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International Journal of Mass Spectrometry 182/183 (1999) 63–71



# Gas phase ion chemistry in germane/ammonia, methylgermane/ammonia, and methylgermane/phosphine

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Received 20 July 1998; accepted 13 September 1998

## Abstract

Gaseous mixtures of germane or methylgermane with ammonia and methylgermane with phosphine have been studied by ion trap mass spectrometry. Rate constants of reactions of the primary ions and of the most important secondary ion species are reported, together with the calculated collisional rate constants and efficiencies of reaction. The  $\text{GeH}_n^+$  ( $n = 0-3$ ) ions, formed by electron ionization of both  $\text{GeH}_4$  and  $\text{CH}_3\text{GeH}_3$ , react with ammonia yielding, among others, the  $\text{GeH}_n^+$  ( $n = 2-4$ ) ion family, which, in a successive and slow reaction with  $\text{NH}_3$ , only give the unreactive ammonium ion. Also, the  $\text{CH}_3\text{GeH}_n^+$  ( $n = 1, 2$ ) species do not form Ge–N bonds, whereas secondary ions of germane, such as  $\text{Ge}_2\text{H}_2^+$ , produce species containing germanium and nitrogen together. In the  $\text{CH}_3\text{GeH}_3/\text{PH}_3$  mixture a great number of ions are formed with rather high rate constants from primary ions of both reagent molecules and from phosphorus containing secondary ions.  $\text{GePH}_n^+$  ( $n = 2-4$ ) ions further react with methylgermane leading to cluster ions with increasing size such as  $\text{Ge}_2\text{PH}_n^+$  and  $\text{Ge}_2\text{CPH}_n^+$ . The experimental conditions favoring the chain propagation of ions containing Ge and N, or Ge and P, with or without C, important in the chemical vapor deposition of materials of interest in photovoltaic technology, are discussed. (Int J Mass Spectrom 182/183 (1999) 63–71) © 1999 Elsevier Science B.V.

*Keywords:* Ammonia; Germanium hydrides; Ion trap mass spectrometry; Kinetics; Phosphine

## 1. Introduction

Gaseous reactions involving ions from silane and germane have attracted a great deal of interest in the last few years and they have been investigated in depth by both experimental [1–12] and theoretical methods [4,10,12–15]. These studies are important from a fundamental point of view because interesting insights into the chemistry of these systems, unperturbed by the effects of the environment (such as

solvation effects) can be obtained. Moreover, it is possible to investigate the role of ion precursors leading to the deposition of amorphous solid materials from gaseous mixtures by chemical vapor deposition (CVD) methods, after appropriate activation [16]. In fact, the synthesis of new materials from the gas phase is acquiring increasing importance and, in particular, the preparation of amorphous semiconductors at a very high purity degree by deposition from mixtures of gaseous compounds is very promising.

As part of a study on gas phase reactivity and determination of rate constants of ion/molecule reactions of volatile hydrides of elements from groups 14 and 15 of the periodic system by ion trap mass

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Dedicated to the memory of Ben S. Freiser.

spectrometry, we report here results concerning ammonia/germane, ammonia/methylgermane, and phosphine/methylgermane mixtures, whereas results on phosphine/germane have already been published [17]. The two systems containing ammonia have been previously investigated by different mass spectrometric methods, i.e. conventional chemical ionization mass spectrometry and Fourier transform mass spectrometry, at rather different partial and total pressures of reagent gases [18,19]. The reactions observed in these systems are useful to investigate the best experimental conditions for direct nitrogen or phosphorus doping during the deposition of amorphous germanium and germanium carbide solids by radiolytical activation of suitable gaseous mixtures.

The gas phase behavior and the reaction mechanisms are compared with those obtained in previous studies on corresponding silicon containing systems:  $\text{NH}_3/\text{SiH}_4$  [8],  $\text{NH}_3/\text{CH}_3\text{SiH}_3$  [20], and  $\text{PH}_3/\text{CH}_3\text{SiH}_3$  [21]; and on the  $\text{GeH}_4/\text{PH}_3$  mixture [17]. The rate constants for the first nucleation reactions are determined and compared with collisional rate constants calculated according to the Langevin and average dipole orientation (ADO) theories [22].

## 2. Experimental

Ammonia and phosphine were obtained commercially in high purity. Germane and methylgermane were prepared as described in the literature [23,24]. Prior to use, each of them was introduced into a separate flask containing anhydrous sodium sulfate as drier. The flasks were then directly connected to the gas inlet system of the instrument. Helium was supplied at an extra-high purity degree and used without further purification. Frequent bake-up periods of the manifold and of the lines for the introduction of reactant gases and helium, together with the drier, were used to reduce the water background in the trap.

A Finnigan ITMS ion trap mass spectrometer was used for all experiments. The temperature was maintained at 333 K in order to obtain results comparable to previously reported data on related systems. Ions were always detected in the 14–300 u mass range. The gas inlet system of the instrument was modified

to permit the simultaneous introduction of three gases (two reagents and helium buffer gas) through different lines into the trap. A Bayard Alpert ionization gauge was used to measure the pressures. Ammonia, phosphine, germane, and methylgermane were admitted to the trap at pressures in the range  $2\text{--}6 \times 10^{-7}$  Torr and helium was added up to a pressure of  $\sim 5.0 \times 10^{-4}$  Torr.

Because accurate pressure measurements are necessary in kinetic experiments, the ion gauge was calibrated measuring the rate constant of the known self-protonation of methane [22]. The indicated pressure was further corrected on the basis of the relative sensitivity of the gauge to different gases ( $\text{NH}_3$ : 1.12;  $\text{PH}_3$ : 1.98;  $\text{GeH}_4$ : 1.94;  $\text{CH}_3\text{GeH}_3$ : 2.67; He: 0.20) [25–27].

The scan modes used to determine reaction rate constants, as well as the procedures for calculations, have been described in detail previously [7,12,17]. Isolation of ions at selected mass-to-charge ratio values was obtained by the superimposition of dc and rf voltages or by the resonance ejection method. In this latter case, no field is directly applied on the ion species under examination and they should have a lower excitation energy content than in the former method. The similarity of rate constants determined by the two isolation procedures is consistent with thermalization of ions by unreactive collisions with helium buffer gas. This hypothesis is also confirmed by the single exponential decay of the abundances of the reacting ions. In some cases, double isolation steps were required, and were always performed by applying the dc voltage.

The rate constants were measured for all primary ions of the reactant gases and for some secondary ions leading to significant ion/molecule reaction products. Every value reported is the average of at least three different experiments; uncertainties, attributed to a combination of errors, fall within 20% of error. In all experiments ions were formed by electron ionization at about 35 eV and for times ranging from 5–20 ms. If necessary, a reaction time followed the ionization event in order to maximize the abundance of the ions to be stored. Isolation of the selected ion species, their reactions with neutral molecules present in the trap for

Table 1

Rate constants for reactions of  $\text{GeH}_n^+$  ( $n = 0-3$ ),  $\text{Ge}_2\text{H}_2^+$ , and  $\text{GeNH}_n^+$  ( $n = 2-4$ ) ions in  $\text{GeH}_4/\text{NH}_3^a$ 

| Reaction                                 | $k_{\text{exp}}$                          | $\Sigma k_{\text{exp}}$ | $k_L$ or $k_{\text{ADO}}^b$ | Efficiency <sup>c</sup> |
|--|---|-------------------------|-----------------------------|-------------------------|
| $\text{Ge}^+ + \text{GeH}_4$             | → isotopic scrambling                     | 1.4                     |                             |                         |
|  | → $\text{Ge}_2\text{H}_2^+ + \text{H}_2$  | 5.8                     | 7.2                         | 0.84                    |
| $\text{Ge}^+ + \text{NH}_3$              | → $\text{GeNH}_2^+ + \text{H}$            | 0.64                    | 0.64                        | 0.038                   |
| $\text{GeH}^+ + \text{GeH}_4$            | → $\text{Ge}_2\text{H}_3^+ + \text{H}_2$  | 5.3                     | 5.3                         | 0.62                    |
| $\text{GeH}^+ + \text{NH}_3$             | → $\text{NH}_4^+ + \text{Ge}$             | 0.86                    |                             |                         |
|  | → $\text{GeNH}_2^+ + \text{H}_2$          | 0.57                    | 1.43                        | 0.085                   |
| $\text{GeH}_2^+ + \text{GeH}_4$          | → $\text{GeH}_3^+ + \text{GeH}_3$         | 3.3                     |                             |                         |
|  | → $\text{Ge}_2\text{H}_2^+ + 2\text{H}_2$ | 3.7                     | 7.0                         | 0.82                    |
| $\text{GeH}_2^+ + \text{NH}_3$           | → $\text{NH}_4^+ + \text{GeH}$            | 11                      |                             |                         |
|  | → $\text{GeNH}_3^+ + \text{H}_2$          | 2.7                     |                             |                         |
|  | → $\text{GeNH}_4^+ + \text{H}_2$          | 2.3                     | 16                          | 0.96                    |
| $\text{GeH}_3^+ + \text{GeH}_4$          | → isotopic scrambling                     | 3.4                     | 3.4                         | 0.40                    |
| $\text{GeH}_3^+ + \text{NH}_3$           | → $\text{NH}_4^+ + \text{GeH}_2$          | 6.1                     |                             |                         |
|  | → $\text{GeNH}_4^+ + \text{H}_2$          | 0.53                    | 6.6                         | 0.39                    |
| $\text{Ge}_2\text{H}_2^+ + \text{GeH}_4$ | → $\text{Ge}_3\text{H}_4^+ + \text{H}_2$  | 1.0                     | 1.0                         | 0.14                    |
| $\text{Ge}_2\text{H}_2^+ + \text{NH}_3$  | → $\text{NH}_4^+ + \text{Ge}_2\text{H}$   | 2.6                     |                             |                         |
|  | → $\text{Ge}_2\text{NH}_3^+ + \text{H}_2$ | 1.1                     | 3.7                         | 0.23                    |
| $\text{GeNH}_2^+ + \text{NH}_3$          | → $\text{NH}_4^+ + \text{GeNH}$           | 0.30                    | 0.30                        | 0.018                   |
| $\text{GeNH}_3^+ + \text{NH}_3$          | → $\text{NH}_4^+ + \text{GeNH}_2$         | 2.4                     | 2.4                         | 0.15                    |
| $\text{GeNH}_4^+ + \text{NH}_3$          | → $\text{NH}_4^+ + \text{GeNH}_3$         | 1.3                     | 1.3                         | 0.079                   |

<sup>a</sup> Rate constants are expressed as  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ; experiments were run at 333 K; uncertainty is within 20%.<sup>b</sup> Rate constants have been calculated according to the Langevin theory [22] for  $\text{GeH}_4$ , taking its polarizability ( $\alpha = 4.966 \times 10^{-24} \text{ cm}^3$ ) from [28], and according to the ADO theory [22] for  $\text{NH}_3$  taking its dipole moment ( $\mu_D = 1.471 \times 10^{-18} \text{ esu cm}$ ) from [29] and its polarizability ( $\alpha = 2.145 \times 10^{-24} \text{ cm}^3$ ) from [30].<sup>c</sup> Efficiency has been calculated as the ratio  $\Sigma k_{\text{exp}}/k_{\text{Langevin}}$  or  $\Sigma k_{\text{exp}}/k_{\text{ADO}}$ .

variable delay times, and acquisition were the successive events. In experiments requiring multiple isolation steps, reaction of the selected ions with neutral gases was followed by isolation of a secondary ion product, that, in turn, was allowed to react for an additional time before acquisition. Typically, the reaction time was varied from 0–40 ms by 0.2 ms steps, but, for very fast processes, a maximum reaction time of 20 ms (steps of 0.1 ms) was considered. Ionic species that were selectively stored from germane or methylgermane contained the  $^{70}\text{Ge}$  ( $\text{Ge}^+$ ,  $\text{GeH}^+$ ,  $\text{CH}_3\text{Ge}^+$ , and  $\text{CH}_3\text{GeH}^+$ ) or  $^{76}\text{Ge}$  ( $\text{GeH}_2^+$ ,  $\text{GeH}_3^+$ ,  $\text{CH}_3\text{GeH}_2^+$ ) isotope.

### 3. Results and discussion

#### 3.1. $\text{GeH}_4/\text{NH}_3$ mixture

Ionization of  $\text{GeH}_4$  and  $\text{NH}_3$  with electrons at 35 eV produces the ion families  $\text{GeH}_n^+$  ( $n = 0-3$ ) and  $\text{NH}_n^+$  ( $n = 2, 3$ ). Table 1 reports the rate constants of

reactions of the  $\text{GeH}_n^+$  ( $n = 0-3$ ) ions and of the most abundant and interesting secondary ions with the molecules present in the trap. Collisional rate constants (Langevin and ADO theories [22]) and efficiencies of reactions are also shown in Table 1. Processes starting from  $\text{NH}_2^+$  and  $\text{NH}_3^+$  are not shown because they mainly give very fast hydrogen abstraction from both ammonia and germane to form  $\text{NH}_3^+$  and  $\text{NH}_4^+$ , respectively. Reaction between  $\text{NH}_2^+$  and  $\text{GeH}_4$  also produces a very small amount of  $\text{GeH}_3^+$ .

The  $\text{GeH}_n^+$  ( $n = 0-3$ ) primary ions of germane react in self-condensation processes with rate constants that are in good agreement with those previously determined in experiments of  $\text{GeH}_4$  alone [7]. When the neutral reactant is ammonia, condensation reactions are observed for all  $\text{GeH}_n^+$  ( $n = 0-3$ ) ions, leading to the formation of  $\text{GeNH}_n^+$  ( $n = 2-4$ ) and loss of a hydrogen atom or molecule. However,  $\text{Ge}^+$ ,  $\text{GeH}^+$ , and  $\text{GeH}_3^+$  react very slowly, displaying rate constants in the  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  order of magnitude,

whereas  $\text{GeH}_2^+$  gives both  $\text{GeNH}_3^+$  and  $\text{GeNH}_4^+$ , in reactions taking place with  $k = 2.7$  and  $2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively. For these  $\text{GeH}_n^+$  ( $n = 0-3$ ) ion species the fastest process consists of transfer of a proton to  $\text{NH}_3$  to yield the ammonium ion,  $\text{NH}_4^+$  that is unreactive under the experimental conditions used in this study. Moreover, such reactions occur at increasing rates as the number of hydrogen atoms bonded to germanium in the reacting ion increases. Among the primary ions of germane,  $\text{GeH}_2^+$  shows the highest reactivity towards ammonia, considering both the number of products and the total rate constant of reaction.

Even if not observable in Table 1, unusual behavior has been noted in experiments in which  $\text{GeH}_2^+$  or  $\text{GeH}_3^+$  ion species are selectively stored for variable delay times, up to 40 ms. Under these experimental conditions, the total ion current continuously increases, becoming twice, or even more, the ion current value measured after the isolation event. Moreover, the excess current is totally attributed to the  $\text{NH}_4^+$  species. This trend has never been observed in previously examined systems, in which the current transported by specific ion species can decrease (reaction), increase (formation), increase and then decrease (formation followed by reaction), but the total amount of current and, therefore, of ions, remains stable during the whole experiment. Therefore, it has been hypothesized that a very favorable reaction between neutral moieties leads to the formation of an ion pair, of which the positively charged species is  $\text{NH}_4^+$ . It follows that one of the neutrals is ammonia and the second must be strictly related to  $\text{GeH}_2^+$  or  $\text{GeH}_3^+$ . Reactions (1) and (2) are proposed:



In the first process there is experimental support of both the reacting ( $\text{GeH}_{2/3}^+$ ) and product ( $\text{NH}_4^+$ ) cations. To the contrary, in the second reaction the only evidence is the increase of abundance of the ammonium ion  $\text{NH}_4^+$ . This suggested mechanism in which  $\text{GeH}_{2/3}^+$  ions behave like biprotic acids requires the presence of two hydrogen atoms bonded to germa-

nium and is consistent with its absence for  $\text{Ge}^+$  and  $\text{GeH}^+$ .

Among secondary ions, only  $\text{Ge}_2\text{H}_2^+$  forms a species containing germanium and nitrogen atoms together at an appreciable rate. All the  $\text{GeNH}_n^+$  ( $n = 2-4$ ) ions react rather slowly yielding the unreactive  $\text{NH}_4^+$  species that is also the product of the fastest reaction of  $\text{Ge}_2\text{H}_2^+$ .

Comparison of the gas phase ion/molecule reactions in this system with those of the  $\text{NH}_3/\text{SiH}_4$  mixture shows that, generally, the corresponding silicon containing ions are formed in similar processes [8]. In fact, primary ions of silane,  $\text{SiH}_n^+$  ( $n = 0-3$ ), react with ammonia yielding both  $\text{SiNH}_n^+$  ( $n = 2-4$ ) species (condensation of a  $\text{NH}_3$  molecule and loss of H or  $\text{H}_2$ ) and  $\text{NH}_4^+$  (proton transfer to  $\text{NH}_3$ ), even if, in this case, formation of the ammonium ion is the slowest process. Efficiencies of reaction differ significantly, being higher for the  $\text{Si}^+$  and  $\text{SiH}^+$  ions compared with  $\text{Ge}^+$  and  $\text{GeH}^+$ , and lower for  $\text{SiH}_2^+$  and  $\text{SiH}_3^+$  ion species compared with  $\text{GeH}_2^+$  and  $\text{GeH}_3^+$ . Moreover, secondary ions, such as  $\text{SiNH}_n^+$  ( $n = 2, 3$ ), besides the silicon analogue of  $\text{Ge}_2\text{NH}_3^+$ , give the  $\text{SiN}_2\text{H}_n^+$  ( $n = 4, 5$ ) ions by reaction with ammonia. Ions of the same family,  $\text{SiNH}_n^+$  ( $n = 2-4, 6$ ), are also formed from  $\text{Si}_2\text{H}_n^+$  ( $n = 2-5$ ) by elimination of a neutral moiety containing a silicon atom, whereas this kind of process has never been observed for the germanium systems. Finally,  $\text{NH}_2^+$  and  $\text{NH}_3^+$ , too, are able to produce new Si-N bonds in reactions with silane, forming  $\text{SiNH}_4^+$  and  $\text{SiNH}_6^+$ , with the corresponding reaction of germanium containing ions being absent in the  $\text{GeH}_4/\text{NH}_3$  mixture.

### 3.2. $\text{CH}_3\text{GeH}_3/\text{NH}_3$ mixture

Electron ionization of methylgermane leads to the formation of two ion families,  $\text{GeH}_n^+$  ( $n = 0-3$ ) and  $\text{CH}_3\text{GeH}_n^+$  ( $n = 0-2$ ). They all react with their neutral precursors in agreement with previously reported data on self-condensation of methylgermane [35]. The  $\text{GeH}_n^+$  ( $n = 0-3$ ) ion species react with ammonia in analogous processes, and possess rate constants that fall within experimental error of the same ions of germane, as shown in Table 2 and Table

Table 2

Rate constants for reactions of  $\text{GeH}_n^+$  ( $n = 0-3$ ),  $\text{CH}_3\text{GeH}_n^+$  ( $n = 1, 2$ ), and  $\text{GeNH}_n^+$  ( $n = 2, 4$ ) ions in  $\text{CH}_3\text{GeH}_3/\text{NH}_3^a$ 

| Reaction  | $k_{\text{exp}}$ | $\Sigma k_{\text{exp}}$ | $k_{\text{ADO}}^b$ | Efficiency <sup>c</sup> |
|---|------------------|-------------------------|--------------------|-------------------------|
| $\text{Ge}^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{Ge}^+ + \text{GeH}_3$               | 4.3              |                         |                    |                         |
| $\rightarrow \text{Ge}_2\text{CH}_4^+ + \text{H}_2$   | 8.5              | 12.8                    | 10.88              | 1.18                    |
| $\text{Ge}^+ + \text{NH}_3 \rightarrow \text{GeNH}_2^+ + \text{H}$                                      | 0.52             | 0.52                    | 16.77              | 0.031                   |
| $\text{GeH}^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{Ge}^+ + \text{GeH}_4$              | 0.88             |                         |                    |                         |
| $\rightarrow \text{Ge}_2\text{CH}_5^+ + \text{H}_2$   | 8.1              | 9.0                     | 10.84              | 0.83                    |
| $\text{GeH}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Ge}$                                      | 0.61             |                         |                    |                         |
| $\rightarrow \text{GeNH}_2^+ + \text{H}_2$  | 0.70             | 1.31                    | 16.75              | 0.078                   |
| $\text{GeH}_2^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{GeH}_2^+ + \text{GeH}_3$         | 7.2              | 7.2                     | 10.80              | 0.673                   |
| $\text{GeH}_2^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{GeH}_2$                                 | 9.3              |                         |                    |                         |
| $\rightarrow \text{GeNH}_3^+ + \text{H}_2$  | 3.6              |                         |                    |                         |
| $\rightarrow \text{GeNH}_4^+ + \text{H}$  | 2.5              | 15.4                    | 16.73              | 0.92                    |
| $\text{GeH}_3^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{GeH}_2^+ + \text{GeH}_4$         | 13               | 13                      | 10.77              | 1.21                    |
| $\text{GeH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{GeH}_2$                                 | 7.6              |                         |                    |                         |
| $\rightarrow \text{GeNH}_4^+ + \text{H}_2$  | 0.75             | 8.4                     | 16.71              | 0.50                    |
| $\text{CH}_3\text{GeH}^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{GeC}_2\text{H}_7^+ + \text{GeH}_3$ | 1.7              |                         |                    |                         |
| $\rightarrow \text{Ge}_2\text{C}_2\text{H}_8^+ + \text{H}_2$  | 2.9              | 4.6                     | 10.33              | 0.44                    |
| $\text{CH}_3\text{GeH}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{CH}_3\text{Ge}$                | 7.1              | 7.1                     | 16.48              | 0.43                    |
| $\text{CH}_3\text{GeH}_2^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{isotopic scrambling}$            | 4.1              | 4.1                     | 10.29              | 0.40                    |
| $\text{CH}_3\text{GeH}_2^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{CH}_3\text{GeH}$             | 8.5              | 8.5                     | 16.47              | 0.52                    |
| $\text{GeNH}_2^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{GeNH}$                                 | 0.39             | 0.39                    | 16.49              | 0.024                   |
| $\text{GeNH}_4^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{GeNH}_3$                               | 1.3              | 1.3                     | 16.46              | 0.079                   |

<sup>a</sup> Rate constants are expressed as  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ; experiments were run at 333 K; uncertainty is within 20%.<sup>b</sup> Rate constants have been calculated according to the ADO theory [22] taking dipole moment of  $\text{NH}_3$  ( $\mu_D = 1.471 \times 10^{-18} \text{ esu cm}$ ) from [29] and of  $\text{CH}_3\text{GeH}_3$  ( $\mu_D = 0.644 \times 10^{-18} \text{ esu cm}$ ) from [31], polarizability of  $\text{NH}_3$  ( $\alpha = 2.145 \times 10^{-24} \text{ cm}^3$ ) from [30], and calculating that of  $\text{CH}_3\text{GeH}_3$  ( $\alpha = 6.735 \times 10^{-24} \text{ cm}^3$ ) as in [32].<sup>c</sup> Efficiency has been calculated as the ratio  $\Sigma k_{\text{exp}}/k_{\text{ADO}}$ .

1. Besides self-condensation reactions,  $\text{CH}_3\text{GeH}^+$  and  $\text{CH}_3\text{GeH}_2^+$  give only proton transfer to  $\text{NH}_3$ , and these have very similar rate constants:  $7.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $8.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively. Moreover,  $\text{CH}_3\text{Ge}^+$  is unreactive towards ammonia under the experimental conditions examined here and  $\text{GeNH}_2^+$ , together with  $\text{GeNH}_4^+$ , behaves as in the  $\text{GeH}_4/\text{NH}_3$  system, forming  $\text{NH}_4^+$  as the only product. Again,  $\text{NH}_n^+$  ( $n = 2, 3$ ) ions are not reported in Table 2 because they are mainly involved in fast hydrogen abstraction processes from both neutrals present in the trap. The ion/molecule reactions of the  $\text{GeNH}_3^+$  species have not been studied because this ion is isobaric with  $\text{CH}_3\text{GeH}_2^+$  and there was no experiment suitable to selectively isolate it. Indeed,  $\text{GeNH}_2^+$  is also isobaric with the carbon containing ion  $\text{CH}_3\text{GeH}^+$ , but it was isolated in double isolation experiments starting from selective storage of  $\text{GeH}^+$ . Unfortunately, the same kind of experiment was not possible for the

separation of  $\text{GeNH}_3^+$  from  $\text{CH}_3\text{GeH}_2^+$  because they are formed in parallel reactions from  $\text{GeH}_2^+$  with the neutrals present in the trap. The reactivity of the  $\text{CH}_3\text{GeH}_n^+$  ( $n = 1, 2$ ) species, which are primary ions as well, was obtained by isolating them immediately after the ionization event when the contribution of the nitrogen containing species can be considered negligible.

The  $\text{NH}_3/\text{CH}_3\text{SiH}_3$  system, reported previously [20], shows ion/molecule reactions similar to those described for the  $\text{CH}_3\text{GeH}_3/\text{NH}_3$  mixture. However, processes starting from silicon containing ions with ammonia generally proceed faster than from the corresponding ions of methylgermane, also forming a higher number of products. In particular, a species containing silicon, carbon, and nitrogen together ( $\text{SiCNH}_6^+$ ) is observed from reactions of  $\text{CH}_3\text{SiH}_n^+$  ( $n = 1, 2$ ) with ammonia and from  $\text{SiNH}_4^+$  with methylsilane. This latter ion species is also the pre-

Table 3

Rate constants for reactions of  $\text{GeH}_n^+$  ( $n = 1-3$ ),  $\text{CH}_3\text{GeH}^+$ , and  $\text{PH}_n^+$  ( $n = 0-3$ ) ions in  $\text{CH}_3\text{GeH}_3/\text{PH}_3^a$ 

| Reaction  | $k_{\text{exp}}$   | $\Sigma k_{\text{exp}}$ | $k_{\text{ADO}}^b$ | Efficiency <sup>c</sup> |
|---|--|-------------------------|--------------------|-------------------------|
| $\text{GeH}^+ + \text{CH}_3\text{GeH}_3$            | $\rightarrow \text{CH}_3\text{Ge}^+ + \text{GeH}_4$              | 0.92                    |                    |                         |
|   | $\rightarrow \text{Ge}_2\text{CH}_5^+ + \text{H}_2$              | 9.4                     | 10.3               | 0.95                    |
| $\text{GeH}^+ + \text{PH}_3$                        | $\rightarrow \text{GePH}_2^+ + \text{H}_2$                       | 1.8                     | 1.8                | 0.154                   |
| $\text{GeH}_2^+ + \text{CH}_3\text{GeH}_3$          | $\rightarrow \text{CH}_3\text{GeH}^+ + \text{GeH}_4$             | 3.0                     |                    |                         |
|   | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{GeH}_3$           | 6.1                     | 9.1                | 0.84                    |
| $\text{GeH}_2^+ + \text{PH}_3$                      | $\rightarrow \text{PH}_4^+ + \text{GeH}$                         | 11                      |                    |                         |
|   | $\rightarrow \text{GePH}_3^+ + \text{H}_2$                       | 2.7                     | 13                 | 1.06                    |
| $\text{GeH}_3^+ + \text{CH}_3\text{GeH}_3$          | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{GeH}_4$           | 9.1                     | 9.1                | 0.84                    |
| $\text{GeH}_3^+ + \text{PH}_3$                      | $\rightarrow \text{PH}_4^+ + \text{GeH}_2$                       | 1.6                     |                    |                         |
|   | $\rightarrow \text{GePH}_4^+ + \text{H}_2$                       | 0.84                    | 2.4                | 0.20                    |
| $\text{CH}_3\text{GeH}^+ + \text{CH}_3\text{GeH}_3$ | $\rightarrow \text{GeC}_2\text{H}_7^+ + \text{GeH}_3$            | 2.1                     |                    |                         |
|   | $\rightarrow \text{Ge}_2\text{CH}_6^+ + \text{CH}_4$             | 1.2                     |                    |                         |
|   | $\rightarrow \text{Ge}_2\text{C}_2\text{H}_8^+ + \text{H}_2$     | 2.5                     | 5.8                | 0.56                    |
| $\text{CH}_3\text{GeH}^+ + \text{PH}_3$             | $\rightarrow \text{GePH}_3^+ + \text{CH}_4$                      | 3.3                     | 3.3                | 0.28                    |
| $\text{P}^+ + \text{CH}_3\text{GeH}_3$              | $\rightarrow \text{CH}_3\text{Ge}^+ + \text{PH}_3$               | 2.3                     |                    |                         |
|   | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{PH}$              | 9.0                     |                    |                         |
|   | $\rightarrow \text{PCH}_2^+ + \text{GeH}_4$                      | 0.75                    | 12.0               | 0.84                    |
| $\text{P}^+ + \text{PH}_3$                          | $\rightarrow \text{PH}_3^+ + \text{P}$                           | 5.9                     |                    |                         |
|   | $\rightarrow \text{P}_2\text{H}^+ + \text{H}_2$                  | 6.0                     |                    |                         |
|   | $\rightarrow \text{P}_2\text{H}_2^+ + \text{H}$                  | 0.64                    | 12.5               | 1.08                    |
| $\text{PH}^+ + \text{CH}_3\text{GeH}_3$             | $\rightarrow \text{CH}_3\text{Ge}^+ + \text{PH}_3 + \text{H}$    | 1.8                     |                    |                         |
|   | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{PH}_2$            | 7.6                     |                    |                         |
|   | $\rightarrow \text{PCH}_2^+ + \text{GeH}_3 + \text{H}_2$         | 0.64                    | 10.0               | 0.71                    |
| $\text{PH}^+ + \text{PH}_3$                         | $\rightarrow \text{PH}_3^+ + \text{PH}$                          | 5.9                     |                    |                         |
|   | $\rightarrow \text{P}_2^+ + 2\text{H}_2$                         | 2.3                     |                    |                         |
|   | $\rightarrow \text{P}_2\text{H}_2^+ + \text{H}_2$                | 3.9                     |                    |                         |
|   | $\rightarrow \text{P}_2\text{H}_3^+ + \text{H}$                  | 1.2                     | 13.3               | 1.16                    |
| $\text{PH}_2^+ + \text{CH}_3\text{GeH}_3$           | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{PH}_3$            | 9.0                     | 9.0                | 0.64                    |
| $\text{PH}_2^+ + \text{PH}_3$                       | $\rightarrow \text{P}_2\text{H}^+ + 2\text{H}_2$                 | 3.0                     |                    |                         |
|   | $\rightarrow \text{P}_2\text{H}_3^+ + \text{H}_2$                | 7.6                     | 10.6               | 0.93                    |
| $\text{PH}_3^+ + \text{CH}_3\text{GeH}_3$           | $\rightarrow \text{PH}_4^+ + \text{CH}_3\text{GeH}_2$            | 11                      |                    |                         |
|   | $\rightarrow \text{PCH}_4^+ + \text{GeH}_3 + \text{H}_2$         | 0.56                    |                    |                         |
|   | $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{PH}_3 + \text{H}$ | 0.90                    | 12.5               | 0.90                    |
| $\text{PH}_3^+ + \text{PH}_3$                       | $\rightarrow \text{PH}_4^+ + \text{PH}_2$                        | 12                      | 12                 | 1.06                    |

<sup>a</sup> Rate constants are expressed as  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ; experiments were run at 333 K; uncertainty is within 20%.<sup>b</sup> Rate constants have been calculated according to the ADO theory [22] taking dipole moment of  $\text{PH}_3$  ( $\mu_D = 0.574 \times 10^{-18} \text{ esu cm}$ ) from [33] and of  $\text{CH}_3\text{GeH}_3$  ( $\mu_D = 0.644 \times 10^{-18} \text{ esu cm}$ ) from [31], polarizability of  $\text{PH}_3$  ( $\alpha = 4.84 \times 10^{-24} \text{ cm}^3$ ) from [34], and calculating that of  $\text{CH}_3\text{GeH}_3$  ( $\alpha = 6.735 \times 10^{-24} \text{ cm}^3$ ) as in [32].<sup>c</sup> Efficiency has been calculated as the ratio  $\Sigma k_{\text{exp}}/k_{\text{ADO}}$ .

cursor of ions containing two nitrogen atoms ( $\text{SiN}_2\text{H}_5^+$  and  $\text{SiN}_2\text{H}_6^+$ ) when it reacts with ammonia. This behaviour differs from that of the  $\text{CH}_3\text{GeH}_3/\text{NH}_3$  mixture, in which the corresponding germanium containing ions have never been detected. Again, efficiencies of the primary  $\text{SiH}_n^+$  ( $n = 0-3$ ) ions reacting with ammonia are higher than those of the germanium analogues for  $n = 0, 1$  and lower for  $n = 2, 3$ .

### 3.3. $\text{CH}_3\text{GeH}_3/\text{PH}_3$ mixture

Table 3 shows the rate constants for ion/molecule reactions of the primary ions of both methylgermane and phosphine in a  $\text{CH}_3\text{GeH}_3/\text{PH}_3$  mixture, together with the collisional rate constants and efficiencies of reactions. Again, self-condensation processes of germanium containing ions with  $\text{CH}_3\text{GeH}_3$  and of phosphorus containing ions with phosphine are in good



Table 4

Rate constants for reactions of  $\text{PH}_4^+$ ,  $\text{P}_2\text{H}_n^+$  ( $n = 0-3$ ),  $\text{GePH}_3^+$ , and  $\text{PCH}_n^+$  ( $n = 2, 4$ ) ions in  $\text{CH}_3\text{GeH}_3/\text{PH}_3^a$ 

| Reaction   | $k_{\text{exp}}$ | $\Sigma k_{\text{exp}}$ | $k_{\text{ADO}}^b$ | Efficiency <sup>c</sup> |
|--|------------------|-------------------------|--------------------|-------------------------|
| $\text{PH}_4^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{PCH}_4^+ + \text{GeH}_4 + \text{H}_2$     | 0.48             | 0.48                    | 13.75              | 0.035                   |
| $\text{P}_2^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{GeH}_2^+ + \text{P}_2\text{H}$  | 2.6              |                         |                    |                         |
| $\rightarrow \text{PH}_3^+ + \text{GePCH}_3$   | 5.1              | 7.7                     | 11.40              | 0.67                    |
| $\text{P}_2^+ + \text{PH}_3 \rightarrow \text{PH}_3^+ + \text{P}_2$                                  | 11.6             | 11.6                    | 9.93               | 1.17                    |
| $\text{P}_2\text{H}^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{PCH}_4^+ + \text{GePH}_3$          | 0.59             |                         |                    |                         |
| $\rightarrow \text{CH}_3\text{Ge}^+ + \text{P}_2\text{H}_4$  | 4.1              |                         |                    |                         |
| $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{P}_2\text{H}_2$                                       | 4.6              | 9.3                     | 11.34              | 0.82                    |
| $\text{P}_2\text{H}^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{P}_2$                          | 8.2              | 8.2                     | 9.90               | 0.83                    |
| $\text{P}_2\text{H}_2^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{PCH}_4^+ + \text{GePH}_4$        | 0.92             |                         |                    |                         |
| $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{P}_2\text{H}_3$                                       | 0.74             |                         |                    |                         |
| $\rightarrow \text{GeCPH}_6^+ + \text{PH}_2$   | 4.8              | 6.5                     | 11.28              | 0.57                    |
| $\text{P}_2\text{H}_2^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{P}_2\text{H}$                | 8.2              |                         |                    |                         |
| $\rightarrow \text{P}_2\text{H}_3^+ + \text{PH}_2$   | 1.6              | 9.8                     | 9.87               | 0.99                    |
| $\text{P}_2\text{H}_3^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{PCH}_4^+ + \text{GePH}_5$        | 0.64             |                         |                    |                         |
| $\rightarrow \text{CH}_3\text{GeH}_2^+ + \text{P}_2\text{H}_4$                                       | 4.4              | 5.0                     | 11.24              | 0.45                    |
| $\text{P}_2\text{H}_3^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{P}_2\text{H}_2$              | 4.4              | 4.4                     | 9.85               | 0.45                    |
| $\text{GePH}_3^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{GeCPH}_3^+ + \text{GeH}_4 + \text{H}_2$ | 0.54             |                         |                    |                         |
| $\rightarrow \text{Ge}_2\text{CH}_6^+ + \text{PH}_3$   | 1.4              | 1.9                     | 9.87               | 0.19                    |
| $\text{PCH}_2^+ + \text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{GeH}_2^+ + \text{PCH}_3$      | 2.7              | 2.7                     | 12.60              | 0.21                    |
| $\text{PCH}_2^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{PCH}$                                | 0.36             | 0.36                    | 13.42              | 0.027                   |
| $\text{PCH}_4^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{PCH}_3$                              | 0.40             | 0.40                    | 13.29              | 0.030                   |

<sup>a</sup> Rate constants are expressed as  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ; experiments were run at 333 K; uncertainty is within 20%.<sup>b</sup> Rate constants have been calculated according to the ADO theory [22] taking dipole moment of  $\text{PH}_3$  ( $\mu_D = 0.574 \times 10^{-18} \text{ esu cm}$ ) from [33] and of  $\text{CH}_3\text{GeH}_3$  ( $\mu_D = 0.644 \times 10^{-18} \text{ esu cm}$ ) from [31], polarizability of  $\text{PH}_3$  ( $\alpha = 4.84 \times 10^{-24} \text{ cm}^3$ ) from [34], and calculating that of  $\text{CH}_3\text{GeH}_3$  ( $\alpha = 6.735 \times 10^{-24} \text{ cm}^3$ ) as in [32].<sup>c</sup> Efficiency has been calculated as the ratio  $\Sigma k_{\text{exp}}/k_{\text{ADO}}$ .

agreement with previously reported rate constants [35–37].  $\text{Ge}^+$  and  $\text{CH}_3\text{GeH}_2^+$  ion species are not shown in Table 3 because they do not react with phosphine under the experimental conditions examined here. A common reaction of the  $\text{GeH}_n^+$  ( $n = 1-3$ ) ions is condensation with  $\text{PH}_3$  and loss of a hydrogen molecule to form the  $\text{GePH}_n^+$  ( $n = 2-4$ ) species, occurring rather slowly, in agreement with rate constants determined in the  $\text{GeH}_4/\text{PH}_3$  mixture [17].  $\text{GeH}_2^+$  produces a  $\text{PH}_4^+$  ion in a very fast reaction ( $k = 11 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) and  $\text{GeH}_3^+$  forms the same ion more slowly ( $k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ). All the  $\text{PH}_n^+$  ions react with methylgermane with high efficiency, which ranges from 0.64–0.90, producing many ion species. However, no ion containing germanium and phosphorus atoms bonded together is observed. In fact, the main process for the  $\text{PH}_n^+$  ( $n = 0-2$ ) ions is hydride abstraction from  $\text{CH}_3\text{GeH}_3$  yielding  $\text{CH}_3\text{GeH}_2^+$  in fast reactions:  $k = 9.0, 7.6,$

and  $9.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively.  $\text{CH}_3\text{Ge}^+$  ions are formed from both  $\text{P}^+$  and  $\text{PH}^+$  in slower reactions:  $k = 2.3$  and  $1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Moreover, very slow condensation processes are observed, leading to the formation of  $\text{PCH}_2^+$  and  $\text{PCH}_4^+$  species. These reactions take place with elimination of a germane molecule or of a neutral moiety whose mass corresponds to the  $\text{GeH}_5$  formula and, based on enthalpies of formation, can be hypothesized to be  $\text{GeH}_3 + \text{H}_2$ .

In Table 4 the rate constants for reactions of the most abundant secondary ions with  $\text{CH}_3\text{GeH}_3$  and  $\text{PH}_3$  are reported. Formation of the  $\text{PCH}_4^+$  species is observed from a variety of reacting ions, such as  $\text{PH}_4^+$  and  $\text{P}_2\text{H}_n^+$  ( $n = 1-3$ ), with rate constants always in the  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  order of magnitude. It is worth noting that  $\text{PH}_4^+$  reacts with methylgermane, whereas it is generally very stable and has been shown to be unreactive towards phosphine, silane, methylsilane,

and germane [36,37,12,21,17]. The most common product of reactions between phosphorus containing ions with  $\text{CH}_3\text{GeH}_3$  is  $\text{CH}_3\text{GeH}_2^+$ , which, as reported above, does not react further with phosphine.  $\text{GeCPH}_3^+$  and  $\text{GeCPH}_6^+$ , formed from  $\text{GePH}_3^+$  and  $\text{P}_2\text{H}_2^+$  reacting with methylgermane, are the only species in which germanium and phosphorus atoms are present together. The  $\text{GePH}_n^+$  ( $n = 2-4$ ) ions show very low abundances and it has been possible to determine only rate constants for reactions of the  $\text{GePH}_3^+$  species, giving  $\text{GeCPH}_3^+$  and  $\text{Ge}_2\text{CH}_6^+$ . However, storing the complete ion family for reaction times up to 500 ms, formation has been observed of heavier ions such as  $\text{Ge}_2\text{PH}_n^+$  and  $\text{Ge}_2\text{CPH}_n^+$  that are too weak to be identified more precisely.

Comparison of efficiencies of reactions between the phosphorus containing ions and  $\text{CH}_3\text{GeH}_3$  with respect to  $\text{GeH}_4$  [17] shows that reactions of primary ions  $\text{PH}_n^+$  ( $n = 0-3$ ) are more efficient with methylgermane, whereas for secondary ion species,  $\text{P}_2\text{H}_n^+$  ( $n = 0-3$ ), processes with germane display a higher efficiency.

The gas phase ion/molecule reactions in the  $\text{CH}_3\text{GeH}_3/\text{PH}_3$  mixture can also be compared with those in the  $\text{CH}_3\text{GeH}_3/\text{NH}_3$  system. Formation of Ge–N bonds from  $\text{GeH}_n^+$  ( $n = 2-4$ ) ions proceeds at rates comparable with those of formation of Ge–P bonds in the phosphorus correspondent ions. However, further reactions of these ions only give  $\text{NH}_4^+$  in the presence of ammonia, whereas ionic clusters of increasing size are formed (though very slowly) from  $\text{GePH}_n^+$  ( $n = 2-4$ ).

In the  $\text{PH}_3/\text{CH}_3\text{SiH}_3$  mixture, which has been described previously [21], primary ions of methylsilane,  $\text{SiH}_n^+$  ( $n = 0-3$ ), react with phosphine to give  $\text{SiPH}_n^+$  ( $n = 1-4$ ) species with higher rate constants of reaction than  $\text{GeH}_n^+$  ( $n = 1-3$ ). In contrast,  $\text{PH}_4^+$ , which is formed very rapidly from  $\text{GeH}_2^+$ , is a minor product of the correspondent  $\text{SiH}_2^+$ .  $\text{CH}_3\text{SiH}_2^+$  ions are the most common product of reactions between phosphorus containing ions (both primary and secondary) and methylsilane, as  $\text{CH}_3\text{GeH}_2^+$  in the  $\text{CH}_3\text{GeH}_3/\text{PH}_3$  mixture. The only difference is the higher rate constant of formation of  $\text{CH}_3\text{SiH}_2^+$  with respect to the germanium analogue.

#### 4. Conclusions

Comparison of the ion/molecule reactions in the  $\text{GeH}_4/\text{NH}_3$  and  $\text{CH}_3\text{GeH}_3/\text{NH}_3$  mixtures with the silicon containing analogues ( $\text{NH}_3/\text{SiH}_4$  and  $\text{NH}_3/\text{CH}_3\text{SiH}_3$ ) has shown that similar processes occur even if the presence of germanium leads to a lower number of ionic products. Most of the ionic reactions give the unreactive  $\text{NH}_4^+$  ions as a final product. Moreover, in the  $\text{GeH}_4/\text{NH}_3$  system, ions containing two germanium atoms contribute to the formation of larger clusters through reactions with ammonia. Therefore, the experimental conditions favoring the formation of species with Ge and N, as precursors of nitrogen-doped amorphous germanium, are those giving high amount of  $\text{Ge}_2\text{H}_n^+$  species, i.e. mixtures containing a large excess of germane with respect to ammonia. It was not possible to verify this trend in the methylgermane/ammonia system because of the poor yield of secondary ions containing two germanium atoms.

Similar considerations can be drawn from the  $\text{CH}_3\text{GeH}_3/\text{PH}_3$  mixture with regard to the preparation of phosphorus-doped amorphous germanium carbides. In this system a higher number of reactions are observed, with respect to the ammonia mixture, starting from primary ions of both methylgermane and phosphine. However, few ions contain Ge and P together, and they are  $\text{GePH}_n^+$  ( $n = 2-4$ ) formed by the reaction of  $\text{GeH}_n^+$  ( $n = 1-3$ ) and  $\text{CH}_3\text{GeH}^+$  ions with  $\text{PH}_3$ . These species slowly give catenation processes with methylgermane, leading to clusters of growing size, such as  $\text{Ge}_2\text{PH}_n^+$  and  $\text{Ge}_2\text{CPH}_n^+$ . Therefore, a high concentration of methylgermane is required in order to make these last processes more efficient, i.e., reacting mixtures with high partial pressure of  $\text{CH}_3\text{GeH}_3$  with respect to phosphine.

#### Acknowledgements

The authors thank Ministero dell'Università e della Ricerca Scientifica e Tecnologica and Università di Torino for financial support.



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