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Structural Characterization of the Silicon Trioxide Radical Cation ($SiO_3{}^{\bullet+}$) by Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry and ab Initio MO Calculations

Detlef Stöckigt, Norman Goldberg, Jan Hrušák, Detlev Sülzle,[†] and Helmut Schwarz[*]

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

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Abstract: Gas-phase experiments are performed aimed at a structural characterization of $SiO_3{}^{\bullet+}$, which is—as reported earlier [(a) Creasy, W. R.; O'Keefe, A.; McDonald, J. R. *J. Phys. Chem.* **1987**, *91*, 2848. (b) Wlodek, S.; Bohme, D. K. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1643.]—readily available by oxidizing $SiO_2{}^{\bullet+}$ with N_2O, and the combined experimental/theoretical results point to the formation of the covalently bonded trioxide **1**. The absence of oxygen exchange in the thermoneutral reaction of $SiO_3{}^{\bullet+}$ with ${}^{18}O_2$ as well as collision-induced dissociation (CID) experiments of $SiO_3{}^{\bullet+}$ rule out definitively a loosely bound ion–dipole complex $[O_2–SiO_2]^{\bullet+}$ for the initially generated $SiO_3{}^{\bullet+}$ radical cation. In the near-thermal ion–molecule reactions of $SiO_3{}^{\bullet+}$ with X (X = H_2O, N_2O, CH_3CN, and C_2H_4), the $SiO(X)^{\bullet+}$ products are formed with collision rate, and the kinetic isotope effects are negligibly small (1.1–1.3) when D_2O, CD_3CN, and C_2D_4 are employed. The product $SiO(H_2{}^{18}O)^{\bullet+}$, generated from $SiO_3{}^{\bullet+}$ and $H_2{}^{18}O$, upon collisional activation gives rise to $SiOH^+$ and $Si^{18}OH^+$ in a nearly 1:1 ratio, thus pointing to a symmetrical intermediate. From bracketing experiments the standard enthalpy of formation of $SiO_3{}^{\bullet+}$ is estimated as $186 < \Delta H^{\circ}{}_{f,298}(SiO_3{}^{\bullet+}) < 212$ kcal/mol. Preliminary ab initio MO calculations (MP4SDTQ/6-31G*//MP2(Full)6-31G*) of several $SiO_3{}^{\bullet+}$ isomers provide the following information: The ${}^4A_1{}'$ state of the D_{3h}-symmetrical structure **1** is found to correspond to the global minimum, and the slightly distorted C_{2v} structure **2** (${}^2A_1$) is 11.2 kcal/mol less stable than **1**. The weakly bound ion–dipole complexes **5** and **6**, which may serve as intermediates in the collision-induced dissociation of **1**, are only destabilized by 2.2 and 5.5 kcal/mol relative to **1**. For the C_{2v}-symmetric structures **3** and **4**, there is no computational evidence that these radical cations exist as minima on either the doublet or quartet potential energy surfaces of $SiO_3{}^{\bullet+}$.

Introduction

While silicon oxides are ubiquitous on planet Earth's surface, these molecules are much less present[1] in extraterrestrial environments, and the anomalous distribution of atomic silicon in the ionosphere[2] has triggered numerous experimental and theoretical studies aimed at providing evidence for the pathways by which the depletion of ground-state $Si^{\bullet+}({}^2P)$ occurs. Reactions 1 and 2 were proposed[3] to be responsible for the formation of protonated silicon monoxide ($SiOH^+$),[4] which upon ion–electron recombination (eq 2) is suggested to give rise to silicon monoxide in interstellar gas clouds.

$$Si^{\bullet+} + H_2O \longrightarrow SiOH^+ + H^{\bullet} \qquad (1)$$

$$SiOH^+ + e^- \longrightarrow SiO + H^{\bullet} \qquad (2)$$

Higher silicon oxides (SiO_x; $x \geq 2$) are also of interest in the context of studying the intriguing electronic and structural properties of polyoxides. While there exist several reports on the trioxides of carbon,[5] nitrogen,[6] and phosphorus,[7] data on the successful preparation or on a thorough theoretical characterization of the analogous neutral silicon trioxide SiO_3 have not yet been reported in the literature. The radical cations of silicon oxides, $SiO_x{}^{\bullet+}$ (x = 1–4), are available by a stepwise oxidation of atomic silicon ion (eq 3), and the rates of ion formation were measured[8] by using the selected ion flow tube (SIFT) technique.[9]

$$Si^{\bullet+} \longrightarrow SiO^{\bullet+} \longrightarrow SiO_2^{\bullet+} \longrightarrow SiO_3^{\bullet+} \longrightarrow SiO_4^{\bullet+} \qquad (3)$$

Due to the limitation of the SIFT method, a structural characterization of the higher silicon oxides $SiO_x{}^{\bullet+}$ (x = 3, 4) could not be achieved.[10] In this article we will report the results of near-thermal ion–molecule as well as collision-induced dissociation (CID) reactions of $SiO_3{}^{\bullet+}$ using the technique of Fourier-

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[†] Present address: SCHERING AG, PCH-PCS, Müllerstrasse 170, D-13342 Berlin, Germany.

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transform ion cyclotron resonance (FTICR).[11,12] The experimental findings are complemented by preliminary ab initio MO studies of chemically feasible $SiO_3^{\bullet+}$ isomers, including doublet and quartet states.[13]

Experimental and Computational Details

The apparatus (a Spectrospin CMS-47X equipped with an external ion source[14]) and its operation have been described in detail previously.[15] Atomic $Si^{\bullet+}$ is formed via laser desorption/ionization[16] by focusing the beam of a Nd:YAG laser (Spectron Systems, fundamental frequency 1064 nm) onto a silicon wafer which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the $Si^{\bullet+}$ ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. In order to quench the excited $Si^{\bullet+}(^4P)$ state, which is cogenerated (<5%) under the present conditions, argon was admitted to the ICR cell with a constant pressure of ca. 2×10^{-7} mbar. Argon was also used as a collision gas in the CID experiments.[17] Any excited $Si^{\bullet+}$ states which may have survived the quenching procedure were removed by introducing H_2 or D_2 via a selenoid-pulsed valve;[18] from previous studies[4b] it is known that excited $Si^{\bullet+}$ cations (^4P and higher states) undergo facile reactions with molecular hydrogen, while ground-state $Si^{\bullet+}(^2P)$ is nonreactive. Isolation of the most abundant isotope of silicon, i.e. $^{28}Si^{\bullet+}$, was achieved by using FERETS,[19] and great care has been taken to avoid any off-resonance excitation of the ions of interest.[20] The radical cation $SiO_3^{\bullet+}$ was generated as described earlier[8,10b] by reacting $Si^{\bullet+}$ with a mixture of N_2O/Ar (1:10) which was pulsed-in using a second valve. The pressure in the reservoir was ca. 1 mbar, and the valve was opened for 30 ms. After 2 s the reagent gas was pumped away and the $SiO_3^{\bullet+}$ ions were collisionally cooled and isolated as described above. The reagent gases used to probe the ion–molecule reactions of $SiO_3^{\bullet+}$ were introduced via a second leak valve; depending on the ion gauge sensitivity, the pressure of the various gases, as measured with an ionization gauge (Balzers IMG 070), was ca. $(5–10) \times 10^{-9}$ mbar. High-resolution and double-resonance experiments were performed as described earlier.[15,21] For the determination of the rate constants, ion gauge sensitivities, relative to N_2, were taken from the literature[22] as were the polarizabilities[23] and dipole moments.[23] The experimentally determined rate constants, k_R, which were obtained from the plot of $\log[SiO_3^{\bullet+}]$ versus time, were compared with collision rate constants (k_{coll}) as calculated by Su and Chesnavich.[24] A typical example is given in Figure 1 for the reaction of $SiO_3^{\bullet+}$ with H_2O. The rate constants have error bars not exceeding ±25%, and the errors are mostly due to different ion gauge sensitivities for different substances used for the calibration.[25] All ICR experiments were conducted at room temperature (298 K). The thermochemical data used are summarized in Table 1.

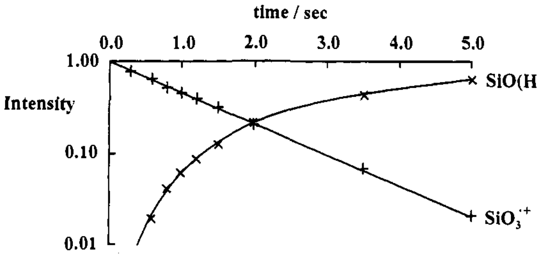

Figure 1. Time evolution of the $SiO_3^{\bullet+}$ (+) and $SiO(H_2O)^{\bullet+}$ (×) ion intensities in the reaction $SiO_3^{\bullet+} + H_2O \rightarrow SiO(H_2O)^{\bullet+} + O_2$. While the neutral molecules are at room temperature ($p_{H_2O} \approx 1.5 \times 10^{-8}$ mbar), the ions are not.

Table 1. Standard Enthalpy of Formation ($\Delta H^\circ_{f,298}$) for Ions and Neutrals As Discussed in the Text[a]

ion	$\Delta H^\circ_{f,298}$ (kcal/mol)	neutral	$\Delta H^\circ_{f,298}$ (kcal/mol)
$Si^{\bullet+}$	295	N_2O	20
$SiO^{\bullet+}$	240	H_2O	–58
$SiO_2^{\bullet+}$	192[b]	SiO_2	–73[b]
$SiO_3^{\bullet+}$	199[c]	C_2H_4	13
$O_2^{\bullet+}$	279	CH_3CN	18

[a] Unless stated otherwise, all values are taken from ref 26. Uncertainties are ±2 kcal/mol except for $SiO_2^{\bullet+}$ and $SiO_3^{\bullet+}$ (see text and ref 30). [b] Taken from ref 8b. [c] This work. Also, see comments in ref 30.

The ab initio MO calculations of the $SiO_3^{\bullet+}$ isomers pertinent to this study were performed on an IBM/RISC 6000 workstation using the GAUSSIAN 92 program package.[27] For the geometry optimization the standard polarized split valence basis set 6-31G* [28] has been used in the framework of the Møller–Plesset (MP) perturbation theory,[29] terminated at the second order. For the evaluation of relative stabilities, fourth-order perturbation theory has been applied including single, double, triple, and quadruple excitations (MP4SDTQ). While in the MP2-calculated geometries all electrons have been included in the correlation (MP2-(Full)), in the MP4SDTQ calculations only the valence electrons were correlated. In addition to the single-determinant-based perturbational treatment, we performed single-point MCSCF calculations (correlating seven electrons in nine orbitals) using the MP2(Full)-optimized geometries. This procedure was necessary because the expectation values $\langle S^2 \rangle$ for the spin projection operator indicated quite large spin contaminations of the wave functions for some of the doublet-state isomers of $SiO_3^{\bullet+}$.

Results and Discussion

As reported earlier,[8] the $SiO_3^{\bullet+}$ species is accessible by consecutive oxidation commencing with atomic silicon ions. Attempts to oxidize $SiO_3^{\bullet+}$ with N_2O to $SiO_4^{\bullet+}$ (*m*/*z* 92) failed under ICR conditions. At the detection limit of the ICR machine, no $SiO_4^{\bullet+}$ is formed; rather, the ionic products, shown in eq 4, are obtained. The occurrence of reaction 4a, together with the formation of $SiO_3^{\bullet+}$ (eq 5), permits an estimate of the standard enthalpy of formation of $SiO_3^{\bullet+}$ by using the thermochemical data given in Table 1, and we arrive at 186 < $\Delta H^\circ_{f,298}(SiO_3^{\bullet+})$ < 212 kcal/mol.[30,31]

$$SiO_3^{\bullet+} + N_2O \xrightarrow{0.9} O_2^{\bullet+} + SiO_2 + N_2 \qquad (4a)$$

$$\xrightarrow{0.1} [SiN_2O_2]^{\bullet+} + O_2 \qquad (4b)$$

$$SiO_2^{\bullet+} + N_2O \rightarrow SiO_3^{\bullet+} + N_2 \qquad (5)$$

Next, we will describe several experiments aimed at obtaining insight in the connectivities of the $SiO_3^{\bullet+}$ radical ion, for which several structures are chemically feasible.

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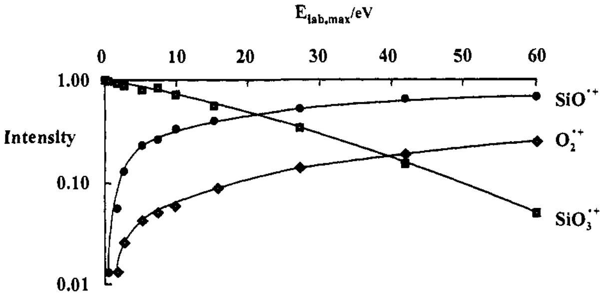

Figure 2. CID experiments of $SiO_3^{\bullet+}$ (collision gas, argon).

If $SiO_3^{\bullet+}$ is subjected to CID experiments with argon as a collision partner, over the whole kinetic energy range applied (Figure 2) the only products formed correspond to $SiO^{\bullet+}$ and $O_2^{\bullet+}$ favoring reaction 6a for all kinetic energies. This is not surprising, as—on the basis of thermochemical data—path 6a is 15 kcal/mol less energy demanding than reaction 6b.

$$\mathrm{SiO_3^{\bullet+}} \xrightarrow{\text{CID}} \begin{cases} \mathrm{SiO^{\bullet+} + O_2} & \text{(6a)} \\ \mathrm{O_2^{\bullet+} + SiO} & \text{(6b)} \end{cases}$$

In the collision experiments no products are observed for the deoxygenation of $SiO_3^{\bullet+}$ (eq 7). While this process is energetically 3 kcal/mol less demanding than process 6b, the large uncertainty (±20 kcal/mol)[8b] in the standard enthalpy of formation of $SiO_2^{\bullet+}$ makes this supposition less convincing, and reaction 7 may well be the most energetically demanding of the three channels.

$$\mathrm{SiO_3^{\bullet+}} \overset{\text{CID}}{\nrightarrow} \mathrm{SiO_2^{\bullet+} + O} \qquad (7)$$

The CID results suggest that, in the course of the collision events, the $SiO_3^{\bullet+}$ species prior to dissociation quite likely isomerizes to an ion–dipole intermediate which contains the two building blocks SiO and O_2. This intermediate, in turn, serves as the immediate precursor for the formation of the products shown in eq 6a,b and in Figure 2, i.e. $SiO^{\bullet+}/O_2$ and $O_2^{\bullet+}/SiO$. In addition to the thermochemical arguments (see above), formation of $SiO_2^{\bullet+}/O$ is not expected to take place from an ion–dipole complex $[O_2–SiO]^{\bullet+}$.

While a loosely bound ion–dipole complex is most likely involved as an intermediate in the CID experiment, such a structure cannot be assigned to the $SiO_3^{\bullet+}$ species *initially generated* in the sequential oxidation of the atomic silicon cation (eqs 3 and 5). This conclusion is based on the observation that the thermoneutral exchange process with dioxygen (eq 8) does not take place. If the $SiO_3^{\bullet+}$ product of eq 5 would correspond to a loosely interacting ion–dipole complex $[O_2–SiO]^{\bullet+}$, replacement of O_2 by its isotopomer $^{18}O_2$ is expected to occur, as these kind of complexes are known to undergo facile exchange reactions.[32]

$$\mathrm{SiO_3^{\bullet+} + {}^{18}O_2} \nrightarrow \mathrm{SiO_{3-x}{}^{18}O_x^{\bullet+} + O_x{}^{18}O_{2-x}} \qquad (8)$$

However, replacement of molecular oxygen is the dominant reaction channel in the ion–molecule reactions of $SiO_3^{\bullet+}$ with various neutral molecules M (eq 9).

Table 2. Rate Constants (in Units of 10^{-10} cm^3 molecule^{-1} s^{-1}) for the Reactions of $SiO_3^{\bullet+}$ with Neutral Molecules M at 298 K

M	products	k_R	k_{coll}	reaction efficiency[c]
N_2O	$[SiN_2O_2]^{\bullet+} + O_2$[a,b]	8	8.1	0.99
H_2O	$SiO(H_2O)^{\bullet+} + O_2$	23	23.8	0.97
CH_3CN	$SiO(CH_3CN)^{\bullet+} + O_2$[b]	34	36.0	0.94
C_2H_4	$SiO(C_2H_4)^{\bullet+} + O_2$[b]	11	10.7	1.03

[a] For the other products, see eq 4a. [b] See ref 30. [c] Defined as k_R/k_{coll}.

$$\mathrm{SiO_3^{\bullet+} + M} \longrightarrow \mathrm{[O_2–Si(O)M]^{\bullet+}} \longrightarrow \mathrm{Si(O)M^{\bullet+} + O_2} \qquad (9)$$

While the O_2 expulsion is not observed for M = O_2, N_2, H_2, CO, CO_2, and CH_4, respectively, thus indicating that the reactions do not take place at all or with rate constants $k_R < 10^{-13}$ cm^3 molecule^{-1} s^{-1}, the processes are extremely efficient with M = C_2H_4 and the polar molecules M = N_2O, H_2O, and CH_3CN (Table 2). The efficiency of O_2 expulsion is demonstrated by a comparison of the experimentally determined rate constants, k_R, with the calculated[24] collision rate constants, k_{coll}. As shown in the last column of Table 2, evaporation of O_2 occurs for all molecules near or with collision rate, and when the ion–molecule reactions of $SiO_3^{\bullet+}$ are performed with D_2O, C_2D_4, and CD_3CN, the kinetic isotope effects (KIEs) on the rate constants are negligibly small (KIE ≈ 1.1–1.3).

For the mechanism of O_2 substitution by M (eq 9) several scenarios are conceivable. As often invoked in gas-phase ion–molecule reactions, the process may proceed via an ion–dipole intermediate $[O_2–Si(O)M]^{\bullet+}$, as indicated in eq 9. However, as suggested by a reviewer, the reaction of $SiO_3^{\bullet+}$ with M could also be viewed as bond rearrangement processes, triggered by an initial electrostatic interaction of the positive charge on $SiO_3^{\bullet+}$ (mostly located on the silicon atom as shown further below) with M. Indeed, the results obtained for the reaction of $SiO_3^{\bullet+}$ with $H_2{}^{18}O$ point to the operation of bond rearrangements.

While most of the ionic products $Si(O)M^{\bullet+}$ formed in process 9 were not structurally characterized, some insight was obtained for the reaction with M = $H_2{}^{18}O$. Collision-induced decomposition of the resulting $SiO(H_2{}^{18}O)^{\bullet+}$ product gives rise to a 1:1 formation of $SiOH^{\bullet+}/Si^{18}OH^{\bullet+}$ (eq 10) throughout the kinetic energy regime applied. This indicates that symmetric silicon dihydroxide ion $SiOH(^{18}OH)^{\bullet+}$ acts as an intermediate in the course of the reaction. However, this experiment does not permit an unequivocal determination of the stage of the overall reaction at which the isomerization $SiO(H_2{}^{18}O)^{\bullet+} \rightarrow SiOH(^{18}OH)^{\bullet+}$ takes place.[33]

$$\mathrm{SiO_3^{\bullet+} + H_2{}^{18}O} \xrightarrow[-O_2]{} \mathrm{SiO(H_2{}^{18}O)^{\bullet+}} \rightleftharpoons \mathrm{SiOH(^{18}OH)^{\bullet+}} \xrightarrow{\text{CID}} \begin{cases} \mathrm{SiOH^{+}} \\ \mathrm{Si^{18}OH^{+}} \end{cases} \qquad (10)$$

Although the experimental findings are in keeping with the formation of a *covalently* bonded $SiO_3^{\bullet+}$ species in the oxidation of $SiO_2^{\bullet+}$ with N_2O,[34] unambiguous structural assignment, i.e. a distinction between **1**, **2**, and **3** (Chart 1), is not possible on the basis of these experiments alone. While ion–dipole complexes of the general structure $[O_2–SiO]^{\bullet+}$ are involved as intermediates in the collision-induced decomposition of $SiO_3^{\bullet+}$ (eq 6) and perhaps also in the ion–molecule reactions of $SiO_3^{\bullet+}$ with neutral molecules M (eq 9), these species neither are formed as the initial oxidation product (eq 5) nor correspond to the global minimum on the potential energy surface (PES) of $SiO_3^{\bullet+}$. The latter aspect is supported by ab initio MO calculations which will be referred to briefly.[13] At all theoretical levels used, the global minimum

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[30] We agree with the comment of a reviewer that, in view of the very large uncertainty in $\Delta H^\circ_{f,298}(SiO_2^{\bullet+})$ of ±20 kcal/mol[8] and the problems inherently associated with deriving thermochemical data from bracketing experiments, the estimate of $\Delta H^\circ_{f,298}(SiO_3^{\bullet+})$ is only qualitative. In line with this, no corrections were made for entropy effects.

[31] While the elemental composition of the ionic product of reaction 4b as well as the products formed in the reactions of $SiO_3^{\bullet+}$ with other neutral molecules M (eq 9) has been established by high-resolution FTICR, no attempts were made to structurally characterize the resulting radical cations.

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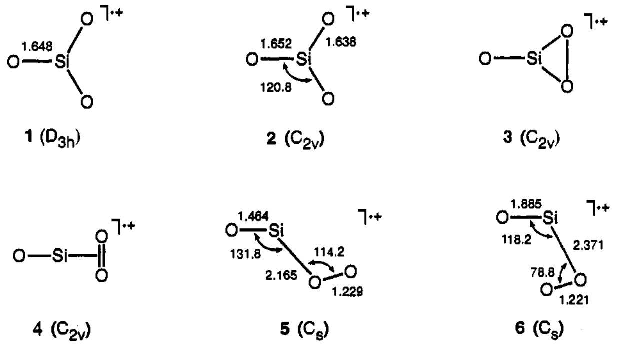
[33] Ligand switching reactions strongly suggest that from the initially formed $SiO(H_2{}^{18}O)^{\bullet+}$ ion both H_2O and $H_2{}^{18}O$ are exchanged in a 1:1 ratio. This points to a facile reversible isomerization $SiO(H_2{}^{18}O)^{\bullet+} \rightleftarrows Si(OH)(O^{18}H)^{\bullet+}$ prior to CID experiments. This view is also underlined by preliminary ab initio MO studies (Fiedler, A. Unpublished results).

[34] We do not object to a reviewer's comment that "formation of $SiO_3^{\bullet+}$ from $SiO_2^{\bullet+}$ by oxygen atom transfer from N_2O can be expected to result in structure **1**. It is energetically favoured as well as mechanistically (electrostatic considerations suggest that the O-atom attack will be on the positively charged Si site in $SiO_2^{\bullet+}$)".

Chart 1. MP2(Full)/6-31G*-Calculated Geometries of Some $SiO_3^{\bullet+}$ Isomers[a]



[a] Bond lengths are given in Å and bond angles in deg. **1** corresponds to the quartet state $^4A_1'$, **2** to a doublet state ($^2A_1$); **5** and **6** ($^4A''$) are ion–dipole complexes of $SiO^{\bullet+}$ ($^2\Sigma$) and O_2 ($^3\Sigma_g^-$).

corresponds to the D_{3h}-symmetrical structure **1**. The MP2-calculated bond length (Chart 1) of 1.648 Å is almost identical with the SiO bond length of 1.650 Å obtained at MP4SDTQ.[35] The three unpaired electrons of the $^4A_1'$ state of **1** occupy the a_1' ($\epsilon_i = -0.905$ hartree) and $2e'$ ($\epsilon_i = -0.866$ hartree) orbitals, which are localized on the three oxygen atoms. The positive charge, as calculated by a Mulliken population analysis, is located on the central silicon atom (1.69 e) while each of the three oxygen atoms is negatively charged (−0.23 e). The $\langle S^2 \rangle$ value of 3.770 for **1** indicates only a small contamination of the single-determinant wave function, and this result is consistent with the data from a MCSCF calculation according to which this configuration contributes to the wave function with 97%.

In contrast, for the doublet electromer of **1**, the wave function is heavily contaminated by higher spin contributions, as suggested by a value of $\langle S^2 \rangle = 1.768$. In addition, according to the MP2-(Full) geometry optimization, the doublet state of **1** is distorted from D_{3h}- to C_{2v}-symmetry, and the structural data of the electromer **2** ($^2A_1$) are given in Chart 1. The electronic structure of **2** ($^2A_1$) is quite similar to that of **1** ($^4A_1'$). The three unpaired electrons are localized at the oxygen atoms, and the Mulliken population analysis places the positive charge on the silicon center (1.67 e), while the oxygen atoms are negatively charged (−0.23 e for the "axial" oxygen and −0.22 e for each of the two "in plane" oxygen atoms). MCSCF calculations indicate that the wave function consists of two contributions (46% and 52% each) which differ only in the α,β spins at the oxygen atoms. With regard to the relative stability, **2** is calculated (MP4SDTQ//MP2(Full)/6-31G*) to be 11.2 kcal/mol less stable than **1**.

All attempts to locate the C_{2v}-symmetrical structure **3** on either the quartet or doublet potential energy surface of $SiO_3^{\bullet+}$ failed, in that the geometry optimization resulted in structures **1** or **2**. Similarly, the T-shaped, C_{2v}-symmetric ion–dipole complex **4** could not be located as a stationary point of the $SiO_3^{\bullet+}$ potential energy surface. However, the complexes **5** and **6** were found to exist as genuine minima on the quartet surface. These two C_s-symmetrical structures correspond to weakly bound complexes of $SiO^{\bullet+}$ ($^2\Sigma^-$) and O_2 ($^3\Sigma_g^-$) as indicated by the long distances of 2.165 (**5**) and 2.371 Å (**6**) separating the two building blocks. In addition, the perturbation of the O_2 molecules in **5** and **6** by the $SiO^{\bullet+}$ radical cation is rather small; this follows directly from a comparison of the O–O bond lengths in **5** and **6** (1.229 and 1.221 Å) as compared with the MP2(Full)-calculated O–O bond length of 1.225 Å for the free oxygen molecule. Interestingly, **5** and **6** are only slightly less stable than **1** (5.0 and 2.0 kcal/mol) and therefore may indeed serve as intermediates en route in the collision-induced dissociation of **1** (eq 6): The evaporation of O_2 to generate $SiO^{\bullet+}$ is the energetically favored reaction channel (see Figure 2) over the whole energy regime. Formation of $O_2^{\bullet+}$, which was accompanied by loss of SiO (reaction 6b), is also favorable, since it only requires electron transfer from O_2 to $SiO^{\bullet+}$ prior to separation of the ion–dipole complexes **5** and **6**.

In conclusion, while more elaborate quantum mechanical calculations are necessary to map out the complete potential energy surface of $SiO_3^{\bullet+}$,[13] the combined experimental/theoretical results strongly suggest that $SiO_3^{\bullet+}$ formed in the gas-phase oxidation of $SiO_2^{\bullet+}$ with N_2O (eq 5)[8] corresponds to the D_{3h}-symmetric species **1**.

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(35) This excellent agreement prompted us not to employ the very expensive MP4SDTQ calculations for the geometry optimization of the other $SiO_3^{\bullet+}$ species shown in Chart 1.