

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

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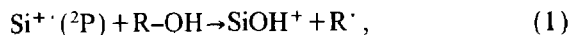
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The high-energy isomer HSiO^+ of protonated SiO has been generated by a fast O-atom transfer reaction between SiH^+ and N_2O in helium and hydrogen buffer gases at 0.35 Torr and 295 ± 2 K. Formation of HSiO^+ by O-atom transfer proceeds in competition 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

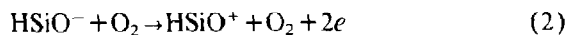
Protonated silicon monoxide now has a rich history of experimental and theoretical investigation largely stimulated by the importance of this ion in ionospheric [1] and interstellar [2] chemistry. Many chemical reactions have been identified which protonate SiO, but they all are thermodynamically controlled to yield the ground-state isomer SiOH^+ which is protonated at the oxygen-site of SiO [3]. For example, $\text{Si}^+(\text{}^2\text{P})$ has been shown to react rapidly with the molecules H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCOOH and CH_3COOH in R-OH insertion reactions of type



for which $k > 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [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^+ ($\approx 35 \text{ kcal mol}^{-1}$) 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



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 $122 \pm 7 \text{ kcal mol}^{-1}$ #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 ¹Σ⁺ state relatively uncontaminated with ²⁹Si⁺ (<0.01%) and the first excited electronic state ³Π SiH⁺ (<0.05%). The contribution of ²⁹Si⁺ could be estimated by monitoring ²⁸Si⁺ while the observed production of SO₂H⁺ from SO₂ provided an upper limit to the presence of ³Π SiH⁺. The first excited state should transfer a proton to SO₂ since its deprotonation energy, 148 kcal mol⁻¹, which is derived from its appearance energy [11], lies below the proton affinity of SO₂. The buffer and reagent gases were of the usual purity [10].

^{a1} 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 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 SO₂. SO₂ 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. N₂O 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 N₂OH⁺. The more stable SiOH⁺ isomer was found to be unreactive with SO₂ and N₂O, *k* < 10⁻¹² cm³ 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 N₂OH⁺ in the experiments with N₂O) with the addition of SO₂ downstream, or from the appearance of SO₂H⁺.

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 N₂O 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 cm³ 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)} | <i>k</i> _{exp} ^{c)} | <i>k</i> _c ^{d)} | Δ <i>H</i> 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 ₂ O (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 N₂O, in hydrogen buffer gas at 0.35 Torr as well.

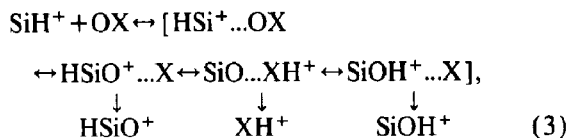
^{d)} The collision rate coefficients are derived using the combined variational transition-state theory-classical trajectory model of ref. [13].

^{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 N₂O and the monitor reaction with SO₂ lead to isomerization to SiOH⁺.

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, $k \leq 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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

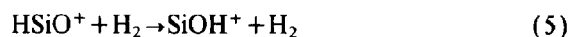


even when the O-atom transfer is endothermic overall, providing that the endothermicity is less than, or comparable to, the ion-neutral interaction energy, $\approx 10\text{--}15 \text{ kcal mol}^{-1}$ [9,14]. The O-atom transfer reaction with N_2O is of course exothermic overall so that HSiO^+ and N_2 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 $\text{X}=\text{CO}$, for which the proton affinity is known to be 141.9 kcal mol^{-1} [12], and probably also for $\text{X}=\text{SO}$, 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, $-3 \pm 5 \text{ kcal mol}^{-1}$, (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 de-

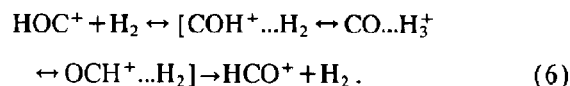
parture of $\text{OH}^+ + \text{SiO}$ as separate species is endothermic by $13 \pm 2 \text{ kcal mol}^{-1}$).

In the reaction with N_2O for which $\text{X}=\text{N}_2$, the transfer of a proton from HSiO^+ to N_2 is endothermic by $15 \pm 3 \text{ kcal mol}^{-1}$ 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



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]



The formation of the intermediate $[\text{CO} \dots \text{H}_3^+]$ is essentially thermoneutral and, in fact, $\text{CO} + \text{H}_3^+$ 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. $\approx 31 \text{ kcal mol}^{-1}$.

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 $\approx 12 \text{ kcal mol}^{-1}$ above the ground-state isomer SiSH^+ [6].

Acknowledgement

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