Positive ion chemistry of SiH$_4$/GeF$_4$ gaseous mixtures studied by ion trap mass spectrometry and \textit{ab initio} calculations

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The positive ion chemistry occurring in SiH$_4$/GeF$_4$ gaseous mixtures was investigated by ion trap mass spectrometry and \textit{ab initio} theoretical calculations. The GeF$_3^+$ cation, the only fragment obtained from ionised GeF$_4^-$, was unreactive towards SiH$_4$. All the primary ions SiH$_n^+$ ($n=0$–3) react instead with GeF$_4$ to form SiF$_2^+$ or SiH$_2$F$.^+$. The latter species reacts in turn with SiH$_4$ and GeF$_4$ to form SiH$_3^+$ and SiHF$_3^+$. The potential energy profiles conceivably involved in these reactions were investigated by \textit{ab initio} calculations performed at the MP2 and coupled cluster [CCSD(T)] level of theory.

\textbf{Keywords}: gas-phase ion chemistry, germanium tetrafluoride, ion trap mass spectrometry, silane, theoretical calculations

\section*{Introduction}

The gas-phase ion chemistry of SiH$_4$ and of various of its mixtures with other compounds is of both fundamental and applied interest. These systems are, in fact, employed to deposit electronic and opto-electronic materials by chemical vapour deposition techniques,$^1$ and it is of interest to investigate the conceivable role of ionic species in the early stages of the polymerisation. Thus, over the last four decades, numerous experimental and theoretical studies have been reported concerning the ion–molecule reactions occurring in ionised SiH$_4^-$ and in mixtures of SiH$_4$ with hydrogen,$^{13}$ hydrocarbons,$^{14–22}$ inorganic oxides,$^{23,24}$ water$^{25}$ and ammonia.$^{26,27}$ In particular, to investigate the contribution of Si–C ion clusters and Si–C ionic species “doped” with N or P atoms in the formation of photovoltaic silicon carbides,$^{28–30}$ some of us extensively studied the ionic reactions occurring in binary$^{31–38}$ and ternary mixtures$^{39–46}$ containing SiH$_4$, saturated and unsaturated hydrocarbons and ammonia or phosphine. Ionised mixtures of SiH$_4$ and CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$ and CF$_3$ have also been investigated. The primary SiH$_n^+$ ($n=0$–3) showed a distinct tendency to attack the Cl or F atoms of the halocarbons to form neutral and/or ionic products with Si–Cl or Si–F bonds. The CF$_x^+$ ($x=1$–3) also reacted with SiH$_4$ by both H$^-$ abstraction and formation of products with extensive redistribution of F and H between carbon and silicon centres. Consistent with these findings, our recent study on the ion chemistry of SiH$_4$/NF$_3$ mixtures$^{48–50}$ revealed that the primary SiH$_x^+$ ($x=1$–3) react efficiently with NF$_3$ to form the silicon–fluorine cations SiHF$_x^+$ ($x=1$, 2), SiH$_2$F$^+$ and SiF$_3^+$ ($x=1$–3). The fluorinated Si$_2$ clusters Si$_2$H$_2$F$^+$, Si$_2$H$_3$F$^+$ and Si$_2$H$_4$F$^+$ were also observed. The primary NF$_x^+$ ($x=1$–3) react instead with SiH$_4$ mainly by charge transfer, even though additional products were observed which suggest the formation of intimate...
Experimental and computational details

Silane (99.99% purity grade) and helium (99.9999%) were purchased from Sigma-Aldrich. All the gases were used without further purification.

The experiments were performed with a Finnigan ITMS instrument (Austin, TX, USA) maintained at 333 K. Reagent gases and buffer helium were introduced into the trap at typical pressures of about 1.3 × 10⁻³ to 1.3 × 10⁻⁵ Pa (the SiH₄/GeF₄ ratio is about 1:1), and about 1.3 × 10⁻² Pa, respectively, empirically set to maximise the abundance of the signals and measured by a Bayard Alpert ion gauge. The nominal values were corrected for different sensitivity toward different gases and for a calibration factor which depends on the geometry of the instrument. These pressure domains ensure appreciable signal-to-noise ratios but prevent too high ion densities into the trap. This avoids space–charge effects which may compromise m/z ratio assignments or cause problems of mass discrimination. The q values of the reactant ions, determined by setting the low-mass cut-off value, were selected to ensure that the q value of any product ion (m/z ratio higher and lower than the precursor ion) falls well within the 0.15–0.908 range. This avoids ion loss due to ion ejection (q > 0.908) or to low trapping fields (q < 0.15). Ion densities are also optimised with respect to ionisation times by an automatic gain control. In addition, our investigated range of m/z ratios between 14Th and 400Th avoids the reduction of mass accuracy which occurs when resonance ejection is used to extend the standard highest limit of 650Th of the commercial ion trap. Therefore, even though we did not perform specific determinations of the dynamic range, we may reasonably assume that it is linear for all the experiments performed. In the ITMS, the ionising electron energy is a function of both the amplitude of the rf voltage applied to the ring electrode during ionisation and the phase of the rf as the electrons enter the trap. Therefore, no single electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned. However, simulations of the electron energy can be assigned.
of SiH$_4^{+0}$ showed reactivity towards GeF$_4$. The secondary ion, SiH$_2^+$, is also reactive towards both SiH$_4$ and GeF$_4$. The details of our observed processes are collated in Table 1.

The open-shell cations, Si$^+$ and SiH$_2^+$, react with GeF$_4$ and undergo the F-atom abstractions described by the reactions:

\[
\text{Si}^+ + \text{GeF}_4 \rightarrow \text{SiF}^+ + \text{GeF}_3 \quad \text{(1)}
\]

\[
\text{SiH}_2^+ + \text{GeF}_4 \rightarrow \text{SiH}_2\text{F}^+ + \text{GeF}_3 \quad \text{(2)}
\]

These processes are theoretically predicted to be exothermic by 112 kJ mol$^{-1}$ and 68 kJ mol$^{-1}$, respectively, and these values reflect average Si–F bond energies which are in general larger than Ge–F (for example, 596 kJ mol$^{-1}$ vs 470 kJ mol$^{-1}$ passing from SiF$_3$ to GeF$_3$). The estimated enthalpy change of Reaction (1) differs in particular from the experimental value by nearly 50 kJ mol$^{-1}$ and this deviation can be taken as an estimate of the accuracy of the presently employed CCSD(T)/MP2 level of theory. Both Reactions (1) and (2) conceivably occur by the attack of Si$^+$ or SiH$_2^+$ to a F atom of GeF$_4$, with formation of the Si–F bond and concomitant cleavage of the weaker Ge–F bond. The reaction between Si$^+$ and GeF$_4$ deserves an additional comment, however. The electron ionisation of SiH$_4$ in general produces both ground (2P) and excited Si$^+$ states (about 30%). The formation of electronically excited Si$^+$ is also expected under our ITMS conditions. Collisions with helium are, in fact, only partially effective in quenching excited electronic states. Consistent with this expectation, we noticed the contribution of excited Si$^+$ to the reaction between Si$^+$ and NF$_3$. We observed the formation of both SiF$^+$ and NF$_2$ (definitely exothermic for both ground and excited Si$^+$), and of NF$_3$ and SiF, which is endothermic by 38 kJ mol$^{-1}$ for ground state Si$^+$ but largely exothermic for excited Si$^+$. Likewise, it was observed that the reaction of Si$^+$ with CF$_3$ at collision energies of 1 eV (laboratory frame) produces SiF$^+$ and CF$_3$ as well as CF$_2^+$ and SiF. The energy dependence of the cross sections suggested that both processes were exothermic. However, while the formation of SiF$^+$ is exothermic for both ground and excited Si$^+$, the formation of CF$_3$ is endothermic by nearly 50 kJ mol$^{-1}$ for ground state Si$^+$ and exothermic only for excited Si$^+$. As for Reaction (1), the observed formation of SiF$^+$ and GeF$_3$ is exothermic for both ground and excited Si$^+$ (see Table 1). The time dependence of ln[Si +] resulted in a straight line of constant slope over the entire time interval explored (0–40 ms), thus suggesting a single ionic population or two ionic populations which react at identical reaction rates. In addition, we did not observe any product firmly ascribable to excited Si$^+$. Therefore, at variance with the reaction of Si$^+$ with NF$_3$ and CF$_3$, we cannot distinguish the relative contribution of the ground and/or excited state to the fraction of the Si$^+$ ionic population which reacts with GeF$_4$ according to Reaction (1) (about 30%).

The closed-shell cations SiH$^+$ and SiH$_3^+$ react with GeF$_4$ and undergo the formal H/F exchange reactions described by the reactions:

\[
\text{SiH}^+ + \text{GeF}_4 \rightarrow \text{SiH}_2\text{F}^+ + \text{GeF}_3 \quad \text{(3)}
\]

\[
\text{SiH}_3^+ + \text{GeF}_4 \rightarrow \text{SiH}_2\text{F}^+ + \text{GeF}_3 \quad \text{(4)}
\]

Both these processes are predicted to be exothermic and this essentially reflects the formation of the strong Si–F bonds of SiF$^+$ and SiH$_2^+$F$^+$. These products conceivably arise from the direct attack of SiH$^+$ and SiH$_3^+$ to a F atom of GeF$_4$, to form H$_2$Si–F–GeF$_3$ and H$_3$Si–F–GeF$_3$ intermediates, which undergo the eventual extrusion of GeHF$_3$. This process could occur directly, or pass through additional intermediates. To distinguis among the various conceivable paths, we performed ab initio calculations on the mechanisms of Reactions (3) and (4).
The obtained results are summarised in Figures 1–4, which show the optimised geometries and the relative energies at 0 K of the species involved in these processes.

Both Reactions [3] and [4] commence by the addition of the reactant ions SiH$^+$ or SiH$_3^+$ to GeF$_4$ so to form the fluoro-coordinated complex 1_SiH$^+$ (Figure 1) or 1_SiH$_3^+$ (Figure 3). Both these processes are exothermic (Figures 2 and 4), even though the complexation energy of SiH$_3^+$ is larger than SiH$^+$ by 40 kJ mol$^{-1}$. This higher Lewis acidity of SiH$_3^+$ also reflects in the optimised geometries of 1_SiH$^+$ and 1_SiH$_3^+$. The former species features, in fact, a longer Si–F$_1$ bond distance (1.952 Å vs 1.830 Å) and a shorter Ge–F$_1$ bond distance (1.823 Å vs 1.843 Å). Consistently, the charge shift from GeF$_4$ to SiH$^+$ which accompanies the formation of 1_SiH$^+$, computed as 0.180 e, is larger than the charge shift of 0.106 e which accompanies the formation of 1_SiH$^+$ from SiH$^+$ and GeF$_4$.

The subsequent fates of 1_SiH$^+$ and 1_SiH$_3^+$ and the detailed mechanisms of Reactions [3] and [4] are somewhat different. As shown in Figure 2, the former species passes through the four-centres transition structure TS_SiH$^+$ (Figure 1) and undergoes the H/F exchange between the silicon and the germanium atom to form 2_SiH$^+$, an ion–molecule complex arising from the coordination of the Si atom of SiH$^+$ to the F atom of GeHF$_3$. This reaction intermediate directly dissociates into its constituting moieties and this explains the observation of SiF$^+$ from Reaction (3). On the other hand, as shown in Figure 4, 1_SiH$_3^+$ passes through the four-centres transition structure TS_SiH$_3^+$ (Figure 3), and undergoes the H/F exchange between the silicon and the germanium atom so to form the reaction intermediate 1¢_SiH$_3^+$. This species formally arises from the coordination of the silicon atom of SiH$_3$F$^+$ to the hydrogen atom of GeHF$_3$ and resides in a very flat region of the potential energy surface. Its dissociation into the constituting moieties is endothermic by only 10 kJ mol$^{-1}$, and this explains the experimental observation of SiH$_2$F$^+$ from Reaction 4. We explored also the conceivable role in Reaction [4] of isomer 2_SiH$_3^+$, which is the corresponding analogue of 2_SiH$^+$. We ascertained in particular that, passing through the four-centres transition structure TS'_SiH$_3^+$ (Figure 3), isomer 1¢_SiH$_3^+$ could actually collapse into the significantly more stable 2_SiH$_3^+$. However, as shown in Figure 4, the transition structure TS'_SiH$_3^+$ is less stable than the dissociation limit SiH$_2$F$^+$ + GeHF$_3$. Therefore, it is reasonable to suggest that isomer 1¢_SiH$_3^+$ directly dissociates into its constituting fragments rather than isomerise into 1_SiH$_3^+$, and that the latter intermediate is not involved in the mechanism of Reaction [4]. Additional evidence, in this regard, comes from the theoretical prediction (see Figure 4) that the dissociation limit of lowest energy of 1_SiH$_3^+$ is GeHF$_2$ + SiH$_2$F$_2$ rather than SiH$_2$F$^+$ + GeHF$_3$. However, the GeHF$_2$ ionic product was not experimentally observed.

Isomer 2_SiH$_3^+$ is the corresponding analogue of 2_SiH$^+$ and arises from the coordination of the Si atom of SiH$_3$F$^+$ to the F...
atom of GeHF₃. Interestingly, the optimised geometries and charge distributions of 2_SiH⁺ and 2_SiH₃⁺ suggest that, likewise, SiH₂⁺ is a Lewis acid stronger than SiH⁺, and SiH₂F⁺ is a Lewis acid stronger than SiF⁺. We note, in particular, that the dissociation energy of 2_SiH₃⁺ into SiH₂F⁺ and GeHF₃ is larger by 80 kJ mol⁻¹ than the dissociation energy of 2_SiH⁺ into SiF⁺ and GeHF₃. Consistently, the former species possesses a shorter Si–F₁ bond distance (1.777 Å vs 1.922 Å) and a longer Ge–F₁ bond distance (1.918 Å vs 1.868 Å) and the charge shift from GeHF₃ to SiH₂F⁺, which accompanies the formation of 2_SiH₃⁺, computed as 0.206 e, is larger than the charge shift of 0.115 e which accompanies the formation of 2_SiH⁺ from SiF⁺ and GeHF₃.

As shown in Figures 2 and 4, the rate-determining step of Reactions (3) and (4) is the rearrangement of 1_SiH⁺ or 1_SiH₃⁺ into 2_SiH⁺ or 1'_SiH⁺, respectively, passing through TS_SiH⁺ and TS_SiH₃⁺. These transition structures are predicted to be more stable than the entrance channel SiH⁺ or SiH₂⁺ + GeF₄ by 10–14 kJ mol⁻¹. These values are indeed comparable with the estimated uncertainty of our calculations and the theoretical results essentially suggest that the transition structures involved in the rate-determining steps of Reactions (3) and (4) are comparably stable or only slightly more stable than the reactants. Therefore, in keeping with the experiments, their efficiencies are expected to be significantly less than unity.

The SiH₂F⁺ cation obtained from Reaction (4) reacts with SiH⁺ by hydride transfer and, with GeF₄, undergoes the formal H/F atom exchange according to the reaction:

\[
\text{SiH}_2F^+ + \text{GeF}_4 \rightarrow \text{SiHF}_2^+ + \text{GeF}_3
\]

The mechanism of this process is reasonably similar to those outlined for Reactions (3) and (4).

**Comparison between ionised SiH₄/GeF₄ and SiH₄/CF₄**

So far, the reactions of SiH₄⁺ ions with CF₄ at collision energies of 1 eV (laboratory frame) have been investigated by tandem mass spectrometry.⁶⁶,⁶⁷ Compared with GeF₄, the reactivity patterns include, in general, a larger number of products. The open-shell SiH₂⁺ reacts with CF₄ predominantly by F atom abstraction. However, at variance with GeF₄, the product of the reaction between SiH₂⁺ and CF₄ is CF₂⁺ rather than SiH₂F⁺. This suggests that the experimentally unknown ionisation energy of SiH₂F⁺, so far theoretically estimated as 8.12 eV,⁷¹ is indeed lower than GeF₃, ≤ 10.3 ± 0.3 eV,⁷⁰ but higher than CF₃, 8.76 eV. The minor exothermic products SiF⁺, SiHF⁺, SiH₂F⁺, CF₂ and CHF₂ were also observed. The reaction of SiH⁺ with CF₄ produces comparable amounts of SiF⁺ [by a reaction analogue to Reaction (3)] and CF₂, which is also by far the prevailing product from the reaction between SiH₂⁺ and CF₄. The latter process also leads to minor SiH₂F⁺ and CHF₂. Overall, while...
the major reaction of SiH₃⁺ [n = 1−3] with GeF₄ is the F abstraction or H/F exchange reaction, the major reaction of positive silicon ions with CF₃⁺ is the F⁻ abstraction.

It is also of interest to compare the reactivity toward SiH₄ of GeF₃⁺ and CF₃⁺. Thus, at collision energies of 1 eV (laboratory frame), the latter cation forms SiH₃⁺ (nearly 72% of the total cross section), CH₂F⁺ (nearly 20%), and the minor CH₃⁺ and CH₂F⁺. The endothermic formation of SiH₃F⁺ and SiHF₂⁺ was also detected. Even though this rich reactivity pattern may at least partially reflect the translationally excited character of CF₂⁺, the latter species is certainly more reactive toward SiH₄ than GeF₃⁺. A factor which contributes to this observed difference is the weaker character of the Ge–H with respect to the C–H bond. For example, while the formation of CHF₃ from
CF₃ and SiH₃ is exothermic by 122 kJ mol⁻¹, the conceivable formation of GeHF₃ from GeF₃ and SiH₃ is estimated to be endothermic by 6 kJ mol⁻¹ (this estimate is based on the experimental enthalpy of formation of GeF₃, quoted as 58 kJ mol⁻¹ by Harland et al., and the theoretical enthalpy of formation of GeHF₃, derived as −888 kJ mol⁻¹ from the G4 atomisation energy of 1715 kJ mol⁻¹).

**Conclusions**

Our investigation of the positive ion chemistry occurring in mixtures of SiH₃ and GeF₃ did not reveal any formation of Si–Ge ionic species. This suggests that, when employed to deposit silicon–germanium thin films by plasma techniques, the species involved in the early stages of the polymerisation are neutral rather than ionic. This information could contribute to optimising the running conditions during deposition processes.

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