International Journal of Mass Spectrometry 219 (2002) 537–547
www.elsevier.com/locate/ijms

Silicon vs. carbon containing ions: 1,3-proton transfers within the $(CH_3)(X)Si(OR)(^+OHR')$ units

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Received 1 February 2002; accepted 28 March 2002

Abstract

In the cell of an FT-ICR spectrometer, $(CH_3)(X)C(OCR)(^+OHR')$ and $(CH_3)(X)Si(OCR)^+OHR'$ (R and R′ = H, CH_3 or C_2H_5; X = H or CH_3) covalent ions were generated by reaction of the $(CH_3)(X)^+Si–OCR'$ cations with water or alcohols. In the so-formed covalent ions, experiment shows that 1,3-H^+ transfers from oxygen to oxygen are often easy in silicon containing ions while they are not observed in the corresponding ions containing only carbon. Calculations indicate that the energy required for a 1,3-H^+ transfer from oxygen to oxygen is almost identical whether the transition state contains a silicon atom or not. The greater strength of the Si–O bond in cations, compared to that of the C–O bond or, in other words, the great electrophilic character of cations possessing a Si^+, is the main factor explaining the difference in the behavior of the studied silicon containing ions and ions containing exclusively carbon. (Int J Mass Spectrom 219 (2002) 537–547)

Keywords: Silicon contain ions; 1,3-Proton transfer; Ion–molecule reactions; FT-ICR; Calculations

1. Introduction

It is well known that in solution, silicon chemistry differs from carbon chemistry [1]. Several reviews have shown that, in the gas phase, the properties of silicon containing ions and of their carbon containing homologues are also strongly different [2,3].

An example is the thermochemical data of these ions. For instance, while CO is preferentially protonated at oxygen. SiO protonated at silicon [4]. Furthermore, low coordinate silicon compounds such as silenes [5] and silanones [6] possess a proton affinity much higher than those of alkenes or ketones.

An other example is their reactivity. For instance, the cations in which the positive charge is located at a silicon atom are strong electrophile reagents, leading to covalent bond formation with a large variety of molecules including water, alcohols, amines, or ketones [2,3,7–9].

In a recent work, it has been shown that the 1,3-methyl cation transfer reactions from silicon to silicon are very easy while they are very difficult from carbon to carbon (Scheme 1). This has been explained by a strong interaction between the two silicon atoms in the transition state [10].

In carbon chemistry, the unimolecular 1,3-H^+ transfers usually involve a high-energy barrier. It is the case for the transfers from carbon to oxygen corresponding to keto–enol tautomerization [11] as well as for unimolecular 1,3-H^+ transfers from oxygen to oxygen which do not occur [12] (Scheme 2). However, the exothermic transfers from oxygen to

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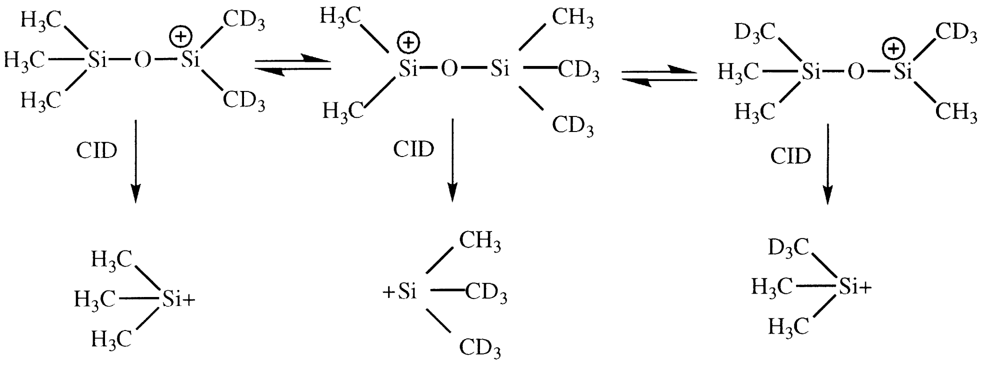
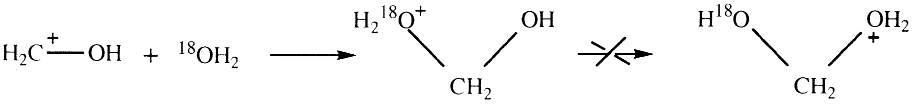
PII S1387-3806(02)00707-8



Scheme 1.



Scheme 2.

nitrogen have been described but have been shown to be energy demanding [13].

In this work, 1,3-H^+ transfers from oxygen to oxygen are studied in systems containing a silicon atom in the ion, involved in the transition state.

2. Experimental

2.1. Measurements

The reactions were studied by use of a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source and an infinity cell [14,15]. 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.

2.2. Calculations

The Gaussian 98 software package [16] 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 [17]. 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 an zero point energies and thermal enthalpies at 298.15 K were computed at this level of theory.

2.3. Reactant ions

The reactant ions were produced by fragmentation of commercially available compounds in the external ion source of a Bruker CMS-47X FT-ICR mass spectrometer. For instance:

$$(CH_3)_3C(CH_3)_2Si\text{–}OH^{\bullet+} \rightarrow (CH_3)_2{}^+Si\text{–}OH + (CH_3)_3C^{\bullet}$$

$$(CH_3)_2Si(OCH_3)_2{}^{\bullet+} \rightarrow (CH_3)_2{}^+Si\text{–}OCH_3 + CH_3O^{\bullet}$$

$$(CH_3)_2Si(OCH_2CH_3)_2{}^{\bullet+} \rightarrow (CH_3)_2{}^+Si\text{–}OCH_2CH_3 + CH_3CH_2O^{\bullet}$$

2.4. Intermediate adducts

The so-formed ions were then allowed to react in the cell with neutral molecules giving covalent adducts, via nucleophilic additions [3,7–9]. In general, they are long-lived enough to be stabilized by radiative and/or collisional processes and, therefore, observed in the FT-ICR time-frame. Their fragmentation, followed by a new addition of neutral molecule yields a second generation of covalent intermediates which can be observed or only transient. In this latter case, their intermediacy can be proved by the effect caused by their continuous fast ejection on the abundances of the products which are formed.

$$(CH_3)_2{}^+C\text{–}OCH_3 + CD_3OH \rightarrow (CH_3)_2C(OCH_3)({}^+OHCD_3)$$

$$(CH_3)_2{}^+Si\text{–}OCH_3 + CD_3OH \rightarrow (CH_3)_2Si(OCH_3)({}^+OHCD_3)$$

3. Results and discussion

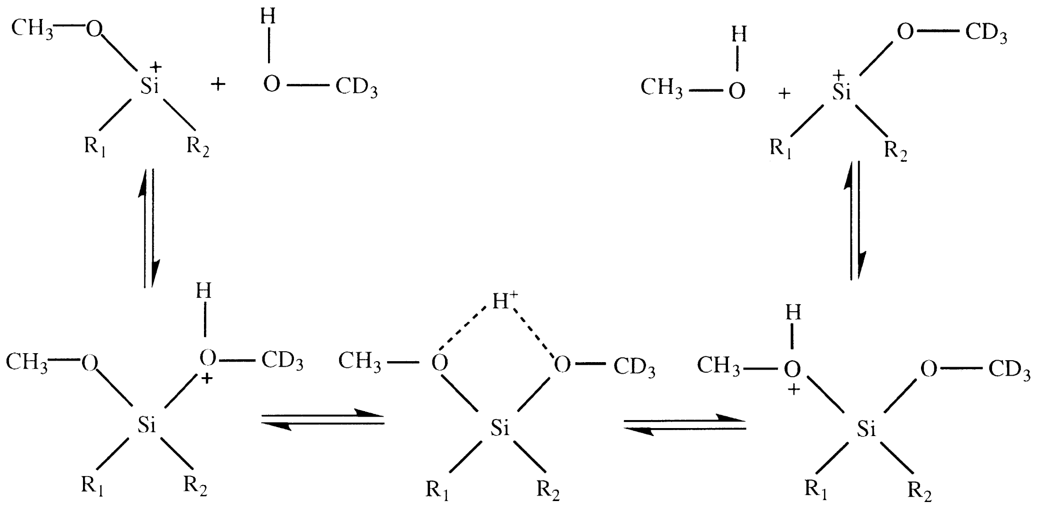
The covalent adducts can isomerize by 1,3-H^+ transfer giving a second adduct. Simple cleavage of this latter adduct leads to the elimination of a neutral molecule which may be considered as a sufficient condition to affirm that the 1,3-H^+ transfer occurs (Scheme 3). However, this condition is not necessary since the intermediate adducts can yield other product ions corresponding to more favorable pathways. Considering the outcome of the reaction shown in Scheme 3, it may he noted that, finally, the overall press can he considered as a substitution reaction.

In a first approach, the reaction of $(CH_3)_2{}^+Si\text{–}OR$ and $CH_3{}^+SiH\text{–}OR$ ions (R = H, CH_3, CH_2CH_3) with water, methanol, and ethanol, will he successively discussed in order (i) to check whether the substitution reaction takes place or not and (ii) to study the specific reactions of each intermediate complex.

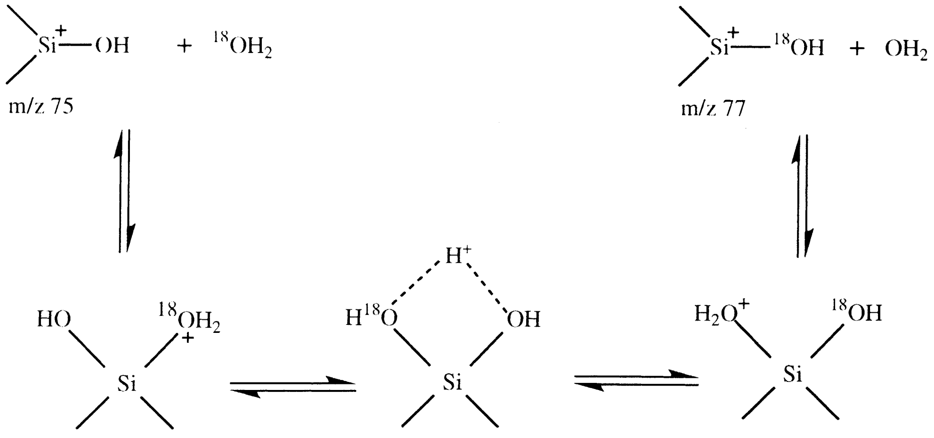
3.1. Reactions of the $(CH_3)_2{}^+Si\text{–}OR$ ions ($R = H, CH_3, CH_2CH_3$)

The reaction of the $(CH_3)_2{}^+Si\text{–}OH$ ($m/z = 75$) cation with $H_2{}^{18}O$ is rapid and yields a $m/z = 77$ product (Scheme 4, Fig. 1). Exact mass determination and reactivity of this product indicates that it corresponds to the $(CH_3)_2{}^+Si\text{–}{}^{18}OH$ structure. The substitution reaction and, therefore, the 1,3-H^+ transfer within the intermediate covalent structure are rapid ($k = 3 \times 10^{-9}\ cm^3\ mol^{-1}\ s^{-1}$).

The $(CH_3)_2{}^+Si\text{–}OH$ ($m/z = 75$) cation rapidly disappears in the presence of methanol to give the $(CH_3)_2{}^+Si\text{–}OCH_3$ ($m/z = 89$) product. The 1,3-H^+ transfer is rapid ($k = 1.1 \times 10^{-9}\ cm^3\ mol^{-1}\ s^{-1}$).



Scheme 3.



Scheme 4.

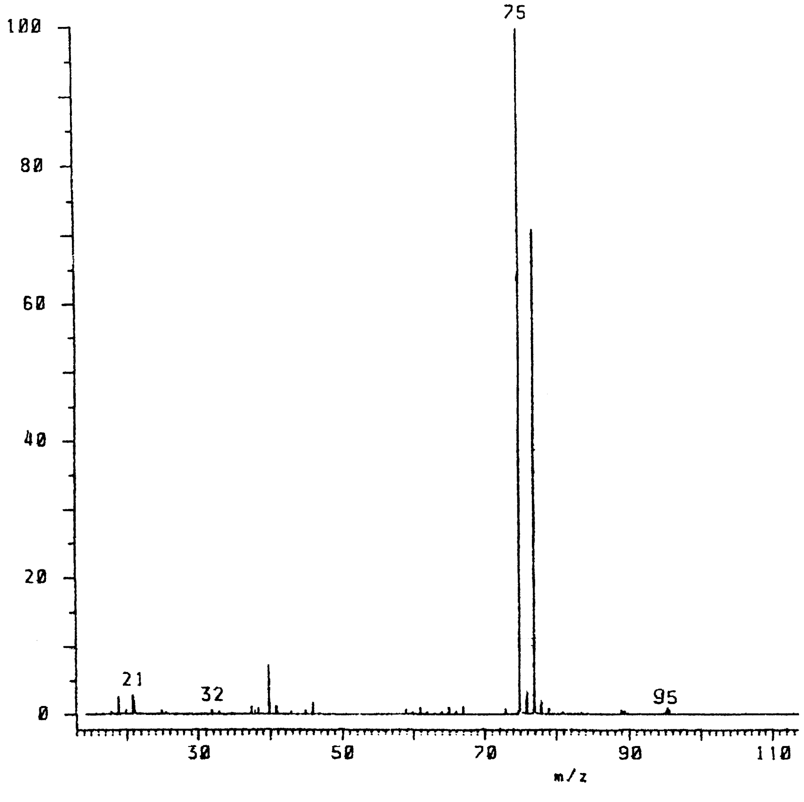
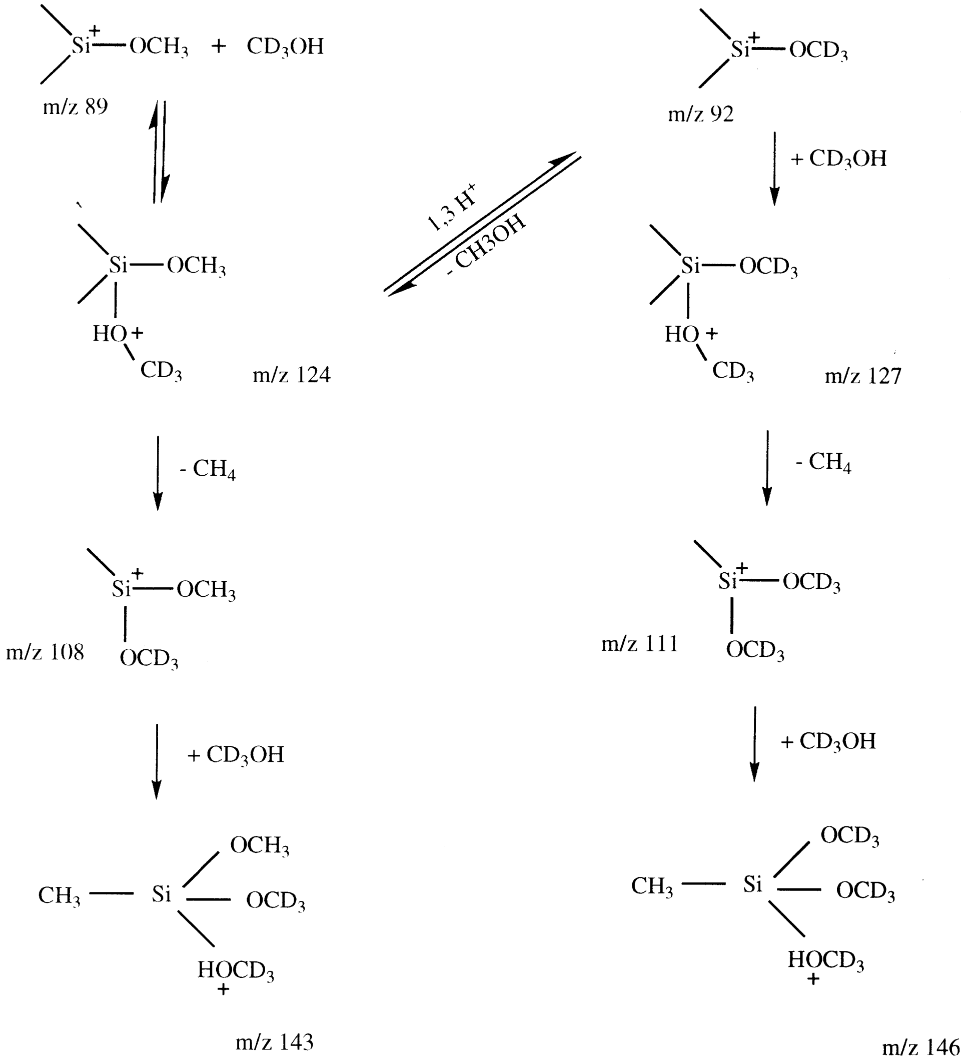


Fig. 1. FT-ICR spectrum observed after the reaction of $m/z = 75$ ion with $H_2{}^{18}O$ (2×10^{-8} mbar) at 3 s reaction time.

Addition of a molecule of water to the $(CH_3)_2{}^+$Si–OCH_3 (m/z = 89) cation yields the $(CH_3)_2$Si($^+OH_2$)OCH_3 adduct, m/z = 107, whose lifetime is long enough to be observed. A similar phenomenon has been described for the reaction of the $(CH_3)_3Si^+$ cation with water and may be the consequence of the strong exothermicity of the reaction [3]. The $(CH_3)_2{}^+$Si–OH (m/z = 75) product is not formed. Nothing, in this case, can confirm or discard the occurrence of the 1,3-H^+ transfer within the complex.

The reaction of $(CH_3)_2{}^+$Si–OCH_3 (m/z = 89) with CD_3OH leads first to an observed $(CH_3)_2$Si($CD_3{}^+$OH)OCH_3 (m/z = 124) adduct which yields m/z = 92 as dominant product after 1,3-H^+ transfer (Scheme 5, Fig. 2). High resolution and reactivity of this product is in agreement with the $(CH_3)_2{}^+$Si–OCD_3 structure. The reaction is rapid ($k = 6 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}, Fig. 3).

The successive reaction of the so-formed products are also interesting (Scheme 5). The $(CH_3)_2$Si$^+$($OHCD_3$)OCH_3 (m/z = 124) adduct eliminates a



Scheme 5.

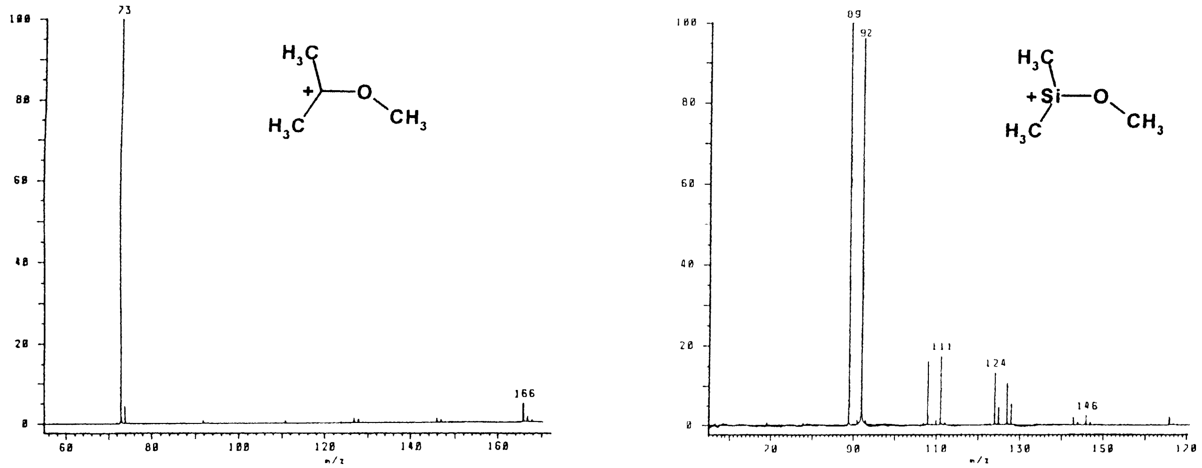


Fig. 2. Comparison of the FT-ICR spectra observed after the reaction a 10 s (pression 2×10^{-8} mbar) of $m/z = 73$ and 89 with CD_3OH.

methane molecule, as observed in similar cases [7–9], to form the $CH_3{}^+Si(OCD_3)(OCH_3)$ ($m/z = 108$) product. Similarly, $(CH_3)_2{}^+Si–OCD_3$ ($m/z = 92$) undergoes addition of new molecule of CD_3OH to give the $m/z = 127$ adduct and then the product ion ($m/z = 111$).

The labeled product ions $m/z = 108$ and 111 display the same behavior than the $CH_3{}^+Si(OCH_3)_2$ cation ($m/z = 105$) generated by simple cleavage of ionized $(CH_3)_2Si(OCH_3)_2$. They add a molecule of methanol (Scheme 5) and undergo a rapid 1,3-H^+ transfer.

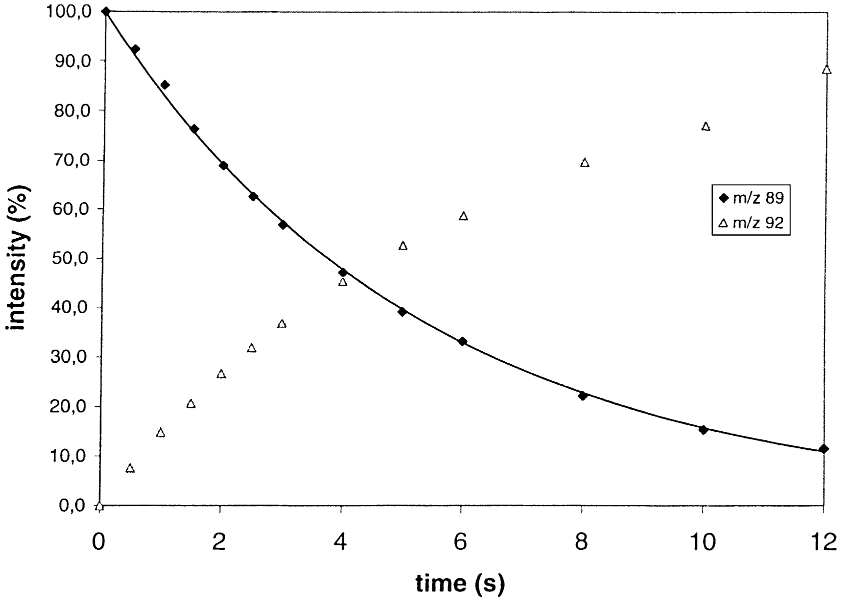


Fig. 3. Kinetics of the reaction of $m/z = 89$ with CD_3OH 2×10^{-8} mbar.

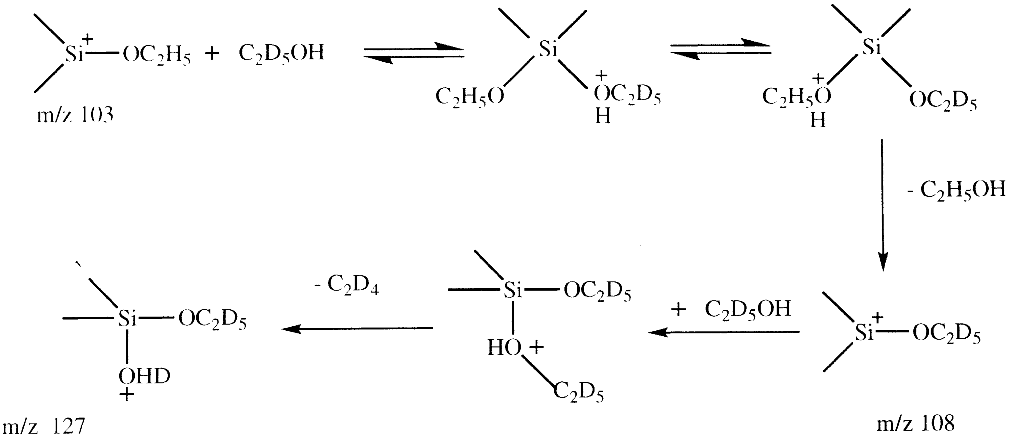
Reaction of the $(CH_3)_2{}^+Si–OC_2H_5$ cation (m/z = 103) with water only yields the transient adduct $(CH_3)_2Si(^+OH_2)OCH_2CH_3$. Most probably, the observed elimination of an ethylene molecule involves its conversion into the $(CH_3)_2Si(OH)^+OHCH_2CH_3$ to form the final product $(CH_3)Si(^+OH_2)OH$ (m/z = 93), since ions of the type $R^+O(H)CH_2CH_3$ easily eliminate ethylene. The substitution is not observed; the 1,3-H^+ transfer is uncertain but probable.

In the presence of ethanol, $(CH_3)_2{}^+Si–OH$ (m/z = 75) gives the $(CH_3)_2Si(OH)(^+OHCH_2CH_3)$ adduct (m/z = 121) which undergoes two competing reactions occurring almost at the same rate. On the one hand, it eliminates an ethylene molecule giving the $(CH_3)_2Si(^+OH_2)(OH)$ (m/z = 93) product ion as just mentioned. On the other hand, it isomerizes into $(CH_3)_2Si(^+OH_2)(OCH_2CH_3)$ via a rapid 1,3-H^+ transfer leading then to $(CH_3)_2{}^+Si–OC_2H_5$ cation (m/z = 103) by loss of water.

The $(CH_3)_2Si(^+OHCH_2CH_3)OCH_3$ transient adduct formed by reaction of the $(CH_3)_2{}^+Si–OCH_3$ cation (m/z = 89) with ethanol is only transient, since it reacts via two rapid and competing reactions. First, for about two-thirds, it eliminates ethylene to yield $(CH_3)_2Si(^+OH_2)(OCH_3)$ (m/z = 107). Second, for about one-third, 1,3-H^+ transfer gives $(CH_3)_2Si(^+OHCH_3)(OCH_2CH_3)$ and then $(CH_3)_2{}^+Si–OC_2H_5$ (m/z = 103). Substitution and transfer reactions occur easily.

Reaction of $(CH_3)_2{}^+Si–OC_2H_5$ with methanol yields two primary products m/z = 89 (loss of ethanol, 5%) and m/z = 107 (loss of ethylene, 95%). Therefore, formation of the substituted product $(CH_3)_2{}^+Si–OCH_3$ (m/z = 89) is slow due to its slight endothermicity. However, the high abundance of m/z = 107 suggests that the first adduct formed, $(CH_3)_2Si(^+OHCH_3)(OCH_2CH_3)$ converts rapidly by 1,3-H^+ transfer, into $(CH_3)_2Si(^+OHCH_2CH_3)(OCH_3)$ prior to loss of ethylene.

The $(CH_3)_2{}^+Si–OC_2H_5$ ion reacts with C_2D_5OH to give a very complicated sequence of reactions, since the $(CH_3)_2Si(^+OHCH_2CH_3)(OC_2CD_3)$ adduct and its isomer $(CH_3)_2Si(^+OHCD_2CD_3)(OCH_2CH_3)$, formed after 1,3-$H^+$ transfer, gives a succession C_2H_4 and C_2D_4 eliminations and of C_2D_5OH additions on the intermediate cations. Furthermore, the abundance of the $(CH_3)_2{}^+Si–OC_2H_5$ substitution product (m/z = 108) is only 5%. However, its fast continuous ejection demonstrate that the $(CH_3)_2Si(^+OHD)(OC_2D_5)$ (m/z = 127, 30%) is only formed by the further reactions of $(CH_3)_2{}^+Si–OC_2H_5$ shown in Scheme 6. Therefore, at least of one third of the products are formed after the 1,3-H^+ transfer. Since $(CH_3)_2{}^+Si–OC_2H_5$ disappears at collision rate, this transfer is rapid.



Scheme 6.

3.2. Reaction of the $CH_3{}^+SiH–OR$ ion ($R = H$, CH_3, CH_2CH_3)

The $CH_3{}^+SiH–OCH_3$ ($m/z = 75$) cation reacts with water to give the transient adduct $CH_3SiH({}^+OH_2)(OCH_3)$ ($m/z = 93$). This adduct possesses one hydrogen atom and one methyl group bonded to the silicon atom. As soon as ions possessing a $CH_3SiH({}^+OHR)$ structure is observed [7–9], it eliminates hydrogen to give $m/z = 91$ and methane to yield $m/z = 77$, which are the only products. Substitution giving $CH_3{}^+SiH–OH$ ($m/z = 61$) is not observed.

The $CH_3SiH({}^+OHCH_3)(OH)$ transient adduct ($m/z = 93$), formed by reaction of $CH_3{}^+SiH–OH$ with methanol, slowly eliminates H_2. The rapid reaction is the 1,3-H^+ transfer leading to the $CH_3{}^+SiH–OCH_3$ ($m/z = 75$) substituted product, which undergoes sequential reactions (addition of methanol, eliminations of hydrogen or methane molecules).

Reaction of the $CH_3{}^+SiH–OCH_3$ (m/z=75) cation with CD_3OH yields rapidly to the substitution product $CH_3{}^+SiH–OCD_3$ ($m/z = 78$). At the same rate, the intermediate adducts, $CH_3{}^+SiH({}^+OHCD_3)(OCH_3)$ and $CH_3{}^+SiH({}^+OHCH_3)(OCD_3)$ eliminate H_2 and CH_4 in agreement with the mechanism shown in Scheme 7, to give $CH_3{}^+Si(OCH_3)(OCD_3)$ and $H^+Si(OCH_3)(OCD_3)$. After addition of a new molecule of CD_3OH, the reaction ends up, for long reaction times with the formation of the $H^+Si(OCD_3)_2$, $CH_3{}^+Si(OCD_3)_2$, and ${}^+Si(OCD_3)_3$ products.

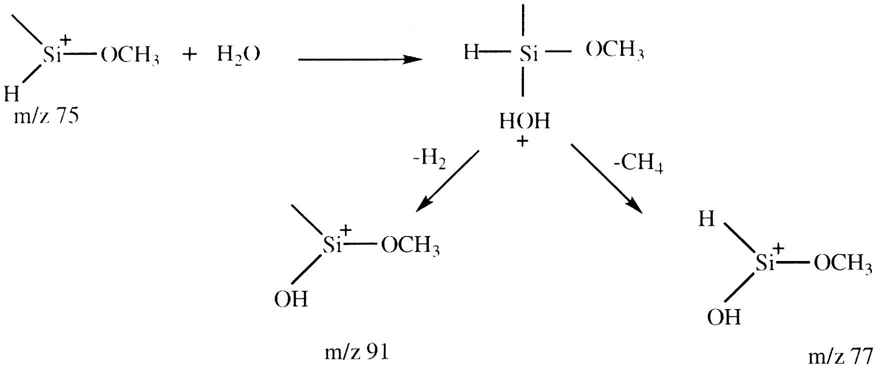
At the beginning of the reaction between the $CH_3{}^+SiH–OCH_3$ ($m/z = 75$) cation and ethanol, two pathways are open. First, the $CH_3{}^+SiH({}^+OHCH_2CH_3)(OCH_3)$ intermediate loses ethylene. Second, after a rapid 1,3-H^+ transfer, the substitution product $CH_3{}^+SiH–OCH_2CH_3$ ($m/z = 89$) is observed. For longer reaction times this latter ion undergoes the expected further reactions: addition of ethanol followed by ethylene loss

3.3. Carbon vs. silicon containing ions

Results obtained for the silicon containing ions can be summarized as follows: the substitution reaction is (i) rapid when exothermic or thermoneutral, (ii) slow when the reaction is slightly endothermic (substitution of the ethoxy group by a methoxy group), and (iii) unobserved when the substitution reaction is significantly endothermic.

Conversely, 1,3-H^+ transfer from oxygen to oxygen is of course rapid when the substitution reaction is rapid. However, it has been possible to show, in several cases, that the transfer is also observed when the substitution is endothermic.

The reactions of the $(CH_3)_2{}^+C–OH$, $(CH_3)_2{}^+C–OCH_3$, and $(CH_3)_2{}^+C–OCH_2CH_3$ cations with water, methanol or ethanol, were also studied. The substitution reaction is never observed and there is no data indicating that the 1,3-H^+ transfer from oxygen to oxygen takes place, in agreement with previous results [12].



Scheme 7.

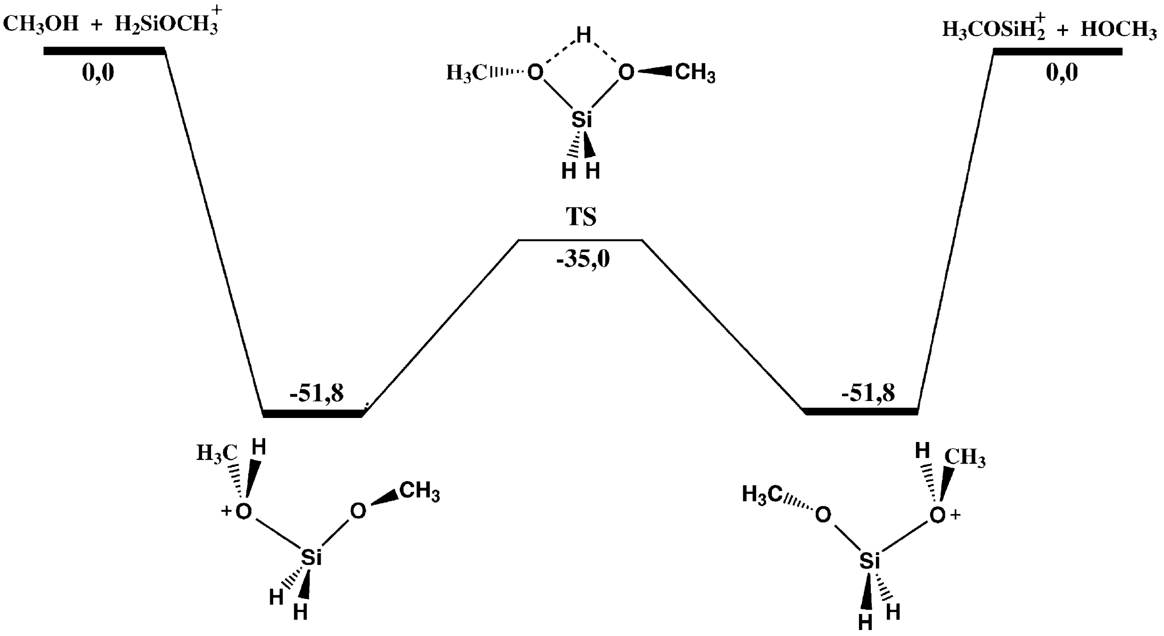


Fig. 4. Energy profile (kcal mol^{-1}).

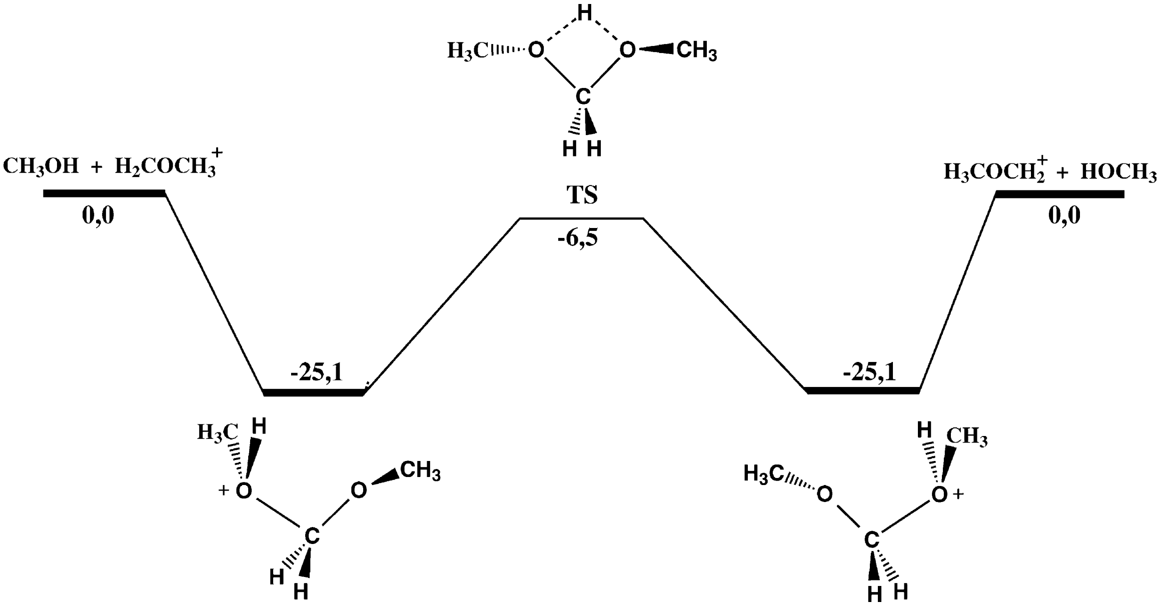


Fig. 5. Energy profile (kcal mol^{-1}).

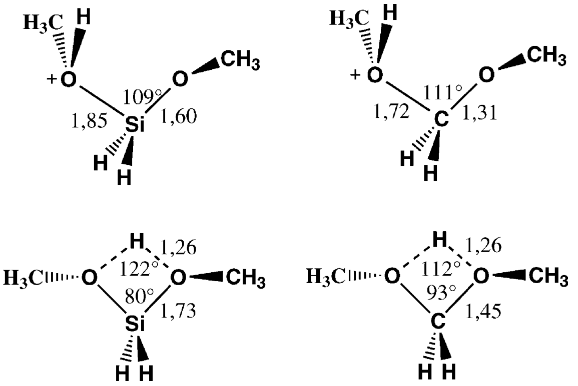


Fig. 6. Calculated stable structures and transition states.

3.4. Calculations

The calculated energy profile for the $(CH_3)_2{}^+$Si–OCH_3/CH_3OH and $(CH_3)_2{}^+$C–OCH_3/CH_3OH systems are reported, respectively, in Figs. 4 and 5 and the structures of stables adducts and of transition states are shown in Fig. 6.

4. Discussion

In the $(CH_3)_2{}^+$Si–OCH_3/CH_3OH system, the relative energies of the reactants and of the transition state (Fig. 4) clearly explain why the 1,3-H$^+$ transfer is rapid when the substitution reaction is exothermic or thermoneutral.

Some processes are almost thermoneutral. For instance, the substitution of an ethoxy group by a methoxy group can be estimated to be only 2 or 3 kcal mol^{-1} endothermic if it is considered that the difference in the proton affinity of $(CH_3)Si{=}O$ and $(CH_3CH)Si{=}O$ is about 2 kcal mol^{-1} [6]. In such cases, the thermal energy of the reactant allows the reaction to take place. When the substitution reaction is endothermic and not observed, the transition state for proton transfer is low compared to the energy of the reactants and different other exothermic reactions are possible after this step.

For the $(CH_3)_2{}^+$C–OCH_3/CH_3OH system Fig. 4 shows that the transition state energy for 1,3-H$^+$ transfer lies only some kcal mol^{-1} under the energy of the reactants. It may be noted that the difference may be slightly lower, since DFT calculations underestimate the transition states energies. Starting from the intermediate covalent structures, two ways are open: the simple cleavage giving back the reactants and the proton transfer which are very close in energy. Since the covalent intermediate is hot, the entropic factor which favors the simple cleavage is determining and the proton transfer is, therefore, not observed.

The transition state energies for the 1,3-H$^+$ transfers indicates that the energy barriers for a 1,3-H$^+$ transfer is identical for both systems. This conclusion contrasts with that obtained for the 1,3-$CH_3{}^+$ transfers in disioxane-type ions.

The difference between both systems comes from the stabilization energy of the covalent intermediate and, therefore, of the internal energy available, which is about 52 kcal mol^{-1} for the studied silicon containing ions, and only 25 kcal mol^{-1} for carbon containing ions. This shows the strong electrophilic character of Si$^+$ containing ions. The difference makes the 1,3-H$^+$ transfer easy in the first case and very difficult in the second.

5. Conclusion

From this study four main conclusions can be drawn.

(i) The 1,3-H$^+$ transfers from oxygen to oxygen are easy in silicon containing ions while they are not observed in the corresponding ions containing only carbon.
(ii) Starting from a covalent structure, the energy required for a 1,3-H$^+$ transfer from oxygen to oxygen is almost identical whether the transition state contains a silicon atom or not.
(iii) The greater strength of the Si–O bond in cations, compared to that of the C–O bond or, in other words, the great electrophilic character of ions possessing a Si$^+$, is the main factor explaining the

difference in the behavior of the studied silicon or carbon containing ions.

(iv) Finally, specific reactions of silicon containing ions have been observed in this work. For instance, ions possessing a $CH_3SiH(^+OHR)$ structure can eliminate H_2 and CH_4.

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