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International Journal of Mass Spectrometry 228 (2003) 551–562

www.elsevier.com/locate/ijms

Ligand exchange ion–molecule reactions of simple silyl and germyl cations

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Received 20 December 2002; accepted 19 March 2003

Dedicated to Prof. Dr. Helmut Schwarz on the occasion of his 60th birthday for his inspiring contributions to gas-phase ion chemistry and his contagious zest for science.

Abstract

The gas-phase reaction of Me_3Si^+ with $Si(OMe)_4$, studied under FT-ICR conditions, reveals that aside from the expected silyl ion–*n*-donor base association an exchange mechanism exists that gives rise to Me_2SiOMe^+. Further reaction of this ion was observed to result in a second exchange of a methyl group by a methoxy group in the silyl ion. The similar reaction between Me_3Si^+ and $Ge(OMe)_4$ yields not only the silyl ions with progressive exchange of methyl by methoxy but the different germyl ions, $Me_nGe(OMe)_{3-n}{}^+$ ($n = 0$–3). Ab initio calculations for the simple model system $MeSiH_2{}^+ + MeOGeH_3$ reveal that these reactions proceed by initial formation of a very strong Lewis acid–base complex where migration of the germyl or silyl group can result in a moiety held together by an alkyl bridge. Methide abstraction in this intermediate can then give rise to silyl and germyl cations. The present results suggest that other Si and Ge systems may display this very same kind of rich chemistry.

Keywords: Silyl ions; Germyl ions; Sily and germyl migration; Methide abstraction

1. Introduction

The search for stable silyl and germyl cations in condensed phases has been an elusive and challenging task, and a subject of considerable speculation in recent years [1–6]. These ions are expected to be very powerful electrophiles and can be key short-lived intermediates in mediating reactions of silicon-, and germanium-containing organic substrates. By contrast, gas-phase $SiR_3{}^+$ and $GeR_3{}^+$ ions, bearing equivalent (R = alkyl) groups, or their asymmetric analogs with non-equivalent alkyl groups and/or hydrogens as substituents, are relatively common fragments in the mass spectra of organosilanes and organogermanes [7].

The gas-phase ion chemistry of simple silyl cations has been relatively well studied because of the intrinsic interest in their chemistry, and their possible role in semiconductor technology (for general overviews on this subject, see [8]). In particular, the association of Me_3Si^+ with organic bases has been explored from a qualitative and quantitative point of view (for a thorough review, see [9]). Considerably less attention

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doi:10.1016/S1387-3806(03)00164-7

has been dedicated to the gas-phase ion chemistry of germanium-containing ions as recently reviewed by one of the authors [10,11]. In fact, important properties such as the thermochemistry and reactivity of even simple germyl cations remain largely unexplored. However, several reports have already shown that gaseous Me_3Ge^+ ions can undergo association with a number of *n*-donor bases [12] in a similar fashion to the corresponding silyl cation. On the other hand, little is known about the possible propensity of germyl groups to undergo migrations in mass spectrometric processes. This kind of behavior has been illustrated for silyl-containing systems where mass spectral fragmentations [13] and recent results from ion–molecule reaction [14,15] studies reveal that silyl groups are prone to undergo rearrangements and/or migrations that can often account for the dominant reaction pathways.

In recent years, our group has actively pursued the investigation of the gas-phase ion chemistry of homoleptic silicon and germanium alkoxides in order to elucidate the basic mechanisms of transient Si and Ge species that may play a role in sol–gel processes and in vapor deposition processes [16–19]. In the course of these investigations, and in comparing the reactivity of simple silyl and germyl cations, it became apparent that unusual exchange reactions occur in these systems involving alkyl and alkoxy ligands. In this paper, some of these reactions are described and ab initio calculations of model systems are used to propose a mechanism for these exchange reactions.

2. Experimental

Gas-phase ion–molecule reactions were studied in a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer built in this Institute and interfaced to an IonSpec Omega Fourier Transform Data System. The general characteristics of the spectrometer and its application towards the elucidation of gas-phase ion reaction sequences have been illustrated in recent publications from these laboratories [15,17,18,20]. This spectrometer typically operates at a fixed magnetic field of 1.0 T provided by a 9 in. electromagnet. The cell of the spectrometer is a modified near-cubic 15.6 cm^3 one-region cell in which center holes have been drilled on both transmitter plates to allow for laser irradiation of the ion cloud. The temperature of the cell under normal operating conditions (with the ionizing filament turned on) is typically 333 ± 5 K as measured with a Pt wire thermometer located near one of the transmitter plates.

Positive ions were generated from the corresponding neutral using a 40 ms ionization pulse of 18 eV electrons. The typical pressure of the neutral precursor of ions was usually in the $2–6 \times 10^{-8}$ Torr range as monitored by a nude ion gauge located just before the turbomolecular pump. The reactivity of ions of a given *m*/*z* was determined by ejection of all unwanted ions from the ICR cell with a combination of short radio-frequency pulses. The reactivity of different fragment ions (with their full isotopomeric components) was determined by ejecting all unwanted ions from the ICR cell with a combination of radio-frequency pulses. The additional neutral reagents were introduced in the cell through leak valves to a final pressure of 10^{-7} Torr.

At the typical working pressures, considerable reaction is observed in the first few hundreds of milliseconds of trapping time, and secondary reactions are also observed to occur readily as discussed later.

All the reagents were commercially available and were used without further purification. Fresh samples of silicon and germanium alkoxides were frequently employed to minimize the problems of hydrolysis of these compounds. All samples were repeatedly distilled under vacuum prior to introduction in the cell.

3. Ab initio calculations

Ab initio calculations were carried out with the Gaussian 94 suite of programs [21] for simple model systems to provide some basic understanding of the nature of the intermediates and transition states involved in the exchange reactions. The level of calculations was kept at a moderate level for the sake of convenience and because of present limitations on computer capabilities.

The structure of the reagent species, intermediates, and products were initially optimized at the HF/6-31G* level. Stationary points were characterized by harmonic frequency analysis, and the frequencies were used to determine zero point vibrational energies (ZPEs) without any scaling procedure. Electronic energy calculations were then carried out at the MP2/6-31G* level using these optimized structures. Transition states were studied at the same level of theory and their nature confirmed by the presence of a single imaginary frequency, and by performing IRC calculations.

4. Results and discussion

Me_3Si^+ and Me_3Ge^+ ions generated from Me_4Si and Me_4Ge, respectively were found to be unreactive towards their parent neutral under the typical low pressure experimental conditions of our FT-ICR experiments. This is in complete agreement with previous findings [22]. At higher pressures ($\sim 10^{-3}$ Torr), mass spectrometric experiments have shown that Me_3Si^+ undergoes an association reaction with Me_4Si to yield $Me_7Si_2^+$ [23,24]. The structure of this species has not been clearly established although a methyl-bridge structure has been proposed to be consistent with experimental observations.

Similar studies carried out in a mixture of Me_4Si and Me_4Ge reveal that Me_3Si^+ ions can readily abstract a methide species from Me_4Ge to yield Me_3Ge^+ as shown below

$$Me_3Si^+ + GeMe_4 \rightarrow Me_3Ge^+ + SiMe_4 \qquad (1)$$

This intriguing type of ion–molecule reaction involving the formal transfer of $(Me)^-$ proceeds readily under our FT-ICR conditions. Reactions has been well characterized previously [25,26], and a $\Delta H_1^\circ = -10.2 \pm 1.2\,\mathrm{kcal\,mol^{-1}}$ has been obtained from equilibrium measurements [25]. Similar type reactions have also been observed for Me_3Si^+, Me_3C^+, Me_2CH^+, and Me_2Cl^+ with phenyltrimethylgermanes [27,28].

In order to understand the potential energy surface for reaction (1) and its possible implications with other reactions involving these ions, we opted to carry out theoretical calculations on the prototype model reaction involving H_3Si^+ and $MeGeH_3$,

$$H_3Si^+ + MeGeH_3 \rightarrow H_3Ge^+ + MeSiH_3 \qquad (2)$$

The results from these calculations (Table 1) reveal that reaction (2) proceeds through a single well potential with the minimum corresponding to a structure where a methyl group is shared by partially charged H_3Si and H_3Ge moieties (see Fig. 1). The calculated exothermicity ($-5.4\,\mathrm{kcal\,mol^{-1}}$) is close to the value measured for reaction (1) but the stability for the $[H_3Si\cdots Me\cdots GeH_3]^+$ intermediate would appear to be somewhat overestimated. For the related $Me_7Si_2^+$ species, the experimental binding energy has been determined to be $22.3 \pm 0.4\,\mathrm{kcal\,mol^{-1}}$ [25].

The putative intermediate of the methide abstraction reaction (2) is predicted to have a linear arrangement of the heavy atoms, i.e., $\angle SiCGe = 180^\circ$, and the

Table 1
Calculated electronic energies (in a.u.) and zero point energies (in $\mathrm{kcal\,mol^{-1}}$) for the relevant species of the model reaction (2)[a]

	E (MP2/6-31G*//HF/6-31G*)	ZPE	Relative energies
$MeGeH_3$	−2114.804942	39.4	
SiH_3^+	−290.391219	15.1	
$MeGeH_3 + SiH_3^+$			0
$[H_3Ge\cdots Me\cdots SiH_3]^+$	−2405.253406	57.0	−33.3
$MeSiH_3$	−330.485042	40.9	
GeH_3^+	−2074.720060	13.7	
$MeSiH_3 + GeH_3^+$			−5.4

[a] See Fig. 1 for the energy diagram.

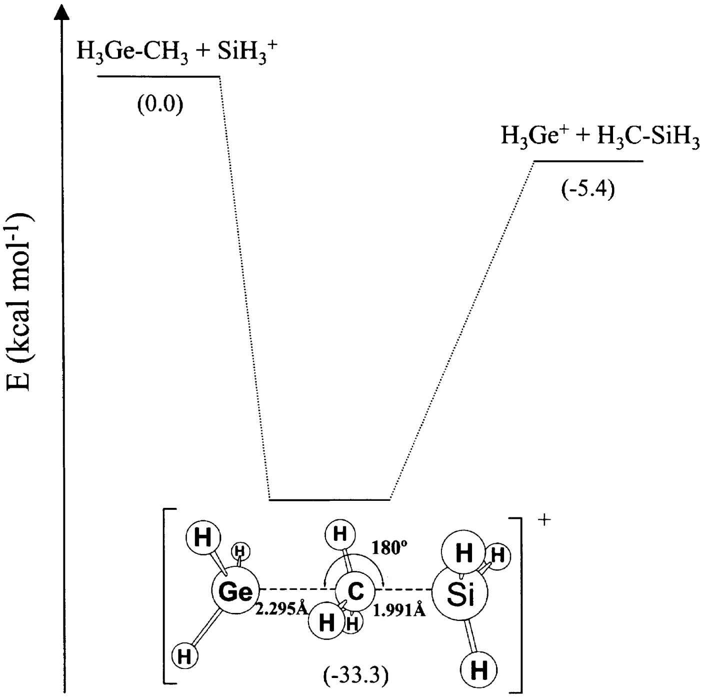


Fig. 1. Calculated energy diagram for the methide abstraction reaction of H_3Si^+ and $MeGeH_3$. The structure of the intermediate for this single well potential is also shown in the diagram.

methyl group slightly tilted toward a nascent neutral methylsilane molecule. Although the geometric arrangement is somewhat surprising, the idea of the methyl group bridging the Si and Ge center agrees with previous qualitative interpretations of the likely structure for $Me_7Si_2^+$ [24,25].

A considerably more facile addition reaction is observed in the reaction of either Me_3Si^+ or Me_3Ge^+ with the silicon and germanium alkoxides acting as *n*-bases. This is shown in reaction (3) for Me_3Si^+ and $E = Si, Ge$, where the structure of the product ion has been represented as that resulting from the expected association between the electrophilic ion and the alkoxy-oxygen lone pair (see below also).

$$Me_3Si^+ + E(OMe)_4 \rightarrow [Me_3Si\text{–}O^+(Me)\text{–}E(OMe)_3] \quad (3)$$

Similar results are observed for Me_3Ge^+.

Although reaction (3) is by far the most important reaction for these systems, the most interesting observation was the fact that new silyl ions are also generated through a ligand exchange reaction between the ion and the neutral. A good example is shown in reaction (4) that was found to be competitive with reaction (3)

$$Me_3Si^+ + Si(OMe)_4 \rightarrow MeOSiMe_2^+ + MeSi(OMe)_3 \quad (4)$$

The resulting $MeOSiMe_2^+$ ions were also observed to promote further ligand exchange with neutral $Si(OMe)_4$, under our experimental conditions, to yield $(MeO)_2SiMe^+$, as well as an association reaction of this ion with the silicon alkoxide in a process similar to that shown in reaction (3).

A similar ligand exchange reaction is observed if the reaction is initiated with $(MeO)_3Si^+$ reacting with Me_4Si. In this case, Me_3Si^+ is formed rapidly by the methide abstraction reaction (5)

$$(MeO)_3Si^+ + Me_4Si \rightarrow Me_3Si^+ + MeSi(OMe)_3 \quad (5)$$

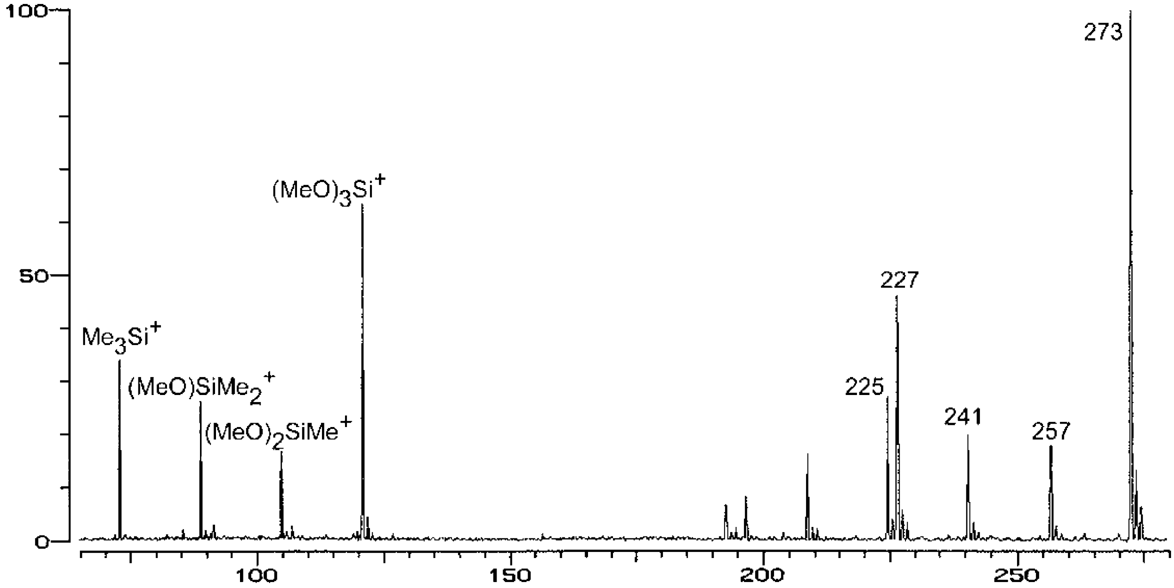


Fig. 2. FT-ICR spectrum obtained 700 ms after isolation of $(MeO)_3Si^+$ in the presence of an approximately equimolar mixture of $Si(OMe)_4$ and $SiMe_4$ at about 1×10^{-7} Torr. This spectrum clearly shows the ligand exchange process and formation of all the different silyl cations. Please notice that the high mass ions result from addition of the silyl ions to $Si(OMe)_4$ and ions originating from loss of 46 mass units from the addition products. For example, *m/z* 273, $Si_2(OMe)_7{}^+$ and its fragmentation product *m/z* 227 $Si_2(O)(OMe)_5{}^+$; *m/z* 257, $MeSi_2(OMe)_6{}^+$ and its fragmentation product *m/z* 211 assumed to be $MeSi_2(OMe)_4{}^+$; *m/z* 241, $Me_2Si_2(OMe)_5{}^+$ and so on.

Successive ligand exchange reactions follow as mentioned above. Fig. 2 shows the FT-ICR spectrum obtained after isolation of the $(MeO)_3Si^+$ ion and after 700 ms of reaction time in an approximately equimolar mixture of Me_4Si and $(MeO)_4Si$ at 10^{-7} Torr. This spectrum shows the different addition products resulting from reactions similar to (3), and the fragmentation of energy rich addition product by elimination of CH_4 and CH_2O, or Me_2O, as discussed in [17] and shown for example in reaction (6)

$$\begin{aligned}&(MeO)_3Si^+ + Si(OMe)_4\\ &\quad\rightarrow [(MeO)_3Si\text{–}O^+(Me)\text{–}Si(OMe)_3]^* \quad (m/z\,273)\\ &\quad\rightarrow (MeO)_3SiOSi(OMe)_2{}^+ (m/z\,227)\\ &\qquad + (Me_2O, \quad \text{or} \quad CH_4 + CH_2O) \qquad (6)\end{aligned}$$

The different silyl ions are explicitly identified in the spectrum, whereas the higher mass ions are identified in the caption of Fig. 2.

A more complex and diversified set of ligand exchange reactions is observed in the reaction of Me_3Si^+ with $Ge(OMe)_4$. Although direct association, reaction (3), is again the predominant pathway, a full range of both silyl, $MeOSiMe_2{}^+$ and $(MeO)_2SiMe^+$, and germyl, $(MeO)_3Ge^+$, $(MeO)_2GeMe^+$, $MeOGeMe_2{}^+$ and Me_3Ge^+, cations are produced through the sequence outlined in reactions (7) and (8),

$$\begin{aligned}&Me_3Si^+ + Ge(OMe)_4 \rightarrow MeOSiMe_2{}^+\\ &\quad + MeGe(OMe)_3 \qquad (7a)\end{aligned}$$

$$\begin{aligned}&Me_3Si^+ + Ge(OMe)_4 \rightarrow (MeO)_3Ge^+\\ &\quad + MeOSiMe_3 \qquad (7b)\end{aligned}$$

$$\begin{aligned}&(MeO)_3Ge^+ + Me_4Si \rightarrow (MeO)_2GeMe^+\\ &\quad + Me_3SiOMe \qquad (8)\end{aligned}$$

This clearly illustrated in the FT-ICR spectrum obtained 700 ms after ion isolation (Fig. 3) under conditions similar to that of Fig. 2. As in the previous case, the silyl cation formed in reaction (7a) undergoes

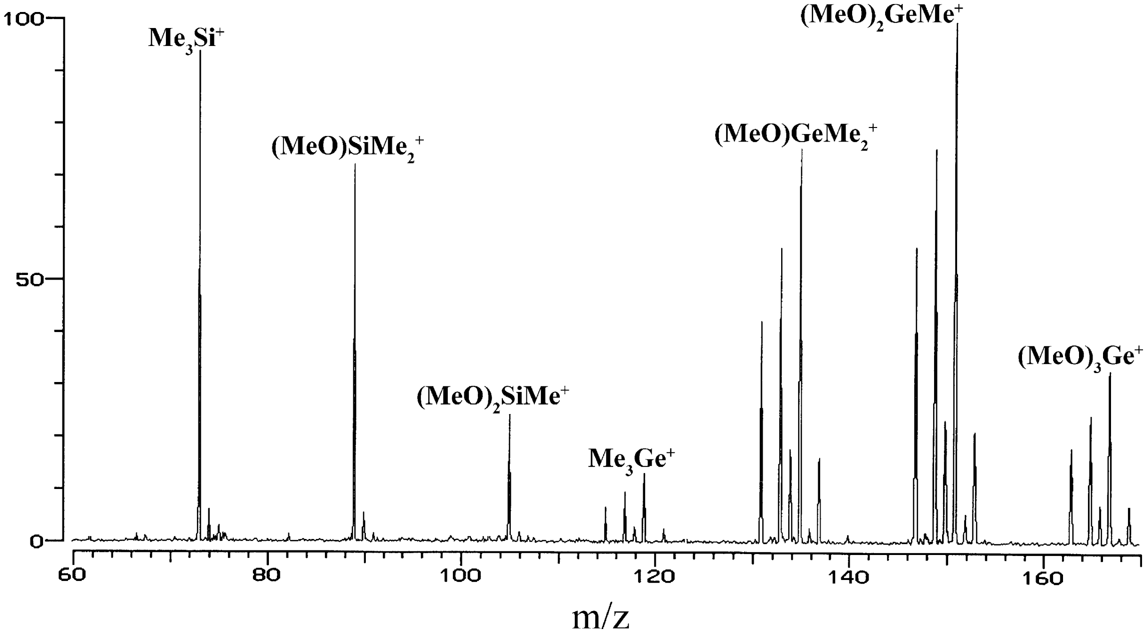


Fig. 3. FT-ICR spectrum obtained 700 ms after isolation of Me_3Si^+ in the presence of an approximately equimolar mixture of $Ge(OMe)_4$ and $SiMe_4$ at about 1×10^{-7} Torr. This spectrum covering only the *m/z* 60–170 range clearly shows the formation of the different silyl and germyl cations as discussed in reactions (7) and (8).

secondary reactions to yield $(MeO)_2SiMe^+$. Likewise, $(MeO)_2GeMe^+$ can promote further ligand exchange reactions with Me_4Si. The mass spectrum displayed in Fig. 3 refers only to the region of the silyl and germyl cations because at higher values of *m/z* the spectrum is dominated by product ions formed by association of the different silyl and germyl cations with neutral $Ge(OMe)_4$.

The different germyl cations formed through reactions like (8) are also clearly identified in systems where $(MeO)_3Ge^+$ is first isolated and allowed to react with Me_4Si.

Several approaches can be used to explore the mechanism of these reactions by theoretical calculations. Again, we chose a simple model system for our ab initio calculations that would minimize the painstaking problem associated with multiple local minima when dealing with large number of methyl substituents and corresponding to all the possible rotamers. To this effect, the reaction between H_2SiMe^+ and $MeOGeH_3$ was singled out as our model system in the hope that sufficient information could be gained from this system. Different pathway possibilities had to be considered for this system that are relevant to the silyl–germyl exchange reactions. These are:

(a) ligand exchange and formation of a new silyl ion,

$$H_2SiMe^+ + MeOGeH_3 \rightarrow H_2SiOMe^+ + MeGeH_3 \quad (9a)$$

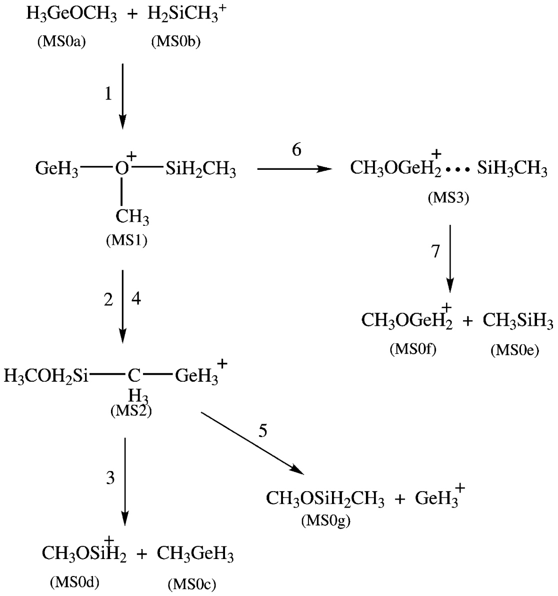
(b) methoxide abstraction and formation of a germyl ion,

$$H_2SiMe^+ + MeOGeH_3 \rightarrow H_2Si(Me)(OMe) + H_3Ge^+ \quad (9b)$$

(c) hydride abstraction,

$$H_2SiMe^+ + MeOGeH_3 \rightarrow H_3SiMe + MeOGeH_2^+ \quad (9c)$$

Reaction (9c) is not an available pathway for the fully substituted silicon and germanium species studied in



Scheme 1.

Table 2

Relative energies of reagents, intermediate species, transition states, and products for the $MeSiH_2^+ + MeOGeH_3$ model reaction (see Scheme 1 and Fig. 4)[a]

	MP2/6-31G*// HF/6-31G*	ΔZPE	Δ*E*
MS0a + MS0b	0.00	0.00	0.00
MS1	−76.62	3.71	−72.91
MS2	−38.34	2.48	−35.86
MS3	−39.44	2.42	−37.02
TS2	−31.99	2.18	−29.81
TS4	−31.69	2.60	−29.09
TS6	−30.97	2.06	−28.91
MS0c + MS0d	−20.23	1.01	−19.22
MS0e + MS0f	−12.33	0.97	−11.36
MS0g + H_3Ge^+	−2.84	0.26	−2.58

[a] Units in $kcal\,mol^{-1}$.

the experimental work, but it was included for the sake of comparison.

The theoretical calculations predict that all three channels of our model reaction system (9) are exothermic. The general mechanism for the set of reactions (9) can be visualized in Scheme 1 where reagents, intermediates and products are identified by a code-name, and the different steps of the mechanisms are numerically identified. Scheme 1 is based on theoretical calculations at the MP2/6-31G*//HF/6-31G* level and the relative energies are tabulated in Table 2. The calculated structures for the different intermediates and transition states are shown in Figs. 4 and 5, and the overall energy diagram of the reaction shown in Fig. 6.

According to our theoretical calculation and Scheme 1, reaction (9) is predicted to proceed by initial addition of the silyl ion to the oxygen center to yield the MS1 intermediate. This is in agreement with our proposal that association reactions like those in (3) result in binding of the silyl cation to the alkoxy oxygen of the neutral silicon or germanium alkoxide. The MS1 intermediate is calculated to be unusually stable (72.9 $kcal\,mol^{-1}$) with respect to the reagents, and higher level calculations were performed to investigate possible deficiencies in our methodology. Slightly higher values are found in these calculations, namely 76.1 $kcal\,mol^{-1}$ at the CCSD(T)/6-31G* level, and 75.0 $kcal\,mol^{-1}$ at the MP2/6-311G(2df, 2p) level. Additional calculations are probably necessary to optimize the structure at a higher level of theory before a more definitive conclusion can be reached on the predicted stability of this intermediate. Nevertheless, for the sake of understanding the pathways for the ligand exchange mechanism in the silyl cation, and formation of a germyl cation, as in reactions (7) and (8), it is important to follow the possible pathways available to the MS1 intermediate:

(a) Migration of the silyl group from the oxygen center to one of the hydrogens bound to germanium proceeds through TS6 to yield the germyl ion—monosilane complex (MS3) that upon breaking apart yields the product of a formal hydride abstraction, reaction (9c).

(b) A second pathway is found where a nascent germyl ion migrates from oxygen to the methyl group bound to Si through TS2. This results in the formation of the MS2 intermediate, a silyl–germyl moiety exhibiting a methyl bridge similar to that described for the intermediate in the methide abstraction (1) and (2) (see Fig. 1). Interestingly enough, a second transition state

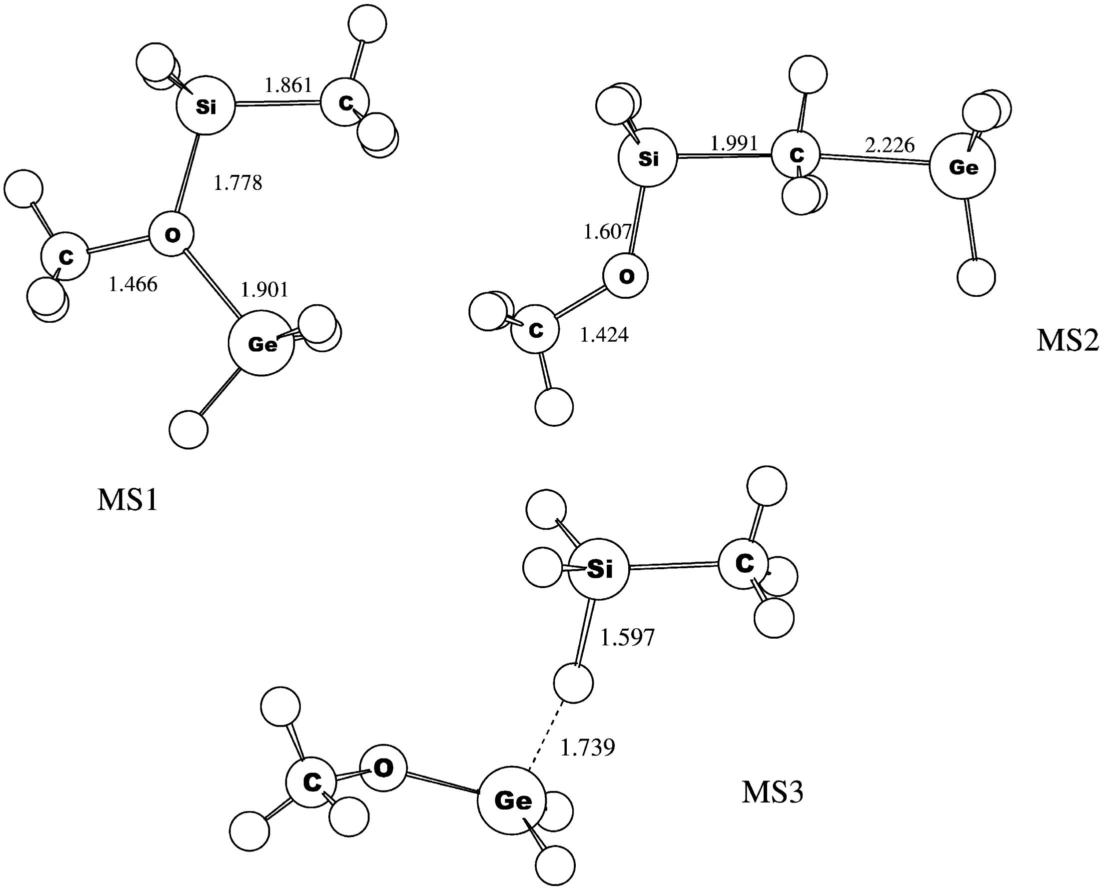
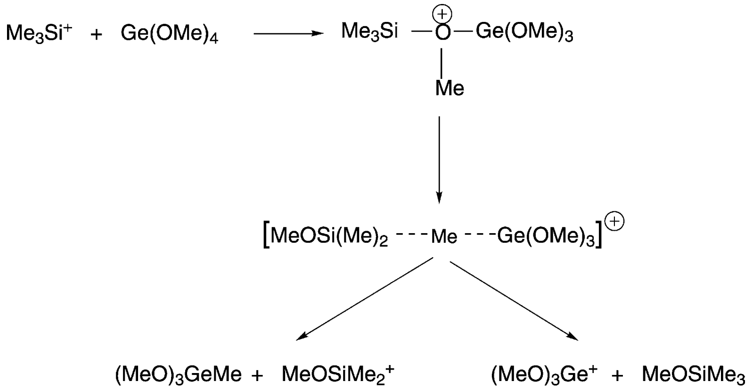


Fig. 4. Optimized structure for the intermediates of the prototypical reaction $MeSiH_2^+ + MeOGeH_3$ as identified in Scheme 1.



Scheme 2.

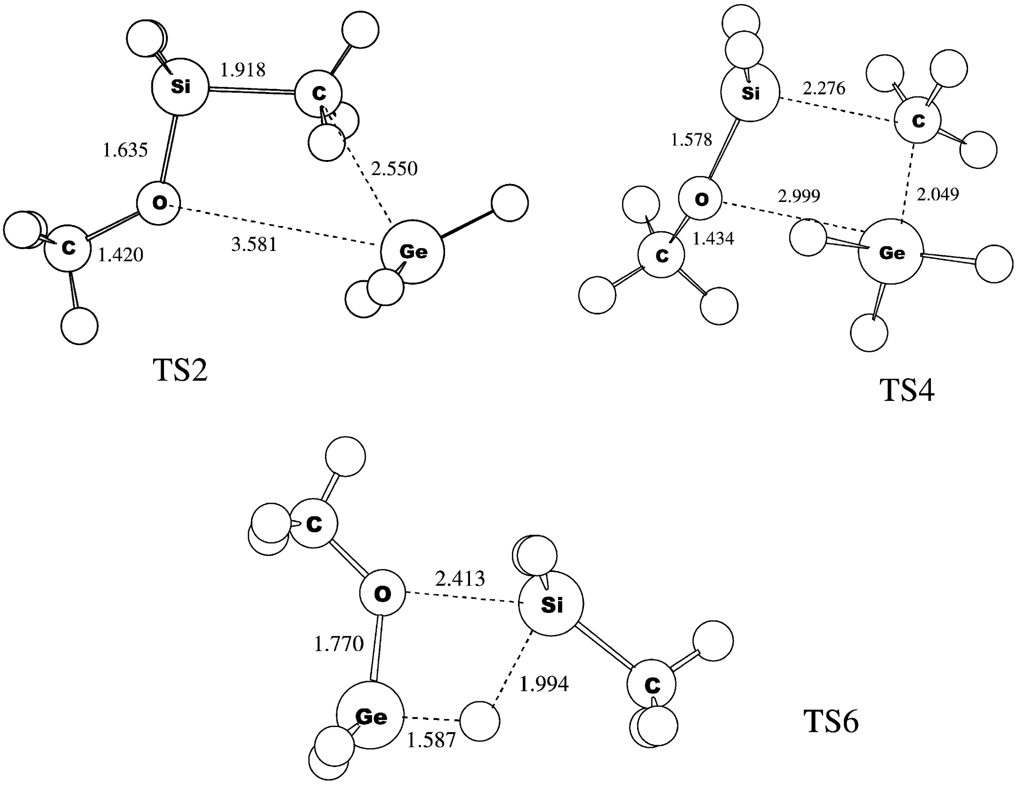


Fig. 5. Optimized structure for the different transition states encountered for the different steps of the prototypical reaction $MeSiH_2^+ + MeOGeH_3$ (see Scheme 1).

TS4, more closely associated with a four center mechanism, was also found to mediate the transformation of the MS1 intermediate to MS2. This MS2 intermediate can then proceed either to the products of reaction (9a) by methide abstraction of the germyl group in the complex, or to the products of reaction (9b) by methide abstraction of the silyl group in the complex.

The calculated energies for the different transition states encountered for the evolution of the MS1 intermediate toward products are very similar, and considering that the MS2 and MS3 are relatively shallow intermediates (when compared to MS1), it is reasonable to assume that the product distribution of our hypothetical reaction (9) would follow the relative stabilities of the different products.

The above calculations are a good indication of how to rationalize the mechanism of reactions (7) and (8). In the case of reaction (7), and based on the results of our model system, we can propose the reaction sequence shown in Scheme 2. Here, the initial formation of the associated product from reaction (3) is followed by migration to give rise to the methyl bridge intermediate and methide abstraction by either the germyl or silyl group to yield the products of reactions (7a) and (7b).

By comparison, reaction (8) is envisioned to occur in the opposite sequence with initial methide abstraction in the intermediate followed by migration as outlined in Scheme 3.

A particularly important consideration in these exchange reactions is the fact that they have only been observed with Me_3Si^+ as the reagent ion, or Me_4Si as

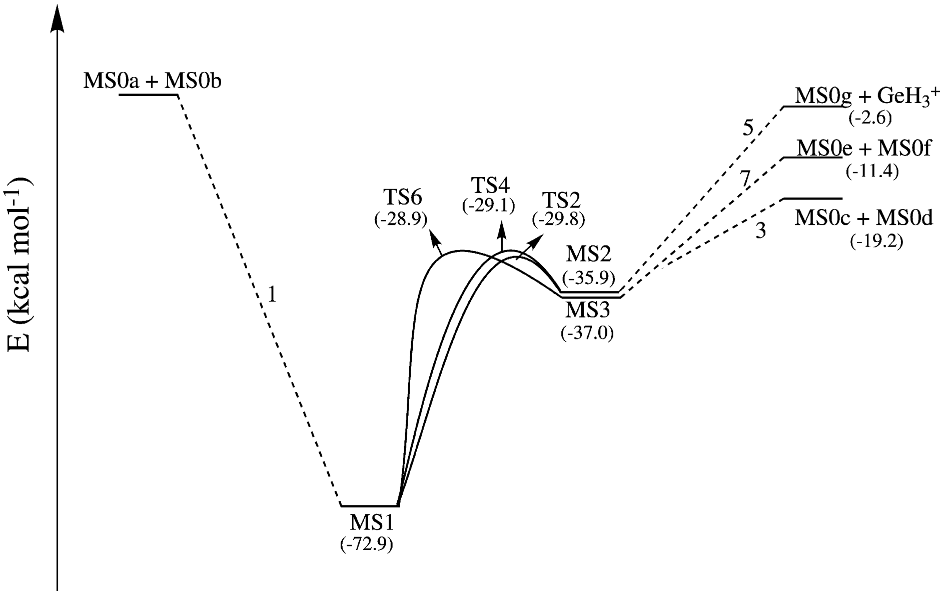
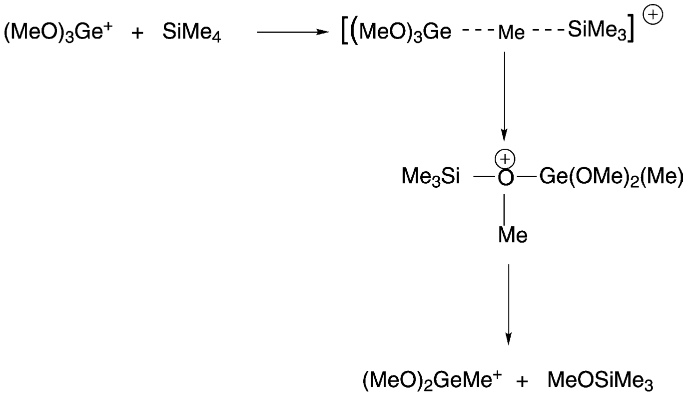


Fig. 6. Energy diagram calculated for the prototypical reaction $MeSiH_2^+ + MeOGeH_3$ (see Scheme 1 for nomenclature). Energies in kcal mol^{-1}.

the neutral reagent. For example:

(a) the reaction of Me_3Ge^+ with $Ge(OMe)_4$ results in the exclusive formation of the $Me_3GeO^+(Me)Ge(OMe)_3$ adduct;
(b) the reaction of Me_3Ge^+ with $Si(OMe)_4$ results in the exclusive formation of the $Me_3GeO^+(Me)Si(OMe)_3$ adduct;
(c) no reaction is observed under our experimental conditions for $(MeO)_3Si^+$ in the presence of Me_4Ge.

It is not clear from these experiments whether (a) and (b) proceed to yield a much more stable intermediate, or these intermediates are less prone to undergo fragmentation reactions. In case (c), it is not known



Scheme 3.

whether the initial methide abstraction is energetically unfavorable and thus no ligand exchange occurs for this pair of reagents. On the other hand, the above observations coupled with the results of reactions (7a) and (8) suggest that an important and likely driving force for these reactions can be attributed to the much larger Si–O than Ge–O bond strength.

The migration and rearrangements reported in this paper are reminiscent of the migration first reported by Wright and West in silyl and germyl ethers in the presence of strong base [29] that have been recently investigated at high level of theory by Antoniotti and Tonachini [30]. Furthermore, migrations have also been reported in systems containing a direct Si–Ge bond [31] through an apparent alkyl or aryl bridge. Thus, we feel that the some important areas of investigation can be pursued in this area by gas-phase ion chemistry and our group will continue to explore some of this fascinating chemistry.

Acknowledgements

The present work was made possible by support from the Brazilian Research Council (CNPq) through the Millenium Institute for Complex Materials. We also thank FAPESP for graduate (LAX) and post-doctoral (JRP) fellowships.

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