Formation of the high-energy isomer $HSiO^+$ by chemical reaction in the gas phase

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The high-energy isomer $HSiO^+$ of protonated SiO has been generated by a fast O-atom transfer reaction between SiH^+ and N_2O in helium and hydrogen buffer gases at 0.35 Torr and 295 ± 2 K. Formation of $HSiO^+$ by O-atom transfer proceeds in competition with formation of the ground-state $SiOH^+$ isomer, which is formally an insertion reaction. Other insertion reactions were observed in the reactions of SiH^+ with CO_2 and SO_2. The mechanism of insertion is rationalized in terms of sequential O-atom transfer and isomerization of $HSiO^+$ to $SiOH^+$ within the intermediate complex, where the isomerization may be achieved via a proton shuttle within the complex or unimolecularly, when sufficient excess energy is available in the initial O-atom transfer. The high-energy isomer $HSiO^+$ does not convert to $SiOH^+$ by reaction with H_2 at the operating conditions of the experiments.

1. Introduction

Protonated silicon monoxide now has a rich history of experimental and theoretical investigation largely stimulated by the importance of this ion in ionospheric [1] and interstellar [2] chemistry. Many chemical reactions have been identified which protonate SiO, but they all are thermodynamically controlled to yield the ground-state isomer $SiOH^+$ which is protonated at the oxygen-site of SiO [3]. For example, $Si^+(^2P)$ has been shown to react rapidly with the molecules H_2O, CH_3OH, C_2H_5OH, HCOOH and CH_3COOH in R–OH insertion reactions of type

$$Si^{+\cdot}(^2P) + R\text{–}OH \rightarrow SiOH^+ + R^\cdot , \qquad (1)$$

for which $k > 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [4].

Calculations have shown that the silicon-protonated isomer lies higher in energy by as much as 55 to 65 kcal mol^{-1} [5–7]. This large difference in energy has made the high-energy $HSiO^+$ isomer elusive and inaccessible to the reactions investigated so far. Nevertheless, the calculations have shown that $HSiO^+$ corresponds to a minimum in the $SiHO^+$ potential energy surface and they predict the existence of a substantial barrier for the interconversion of $HSiO^+$ to $SiOH^+$ (≈ 35 kcal mol^{-1}) so that it should be possible to isolate $HSiO^+$ [5–7]. Indeed, very recent mass-spectrometric experiments have shown that the high-energy isomer may be formed by the charge reversal reaction

$$HSiO^- + O_2 \rightarrow HSiO^+ + O_2 + 2e \qquad (2)$$

at 8 keV kinetic energy [7] and that it is stable for at least 10 ms when formed in this manner.

We report here the results of a successful search for a chemical route to the formation of the $HSiO^+$ ion, the higher-energy isomer of $SiOH^+$, at thermal energies. A consideration of the formation of the carbon analogue HCO^+ by ion/molecule reactions was not helpful in this regard since, in this case, HCO^+ is the low-energy isomer which is readily produced by the direct protonation of CO. Instead, it was constructive to view SiH^+ as an O-atom acceptor and to search for appropriate O-atom donor molecules. HSi^+ has an O-atom affinity of 122 ± 7 kcal mol^{-1} [#1] and so should be able to accept an O atom from N_2O (40.0) and possibly O_2 (119.2) where O-atom af-

For footnote see next page.

finities in kcal mol^{-1} have been given in parentheses [9].

2. Experimental results and discussion

The experiments were performed with a selected-ion flow tube (SIFT) mass spectrometer which has been described in detail [10]. SiH^+ was produced by direct electron impact ionization of trichlorosilane vapor. The selected SiH^+ appeared to be primarily in its ground $^1\Sigma^+$ state relatively uncontaminated with $^{29}Si^{+\cdot}$ (<0.01%) and the first excited electronic state $^3\Pi$ SiH^+ (<0.05%). The contribution of $^{29}Si^+$ could be estimated by monitoring $^{28}Si^+$ while the observed production of SO_2H^+ from SO_2 provided an upper limit to the presence of $^3\Pi$ SiH^+. The first excited state should transfer a proton to SO_2 since its deprotonation energy, 148 kcal mol^{-1}, which is derived from its appearance energy [11], lies below the proton affinity of SO_2. The buffer and reagent gases were of the usual purity [10].

The production of the high-energy isomer $HSiO^+$ (which, of course, could not be distinguished from the ground-state $SiOH^+$ isomer directly with our mass spectrometer) was monitored with SO_2. SO_2 has a proton affinity (152.1 kcal mol^{-1} [12]) intermediate between the proton affinities of the two sites of protonation in SiO (131.6 and 192.4 kcal mol^{-1} for the Si and O sites computed at the MP4/6-31G**//6-31G** level of theory [6]), so that it undergoes proton-transfer selectively with the high-energy isomer. N_2O also has an intermediate proton affinity (138.8 kcal mol^{-1} [12]) but was not useful as a monitor gas because of the mass coincidence of $SiHO^+$ and N_2OH^+. The more stable $SiOH^+$ isomer was found to be unreactive with SO_2 and N_2O, $k < 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, so that the relative abundance of $HSiO^+$ could be determined from the fractional disappearance of m/z 45 containing $HSiO^+$ (and N_2OH^+ in the experiments with N_2O) with the addition of SO_2 downstream, or from the appearance of SO_2H^+.

Table 1 provides a summary of product distributions and bimolecular rate coefficients obtained for reactions of SiH^+. Of the four reactions investigated, only the reaction with N_2O produces the high-energy isomer $HSiO^+$. The evidence for its formation is unambiguous and only in this case is it exothermic. At least 1 in 4 reactive collisions produces $HSiO^+$ while

Table 1
Product distributions and bimolecular rate coefficients (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) for reactions of SiH^+ with various molecules measured at 295 ± 2 K using the SIFT technique

Molecule (PA) [a]	Products	PD [b]	k_{exp} [c]	k_c [d]	ΔH^0_{298} [e]
O_2 (101.9)	$HSiO_2^+$	1.0	0.005	0.76	
	$SiOH^+ + O$				−64
	$HSiO^+ + O$				−3
CO_2 (130.9)	$SiOH^+ + CO$	0.78	0.19	0.91	−52
	$HCO^+ + SiO$	0.22			−5
N_2O (138.8)	$SiOH^+ + N_2$	0.77	0.56	1.0	−139
	$HSiO^+ + N_2$	0.23 [f]			−78
SO_2 (152.1)	$SiOH^+ + SO$	1.0	1.2	1.9	−48

[a] The proton affinity is given in parentheses at 298 K in kcal mol^{-1} from ref. [12].

[b] Primary product ions which contribute more than 5%. The product distributions are estimated to be accurate to ±30%.

[c] The accuracy of the rate coefficients is estimated to be within ±30%. The measurements were made in helium buffer gas at 0.35 Torr and, in the case of N_2O, in hydrogen buffer gas at 0.35 Torr as well.

[d] The collision rate coefficients are derived using the combined variational transition-state theory-classical trajectory model of ref. [13].

[e] The standard enthalpy changes for reaction are uncertain by about 5 kcal mol^{-1}.

[f] The PD for $HSiO^+$ formation is a lower limit if fractions of the sequential reaction with N_2O and the monitor reaction with SO_2 lead to isomerization to $SiOH^+$.

[#1] The enthalpy of formation of $HSiO^+$ (211.6 ± 4 kcal mol^{-1}) was derived from the computed proton affinity of the silicon site of SiO (131.6 ± 2 kcal mol^{-1}) taken from ref. [6] and enthalpies of formation for O, SiH^+, SiO and H^+ were taken from ref. [8].

the remainder of the reactive collisions of SiH^+ lead to $SiOH^+$ in what is, formally, an O-atom insertion reaction. With SO_2 only the insertion is observed and with CO_2 protonated CO also appears as a product ion. The reaction with O_2 was observed to be very slow, $k \leqslant 5\times10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$, and the adduct ion $HSiO_2^+$ seemed to be the only product ion.

The products observed for the insertion reactions may be understood in terms of a proton "shuttle" mechanism initiated by O-atom transfer within the intermediate complexes

$$\begin{array}{l} SiH^+ + OX \leftrightarrow [HSi^+ ... OX \\ \quad \leftrightarrow \underset{\displaystyle HSiO^+}{\underset{\downarrow}{HSiO^+ ... X}} \leftrightarrow \underset{\displaystyle XH^+}{\underset{\downarrow}{SiO ... XH^+}} \leftrightarrow \underset{\displaystyle SiOH^+}{\underset{\downarrow}{SiOH^+ ... X}}], \end{array} \qquad (3)$$

even when the O-atom transfer is endothermic overall, providing that the endothermicity is less than, or comparable to, the ion–neutral interaction energy, $\approx$10–15 kcal mol^{-1} [9,14]. The O-atom transfer reaction with N_2O is of course exothermic overall so that $HSiO^+$ and N_2 may immediately depart as products. We propose that when such a departure is endothermic by less than the ion–neutral interaction energy, as is the case with CO_2 and SO_2 for which the endothermicities are only 6 and 10 kcal mol^{-1}, respectively, the $HSiO^+$ may isomerize within the complex and lead to the insertion product $SiOH^+$ via a proton "shuttle" with X if the shuttle X has a proton affinity which lies between the proton affinities of the Si and O sites of SiO. This is the case for X=CO, for which the proton affinity is known to be 141.9 kcal mol^{-1} [12], and probably also for X=SO, for which however the proton affinity is not known. For the reaction with CO_2 formation of protonated X is also exothermic overall and occurs with an efficiency of 22%. The failure of the reaction with O_2 to form any of the two isomers is interesting. The O-atom transfer may well be endothermic overall given the uncertainty in the enthalpy change, -3 ± 5 kcal mol^{-1}, (and probably is, given the failure to observe O-atom transfer), but the ion–neutral interaction energy should allow the intramolecular O-atom transfer. Formation of the $SiOH^+$ on the other hand is highly exothermic overall (more than 60 kcal mol^{-1}) but the proton affinity of the shuttle, the O atom in this case, is too low (116 kcal mol^{-1}) to permit the intramolecular isomerization (and the departure of $OH^+ + SiO$ as separate species is endothermic by 13 ± 2 kcal mol^{-1}).

In the reaction with N_2O for which $X=N_2$, the transfer of a proton from $HSiO^+$ to N_2 is endothermic by 15 ± 3 kcal mol^{-1} so that the shuttle mechanism will not serve to isomerize $HSiO^+$ unless more than this amount of internal energy is deposited in the $HSiO^+$ by the O-atom transfer. Indeed, in this case, the excess energy in the initial O-atom transfer is sufficient (78 kcal mol^{-1}) to deposit enough internal energy into $HSiO^+$ for the shuttle mechanism to occur and even for unimolecular isomerization to $SiOH^+$ to occur. The threshold for isomerization has been estimated theoretically to be about 35 kcal mol^{-1} [7].

Finally, we can report that the catalytic conversion reaction

$$HSiO^+ + H_2 \rightarrow SiOH^+ + H_2 \qquad (5)$$

does not take place with a significant rate coefficient at room temperature and 0.35 Torr pressure of H_2. Experiments with hydrogen buffer indicated no change in the characteristics of the reaction of HSi^+ with N_2O. This result is not surprising since $HSiO^+$ does not possess the insertive quality of the carbyne-cation $HOC{:}^+$, the higher-energy isomer in the analogous carbon system, which readily isomerizes to HCO^+ in the presence of H_2 [15]. The mechanism of this isomerization can again be understood in terms of the participation of a proton shuttle, H_2 in this case, as described in [16]

$$\begin{array}{l} HOC^+ + H_2 \leftrightarrow [COH^+ ... H_2 \leftrightarrow CO ... H_3^+ \\ \quad \leftrightarrow OCH^+ ... H_2] \rightarrow HCO^+ + H_2 . \end{array} \qquad (6)$$

The formation of the intermediate $[CO...H_3^+]$ is essentially thermoneutral and, in fact, $CO + H_3^+$ are also observed as bimolecular products in the overall reaction of HOC^+ with H_2. The analogous mechanism is not possible for the isomerization of $HSiO^+$ to $SiOH^+$ in the presence of H_2 because of the large difference in the proton affinities of the Si site of SiO and H_2, viz. $\approx$31 kcal mol^{-1}.

The non-reactivity of $HSiO^+$ with H_2 and the large value predicted for the permanent dipole moment of this ion, viz. 6 D [17], have encouraging implications for the possible spectroscopic detection of

$HSiO^+$ in the circumstellar shells of oxygen-rich stars or in dense interstellar clouds.

Current experiments in our laboratory are directed toward a search for analogous chemical routes leading to the formation of the higher-energy isomer of the sulfur analogue $HSiS^+$, which we have predicted to lie ≈ 12 kcal mol^{-1} above the ground-state isomer $SiSH^+$ [6].

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