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Gas-phase reactions of Si⁺ and SiOH⁺ with molecules containing hydroxyl groups: Possible ion-molecule reaction pathways toward silicon monoxide, silanoic acid, and trihydroxy-, tri...

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consistent with a picture that the two reactions are separate. The electron for the electron-transfer reaction quite likely comes from a π orbital in the double bond. This does not involve the chlorine atom. So we picture the reactions as occurring on three potential-energy surfaces. The reactants approach along a covalent surface. They may then encounter one of two surface crossings, both ionic in nature. One of these has the structure $RX^+ + SbF_5^-$ and leads to electron transfer, and the other has the structure $R^+ + SbF_5Cl^-$ and leads to halide transfer. Quite likely, the choice of reaction path—which surface crossing is encountered—is governed by the orientations of the reactant molecules as they collide. When the reaction involves a saturated halide, the ionization potential of the halide is high, and the surface leading to

electron transfer may then be inaccessible. However, halide transfer can still take place.

Acknowledgment. Research support from the National Science Foundation under Grant CHE-8201164 is gratefully acknowledged. We also thank Yound-duk Huh for helping in some of the later experiments.

Registry No. SbF_5 , 7783-70-2; $H_3C(CH_2)_3I$, 542-69-8; $H_3CCH_2CH(CH_3)I$, 513-48-4; $(H_3C)_3Cl$, 558-17-8; $(H_3C)_2CH=CH_2I$, 513-38-2; $(H_3C)_3CCOCl$, 3282-30-2; $H_3C(CH_2)_3COCl$, 638-29-9; $(H_3C)_2CHCH_2COCl$, 108-12-3; $H_3CCH=CHCOCl$, 10487-71-5; $H_2C=C(CH_3)COCl$, 920-46-7; $H_2C=CHCH_2COCl$, 1470-91-3; cyclopropanecarbonyl chloride, 4023-34-1.

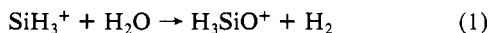
Gas-Phase Reactions of Si^+ and $SiOH^+$ with Molecules Containing Hydroxyl Groups: Possible Ion-Molecule Reaction Pathways toward Silicon Monoxide, Silanoic Acid, and Trihydroxy-, Trimethoxy-, and Triethoxysilane

S. Wlodek, A. Fox, and D. K. Bohme*

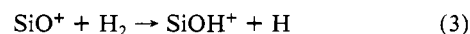
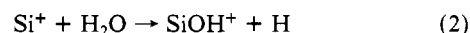
Contribution from the Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ontario, Canada M3J 1P3. Received April 1, 1987

Abstract: Reactions of ground-state Si^+ (2P) and $SiOH^+$ ions have been investigated with H_2 , D_2 , CO , H_2O , CH_3OH , C_2H_5OH , $HCOOH$, and CH_3COOH at 296 ± 2 K with the selected-ion flow tube (SIFT) technique. Both ions were found to be unreactive toward H_2 , D_2 , and CO . Ground-state silicon ions were observed to react with the hydroxyl-containing molecules to produce the silene cation $SiOH^+$, which may neutralize by proton transfer or by recombination with electrons to form silicon monoxide. $SiH_3O_2^+$, which may neutralize to produce silanoic acid, was observed to be the predominant product in the reactions of $SiOH^+$ with H_2O , C_2H_5OH , and $HCOOH$, while direct formation of silanoic acid is likely in the reaction observed between $SiOH^+$ and CH_3COOH . A single mechanism involving O-H insertion of the $SiOH^+$ silylene cation provides a plausible explanation for all of the results obtained with this ion. Also, further chemistry was observed to be initiated by $SiH_3O_2^+$. Solvation was the predominant channel seen with water and ethanol while $SiCH_3O_3^+$ and $SiH_5O_3^+$ were the predominant products observed with formic acid. Several reaction sequences were identified in methanol, ethanol, and formic acid which are postulated to lead to the complete saturation of Si^+ forming ions of the type $HSi(OCH_3)_3H^+$, $HSi(OC_2H_5)_3H^+$, and $HSi(OH)_3H^+$ which may neutralize to generate trimethoxysilane, triethoxysilane and trihydroxysilane, respectively.

It is well-known that the gas-phase chemistry of silicon is quite different from that of carbon.^{1,2} For example, the silicon-oxygen double bond is much less commonly known than the carbon-oxygen double bond. Experimental evidence for the existence of silicon analogues of the simple carbon molecules of formaldehyde and formic acid has been achieved only recently with matrix experiments at 17 K in a study of photoinduced reactions of oxygen atoms with silane.³ There is a strong indication that the silicon analogue of formaldehyde is formed in the gas phase as well. The emission recently observed from the product of the reaction of ozone with silane can be ascribed to an energy-rich H_2SiO molecule.⁴ Also the ion/molecule reaction 1 has been observed in the gas phase.^{5,6} The ionic product of this reaction is likely



to be protonated silanone and to yield silanone upon neutralization by proton transfer or recombination with electrons. Protonated silicon monoxide has also been shown to be produced in the gas phase by the ion/molecule reactions 2 and 3.⁷ Reaction 2 is believed to be responsible for the formation of $SiOH^+$ in the



Earth's atmosphere (in which silicon is introduced by meteor ablation).⁷ Also, reaction 3 has been suggested as a critical step in the production of silicon monoxide in interstellar gas clouds by the neutralization of $SiOH^+$.^{8,9}

Here we report results of gas-phase measurements of the chemistry initiated by Si^+ in the vapors of water, methanol, ethanol, formic acid, and acetic acid. The study provides several new pathways for the formation of $SiOH^+$ which itself is found to be reactive. For example, $SiOH^+$ ions were found to dehydrate formic acid and ethanol molecules to form $SiH_3O_2^+$ ions. The deprotonation of the latter ions by proton transfer to a molecule

(1) Burger, H.; Eujen, R. *Topics in Current Chemistry: Silicon Chemistry I*; Davison, A., Dewar, M. J. S., Hafner, K., Heilbronner, E., Hofman, U., Lehn, J. M., Niedenzu, K., Schafer, K., Wittig, G., Eds.; Springer-Verlag: West Berlin, 1974.

(2) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(3) (a) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567. (b) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1985**, *89*, 3261.

(4) Glinski, R. J.; Gole, J. L.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5891.

(5) Cheng, T. M. H.; Lampe, F. W. *J. Phys. Chem.* **1973**, *77*, 2841.

(6) Shin, S. K.; Beauchamp, J. L. *J. Phys. Chem.* **1986**, *90*, 1507.

(7) Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E.; Viehland, L. A. *J. Chem. Phys.* **1981**, *75*, 669.

(8) Millar, T. J. *Astrophys. Space Sci.* **1980**, *72*, 509.

(9) Clegg, R. E. S.; van IJzendoorn, L. J.; Allamandola, L. J. *Mon. Not. R. Astron. Soc.* **1983**, *203*, 125.

Table I. Rate Constants (in units of 10^{-9} cm³ molecule⁻¹ s⁻¹) and Product Distributions for Reactions of Si⁺ (²P) at 296 ± 2 K

neutral reactant	products	product distribution ^a	k_{exptl}^b	k_c^c
H ₂ (D ₂)	no reaction		≤0.0002 ≤0.0001 ^d	1.5 (1.1)
CO	no reaction		≤0.00002	0.91
H ₂ O	SiOH ⁺ + H	1.0	0.23 0.23 ^d	2.7
CH ₃ OH	SiOH ⁺ + CH ₃ SiOCH ₃ ⁺ + H	0.75 0.25	2.2	2.4
C ₂ H ₅ OH	SiOH ⁺ + C ₂ H ₅	1.0	2.5	2.4
HCCOOH	SiOH ⁺ + CHO	1.0	2.3	1.9
CH ₃ COOH	SiOH ⁺ + CH ₃ CO CH ₃ CO ⁺ + SiOH	0.70 0.30	3.0	2.3

^aPrimary product ions which contribute more than 5%. The product distributions have been rounded off to the nearest 5% and are estimated to be accurate to ±30%. ^bThe accuracy of the rate constants is estimated to be better than ±30%. ^cCollision rate constants are derived from the combined variational transition state theory—classical trajectory study of: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183. ^dReference 7.

M or recombination with electrons may lead to neutral silanoic acid according to reaction 4. Also, further reactions were



identified which provide routes toward the complete saturation of Si⁺ and the production of substituted silane ions which provide interesting opportunities for the formation of new silicon/oxygen compounds.

Experimental Section

The measurements were performed with the selected-ion flow tube (SIFT) apparatus in the Ion Chemistry Laboratory.^{10,11} Silicon ions were generated by electron ionization of either pure SiCl₄ (Aldrich) or a 10 mol % mixture of SiCl₄ in deuterium with electron energies in the range from 40 to 50 eV. The ions were mass selected and injected into helium buffer gas at pressures of ca. 0.35 Torr and energies of ca. 15 to 30 V. The deuterium was added to remove the excited Si⁺ (⁴P) ions. Impurity ions observed downstream had intensities ≤15% of the Si⁺ signal. The main impurity ions were SiOH⁺ and SiCl⁺, which are thought to arise from the reactions of Si⁺ with H₂O impurity in the helium buffer gas and SiCl₄ leaking from the source, respectively. In some experiments Si(CH₃)₃ (Stohler Isotope Chemicals) was used instead of SiCl₄, and SiOH⁺ and Si(CH₃)₃⁺ were the main impurity ions (≤10%) in this case. SiOH⁺ ions were produced by introducing water vapor upstream in the flow tube in which Si⁺ ions were initially dominant or by electron ionization of (CH₃)₃SiOH prepared by the hydrolysis of (CH₃)₃SiCl.¹² All experiments were done at 296 ± 2 K.

Reagent vapors were derived from HCCOOH, CH₃COOH, CH₃OH (BDH Chemicals, ≥98, 99.7, and 99.5%, respectively), C₂H₅OH (Consolidated Alcohols, absolute), and C₂D₅OD (MSD Isotopes, ≥99 atom % D). All the reagent and source gases and the helium buffer gas were of a minimum purity of 99.5 mol %.

Results and Discussion

Reactions of Si⁺. The rate constants and product distributions determined for the reactions of Si⁺ investigated in this study are summarized in Table I. Care had to be taken in these measurements to ensure that the Si⁺ ions were in their ground electronic state. When Si⁺ was generated from 100% SiCl₄, about 80% of the selected Si⁺ ions reacted with deuterium by D atom transfer to give SiD⁺ as is indicated in Figure 1a and in reaction 5. D atom transfer is endothermic with the ground state of Si⁺



so that the reactive component of Si⁺ in Figure 1a and the state of Si⁺ in reaction 5 are likely to be the first excited state, Si⁺ (²P), which has an energy about 5.3 eV above the ground state, Si⁺

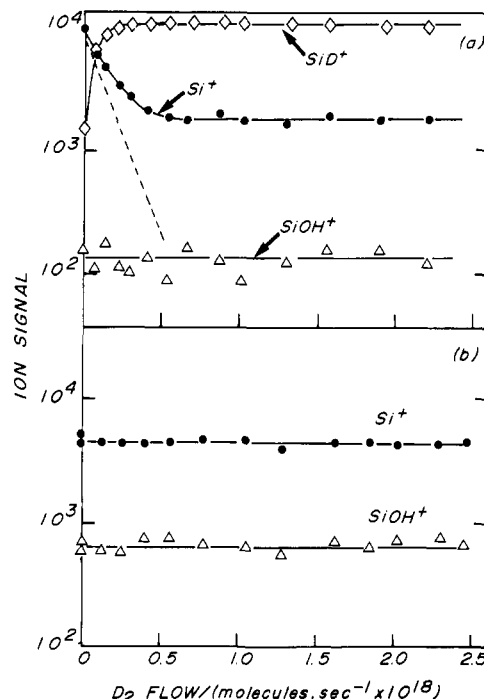


Figure 1. The response observed for selected silicon ions toward deuterium added into the reaction region of the SIFT apparatus: (a) Si⁺ generated from pure SiCl₄, (b) Si⁺ generated from a 10 mol % mixture of SiCl₄ in deuterium. The electron energy is 50 eV and the nominal ion injection energy is 36 V. Helium was used as the buffer gas. $P = 0.35$ Torr, $\bar{v} = 6.7 \times 10^3$ cm s⁻¹, $L = 46$ cm, and $T = 293$ K. The SiOH⁺ ions are present due to the reaction of Si⁺ with the water vapor impurity in the buffer gas. The dashed decay is due exclusively to the reactive component of the selected Si⁺.

(²P).¹³ An analysis of the decay of this reactive component provided a rate constant of $(7.7 \pm 2.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ for reaction 5. The Si⁺ ions generated and selected from a mixture of SiCl₄ and D₂ in the ion source showed no reactivity toward deuterium as is evident in Figure 1b. The Si⁺ ions generated in this fashion should therefore be in their ground (²P) state. Deuterium was added into the ion source in all of the measurements indicated in Table I so that these should all correspond to reactions involving ground-state Si⁺ (²P) ions.

No reactions were observed between Si⁺ (²P) and the molecules H₂, D₂, and CO.

As is evident from Table I, reactions were observed with all of the other molecules, and SiOH⁺ was the main product in each case. Other product ions were also significant in the reactions with methanol (SiOCH₃⁺) and acetic acid (CH₃CO⁺). In the latter reaction the other possible product ion with m/z 43, SiCH₃⁺, can be ruled out because of endothermicity.¹⁴ Figure 2 presents results obtained for a measurement of the reaction of Si⁺ with formic acid.

There are two possible isomers of protonated silicon monoxide: SiOH⁺ and HSiO⁺. Quantum chemical calculations have shown

(13) Martin, W. C.; Zalubas, R. *J. Phys. Chem. Ref. Data* **1983**, *12*, 323.

(14) A value of 264 kcal mol⁻¹ can be derived for the heat of formation of SiCH₃⁺ from the available appearance potential of 14.05 ± 0.05 eV from CH₃SiH₃ and the heat of formation of -7.8 kcal mol⁻¹ for CH₃SiH₃. Production of SiCH₃⁺ is then endothermic for the reaction of Si⁺ with CH₃COOH to produce COOH, CO + OH, or CO₂ + H by at least 30 kcal mol⁻¹, and for the reaction of SiOH⁺ with CH₃COOH to produce H₂O + CO₂, HCCOOH + O, CO + H₂O₂, or CO + H₂O + O by at least 62 kcal mol⁻¹. A heat of formation for SiOH⁺ of 154 ± 3 kcal mol⁻¹ can be derived from the proton affinity for SiO of 189 ± 3 kcal mol⁻¹. The appearance potential and remaining heats of formation were taken from the following: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Ser.* **6**, Suppl. 1 **1977**. Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* **1969**, *26*, 41. The heat of formation of CH₃SiH₃ was taken from: Bell, T. N.; Perkins, K. A.; Perkins, P. G. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1779.

(10) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.

(11) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *55*, 69.

(12) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw Hill: New York, 1965; p 78.

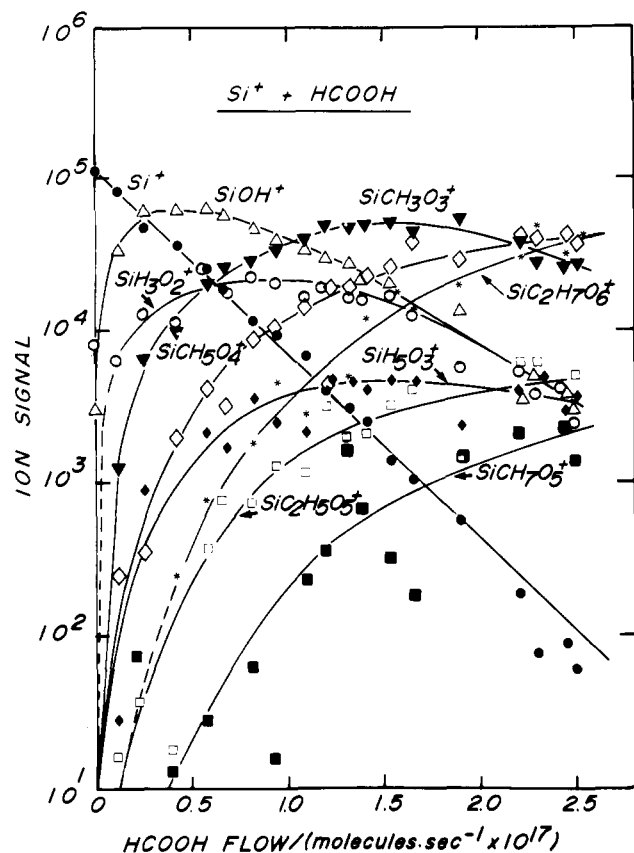


Figure 2. The observed variations in ion signals recorded for the addition of formic acid vapor into the reaction region of the SIFT apparatus in which Si^+ is initially established as the dominant ion in helium buffer gas. $P = 0.346$ Torr, $\bar{v} = 6.4 \times 10^3$ cm s $^{-1}$, $L = 46$ cm, and $T = 295$ K. The Si^+ is derived from a 10 mol % mixture of SiCl_4 in D_2 at an electron energy of 75 eV.

that the isomer protonated at oxygen is 66.5 kcal mol $^{-1}$ more stable than the isomer protonated at silicon.¹⁵ This energy difference is sufficient to exclude the formation of the isomer protonated at silicon, which would occur by insertion into the O–H bond of the oxidized hydrocarbons that were investigated.

Since the isomer protonated at oxygen is the preferred product, C–OH bond insertion should be the preferred mechanism for the reactions with the alcohols and carboxylic acids. The additional formation of some SiOCH_3^+ in the case of methanol is likely to result from Si^+ insertion into the O–H bond with concomitant elimination of the H atom. Insertion into the C–OH bond with concomitant H atom elimination could lead to the isomeric ion CH_3SiO^+ , but this isomer has been found to be much less stable.¹⁶ The reason for the absence of an analogous channel with ethanol is not clear but may be due to enhanced dissipation of internal energy in the alkyl group and thus a reduced probability of H atom dissociation. The significant difference in the efficiency of the reaction of Si^+ with water is also worthy of note. The efficiency measured for the water reaction is about one-tenth of the approximately unit efficiency of the other reactions. This difference may be explained in terms of a difference in the strength of the bond involved in the insertion of the Si^+ , the O–H bond in water being more than 20 kcal mol $^{-1}$ stronger than the C–OH bond in the alcohols and acids.

Reactions of SiOH^+ . Table II summarizes the rate constants and product distributions determined for the reactions studied with SiOH^+ . No differences in reactivity were observed for SiOH^+ generated chemically by reaction 3 and SiOH^+ generated by electron ionization of $(\text{CH}_3)_3\text{SiOH}$.

Table II. Rate Constants (in units of 10^{-9} cm 3 molecule $^{-1}$ s $^{-1}$) and Product Distributions for Reactions of SiOH^+ at 296 ± 2 K

neutral reactant	products	product distribution ^a	k_{exptl}^b	k_c^c
H_2	no reaction		≤ 0.0002	1.5
CO	$\text{SiOH}^+\cdot\text{CO}$		≤ 0.0003	0.82
H_2O	SiH_3O_2^+		0.01	2.5
CH_3OH	$\text{SiOCH}_3^+ + \text{H}_2\text{O}$	0.90	1.15	2.1
$\text{C}_2\text{H}_5\text{OH}$	$\text{SiH}_3\text{O}_2^+ + \text{C}_2\text{H}_4$	0.10	2.4	2.1
	$\text{SiOC}_2\text{H}_5^+ + \text{H}_2\text{O}$	0.60		
	$\text{C}_2\text{H}_5\text{OH}_2^+ + \text{SiO}$	0.30		
	$\text{SiH}_3\text{O}^+ + \text{C}_2\text{H}_4\text{O}$	0.07 ^d		
	SiH_5O_3^+	0.03 ^d		
HCOOH	$\text{SiH}_3\text{O}_2^+ + \text{CO}$	≥ 0.9	1.0	1.7
	$\text{SiOH}^+\cdot\text{HCOOH}$	≤ 0.1		
CH_3COOH	$\text{CH}_3\text{CO}^+ + (\text{SiH}_2\text{O}_2)$	0.90	2.3	2.0
	$\text{CH}_3\text{COOH}_2^+ + \text{SiO}$	0.10		

^a Primary product ions which contribute more than 5% (with one exception). Product distributions have been rounded off to the nearest 5% (with two exceptions) and are estimated to be accurate to $\pm 30\%$. ^b The accuracy of the rate constants is estimated to be better than $\pm 30\%$. The measurements were made in helium buffer gas at 0.35 Torr and 1.1×10^{16} atoms cm $^{-3}$. ^c The collision rate constants are derived from the combined variational transition state theory—classical trajectory study of: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183. ^d From experiments with $\text{C}_2\text{D}_5\text{OD}$.

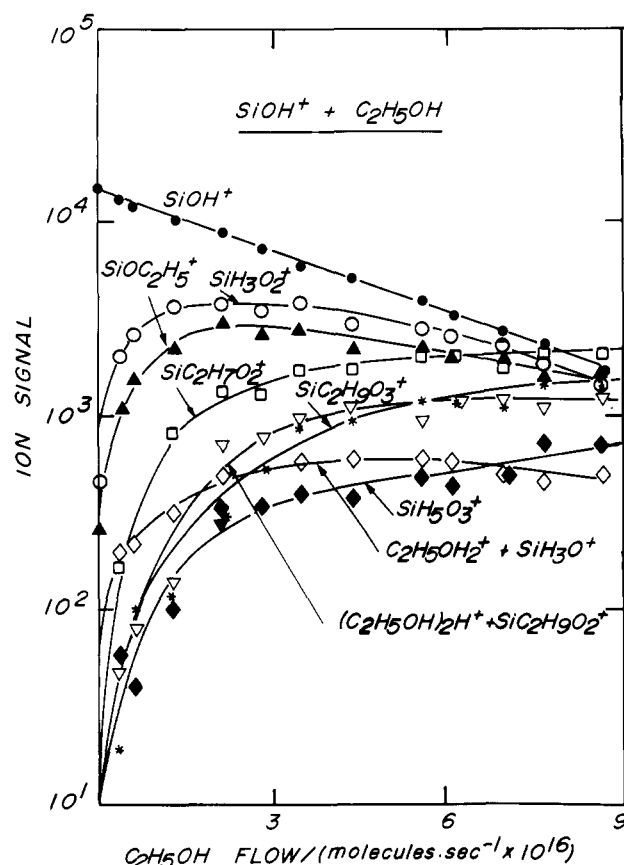


Figure 3. The observed variations in ion signals recorded for the addition of ethanol vapor into the reaction region of the SIFT apparatus in which SiOH^+ is initially established as the dominant ion in helium buffer gas. $P = 0.352$ Torr, $\bar{v} = 6.9 \times 10^3$ cm s $^{-1}$, $L = 46$ cm, and $T = 294$ K. The SiOH^+ is derived from $(\text{CH}_3)_2\text{SiOH}$ at an electron energy of 75 eV. The ion at m/z 119 ($\text{SiO}_2\text{C}_4\text{H}_{11}^+$ or $\text{HSi}(\text{OC}_2\text{H}_5)_2^+$) was not monitored in this experiment.

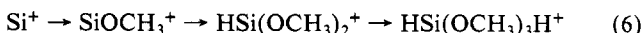
The reactions of SiOH^+ with H_2 , D_2 , CO , and H_2O were not rapid. No reaction was observed with hydrogen or deuterium. $k \leq 2 \times 10^{-13}$ cm 3 molecule $^{-1}$ s $^{-1}$. Carbon monoxide was observed to form an adduct but with a specific rate less than 3×10^{-13} cm 3 molecule $^{-1}$ s $^{-1}$. The addition reaction with H_2O was much faster, $k = 1.0 \times 10^{-11}$ cm 3 molecule $^{-1}$ s $^{-1}$, but still two orders of mag-

(15) Qi, T. Y.; Pauzet, F.; Berthier, G. *Astron. Astrophys.* **1984**, *135*, L1.

(16) Calculations at the MP2/6-31G**//6-31G* level have indicated an energy difference of 30.3 kcal mol $^{-1}$. A. C. Hopkinson, private communication.

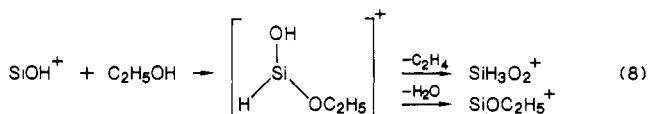
nitude below its collision limit. In total five molecules of water were observed to add to SiOH^+ but the kinetics were established only for the addition of the first water molecule.

The remaining reactions with SiOH^+ were all rapid and predominantly bimolecular. Figure 3 shows the evolution of the products formed in the rapid reaction of SiOH^+ with ethanol. Dehydration of the neutral reactant to form SiH_3O_2^+ was the major channel in the reactions with ethanol and formic acid. Another significant channel with ethanol and the major channel with methanol resulted in the elimination of H_2O to form ions of the type $\text{SiOC}_2\text{H}_5^+$ and SiOCH_3^+ , respectively. The latter two ions were both observed to rapidly add solvent molecules, one with ethanol and two with methanol. The nature of the bonding in the solvated ions is uncertain, but the high rates are suggestive of covalent bond formation which may proceed by O-H bond insertion to form the ions $\text{HSi}(\text{OC}_2\text{H}_5)_2^+$, $\text{HSi}(\text{OCH}_3)_2^+$, and $\text{HSi}(\text{OCH}_3)_3\text{H}^+$. Altogether, the sequential reactions initiated by Si^+ in methanol and ethanol may act to saturate the Si center in the manner shown by reactions 6 and 7. The terminal ions in

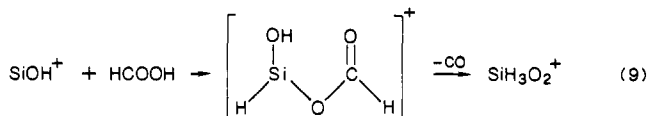


these sequences may neutralize by proton transfer or recombination with electrons to form trimethoxy- and triethoxysilane, respectively. The acetyl ion, CH_3CO^+ , was the main product observed for the reaction of SiOH^+ with acetic acid (the alternative formation of SiCH_3^+ , which has the same m/z as CH_3CO^+ , could be excluded on energetic grounds).

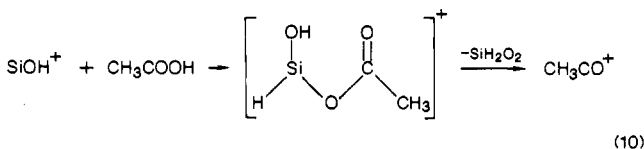
All of the major product ions of the reactions observed with SiOH^+ can be rationalized in terms of a single mechanism involving O-H bond insertion. The SiOH^+ has silylene character¹⁷ and O-H bond insertion seems to be preferred in analogous reactions with neutral carbenes.¹⁸ The intermediate ion formed by the insertion, HOSiHOR^+ , may be collisionally stabilized in the buffer gas or it may decompose. The former appears to be the case with H_2O , CH_3OH , and possibly HCOOH . The path of decomposition will depend on the nature of R. For $\text{R} = \text{CH}_3$ only elimination of H_2O was observed. With ethanol both C_2H_4 and water are eliminated from the postulated intermediate shown in reaction 8. For $\text{R} = \text{HCO}$ elimination of CO predominates



as shown in reaction 9, and for $\text{R} = \text{CH}_3\text{CO}$, the acetyl ion is



formed as is shown in reaction 10. The structure of the SiH_3O_2^+ ions favored by this mechanism is that of protonated silanoic acid, $\text{HSi}(\text{OH})_2^+$, and that of SiH_2O_2 is likely to be neutral silanoic acid, HSiOOH .



Some proton transfer was observed in the reactions of SiOH^+ with acetic acid and ethanol. The minor proton-transfer channel

(17) The silylene character of SiOH^+ is evident from the geometry-optimized canonical coefficient matrix for SiOH^+ at the 6-31G** level. The highest occupied molecular orbital has predominantly 3s character on the silicon atom and the net atomic charges are consistent with the valence structure $:\text{Si}^+-\text{O}-\text{H}$. Unpublished results from this laboratory.

(18) Stang, P. J. *Chem. Rev.* 1978, 78, 383.

in ethanol was characterized in experiments in which SiOD^+ was generated from, and reacted with, $\text{C}_2\text{D}_5\text{OD}$, and which showed that both $\text{C}_2\text{D}_5\text{OD}_2^+$ and SiD_3O^+ (D_2SiOD^+) were products. Ethanol and acetic acid have the highest proton affinities of the substrates chosen for study, 188.3 and 190.2 kcal mol⁻¹, respectively.¹⁹ A more extensive study in our laboratory of the occurrence and non-occurrence of proton transfer with SiOH^+ has provided a proton affinity for SiO of 190 ± 3 kcal mol⁻¹.²⁰ The proton transfer observed with ethanol appears to be slightly endothermic.

Reactions of SiH_3O_2^+ . The SiH_3O_2^+ ion is a predominant product in the reactions of SiOH^+ with water, ethanol, and formic acid. The mechanistic arguments presented in the previous section strongly suggest that this ion is protonated silanoic acid, $\text{HSi}(\text{OH})_2^+$. Other isomers such as, for example, weakly hydrated SiOH^+ , $\text{SiOH}^+\cdot\text{H}_2\text{O}$, are much less likely. The reactivity of the SiH_3O_2^+ was revealed by the secondary reactions of this ion with the molecules from which it was formed. With water and ethanol the SiH_3O_2^+ ion was observed to react by association to add one molecule probably by O-H bond insertion to form the saturated ion $\text{HSi}(\text{OH})_3\text{H}^+$. The reaction with ethanol produced two bimolecular products as well as proceeding by association as shown by reaction 11. Likely structures for the three product ions are $\text{HSi}(\text{OC}_2\text{H}_5)\text{OH}^+$, $\text{HSi}(\text{OH})_3\text{H}^+$ and $\text{HSi}(\text{OC}_2\text{H}_5)(\text{OH})_2\text{H}^+$, respectively.

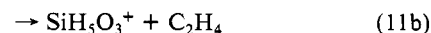
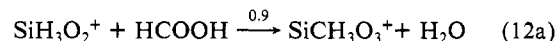
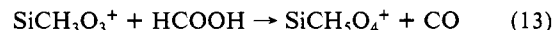


Figure 2 reveals the full scope of the chemistry initiated by SiH_3O_2^+ in formic acid. The primary channels are indicated in reaction 12. The major channel leads to H_2O elimination while



the minor channel may be viewed as dehydration of the formic acid. Several isomers are possible for both product ions. $\text{SiCH}_3\text{O}_3^+$ may be $\text{HSi}(\text{OCHO})\text{OH}^+$ or (less likely) $\text{SiOH}^+\cdot\text{HCOOH}$ which could result from O-H insertion or solvent switching, respectively. The isomer of SiH_5O_3^+ produced in reaction 12b is likely to be the fully saturated cation $\text{HSi}(\text{OH})_3\text{H}^+$ which may be formed by C-OH bond insertion. This ion may neutralize by proton transfer or recombination with electrons to produce trihydroxysilane, $\text{HSi}(\text{OH})_3$.

Reaction 13 appears to predominate in the collisions of $\text{SiCH}_3\text{O}_3^+$ with formic acid. Several isomers are possible for



$\text{SiCH}_5\text{O}_4^+$, including $\text{SiCH}_3\text{O}_3^+\cdot\text{H}_2\text{O}$, $\text{SiH}_3\text{O}_2^+\cdot\text{HCOOH}$, and $\text{HSi}(\text{OCHO})(\text{OH})_2\text{H}^+$. The latter isomer is probably preferred given that $\text{SiCH}_3\text{O}_3^+$ is likely to be $\text{HSi}(\text{OCHO})\text{OH}^+$. It is fully saturated at the silicon center and again may be formed by C-OH bond insertion.

Finally, SiH_5O_3^+ , $\text{SiCH}_3\text{O}_3^+$, and $\text{SiCH}_5\text{O}_4^+$ each appeared to add one molecule of formic acid by association.

Conclusions

Atomic silicon cations have been produced in their excited state, Si^+ (⁴P), and ground state, Si^+ (²P), by the electron ionization of silicon tetrachloride at 40–50 eV. In contrast to the ground-state silicon ions which were found to be unreactive, the excited-state silicon ions were found to react rapidly with hydrogen and deuterium to form SiH^+ and SiD^+ , respectively. Hydrogen or deuterium may therefore be used to selectively remove the excited state from a mixture of ground- and excited-state ions, as has been

(19) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* 1984, 13, 695.

(20) Unpublished results from this laboratory.

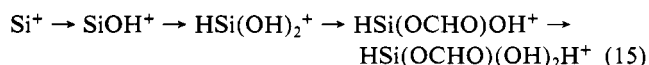
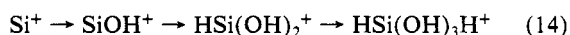
done in the study reported here.

Si^+ (^2P) ions were found to react rapidly at 296 ± 2 K with several simple molecules containing hydroxyl groups. SiOH^+ , conceivably formed by H-OH or C-OH bond insertion, was observed to be the predominant product ion with water, methanol, ethanol, formic acid, and acetic acid. Reactions of atomic silicon ions which produce SiOH^+ are of interest in molecular synthesis. For example, in interstellar and other ionized gaseous environments in which SiOH^+ may neutralize by electron/ion recombination or proton transfer, such reactions provide possible routes toward the formation of silicon monoxide.^{8,9}

The chemistry of SiOH^+ was seen to have interesting consequences. An ion likely to be protonated silanoic acid was observed to be produced from SiOH^+ by addition with water and by dehydration with ethanol and formic acid. Neutral silanoic acid is a likely direct product of the reaction with acetic acid in which the acetyl ion was observed to be eliminated. The reactions with ethanol, formic acid, and acetic acid were observed to be rapid and bimolecular. A single mechanism involving O-H bond insertion of the SiOH^+ silene cation provides a plausible explanation for all of the results obtained with this ion.

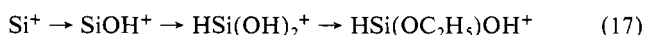
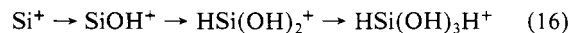
Insertion appears to be a common mechanistic feature of the bimolecular reactions observed with Si^+ and SiOH^+ . The overall energetics of the reactions with Si^+ constrain this ion to insert into the C-OH bond of the hydroxyl-containing molecules investigated. The energetics of the reactions of SiOH^+ are less well known but the predominant reaction features observed can be rationalized in terms of O-H bond insertion characteristic of analogous reactions of neutral carbenes.

With the molecules containing hydroxyl groups Si^+ initiates reaction sequences which appear to saturate the silicon center. With formic acid complete saturation appears to be achieved in three bimolecular steps as shown in reaction 14, or in four steps as shown in reaction 15. With acetic acid the silicon appears



in the neutral product in the second step so that further saturation

could not be followed in the experiment. With water, methanol, and ethanol the bimolecular reaction sequence stopped at SiOH^+ after one step, at SiOCH_3^+ after one or two steps, and at $\text{SiOC}_2\text{H}_5^+$ after two steps, respectively. With ethanol the experimental data were consistent with the additional bimolecular reaction sequences shown in 16 and 17. In some instances the



terminal ions of the bimolecular reaction sequences were observed to add further molecules of reactant in what are presumably termolecular association reactions. These may also lead to more saturated Si ions as, for example, in the reaction sequences 6 and 7 which may lead to $\text{HSi}(\text{OCH}_3)_3\text{H}^+$ and $\text{HSi}(\text{OC}_2\text{H}_5)_3\text{H}^+$, respectively.

The ion/molecule reaction sequences initiated by Si^+ investigated in this study increase the oxygen/silicon coordination number and so are of interest in molecular synthesis. For example we have seen how silicon monoxide and silanoic acid may be produced. Neutralization by proton transfer or recombination with electrons of the terminal ions in the reaction sequences 6, 7, and 15 may produce $\text{HSi}(\text{OCH}_3)_3$, $\text{HSi}(\text{OC}_2\text{H}_5)_3$, and $\text{HSi}(\text{OCHO})(\text{OH})_2$, respectively. Also, it is not difficult for the $\text{HSi}(\text{OH})_3\text{H}^+$ produced as a terminal ion in the reaction sequences 14 and 16 to generate trihydroxysilane by neutralization. Subsequent hydride abstraction or reionization of this molecule followed by a dehydrative reaction between the unsaturated $\text{Si}(\text{OH})_3^+$ fragment ion and carboxylic acid, in analogy with reaction 12b, may generate tetrahydroxysilane, $\text{Si}(\text{OH})_4$, on neutralization. Tetrahydroxysilane is a building block for condensational synthesis of hydrated silicate networks.^{21,22}

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(21) Abe, Y.; Misono, T. *J. Polym. Sci. Polym. Lett.* **1984**, *22*, 565.

(22) Meinhold, R. H.; Rothbaum, H. P.; Newman, R. H. *J. Colloid Interface Sci.* **1985**, *108*, 234.

The Influence of Oxygen Variation on the Crystal Structure and Phase Composition of the Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

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Abstract: On the basis of iodometric determinations of the oxidation state of Cu in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, TGA experiments, and equilibrium reactions, the highest oxygen content of 6.96 (2) is achieved when annealing in O_2 at about 440 °C. Annealing in air or oxygen in the range 350–450 °C produced material which analyzed as 6.94 (2). The orthorhombic phase exists over the composition range $\text{O}_{6.96}$ – $\text{O}_{6.60}$. The tetragonal composition $\text{YBa}_2\text{Cu}_3\text{O}_6$ is prepared by heating the mixture in an inert atmosphere, Ar or N_2 , at temperatures in excess of 700 °C. The oxygen solution range for this phase ranges from $\text{O}_{6.0}$ to $\text{O}_{6.15}$. Compositions with nominal oxygen contents of 6.15–6.60 may be mixtures of the tetragonal and orthorhombic phases.

The superconducting compounds with general formulas $\text{Ln}_{2-x}\text{M}_x\text{CuO}_{4-x}$ (M = Ba, Sr) and $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ display variations in oxygen content that strongly influence the superconducting property. During the investigation of the range of values of x in

the latter stoichiometry we prepared single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_6$ and determined its crystal structure.¹ This compound is tetragonal and is a semiconductor. The change of crystal system upon loss of oxygen may imply a limited range of oxygen solubility for each phase, and we carried out a systematic investigation of the vari-

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(1) Swinnea, J. S.; Steinfink, H. J. *Mater. Res.* **1987**, *2*, 424.