Combined quantum chemical and mass spectrometric study of $[Si,C,H_3,O]^+$ isomers

Max C. Holthausen,* Detlef Schröder, Waltraud Zummack, Wolfram Koch and Helmut Schwarz

Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

The potential energy surface of $[Si,C,H_3,O]^+$ has been explored by means of *ab initio* MO calculations at the G2 level of theory as well as by mass spectrometric techniques. The silicon–methoxide cation H_3COSi^+ has been identified as the global minimum ($\Delta_fH = 151$ kcal mol^{-1}), followed by the silaacetyl cations H_3SiCO^+ ($\Delta_fH = 172$ kcal mol^{-1}) and H_3CSiO^+ ($\Delta_fH = 180$ kcal mol^{-1}). A number of other intermediates, the transition structures associated with the mutual interconversion reactions and the energetics of possible fragmentation channels are explored computationally. It turns out that the energy demands for the unimolecular isomerizations of most of the isomers are substantially lower than those of fragmentations. Consequently, an identification of the different isomers based solely on mass spectrometric information is made difficult by intramolecular rearrangements which precede the structure-indicative fragmentation reactions, even though H_3SiCO^+ is clearly distinguishable from H_3CSiO^+ and H_3COSi^+. However, when the experimental findings are combined with the computationally predicted $[Si,C,H_3,O]^+$ potential-energy surface and with thermochemical information, this difficulty can be overcome, and a coherent picture of this complex system emerges. In addition, the existence of the neutral radicals $H_3COSi^{\cdot}$, $H_3CSiO^{\cdot}$, as well as $H_3SiCO^{\cdot}$ and/or $H_3SiOC^{\cdot}$ is explored by means of neutralization–reionization mass spectrometry.

Silicon-containing molecules have attracted considerable interest during the last two decades,[1,2] due to their relevance in technology, applied chemistry and organic synthesis. In addition, neutral and cationic silicon compounds[3] have been suggested to play an important role in interstellar chemistry. The element silicon is quite abundant in inter- and circum-stellar environments[4] and molecules such as SiC_n ($n = 1,2,4$), SiH_4 or SiN have been identified.[4c] Furthermore, from a conceptual point of view, silicon occupies a unique position in understanding the different behaviour of the elements Li–Ne compared with heavier main group elements.[5] Particular attention has been paid to the comparison of silicon chemistry to that of its lower homologue carbon, which differs substantially, as for example shown by the huge difference in the stability of multiple bonded carbon and silicon systems.

In the last few years, gas-phase reactions of atomic Si^+ cations with a variety of molecules have been examined by different experimental and theoretical means,[6] as recently reviewed by Böhme.[7] Owing to the large oxophilicity of silicon, the reactions of Si^+ with oxygen bases have attracted particular attention.[8] For example, Si^+ ions have been shown to react rapidly with ROH molecules; while the predominant product corresponds to $HOSi^+$, formation of $ROSi^+$ ions also takes place.[7] For the simplest case (R = H), it is now well established that of the two possible isomers $HSiO^+$ and $HOSi^+$ the latter is more stable by almost 60 kcal mol^{-1}, and only $HOSi^+$ is generated in the reaction of Si^+ with H_2O.[9] This result is in distinct contrast to the corresponding carbon-containing system, where the formyl cation HCO^+ is substantially more stable than the isoformyl cation HOC^+.[10] For $R = CH_3$,[11] the situation is more complex due to the large number of conceivable isomers of the elemental composition $[Si,C,H_3,O]^+$. Of particular interest in this context are the four structures with connectivities H_3XYO^+ and H_3YXO^+ (X and Y being either Si or C) since they can be compared to their all-carbon counterparts H_3CCO^+ and H_3COC^+. In a previous investigation, two of us studied computationally the relative stabilities and the interconversion barrier of the 2-silaacetyl cation H_3SiCO^+ and *O*-silylated carbon monoxide H_3SiOC^+ at fairly high levels of theory.[12] The 2-silaacetyl cation was found to be more stable than the *O*-silylated carbon monoxide by some 20 kcal mol^{-1} with an activation barrier of *ca.* 33 kcal mol^{-1} relative to H_3SiCO^+. While this is qualitatively the same order of stability as found for the pure carbon analogue, where the acetyl cation H_3CCO^+ is more stable than H_3COC^+,[13] yet a different conclusion was drawn by Luna and Yáñez[14] for the pair H_3CSiO^+ and H_3COSi^+, *i.e.* where CO is formally replaced by SiO. In their recent computational study employing the G2 scheme to the $[Si,C,H_4,O]^+$ potential energy surface (PES), these two $[Si,C,H_3,O]^+$ isomers were included as possible fragmentation products. These authors report an energy difference of 29 kcal mol^{-1} in favour of the H_3COSi^+ isomer; however, no information about the transition structure and the associated activation energy connecting these two minima was provided. Apart from these two studies of selected aspects of the PES of $[Si,C,H_3,O]^+$, no further attempts to identify the relevant stationary points on this surface have been made. In the following, we report the results of a comprehensive and detailed combined theoretical and mass spectrometric study of the relevant parts of the $[Si,C,H_3,O]^+$ potential energy surface, with particular emphasis on the various isomers, their interconversion pathways and fragmentation channels. In addition, the existence of the neutral radicals $H_3CSiO^{\cdot}$ and $H_3COSi^{\cdot}$, as well as $H_3SiCO^{\cdot}$ and/or $H_3SiOC^{\cdot}$ is explored by means of neutralization–reionization mass spectrometry and their stabilities are assessed computationally.

Computational and experimental details

The G2 approach has been described in great detail in the literature.[15] Briefly, this composite scheme consists of geometry optimizations at the MP2(full)/6-31G(d) level of theory,[16] followed by a series of single point calculations and empirical corrections to achieve effectively relative energies of QCISD(T)/6-311+G(3df,2p) quality. Usually, thermochemical data can be reproduced to within ±2 kcal mol^{-1}, even though cases where such high accuracy cannot be achieved are also known.[17] Each stationary point was characterized as a minimum, transition structure (TS) or chemically irrelevant higher-order saddle point by checking the number of negative eigenvalues of the analytically derived MP2/6-31G(d) force constant matrix, from which also the harmonic frequencies, needed for the zero point vibrational energy (ZPVE) corrections, were obtained. In a few cases, we also computed the intrinsic reaction coordinate (IRC)[18] in order to establish unambiguously the minima connected with a particular TS. All calculations were performed employing Gaussian 92[19] installed on IBM RS/6000 workstations.

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described elsewhere.[20] $[Si,C,H_3,O]^+$ cations were generated by either electron ionization (EI) or chemical ionization (CI) of appropriate precursors (see below). The ions of interest, having 8 keV kinetic energy, were mass-selected using B(1)E(1) at a resolution of $m/\Delta m \geq 4000$, which was necessary in order to resolve $[Si,C,H_3,O]^+$ from isobaric $[Si,C_2,H_7]^+$ and $[C_3,H_7,O]^+$ ions (all $m/z = 59$ for the ^{28}Si isotope). $[Si,C,H_3,O]^-$ anions were generated by chemical ionization of a mixture of tetramethyl silane or trimethyl silanol with N_2O as electron moderator and reagent gas in the negative chemical ionization mode.[21] Collisional activation (CA) was brought about by helium (80% transmission, T) in the field-free region preceding B(2), and the fragment ions were monitored by scanning B(2). Despite reasonable ion intensities, the experimental errors in the measurements of the peak heights in the CA mass spectra of the $[Si,C,H_3,O]^+$ isomers were higher than usual in this type of tandem MS experiments. These enlarged errors indicate that mixtures of ions, interconversion processes and competing fragmentation pathways[22] may play a role in the experiment and may obscure the identification of certain isomers (see below). Neutralization–reionization (NR)[23] experiments of cations were performed by colliding B(1)/E(1) mass-selected cations with xenon (80% T), deflecting the remaining ions by applying a potential of 1 kV, reionizing the fast neutrals by collision with oxygen (80% T) and scanning B(2) to monitor the cations formed. NR spectra of anions were obtained similar to those of cations, but using oxygen in both collision cells (each, 80% T) and detecting the cations which are formed upon reionization of the fast moving neutrals. Unfortunately, the NR method could not be applied to all $[Si,C,H_3,O]^+$ ions, because the ion intensities at mass resolutions sufficient to resolve isobaric interferences were too low for most of the precursors. All spectra were accumulated and on-line processed with the AMD/Intectra data system; 5–20 scans were averaged to improve the signal-to-noise ratio. In order to account for interferences which may arise from ^{29}Si and ^{30}Si isotopologues, the corresponding ions containing ^{28}Si were measured separately and the intensities were corrected to the natural isotope abundancies, *e.g.* the spectrum of $[^{28}Si,C,H_2,O]^+$ was used to correct that of $[^{28}Si,C,H_3,O]^+$ for interfering $[^{29}Si,C,H_2,O]^+$. In the case of chemical ionization of a mixture of SiH_4 and CO, interfering contributions from $Si_2H_n^+$ ions ($n = 0$–3) were also included in these corrections.

Chemicals were either commercially available or prepared according to well known laboratory procedures and purified by distillation. Trimethylsilanol was synthesized as an azeotrope containing *ca.* 7% of hexamethyl disiloxane and used without further purification.[24] Silane was generated in an on-line apparatus[25] in which magnesium silicide (Strem Chemicals, Inc.) was hydrolysed with diluted sulfuric acid at 0 °C.

Results and discussion

As will become obvious further below, the experimental characterization and in particular the differentiation of the $[Si,C,H_3,O]^+$ isomers generated from the various precursor molecules is all but trivial. In fact, the interpretation is hampered by the presence of mixtures, facile interconversion processes between the isomers, either prior to or after collisional activation, as well as competing fragmentation channels. Therefore, we will commence the discussion with the theoretical results, followed by the evaluation of the energetics of possible fragmentation channels. Finally, the experimental findings are interpreted in light of the computational predictions.

Theoretical section

In general, one can classify the $[Si,C,H_3,O]^+$ isomers as members of two different groups of related species which are discussed separately. The first group consists of the silicon–methoxide cation H_3COSi^+, **1**, and the related isomers **2**–**6** (Fig. 1). The second group contains the 2-silaacetyl cation H_3SiCO^+, **7**, and the isomers **8**–**11** (see below). This classification is based on the following reasoning: although all species can undergo several isomerization processes, no low-energy pathway for a feasible (stepwise) intramolecular isomerization connecting these two classes of isomers was found. A second criterion by which these two groups differ deals with the connectivity of the hydrogen atoms: the ions which are accessible from **1** at lower energies do contain at least two C–H bonds, while those ions which are derived from **7** mostly contain several Si–H bonds.

Silicon–methoxide cation H_3COSi^+ 1 and the related structures 2–6. The silicon–methoxide cation, **1**, represents the global minimum on the potential energy surface of $[Si,C,H_3,O]^+$ (Tables 1 and 2). The geometry of **1** can be described as that of a neutral SiO unit which is cationized by a methyl group at the oxygen terminus. For example, the Si–O bond ($r_{Si-O} = 1.556$ Å) in **1** is hardly elongated compared with isolated neutral SiO

Table 1 Calculated relative stabilities (kcal mol^{-1}) of the $[Si,C,H_3,O]^+$ isomers **1**–**6** at the G2 level of theory and the transition structures connecting the minima

	E_{rel}/kcal mol^{-1}
H_3COSi^+ (**1**)	0.0
TS **1/2**	63.5
H_3CSiO^+ (**2**)	29.4
TS **1/3**	55.3
H_2COSiH^+ (**3**)	47.3
TS **3/3′**	55.8
H_2COSiH^+ (**3′**)	44.1
TS **3′/4**	68.2
c-H_2COSiH^+ (**4**)	56.5
TS **4/5**	87.2
c-$H_2CO(H)Si^+$ (**5**)	43.9
TS **2/5**	94.6
TS **5/6**	62.6
H_2CSiOH^+ (**6**)	43.4

Table 2 Calculated relative stabilities (kcal mol^{-1}) of the $[Si,C,H_3,O]^+$ isomers **7**–**13** at the G2 level of theory and some transition structures connecting the minima[a]

	E_{rel}/kcal mol^{-1}
H_3SiCO^+ (**7**)	20.8
TS **7/8**	49.8
H_3SiOC^+ (**8**)	35.9
TS **7/9**	69.0
c-$H_2SiOC(H)O^+$ (**9**)	55.7
TS **9/4**	109.5
TS **9/10**	120.1
H_2SiCOH^+ (**10**)	79.3
TS **8/11**	109.4
H_2SiOCH^+ (**11**)	91.7
$HSiC(H)OH^+$ (**12**)	66.7
$SiC(H)OH_2^+$ (**13**)	83.0

[a] Energies relative to the global minimum H_3COSi^+, **1**.

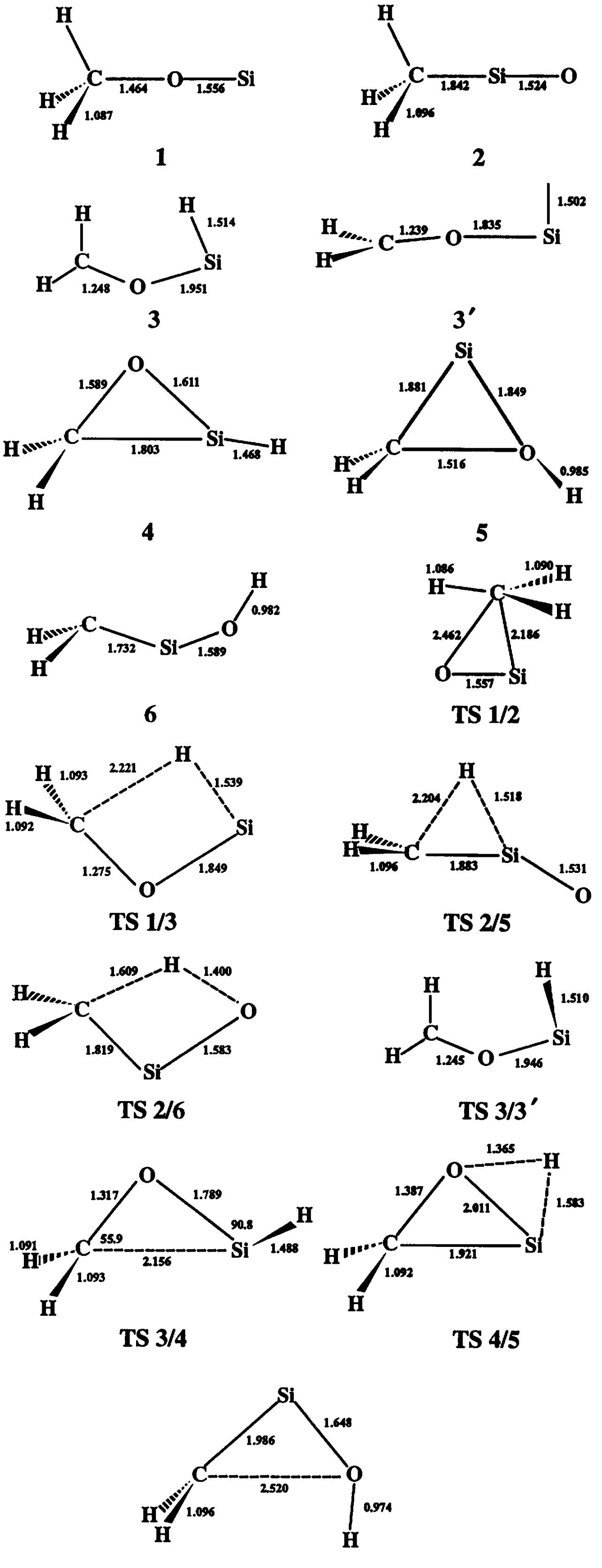

Fig. 1 Selected bond lengths (in Å) of **1**–**6** and connecting transition structures

($r_{Si\text{-}O}$ = 1.542 Å). On the other hand the bonding between the carbon and the oxygen atom in **1** has significant covalent character, as is apparent from the relatively short C–O bond length of 1.464 Å (*cf.* $r_{C\text{-}O} \approx 1.43$ Å for a C–O single bond[26]) and the almost perfect tetrahedral environment of the carbon atom. The high stability of **1** can be accounted for by the fact that while the strong Si–O bond is hardly perturbed, simultaneously a reasonably strong C–O interaction arises. The assignment of **1** as the global minimum of the $[Si,C,H_3,O]^+$ potential energy surface is also consistent with a consideration of C–H, O–H, Si–H, C–O, Si–O and Si–C bond dissociation energies (E_d),[10] which imply that species with an intact methyl group together with a Si–O–C, C–Si–O or Si–C–O connectivities are the most stable ones,[27] and among these structures, **1** represents the minimum.

Isomer **2** is closely related to **1** in that it can be described as SiO which is methyl-cationized at the silicon site, *i.e.* the 1-sila analogue of the well known acetyl cation. However, as already pointed out earlier by Luna and Yàñez,[14] CH_3OSi^+ is by no less than 29.4 kcal mol^{-1} more stable than CH_3SiO^+. The large stability of **1** can be attributed to the fact that methyl cationization of dipolar SiO is more facile at the negative oxygen terminus than at the positive silicon atom. The transition structure TS**1/2** associated with the interconversion **1**$\rightleftharpoons$**2** is well above the related minima (E_{rel} = 63.5 kcal mol^{-1}), and the relatively large C–O and C–Si distances and the almost planar environment of the CH_3 moiety, characterizes TS **1/2** as the movement of a methyl group around the SiO dipole with an imaginary frequency of *i*386 cm^{-1}. Thus, TS **1/2** can be described as an ion–dipole complex of a methyl cation and silicon monoxide, in which the positive charge is expected to be located at the methyl, because its ionization energy (IE) of 9.8 eV is significantly lower than that of SiO (11.4 eV).

In the present context, it is instructive to compare **1** and **2** to the $[Si,O,H]^+$ system:[7,9,28] as far as thermochemical stabilities are concerned, the presence of a methyl group lowers the energy difference of 56.2 kcal mol^{-1} between the more stable $SiOH^+$ and $HSiO^+$ to 29.4 kcal mol^{-1} between **1** and **2**. Concomitantly, the activation barriers associated with the corresponding transition structures differ by approximately the same amount, *i.e.* 91.5 kcal mol^{-1} for $SiOH^+ \rightarrow HSiO^+$ *versus* 63.5 kcal mol^{-1} for the interconversion **1**→**2**. Thus, the extreme stability difference for the two isomers of protonated SiO is reduced when H^+ is replaced by CH_3^+. Interestingly, this trend is in sharp contrast to what is known for the carbon case,[13,29,30] *i.e.* HCO^+ is 37.3 kcal mol^{-1} lower in energy than COH^+, and CH_3CO^+ is even 51.5 kcal mol^{-1} more stable than CH_3OC^+. The explanation for this substituent effect on the opposing stabilities of carbon and silicon compounds $[C,H_3,O,X]^+$ (X = C, Si) is mostly due to thermodynamic reasons which favour the formal oxidation state +II in **1** compared with CH_3OC^+.

For cationic systems such as $[Si,C,H_3,O]^+$, isomerization processes involving transfers of hydrogen atoms of protons[31] are of prime interest for the evaluation of the potential energy surface as well as for the mass spectrometric characterization of the various possible isomers. The first conceivable isomer starting from **1** involves a 1,3-H transfer from carbon to silicon leading to H_2COSiH^+ for which two minima were obtained, **3** (E_{rel} = 47.3 kcal mol^{-1}) and **3′** (E_{rel} = 44.1 kcal mol^{-1}). Qualitatively, both species can be described in terms of a SiH^+ cation [IE(SiH) = 7.89 eV] interacting with the oxygen terminus of formaldehyde [IE(CH_2O) = 10.87 eV].[10] The geometrical features of **3** and **3′** are quite similar; remarkable are the relatively long Si–O and short C–O bond lengths. The major difference between **3** and **3′** is in the in-plane *syn* arrangement between H_2CO and SiH moieties in the former as opposed to the perpendicular situation in the latter isomer. In accordance with the qualitative description of **3** and **3′** as formaldehyde–SiH^+ complexes, the bond dissociation energy (D) of only 46.8 kcal mol^{-1} for the Si–O bond in **3′** to yield SiH^+ and CH_2O is rather low considering the high oxophilicity of silicon. The potential energy surface in the vicinity of **3** and **3′** is very flat, and parts of it were therefore evaluated by IRC calculations, which revealed that the lowest pathway connecting **1** and the H_2COSiH^+ region of the PES involves TS **1/3** (E_{rel} = 55.3 kcal mol^{-1}) and leads initially to the less stable isomer **3**. The activation barrier associated with the interconversion into the more stable perpendicular isomer **3'** occurs *via* TS **3/3'** (E_{rel} = 55.8 kcal mol^{-1}) which is only 8.5 kcal mol^{-1} higher in energy than **3**. However, the activation barrier for the rearrangement **1**→**3** is below TS **1/2** (E_{rel} = 63.5 kcal mol^{-1}), such that **1** is expected to interconvert more readily into **3** than into **2**.

The next isomer to be considered is the cyclic species **4** which can be formed from **3'** by ring closure *via* TS **3'/4** (E_{rel} = 68.2 kcal mol^{-1}) as confirmed by IRC. **4** can be described as a 1-silaoxiranyl cation in which all atoms are connected by chemical bonds as indicated by the Si–C, Si–O and C–O bond distances. Despite this seemingly favourable bonding situation, **4** is computed to lie 56.5 kcal mol^{-1} higher in energy than **1**, and is also 12.4 kcal mol^{-1} less stable than the ring-opened isomer **3'**. The low stability of **4** can be rationalized by the competition of silicon and carbon in bond formation with oxygen in the three-membered ring, which leads to a substantial elongation of the C–O bond length. Ring strain seems not to be important for **4** and the other cyclic structures reported in the following, as the corresponding frequencies are quite low and the potential around silicon is rather flat.

Another cyclic structure evolves from **4** *via* a 1,2-H transfer from silicon to oxygen to yield **5**. However, the corresponding TS **4/5** (*i*1302 cm^{-1}) is quite high in energy (E_{rel} = 87.2 kcal mol^{-1}), such that the route **1**→**3**→**4**→**5** is unlikely to occur, because dissociation of **1** (or **2**) into SiO and CH_3^+ will compete efficiently. Although the hydrogen atom attached to oxygen weakens the binding in the ring, **5** is relatively low in energy (E_{rel} = 43.9 kcal mol^{-1}). Part of this stabilization may be due to the lower strain in **5** compared with **4**, because the Si–O bond is elongated significantly to 1.849 Å, but the major contribution can be traced back to the thermodynamic driving force associated with the formation of an O–H bond in **5**.

Even though we carefully searched for such species, no minimum corresponding to the result of a formal [1,2]-H shift from either **1** or **2** could be located. We did, however, find a saddle point (TS **2/5**, E_{rel} = 94.6 kcal mol^{-1}), which at first glance seems to connect **2** with the target isomer $H_2CSi(H)O^+$. A subsequent analysis of the IRC reveals that TS **2/5** is in fact the saddle point for the direct interconversion of **2** into **5**. After the activation barrier is surpassed, the C–Si–O angle begins to decrease and a bond between the terminal oxygen and carbon atoms is formed when progressing along the reaction coordinate. Owing to the very high activation energy connected with TS **2/5**, which is well above the threshold for fragmentation of **2** into CH_3^+ + SiO (see below), this rearrangement is not expected to play any significant role in the present context.

Besides TS **4/5** and the very energy demanding TS **2/5**, there exists another pathway for the rearrangement of **5**, which involves ring-opening of the C–O bond *via* TS **5/6** to the acyclic isomer **6**, *i.e.* *O*-protonated 1-silaketene.[32] Since TS **5/6** is much lower in energy than TS **4/5**, the interconversion **5**→**6** is expected to be relatively facile. In addition, acyclic **6** (E_{rel} = 43.4 kcal mol^{-1}) is slightly more stable than **5**, probably due to the formation of the favourable $SiOH^+$ substructure.[7,33] With respect to the geometry, the SiOH unit in **6** is hardly perturbed compared with the free $SiOH^+$ molecule (r_{Si-O} = 1.540 Å, r_{O-H} = 0.963 Å),[9] while the bending of the Si–O–H unit (127°) reflects the influence of the additional methylene group in **6**, compared with the linear structure of isolated $SiOH^+$. The binding of the methylene group to the $HOSi^+$ substructure can be described in terms of a single σ-bond with significant pyramidalization of the carbon atom. This description is also in line with the relatively weak $D(H_2C\text{–}SiOH^+)$ = 53.1 kcal mol^{-1}, such that loss of a methylene represents an energetically low-lying fragmentation channel in the $[Si,C,H_3,O]^+$ system.[34]

The conclusion of this section is that **1** is by far the most stable $[Si,C,H_3,O]^+$ isomer (Fig. 2). However, once **1** has accumulated enough internal energy, as is the case in the keV collisions of our experimental set up, it may well undergo rearrangement processes leading to the isomers **2**–**6** prior to fragmentation.

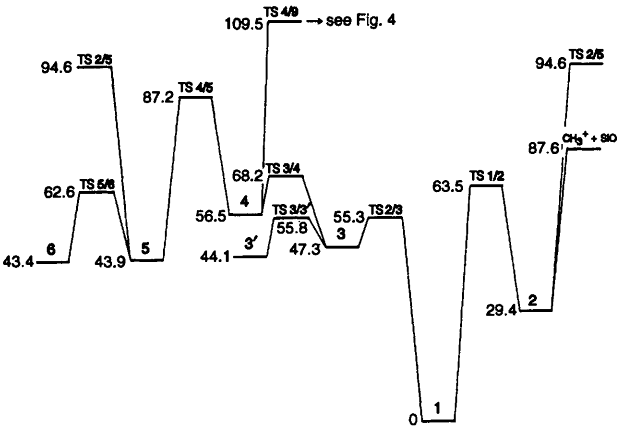

Fig. 2 Potential energy surface for isomers **1**–**6**

Table 2 Calculated relative stabilities (kcal mol^{-1}) of the $[Si,C,H_3,O]^+$ isomers **7**–**13** at the G2 level of theory and some transition structures connecting the minima[a]

	E_{rel}/kcal mol^{-1}
H_3SiCO^+ (**7**)	20.8
TS **7/8**	49.8
H_3SiOC^+ (**8**)	35.9
TS **7/9**	69.0
c-$H_2SiOC(H)O^+$ (**9**)	55.7
TS **9/4**	109.5
TS **9/10**	120.1
H_2SiCOH^+ (**10**)	79.3
TS **8/11**	109.4
H_2SiOCH^+ (**11**)	91.7
$HSiC(H)OH^+$ (**12**)	66.7
$SiC(H)OH_2^+$ (**13**)	83.0

[a] Energies relative to the global minimum H_3COSi^+, **1**.

2-Silaacetyl cation H_3SiCO^+ 7 and the related isomers 8–11. A theoretical study of the 2-silaacetyl cation **7**, its isomer **8**, and their mutual interconversion has already been reported.[12] Both species can be considered as *C*- or *O*-silylated carbon monoxide, respectively, and the binding situations in **7** and **8** can indeed be viewed as those of ion–dipole complexes of a silyl cation with a CO molecule. The carbon-silylated isomer **7** (E_{rel} = 20.8 kcal mol^{-1}, Table 2, Fig. 3) is considerably more stable than **8** (E_{rel} = 35.9 kcal mol^{-1}). However, the activation barrier connecting both isomers *via* TS **7/8** (E_{rel} = 49.8 kcal mol^{-1}) is in the vicinity of the energy demand for the loss of the CO molecule (E_{rel} = 54.0 kcal mol^{-1}). The absolute numbers obtained here at the G2 level of theory differ only slightly from our previous data,[12] and the qualitative picture remains unchanged. Further, although the energy regime of the present experiments are well above TS **7/8**, the unimolecular interconversion **7**⇌**8** is unlikely to compete efficiently with dissociation, because the rate for isomerization will certainly be smaller than that for the practically barrier-free, direct fragmentation process (Fig. 4). As alluded to in our previous study,[12] the direct bond cleavage will therefore be favoured at higher internal energies due to the larger entropy contribution compared with the rearrangement.

Various computational attempts have been made to search for low-energy pathways for the interconversion of **7** and **8** into the isomers related to the silicon-methoxide cation **1**. The Si–H bonds, as in **7** and **8**, are relatively weak such that rather low activation barriers for hydrogen migrations to either carbon or oxygen are expected. However, no energetically reasonable

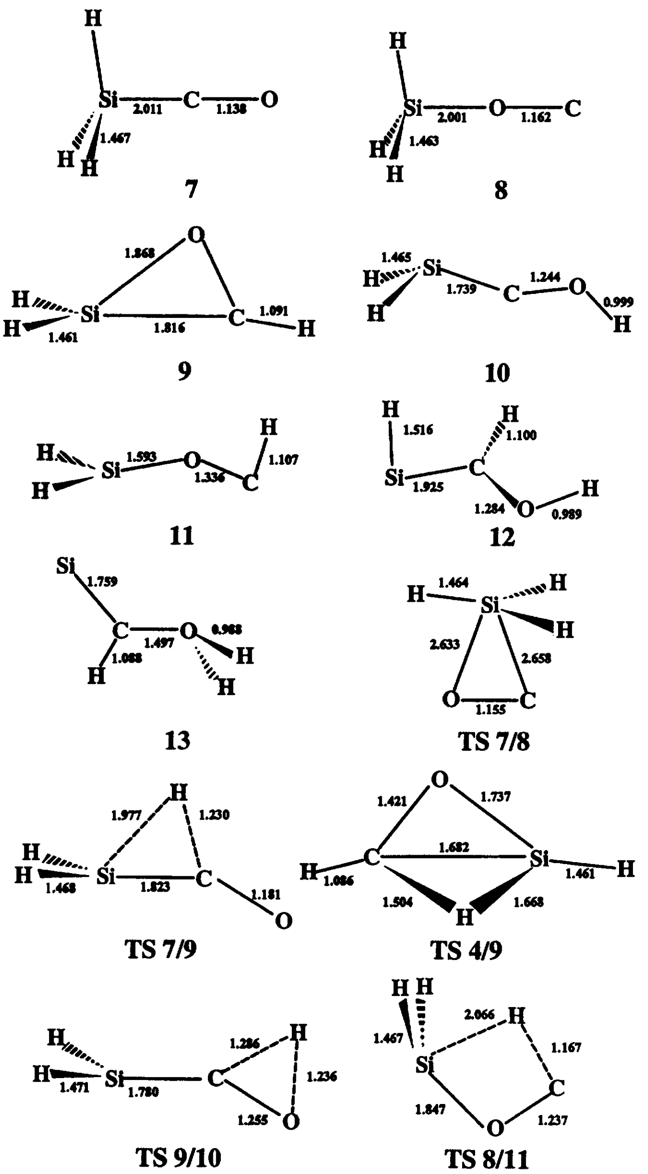

Fig. 3 Selected bond lengths (in Å) of 7–13 and selected transition structures

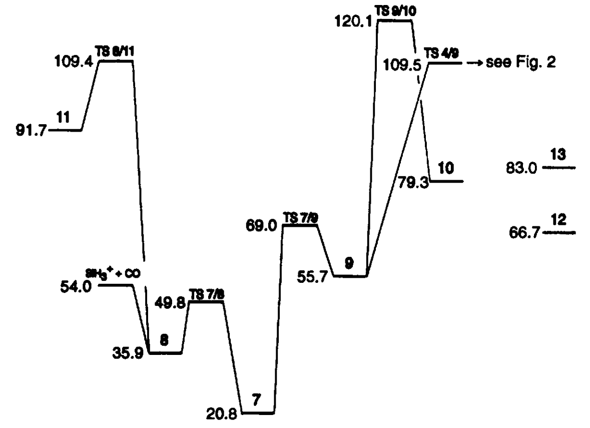

Fig. 4 Potential energy surface for isomers 7–11 (E_{rel} refers to the most stable isomer 1)

transition structures for these processes were found. This reinforces our conclusion that the two groups of isomers, 1–6 and 7–11, cannot communicate with each other. Thus, 7 and 8, either individually or as a mixture, should be mass spectrometrically distinguishable from the isomers 1–6 by means of the facile formation of SiH_3^+ from 7 to 8, a fragment which is rather difficult to achieve from the other isomers.

The transition structure with the lowest activation barrier for hydrogen migration, TS 7/9, is located 15.0 kcal mol^{-1} above the CO-loss channel and leads to the formation of the cyclic ion 9 (E_{rel} = 55.7 kcal mol^{-1}). Formally, the so-formed isomer is structurally related to its tautomer 4, *i.e.* 9 corresponds to the 2-silaoxiranyl cation. However, a closer inspection of the geometry of 9 suggests that the bonding situation can be better described as that of a silylene unit [IE(SiH_2) = 8.9 eV] coordinated to a formyl cation [IE($HCO^•$) = 8.6 eV] as indicated by the similar and long Si–C and Si–O distances (1.816 and 1.868 Å, respectively), together with the short C–O bond (1.275 Å); the latter points toward a significant C–O double bond character in 9. Although a 1,2-H migration from the silicon to the carbon atom in 9 would lead to 4 and by such connect this part of the potential-energy surface with that of the isomers 1–6, the corresponding transition structure TS 4/9 is very high in energy and well above the dissociation channels. Hence, this rearrangement can safely be excluded from playing a role in the experiments. Other pathways to bring about this rearrangement could not be located irrespective of various starting geometries used. In addition, the high energy isomer **10** (E_{rel} = 79.3 kcal mol^{-1}) has been found in which 1,2-H transfer from the carbon to the oxygen atom is accompanied by ring-opening. The huge barrier associated with TS 9/10 can be attributed to the breaking of the thermodynamically favourable Si–O bond; owing to the high energy demand of TS 9/10 this pathway was not pursued any further.

The *O*-silylated isomer 8 may also isomerize, but the well depth of 8 (E_{rel} = 35.9 kcal mol^{-1}) with respect to the threshold for loss of carbon monoxide (E_{rel} = 54.0 kcal mol^{-1}) is even smaller than for 7, such that only very low-lying rearrangement processes will play a role for the chemistry of this species. In fact, apart from TS 7/8 no other saddle point originating from 8 and satisfying the requirement of being below the dissociation into H_3Si^+ and CO could be identified. The only other TS found starting from 8 involves a 1,3-hydrogen transfer from the silicon to the carbon to yield 11. Because TS 8/11 as well as the corresponding product 11 are very high in energy, this part of the PES was not pursued furthermore; the same applies for the isomers 12 and 13.

The relatively high energy demands of some isomers and particularly of the associated transition structures may render the triplet surface of $[Si,C,H_3,O]^+$ energetically accessible. However, spin–orbit coupling is small for silicon,[35] such that curve-crossing between different spin states is not likely to play a role for the $[Si,C,H_3,O]^+$ isomers considered here. Therefore, neither the triplet surface nor possible changes in multiplicities in the course of the reactions were examined in this study. Note, however, that in the course of the experimental generation of $[Si,C,H_3,O]^+$ by electron ionization, electronically excited states may well be formed[36] and may add to the complexity of the system.

Energetics of the fragmentation channels

For the evaluation of the thermodynamic and kinetic stabilities of the $[Si,C,H_3,O]^+$ isomers as well as for their experimental characterization by mass spectrometric means, reliable knowledge of the energetics of possible fragmentation pathways is of paramount importance. For all ions under study, intense $H^•$ and H_2 losses (leading to $[Si,C,H_2,O]^{•+}$ and $[Si,C,H,O]^+$ ions, respectively)[37] were observed. Nevertheless, these hydrogen losses are not indicative of the respective connectivities. Therefore, we will restrict this section to those channels in which at least one heavy atom (Si,O,C) is also lost. In the following, we briefly discuss the computed thresholds for these fragmentation pathways together with the experimental thermochemistry[10] (Table 3).

Table 3 Combined heats of formation ($\Delta_f H$ in kcal mol^{-1}) for selected fragmentation channels (mass differences Δm in amu) of $[Si,C,H_3,O]^+$

	Δm[a]	$\Delta_f H$ (calc)[b]/kcal mol^{-1}	$\Delta_f H$(exp)[c]/kcal mol^{-1}	$\Delta_f H$(calc) − (exp)/kcal mol^{-1}
$SiOH^+ + CH_2(^3B_1)$	−14	248[d]	244	+4
$SiO^{\cdot +} + CH_3^{\cdot}$	−15	281[d]	275	+6
$SiCH_3^+ + O$	−16	294[e]	293[f]	+1
$SiCH_2^{:+} + OH^{\cdot}$	−17	290[e]	292[f]	−2
$SiCH^+ + H_2O$	−18	269[e]	280[f]	−11[g]
$CH_2OH^+ + Si$	−28	277[d,h]	276	+1
$SiH_3^+ + CO$	−28	205[d]	210	−5
$CH_2O^{\cdot +} + SiH^{\cdot}$	−29	314[d,h]	315	−1
$SiH_2^{\cdot +} + HCO^{\cdot}$	−29	285[d]	283	+2
$HCO^+ + SiH_2\,(^1A_1)$	−30	263[i]	266	−3
$SiH^+ + H_2CO$	−30	243[d]	246	−3
$CO^{\cdot +} + SiH_3^{\cdot}$	−31	344[d,h]	345	−1
$Si^{\cdot +} + H_3CO^{\cdot}$	−31	301[d,h]	300	+1
$CH_3^+ + SiO$	−44	239[d]	237	+2

[a] Mass differences (Δm) for the corresponding neutral lost are expressed in amu. [b] For the evaluation of $\Delta_f H$ from *ab initio* energies, see text and footnote *g* of this Table. [c] Ref. 10. [d] G2 energies; this work. [e] Theoretical values of PMP4 calculations taken from ref. 39*d*. [f] Experimental values taken from ref. 39*a*. [g] For a discussion of the discrepancy between theoretical and experimental data, see ref. 39*d*. [h] These fragmentation channels are expected to be quite accurately described by both theoretical and experimental methods and are used for the conversion of the G2 energies into heats of formation. [i] Theoretical values taken from ref. 15.

In order to compare the G2 energies with experimental heats of formation ($\Delta_f H$), we combined the calculated and experimental reaction enthalpies for those reactions in Table 3 which are expected to be described most accurately experimentally[10] as well as theoretically, *i.e.* the channels leading to $Si^{\cdot +} + CH_3O^{\cdot}$, $Si + CH_2OH^+$, $CO^{\cdot +} + H_3Si^{\cdot}$ and $CH_3^+ + SiO$. In agreement with ref. 14 we can obtain $\Delta_f H$ (**1**) = 151 ± 1 kcal mol^{-1} for the global minimum **1**, and express the relative energies (E_{rel}) predicted by G2 calculations in terms of heats of formation ($\Delta_f H$).

For most of the reactions listed in Table 3 the agreement between the theoretically predicted energies and the experimental thermochemistry is good and within ±3 kcal mol^{-1}. Accordingly, by far the most energetically favoured fragmentation channel of the $[Si,C,H_3,O]^+$ system corresponds to the formation of SiH_3^+ and carbon monoxide. However, for this channel a somewhat larger discrepancy between computed and experimental data of 5 kcal mol^{-1} is found. Slightly larger deviations than is usually found for the G2 scheme are also observed for the $SiOH^+ + CH_2$ and $SiO^{\cdot +} + CH_3^{\cdot}$ dissociation reactions. The significant discrepancy of 11 kcal mol^{-1} for the $SiCH^+ + H_2O$ channel was interpreted in terms of experimental uncertainties as discussed in a recent theoretical work by Böhme and co-workers from which these data were taken.[39d] The calculated IE($H_3Si^{\cdot}$) of 8.05 eV is in good agreement with the experimental figure (8.11 ± 0.07 eV), and also calculated reaction enthalpy of −137.9 kcal mol^{-1} for the process $HSi^+ + 2H^{\cdot} \rightarrow H_3Si^+$ is close to the experimental figure of −140 kcal mol^{-1}. However, for the process $H_3C^+ + SiO \rightarrow H_3Si^+ + CO$, we calculate a reaction enthalpy ($\Delta_R H$) of −33.6 kcal mol^{-1} compared with the experimental figure of $\Delta_R H = -28.0$ kcal mol^{-1}. Thus, we conclude that there exists a need for a further refinement of the theoretical as well as the experimental data in silicon gas-phase chemistry. Notwithstanding, the accuracy of the G2 method is certainly sufficient to allow for a comparison of the energetics of the fragmentation channels as required for the interpretation of the experimental findings for $[Si,C,H_3,O]^+$ isomers.

Of prime interest for the fragmentation behaviour of $[Si,C,H_3,O]^+$ ions in mass spectrometric experiments are the relative energies of these fragmentation pathways. As mentioned above, the lowest lying channel corresponds to the formation of $SiH_3^+ + CO$. However, this direct bond cleavage process is only feasible for **7** and its related isomers **8**–**11**, while for the isomers **1**–**6** this fragmentation is not accessible due to the existence of significant kinetic barriers (see above). The next two low-lying channels also involve the formation of stable neutrals, *i.e.* losses of neutral SiO and neutral formaldehyde accompanied by the generation of the cations CH_3^+ and SiH^+, respectively. Interestingly, and intuitively quite unexpected, the thermochemical energy demand for the loss of a free triplet methylene is fairly low (E_{rel} = 96.5 kcal mol^{-1}). Even if strict spin conservation is assumed, this dissociation, leading then to singlet methylene, is still comparably low in energy (E = 105.5 kcal mol^{-1}). Therefore, methylene loss will contribute significantly to the fragmentation patterns, whenever the Si–O–H connectivity is present or easily affordable in the respective $[Si,C,H_3,O]^+$ isomers. All other fragmentation pathways involving losses of heavy atoms are significantly higher in energy, and hence will only give rise to intense signals in the mass spectra, when (*i*) high kinetic barriers prevent isomerization processes and (*ii*) excitation occurs well above their threshold energies (the latter is, of course, the case in keV collision experiments performed here).

Recapitulating the discussion of the computed PES of $[Si,C,H_3,O]^+$, we emphasize two aspects. (*i*) The minima on this potential energy surface can be divided into two classes of isomers, consisting of ions **1**–**6** and **7**–**11**, respectively. No energetically feasible pathway through which these two classes of isomers can communicate with each other could be identified. (*ii*) The possible fragmentation channels are significantly higher in energy than most of the barriers connecting the isomers **1**–**6**. Thus, interconversions of these isomers into each other upon ion generation or in post-collisional rearrangements are likely to precede fragmentation.

Experimental results

$[Si,C,H_3,O]^+$ ions were generated from a variety of silicon compounds as precursors, and a structural characterization was attempted by collisional activation (CA). A severe complication of these experiments arises from the accidental mass overlap of atomic silicon with the CO molecule (both 28 amu), such that the mass difference of $\Delta m = -28$ may correspond to losses of atomic Si and/or CO. Similarly, $\Delta m = -29$ may correspond to losses of $SiH^{\cdot}$ and/or $HCO^{\cdot}$, $\Delta m = -30$ to losses of SiH_2 and/or CH_2O, and $\Delta m = -31$ to eliminations of $SiH_3^{\cdot}$ and/or $CH_3O^{\cdot}$. The same applies for the corresponding ionic fragments in the mass range 28–31 amu, *i.e.* SiH_n^+ or CH_nO^+ (n = 0–3). Unfortunately, in this particular case even the often simple and powerful use of isotopic labelling would not resolve this pitfall and only the investigation of doubly labelled compounds (*e.g.* ^2H and ^{13}C) would suffice, which has not been attempted. As discussed below, the assignments of the major contributions to the fragments in this mass range are based on plausibility considerations with respect to the corresponding ionic products in accordance with the other fragments and thermochemistry. In the presentation of the experimental data we will follow the two classes of isomers **1**–**6** and **7**–**11** as outlined in the theoretical section.

The CA mass spectra of $[Si,C,H_3,O]^+$ ions from different precursors are shown in Table 4. All $[Si,C,H_3,O]^+$ ions studied exhibit relatively intense losses of hydrogen ($\Delta m = -1, -2, -3$). As these processes are not specific for the structures of the ions generated from the different precursors, we will focus the discussion of the fragmentation patterns on the other, more structure-indicative reactions in which at least one heavy atom is part of the neutral species lost.

Silicon–methoxide H_3COSi^+ 1 and related isomers 2–6. At first, we address the $[Si,C,H_3,O]^+$ ions which are generated by electron ionization of tetramethoxysilane, $Si(OCH_3)_4$, and discuss their collision-induced fragmentation behaviour in some more detail. The base peak of the spectrum corresponds to the loss of a hydrogen atom, losses of H_2 as well as $H_2 + H^{\cdot}$ are also quite intense. Even though these signals do not give very much information as far as the ion structure is concerned, the intense $H^{\cdot}$ loss is in line with the formation of the most stable $[Si,C,H_2,O]^+$ isomer $SiOCH_2^{\cdot+}$ by simple C–H bond cleavage of **1**.[37c] A structure-indicative signal is that for the loss of neutral SiO which implies that either an intact methyl group is present in the ion or it can be formed relatively easily. Indeed the occurrence or non-occurrence of the CH_3^+ fragment can be used for a distinction of the two classes of $[Si,C,H_3,O]^+$ ions, *i.e.* **1**–**6** and **7**–**13**, and its presence in the mass spectra relates to the corresponding $[Si,C,H_3,O]^+$ species to the structures **1**–**6**. Note that the intensities were neither corrected for the different transmissions through the analysers nor for the different detection efficiencies of the fragment ions; thus, the fraction of the CH_3^+ channel may be underestimated, because the mass and kinetic energy of this fragment ion are only a quarter of the incident beam.[38] Other fragmentation channels lead to distinct signals for $SiOH^+$ and $SiO^{\cdot+}$, while those for $SiCH_n^+$ ($n = 0$–3)[39] are hardly observed. These observations imply that a Si–O bond is present in the $[Si,C,H_3,O]^+$ ion formed from $Si(OCH_3)_4$, but not a Si–C bond. Together with the observation of an intact methyl group, structure **1** is the most plausible suggestion for the $[Si,C,H_3,O]^+$ ion obtained from $Si(OCH_3)_4$. This assignment is not only in accord with the structure of the precursor molecule, but also in keeping with the mass-overlapping CH_nO^+ and SiH_n^+ ions ($n = 0$–3), whose pattern fully agrees with that expected for **1**, *i.e.* a weak signal formally corresponding to the (unstable) methoxy cation[40] ($\Delta m = -28$) which rapidly fragments to give rise to the more intense signals for $CH_2O^{\cdot+}$ ($\Delta m = -29$), CHO^+ ($\Delta m = -30$) and $CO^{\cdot+}$ ($\Delta m = -31$), together with atomic Si^+ (also, $\Delta m = -31$).

Additional evidence for the structural assignment is provided by the NR mass spectrum of the $[Si,C,H_3,O]^+$ ion generated from $Si(OCH_3)_4$ in which an intense signal for SiO^+ predominates, while signals for $SiOH^+$ and also $SiCH_n^+$ ($n = 0$–3) are hardly observed [Fig. 5(*a*)]. In addition, the recovery signal for reionized $[Si,C,H_3,O]^+$ demonstrates that the corresponding neutral radical is stable within the microsecond timescale. This finding also accounts for the intense $SiO^{\cdot+}$ signal in that it originates from reionized neutral SiO which is formed by dissociation of rovibronically excited **1** upon neutralization, *i.e.* $Si(OCH_3)^+ \rightarrow Si(OCH_3)^{\cdot *} \rightarrow SiO + CH_3^{\cdot}$. Nevertheless, in view of the theoretically predicted potential energy surface of $[Si,C,H_3,O]^+$ and the experimental findings presented further below, the structural assignment of this ion cannot be unequivocal, since all fragmentation channels which were discussed in the elucidation of the connectivity are situated well above the barriers for isomerization between **1**–**6**. In particular, the distinction of the isomers is severely hampered by the overlapping signals for SiH_n^+ and CH_nO^+ ($n = 0$–3) in the CA as well as in the NR spectra.

The CA mass spectrum of the $[Si,C,H_3,O]^+$ ion generated from trimethylsilyl methyl ether, $(CH_3)_3SiOCH_3$, is quite similar, but not identical, to that derived from $Si(OCH_3)_4$; the major differences are the smaller ratio of $H^{\cdot}$ and H_2 losses and the slightly more intense signals corresponding to $SiCH_n^+$ ($n = 0$–2) when $(CH_3)_3SiOCH_3$ is used as a precursor. These differences are due to the structure of the precursor molecule which contains both $Si–OCH_3$ and $CH_3–SiO$ units, such that a mixture of isomers **1** and **2** is probably formed upon electron ionization.

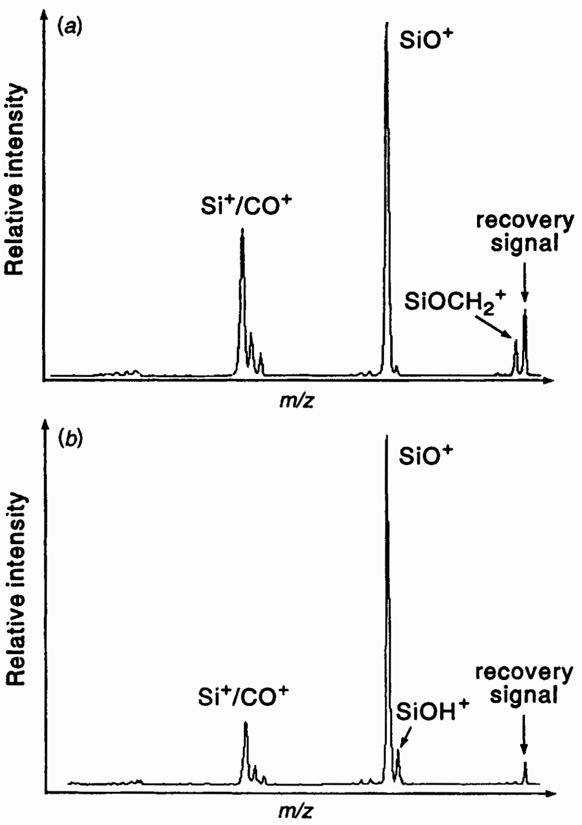

Fig. 5 NR mass spectra ($Xe–O_2$, both 80% T) of $[Si,C,H_3,O]^+$ cations generated by electron ionization of (*a*) tetramethoxysilane and (*b*) diacetyldimethylsilane

A significant change in the CA mass spectra is observed when either tri- or di-acetylmethylsilanes, $(CH_3COO)_3SiCH_3$ and $(CH_3COO)_2Si(CH_3)_2$, respectively, are used as precursors. The base peaks of the spectra are shifted to the SiO^+ and $SiOH^+$ cations, respectively, and, even more significant, the $SiCH_n^+$ fragments ($n = 0$–3) gain in intensity and indicate the existence of a Si–C bond. Tentatively, we assign these CA mass spectra to the formation of **2**, which is also in line with the $CH_3–SiO$ connectivities in the precursor molecules. However, the intense signal for $SiOH^+$ conflicts with such a straightforward assignment, because this fragment ion cannot be directly generated from **2**. The presence of $SiOH^+$ in the spectrum requires hydrogen migration from **2** to an isomer which gives rise to the fragmentation channel $CH_2 + SiOH^+$. The NR spectrum of the $[Si,C,H_3,O]^+$ ion generated by electron ionization of $(CH_3COO)_2Si(CH_3)_2$ is also dominated by the $SiO^{\cdot+}$ peak, but it also shows a significant signal for $SiOH^+$ [Fig. 5(*b*)]. Although we cannot decide whether the so-formed ion exhibits structures **2**–**6**, the NR spectrum can be clearly distinguished from that of **1** [Fig. 5(*a*)] by the almost complete absence of the $[Si,C,H_2,O]^+$ signal in Fig. 5(*b*). Owing to the connectivity of the precursor molecule, structure **2** seems to be a reasonable suggestion.

With respect to the height of the calculated barriers for the $[Si,C,H_3,O]^+$ isomers, the ambiguity of the CA and also the NR mass spectra of the $[Si,C,H_3,O]^+$ ions from different precursors, points to the formation of isomeric mixtures upon electron ionization. Another approach to the connectivity **2**

Table 4 Mass differences (Δm in amu) in the collisional activation mass spectra of $[Si,C,H_3,O]^+$ cations from different precursors (data are given as percentages of the base peak)[a,b]

	Δm (amu)													
Fragment ions[c]	−1 $SiCH_2O^+$	−2 $SiCHO^+$	−3 $SiCO^+$	−14 $SiOH^+$	−15 SiO^+	−16 $SiCH_3^+$	−17 $SiCH_2^+$	−18 $SiCH^+$	−19 SiC^+	−28 $SiH_3^+CH_3O^+$	−29 $SiH_2^+CH_2O^+$	−30 SiH^+CHO^+	−31 Si^+CO^+	−44 CH_3^+
$Si(OCH_3)_4$	100	25	40	25	50		1	2		2	10	20	40	15
$(CH_3)_3SiOCH_3$	100	55	50	45	75		2	3	1	1	5	15	30	20
$(CH_3COO)_3SiCH_3$	30	50	25	95	100	4	8	10	4	1	5	10	20	20
$(CH_3COO)_2Si(CH_3)_2$	25	60	25	100	95	4	8	8	2	1	4	10	25	25
$(CH_3)_3SiOC_2H_5$	40	70	25	100	70	2	10	10	2	1	4	10	15	25
$(CH_3)_3SiOH$	35	60	30	100	60	2	8	10	2	1	2	5	12	15
$(CH_3)_3SiCH_2OH$	15	60	10	100	25	1	6	4	1	1	2	4	8	10
SiH_4/CO[d]	70	25	60	2	3		2	5	4	100	8	35	30	

[a] For the sake of clarity intensities of less than 1% are omitted. Unless noted otherwise, the ions were generated by electron ionization (70 eV). [b] A series of other conceivable precursors could not be used because they give rise to intense dictations $[m/z\ 118]^{2+}$, which cannot be mass-resolved from $[Si,C,H_3,O]^+$, *e.g.* $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_3SiOOSi(CH_3)_3$, *c*-$[(CH_3)(H)SiO]_4$ and *c*-$[(CH_3)_2SiO]_4$. [c] The formulae of the fragment ions stand for their elemental compositions and should not imply any ion structures. [d] Chemical ionization of a mixture of SiH_4 and CO.

involves the corresponding $[Si,C,H_3,O]^-$ anions. Therefore, either tetramethylsilane or trimethylsilanol were subjected to negative chemical ionization with N_2O as electron moderating and oxidizing agent. Despite the relatively low intensity of the so-formed $[Si,C,H_3,O]^-$, the precursors and the low probability of rearrangements in anions[41] render it quite plausible that CH_3SiO^- is formed exclusively.

If the $[Si,C,H_3,O]^-$ anion is subjected to an NR experiment from the anion to the cations, a distinct recovery signal for $[Si,C,H_3,O]^+$ is observed (Fig. 6), which can be traced back to the reionization of the intermediate neutral 1-silaacetyl radical. The other ionic fragments observed support the proposal of structure **2**; in particular, the distinct signals for $SiCH_n^+$ together with CH_n^+ ($n = 0$–3). In view of the calculated barrier height of 34.1 kcal mol^{-1} for the rearrangement of **2** into the more stable **1**, the connectivity of **2** may well be retained in the cation, but the charge-reversed $[Si,C,H_3,O]^+$ signal was too weak in intensity for a further characterization. Note however, that the distinct signals for SiH_n^+ and/or CH_nO^+ ($n = 1$–3) indicate some extent of isomerization of the so-formed **2** prior to dissociation; most likely interconversion occurs in the reionization step.

The CA spectra of the $[Si,C,H_3,O]^+$ ions generated from the next two precursors listed in Table 4, trimethylsilyl ethyl ether $(CH_3)_3SiOC_2H_5$ and trimethylsilanol $(CH_3)_3SiOH$, are similar to those derived from the acetyl silanes, with the $SiO^{\cdot+}$ signal somewhat less intense compared with $SiOH^+$. These similar, but yet different spectra provide another indication of the generation of mixtures of isomeric $[Si,C,H_3,O]^+$ ions upon electron ionization of the precursor molecules. In addition, the CA mass spectra of the $[Si,C,H_3,O]^+$ ions turned out to be dependent on the precise conditions in the ion source (pressure, electron energy, repeller voltage *etc.*) which further supports the suggested formation of mixtures. Finally, in the CA mass spectrum of $[Si,C,H_3,O]^+$ derived from (trimethylsilyl)methanol $(CH_3)_3SiCH_2OH$, the ratio between $SiOH^+$ and SiO^+ amounts to 4:1 compared with a 1:2 ratio for the ion generated from $Si(OCH_3)_4$. In view of the thermodynamics of the corresponding exit channels (Table 3), the large amount of methylene loss concomitant with formation of $SiOH^+$ clearly points towards a different connectivity of the so-formed ion, or, more likely, a different isomer than **1** represents the majority of the mass selected $[Si,C,H_3,O]^+$ generated from this precursor. Within the context of the computational results, we propose that either the acyclic isomer **6** and/or cyclic species **5** constitute the major components of the $[Si,C,H_3,O]^+$ ions obtained upon electron ionization of $(CH_3)_3SiCH_2OH$.

In conclusion, the differentiation of the $[Si,C,H_3,O]^+$ isomers from the first group (ions **1**–**6**) by means of CA mass spectroscopy is not straightforward, and obviously mixtures of isomers, rearrangement processes, as well as competing fragmentation channels obscure the assignment of connectivities for the different ions being formed.

2-Silaacetyl cation H_3SiCO^+ 7 and related isomers 8–11. For the $[Si,C,H_3,O]^+$ ion generated by chemical ionization of SiH_4 in the presence of CO the situation is much less complicated. The CA mass spectrum of the $[Si,C,H_3,O]^+$ ion formed (last entry in Table 4) is fully in line with the description of this ion as an adduct of a silyl cation with carbon monoxide, *i.e.* **7** or **8**, in that the loss of carbon monoxide ($\Delta m = -28$) dominates the spectrum. Moreover, the distinct differences in the CA spectrum of the so-formed ion from those derived from the other precursor molecules (in particular, the absence of CH_3^+, see above) excludes isomerizations involving a cleavage of the C–O bond and indicates that complete migration of the hydrogen atoms from the silicon to carbon is negligible. As far as the site of silylation of the carbon monoxide molecule is concerned, the structure-indicative signals for $SiOH^+$ and SiO^+ concomitant with those for $SiCH_n^+$ ($n = 0$–3) imply that chemical ionization leads to a mixture of the *C*- and *O*-silylated isomers **7** and **8**. Although our calculations reveal that **8** is less stable by 15.1 kcal mol^{-1} than **7**, it is very feasible that under the non-equilibrium conditions of a low-pressure chemical-ionization source a mixture of both isomers might be generated and, hence, sampled in the detection. The assumption of a mixture of **7** and **8** is also in line with earlier[12] and the present computational findings that TS **7/8** ($E_{rel} = 49.8$ kcal mol^{-1}) is energetically close to H_3Si^+–CO bond cleavage ($E_{rel} = 54.0$ kcal mol^{-1}). Further, unimolecular isomerization $\mathbf{7} \rightleftharpoons \mathbf{8}$ is not likely to occur upon collisional activation, since the direct dissociation to lose a CO molecule would compete efficiently (see above).

The NR spectrum of the so-formed ion (Fig. 7) is also completely different from those displayed in Figs. 5 and 6, in that the signal for $SiO^{\cdot+}$ is very weak, while $[Si,C,H_n,O]^+$ ($n = 0$–3) and $Si^{\cdot+}$ dominate the spectrum. Further, the presence of a recovery signal for reionized $[Si,C,H_3,O]^+$ indicates that the corresponding neutral radical is accessible by NRMS (see below).

Comparison of $[Si,C,H_3,O]^+$ cations and neutral $[Si,C,H_3,O]$ radicals. It is instructive to compare the thermochemistry of **1**, **2** and **7** and the corresponding neutral radicals with their carbon analogues. As discussed above, the stability difference of 29.4 kcal mol^{-1} in favour of H_3COSi^+ compared with H_3CSiO^+ is reversed in the carbon case, *i.e.* CH_3CO^+ is 51.6 kcal mol^{-1} more stable than CH_3OC^+.[13] Thus, methyl cationization of the oxygen atom is much more favourable for SiO than for CO. Quite the opposite situation is found for permutative methyl cationization of the other atom, *i.e.* C or Si. Compared with $D(H_3C^+$–$CO) = 79.7$ kcal mol^{-1} for the acetyl cation, $D(H_3C^+$–$SiO)$ decreases from 58.2 kcal mol^{-1} in the 1-silaacetyl cation **2** to an $D(H_3Si^+$–$CO)$ value of only 33.2 kcal

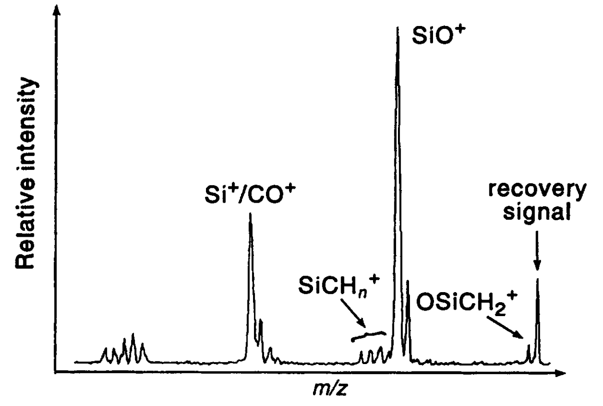

Fig. 6 NR mass spectrum (O_2, 80% T, O_2, 60% T) of $[Si,C,H_3,O]^-$ anions generated by chemical ionization of $Si(CH_3)_4$ with N_2O as reagent gas. (Here, the anions are neutralized first, and then the neutrals are reionized to cations which are then detected.)

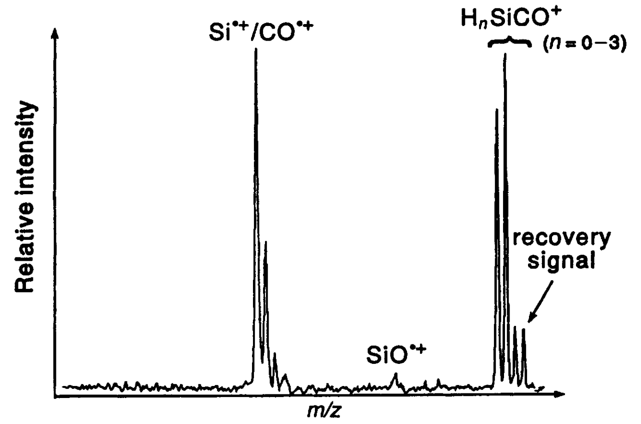

Fig. 7 NR mass spectrum (Xe–O_2, both 80% T) of the $[Si,C,H_3,O]^+$ cations generated by chemical ionization of a mixture of silane and carbon monoxide

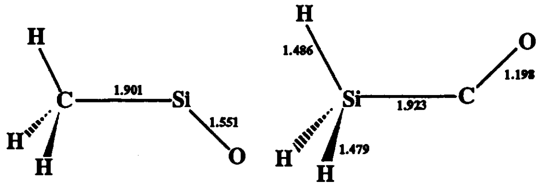

Fig. 8 Selected bond lengths (in Å) of the neutral silaacetyl radicals $H_3CSiO^{\bullet}$ and $H_3SiCO^{\bullet}$

mol^{-1} in the 1-silaacetyl cation **7**. These significantly lower values indicate a decreasing covalent character of the binding in the series $H_3C^+–CO > H_3C^+–SiO > H_3Si^+–CO$.

In order to assess the change of this series upon one-electron reduction, we calculated the neutral 1- and 2-silaacetyl radicals $CH_3SiO^{\bullet}$ and $H_3SiCO^{\bullet}$ at the G2 level of theory (Fig. 8). Indeed, the situation is quite different for the neutral radicals. While for 1-silaacetyl $D(H_3C–SiO) = 20.0$ kcal mol^{-1} is even larger than $D(H_3C–CO)$ of the acetyl radical (14.2 kcal mol^{-1}), we found $D(H_3Si–CO)$ for 2-silaacetyl to be as small as 5.5 kcal mol^{-1}. In view of the latter figure, it seems questionable whether a high-energy collision experiment such as NRMS allows for the generation of neutral 2-silaacetyl, and perhaps neutral $H_3SiOC^{\bullet}$ gives rise to the recovery signal observed in Fig. 7. Further, Ho and Melius predicted Δ_fH of neutral $H_3COSi^{\bullet}$ as 8.4 ± 2.7 kcal mol^{-1} on a similarly accurate level of theory.[27] Thus, upon neutralization of positively charged **1**, the neutral silicon methoxide radical still exhibits a reasonably strong Si–O bond (*ca.* 103 kcal mol^{-1}), however, the CH_3 group affinity of the SiO unit at the O-terminus is rather low, *i.e.* $D(H_3C^{\bullet}–OSi) \approx 2.5$ kcal mol^{-1}. However, neutral $H_3COSi^{\bullet}$ may be stabilized by a kinetic barrier against its dissociation into a $CH_3^{\bullet}$ radical and SiO in which quite different bonding situations prevail. Finally, the theoretical results predict the IE values of $CH_3OSi^{\bullet}$, $CH_3SiO^{\bullet}$ and $H_3SiCO^{\bullet}$ as 6.2, 8.1 and 6.7 eV, respectively, compared with an IE value of 7.0 eV for the acetyl radical.

Conclusions

The present study of $[Si,C,H_3,O]^+$ isomers reveals that the silicon–methoxide cation **1**, the 1-silaacetyl cation **2**, and the 2-silaacetyl cation **7** represent deep minima of the potential energy surface of $[Si,C,H_3,O]^+$, and substantial barriers prevent facile interconversion processes. The silicon–methoxide cation **1** represents the global minimum of the $[Si,C,H_3,O]^+$ system, while in the corresponding carbon system of the $[C_2,H_3,O]^+$ isomers, the acetyl cation is by far the most stable species.[13] This difference underlines once more the tendency of silicon to avoid the formation of multiple bonds. In comparison to the acetyl cation, the methyl group in the 1-silaacetyl cation **2** bears much more positive charge, and the 2-silaacetyl cation **7** can even be regarded as a complex of a SiH_3^+ cation with carbon monoxide.

Further, the present results prompted us to draw some more general conclusions concerning the suitability of applied experimental and theoretical methods. On the one hand, the experimental characterization of different $[Si,C,H_3,O]^+$ isomers by tandem mass spectrometry is not at all straightforward and is hampered by the presence of mixtures in the precursor ions, post-collisional isomerizations and competition of different fragmentation channels. In fact, the distinction of the isomers **1**–**6** turns out to be rather difficult, while **7** and **8** can clearly be distinguished from the former. Even the otherwise powerful NRMS technique does not remove this ambiguity, because the experimental and theoretical findings together with thermochemical considerations question whether the fractions of the different $[Si,C,H_3,O]^+$ ions which are reionized retain the structure of the corresponding precursors. The theoretical approach at the G2 level of theory is much more powerful with respect to the minima and interconversion processes of the $[Si,C,H_3,O]^+$ isomers, but the number of energetically conceivable isomers which have to be considered is large and some of the minima and barriers are located in extremely flat regions of the potential energy surface such that these require costly IRC calculations for an unequivocal identification. Most significantly, due to the high energy demands of the possible fragmentations on the singlet surface, the involvement of triplet $[Si,C,H_3,O]^+$ species in the dissociation processes cannot completely be ruled out. Yet, the inclusion of higher multiplicities would lead to an even larger complexity of the computational approach, which is beyond our present capabilities. Thus, the present example demonstrates that despite the enormous improvement of both experimental and theoretical tools within the last decades, even main-group element compounds containing only a few heavy atoms do in some cases still represent ambitious challenges to both experimentalists as well as theoreticians.

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