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Gas phase ion chemistry of $(CH_3)_3SiCF_3$ and $(CH_3)_3SiC_2F_5$, FTICR experiments and theory

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ABSTRACT

The ion chemistry of the fluoroalkyltrimethylsilanes $(CH_3)_3SiCF_3$ and $(CH_3)_3SiC_2F_5$ has been investigated in the gas phase with Fourier transform ion cyclotron resonance spectrometry. The formation of positive and negative ions was studied. Reaction pathways for primary ions with neutral molecules at different pressures for various trapping times were monitored. The major product ions were siliconate (SiX_5^-) and fluoronium ions like $(CH_3)_6FSi_2^+$. Siliconate ions were also generated by F^--transfer reactions with SF_6^- and SF_5^-. The results of the mass spectrometric investigations are supported by DFT-calculations.

1. Introduction

In the chemistry of silicon compounds, trivalent siliconium ions are often proposed as intermediates. While they have not been isolated in solution yet, with ICR mass spectrometry it is possible to monitor the reactions of these ions in the gas phase.

$Si(CH_3)_3^+$ is usually a major fragment ion of methylsilanes [1,2] and readily participates in association reactions with Lewis-bases [3]. Rearrangement reactions are often observed for the ions of alkylsilanes [4].

Electronegative substituents like fluorine enhance Lewis-acidity and lead to an increased formation of adducts with Lewis-bases [5]. In this study the influence of fluorinated alkyl-groups on the ion chemistry of silanes was examined.

Hypervalent species of silicon are interesting model compounds for studies of nucleophilic substitution reactions. Pentavalent siliconates are stable intermediates in substitution reactions at silicon e.g., perfluoroalkylations with Ruppert's reagent $(CH_3)_3SiCF_3$ [6]. These compounds are prepared by addition of fluoride to $R_fSi(CH_3)_3$. So far the intermediates of the $[R_fSi(CH_3)_3F]^-$ type have not been isolated in the condensed phase but have been detected with NMR experiments [7]. In solution any trace of protic solvent will usually hydrolyze the siliconate to yield $Si(CH_3)_3F$ and R_fH.

Pentavalent siliconates with two fluorinated alkyl groups however, $[(R_f)_2Si(CH_3)_3]^-$ have already been prepared [8].

As m/z values give only the elemental composition, geometry optimizations with quantum chemistry program packages like GAUSSIAN are a standard method to find possible structures of the ions involved in ion/molecule reactions. Schwarz and coworkers have applied the method for many ion/molecule reactions and structures [21,22]. In addition the calculations give at least a qualitative indication that a proposed structure is a minimum on the potential energy surface. DFT methods offer an acceptable performance at low computational cost and time, compared to high level ab initio methods [23].

2. Methods

2.1. Experimental

2.1.1. Instrumentation

The mass spectra were acquired with two instruments. The first instrument was the modified prototype Bruker CMS47X FT ICR spectrometer with a 7 T superconducting magnet with an 89 mm room temperature bore, described previously [9]. The standard vacuum system was evacuated with an oil diffusion pump (Varian VHS 600) with a liquid nitrogen cooled cryo-baffle and additional forepump (Edwards RV12). The pressure in the inlet system was 2×10^{-2} mbar. In the UHV system a base pressure of 1×10^{-8} mbar was reached. The pressure was measured with a Bayard-Alpert type hot-cathode gauge (Varian UHV-24p), in the inlet system with a Pirani gauge.

The Bruker ICR instrument was equipped with a standard closed cylindrical ICR-cell with segmented detection and excitation

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electrodes. It had a radius of 21 mm and an aspect ratio of 1. The electrodes were made of stainless steel, VESPEL was used as insulator material. An externally mounted rhenium filament served as cathode.

The second instrument was a modified mobile SIEMENS Quantra ICR spectrometer [10] that was used chiefly for the acquisition of spectra series. The spectrometer is constructed for gas analysis and is equipped with piezo inlet valves that admit only minute sample quantities into the vacuum system. Thus during measurements the pressure does not rise significantly above the base pressure of $\sim 10^{-10}$ mbar. For the study of ion-molecule reactions much higher pressures and a continous sample inlet are needed. As the getter pump would have been overloaded during the ion/molecule reactions, the spectrometer was fitted with an external turbopump (Pfeiffer TPU 270) and the getter pump was switched off during measurements. The pressure in the vacuum system was determined with an additional hot-cathode gauge and regulated using an all-metal UHV valve (Vacom, Germany). The reactions were carried out at sample pressures ranging from 5×10^{-8} mbar to 5×10^{-6} mbar. The inlet system was modified for continous gas inlet. One of the piezo valves was replaced with a leak valve (Varian, Variable Leak Valve 951-5106) to which a homebuilt inlet system was fitted. It was evacuated with a rotary vane pump (Edwards RV12) and was suitable for gaseous compounds with vapour pressures larger than 2×10^{-2} mbar. Reaction times for ion/molecule reactions lasted for up to 20 s.

In both instruments positive ions were generated by electron impact. Electron energy usually was 70 eV. Negative ions were generated by dissociative electron attachment at 20 eV from the parent compounds. Additional experiments to create siliconate ions following the method described by Beauchamp [5] were performed. For this purpose SF_6^- and SF_5^- anions were generated from sulfur hexafluoride at 1 eV electron energy. Then neutral compounds were introduced into the vacuum system and the formation of siliconates was monitored for up to 15 s. Addition reactions of ethanolate ions created from ethyl nitrite at 20 eV were examined as well.

Ion intensities were read out from the raw data with a VisualBasic Application written by Kühne.[1] Plots showing the evolution of intensities were generated with Diadem 10.2 (National Instruments).

2.1.2. Chemicals

The following chemicals were used in this study.

Sulfurhexafluoride, AirLiquide.
Ethylnitrite, Sigma Aldrich.

These chemicals were used without further purification. They were mass spectrometrically pure. Samples of $(CH_3)_3SiCF_3$, $(CH_3)_3SiC_2F_5$ and were prepared according to standard procedures.

2.1.3. Calculations

Geometry optimizations with DFT-methods were performed with the GAUSSIAN 03 W software package [11] at the B3LYP/6-31+G(d) level. Stationary points on the PES were identified through frequency analysis as minima (no imaginary frequency) or transition states (one imaginary frequency). Zero-point-energies were corrected with the scaling factor for the 6-31G(d) basis set. Single point energies were calculated for the optimized geometries with a larger basis set at the B3LYP/6-311++G(2df,2pd) level.

Table 1
Mass spectrum of $(CH_3)_3SiCF_3$ after a reaction time of 2 s at $p = 7 \times 10^{-7}$ mbar

	m/z_{measured}	$m/z_{\mathrm{calculated}}$	$\Delta m/z$
$(CH_3)_3Si^+$	73.057	73.047	0.01
$(CH_3)_2FSi^+$	77.026	77.022	0.04
$(CH_3)F_2Si^+$	81.006	80.997	0.009
$(CH_3)_3CF_2Si^+$	123.054	123.044	0.01
$(CH_3)_6FSi_2^+$	165.154	165.093	0.061

3. Results and discussion

3.1. Ion chemistry of $CF_3Si(CH_3)_3$

3.1.1. Positive ions

The mass spectrum of $(CH_3)_3SiCF_3$ (Table 1) shows four fragment ions and an additional signal at $m/z = 165$. The mass of this peak is higher than the molecular mass and is the product of an ion/molecule reaction. The molecular ion itself was not observed.

Observation of ion intensities over a time period of 20 s at $p = 1.2 \times 10^{-7}$ mbar shows that $(CH_3)_2FSi^+$ is formed as a primary ion. During the course of the reaction its signal intensitiy decreases whereas the intensities of $(CH_3)_3Si^+$ and less pronouncedly of $(CH_3)_3CF_2Si^+$ rise. This is a clear indication that these two ions are products of ion/molecule reactions of $(CH_3)_2FSi^+$ with neutral molecules. The reaction of $(CH_3)_2FSi^+$ ($m/z = 77$) at $p = 1.5 \times 10^{-7}$ mbar after ejection of all other ions gives the same result.

After about 11 s the intensity of $((CH_3)_3Si)_2F^+$ starts to rise as the product of an ion/molecule reaction of the product ion $(CH_3)_3Si^+$ with neutral $(CH_3)_3SiCF_3$. At higher pressures (7.3×10^{-7} and 1.2×10^{-6} mbar) the reaction is completed after about 2 s (Fig. 1). The reactions of the positive ions of $(CH_3)_3SiCF_3$ are summarized in Scheme 1.

DFT-calculations show that the primary ion $(CH_3)_2FSi^+$ is formed in a dissociative rearrangement reaction of the molecular ion. Obviously, $(CH_3)_3SiCF_3^+$ is not a stable ion but decomposes in a spontaneous reaction to yield $(CH_3)_2FSi^+$ and a CH_3CF_2 radical as stable products. A reaction barrier of 17 kcal/mol (0.74 eV) is predicted by the Gaussian results. This barrier can be passed due to the excess energy from electron ionization. The overall reaction is exothermic by 40 kcal/mol.

For the final product of the ion/molecule reactions a fluorine-bridged ion, $(CH_3)_6FSi_2^+$ is calculated as a stable structure. This type of ion has already been described by Beauchamp as being formed by clustering of $(CH_3)_3Si^+$ with $(CH_3)_3SiF$ in the gas phase [12].

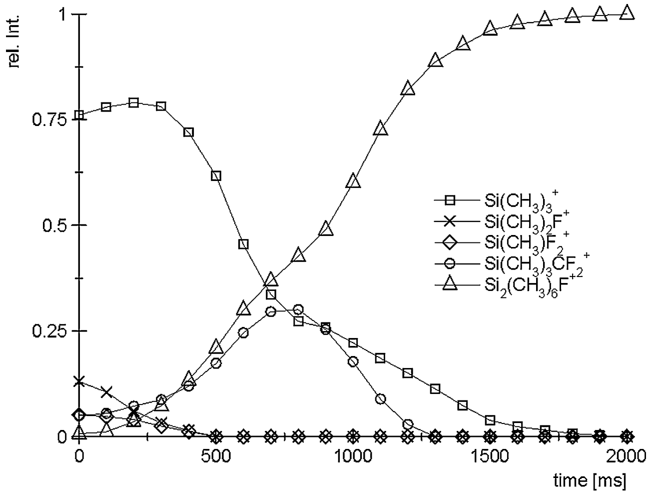

Fig. 1. Relative intensities of the ions of CF_3SiMe_3 at $p = 1.2 \times 10^{-6}$ mbar pressure.

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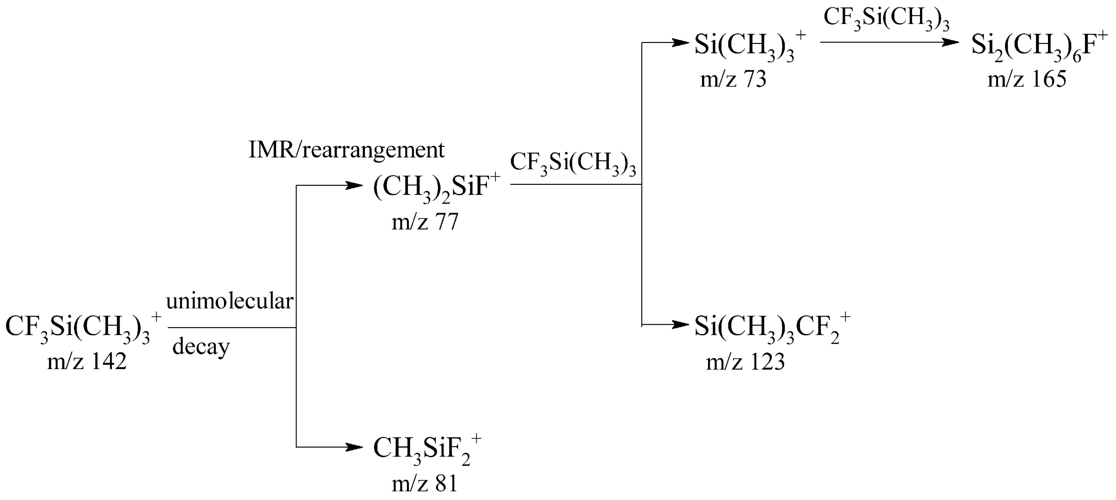
[1] D. Kühne, private communication (2005).



Scheme 1. Reactions of the positive ions of $(CH_3)_3SiCF_3$.

The formation of $Si(CH_3)_3{}^+$ from a reaction of $SiF(CH_3)_2{}^+$ is similar to a reaction path found by Beauchamp [12] for the ion chemistry of fluorosilanes:

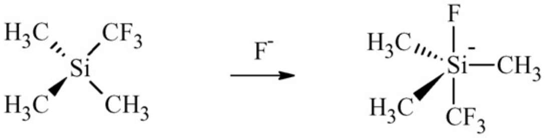
$$(CH_3)_mSiF_{4-m} + (CH_3)_nSiF^+_{3-n} \xrightarrow{m>n} (CH_3)_mSiF^+_{3-m} + (CH_3)_nSiF_{4-n} \quad (1)$$

Highly electronegative substituents bound to silicon enhance its Lewis acidity and its fluoride affinity. That is why higher methylated silicon-cations are formed in the above reaction of fluorinated silanes.

A reaction of $Si(CH_3)_2F^+$ with $CF_3Si(CH_3)_3$ in line with this scheme accompanied by a difluorocarbene-elimination would lead to the formation of $Si(CH_3)_3{}^+$. This kind of behaviour is well known from reactions of $CF_3Si(CH_3)_3$ and CF_3SiF_3 in organic synthesis [13,14]. However, a different and more probable pathway in the gas phase is a direct transfer of $CF_3{}^-$ to $Si(CH_3)_2F^+$. This path is energetically more favourable than the F^- transfer by 12.3 kcal/mol. The results of DFT-calculations rather favor an F^--elimination leading to the formation of $Si(CH_3)_3CF_2{}^+$. Experiments with ejection of $m/z = 123$, though, show that the formation of $Si(CH_3)_3CF_2{}^+$ is only a side reaction and not an intermediate step of the reaction sequence leading to $Si(CH_3)_3{}^+$ (Scheme 2).

3.1.2. *Negative ions*

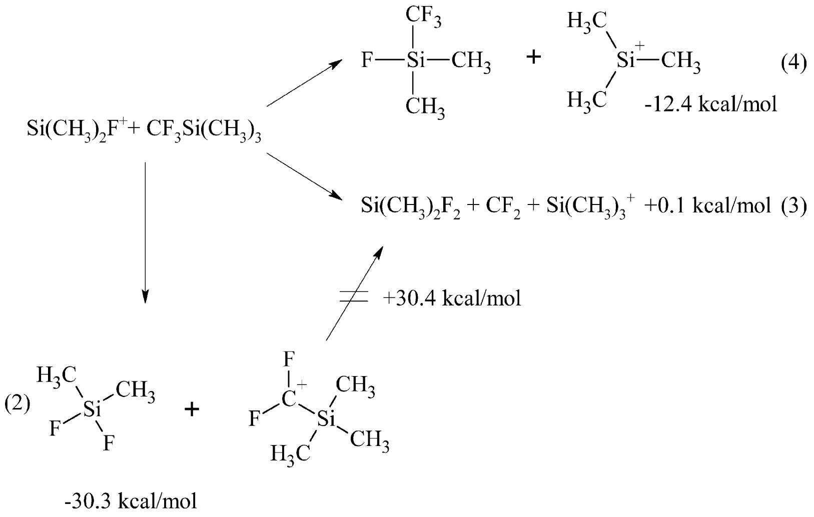
Anions containing silicon are usually more stable than carbanions. A silicon carrying the negative charge or a charge in α-position to the silicon results in a positive electron affinity [15]. Therefore a nucleophilic substitution reaction on silicon does not proceed via the double-well potential that is known from carbon chemistry. The "transition state" is a minimum on the potential surface instead [16]. Electronegative substituents on silicon further enhance the stability of these pentacoordinated species.



(5)

The same kind of reactivity is observed in the gas phase. Ion/molecule reactions of $(CH_3)_3SiCF_3$ lead to the formation of two pentavalent siliconates, $m/z = 161$ ($[(CH_3)_3SiFCF_3]^-$) and $m/z = 211$ ($[(CH_3)_3Si(CF_3)_2]^-$).

DFT-calculations predict a trigonal bipyramidal structure for the siliconates with the electronegative substituents in the axial position. There is also a minimum on the potential surface for a



Scheme 2. Reactions of $Si(CH_3)_2F^+$ ($m/z = 77$) with $(CH_3)_3SiCF_3$.

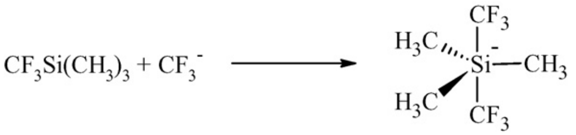
Table 2
Comparison of experimental [8] and our calculated values for $(CF_3)_2Si(CH_3)_3^-$

Bond length/angle	Exp. value [8]	Gaussian
$Si–C_{ax1}$	206.2 pm	213.5 pm
$Si–C_{ax2}$	205.6 pm	210.5 pm
$C_{ax1}–Si–C_{ax2}$	179.4°	179.9°

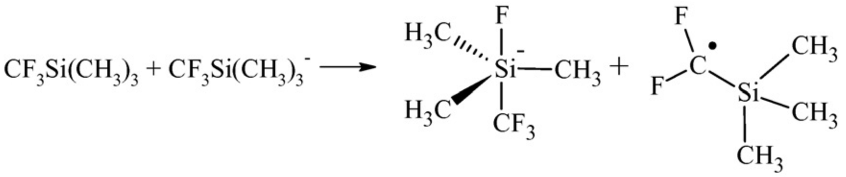
structure with a fluorine in equatorial position. However, the structure with F in axial position is predicted to be more stable by 7.6 kcal/mol. A structure with an equatorial CF_3-group is calculated to be 10 kcal/mol higher than the energetically lowest conformation.

The calculated bond lengths for the axial Si–C bonds are much longer than experimental values from X-Ray diffraction studies by Bissky [8] (Table 2). The same applies to comparisons of DFT-calculations of other siliconates with measured bond lengths [17] so this appears to be an effect of the DFT algorithms.

DFT-calculations also suggest that $(CF_3)_2Si(CH_3)_3^-$ (6) is formed through addition of a CF_3^--anion whereas $CF_3Si(CH_3)_3F^-$ (7) is produced by way of an F^--transfer from the anion of the starting compound $CF_3Si(CH_3)_3^-$.



(6)

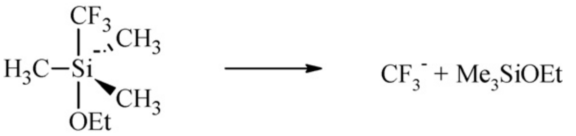


(7)

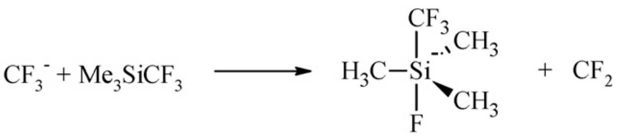
3.1.3. Reactions of $CF_3Si(CH_3)_3$ with EtO^- and SF_6

$[(CH_3)_3SiFCF_3]^-$ has also been prepared in an ion/molecule reaction with SF_6 as a fluoride-donor. For this purpose SF_6^- and SF_5^- were generated at high pressure (1×10^{-6} mbar) by dissociative electron capture.

Reaction with $C_2H_5O^-$ as a nucleophile leads to a substitution reaction instead of an addition. CF_3^- is released from the transient intermediate $[(CH_3)_3Si(OC_2H_5)CF_3]^-$. The mass spectra show peaks of CF_3^- and $[(CH_3)_3SiFCF_3]^-$. The formation of $[(CH_3)_3SiFCF_3]^-$ might be interpreted as a reaction of CF_3^- with neutral $(CH_3)_3SiCF_3$ accompanied by a difluorocarbene-elimination.

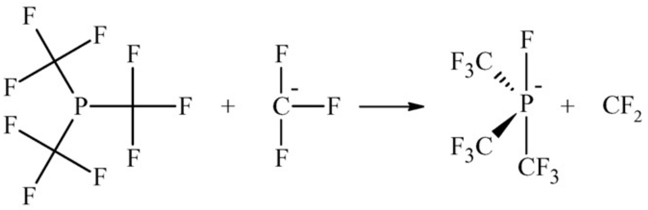


(8)



(9)

A corresponding reaction has already been found in the chemistry of phosphanes[2] [18], formally hypervalent phosphoranides are formed by reaction (10):



(10)

However, DFT-calculations do not support a reaction path of CF_3^- via a fluoride-attack at silicon for the reaction of the silanes with CF_3^-. No stable minimum could be found for an attack of the CF_3^--ion via one of the fluorines. In addition a reaction energy of +7 kcal/mol is predicted by DFT-methods for reaction (9). Therefore we propose a different mechanism instead with fluoride transfer from $[(CH_3)_3Si(OC_2H_5)CF_3]^-$ and formation of $[(CH_3)_3Si(F)CF_3]^-$ and $(CH_3)_3SiCF_2OC_2H_5$.

$$[CF_3Si(CH_3)_3OC_2H_5]^- + CF_3Si(CH_3)_3 \rightarrow [CF_3Si(CH_3)_3F]^- + C_2F_5OCF_2Si(CH_3)_3, \quad \Delta E = -12\,\text{kcal/mol} \tag{11}$$

To a small degree deprotonation is observed as well leading to the anion of $m/z = 141$ ($[(CH_3)_2CH_2SiCF_3]^-$).

Furthermore, the results of the reaction of $C_2H_5O^-$ with $(CH_3)_3SiCF_3$ indicate that Fluorine binds stronger to silicon than CF_3. A recent investigation by Krouse and Wenthold [19] in a flowing afterglow-triple quadrupole mass spectrometer has shown that F^- releases $C_2H_5O^-$ from $(CH_3)_3SiOC_2H_5$ while this study shows that $C_2H_5O^-$ binds stronger to silicon than CF_3^-. From these results one can derive the following order of nucleophilicities:

$$F^- > C_2H_5O^- > CF_3^-$$

In contrast to the aforementioned results from Krouse the intermediate siliconates could not be observed in our spectra. This may be attributed to the higher pressure in a flow tube that serves to dissipate the excess energy of the siliconate formation thus preventing fragmentation of the adduct ion.

A well-known reaction path for alkoxide anions with silanes is the formation of siloxide anions [20]. However no siloxide ions were observed in the spectra of the silanes examined in this study.

Reaction energies calculated with Gaussian support these results. The deprotonation of the silane is energetically unfavourable compared to the addition of CF_3^- or $C_2H_5O^-$:

$$CF_3Si(CH_3)_3 + C_2H_5O^- \rightarrow CF_3Si(CH_3)_2CH_2^- + C_2H_5OH, \quad \Delta E = -2.4\,\text{kcal/mol} \tag{12}$$

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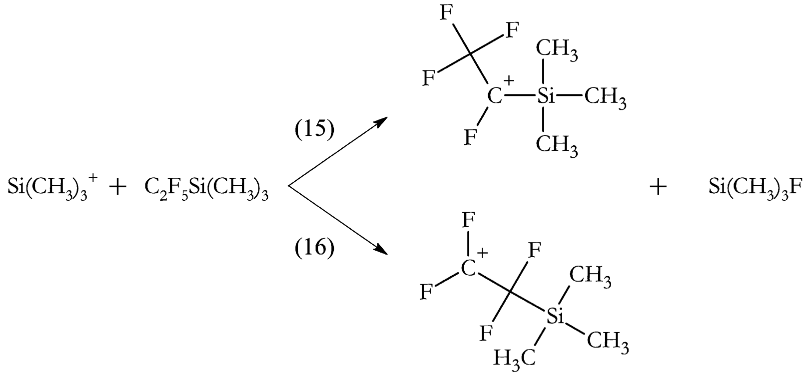
[2] Own results (unpublished) for $(CF_3)_2PCl$.



Scheme 3. Fluoride abstraction from $(CH_3)_3SiC_2F_5$ with $Si(CH_3)_3^+$.

$$CF_3Si(CH_3)_3 + C_2H_5O^- \rightarrow CF_3Si(CH_3)_3OC_2H_5^-,$$
$$\Delta E = -36.8\,\text{kcal/mol} \qquad (13)$$

$$CF_3Si(CH_3)_3 + F^- \rightarrow CF_3Si(CH_3)_3F^-, \quad \Delta E = -50\,\text{kcal/mol} \qquad (14)$$

3.2. Ion chemistry of $C_2F_5Si(CH_3)_3$

3.2.1. Positive ions

No molecular ion is observed in the spectra of $C_2F_5Si(CH_3)_3$. $Si(CH_3)_3^+$ reacts quickly to $Si(CH_3)_2F^+$. At $p = 5 \times 10^{-8}$ mbar immediately after the ionization period there is more $Si(CH_3)_3^+$ ($m/z = 73$) than $Si(CH_3)_2F^+$ ($m/z = 77$) in the cell. In the course of time the signal intensity of $m/z = 73$ decreases whereas the signal of $m/z = 77$ grows. This shows that in contrast to the ion chemistry of $CF_3Si(CH_3)_3$ in this case $Si(CH_3)_2F^+$ is formed as a secondary ion in a reaction of the primary ion $Si(CH_3)_3^+$.

Isolation of $m/z = 73$ yields the same result. Higher pressures between 10^{-7} and 10^{-6} mbar give the same changes in ion abundances over shorter time periods.

At all pressures $Si_2(CH_3)_6F^+$ ($m/z = 165$) is the final product of the ion/molecule reactions of $C_2F_5Si(CH_3)_3$.

In this reaction $Si(CH_3)_3^+$ is the primary ion. One reason may be the considerably elongated F_3CF_2C–Si-bond in the molecular ion compared with the F_3C–Si bond in $CF_3Si(CH_3)_3^+$ that is predicted by DFT calculations.

Gaussian simulations give further details of the mechanism of this reaction. $Si(CH_3)_3^+$ removes an F^- from neutral $C_2F_5Si(CH_3)_3$ either from the α-oder β-carbon (Scheme 3). This results in two possible isomeric structures for $C_2F_4Si(CH_3)_3^+$. Both isomers are not stable and the reaction continues to yield $Si(CH_3)_3^+$ and $Si(CH_3)_2F^+$ accompanied by elimination of C_2F_4 and $C_2F_3CH_3$ (Scheme 4).

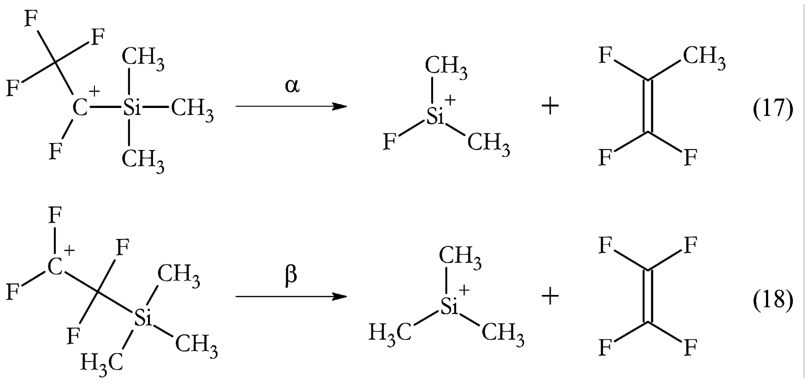
According to the calculations the fluoride abstraction proceeds via a fluorine-bridged intermediate.

3.2.2. Negative ions

Attempts to create the siliconate-anions of $C_2F_5Si(CH_3)_3$ through electron attachment were not successful. The spectra showed only the signal of $C_2F_5^-$.

3.2.3. Reactions of $C_2F_3Si(CH_3)_3$ with $C_2H_5O^-$ and SF_6

Siliconates however could be created by ion/molecule reactions. Analogously to the experiments with $CF_3Si(CH_3)_3$ ethylnitrite was used to generate ethanolate anions. Unlike $CF_3Si(CH_3)_3$, no fluoride addition could be observed but the spectra show only the signal of the $C_2F_5^-$-ion (20). Apparently in the pressure region up to $p = 1 \times 10^{-7}$ mbar the ethanolate ion reacts in a substitution reaction with $C_2F_5Si(CH_3)_3$. An addition of $C_2F_5^-$ is observed only at higher pressure yielding an ion at $m/z = 311$ ($[(C_2F_5)_2Si(CH_3)_3]^-$). At $m/z = 211$ a siliconate with fluoride bound to Si ($[(C_2F_5)FSi(CH_3)_3]^-$) is found in small amounts as well. Similar to the siliconates of $CF_3Si(CH_3)_3$ the conformer with both $C_2F_5^-$-groups in axial position is predicted to be more stable (9 kcal/mol) by the results of DFT-calculations. The substitution of $C_2F_5^-$ by $C_2H_5O^-$ is more exothermic than the corresponding reaction of $CF_3Si(CH_3)_3$ by 7 kcal/mol (19). Presumably the higher pressure leads to an enhanced collisional cooling of the siliconate



Scheme 4. Dissociative rearrangement reactions of the isomeric $(CH_3)_3SiC_2F_4^+$-ions.

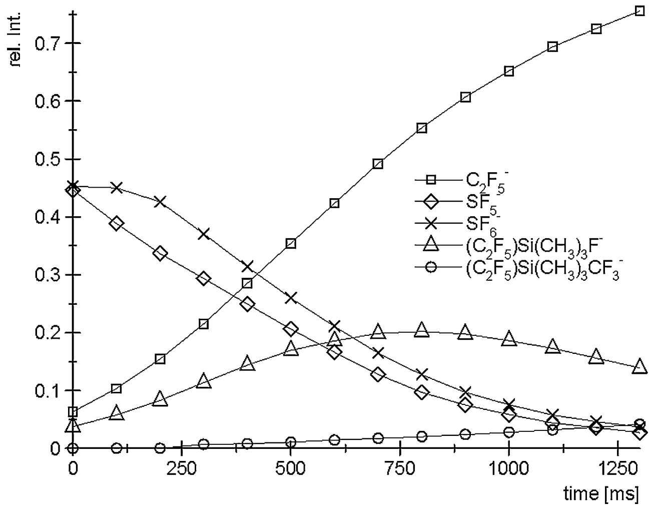


Fig. 2. Relative intensities of the reaction products of $(CH_3)_3SiC_2F_5$ with SF_5^- and SF_6^- at $p = 5.5 \times 10^{-7}$ mbar.

$[(C_2F_5)_2Si(CH_3)_3]^-$.

$$CF_3Si(CH_3)_3 + C_2H_5O^- \rightarrow \underset{-36.8\,\text{kcal/mol}}{[CF_3Si(CH_3)_3OC_2H_5]}$$

$$\rightarrow \underset{-24.3\,\text{kcal/mol}}{CF_3^- + C_2H_5OSi(CH_3)_3} \qquad (19)$$

$$C_2F_5Si(CH_3)_3 + C_2H_5O^- \rightarrow \underset{-38.6\,\text{kcal/mol}}{[C_2F_5Si(CH_3)_3OC_2H_5]^-}$$

$$\rightarrow \underset{-31.25\,\text{kcal/mol}}{C_2F_5^- + C_2H_5OSi(CH_3)_3} \qquad (20)$$

Reactions of $C_2F_5Si(CH_3)_3$ with SF_6^- and SF_5^- yield similar results. Mainly the $C_2F_5^-$ ion is released from the silane in a displacement reaction. $[(C_2F_5)FSi(CH_3)_3]^-$ is also formed (Fig. 2) $[(C_2F_5)_2Si(CH_3)_3]^-$ is observed only in trace amounts.

4. Conclusion

Siliconium ions R_3Si^+ ($R = CH_3$ or F) are the major fragments in the mass spectra of $(CH_3)_3SiCF_3$ and $(CH_3)_3SiC_2F_5$. An F/CH_3 exchange occurs via a displacement reaction of the molecular ion of $(CH_3)_3SiCF_3$. Clustering of fragment ions with neutral molecules leads to formation of fluoronium ions $[((CH_3)_3Si)_2F]^+$ but no fluoronium ions of the type $[((CH_3)_{3-n}F_nSi)_2F]^+$ are detected.

Pentavalent siliconates can be prepared through dissociative electron attachment from $CF_3Si(CH_3)_3$.

Ion/molecule reactions with ethanolate and fluoride anions produced from C_2H_5ONO and SF_6 leads to formation of siliconates. With SF_6^- and SF_5^- fluoride transfer reactions are detected. Displacement reactions are observed as well.

Acknowledgements

Samples of $CF_3Si(CH_3)_3$ and $C_2F_5Si(CH_3)_3$ were provided by PD. Dr. P. Kirsch. Merck, Japan. Special thanks to Siemens AG for providing the Quantra mobile ICR mass spectrometer.

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