Ion Chemistry in XH_4/Allene (X = Ge, Si) Gaseous Mixtures – Formation of X–C Bonds

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Keywords: Ion-molecule reactions / Mass spectrometry / Allene / Germanium / Silicon

The gas-phase ion chemistry of germane/allene and silane/allene mixtures has been studied, with the aim of obtaining information on the experimental conditions leading to the formation of clusters of increasing size containing Ge or Si bonded to carbon atoms. Mechanisms of ion/molecule reactions have been elucidated by ion-trap mass spectrometry using single and multiple isolation steps. Rate constants for the most important reactions have been determined experimentally and compared with collisional rate constants. The germane/allene mixtures display a low reactivity and the most abundant germanium and carbon containing ion is $GeCH_3^+$. However, chain propagation proceeds after the first nucleation step, even if rather slowly, with the formation of large clusters such as $Ge_4C_3H_3^+$ at low abundance. In contrast, the silane/allene mixtures are very reactive and many different processes are observed, with the formation of several silicon and carbon containing ions with appreciable efficiency. Chain propagation proceeds mainly through reactions of silicon-containing ions with allene molecules and the subsequent formation of large clusters such as $Si_3C_3H_5^+$ and $Si_4C_3H_7^+$.

Introduction

In the last few years, hydrogenated amorphous compounds of elements of the Group 14 have been extensively studied for their possible applications in electronic and optoelectronic devices.[1] Amorphous semiconductors based on germanium carbides, a-GeC:H, or silicon carbides, a-SiC:H, have recently been considered[2] in order to obtain collectors of wide range light.

The preparation of these materials is generally carried out by laser-assisted, X-ray-assisted, or other assisted chemical-vapour deposition (CVD) techniques, starting from suitable mixtures of gaseous hydrides containing germanium or silicon with hydrocarbons. It has been observed that the amount of Ge and C, or Si and C in the final solid is a function of the molar composition of the gaseous system, but it does not depend on it in a direct or predictable way. Therefore, it is very important to know which are the main processes taking place in the mixtures under examination, and which occur more rapidly, contributing to a larger extent to the growth of the polymer containing carbon bonded to germanium or silicon atoms. These results provide information on the relationship between the partial pressure of the gaseous reactants and the abundance of the corresponding elements in the solid material.

In previous studies, the mechanisms and kinetics of ionic reactions involved in radiolytically assisted CVD of volatile silicon and germanium hydrides in different mixtures (SiH_4/NH_3, SiH_4/PH_3, CH_3SiH_3/NH_3, CH_3SiH_3/PH_3, GeH_4/NH_3, GeH_4/PH_3, CH_3GeH_3/NH_3, CH_3GeH_3/PH_3) were determined by ion-trap mass spectrometry.[3] Germane or methylgermane/hydrocarbon mixtures, including GeH_4/allene and CH_3GeH_3/allene systems, were also studied by Fourier transform and chemical-ionisation mass spectrometry under different experimental conditions from the present work.[4] More recently, systems containing silane with propane or propene,[5] ethane or ethyne,[6] and ethene,[7] have been studied in an ion-trap instrument with the aim of investigating the formation of ion species containing Si–C bonds.

In this paper we report on the mechanisms of ion/molecule reactions in silane/allene and germane/allene mixtures studied by ion-trap mass spectrometry. Self-condensation processes in allene have also been investigated. The results are interesting both for fundamental and applied chemistry, as they give insights on pathways leading to the formation of silicon-carbon or germanium-carbon containing ions as possible precursors of amorphous silicon or germanium carbides.

The rate constants of the first steps of the chain propagation have been experimentally determined and compared with the collisional rate constants, calculated according to the Langevin theory.[8] A comparison can be also drawn on the gas-phase reactivity of germane and silane towards allene.

Results and Discussion

Tables 1–6 report experimental and collisional rate constants (Langevin theory) of the ion/molecule reactions taking place in the systems studied, and reaction efficiencies calculated as their ratio. When heats of formation were available,[9–17] enthalpies at 298 K were calculated to confirm the feasibility of the observed processes. The most

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Table 1. Reactions of $C_2H_n^+$,$C_3H_n^+$, $C_4H_n^+$ and $C_5H_5^+$ ions in allene

Reactant Ions	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
$C_2H_2^+$	$C_3H_4^+$ (10), $C_3H_5^+$ (0.95)	11	13.76	0.80
$C_2H_3^+$	$C_3H_5^+$ (7.7)	7.7	13.60	0.57
$C_2H_4^+$	$C_2H_5^+$ (0.20), $C_3H_3^+$ (7.3), $C_3H_4^+$ (1.2), $C_3H_5^+$ (0.58)	9.3	13.46	0.69
C_3H^+	$C_2H_3^+$ (0.87), $C_3H_3^+$ (0.50), $C_4H_3^+$ (7.6)	9.0	12.46	0.72
$C_3H_2^+$	$C_3H_3^+$ (6.2), $C_4H_4^+$ (4.1), $C_6H_5^+$ (0.78)	11	12.37	0.90
$C_3H_3^+$	$C_4H_5^+$ (0.22), $C_6H_5^+$ (0.90)	1.1	12.29	0.090
$C_3H_4^+$	$C_3H_5^+$ (0.86), $C_6H_7^+$ (5.9)	6.8	12.21	0.56
$C_3H_5^+$	$C_4H_5^+$ (0.75), $C_6H_7^+$ (2.0), $C_6H_8^+$ (4.8)	7.6	12.14	0.63
$C_4H_3^+$	$C_5H_5^+$ (4.8)	4.8	11.54	0.42
$C_4H_4^+$	$C_5H_4^+$ (0.26), $C_7H_7^+$ (4.7)	5.0	11.49	0.44
$C_4H_5^+$	$C_6H_5^+$ (0.86), $C_7H_7^+$ (0.72), $C_7H_8^+$ (0.20)	1.8	11.44	0.16
$C_5H_5^+$	$C_5H_7^+$ (0.46), $C_6H_7^+$ (0.38)	0.84	10.98	0.076

[a] Rate constants are expressed as 10^{-10} $cm^3molecule^{-1}s^{-1}$; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory calculating polarizability of C_3H_4 as in ref.[19] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_L$.

Table 2. Reactions of $C_2H_n^+$,$C_3H_n^+$ and $C_4H_n^+$ ions with germane and of GeH_n^+ ions with allene in a GeH_4/C_3H_4 mixture

Reactants	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
$C_2H_2^+$ + GeH_4	Ge^+ (2.0), GeH^+ (1.5), GeH_2^+ (1.6), GeH_3^+ (2.6), $GeCH_3^+$ (0.36), $GeC_2H_3^+$ (0.64)	8.7	11.83	0.74
$C_2H_3^+$ + GeH_4	GeH^+ (1.7), GeH_3^+ (2.6), $GeCH_3^+$ (0.78)	5.1	11.66	0.44
$C_2H_4^+$ + GeH_4	GeH^+ (0.81), GeH_2^+ (1.7), $GeCH_3^+$ (0.48)	3.0	11.51	0.26
C_3H^+ + GeH_4	Ge^+ (1.1), GeH^+ (1.8), $GeCH_3^+$ (0.94), $GeC_3H_3^+$ (0.72)	4.6	10.44	0.44
$C_3H_2^+$ + GeH_4	$GeCH_3^+$ (1.8)	1.8	10.34	0.17
$C_3H_3^+$ + GeH_4	$GeCH_3^+$ (0.40)	0.40	10.25	0.039
$C_3H_5^+$ + GeH_4	$GeCH_3^+$ (1.2)	1.2	10.08	0.12
$C_4H_3^+$ + GeH_4	$GeCH_3^+$ (0.96), $GeC_2H_3^+$ (0.92)	1.9	9.42	0.20
$C_4H_5^+$ + GeH_4	$GeCH_3^+$ (0.52)	0.52	9.31	0.056
Ge^+ + C_3H_4	$GeC_3H_3^+$ (2.8)	2.8	10.76	0.26
GeH^+ + C_3H_4	$GeCH_3^+$ (8.9)	8.9	10.73	0.83
GeH_2^+ + C_3H_4	$GeCH_2^+$ (0.65), $GeCH_3^+$ (0.84), $GeC_2H_3^+$ (1.1), $GeC_3H_3^+$ (1.1), $GeC_3H_5^+$ (1.2)	4.9	10.71	0.46

[a] Rate constants are expressed as 10^{-10} $cm^3molecule^{-1}s^{-1}$; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory calculating polarizability of C_3H_4 as in ref.[19], and taking polarizability of GeH_4 from ref.[20] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_L$.

stable isomer for every species was considered in the calculations of the reaction enthalpies.

Allene Self-Condensation

The ion chemistry of allene has been previously studied by different mass spectrometric techniques.[18] Overall rate constants have been reported for reactions of the $C_3H_n^+$ (n = 1–4) ions with neutral allene,[18f] and are generally higher than those reported in the present paper (see Table 1). Such discrepancy is probably due to the different conditions of sample pressure at which the instruments operate, and to the presence of a buffer gas in the ion-trap mass spectrometric experiments, giving a lower population of excited ions with respect to other methods.

Ionisation of allene gives rise to the $C_3H_n^+$ (n = 1–4) and $C_2H_n^+$ (n = 2–4) ion families. Formation of $C_2H_3^+$ and $C_2H_4^+$ involves hydrogen migration before the fragmentation process. If stored for suitable periods of time, all the above-mentioned ions react with neutral allene to yield heavier ion species such as protonated allene ($C_3H_5^+$), $C_4H_n^+$ (n = 3–5), and $C_5H_5^+$ ions.

Many different reactions are observed (Table 1) taking place with elimination of different neutral moieties. Rather common paths involve loss of an ethyne molecule or, to a lesser extent, of an ethene molecule or a C_3H_3 fragment. Elimination of a hydrogen atom or molecule is also observed, but is limited to $C_3H_n^+$ (n = 2–5) and $C_4H_n^+$ (n = 4, 5) ions.

Efficiencies of reaction are rather high for all primary ions and protonated allene, except for $C_3H_3^+$, which reacts very slowly. Reactions of the $C_4H_n^+$ (n = 3–5) ion family show a lower efficiency, which further decreases for the stable $C_5H_5^+$ ion.

Germane/Allene Mixture

Table 2 reports the most significant ion/molecule reactions occurring in a germane/allene mixture. During ionisation, the GeH_n^+ (n = 0–3) ion family is formed, besides primary ions of allene as described above. The main reaction pathway shown by all the $C_2H_n^+$ (n = 2–4) ions, as well as C_3H^+, consists of charge transfer to GeH_4 with successive fragmentation to form ions of the GeH_n^+ (n = 0–3) family. It is worth noting that $GeCH_3^+$ ions are formed by almost all primary and secondary ions of allene, even if these processes are generally rather slow and only in two cases the reaction rate constants are in the 10^{-10} $cm^3molecule^{-1}s^{-1}$ order of magnitude. The exceptions are $C_3H_4^+$, $C_4H_4^+$, and

$C_5H_5^+$, which not only do not give the $GeCH_3^+$ product, but are unreactive towards germane.

Efficiencies of reaction of the primary $C_2H_n^+$ (n = 2–4) and $C_3H_n^+$ (n = 1–4) ion families decrease with increasing number of hydrogen atoms within the same family. Moreover, ions containing two carbon atoms are more efficient than the $C_3H_n^+$ species. Besides $GeCH_3^+$, which is unreactive under the experimental conditions used here, only two ion species, $GeC_2H_3^+$ and $GeC_3H_3^+$, contain Ge–C bonds and are interesting for the chain propagation towards germanium carbide. It is also worth noting that in previous studies on GeH_4/allene mixtures, performed by Fourier transform mass spectrometry, only these three Ge/C containing ions ($GeCH_3^+$, $GeC_2H_3^+$, and $GeC_3H_3^+$) were observed.[4a] Among the germane primary ions, GeH_3^+ is not included in the table as it is unreactive in the reaction times examined here. Germane self-condensation reactions are not reported as they have been already shown in previous papers.[3f,21] All reactions of GeH_n^+ (n = 0–2) ions with allene yield ion products containing germanium and carbon together. Again, $GeCH_3^+$, $GeC_2H_3^+$, and $GeC_3H_3^+$ ions are observed, together with $GeCH_2^+$ and $GeC_3H_5^+$, which are not formed from allene ions reacting with germane.

Unfortunately, mixed ions containing both Ge and C, as well as two-germanium containing ions, generally originate in very slow processes. It follows that, in the time range considered here, their abundance is too low to perform selective isolation with reproducible results. Moreover, as previously also observed in CH_3GeH_3/allene systems,[4b] in which $GeCH_3^+$ is a primary ion displaying a very high abundance, mixed Ge/C ions react very slowly and do not seem to be the precursors of higher order clusters. In particular, they do not react with germane in the reaction time considered, as all mixed ions show a unique germanium atom and up to six carbon atoms in high pressure chemical ionisation experiments.[4b]

However, as the main interest in these systems relies on the catenation of germanium and carbon atoms together to give mixed cluster ions of increasing size, experiments were carried out with isolation and reaction of the whole $Ge_2H_n^+$ (n = 2–4) ion family in the GeH_4/C_3H_4 ($4.7 \times 10^{-7}/1.9 \times 10^{-7}$ Torr) mixture. The mass spectra recorded immediately after the isolation (a), and after 0.5 s (b), 0.9 s (c), and 2 s (d) of reaction are reported in Figure 1. These data do not allow the calculation of the rate constants, nevertheless they give valuable information about $Ge_2H_n^+$ ions reactivity with allene.

At zero reaction time, signals in the mass spectra cover the range of m/z values due to $Ge_2H_2^+$, $Ge_2H_3^+$, and $Ge_2H_4^+$ germane secondary ions, the first one being the most abundant. Increase of the reaction time up to 2 s allowed us to detect several multiplets. Because of the low abundance of some signals, the identification of the number of hydrogen atoms contained in some of the ion species was not straightforward. Therefore, these ions are written with an 'x' as coefficient for hydrogen atoms. Anyway, it is interesting to note that with increasing reaction time the

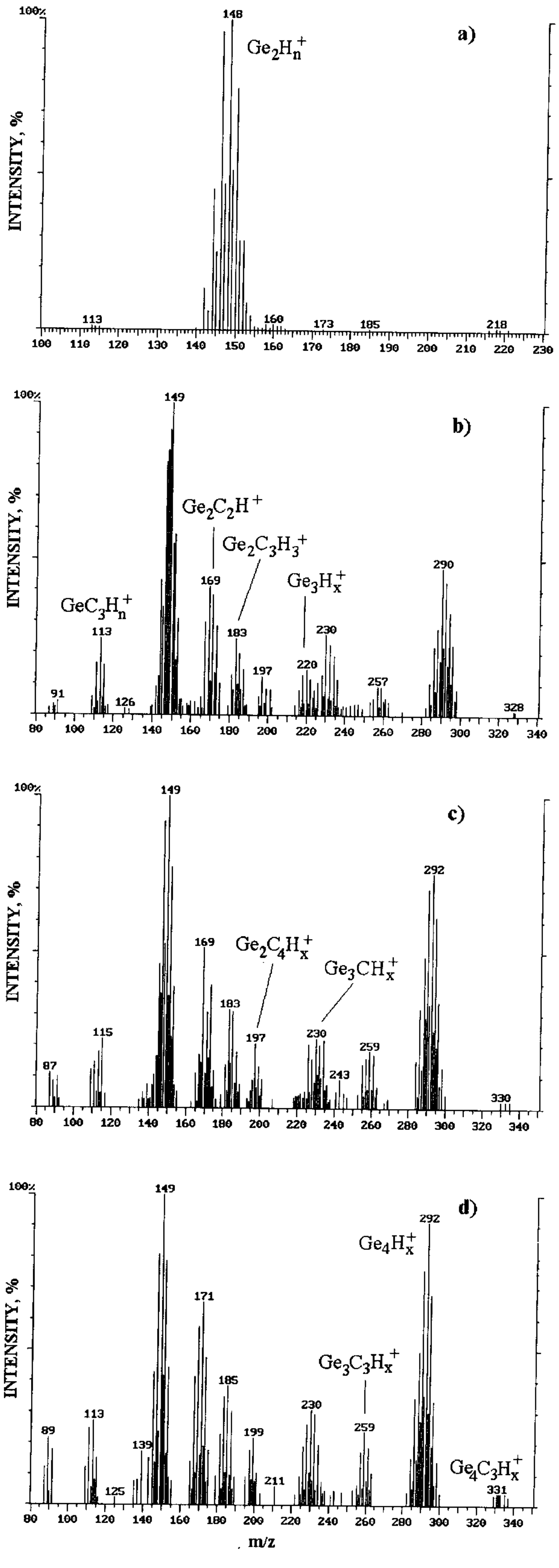


Figure 1. Mass spectra obtained after isolation of the $Ge_2H_n^+$ (n = 2–4) multiplet ions at 0 s (a), 0.5 s (b), 0.9 s (c), and 2 s (d) reaction times.

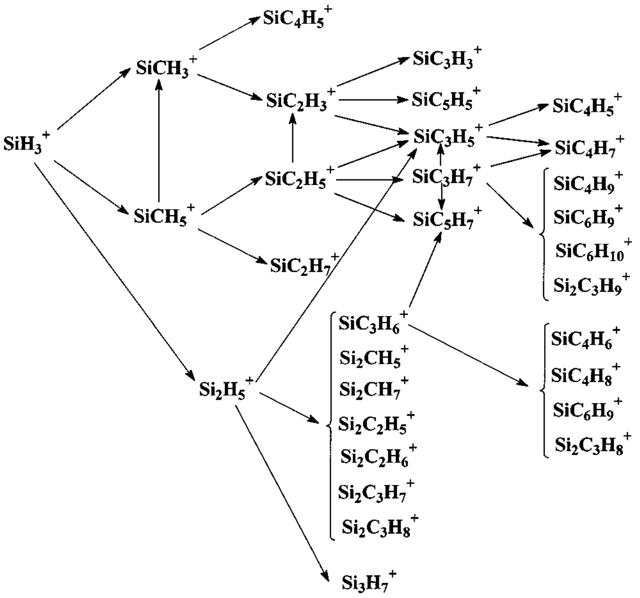
$Ge_2H_n^+$ multiplet reduces to the one corresponding to the $Ge_2H_3^+$ species only. It means that this ion is less reactive than the $Ge_2H_n^+$ (n = 2, 4) species, whose abundance decreases rapidly due to ion/molecule reactions occurring in the mixture. Therefore, the products observed are mainly formed from the $Ge_2H_2^+$ and $Ge_2H_4^+$ ion species reacting with allene, and in particular from $Ge_2H_2^+$, which is the most abundant ion at zero reaction time.

On the basis of the lower and upper limits and of the most intense signal of each multiplet in the spectra, $GeC_3H_n^+$ (n = 3–5), $Ge_2C_2H^+$, $Ge_2C_3H_3^+$, and $Ge_3H_x^+$ (x = 2 for the most abundant species in the multiplet) ion species are formed. Weak signals due to the $Ge_2C_4H_x^+$ (x = 5 for the most abundant species in the multiplet) ions are also observed. As it contains four carbon atoms, it cannot be directly formed from $Ge_2H_n^+$, but it can only originate from $Ge_2C_2H^+$ or $Ge_2C_3H_3^+$. After about 0.9 s reaction time, the signals due to the $Ge_3H_x^+$ ions almost disappear from the mass spectra, while the intensities of higher mass multiplets, assigned to the $Ge_3CH_x^+$ (x = 0 and 2 for the most abundant species in the multiplet), $Ge_3C_3H_x^+$ (x = 5 for the most abundant species in the multiplet), and $Ge_4H_x^+$ (x = 0 and 2 for the most abundant species in the multiplet) ion species, increase remarkably. If the reaction time is further increased, a weak multiplet due to the $Ge_4C_3H_x^+$ ions becomes detectable, the possible precursors being $Ge_3C_3H_x^+$ and $Ge_4H_x^+$ ions.

In separate and successive experiments, some of these ion families were in turn isolated and reacted, in order to determine their direct products. In particular, $Ge_2C_2H^+$ and $Ge_2C_3H_3^+$ ions were isolated together, and the main products of reaction observed after 2 s are $GeC_5H_x^+$ and $GeC_6H_x^+$. These ions were obtained by substitution of a Ge atom by two or three carbons. Moreover, small amounts of $Ge_2C_4H_x^+$ and $Ge_3H_x^+$ ions are also found. Isolation and reaction of the $Ge_3H_x^+$ ion family shows that it produces $Ge_3CH_x^+$ and $Ge_4H_x^+$ ions, but a partial contribution of other species, such as $Ge_2C_2H^+$ or $Ge_2C_3H_3^+$, cannot be ruled out. Finally, it was possible to isolate the $Ge_3CH_x^+$ multiplet, which leads to the formation of the $Ge_3C_3H_x^+$ ion species.

Silane/Allene Mixture

Three different mixtures were considered, which consist of silane and allene in the approximate ratios 1:5 (1.8 × 10^{-7}/8.5 × 10^{-7} Torr), 1:1 (5.0 × 10^{-7}/4.6 × 10^{-7} Torr), and 5:1 (8.6 × 10^{-7}/1.7 × 10^{-7} Torr). Ionisation of the two reacting molecules again produces the allene primary ions and the SiH_n^+ (n = 0–3) ion species from silane. They are trapped in the cell of the mass spectrometer and react with both neutral species with increasing reaction times up to 2 seconds. During this time, several ion families are formed in successive reactions, and products that are obtained after four reaction steps are detected. As an example, Scheme 1 shows the paths of ion/molecule reactions starting from SiH_3^+ primary ion of silane, reacting with silane and allene neutral molecules.



Scheme 1. Paths of ion/molecule reactions starting from SiH_3^+ in a SiH_4/C_3H_4 mixture.

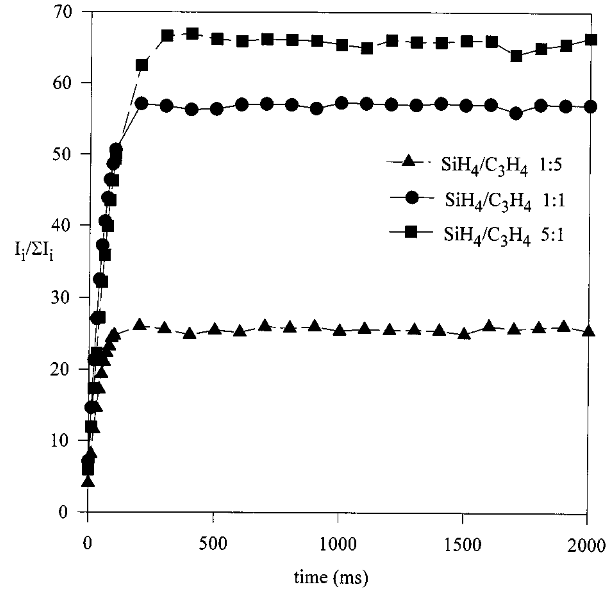


Figure 2. Variation of the total abundances of silicon and carbon containing ions as a function of reaction time for the 1:5, 1:1, and 5:1 silane/allene mixtures.

Figure 2 reports the variation of the total ion abundance of mixed ions as a function of reaction time for the three silane/allene mixtures. In all cases, the abundance rapidly increases to a maximum value, which remains constant up to two seconds of reaction. The highest yield is given by the SiH_4/C_3H_4 5:1 mixture, which is more than twice that of the 1:5 mixture. However, it is worth noting that the behaviour of the 1:1 silane/allene system is rather similar to that of the 5:1 one. Such a trend can be due to the involvement of allene as neutral reagent.

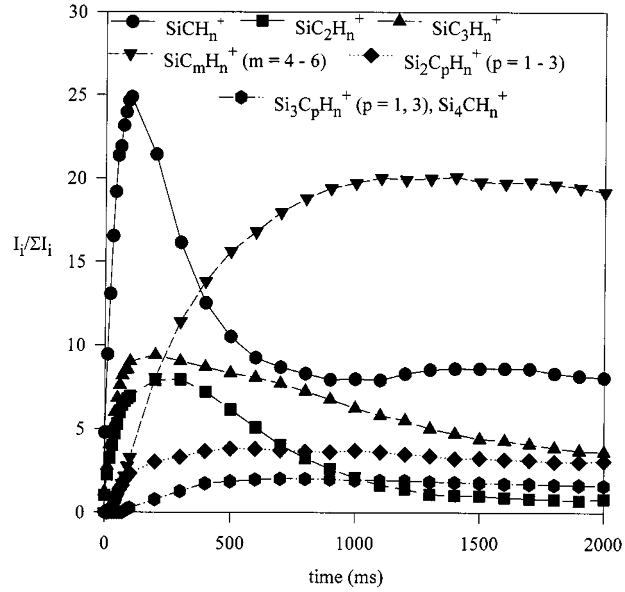


Figure 3. Variation of the abundances with reaction time of the $SiCH_n^+$, $SiC_2H_n^+$, $SiC_3H_n^+$, $SiC_mH_n^+$ (m = 4–6), $Si_2C_pH_n^+$ (p = 1–3), and $Si_3C_pH_n^+$ (p = 1, 3) with $Si_4CH_n^+$ ion families for the 1:1 silane/allene mixtures.

Table 3. Reactions of $C_2H_n^+$, $C_3H_n^+$ and $C_4H_n^+$ ions with silane in a SiH_4/C_3H_4 mixture

Reactant Ions	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
$C_2H_2^+$	$SiCH_3^+$ (2.8), $SiC_2H_3^+$ (2.6), $SiC_2H_5^+$ (1.7)	7.1	12.85	0.55
$C_2H_3^+$	SiH_3^+ (2.6), $SiC_2H_5^+$ (0.77)	3.4	12.72	0.26
C_3H^+	$SiCH_3^+$ (5.3), $SiC_3H_2^+$ (1.8), $SiC_3H_3^+$ (2.4)	9.5	11.75	0.81
$C_3H_2^+$	$SiCH_3^+$ (1.6), $SiC_2H_3^+$ (1.3)	2.9	11.68	0.25
$C_3H_3^+$	$SiCH_3^+$ (0.47), $SiCH_5^+$ (0.89)	1.4	11.61	0.12
$C_3H_4^+$	$SiCH_4^+$ (0.38)	0.38	11.54	0.033
$C_3H_5^+$	$SiCH_5^+$ (3.0)	3.0	11.48	0.26
$C_4H_3^+$	$SiCH_3^+$ (0.40), $SiC_2H_3^+$ (0.56), $SiC_2H_5^+$ (0.89)	1.8	10.98	0.16
$C_4H_4^+$	$SiC_2H_4^+$ (0.38), $SiC_3H_5^+$ (0.26), $SiC_4H_7^+$ (0.34)	0.98	10.94	0.090

[a] Rate constants are expressed as 10^{-10} cm^{3}molecule^{-1}s^{-1}; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory taking polarizability of SiH_4 from ref.[20] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}k_L$.

Variation of the abundances of the $SiCH_n^+$, $SiC_2H_n^+$, $SiC_3H_n^+$, $SiC_mH_n^+$ (m = 4–6), $Si_2C_pH_n^+$ (p = 1–3), and $Si_3C_pH_n^+$ (p = 1–3) together with $Si_4CH_n^+$ ion families are reported in Figure 3 for the 1:1 silane/allene mixture. The total abundance of ions formed in the first reaction step ($SiCH_n^+$, $SiC_2H_n^+$, and $SiC_3H_n^+$) reaches a maximum value after about 100–200 ms of reaction, and then decreases to a rather constant value.

The other ion species show a slower increase, which is as high as 20% for the $SiC_mH_n^+$ ion family, whereas ions produced in successive reaction steps never exceed 4%. However, it is remarkable that the abundance of each ion family examined here does not change substantially after 1 s of reaction.

The rate constants of ion/molecule reactions occurring in the silane/allene system are displayed in tables 3–6. In Table 3, reactions of the $C_2H_n^+$ (n = 2, 3), $C_3H_n^+$ (n = 1–5), and $C_4H_n^+$ (n = 3, 4) ions with silane are listed. The $C_2H_4^+$ ion is not reported, as it has the same nominal mass of the Si^+ species formed from silane, and no experiment was possible that allowed its selection alone. For the same reason, Si^+ is not shown. Allene primary and secondary ions react with silane through different pathways, in which loss of small hydrocarbon molecules (C_2H_2, C_2H_4, C_3H_4), fragments (CH_3, C_2H_3), or H atom, with or without a molecule of hydrogen,occurs. Rate constants are generally low for all reaction paths considered. As observed for the germane/allene mixtures, efficiencies of reaction decrease with increasing number of hydrogen atoms in the families of primary $C_2H_n^+$ (n = 2, 3) and $C_3H_n^+$ (n = 1–4) ions.

Table 4 shows the ion/molecule reactions of the SiH_n^+ (n = 1–3) and $Si_2H_n^+$ (n = 2–5) ions with allene. Self-condensation reactions of silane are not reported, as already discussed in previous papers.[3a,21] Generally, many different products are detected and the reaction efficiencies are high. However, rate constants of single reactions are rather low and the high efficiencies are mainly due to the great number of pathways observed. The only two exceptions are the SiH^+ and SiH_3^+ ions, which yield $SiCH_3^+$with high rate constants, through loss of the stable neutrals, C_2H_2 and C_2H_4, respectively.

As a general remark, reactions with loss of hydrocarbon molecules are the most frequently observed paths. Additions of C_3H_4 and losses of an atom of hydrogen together, or without a molecule of hydrogen are very frequent processes too, with rate constants that are generally lower than the previous ones. Every $Si_2H_n^+$ (n = 2–5) ion shows at least one process characterised by substitution of a neutral fragment containing only silicon and hydrogen by a moiety originating from allene. In fact, loss of a silyl radical is displayed by all the $Si_2H_n^+$ (n = 2–5) ions, except $Si_2H_3^+$, which loses a silylene group. The $Si_2H_n^+$ (n = 4, 5) ions also undergo substitution of a silane by an allene molecule.

In order to follow the growth of ions containing silicon and carbon already bonded together, reactions of the $SiCH_n^+$ (n = 2–5) ion family with both allene and silane are reported in Table 5. As already noticed for ions containing only silicon and hydrogen, reactions of the $SiCH_n^+$ (n = 2–5) species with allene proceed through loss of various neutral molecules (H_2, CH_4, C_2H_2, C_2H_4, and C_3H_6) or by elimination of a variety of hydrocarbon fragments or hydrogen atoms. In contrast, the reactivity of this ion family towards silane is remarkably low, as only $SiCH_2^+$ and $SiCH_4^+$ react

Table 4. Reactions of SiH_n^+ and $Si_2H_n^+$ ions with allene in a SiH_4/C_3H_4 mixture

Reactant Ions	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
SiH^+	$SiCH_3^+$ (14), $SiC_3H_3^+$ (0.50)	14	13.32	1.05
SiH_2^+	$SiCH_2^+$ (2.3), $SiCH_3^+$ (1.5), $SiCH_4^+$ (1.2), $SiC_2H_3^+$ (3.9), $SiC_3H_5^+$ (1.6)	10.5	13.19	0.80
SiH_3^+	$SiCH_3^+$ (7.4), $SiCH_5^+$ (2.4)	9.8	13.06	0.75
$Si_2H_2^+$	$SiC_3H_3^+$ (1.4), $Si_2CH_2^+$ (2.9), $Si_2C_2H_3^+$ (1.8), $Si_2C_3H_3^+$ (0.10), $Si_2C_3H_5^+$ (0.38)	6.6	11.22	0.59
$Si_2H_3^+$	$SiC_3H_5^+$ (0.38), $Si_2CH_3^+$ (1.4), $Si_2CH_5^+$ (0.46), $Si_2C_3H_3^+$ (0.25), $Si_2C_3H_5^+$ (0.38)	2.9	11.18	0.26
$Si_2H_4^+$	$Si_2H_2^+$ (0.23), $SiC_3H_4^+$ (0.28), $SiC_3H_5^+$ (2.8), $Si_2CH_4^+$ (1.5), $Si_2C_2H_5^+$ (1.1), $Si_2C_3H_6^+$ (0.39), $Si_2C_3H_7^+$ (0.79)	7.1	11.15	0.64
$Si_2H_5^+$	$Si_2H_3^+$ (0.65), $SiC_3H_5^+$ (1.1), $SiC_3H_6^+$ (0.76), $Si_2CH_5^+$ (2.3), $Si_2CH_7^+$ (0.31), $Si_2C_2H_5^+$ (0.36), $Si_2C_2H_6^+$ (0.40), $Si_2C_3H_7^+$ (0.53), $Si_2C_3H_8^+$ (0.21)	6.60	11.11	0.59

[a] Rate constants are expressed as 10^{-10} $cm^3molecule^{-1}s^{-1}$; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory calculating polarizability of C_3H_4 as in ref.[19] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}k_L$.

Table 5. Reactions of $SiCH_n^+$ ions with allene and silane in a SiH_4/C_3H_4 mixture

Reactants	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
$SiCH_2^+ + C_3H_4$	$SiCH_3^+$ (1.1), $SiC_2H_2^+$ (3.4), $SiC_2H_3^+$ (0.21), $SiC_3H_2^+$ (2.7), $SiC_3H_3^+$ (2.3), $SiC_4H_5^+$ (0.45)	10	12.06	0.84
$SiCH_2^+ + SiH_4$	$Si_2CH_4^+$ (1.5)	1.5	11.42	0.13
$SiCH_3^+ + C_3H_4$	$SiC_2H_3^+$ (1.4), $SiC_4H_5^+$ (1.0)	2.4	12.00	0.20
$SiCH_4^+ + C_3H_4$	$SiCH_3^+$ (1.0), $SiCH_5^+$ (2.3), $SiC_2H_4^+$ (1.3), $SiC_2H_6^+$ (0.52), $SiC_3H_5^+$ (1.3), $SiC_4H_6^+$ (0.58), $SiC_4H_7^+$ (0.84)	7.8	11.93	0.65
$SiCH_4^+ + SiH_4$	$Si_2CH_6^+$ (0.41)	0.41	11.30	0.036
$SiCH_5^+ + C_3H_4$	$SiCH_3^+$ (5.8), $SiC_2H_5^+$ (0.44), $SiC_2H_7^+$ (0.91)	7.2	11.87	0.60

[a] Rate constants are expressed as 10^{-10} $cm^3molecule^{-1}s^{-1}$; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory calculating polarizability of C_3H_4 as in ref.[19], and taking polarizability of SiH_4 from ref.[20] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}k_L$.

Table 6. Reactions of $Si_3H_5^+$, $Si_4H_7^+$,$SiC_2H_n^+$, and $SiC_3H_n^+$ ions with allene and silane in a SiH_4/C_3H_4 mixture

Reactants	Product Ions and Rate Constants (k_{exp})[a]	Σk_{exp}	k_L[b]	Efficiency[c]
$Si_3H_5^+ + C_3H_4$	$Si_3CH_5^+$ (0.93), $Si_3CH_9^+$ (0.90), $Si_3C_3H_5^+$ (2.6)			
4.4	10.38	0.43		
$Si_4H_7^+ + C_3H_4$	$Si_3C_3H_5^+$ (0.46), $Si_4CH_7^+$ (0.80), $Si_4CH_{11}^+$ (0.78), $Si_4C_3H_7^+$ (1.6)			
3.6	9.96	0.36		
$SiC_2H_3^+ + C_3H_4$	$SiC_3H_3^+$ (0.50), $SiC_3H_5^+$ (0.76), $SiC_5H_5^+$ (1.3)			
2.6	11.35	0.23		
$SiC_2H_5^+ + C_3H_4$	$SiC_2H_3^+$ (2.4), $SiC_3H_5^+$ (0.90), $SiC_3H_7^+$ (0.67), $SiC_5H_7^+$ (1.5)			
5.5	11.26	0.49		
$SiC_3H_5^+ + C_3H_4$	$SiC_4H_5^+$ (1.1), $SiC_4H_7^+$ (0.39)	1.5	10.85	0.14
$SiC_3H_6^+ + C_3H_4$	$SiC_4H_6^+$ (0.74), $SiC_4H_8^+$ (0.32), $SiC_5H_7^+$ (0.97), $SiC_6H_9^+$ (2.2)			
4.2	10.82	0.39		
$SiC_3H_6^+ + SiH_4$	$Si_2C_3H_8^+$ (0.95)	0.95	10.38	0.092
$SiC_3H_7^+ + C_3H_4$	$SiC_3H_5^+$ (0.15), $SiC_4H_7^+$ (1.6), $SiC_4H_9^+$ (0.66), $SiC_5H_7^+$ (1.1), $SiC_6H_9^+$ (1.3), $SiC_6H_{10}^+$ (0.25)			
5.1	10.80	0.47		
$SiC_3H_7^+ + SiH_4$	$Si_2C_3H_9^+$ (0.38)	0.38	10.36	0.037

[a] Rate constants are expressed as 10^{-10} $cm^3molecule^{-1}s^{-1}$; experiments were run at 333 K; uncertainty is within 20%. – [b] Rate constants have been calculated according to the Langevin theory calculating polarizability of C_3H_4 as in ref.[19], and taking polarizability of SiH_4 from ref.[20] – [c] Efficiency has been calculated as the ratio $\Sigma k_{exp}/k_L$.

with SiH_4 through loss of a hydrogen molecule with rather low rate constants.

The reaction of $SiCH_4^+$ to give $SiCH_5^+$ is an hydrogenation process which can involve both silane and allene as neutral reagent. Similarly, ions at nominal mass 58 and 59, could be formed by $SiCH_4^+$ reacting with both silane[5] ($Si_2H_2^+$ and $Si_2H_3^+$) and allene ($SiC_2H_6^+$ and $SiC_2H_7^+$). The hydrogenation process was observed in the SiH_4/C_3H_6 system previously studied,[5] and the use of a pulsed valve allowed us to state that both neutrals react with $SiCH_4^+$ to give $SiCH_5^+$. The procedure was repeated in this SiH_4/C_3H_4 system, isolating and reacting $SiCH_4^+$ in experiments with allene at a constant pressure and pulsing silane into the trap. In this way, it was found that the $SiCH_5^+$ ion is formed from $SiCH_4^+$ and allene, as well as $SiC_2H_6^+$ and $SiC_2H_7^+$ and the corresponding formation rate constants were calculated.

The propagation of the processes leading to cluster ions of increasing size was further studied and results are reported in Table 6. In this table, the reactions of the $Si_3H_5^+$,

$Si_4H_7^+$, $SiC_2H_n^+$ (n = 3, 5) and $SiC_3H_n^+$ (n = 5–7) ions with allene are shown, together with rate constants of reactions of $SiC_3H_n^+$ (n = 6, 7) with silane.

The $Si_3H_5^+$ and $Si_4H_7^+$ ions were chosen as an example of the behavior of tertiary and quaternary silane ions, as they are the most abundant within their corresponding families. Hence, it was possible to isolate and select them. Also the reactivity of the $Si_3H_4^+$ ion was studied, which reacts very slowly to give the $Si_3CH_4^+$ and $Si_3CH_8^+$ products. Unfortunately their abundance was too low to allow the determination of their formation rate constants. The $Si_3H_5^+$ and $Si_4H_7^+$ ions show a very similar behaviour towards allene.

The $SiC_2H_n^+$ (n = 3, 5) ions react only with allene with loss of hydrocarbon and H_2 molecules with rather low rate constants. A similar behaviour is displayed by the $SiC_3H_n^+$ (n = 5–7) ions. Within this family, the number of reactions with allene and the reaction efficiencies increase with increasing number of hydrogen atoms in the reacting ion. Only the $SiC_3H_n^+$ (n = 6, 7) ions react with silane and yield the large clusters $Si_2C_3H_{n+2}^+$ via loss of a hydrogen molecule characterised by low rate constants.

The present results may be compared with those obtained in the SiH_4/C_3H_8 and SiH_4/C_3H_6 systems previously studied.[5] The reactivity of the SiH_4/C_3H_8 system was found to be remarkably low, and hence the comparison may be limited to the SiH_4/C_3H_6 and SiH_4/C_3H_4 mixtures. Silane primary ions show a similar behaviour towards propene and allene. In fact, reaction efficiencies are quite high and the most favourable neutral losses are almost the same in the two systems. However, when allene is the neutral reagent, the number of different reaction paths is high. In contrast, reactions of the SiH_n^+ (n = 1–3) ions with propene proceed through a lower number of paths, but generally with higher rates. A similar trend is displayed by the $Si_2H_n^+$ (n = 2–5) ions in the comparison of the two systems. Because of the several different processes starting from silane ions, the number of Si, C, and H containing ion species formed in the SiH_4/C_3H_4 system is higher than in the SiH_4/C_3H_6 one. Among these, some ions are common to the two systems: $SiCH_n^+$ (n = 4, 5), $SiC_2H_5^+$ and $SiC_3H_7^+$. Their reactivity towards silane is supposed to be the same; nevertheless, reactions of $SiCH_5^+$ and $SiC_2H_5^+$ ions could not be studied in the SiH_4/C_3H_4 system, the reason being the lower abundance of the reacting ions in the SiH_4/C_3H_4 mixture. In fact, $SiCH_5^+$ is formed through fewer processes and with lower rate constants in the presence of allene than with propene. $SiC_2H_5^+$ has a higher number of precursors in the SiH_4/C_3H_4 system, but formation rate constants are remarkably low. Mixed ions, containing silicon, carbon and hydrogen, that are present in both the systems react with comparable efficiencies with allene and propene, the number of reaction paths being higher in the silane/allene mixture as already observed for silane ions. Finally, several hydrocarbon ions are common to the two mixtures: $C_2H_3^+$, $C_3H_n^+$ (n = 1–5), rate constants of their reactions with silane being in good agreement among the two systems.

Conclusions

In the comparison of the two mixtures studied in this paper, the great difference of reactivity between silane and germane towards allene is remarkable. In fact, neutral germane as well as ions originated by its ionisation are considerably less reactive than the corresponding silicon containing species. Primary and secondary ions of silane react with allene through many different paths and with appreciable reaction efficiencies to yield mixed ion clusters of growing size, such as $Si_4C_3H_7^+$ or $SiC_6H_{10}^+$. In contrast, germane primary ions react with allene to give only one product for each ion, the only exception being GeH_2^+ which gives several mixed ions but with low rate constants. Moreover, the distribution of the signal due to an ion species containing two Ge atoms and the consequent overlapping of different multiplets make the single selection procedures difficult. Anyway, the isolation of the whole $Ge_2H_n^+$ (n = 2–4) ion family and its reaction (with reaction times as long as 2 s) allowed the detection of mixed clusters, up to $Ge_4C_3H_x^+$ ions, although in low abundance.

Hydrocarbon ions, formed in self-condensation processes of allene, mainly reacted with germane by charge-exchange processes to give ion products containing Ge and H only, together with a few mixed ion clusters. To the contrary, allene ions react with silane to yield a great number of different products containing Si, C, and H atoms. These ion species react further, preferentially with allene, in successive steps, to give large clusters with increasing number of carbon atoms.

Finally, it appears clear that the cationic mechanism does not give a high contribution to the growth of materials, starting from gaseous mixtures in the GeH_4/C_3H_4 system, while it is more efficient in the SiH_4/C_3H_4 one. Moreover, in the silane/allene mixture, the largest cluster ions are generally formed in reactions of silicon containing ions with allene and the highest yield are observed in mixtures containing silane in excess.

Experimental Section

Allene and silane were commercially supplied in high purity and germane was prepared and purified as described in the literature.[22] Prior to use, each of the reagent gases was dried by means of anhydrous sodium sulfate. Helium was supplied at an extra-high degree of purity, and no further purification was necessary. The experiments were performed on a ITMS Finnigan mass spectrometer and the pressure was measured by a Bayard Alpert ionisation gauge. The read pressures were corrected for the relative sensitivity of the ion gauge with respect to different gases[23,24] and for a calibration factor, calculated as previously reported,[21] in order to get the real pressure in the trap. Helium buffer gas was admitted to the trap at a pressure of about 4×10^{-4} Torr (1 Torr = 133 Pa), and allene, germane and silane at pressures in the 2.0×10^{-7}–10.0×10^{-7} Torr range. The trap temperature was 333 K in order to avoid thermal decomposition of reagents and to obtain results comparable with systems studied previously. In all experiments, ions were detected in the mass range of 14–400 u . In order to prevent side reactions with water background, the manifold and the lines for introduction of reagent gases and helium were frequently baked-out.

The scan modes used to isolate selected ion species or ranges of ions for the determination of reaction mechanisms and rate constants, as well as the procedures for calculations, were previously described in detail.[3,21,25] Ionic species that were selectively isolated from silane contained the ^{28}Si isotope, whereas those isolated from germane contained the ^{70}Ge (Ge$^+$, GeH$^+$) or ^{76}Ge (GeH$_2^+$, GeH$_3^+$) isotope. Selection of ions at a specific *m*/*z* value was performed by using dc voltages and by resonance ejection, as in previous studies.[25] The latter method, applying rf voltages only, is expected to cause a lower excitation of the selected ions with respect to the method in which a dc voltage is used. The rate constants obtained with the two different methods were very similar and this behaviour is consistent with the hypothesis that ions are thermalized by unreactive collisions with the buffer gas. The single exponential decays of the abundance of the reacting ions observed in the kinetic experiments further confirm this hypothesis.

Formation of ions was obtained with an electron beam at about 35 eV for ionisation times in the range 1–20 ms. A reaction time suitable to maximise the abundance of ions to be stored was applied after the ionisation event. Isolation of the selected ions, their reactions with neutrals present in the trap for convenient reaction times (50 ms for rate constants calculation and up to 2 s for mechanisms determination) and acquisition were the successive steps.

In the silane/allene mixture, where Si is isobaric with C_2H_4, some experiments were performed by introducing one reagent gas via a pulsed valve in order to determine the neutral species involved in the ion/molecule reaction under examination and, as a consequence, the composition of the product ion. A General Valve Corporation's Iota One pulse valve was used,[26] and the experimental procedures have been already described.[4] Briefly, the introduction into the ion trap of one of the reactants through a pulsed valve allows us to react selected ions with only the other gas which is continuously leaked into the trap. The pressure of the gas to be pulsed was set behind the valve to about 1×10^{-6} Torr, the valve opening time was 0.1 ms and the time required for the pressure of the pulsed gas to decrease to zero was about 1.5 s.

Acknowledgments

Authors wish to thank MURST and Università di Torino for financial support to this research.

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[1] J. G. Ekerdt, Y.-M. Sun, A. Szabo, G. J. Szulczewski, J. M. White, *Chem. Rev.* **1996**, *96*, 1499.

[2] P. Hess, *Electron. Mat. Chem.* **1996**, *127*, 169.

[3] [3a] J.-F. Gal, R. Grover, P.-C. Maria, L. Operti, R. Rabezzana, G. A. Vaglio, P. Volpe, *J. Phys. Chem.* **1994**, *98*, 11978. – [3b] P. Antoniotti, L. Operti, R. Rabezzana, G. A. Vaglio, J.-F. Gal, R. Grover, P.-C. Maria, *J. Phys. Chem.* **1996**, *100*, 155. – [3c] L. Operti, R. Rabezzana, G. A. Vaglio, P. Volpe, *J. Organomet. Chem.* **1996**, *509*, 151. – [3d] G. Cetini, L. Operti, R. Rabezzana, G. A. Vaglio, P. Volpe, *J. Organomet. Chem.* **1996**, *519*, 169. – [3e] P. Benzi, L. Operti, R. Rabezzana, M. Splendore, G. A. Vaglio, *Int. J. Mass Spectrom. Ion Processes* **1996**, *152*, 61. – [3f] P. Antoniotti, L. Operti, R. Rabezzana, G. A. Vaglio, *Int. J. Mass Spectrom.* **1999**, *182*/*183*, 63.

[4] [4a] P. Benzi, L. Operti, G. A. Vaglio, P. Volpe, M. Speranza, R. Gabrielli, *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 647. – [4b] L. Operti, M. Splendore, G. A. Vaglio, P. Volpe, M. Speranza, G. Occhiucci, *J. Organomet. Chem.* **1992**, *433*, 35.

[5] P. Antoniotti, L. Operti, R. Rabezzana, G. A. Vaglio, P. Volpe, *Int. J. Mass Spectrom.* **1999**, *190*/*191*, 243.

[6] P. Antoniotti, C. Canepa, L. Operti, R. Rabezzana, G. Tonachini, G. A. Vaglio, *J. Organomet. Chem.,* **1999**, *589*, 150.

[7] P. Antoniotti, C. Canepa, L. Operti, R. Rabezzana, G. Tonachini, G. A. Vaglio, *J. Phys. Chem. A* **1999**, *103*, 10945.

[8] M. T. Bowers, *Gas Phase Ion Chemistry,* Academic Press, New York, **1979**.

[9] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. ref. Data Suppl. 1* **1988**, *17*.

[10] B. Ruscic, M. Schwarz, J. Berkowitz, *J. Chem. Phys.* **1990**, *92*, 1865.

[11] R. Bakhtiar, C. M. Holznagel, D. B. Jacobson, *J. Phys. Chem.* **1993**, *97*, 12710.

[12] B. H. Boo, P. B. Armentrout, *J. Am. Chem. Soc.* **1991**, *113*, 6401.

[13] B. H. Boo, P. B. Armentrout, *J. Am. Chem. Soc.* **1987**, *109*, 3549.

[14] S. Wlodek, A. Fox, D. K. Bohme, *J. Am. Chem. Soc.* **1991**, *113*, 4461.

[15] B. H. Boo, J. L. Elkind, P. B. Armentrout, *J. Am. Chem. Soc.* **1990**, *112*, 2083.

[16] B. L. Kickel, E. R. Fisher, P. B. Armentrout, *J. Phys. Chem.* **1992**, *96*, 2603.

[17] S. K. Shin, R. R. Corderman, J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 257.

[18] [18a] J. J. Myher, A. G. Harrison, *J. Phys. Chem.* **1968**, *72*, 1905. – [18b] M. T. Bowers, D. D. Elleman, R. M. O'Malley, K. R. Jennings, *J. Phys. Chem.* **1970**, *74*, 2583. – [18c] A. Nato, M. Niwa, K. Honma, I. Tanaka, *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 287. – [18d] C. Lifshitz, Y. Gleitman, S. Gefen, U. Shainock, I. Dotan, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 1. – [18e] C. Lifshitz, Y. Gleitman, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 17. – [18f] V. G. Anicich, G. A. Blake, J. K. Kim, M. J. McEwan, W. T. Huntress Jr. *J. Phys. Chem.* **1984**, *88*, 4608. – [18g] D. Carrier, J. A. Herman, *Int. J. Mass Spectrom. Ion Processes* **1984**, *59*, 49.

[19] K. J. Miller, *J. Am. Chem. Soc.* **1990**, *912*, 8533.

[20] E. R. Lippincott, J. M. Stutman, *J. Phys. Chem.* **1964**, *68*, 2926.

[21] [21a] P. Benzi, L. Operti, G. A. Vaglio, P. Volpe, M. Speranza, R. Gabrielli, *J. Organomet. Chem.* **1988**, *354*, 39. – [21b] L. Operti, M. Splendore, G. A. Vaglio, A. M. Franklin, J. F. J. Todd, *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 25.

[22] P. Benzi, M. Castiglioni, P. Volpe, L. Battezzati, M. Venturi, *Polyhedron* **1988**, *7*, 597.

[23] M. Decouzon, J.-F. Gal, P.-C. Maria, A. S. Tchinianga, *personal communication*.

[24] J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149.

[25] P. Antoniotti, L. Operti, R. Rabezzana, M. Splendore, G. Tonachini, G. A. Vaglio, *J. Chem. Phys.* **1997**, *107*, 1491.

[26] T. J. Carlin, B. S. Freiser, *Anal. Chem.* **1983**, *55*, 571.

Received July 30, 1999
[I99284]