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Generation and characterization of protonated silicic acid $Si(OH)_3^+$ and its neutral counterpart by tandem mass spectrometry and computational chemistry

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Abstract

Dissociative electron ionization of triethoxysilane, $HSi(OC_2H_5)_3$, and tetraethoxysilane, $Si(OC_2H_5)_4$, generates *m/z* 79 ions of composition $[Si, O_3, H_3]^+$. From tandem mass spectrometry experiments and CBS-QB3 model chemistry calculations, it is concluded that these ions have the structure of protonated silicic acid, $Si(OH)_3^+$ ($\mathbf{1a}^+$), for which ΔH_f (298 K) $= -36.3$ kcal mol^{-1} (for the anti-isomer). Low energy (metastable) ions $\mathbf{1a}^+$ dissociate via loss of H_2O and SiO_2 to yield *m/z* 61 ($HOSi{=}O^+$) and *m/z* 19 (H_3O^+) product ions, respectively. These reactions involve isomerization of $\mathbf{1a}^+$ into the stable isomers $HOSi({=}O)OH_2^+$ ($\mathbf{1b}^+$), and $[H_2O\cdots H\cdots O{=}Si{=}O]^+$ ($\mathbf{1c}^+$), the proton-bound dimer of SiO_2 and H_2O. The dimer ion lies 77 kcal mol^{-1} higher in energy than $\mathbf{1a}^+$, in contrast to the carbon analogues $C(OH)_3^+$ and $[H_2O\cdots H\cdots O{=}C{=}O]^+$ which have comparable heats of formation. From neutralization–reionization experiments it is concluded that the $Si(OH)_3^\bullet$ radical is a stable species in the gas phase, having a calculated ΔH_f (298 K) $= -191.1$ kcal mol^{-1} (for the anti-isomer). (Int J Mass Spectrom 221 (2002) 219–227)

Keywords: Protonated silicic acid; Collision-induced dissociation; Neutralization–reionization; Computational chemistry; Proton affinity; SiO_2

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1. Introduction

Over the past several years, small silicon containing organic molecules and ions have attracted a great deal of attention of both experimentalists and theoreticians due to their importance as reactive intermediates in chemical reactions ranging from synthetic organic chemistry [1] to microprocessor manufacturing [2]. Besides, these species have been suggested to play an important role in interstellar chemistry. Two silicon-bearing molecules, SiO and SiS have been detected in interstellar clouds and four other silicon-containing molecules, SiC, c-SiC_2, SiC_4 and SiH_4, have been detected in circumstellar shells [3,4]. Amongst the experimental methods, neutralization–reionization mass spectrometry (NRMS) [5] has proven to be a powerful and versatile technique for investigating highly reactive elusive radicals/molecules which are fundamentally important. The NRMS methodology has been successfully used by Goldberg and Schwarz to generate and characterize several small silicon-containing organic species [6]. Among the oxygen containing silicon species that have been characterized are SiOH/HSiO [7], CH_2OSi

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[8], $Si_xO_yH_z$ [7,9], $(CH_3)_2SiOH$, CH_3SiOH [10], $SiOCH_3$ [11] and SiNCO [12].

Silicon containing species of the type H_xSiO_y are also known to be key intermediates in silane–oxygen flames and theoretical studies [13] on some of these have been reported in the literature. Such species have also been extensively studied by Bohme and coworkers [14], using the selected-ion flow tube (SIFT) technique. We recently reported on the characterization of ionic and neutral silicon dihydroxide, $Si(OH)_2^{\bullet+/0}$ and silanoic acid $HSi(O)OH^{\bullet+/0}$ by NRMS and computational chemistry [15]. Here we report on the characterization of $Si(OH)_3^+$ and its neutral counterpart in the gas phase by using a combination of tandem mass spectrometric methods and calculations using the CBS-QB3 model chemistry (Fig. 1) [16].

2. Experimental and theoretical methods

The mass spectrometric experiments were performed on VG Analytical Autospec M and ZAB-R mass spectrometers of EBE and BEE geometry, respectively (E = electric sector, B = magnet). Detailed information about these instruments has been previously reported [17,18].

Triethoxysilane (**I**) and tetraethoxysilane (**II**) (obtained from Aldrich) were used as precursor molecules for the m/z 79 $Si(OH)_3^+$ ions of the study. The expected elemental composition of the mass 79 ions in the 70 eV electron ionization (EI) mass spectra of **I** and **II** was confirmed with the Autospec M using a resolution $m/\Delta m = 7000$ (10% valley definition).

The metastable ion (MI), collision-induced dissociation (CID) and neutralization–reionization (NR) spectra recorded on the instruments were similar. The NR/CID survivor spectrum was obtained with the ZAB-R instrument and for reasons of uniformity the related spectra presented in Fig. 2 were also recorded on this instrument. The CID spectra were recorded using oxygen as collision gas. The NR spectra were recorded using *N*,*N*-dimethylaniline (ZAB-R) or Xenon (Autospec M) as reducing agents and oxygen gas for reionization. The ZAB-R spectra were recorded using a small PC-based data system developed by Mommers Technologies Inc. (Ottawa).

Structures and energies of the H_3SiO_3 and H_3CO_3 ions and neutrals pertinent to this study, connecting transition states and dissociation products were probed by the standard CBS-QB3 model chemistry [16]. The calculations were performed using Gaussian 98 Revision A.7 [19]. The calculated energies are presented in Table 1 and the potential energy diagram of Fig. 1. Detailed geometries of selected species are displayed in Fig. 3 (the complete set of geometries is available upon request). Frequency calculations gave the correct number of negative eigenvalues for all minima and transition states and the spin contamination was within the acceptable range. The connections of the transition states have been checked by geometry optimizations and frequency calculations.

3. Results and discussion

3.1. The generation and characterization of the $Si(OH)_3^+$ ion

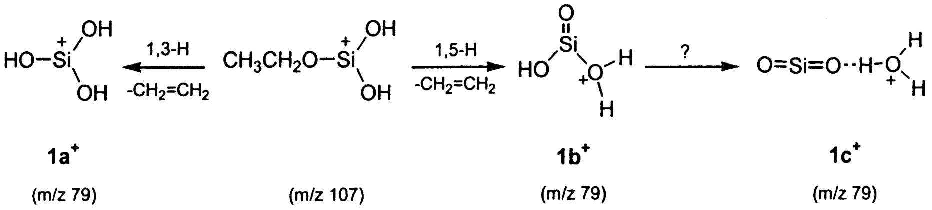
The 70 eV EI mass spectra of triethoxysilane, $HSi(OC_2H_5)_3$ (**I**), and tetraethoxysilane, $Si(OC_2H_5)_4$ (**II**), both display a sizeable (~40% of the base peak) peak at m/z 79, corresponding to ions of elemental composition $[Si, O_3, H_3]^+$. From an analysis of the MI and CID spectra of all potential precursor ions, it follows that the m/z 79 ions from $\mathbf{I}^{\bullet+}$ are generated by the reaction sequence: $164^{\bullet+}$ ($\mathbf{I}^{\bullet+}$) $\rightarrow 163^+ \rightarrow 135^+ \rightarrow 107^+ \rightarrow 79^+$, i.e., loss of $H^\bullet$ followed by three consecutive C_2H_4 losses. For $\mathbf{II}^{\bullet+}$, the m/z 79 ions are also generated by the route $135^+ \rightarrow 107^+ \rightarrow 79^+$, while m/z 135 is generated via two pathways: $208^{\bullet+}(\mathbf{II}^{\bullet+}) \rightarrow 163^+ \rightarrow 135^+$ (consecutive losses of $C_2H_5O^\bullet$ and C_2H_4) and $208^{\bullet+}(\mathbf{II}^{\bullet+}) \rightarrow 179^+ \rightarrow 135^+$ (consecutive losses of $C_2H_5^\bullet$ and $CH_3C(H){=}O$).

If the ethylene losses involve β-hydrogen rearrangements, the resulting m/z 79 ions would have the structure $Si(OH)_3^+$ ($\mathbf{1a}^+$), i.e., silicic acid $(HO)_2Si{=}O$ protonated at the Si=O moiety. Its carbon analogue, viz. carbonyl protonated carbonic acid, $C(OH)_3^+$ ($\mathbf{2a}^+$), has been identified as a stable species in the gas phase. The CID spectrum of this ion is characteristically different from that of its isomer $[O{=}C{=}O\cdots H\cdots OH_2]^+$ ($\mathbf{2c}^+$), the proton-bound dimer of CO_2 and H_2O [20]. A third isomer, hydroxyl protonated carbonic acid, $HOC(=O)OH_2^+$ ($\mathbf{2b}^+$), has so far eluded experimental observation. Semi-empirical calculations [21] indicate that this ion lies higher in energy than $\mathbf{2a}^+$, by 33 kcal mol^{-1}, and is separated by a high barrier for interconversion. Very recently reported [22] high-level ab initio results on this system yield ΔH_f (298 K) $\mathbf{2a}^+ = 35.9$ kcal mol^{-1} (for the anti-isomer); ion $\mathbf{2b}^+$ was found to lie 25 kcal mol^{-1} higher in energy with an interconversion barrier of 52 kcal mol^{-1}. The proton-bound dimer $\mathbf{2c}^+$, on the other hand, is reported to lie 4 kcal mol^{-1} lower in energy. Our CBS-QB3 computational results (Table 1) which provide ΔH_f (298 K) values for $\mathbf{2a}^+$, $\mathbf{2b}^+$ and $\mathbf{2c}^+$ of 35, 61 and 33 kcal mol^{-1}, respectively, are in good agreement with the G2 results of the above study [22]. Thus, ions $\mathbf{2a}^+$ and $\mathbf{2c}^+$ are of comparable stability, while $\mathbf{2b}^+$ lies ca. 27 kcal mol^{-1} higher in energy. In this context, we note that the ΔH_f for the proton-bound dimer ion $\mathbf{2c}^+$ can also be estimated from the empirical relationship of Ref. [23], which correlates the hydrogen bond energy and the proton affinity (PA) difference between the dimer components in heterogeneous proton-bound dimers. This procedure yields, using the appropriate PA values from Ref. [24], ΔH_f ($\mathbf{2c}^+$) = 29 kcal mol^{-1}, which is fairly close to the computationally derived value.

In view of these observations, it seemed reasonable to assume that ions $\mathbf{2b}^+$ and $\mathbf{2c}^+$ have stable silicon analogues, viz. $HOSi(=O)OH_2^+$ ($\mathbf{1b}^+$), and $[O{=}Si{=}O\cdots H\cdots OH_2]^+$ ($\mathbf{1c}^+$). These could conceivably be co-generated in the dissociative ionization of $\mathbf{I}^{\bullet+}$, as is depicted in Scheme 1 for the ethylene loss from the m/z 107 ion, the immediate precursor of the m/z 79 ions.

Our calculations, see Table 1, show that all three ions $\mathbf{1a}^+$–$\mathbf{1c}^+$ are minima on the potential energy surface as are the high energy isomers $\mathbf{1d}^+$ and $\mathbf{1e}^+$ which were not further considered. For ions $\mathbf{1a}^+$–$\mathbf{1c}^+$, unlike the situation with the carbon analogues, the proton-bound dimer $[O{=}Si{=}O\cdots H\cdots OH_2]^+$ is now the least stable isomer of the set, lying 79 kcal mol^{-1} higher in energy than the anti-isomer of $Si(OH)_3^+$. This makes it unlikely that this isomer is co-generated in the C_2H_4 loss from m/z 107. This is probably also true for the hydroxyl protonated silicic acid isomer $\mathbf{1b}^+$, which lies 48 kcal mol^{-1} higher in energy than $\mathbf{1a}^+$ while the isomerization barrier $\mathbf{1b}^+ \rightarrow \mathbf{1a}^+$ is fairly low, 22 kcal mol^{-1} (see Table 1). Thus, it is likely that both $\mathbf{I}^{\bullet+}$ and $\mathbf{II}^{\bullet+}$ yield m/z 79 ions of structure $Si(OH)_3^+$ ($\mathbf{1a}^+$).

Nevertheless, the (identical) MI spectra of the mass 79 ions from $\mathbf{I}^{\bullet+}$ and $\mathbf{II}^{\bullet+}$ provide clear evidence that ions $\mathbf{1b}^+$ and/or $\mathbf{1c}^+$ participate in the dissociation of low energy ions $\mathbf{1a}^+$. The MI spectrum (2ffr, 10 keV ions) displays two peaks, at m/z 61 and m/z 19 with an intensity ratio of 7:1. Both peaks have a Gaussian shape. For the loss of H_2O, yielding the m/z 61 ion $HOSi{=}O^+$, the kinetic energy (KER) release measured from the width at half-height, $T_{0.5}$ [25], is 17 meV. For the loss of SiO_2, yielding the m/z 19 H_3O^+ ion, the KER is slightly but significantly higher, $T_{0.5}$ = 23 meV. It is reasonable to expect that the loss of water involves participation of either $\mathbf{1b}^+$ or $\mathbf{1c}^+$. The less



Scheme 1.

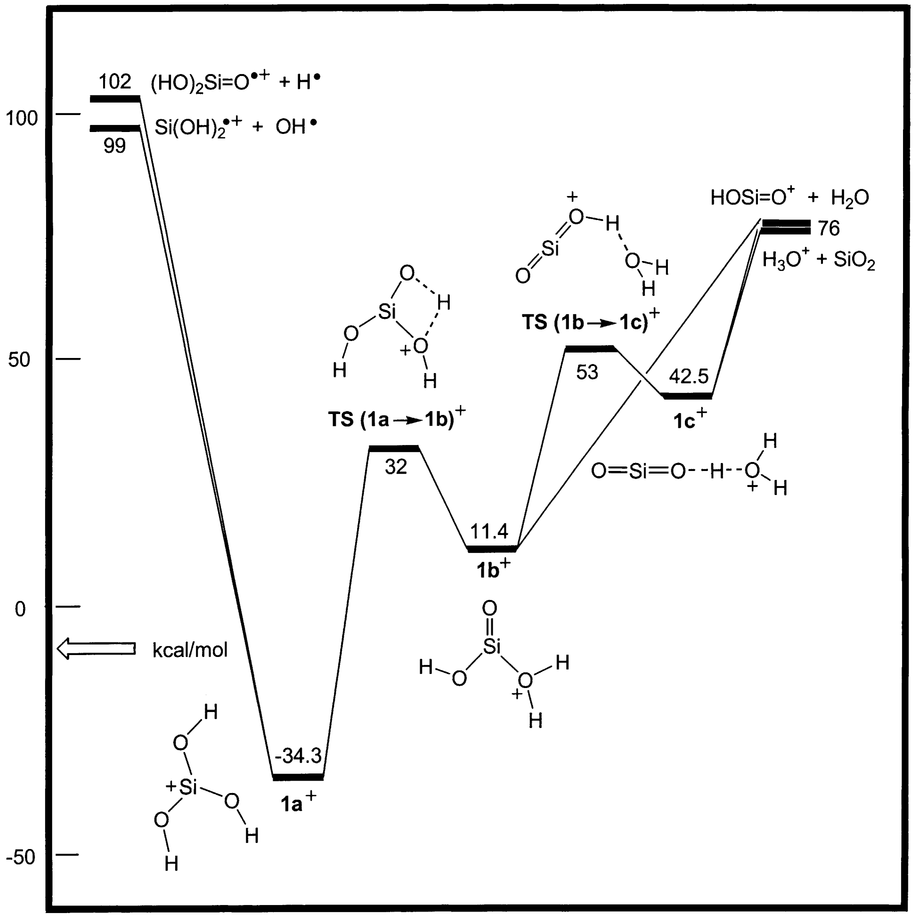


Fig. 1. Potential energy diagram derived from the CBS-QB3 (298 K) calculations of Table 1 describing the isomerization reactions of metastable ions $[Si(OH)_3]^+$.

abundant *m*/*z* 19 H_3O^+ ions on the other hand, could well be generated by direct bond cleavage from the proton-bound dimer **1c**$^+$.

To further probe this proposal, we have calculated the minimum energy requirements for the above metastable dissociations and the two direct bond cleavage reactions that dominate the CID spectrum discussed below. The results are combined in the potential energy diagram of Fig. 1.

It is seen that ions **1a**$^+$ can freely interconvert with their hydroxyl protonated silicic acid isomer **1b**$^+$, at energies well below that required for the H_2O and SiO_2 losses observed in the MI spectrum, while that for the two direct bond cleavage reactions lies even higher in energy. We further note that the energy level for $H_3O^+ + SiO_2$ lies slightly below that for $HOSi{=}O^+ + H_2O$. This implies that the PA of SiO_2 (for which no experimental value is available) is only marginally lower than that of H_2O, 165 kcal mol^{-1} [24]. In line with this, in the optimized geometry of the proton-bound dimer $[O{=}Si{=}O\cdots H\cdots OH_2]^+$, the bridging H is a little closer to the H_2O molecule (1.021 Å vs. 1.273 Å for $H\cdots O{=}Si{=}O$, see Fig. 3). (For the carbon analogue, $[O{=}C{=}O\cdots H\cdots OH_2]^+$, where the PAs of the bridged molecules differ considerably, by 36 kcal mol^{-1} [24], the $O{=}C{=}O\cdots H$ and $H\cdots OH_2$ distances are 1.518 and 1.022 Å, respectively.)

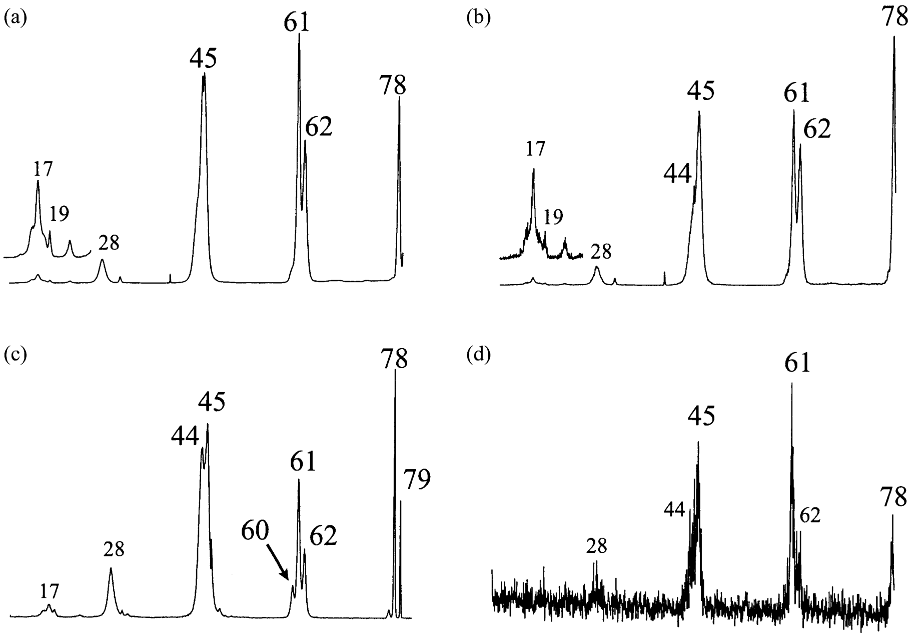


Fig. 2. (a) CID spectrum (3ffr) of 8 keV source generated *m/z* 79 ions $Si(OH)_3^+$; (b) CID spectrum (3ffr) of *m/z* 79 $Si(OH)_3^+$ ions generated from 10 keV *m/z* 107 metastable ions $C_2H_5OSi(OH)_2^+$; (c) NR spectrum (2ffr) of 8 keV *m/z* 79 $Si(OH)_3^+$; (d) CID spectrum (3ffr) of the *m/z* 79 survivor ion in the NR spectrum of (c).

We further note that the calculated stabilization energy of the proton-bound dimer, ca. 33 kcal mol^{-1}, is close to that for symmetric O–H–O bridged proton-bound dimers, ~30.5 kcal mol^{-1} [23]. However, a facile interconversion of $\mathbf{1b}^+$ into the proton-bound dimer apparently does not occur: if the dimer ion were generated from $\mathbf{1b}^+$ below the threshold for dissociation by loss of H_2O, then H_2O and SiO_2 would be lost to the same extent. This does not occur: loss of H_2O dominates the MI spectrum and moreover the associated KER is smaller than that for the loss of SiO_2. Thus, although $TS(\mathbf{1b} \rightarrow \mathbf{1c})^+$ is calculated to lie below the energy levels for the loss of H_2O and SiO_2, the isomerization $\mathbf{1b}^+$ to $\mathbf{1c}^+$ suffers from a substantial kinetic hindrance.

The CID spectra of the source generated *m/z* 79 ions from the two ethoxysilanes are identical. A representative spectrum is presented in Fig. 2a. In line with the proposal, that the stable *m/z* 79 ions are ions $\mathbf{1a}^+$ which can easily interconvert with $\mathbf{1b}^+$ but not $\mathbf{1c}^+$, the spectrum displays intense peaks at *m/z* 78, 62 and 61. Note that *m/z* 19 ions are barely detectable. Other major peaks are *m/z* 45 ($SiOH^+$) and *m/z* 44 ($SiO^{\bullet+}$) which are obviously secondary fragment ions. The spectra also contain a weak doubly charged ion, at *m/z* 39.

Loss of C_2H_4 is the only dissociation of the metastable *m/z* 107 ions $C_2H_5OSi(OH)_2^+$ and the internal energy content of the resulting *m/z* 79 ions is expected to be lower than that of the source generated ions. The energy required for loss of C_2H_4 via a 1,3-H shift leading to $\mathbf{1a}^+$, see Scheme 1, is estimated to be ~30 kcal mol^{-1} [26], considerably less than that required to form $\mathbf{1b}^+$ via a 1,5-H shift, ~45 kcal mol^{-1}, see Fig. 1. Therefore, the metastably generated *m/z* 79 ions from the *m/z* 107 precursor ion may well represent isomerically pure ions $\mathbf{1a}^+$. The CID spectrum of these ions is presented in Fig. 2b. The spectrum is closely similar to that of Fig. 2a but, as seen from the enhanced *m/z* 62:*m/z* 61 peak intensity ratio, the low energy ions are less prone to lose H_2O upon collisional activation. This supports the proposal that the metastably generated *m/z* 79 ions

Table 1
CBS-QB3[a] computational results for the key isomers of the $[Si, O_3, H_3]^{\bullet +}$ system, some carbon analogues and dissociation products

Structure		CBS-QB3 (0 K)	CBS-QB3 (enthalpy)	ΔH_f (0 K)	ΔH_f (298 K)
$Si(OH)_3^+$	**1a**$^+$ (syn)	−516.14491	−516.13846	−31.4	−34.3
$Si(OH)_3^+$	**1a**$^+$ (anti)	−516.14790	−516.14162	−33.3	−36.3
$Si(OH)_3^\bullet$	**1a** (anti)	−515.39565	−516.38837	−188.8	−191.1
$HOSi(=O)OH_2^+$	**1b**$^+$	−516.07208	−516.06564	14.3	11.4
$HOSi(=O)OH_2^\bullet$	**1b**	−516.32300	−516.31565	−143.2	−145.5
$O=Si=O \cdots H \cdots OH_2$	**1c**$^+$	−516.02328	−516.01608	44.9	42.5
$HO(H)Si–O–OH^+$	**1d**$^+$	−515.97150	−515.96540	77.4	74.3
$HO(H)SiO–OH^+$	**1e**$^+$	−515.95878	−515.95159	85.4	83.0
TS (**1a**$^+$ → **1b**$^+$)		−516.04002	−516.03357	34.4	31.5
TS (**1b**$^+$ → **1c**$^+$)		−516.00582	−515.99948	55.8	52.9
TS (**1a** → **1b**)		−516.31712	−516.31097	−139.5	−142.6
$C(OH)_3^+$	**2a**$^+$ (syn)	−264.97708	−264.97205	44.2	40.9
$C(OH)_3^+$	**2a**$^+$ (anti)	−264.98696	−264.98213	38.0	34.6
$HOC(=O)OH_2^+$	**2b**$^+$	−264.94566	−264.94002	63.9	61.0
$O=C=O \cdots H \cdots OH_2^+$	**2c**$^+$	−264.99199	−264.98513	34.8	33.0
$(HO)_2Si=O^{\bullet +}$	m/z 78	−515.43169	−515.42530	50.8	48.9
$(HO)_2Si=O$		−515.82081	−515.81510	−193.3	−195.7
$Si(OH)_2^{\bullet +}$	m/z 62	−440.28228	−440.27705	93.4	91.8
$HOSi=O^+$	m/z 61	−439.63436	−439.62922	134.7	134.0
$HOSi=O^\bullet$ [b]		−439.96896	−439.96419	−75.3	−76.2
$O=Si=O^{\bullet +}$ [c]	m/z 60				221.6
$O=Si=O$ [b]		−439.37501	−439.37077	−67.9	−68.0
$SiOH^+$	m/z 45	−364.52633	−364.52639	151.2	150.9
$SiO^{\bullet +}$ [b]	m/z 44	−363.79760	−363.79428	243.3	243.5
SiO [b]					−23.8
H_3O^+	m/z 19	−76.59652	−76.59265	145.2	143.6

[a] CBS-QB3 energies given in Hartrees, all other components are in kcal mol^{-1}; the calculated ΔH_f (298 K) values for $H^\bullet$, $OH^\bullet$ and H_2O used in Fig. 1 are 52.1, 6.9 and −58.2 kcal mol^{-1}, respectively.

[b] G2 (298 K) calculated values for SiO, SiO_2 and $HOSi=O^\bullet$ are −22.6, −66.2 and −72.9 kcal mol^{-1}, respectively [27]; for SiO and $SiO^{\bullet +}$ experimental values are available, −24.0 and 239.6 kcal mol^{-1}, respectively [24b].

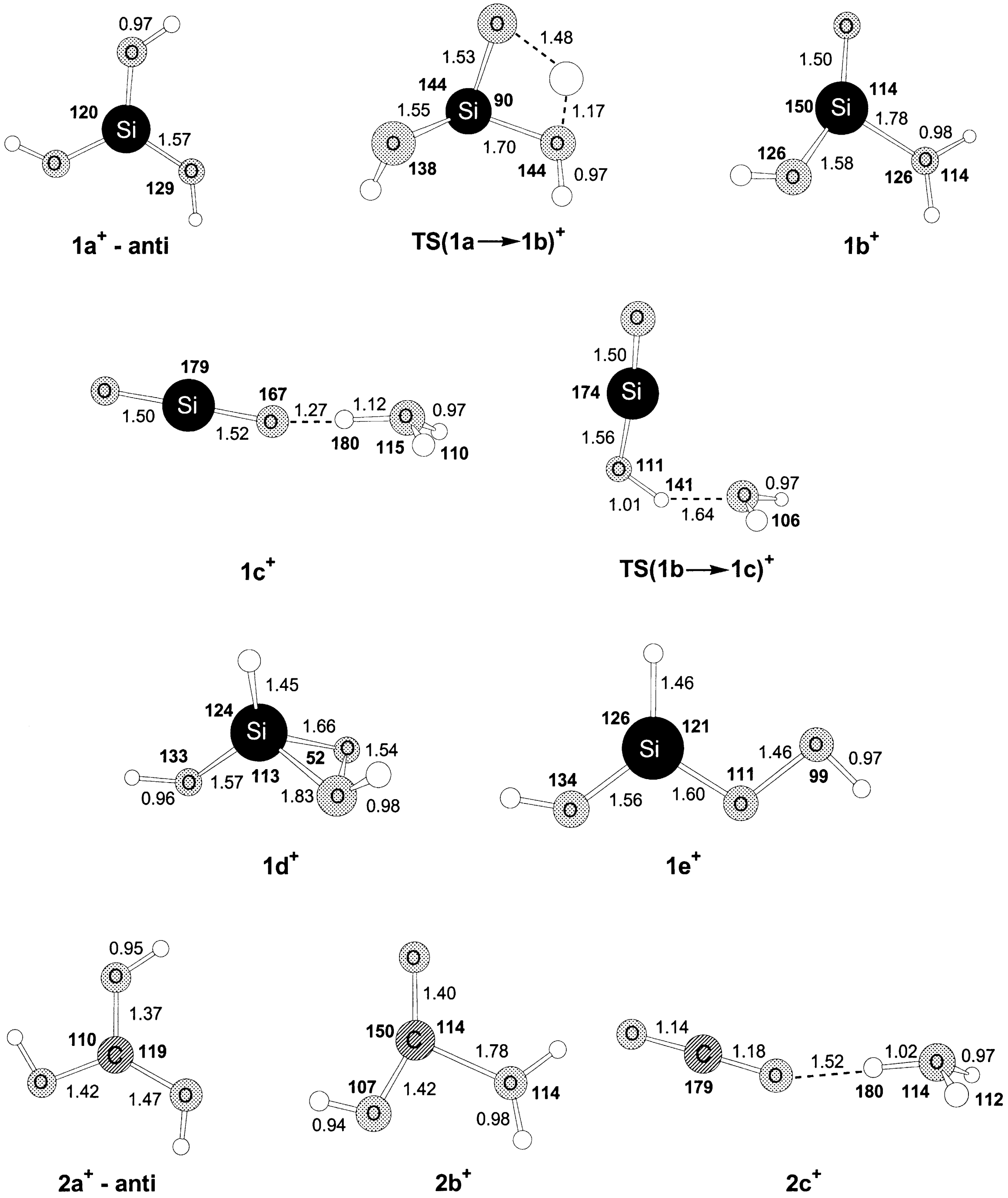
[c] For $SiO_2^{\bullet +}$ spin contamination occurs in the CBS-QB3 calculation. The G2 calculation does not suffer from spin contamination and yields 227.1 kcal mol^{-1}.

are (largely) **1a**$^+$, whereas the source generated ions consist of **1a**$^+$ in admixture with **1b**$^+$.

3.2. Characterization of the neutral species $Si(OH)_3^\bullet$

The neutralization–reionization mass spectra of ions **1a**$^+$ from both precursors are identical and a representative spectrum is shown in Fig. 2c. The spectrum displays a fairly abundant recovery signal at m/z 79 (45% of the base peak at m/z 78). Among ions **1a**$^+$–**1c**$^+$, only **1a**$^+$ is expected to have a stable neutral counterpart and thus the presence of a sizeable recovery signal indicates that the $Si(OH)_3^\bullet$ radical is a stable species on the microsecond time scale of the NR experiment. This is in line with our calculations which show that $Si(OH)_3^\bullet$ (**1a**), is a stable minimum on the potential energy surface with a ΔH_f (298 K) of −191 kcal mol^{-1} (for the anti-isomer). The calculations further indicate, see Table 1, that the neutral counterpart of **1b**$^+$ is only a shallow minimum, which lies 3 kcal mol^{-1} below the transition state for its isomerization into **1a**.

To eliminate the possibility that (part of) the recovery signal in the NR spectrum stems from an isobaric impurity [28], we have obtained its CID spectrum which is presented in Fig. 2d. Although the weak spectrum suffers from a high noise level, there



1a$^+$ - anti

TS(1a⟶1b)$^+$

1b$^+$

1c$^+$

TS(1b⟶1c)$^+$

1d$^+$

1e$^+$

2a$^+$ - anti

2b$^+$

2c$^+$

Fig. 3. Selected optimized geometries of the protonated silicic acid $[Si(OH)_3]^+$, isomers **1a**$^+$–**1e**$^+$ and the carbon analogues **2a**$^+$–**2c**$^+$. Bond angles in degrees and bond lengths in Angstroms.

is little doubt that the survivor ions of Fig. 2c are silicon containing species of structure $Si(OH)_3^+$. Thus, while $Si(OH)_3^\bullet$ is a stable species on the microsecond timescale of the NR experiment, this is not the case for its carbon analogue $C(OH)_3^\bullet$. From the recently reported comprehensive NR study by Gerbaux and Tureček [22], it follows that collisional neutralization of protonated carbonic acid yields transient trihydroxymethyl radicals that dissociate rapidly by loss of a hydrogen atom, so that no survivor species are observed on a timescale $\geq$360 ns.

Two further points deserve comment: (i) comparison of the shapes of the peaks at *m/z* 78, 62 and 61 of the 2ffr CID spectra of **1a**$^+$ with those of its NR spectrum shows that the *m/z* 78 NR peak is less broadened than its CID counterpart, whereas the width of the peaks at *m/z* 61 and 62 shows no change. This suggests that part of the *m/z* 78 ions $(HO)_2Si{=}O^{\bullet+}$ result from collisional ionization of neutral silicic acid molecules $(HO)_2Si{=}O$, generated by loss of $H^\bullet$ from $Si(OH)_3^\bullet$. This reaction is calculated to be endothermic by 47 kcal mol^{-1} (Table 1) and would be associated with only a small reverse activation energy; (ii) the *m/z* 60 peak is not significant in the CID spectrum of **1a**$^+$ and considering the high heat of formation of the $SiO_2^{\bullet+}$ ion, 222 kcal mol^{-1}, this is not surprising. The NR spectrum does display a (moderate) peak at *m/z* 60, which probably originates from collisional ionization of SiO_2. A thermochemically attractive route for its formation involves dehydration of the incipient $Si(OH)_3^\bullet$ radical into $HOSi{=}O^\bullet$ followed by loss of $H^\bullet$. Loss of $OH^\bullet$ from $HOSi{=}O^\bullet$ into SiO has a slightly lower energy requirement and this may explain the enhanced intensity of the *m/z* 44 peak in the NR spectrum.

4. Conclusion

From the combined results of tandem mass spectrometric experiments and CBS-QB3 theoretical calculations, it is concluded that dissociative electron ionization of triethoxysilane, $HSi(OC_2H_5)_3$ and tetraethoxysilane, $Si(OC_2H_5)_4$, yields *m/z* 79 ions having the structure of protonated silicic acid, $Si(OH)_3^+$ (**1a**$^+$). The dissociation of metastable ions **1a**$^+$—via loss of H_2O and SiO_2 to form *m/z* 61 ($HOSi{=}O^+$) and *m/z* 19 (H_3O^+) ions—involves the participation of the high-energy isomers $HOSi({=}O)OH_2^+$ (**1b**$^+$), and $[O{=}Si{=}O\cdots H\cdots OH_2]^+$ (**1c**$^+$), a proton-bound dimer. Neutralization–reionization experiments show that $Si(OH)_3^\bullet$ (**1a**$^\bullet$), is a stable species in the rarefied gas phase, in contrast to its carbon analogue, $C(OH)_3^\bullet$ [22].

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