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Silicon- versus carbon-containing ions: 1,3-CH_3^+ transfers

H. Nedev, J.P. Denhez, D. Leblanc, H.E. Audier*

Laboratoire des Mécanismes Réactionnels, Department de Chimie, CNRS, Ecole Polytechnique, 91128 Palaiseau, France

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Abstract

In the second field-free region of a double focusing mass spectrometer, the spontaneous fragmentation of the $(CH_3)_3C{-}O{-}^+C(CD_3)_2$ ion is not preceded by direct methyl cation migrations. In contrast, a complete exchange of the methyl groups occurs prior to dissociation of the $(CH_3)_3Si{-}O{-}^+Si(CD_3)_2$ ion. This is in agreement with the calculated energy diagram which shows that two factors explain this behavior.

(i) The simple cleavage of $(CH_3)_3C{-}O{-}^+C(CD_3)_2$ giving $(CH_3)_3C^+$ only requires 25.8 kcal mol^{-1} while the corresponding fragmentation in $(CH_3)_3Si{-}O{-}^+Si(CD_3)_2$ necessitates 74.2 kcal mol^{-1}.

(ii) The transition state for the 1,3-CH_3^+ transfer from carbon to carbon lies in energy 59.1 kcal mol^{-1} above the covalent structure $(CH_3)_3C{-}O{-}^+C(CD_3)_2$ and only 12.4 kcal mol^{-1} for the 1,3-CH_3^+ transfer from silicon to silicon.

Calculations and experiments show that the situation is intermediate for the 1,3-CH_3^+ from silicon to carbon. (Int J Mass Spectrom 217 (2002) 245–255) © 2002 Published by Elsevier Science B.V.

Keywords: Silicon; Carbon; CH_3^+ transfers

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1. Introduction

In solution [1] as well as in the gas phase [2–4], silicon chemistry differs strongly from carbon chemistry. In the gas phase, this difference can be exemplified by the protonation site of CO and of SiO. Whereas CO is preferentially protonated at carbon, SiO is protonated at oxygen [5] (Scheme 1). Furthermore, low coordinate silicon compounds such as silenes and silanones possess a proton affinity much higher than those of alkenes or ketones [5,6].

The great stability of the corresponding silicon containing cations, in which the charge is located on a silicon atom, has for consequence an easy cleavage of a Si–C bond in radical cations, as exemplified by the important loss of a methyl radical and by the abundance of the $(CH_3)_3Si^+$ fragment ion when trimethylsylil derivatives dissociate (Scheme 2).

$(CH_3)_3Si^+$ cation is also often involved in ion–neutral complexes [7,8]. The behavior of an ionized trimethylsylil derivative of a steroid is one example, among others, which has been used by Longevialle [7] to demonstrate the existence of ion–neutral complexes and their importance as intermediate species in the gas phase ion chemistry.

The cations in which the positive charge is borne by the silicon atom are strong electrophile reagents, leading to covalent bonds formation with a large variety of molecules including water, alcohols, amines or ketones [4,9–11].

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* Corresponding author. E-mail: hea@dcmr.polytechique.fr

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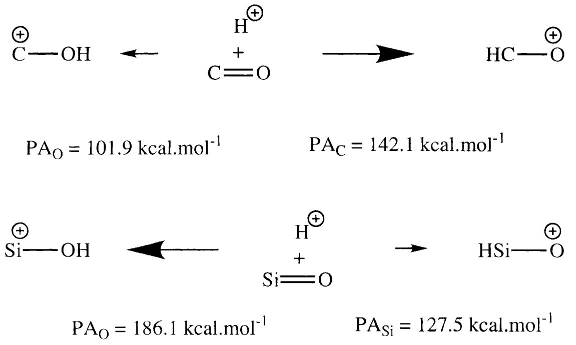
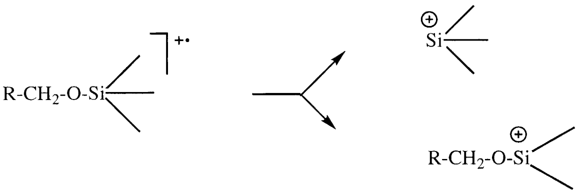


Scheme 1.

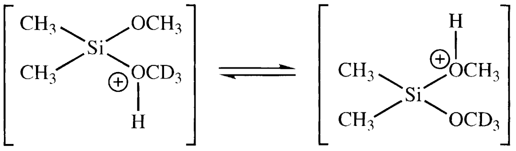


Scheme 2.

The study of the unimolecular fragmentation of the so formed cation products [9–11] suggests that a silicon atom, referred to a carbon atom, can have a great influence in the lowering of the energies of 3- and 4-membered transition states (TSs). This hypothesis could explain why silicon-containing ions undergo original rearrangements such as the isomerization of $CH_3CH_2SiH_2^+$ into $(CH_3)_2SiH^+$ (Scheme 3) [12].

In order to check this hypothesis, two models have been studied in our laboratory.

(i) In the following of a work of Grützmacher and Büchner [13], it has been shown that the 1,3-H^+ transfers from oxygen to oxygen are very difficult in carbon-containing ions but easy when a silicon atom is involved in the 4-membered transition state [6,14] (Scheme 4).



Scheme 4.

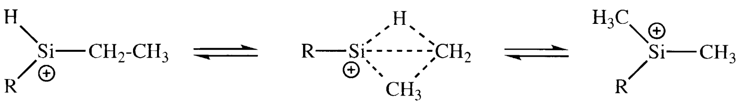
(ii) In this vein, the internal 1,3-methyl cation transfer reactions, from carbon to carbon, from silicon to silicon and from silicon to carbon, are compared and the reactions of the $R_1R_2R_3C–O–^+CR_4R_5$, $R_1R_2R_3Si–O–^+SiR_4R_5$, and $R_1R_2R_3Si–O–^+CR_4R_5$ ions (R=H or CH_3) are investigated in this study.

2. Experimental

2.1. Measurements

Measurements were mainly performed with a VG-ZAB-2F double focusing mass spectrometer. Ions were produced in a high pressure ion source as described further below. Their unimolecular dissociations were studied in the second field-free region (MIKE technique). Collision-induced dissociation were performed by using helium as collision gas.

In some cases, in order to performed high resolution measurements, the reactions were studied with a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source and an infinity cell [15,16]. The neutral reactants were introduced into the cell through a leak valve at a pressure of 1×10^{-8} to 4×10^{-8} mbar depending on the experiment, and then diluted with argon, to give a total pressure of 2×10^{-7} mbar.



Scheme 3.

2.2. Formation of the studied ions

The following ions were studied:

$\mathrm{(CH_3)_2CH{-}O{-}^{+}CHCH_3}$ **1**
$\mathrm{(CH_3)_2CH{-}O{-}^{+}C(CH_3)_2}$ **2**
$\mathrm{(CH_3)_3C{-}O{-}^{+}CHCH_3}$ **3**
$\mathrm{(CH_3)_3C{-}O{-}^{+}C(CH_3)_2}$ **4**
$\mathrm{(CH_3)_3Si{-}O{-}^{+}Si(CH_3)_2}$ **5**
$\mathrm{(CH_3)_2SiH{-}O{-}^{+}CHCH_3}$ **6**
$\mathrm{(CH_3)_2SiH{-}O{-}^{+}C(CH_3)_2}$ **7**
$\mathrm{(CH_3)_2Si^{+}{-}O{-}CH(CH_3)_2}$ **8**
$\mathrm{(CH_3)_2Si{-}O{-}^{+}CHCH_3}$ **9**
$\mathrm{(CH_3)_2Si{-}O{-}^{+}C(CH_3)_2}$ **10**

These ions were generated in the ion source, either

(i) by loss of a methyl radical from the corresponding radical cations when available (Eqs. (1) and (2)) or;
(ii) by reaction of the appropriate cation, formed by protonation–dissociation of the corresponding RX [R=$\mathrm{(CH_3)_3Si}$, $\mathrm{(CH_3)_3C}$, etc.; X=Cl or Br], with acetaldehyde or acetone (Eqs. (3) and (4)).

$$\mathrm{(CH_3)_3C{-}O{-}C(CH_3)_3}^{\bullet+} \rightarrow \mathrm{(CH_3)_3C{-}O{-}^{+}C(CH_3)_2 + CH_3}^{\bullet} \quad (1)$$

$$\mathrm{(CH_3)_3Si{-}O{-}Si(CH_3)_3}^{\bullet+} \rightarrow \mathrm{(CH_3)_3Si{-}O{-}^{+}Si(CH_3)_2 + CH_3}^{\bullet} \quad (2)$$

$$\mathrm{(CH_3)_3C^{+} + OC(CH_3)_2} \rightarrow \mathrm{(CH_3)_3C{-}O{-}^{+}C(CH_3)_2} \quad (3)$$

$$\mathrm{(CH_3)_2SiH^{+} + OC(CH_3)_2} \rightarrow \mathrm{(CH_3)_2SiH{-}O{-}^{+}C(CH_3)_2} \quad (4)$$

Ions formed by loss of a methyl radical from a radical cation and by ion–molecule reaction possess the same structure. For instance, the spontaneous fragmentations as well as the CID of the $\mathrm{(CH_3)_3C{-}O{-}^{+}C(CH_3)_2}$ cation are identical whatever its mode of formation may be (Eqs. (1) and (3)).

2.3. Labeling

Labeled ions where mainly formed by ion–molecule reactions and by using labeled reagents such as $\mathrm{(CD_3)_3CBr}$, $\mathrm{(CD_3)_3SiCl}$, $\mathrm{(CD_3)_2CO}$, $\mathrm{CD_3CDO}$, etc.

The $\mathrm{(CD_3)_3Si{-}O{-}^{+}Si(CH_3)_2}$ and $\mathrm{(CH_3)_3Si{-}O{-}^{+}Si(CD_3)_2}$ labeled ions **5** were generated from ionized $\mathrm{(CH_3)_3Si{-}O{-}Si(CD_3)_3}$, prepared as previously described [9,17].

The $\mathrm{(CH_3)_2Si^{+}{-}O{-}CH(CD_3)_2}$ and $\mathrm{(CH_3)_3Si{-}O{-}^{+}CHCD_3}$ labeled ions **8** and **9** (Eq. (5)) were formed by cleavage of ionized $\mathrm{(CH_3)_3Si{-}O{-}CH(CD_3)_2}$ which was prepared by reaction of $\mathrm{(CH_3)_3SiCl}$ with $\mathrm{(CD_3)_2CHOH}$ [18].

$$\underset{\mathbf{8}}{\mathrm{(CH_3)_2Si^{+}{-}O{-}CH(CD_3)_2}} + \mathrm{CH_3}^{\bullet} \leftarrow \mathrm{(CH_3)_3Si{-}O{-}CH(CD_3)_2}^{\bullet+} \rightarrow \underset{\mathbf{9}}{\mathrm{(CH_3)_3Si{-}O{-}^{+}CHCD_3}} + \mathrm{CD_3}^{\bullet} \quad (5)$$

2.4. Calculations

The Gaussian-98 [19] was used for calculations to determine the different key structures on the potential energy profile. The geometries were optimized at the B3LYP/6-31G(d) level of theory [20]. Diagonalization of the computed Hessian was performed in order to confirm that the structures were energy minima or transition states on the potential energy surface and zero point energies and thermal enthalpies at 298.15 K were computed at this level of theory.

3. Results

Except when indicated, the results reported concern the fragmentation of metastable ions generated in the ion source by ion–molecule reactions.

3.1. Ions without silicon atoms

Spontaneous fragmentation ion **1**, $(CH_3)_2CH–O–^+CHCH_3$, only yields loss of water.

Ion **2**, $(CH_3)_2CH–O–^+C(CH_3)_2$, only leads to protonated acetone (*m*/*z* 59). This fragment is shifted to *m*/*z* 60 in $(CD_3)_2CH–O–^+C(CH_3)_2$ and to *m*/*z* 65 in $(CH_3)_2CH–O–^+C(CD_3)_2$.

The unimolecular reaction ion of **3**, $(CH_3)_3C–O–^+CHCH_3$, mainly gives the *m*/*z* 57 ion (83%), *tert*-$C_4H_9^+$, but also *m*/*z* 83 (17%) corresponding to water loss. Upon collisions, *m*/*z* 57 is strongly dominant. The *tert*-butyl fragment remains at *m*/*z* 57 when the $(CH_3)_3C–O^+–CDCD_3$ ion fragments but is shifted to *m*/*z* 66 in $(CH_3)_3C–O–^+CHCH_3$.

The spontaneous fragmentation of metastable ion **4**, $(CH_3)_3C–O–^+C(CH_3)_2$, only gives protonated acetone (*m*/*z* 59). In the $(CH_3)_3C–O–^+C(CD_3)_2$ labeled ion, the three fragments observed, *m*/*z* 59 (7%), *m*/*z* 60 (14%), and *m*/*z* 65 (79%) correspond to protonated acetone containing, respectively, zero, one and six deuterium atoms. Upon collision, **4** leads to *m*/*z* 59 (65%) but also to the *tert*-butyl cation, *m*/*z* 57 (35%). In the collision-induced dissociations spectrum of $(CH_3)_3C–O–^+C(CD_3)_2$, labeled protonated acetone *m*/*z* 65 remains the base peak (64%) and the *tert*-butyl cation, *m*/*z* 57, is also abundant (28%). However, three fragments *m*/*z* 59 (2% of the base peak), *m*/*z* 60 (3.5%) and *m*/*z* 63, $C_4H_3D_6^+$ (2.5%), are also observed.

3.2. Silicon-containing ions

Ion **5**, $(CH_3)_3Si–O–^+Si(CH_3)_2$, that has been previously studied both with a double focusing mass spectrometer [17] and by FT-ICR [9], leads to methane loss. From the fragmentation of the labeled ions $(CD_3)_3Si–O^+–Si(CH_3)_2$ and $(CH_3)_3Si–O–^+Si(CD_3)_2$, formed by fragmentation of ionized $(CH_3)_3Si–O–Si(CD_3)_3$ in the ion source, it has been shown that a complete exchange of the methyl groups takes place prior to fragmentation [9,17].

The spontaneous fragmentation of metastable ion **6**, $(CH_3)_2SiH–O–^+CHCH_3$, leads to protonated silanone, *m*/*z* 75 (30%), and to $(CH_3)_3Si^+$, *m*/*z* 73 (70%). These fragments are both completely shifted to *m*/*z* 76 when the $(CH_3)_2SiH–O–^+CDCD_3$ ion reacts. High resolution measurements performed with a FT-ICR spectrometer show that *m*/*z* 76 ions correspond to both structures $(CH_3)_2SiOD^+$ and $(CH_3)_2CD_3Si^+$, formation of the latter being favored for the most energetic ions.

The behavior of ion $(CH_3)_2SiH–O–^+C(CH_3)_2$ **7** is similar and gives a *m*/*z* 73 fragment (70%) as well as protonated acetone *m*/*z* 75 (30%). Both are shifted to *m*/*z* 76 in $(CH_3)_2SiH–O–^+C(CD_3)_2$.

The $(CH_3)_2Si^+–O–CH(CH_3)_2$ ion **8** cannot be generated by ion–molecule reaction since $(CH_3)_2Si{=}O$ is not commercially available and is difficult to prepare. Moreover, methyl loss from ionized $(CH_3)_3Si–O–CH(CH_3)_2$ presumably leads to a mixture of *m*/*z* 117 ions, $(CH_3)_2Si^+–O–CH(CH_3)_2$ and $(CH_3)_3Si–O–^+CHCH_3$. Yet, by loss of a methyl radical from ionized $(CH_3)_3Si–O–CH(CD_3)_2$, the labeled ion **8** $(CH_3)_2Si^+–O–CH(CD_3)_2$ can be generated (Eq. (5)). In the second FFR, this ion only yield the *m*/*z* 76 fragment, either $(CH_3)_2CD_3Si^+$ or $(CH_3)_2SiOD^+$. In order to determine its structure, this fragment was allowed to react with pyridine within the ion-source. The fragmentation corresponding adduct–ion ($m/z = 76 + 79 = 155$) was then studied in the second FFR. The abundance of protonated pyridine compared to those observed for the $[(CH_3)_3Si^+$, pyridine] and $[(CH_3)_2SiOH^+$, pyridine] adducts, allows to conclude that for more than 95%, the studied fragment possesses the $(CH_3)_2SiOH^+$ structure.

Unimolecular reactions of ions **9** and **10**, $(CH_3)_3Si–O–^+C(CH_3)_2$ and $(CH_3)_3Si–O–^+CHCH_3$, yield, for more than 97% the *m*/*z* 73 fragment and for less than 3%, *m*/*z* 75. The *m*/*z* 75 fragment is shifted to *m*/*z* 76 in ions $(CH_3)_3Si–O–^+CDCD_3$ and $(CH_3)_3Si–O–^+C(CD_3)_2$. High resolution measurements, performed with FT-ICR, show that *m*/*z* 76 corresponds to $(CH_3)_3Si–OD^+$.

3.3. Energy profiles

The structures of stable species and of transition states are reported in Fig. 1 and the corresponding

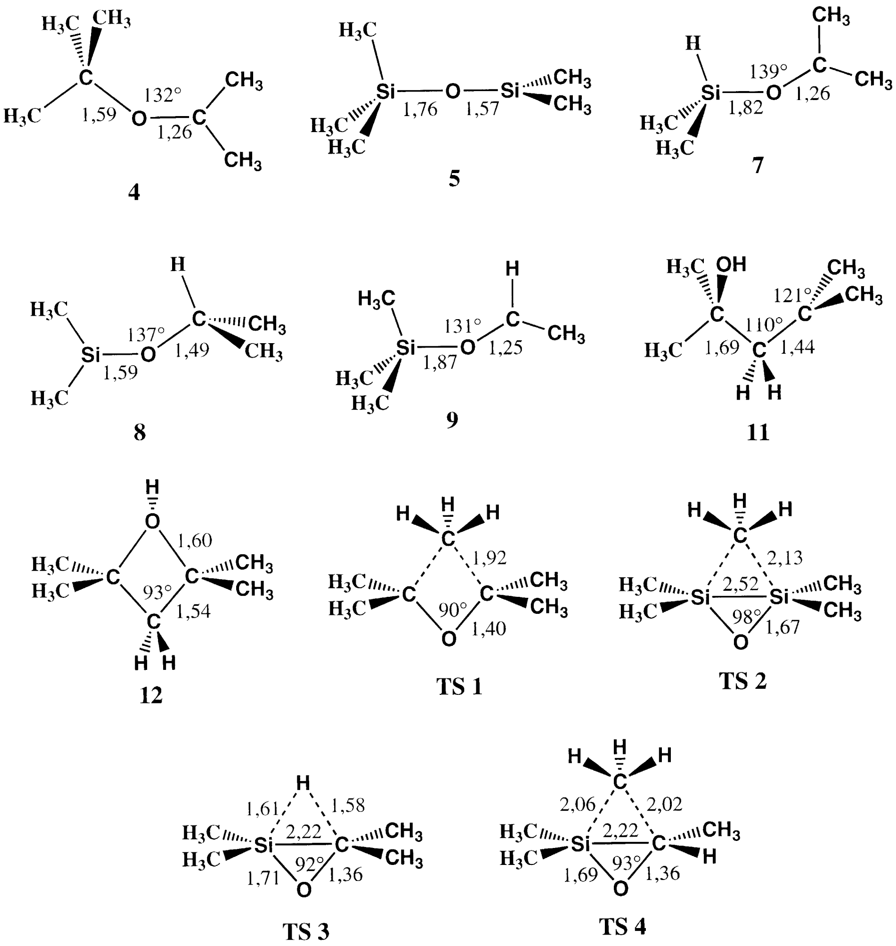


Fig. 1. Stable structures and transition states.

energy profiles are, respectively, shown in Figs. 2–4.

4. Discussion

4.1. Carbon to carbon 1,3-CH_3^+ transfers

Bowen and co-workers [21,22] and Bouchoux et al. [23] have shown that two stable or transient complexes [carbocation, $O{=}CR_1R_2$] and [alkene, $HO^+CR_1R_2$] are intermediate in the fragmentation of ions **1**–**4** (Scheme 5).

The first of these complexes is formed by the initial cleavage of a C–O bond. Conversely, by C–C bond formation within the second complex, this one can isomerize into a protonated ketone leading to its own fragmentations, loss of water more particularly, as studied elsewhere [21–23].

This loss of water is the only spontaneous fragmentation of ion **1**, making this ion unusefull to evidence methyl cation transfers. In contrast, the main products formed by reaction of ions **2** and **3**, spontaneously or upon collision, come from the simple cleavage of both intermediate complexes. For instance, the shift of the protonated acetone fragment in labeled ions **2** as well

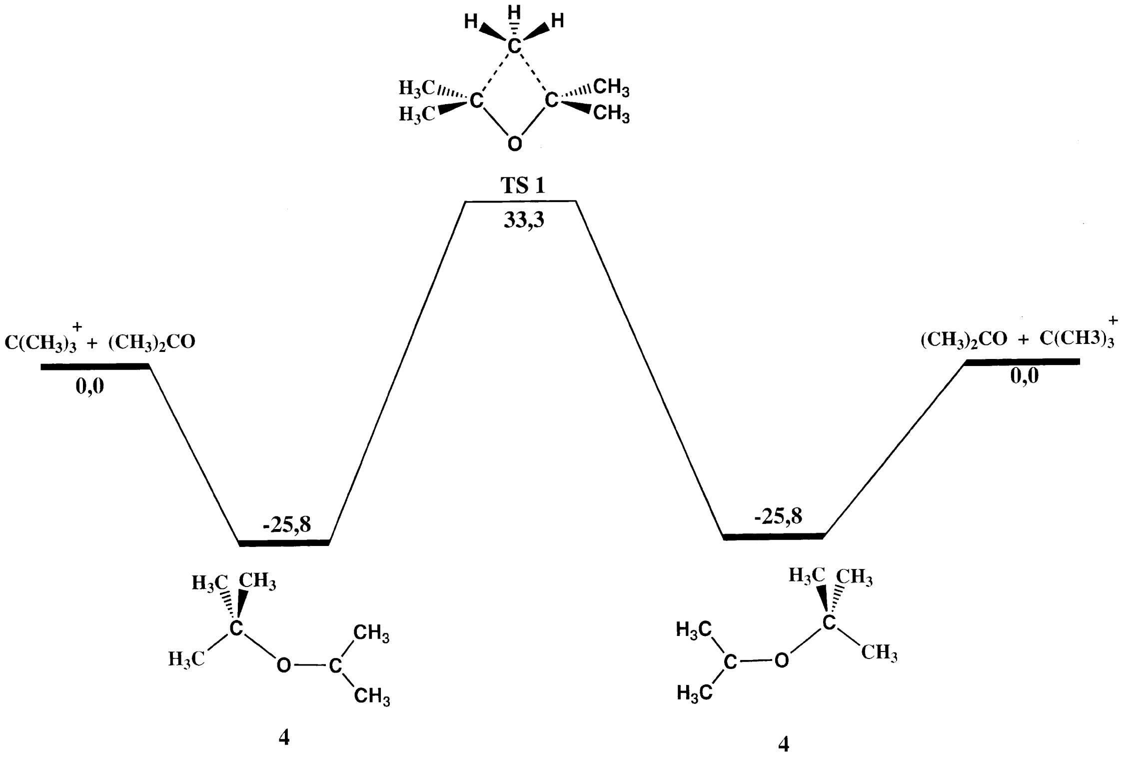


Fig. 2. Energy profile of ion **4**.

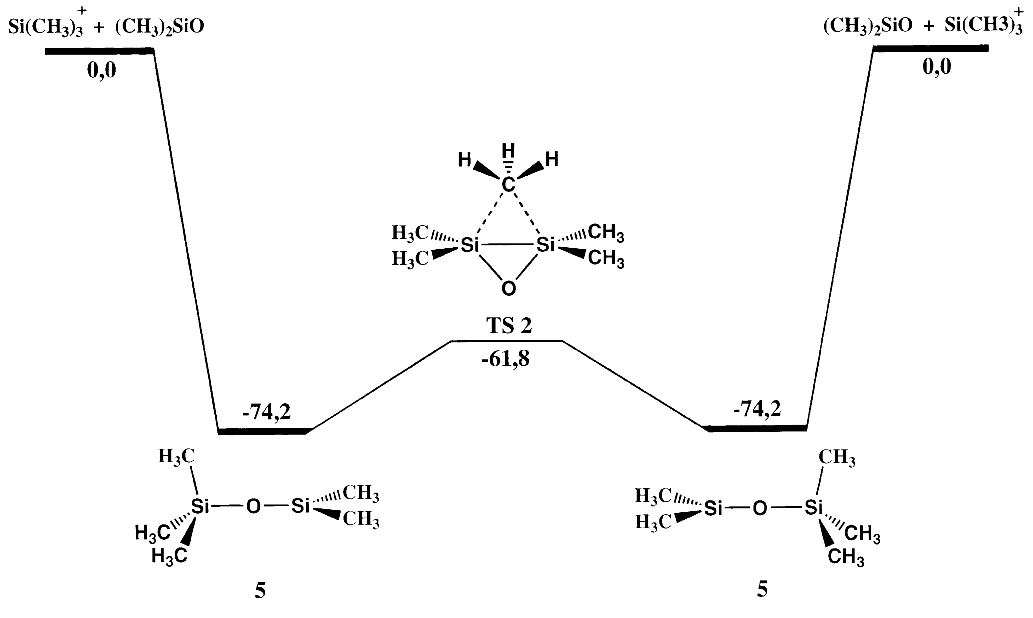


Fig. 3. Energy profile of ion **5**.

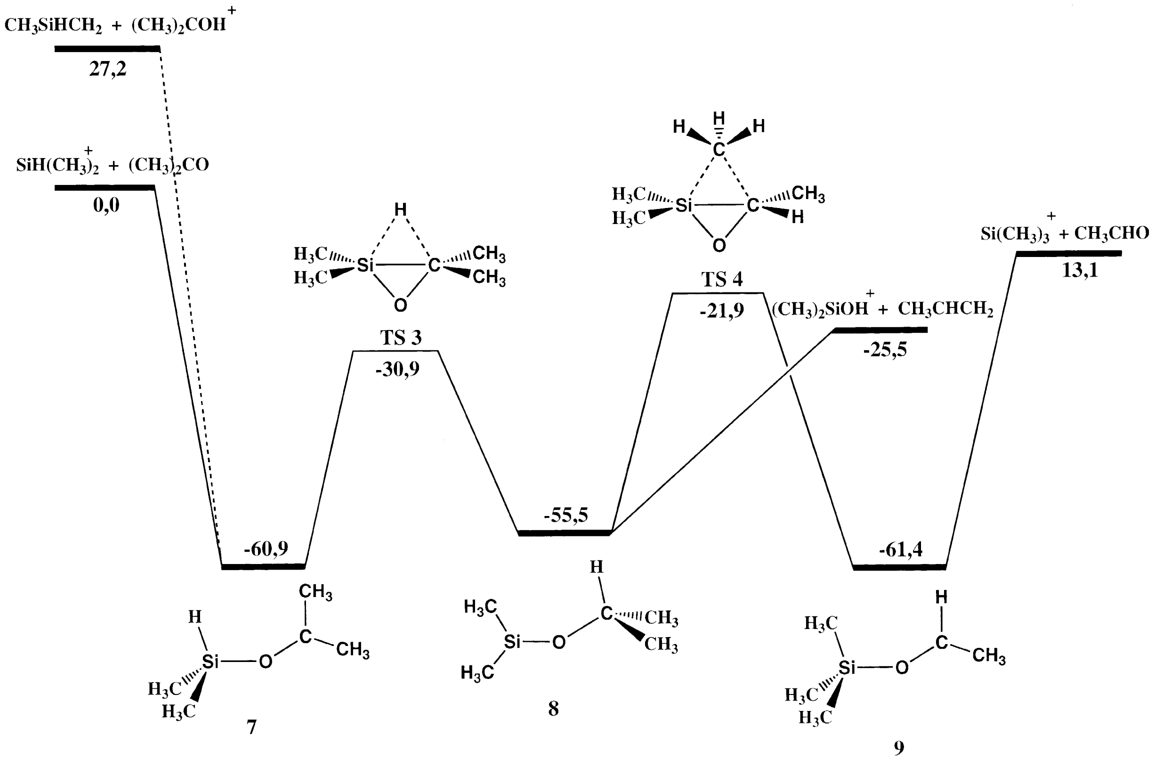
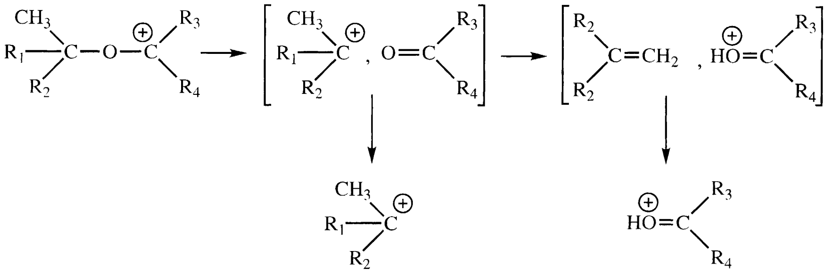


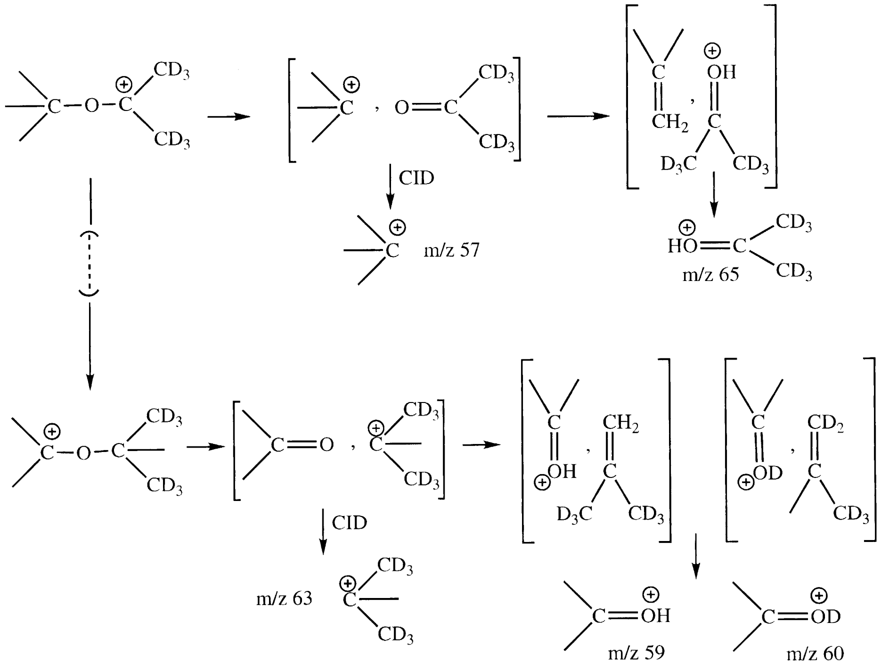
Fig. 4. Energy profile of ions **7**–**9**.

as the shift of the *tert*-$C_4H_9^+$ fragment in labeled **3** show that no CH_3^+ transfer or exchange precedes the dissociation.

In the labeled ion $(CH_3)_3C–O–^+C(CD_3)_2$ **4**, the fragments formed spontaneously (*m*/*z* 65) and upon collisions (*m*/*z* 57 and *m*/*z* 65) come from the cleavage of intermediate complexes (Scheme 6). The minor fragments observed in the MIKE spectrum, *m*/*z* 59 and *m*/*z* 60, which are almost in a 1/2 ratio, can be easily explained if it is assumed that $(CH_3)_3C–O–^+C(CD_3)_2$ slowly converts into $(CH_3)_3C^+–O–C(CD_3)_2CH_3$ (Scheme 6). The abundance ratio [*m*/*z* 59] + [*m*/*z* 60]/[*m*/*z* 65] = 0.26 indicates the proportion of ions **4** which undergo an isomerization process for the decomposing ions. This is in coherence with the CID spectrum in which a small ions 63 peak, $(CD_3)_2CH_3C^+$, is also observed (Scheme 6). It may be noted that CID spectra also indicates that the



Scheme 5.



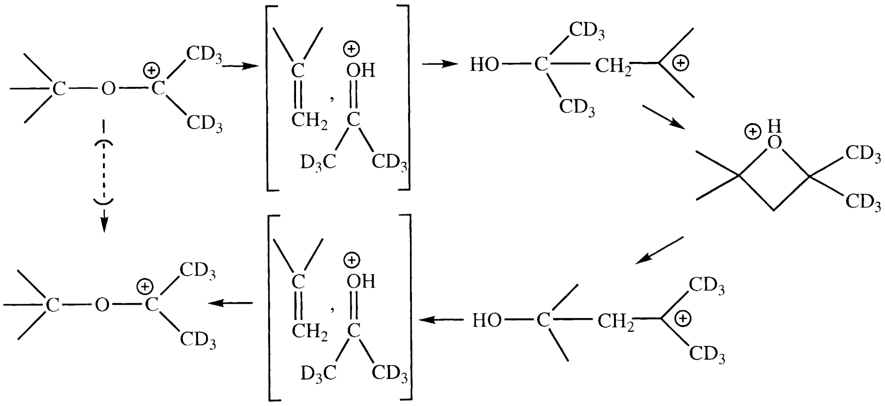
Scheme 6.

ratio of undecomposing $(CH_3)_3C–O–^+C(CD_3)_2$ ions isomerizing into $(CH_3)_3C^+–O–C(CD_3)_2CH_3$ is only about 8% since these ions possess, before they collide, less internal energy than the decomposing ions.

The observed isomerization of $(CH_3)_3C–O–^+C(CD_3)_2$ into $(CH_3)_3C^+–O–C(CD_3)_2CH_3$ can be explained by two mechanisms yielding the same products:

(i) a direct 1,3-CH_3^+ transfer via TS_1 (Fig. 2) or;

(ii) a Bowen–Williams rearrangement [21–23] followed by a symmetrization of the system via the carbocation **11** and the 4-membered intermediate **12**, as it has soon proposed to explain the permutation of the methyl groups in the $CD_3{}^+C(OH)CH_2CH_3$ carbocation (Scheme 7) [24].



Scheme 7.

The energy profile shown in Fig. 2 indicates that the transition state for a direct 1,3-CH_3^+ transfer of the mechanism (i) lies in energy 33.3 kcal mol^{-1} above the reactant energies. Therefore, starting from the covalent structure **4**, both enthalpic and entropic factors are strongly unfavorable to the 1,3-CH_3^+ compared to the simple cleavage.

Contrastingly, the carbocation **11** (Fig. 1, Scheme 7), whose formation is rate determining in the mechanism (ii), and *a fortiori* the symmetric cyclic structure **12** (Fig. 1, Scheme 7), possess calculated energy (−5.6 and −11.6 kcal mol^{-1}, respectively) which are slightly under that of the reactants. This makes the reaction difficult but possible.

In conclusion of this part:

- the excess of internal energy of the covalent ion formed by reaction of $(CH_3)_3C^+$ with acetone is 25.8 kcal mol^{-1};
- the energy required for a 1,3-CH_3^+ transfer within this covalent structure is 59.1 kcal mol^{-1};
- therefore, the direct 1,3-CH_3^+ transfer is impossible.

4.2. Silicon to silicon 1,3-CH_3^+ transfers

A statistical exchange of the methyl groups takes place prior to dissociation of ion **5** (Fig. 3) which means that the 1,3-CH_3^+ transfers may be very easy. This is in perfect agreement with the energy profile (Fig. 3) which shows that the TS_2 for the direct 1,3-CH_3^+ transfer lies only a few kcal mol^{-1} above the energy of the covalent structure **5**.

This low barrier for the 1,3-CH_3^+ transfers could be explained by two factors. First, the 3p orbital of the silicon atom are bigger than the 2p orbital of the carbon atom. Second, the 3d and 3p orbitals of silicon are closer in energy than the 3d and 2p orbitals of carbon. Since TS_2 corresponds to a 4-membered ring, which is a very constrained structure, the size of the 3p-lobes and the polarization d-functions of the silicon atom make this transition state more “flexible” and more stable than the relevant structure of with carbon atoms.

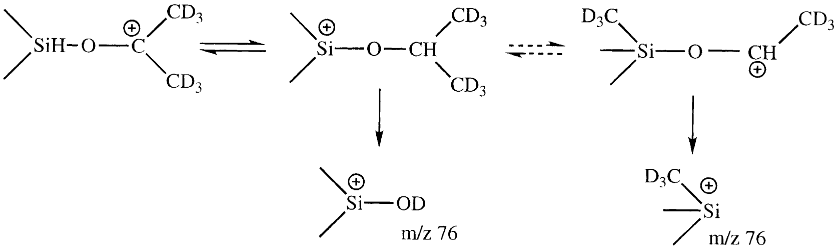
In conclusion of this part:

- the excess of internal energy of the covalent ion formed by reaction of $(CH_3)_3Si^+$ with silanone is 74.2 kcal mol^{-1};
- the energy required for a 1,3-CH_3^+ transfer within this covalent structure is only 12.4 kcal mol^{-1};
- the direct 1,3-CH_3^+ transfer is very easy.

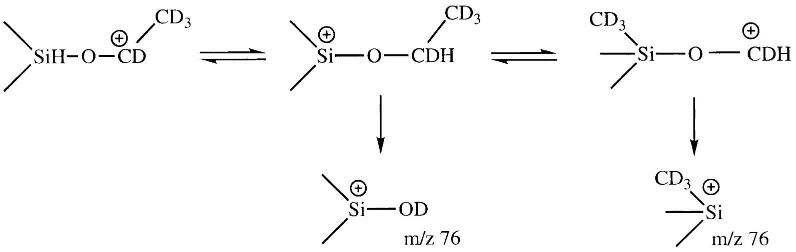
4.3. Silicon to carbon 1,3-CH_3^+ transfers

Formation of protonated acetone and of *tert*-butylsilyl cation when ion **6** reacts and the shifts of these products when labeled ions are used as reactant, suggest that ion **6** isomerizes by 1,3-H^+ transfer and by 1,3-CH_3^+ transfer as shown in Scheme 8.

Comparison of the behavior of isomeric ions **7**–**9** as well as the corresponding calculated energy profile (Scheme 9, Fig. 4) allow to discuss whether these transfers are important or not. Among the studied ions, **8** has a special behavior. Its fragmentation leads mainly to the very stable final state [protonated silanone + propene] (Fig. 4) while only the most



Scheme 8.



Scheme 9.

energetic ions can give $(CH_3)_3Si^+$, after isomerization into **9**. The formation of protonated silanone could be a concerted process, involving therefore, an energy barrier, since the high ΔH_f of silanone [6,25] makes unfavorable the intermediacy of the $[(CH_3)_2Si{=}O, {}^+CH(CH_3)_2]$ complex.

Starting of ion **7**, the lack of $(CH_3)_2SiH^+$ or of protonated acetone is in good agreement with the energy profile since these products correspond to final states which lie too high in energy. Via TS_3 and by a 1,3-H^+ transfer, **7** leads to **8**. The so formed ions **8** possess, in average, an important excess of internal energy since their internal energy is at least that of TS_3. For this reason, they yield of course protonated silanone but they also lead to $(CH_3)_3Si^+$ in a greater abundance than that observed by reaction of ions **8** directly generated in the ion-source; to form $(CH_3)_3Si^+$, ions **7** and **8** must convert into **9** by a 1,3-CH_3^+ transfer via TS_4.

Starting from ion **9**, two ways are open. The first one is the simple cleavage giving $(CH_3)_3Si^+$ which is not the most stable final state but which is strongly entropically favored. The second is the isomerization into **8** giving then protonated silanone as product. This way is the best in energy because TS_4 lies some kcal mol^{-1} under the final state $[(CH_3)_3Si^+ + CH_3CHO]$ but is entropically difficult since it involves two rearrangements. Ion **9** being a "hot ion", it is not surprising to observe that the simple cleavage is significantly dominant. The lack of $(CD_3)_3Si^+$ product when $(CH_3)_3Si–O–{}^+CHCD_3$ dissociates, indicates that the slow isomerization **9** → **8** is irreversible.

The $(CH_3)_3Si–O–{}^+CD_3$ labeled ion **10** has a behavior identical to that of **9**.

5. Conclusion

The spontaneous fragmentation of the $(CH_3)_3C–O–{}^+C(CD_3)_2$ ion is not preceded by direct methyl cation migrations. Two factors explain this result:

- the activation energy to yield $(CH_3)_3C^+$ by simple cleavage is only 25.8 kcal mol^{-1};
- the energy barrier for 1,3-CH_3^+ transfer from carbon to carbon is 59.1 kcal mol^{-1}.

In contrast, a complete exchange of the methyl groups occurs prior to dissociation of the $(CH_3)_3Si–O–{}^+Si(CD_3)_2$ ion. In this case:

- the activation energy to yield $(CH_3)_3C^+$ by simple cleavage is 74.2 kcal mol^{-1} which confirms [6,14] that ions in which the charge is borne by a silicone atom are strong electrophiles;
- the energy barrier for 1,3-CH_3^+ transfer from silicon to silicon is only 12.4 kcal mol^{-1}.

Calculation and experiment show that the situation is intermediate for the 1,3-CH_3^+ from silicon to carbon, which makes these transfers possible but difficult, the energy barrier being about 40 kcal mol^{-1}.

The differences, in the behavior of C- and Si-containing ions, can be explained by the fact that, in the 4-membered transition state for 1,3-CH_3^+ transfer from silicon to silicon, a strong interaction between both silicon atoms, which makes very low the transition state energy. Comparatively, this interaction is not important in the transfer from carbon to carbon since the carbon atom is significantly smaller that the silicon atom.

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