to yield CPH_6^+, by transfer of a hydrogen atom, it is impossible to univocally determine the neutral reactant. In fact, the two

Table 3
Ion/molecule reactions of $C_lP_mH_n^+$ ions with phosphine and ethene[a]

Reaction	k_{exp}	$\sum k_{exp}$	k_{coll}[b]	Efficiency[c]
$CPH_2^+ + PH_3 \rightarrow PH_4^+ + CPH$	5.9			
$CPH_2^+ + PH_3 \rightarrow CP_2H_3^+ + H_2$	2.7	8.6	13.50	0.64
$CPH_2^+ + C_2H_4 \rightarrow C_2H_5^+ + CPH$	0.46			
$CPH_2^+ + C_2H_4 \rightarrow C_3PH_4^+ + H_2$	3.9	4.4	11.61	0.38
$CPH_5^+ + PH_3 \rightarrow PH_4^+ + CPH_4$	1.5			
$C_2PH_2^+ + PH_3 \rightarrow P_2H^+ + C_2H_4$	0.69	0.69	12.87	0.054
$C_2PH_2^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2PH$	1.2			
$C_2PH_2^+ + C_2H_4 \rightarrow C_3H_5^+ + CPH$	0.30			
$C_2PH_2^+ + C_2H_4 \rightarrow C_4PH_4^+ + H_2$	1.5	3.0	11.13	0.27
$C_2PH_3^+ + PH_3 \rightarrow PH_4^+ + C_2PH_2$	0.54			
$C_2PH_3^+ + PH_3 \rightarrow P_2H_2^+ + C_2H_4$	3.1	3.6	12.83	0.28
$C_2PH_3^+ + C_2H_4 \rightarrow C_3PH_4^+ + CH_3$	5.7			
$C_2PH_3^+ + C_2H_4 \rightarrow C_4PH_6^+ + H$	1.0	6.7	11.10	0.60
$C_2PH_4^+ + PH_3 \rightarrow PH_4^+ + C_2PH_3$	1.9			
$C_2PH_4^+ + PH_3 \rightarrow P_2H_3^+ + C_2H_4$	2.0	3.9	12.79	0.30
$C_2PH_4^+ + C_2H_4 \rightarrow C_3H_7^+ + CPH$	1.0			
$C_2PH_4^+ + C_2H_4 \rightarrow C_4PH_6^+ + H_2$	1.5	2.5	11.06	0.23
$C_3PH_6^+ + PH_3 \rightarrow CP_2H_5^+ + C_2H_4$	0.71	0.71	12.33	0.058
$C_3PH_6^+ + C_2H_4 \rightarrow C_5PH_8^+ + H_2$	0.49	0.49	10.72	0.046
$C_4PH_4^+ + PH_3 \rightarrow CP_2H^+ + C_3H_6$	0.56			
$C_4PH_4^+ + PH_3 \rightarrow C_2P_2H_3^+ + C_2H_4$	0.47	1.0	12.09	0.085
$C_4PH_4^+ + C_2H_4 \rightarrow C_5PH_4^+ + CH_4$	1.5			
$C_4PH_4^+ + C_2H_4 \rightarrow C_6PH_6^+ + H_2$	2.6	4.1	10.54	0.39
$CP_2H_3^+ + PH_3 \rightarrow CP_3H_4^+ + H_2$	0.58	0.58	12.23	0.047
$CP_2H_3^+ + C_2H_4 \rightarrow C_3H_7^+ + P_2$	0.68	0.68	10.64	0.063

[a] Rate constants are expressed as $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$; uncertainty is ±10%.

[b] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarisability of PH_3 from ref. [21] and that of C_2H_4 from ref. [23], and taking the dipole moment of phosphine from ref. [22].

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

possible reactions (Eqs. (1) and (2))

$$CPH_5^+ + PH_3 \rightarrow CPH_6^+ + PH_2 \tag{1}$$

$$CPH_5^+ + C_2H_4 \rightarrow CPH_6^+ + C_2H_3 \tag{2}$$

differ for the neutral reagents and products, the ion species being the same. However, if we consider the heats of formation of the neutrals [25] ($\Delta H^\circ_{PH_3} = 22.89\,kJ\,mol^{-1}$, $\Delta H^\circ_{PH_2} = 125.94\,kJ\,mol^{-1}$, $\Delta H^\circ_{C_2H_4} = 52.47\,kJ\,mol^{-1}$, $\Delta H^\circ_{C_2H_3} = 299.0\,kJ\,mol^{-1}$), reaction (1) is more exothermic than reaction (2) by ca. $143\,kJ\,mol^{-1}$, thus resulting the most favoured path.

Formation of C/P ion clusters seems to be slightly favoured when ethene is the neutral reagent, as rate constants for these processes are generally higher with respect to those involving PH_3. The main paths leading to mixed ions imply hydrogen loss, and frequently proceed with appreciable rate constants. It is worth noting the frequent loss of a [C, P, H] neutral species, whose connectivity, according to literature data [26,27], corresponds to H–CP, the H–PC isomer being unstable.

The thermodynamic stability of this molecule may represent a favourable exit channel for all the processes in which its formation is possible.

3.2. Ethene/phosphine/germane mixture

Formation of ion clusters containing Ge, C and P atoms together may proceed through the following paths: (a) reactions of Ge/C ions with PH_3; (b) reactions of Ge/P ions with C_2H_4, and (c) reactions of C/P ions with GeH_4. The Ge/C and Ge/P ion clusters originate in ion/molecule reactions taking place in the GeH_4/C_2H_4 and GeH_4/PH_3 gaseous mixtures, which have been previously investigated [17c,e].

(a) The most abundant Ge/C ion clusters encountered in the GeH_4/C_2H_4 system were $GeCH_5{}^+$, $GeC_2H_4{}^+$ and $GeC_2H_5{}^+$. In the present ternary mixture, the $GeCH_5{}^+$ ions were isolated and reacted but resulted to be unreactive toward PH_3 under our experimental conditions, while it was not possible to isolate the $GeC_2H_5{}^+$ ions as they have the same *m*/*z* ratio of other Ge/P and C/P mixed ions in this system, and no double isolation experiment could afford them with sufficient yield. As far as the $GeC_2H_4{}^+$ ions are concerned, their only isotopic signal in the mass spectra that does not overlap to any of other different ions is $^{70}Ge_{C_2H_4}{}^+$ at *m*/*z* 98, but it is too weak to allow its selection.

(b) For the same reason it was not possible to study the reactivity of the $GePH_n{}^+$ ($n = 2$–4) ions, while the remaining Ge/P ions observed in the GeH_4/PH_3 system, i.e., $GeP_2H_n{}^+$ ($n = 0, 3, 5$) were not abundant enough to be selected.

(c) On the other hand, the C/P ions are much more abundant than Ge-containing mixed ions. Low mass ions, such as $CPH_2{}^+$ (*m*/*z* 45) and $C_2PH_2{}^+$ (*m*/*z* 57), were easily selected, while for higher mass ions a double isolation procedure was necessary in order to unambiguously select them. As an example, the $C_3PH_4{}^+$ ion has the same nominal mass as $^{70}GeH^+$. However, isolation and reaction of the $CPH_2{}^+$ precursor ions allow to obtain $C_3PH_4{}^+$ as the only product at *m*/*z* 71, thus making possible its selection. Reactions of C/P ions with germane are reported in Table 4. The most frequent reaction paths involve substitution of a hydrocarbon molecule by GeH_4, with the formation of $GePH_n{}^+$ ($n = 2, 4$) ions, the thermodynamic stability of the neutral losses (CH_4, C_2H_4) likely favouring this kind of process. However, formation of Ge/C/P ion clusters is observed when a hydrogen molecule is lost. It is noticeable that the $CPH_2{}^+$ ions yield the $GeCPH_4{}^+$ clusters with an appreciable rate constant, while the other two products, $GePH_2{}^+$ and $GeH_3{}^+$, are formed in very slow processes and their formation rate constants could not be determined with a good reproducibility. High mass Ge/C/P ion clusters are formed in reactions of the $C_2PH_4{}^+$ and $CP_2H_3{}^+$ ions, even if the rate constants for these processes are quite low.

3.3. Ethene/ammonia mixture

In this system, the same kind of experiments were performed as in the ethene/phosphine mixture. However, due to the presence of a high number of isobaric species (the CH_2 moiety weights as a nitrogen atom), it was not possible to determine the trend of the abundances of ion families with reaction time. In fact, formula could be univocally assigned to ion signals only following selective isolation of precursor ions. Table 5 reports reaction paths, experimental and collisional rate constants and reaction efficiencies of the main ion/molecule reactions observed in the ethene/ammonia system. Ammonia primary ions $NH_n{}^+$ ($n = 3, 4$) are not reactive toward ethene, and hence are not reported in the table. To the contrary, the NH^+ ions display a great deal of reactions with ethene, with appreciable overall efficiency. However, $CNH_4{}^+$ and $C_2NH_3{}^+$ are the only certain mixed ions arising from NH^+. As far as ion products in the *m*/*z* 26–28 range are concerned, two different structures are possible for each of them, one implying formation of C–N bonds, and the other of hydrocarbon ions. Reaction enthalpies were calculated for each possible reaction path according to literature data [25], in

Table 4
Ion/molecule reactions of $C_lP_mH_n^+$ ions with germane[a]

Reaction	k_{exp}	$\sum k_{exp}$	k_{coll}[b]	Efficiency[c]
$CPH_2^+ + GeH_4 \rightarrow GeCPH_4^+ + H_2$	4.0	4.0	9.793	0.41
$CPH_2^+ + GeH_4 \rightarrow GePH_2^+ + CH_4$				
$CPH_2^+ + GeH_4 \rightarrow GeH_3^+ + CPH_3$				
$C_2PH_2^+ + GeH_4 \rightarrow GePH_2^+ + C_2H_4$	1.8	1.8	9.120	0.20
$C_2PH_4^+ + GeH_4 \rightarrow GePH_2^+ + C_2H_6$	1.2			
$C_2PH_4^+ + GeH_4 \rightarrow GePH_4^+ + C_2H_4$	1.3			
$C_2PH_4^+ + GeH_4 \rightarrow GeC_2PH_6^+ + H_2$	0.58	3.1	9.030	0.34
$C_3PH_4^+ + GeH_4 \rightarrow GePH_2^+ + C_3H_6$	1.2	1.2	8.588	0.14
$CP_2H_3^+ + GeH_4 \rightarrow GePH_2^+ + CPH_5$	1.2			
$CP_2H_3^+ + GeH_4 \rightarrow GeCP_2H_5^+ + H_2$	0.81	2.0	8.414	0.24

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

[b] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarisability of GeH_4 from ref. [28].

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

order to identify the most thermodynamically favoured processes. Results show that formation of $C_2H_2^+$ (m/z 26) and NH_3 starting from NH^+ and C_2H_4 is quite exothermic (ca. -450 kJ mol^{-1}), while formation of CN^+ and of the probable neutral losses CH_3 and H_2 is endothermic by about 165 kJ mol^{-1}, thus indicating the hydrocarbon ion as the thermodynamically favoured product. In the other two cases (ions at m/z 27 and 28), all the possible reactions are thermodynamically favoured. Nevertheless, formation of $C_2H_3^+$ (m/z 27) and NH_2 is more exothermic than formation of CNH^+ and CH_4 by ca. 80 kJ mol^{-1}. To the contrary, the reaction yielding CNH_2^+ (m/z 28) and CH_3 is much more exothermic than that originating $C_2H_4^+$ and NH ($\Delta H^\circ = -638$ kJ mol^{-1} for the former, $\Delta H^\circ = -287$ kJ mol^{-1} for the latter reaction), even if it should be kinetically favoured as it consists of simple charge-exchange process. The NH_2^+ ions yield the two CNH_4^+ and $C_2NH_5^+$ mixed ions at m/z 30 and 43, by loss of a methylene and of a hydrogen moiety, respectively. Again, a product with m/z 28 with two different possible structures is observed, and calculation of reaction enthalpies indicates that CNH_2^+ formation is more favoured by about 400 kJ mol^{-1} [25] than the charge-exchange process yielding $C_2H_4^+$. The ethene primary ions basically react with ammonia through charge or proton transfer, leading to the formation of ionised ammonia and of the very stable ammonium ion. The ionisation energy of NH_3 is lower than those of C_2H_n ($n = 1$, 2, 4), and higher than that of C_2H_3 [25], thus justifying the charge transfer processes observed. Moreover, the high proton affinity of NH_3 makes the formation of NH_4^+ very favourable. The most reactive among ethene primary ions, C_2H^+, originate the $C_2NH_3^+$ mixed ions by hydrogen loss in a process characterised by a rather high rate constant. Ethene secondary ions mainly react to give ammonia protonation. In addition, the $C_3H_3^+$ and $C_3H_5^+$ ions slowly yield two products at m/z 28 and 30, respectively, and two structures are possible for each of them. However, heats of formation of $C_2H_4^+$ and $C_2H_6^+$ are higher than those of the N-containing isobaric ions [25]. Heat of formation of the CNH_2 moiety is not available in the literature, but is quite unlikely that it could be lower than that of the stable ethene molecule. As a consequence, formation of mixed ions is likely more energetically favoured with respect to that of the isobaric hydrocarbon ions.

Comparison of the present results can be drawn with literature data by Smith and Adams [30]. They studied the reactions of NH_n^+ and ND_n^+ ($n = 0$–4) with C_2H_4 and C_2D_4 by SIFT mass spectrometry,

Table 5
Ion/molecule reactions of NH_n^+ ions with ethene, of $C_mH_n^+$ ions with ammonia and of CNH_4^+ ion with ammonia[a]

Reaction	k_{exp}	$\sum k_{exp}$	k_{coll}[b]	Efficiency[c]
$NH^{\bullet +} + C_2H_4 \rightarrow C_2H_2^+ + NH_3$ or $CN^+ + CH_3 + H_2$	1.2			
$NH^{\bullet +} + C_2H_4 \rightarrow C_2H_3^+ + NH_2$ or $CNH^+ + CH_4$	3.4			
$NH^{\bullet +} + C_2H_4 \rightarrow C_2H_4^+ + NH$ or $CNH_2^+ + CH_3$	6.1			
$NH^{\bullet +} + C_2H_4 \rightarrow CNH_4^+ + CH$	1.9			
$NH^{\bullet +} + C_2H_4 \rightarrow C_2NH_3^+ + H_2$	1.2	14	15.43	0.89
$NH_2^+ + C_2H_4 \rightarrow C_2H_4^+ + NH_2$ or $CNH_2^+ + CH_4$	4.8			
$NH_2^+ + C_2H_4 \rightarrow CNH_4^+ + CH_2$	3.0			
$NH_2^+ + C_2H_4 \rightarrow C_2NH_5^+ + H$	1.2	9.2	15.11	0.61
$C_2H^+ + NH_3 \rightarrow NH_3^+ + C_2H$	16			
$C_2H^+ + NH_3 \rightarrow NH_4^+ + C_2$	3.4			
$C_2H^+ + NH_3 \rightarrow C_2NH_3^+ + H$	2.6	22	24.64	0.89
$C_2H_2^{\bullet +} + NH_3 \rightarrow NH_3^+ + C_2H_2$	13	13	24.45	0.53
$C_2H_3^+ + NH_3 \rightarrow NH_4^+ + C_2H_2$	21	21	24.27	0.86
$C_2H_4^{\bullet +} + NH_3 \rightarrow NH_3^+ + C_2H_4$	3.8			
$C_2H_4^{\bullet +} + NH_3 \rightarrow NH_4^+ + C_2H_3$	14	18	24.10	0.74
$C_2H_5^+ + NH_3 \rightarrow NH_4^+ + C_2H_4$	16	16	23.79	0.67
$C_3H_3^+ + NH_3 \rightarrow C_2H_4^+ + CNH_2$ or $CNH_2^+ + C_2H_4$	0.55	0.55	22.78	0.024
$C_3H_4^+ + NH_3 \rightarrow NH_4^+ + C_3H_3$	14	14	22.69	0.62
$C_3H_5^+ + NH_3 \rightarrow NH_4^+ + C_3H_4$	1.0			
$C_3H_5^+ + NH_3 \rightarrow C_2H_6^+ + CNH_2$ or $CNH_4^+ + C_2H_4$	0.34	1.3	22.61	0.059
$C_3H_6^+ + NH_3 \rightarrow NH_4^+ + C_3H_5$	6.1	6.1	22.53	0.27
$C_4H_7^+ + NH_3 \rightarrow NH_4^+ + C_4H_6$	6.8	6.8	21.75	0.32
$C_5H_7^+ + NH_3 \rightarrow NH_4^+ + C_5H_6$	3.0	3.0	21.28	0.14
$C_6H_7^+ + NH_3 \rightarrow NH_4^+ + C_6H_6$	4.4	4.4	20.95	0.21
$CNH_4^+ + NH_3 \rightarrow NH_4^+ + CNH_3$	1.2	1.2	23.79	0.050

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

[b] Collisional rate constants have been calculated according to the Parameterized Trajectory Theory [20] taking the polarisability of C_2H_4 from ref. [23] and that of NH_3 from ref. [29] and the dipole moment of NH_3 from ref. [22].

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

where the use of deuterated reagents allowed to distinguish product species with the same mass-to-charge ratio. Their rate constants generally are in good agreement with our results, the main difference concerning formation of NH_4^+ from NH_3^+ and C_2H_4 in SIFT experiments, which was not observed in ITMS. It is likely that the very fast ammonia protonation process by NH_3^+ ($k = 22 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, [31]) makes difficult the detection of the reaction channel with ethene which yields the same NH_4^+ product.

Reactions of $C_2H_n^+$ (n = 2–5) ions with ammonia were studied by several groups [32]. The agreement with the present results is quite good; even if the rate constants reported are generally higher than those calculated in our laboratory.

CNH_4^+ species are the only mixed ions whose selection was possible, as all the other C/N ions are too weak to prevent their isolation and reaction, even through the double isolation procedure. Unfortunately, they simply react with NH_3 to give the ammonium ion, and no higher mixed clusters are observed.

3.4. Germane/ethene/ammonia mixture

In this system, no reaction leading to Ge/C/N ions formation was detected. The Ge/C ions are those already mentioned in the $GeH_4/C_2H_4/PH_3$ section, i.e., $GeCH_5^+$ and $GeC_2H_n^+$ ($n = 4, 5$), while the mixed Ge/N ions formed from ion/molecule processes between GeH_4 and NH_3 [17d] consist of the $GeNH_n^+$ ($n = 2$–4) ion family. The $GeCH_5^+$ ions have the same *m*/*z* values of $GeNH_3^+$, and the double isolation did not allow to select any of the two isobaric ions with high enough abundance. The $GeC_2H_4^+$ ions resulted to be almost unreactive in the present experimental conditions, the only product detected being NH_4^+, with very low abundance. On the other hand, the $GeC_2H_5^+$ ions react quite efficiently with NH_3. Apart from ammonia protonation ($k = 1.6 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$), a fast exchange process is observed ($k = 7.1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$), with ammonia insertion and ethene neutral loss, leading to the $GeNH_4^+$ ion formation. The $GeNH_n^+$ ($n = 2, 4$) ions did not show any reactivity toward ethene. Finally, the only abundant C/N ions, CNH_4^+, were selected and reacted, but no products of reactions with germane were detected.

4. Conclusions

The different reactivity among the two ternary systems studied in this paper appears striking. The high basicity of NH_3 makes the ammonium ion the only detected product in most of the reactions observed when NH_3 is the neutral reagent, thus preventing clustering reactions. On the other hand, the high affinity of carbon toward phosphorus facilitates C–P bond formation. As a consequence, reactions of ions from ethene with PH_3 yield an appreciable number of C/P mixed ions. Efficiencies of reactions of ammonia and phosphine primary ions toward ethene are comparable. However, ion/molecule reactions in phosphine originate secondary ions containing two P atoms, whose reactions with ethene lead to the formation of C/P clusters, while the only ammonia secondary ion, NH_4^+, resulted to be unreactive. C/P mixed ions are formed through several paths and with good yields in the C_2H_4/PH_3 mixture, and react with C_2H_4 and PH_3 to originate rather heavy clusters such as $C_2P_2H_3^+$ and $C_6PH_6^+$. Mixed ions in the C_2H_4/NH_3 system are mainly formed from low abundance ions, like NH^+, NH_2^+ and C_2H^+, and hence are in turn weak. For this reason it was not possible to study their reactivity, and their contribution to the formation of cluster ions could not be determined. It is worth noting that C/P ions react with GeH_4 with appreciable efficiency with formation of Ge/C/P ion clusters, while the most abundant C/N ions, CNH_4^+, do not react with germane. The binary Ge-containing mixed ions resulted to be little abundant and quite difficult to select in the two systems studied. The only appreciably fast reaction observed takes place between $GeC_2H_5^+$ and NH_3, and does not lead to any Ge/C/N ion formation.

On the basis of the present results, it may be concluded that the high proton affinity of ammonia prevents formation of germanium carbides doped with nitrogen in the $GeH_4/C_2H_4/NH_3$ mixture. The choice of a hydrocarbon molecule as a volatile carbon source more reactive than ethene with respect to ammonia, like propene, may represent a future perspective for this type of research. In fact, in the previously studied propene/ammonia mixture [33], the yield of C/N mixed ions was significantly higher than in the present system. The reactivity of ions from ammonia toward ethene and propene is similar, and slowly leads to the formation of few C/N ions. However, ion/molecule reactions in propene originate a much higher number of hydrocarbon ions than in ethene self-condensation processes. As far as the $GeH_4/C_2H_4/PH_3$ mixture is concerned, it seems to be sufficiently suitable for formation in the gas phase of germanium carbides doped with phosphorus. A disadvantage of this system is the large amount of PH_3 consumed to give the unreactive phosphonium ion. Moreover, it also makes impossible to draw a correlation between the ratios of partial pressures of reactants in the gas phase and the content of Ge, C and P in the solid obtained by radiolysis of the gaseous mixture. Also in this case, the presence of a hydrocarbon more reactive than ethene may lead to significant improvements; comparison of the present system with the C_3H_6/PH_3 mixture previously studied [34] leads to the same conclusions already drawn when the C_2H_4/NH_3 and C_3H_6/NH_3 systems were compared, even if in this comparison the difference in reactivity is less pronounced.

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