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GAS-PHASE FORMATION OF SILICON CARBIDES, OXIDES AND SULPHIDES FROM ATOMIC SILICON IONS

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We have recently embarked on a systematic experimental study of the kinetics and mechanisms of the chemical reactions in the gas phase between ground-state $Si^+(^2P)$ and a variety of astrophysical molecules. The aim of this study is to identify the reactions which trigger the formation of chemical bonds between silicon and carbon, oxygen and sulphur and the chemical pathways which lead to further molecular growth. Such knowledge is valuable in the identification of new extraterrestrial silicon-bearing molecules and for an assessment of the gas-phase transition from atomic silicon to silicon carbide and silicate grain particles in carbon-rich and oxygen-rich astrophysical environments .

Ground-state $Si^+(^2P)$ ions are generated in our laboratory experiments in a Selected-Ion Flow Tube (SIFT) apparatus and reacted in helium buffer gas (at ca 0.35 Torr and 296 K) with added neutral molecules. Reactant and product ions are monitored as a function of the concentration of the added gas. These data provide rate constants and product distributions for the primary reactions. Secondary and higher-order reactions which lead to further ionic growth are also monitored, including the sequential growth of ions in which the silicon becomes increasingly co-ordinated. In natural environments which are partially ionized, such as diffuse or dense interstellar clouds or the atmospheres of certain stars, molecular ions formed in this manner may ultimately be neutralized by recombination with electrons without significantly disrupting their molecular composition and structure, and so provide sources for complex silicon-bearing molecules in these environments.

Ground-state silicon ions havebeen found to be unreactive toward H_2 and so should be available for reactions with other constituents in astrophysical environments in which hydrogen gas predominates (Wlodek et al, 1987).

FORMATION OF SILICON CARBIDES

Si-C bond formation has been found to be efficient with acetylene and cyanoacetylene which react rapidly with $Si^+(^2P)$ to form SiC_2H^+ by H-atom and CN elimination, respectively:

$$Si^+ + C_2H_2 \xrightarrow{0.7} SiC_2H^+ + H \quad (1a)$$

$$\xrightarrow{0.3} SiC_2H_2^+ \quad (1b)$$

$$Si^+ + HC_3N \xrightarrow{0.7} SiC_2H^+ + CN \quad (2a)$$

$$\xrightarrow{0.3} SiC_3HN^+ \quad (2b)$$

A secondary reaction of SiC_2H^+ with acetylene was observed to build up the carbon content further to produce SiC_4H^+ by H_2 elimination:

$$SiC_2H^+ + C_2H_2 \xrightarrow{0.9} SiC_4H_3^+ \quad (3a)$$

$$\xrightarrow{0.1} SiC_4H^+ + H_2 \quad (3b)$$

SiC_2H^+ and SiC_4H^+ may neutralize by recombination with electrons or proton transfer to produce the carbide molecules SiC_2 and SiC_4. Ground-state silicon ions will also extract carbon from amines to form directly the neutral molecules SiCH and $SiCH_3$ as well as the ion $SiCH_2^+$, from acetonitrile to form $SiCH_2^+$, from acetone to form $SiCH_3$, from ethylene to form $SiC_2H_3^+$, and from methylacetylene to form $SiCH_2^+$, SiC_2H^+, and $SiC_3H_3^+$ (Wlodek and Bohme, 1988; Bohme et al, 1988).

Scheme 1 provides a summary of the observed ion chemistry which can be directed to the formation of silicon-carbide molecules.

It is interesting to note that Si^+ reacts only slowly with methane under our experimental conditions, $k = 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, to form adduct ions, probably in a termolecular fashion:

$$Si^+ + CH_4 \longrightarrow SiCH_4^+ \quad (4)$$

Also diacetylene does not entrain silicon, reacting instead to form SiH:

$$Si^+ + C_4H_2 \longrightarrow SiH + C_4H^+ \quad (5)$$

FORMATION OF SILICON OXIDES

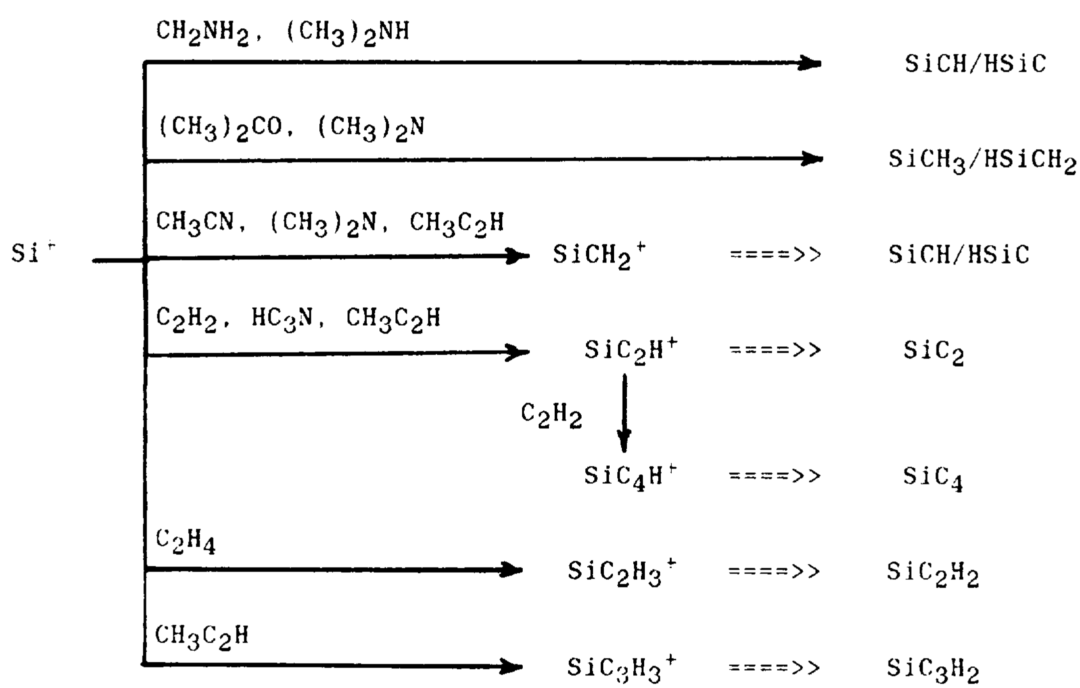
A rich chemistry was observed to be initiated and propagated with hydroxyl-containing molecules (Wlodek et al, 1987). Ground-state silicon ions were found to react with the molecules H_2O, CH_3OH, C_2H_5OH, HCOOH, and CH_3COOH to produce the silene cation $SiOH^+$ which may neutralize to form silicon monoxide:

$$Si^+ + XOH \text{ -----> } SiOH^+ + X \qquad (6)$$

$$SiOH^+ + e\ (B) \text{ -----> } SiO + H\ (BH^+) \qquad (7)$$

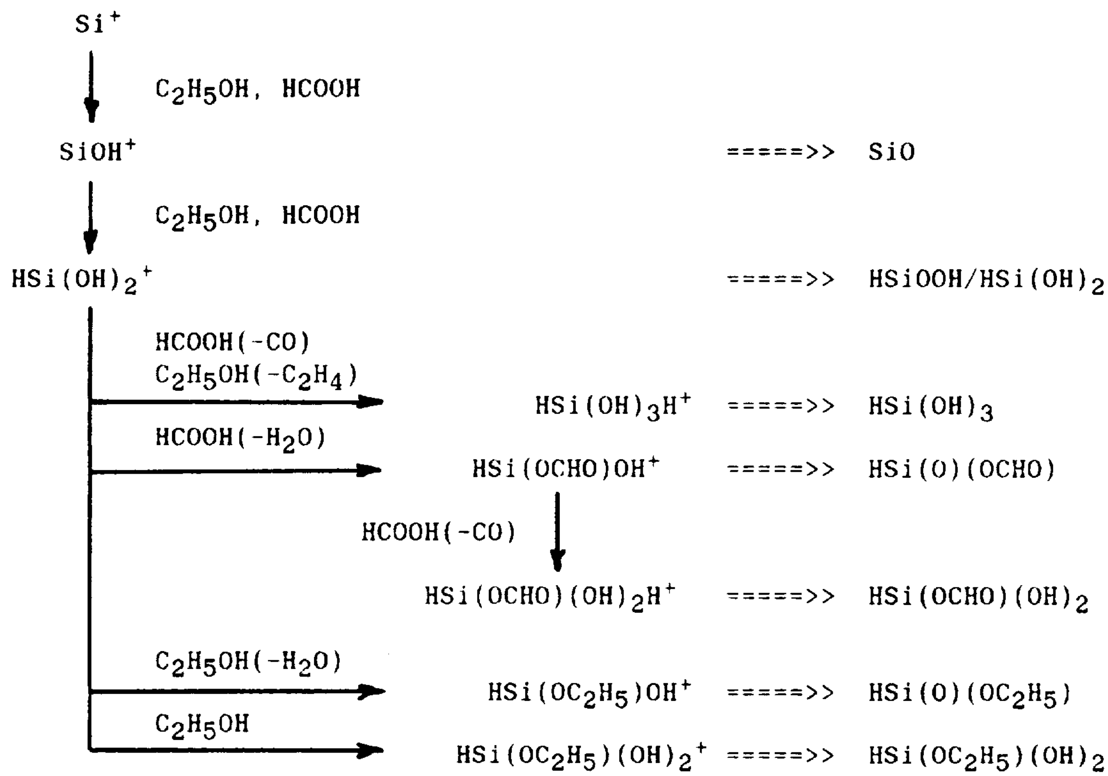
$SiH_3O_2{}^+$, which may neutralize to produce silanoic acid, is the predominat product in the reactions of $SiOH^+$ with H_2O, C_2H_5OH and HCOOH, while direct formation of silanoic acid is likely in the reaction with CH_3COOH. Further chemistry can be propagated by $SiH_3O_2{}^+$. It associates with H_2O and C_2H_5OH and produces $SiCH_3O_3{}^+$ and $SiH_5O_3{}^+$ with formic acid. Reaction sequences identified with CH_3OH, C_2H_5OH and HCOOH are postulated to lead to the complete saturation of Si^+ forming ions of the type $HSi(OCH_3)_3{}^+$, $HSi(OC_2H_5)_3H^+$, and $HSi(OH)_3H^+$ which may neutralize to generate trimethoxysilane, triethoxysilane and trihydroxysilane, respectively. Analogous reactions can be proposed which lead to the formation of tetrahydroxysilane which is a known building block for condensational synthesis of hydrated silica networks.

Scheme 1. Limited reaction scheme for the synthesis of silicon-carbide molecules initiate bu atomic silicon ions. The double arrows represent neutralization reactions such as proton transfer and electron/ion recombination.



Schemes 2 and 3 provide a summary of the observed ion chemistry which can be directed to the formation of silicon-oxide molecules.

Scheme 2. Limited scheme for the synthesis of silicon-oxide molecules with ion chemistry initiates by Si^+ in ethanol and formic acid. The double arrows represent neutralization reactions such as proton transfer and electron/ion recombination.



The oxidation of ground-state atomic silicon ions with diatomic and triatomic molecules not containing hydrogen was explored with O_2, NO, CO, CO_2, NO_2, SO_2, and N_2O. Bimolecular oxidation reactions which may proceed with these molecules include oxygen-atom transfer as indicated in reaction (8) and oxide-anion transfer as indicated in reaction (9). Both

$$Si^+ + XO \longrightarrow SiO^+ + X \qquad (8)$$

$$Si^+ + XO \longrightarrow SiO + X^+ \qquad (9)$$

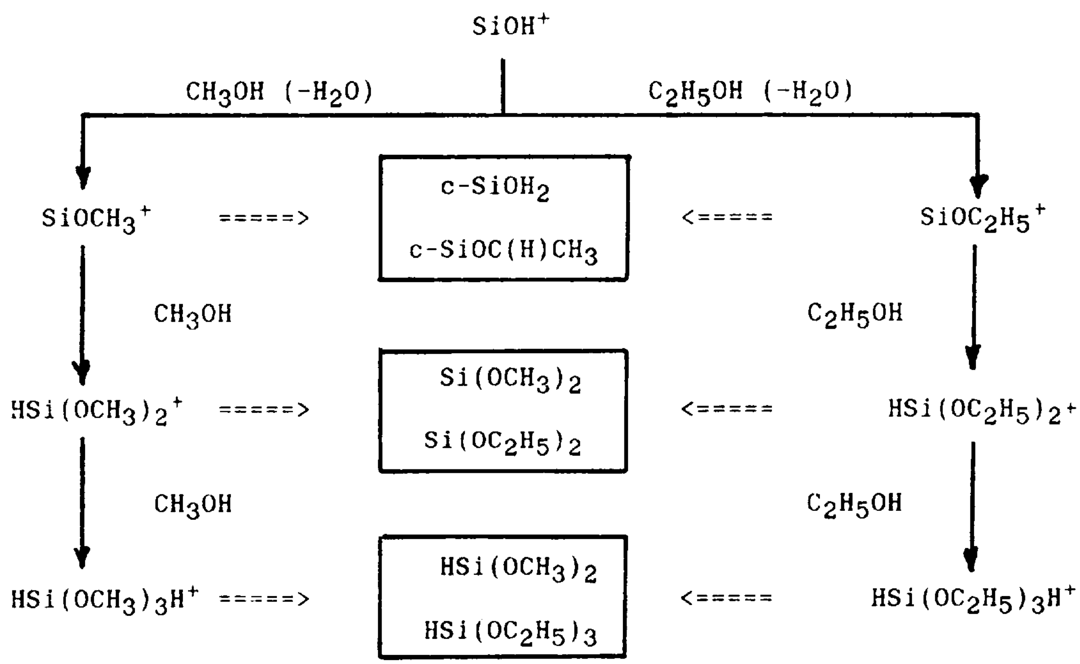
reactions (8) and (9) were observed to occur rapidly when exothermic. Oxygen-atom transfer was observed with N_2O and NO_2, while oxide-anion transfer was observed to occur with NO_2 and SO_2. Slow adduct formation (with O_2, NO and CO_2), or no reaction (with CO) was observed when formation of SiO^+ or SiO was endothermic.

With N_2O oxidation was observed to proceed sequentially to produce polyoxide ions of the type SiO_n^+ as indicated in reaction (10):

$$Si^+ \xrightarrow{N_2O} SiO^+ \xrightarrow{N_2O} SiO_2^+ \xrightarrow{N_2O} SiO_3^+ \xrightarrow{N_2O} SiO_4^+ \qquad (10)$$

The production of these polyatomic ions was observed to compete with adduct formation and elimination of O_2^+ and SiO_2 which becomes important in the last two steps in the reaction sequence. The polyoxide ions pose interesting questions regarding their structure and the molecules which they may spawn upon neutralization.

Scheme 3. Limited reaction scheme for the synthesis of silicon-oxide molecules initiated by $SiOH^+$ in methanol and ethanol. The double arrows represent neutralization reactions such as proton transfer and electron/ion recombination.



FORMATION OF SILICON SULPHIDES

Si-S bond formation was observed to proceed with H_2S and with COS in a reaction analogous to reaction (8):

$$Si^+ + H_2S \longrightarrow SiSH^+ + H \qquad (11)$$

$$Si^+ + COS \longrightarrow SiS^+ + CO \qquad (12)$$

The polysulphide ions SiS_2^+ and SiS_3^+ were observed to be formed sequentially with COS as reactant.

$$Si^+ \xrightarrow{COS} SiS^+ \xrightarrow{COS} SiS_2^+ \xrightarrow{COS} SiS_3^+ \quad (13)$$

Charge-transfer reactions with molecules which have ionization energies lower than the recombination energies of these ions can lead to formation of the polysulphide molecules.

SUMMARY

The experimental studies reported here are providing clues to the formation of a large number of silicon-containing molecules in partially ionized astrophysical environments. For example, the gas-phase ion/molecule reactions which have been identified in our studies so far represent possible contributors to the formation of the following silicon-carbide, silicon-oxide and silicon sulphide molecules:

SiCH, SiC_2, $SiCH_3$, SiC_4, SiO, SiO_2, SiS, SiS_2, HSiOOH, $SiOCH_2$, $HSiC(H)CH_3$, $HSi(OH)_3$, HSi(O)(OCHO), $HSi(O)(OC_2H_5)$, $HSi(OCHO)(OH)_2$, $Si(OCH_3)_2$, $HSi(OCH_3)_3$, $Si(OC_2H_5)_2$, $HSi(OC_2H_5)_3$.

Current investigations are being directed toward ion/molecule reactions of $Si^+(^2P)$ which can lead to bonding with still other heavy atoms, and toward a further elucidation of the kinetics and mechanisms of the higher-order chemistry which can lead to still further growth and perhaps ultimately to the formation of small silicon-carbide and silicon-oxide particles.

Acknowledgment

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