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CHEMISTRY INITIATED BY ATOMIC SILICON IONS IN THE GAS PHASE: FORMATION OF SILICON-BEARING IONS AND MOLECULES

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ABSTRACT

Results of recent gas-phase laboratory studies at York University are reviewed which provide insight into the formation of silicon-bearing ions and molecules initiated by reactions of ground state atomic silicon ions and into the influence of aromatic "surfaces" on this chemistry. Emphasis is given to reactions which lead to the chemical bonding of silicon with hydrogen, carbon, nitrogen, oxygen and sulphur.

INTRODUCTION

For several years now research in the Ion Chemistry Laboratory at York University has been directed towards understanding the growth of silicon-bearing molecules and ions initiated by reactions of atomic silicon ions, particularly as might occur in interstellar and circumstellar chemistry. The more general goal of this research is to identify and characterize chemical reactions which trigger the formation of chemical bonds with atomic silicon and chemical pathways which lead to further molecular evolution. The approach has been systematic and has focused on the kinetics, energetics and mechanisms of ion/molecule reactions leading to the chemical bonding of silicon with hydrogen, carbon, nitrogen, oxygen and sulphur. Because of the fundamental nature of such bonds, the results of these studies are expected to have a broad impact. For example, the new silicon-bearing ions and molecules which have been identified and the manner in which they are formed could be of interest to the theoretical chemist, the laboratory spectroscopist, the atmospheric chemist, the chemical modeller, the radio-astronomer and perhaps even the surface chemist. This article presents a brief overview of the

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results of measurements and calculations which have been completed in the Ion Chemistry Laboratory at York University over the past 3 years.

EXPERIMENTAL

All the measurements were performed with the selected-ion flow tube (SIFT) apparatus which has been described elsewhere [1,2]. Atomic silicon ions were derived by electron impact at 50–100 eV from tetramethylsilane or a 2–3% mixture of tetramethylsilane in deuterium. Electron impact of tetramethylsilane at these energies produces both the ground ^2P state and excited ^4P state of Si^+, but the excited state can be removed either by the charge-transfer reaction (1) or by chemical reaction with deuterium as shown in reaction (2):

$$Si^+(^4P) + Si(CH_3)_4 \rightarrow Si(^2P) + Si(CH_3)_4^{+\cdot} \qquad (1)$$

$$Si^+(^4P) + D_2 \rightarrow SiD^+ + D^\cdot \qquad (2)$$

A pure beam of ground state atomic silicon ions can therefore be selected and injected into the helium buffer gas in the flow tube. The silicon ions are allowed to thermalize by collision with the helium atoms before they enter the reaction region further downstream. The reactions which are initiated when the neutral reactant is finally added into the flow tube therefore proceed at a known temperature which in these experiments is 296 ± 2 K. The pressure of the helium buffer gas is usually set at 0.35 Torr or 1.15×10^{16} He atoms cm^{-3}.

RESULTS AND DISCUSSION

The almost 100 ion/molecule reactions involving silicon which have been identified and characterized so far are compiled in Table 1. This compilation continues to be up-dated and is available separately upon request. Table 2 presents a summary of the experimental and computed values for the proton affinities of SiNH, SiO and SiS which were derived as part of these studies.

Bonding silicon to hydrogen

Both hydrogen-atom and hydride-ion transfer can lead to the bonding of hydrogen atoms to atomic silicon ions, as shown in reactions (3) and (4):

$$Si^{+\cdot} + XH \rightarrow SiH^+ + H^\cdot \qquad (3)$$

$$Si^{+\cdot} + XH \rightarrow SiH^\cdot + X^+ \qquad (4)$$

TABLE 1

Summary of rate constants (k_{exp}, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}) and branching ratios (BR) measured for reactions of silicon-containing ions with molecules in helium buffer gas at 0.35 Torr and 296 ± 2 K

Ion/neutral reaction			BR	k_{exp}	Ref.
$Si^+(^2P) + H_2$	→	No reaction		< 0.0002	3
$Si^+(^2P) + D_2$	→	No reaction		< 0.0002	3
$Si^+(^4P) + D_2$	→	$SiD^+ + D^{\cdot}$	1.0	0.77	3
$Si^{+\cdot} + H_2O$	→	$SiOH^+ + H^{\cdot}$	1.0	0.23	3
$Si^{+\cdot} + NH_3$	→	$SiNH_2^+ + H^{\cdot}$	1.0	0.64	4
$Si^{+\cdot} + NO^{\cdot}$	→	$SiNO^+$	1.0	< 0.01	7
$Si^{+\cdot} + N_2O$	→	$SiO^{+\cdot} + N_2$	1.0	0.40	7
$Si^{+\cdot} + NO_2^{\cdot}$	→	$SiO^{+\cdot} + NO^{\cdot}$	0.68	0.86	7
	→	$NO^+ + SiO$	0.30		
	→	$SiNO_2^+$	0.02		
$Si^{+\cdot} + O_2$	→	$SiO_2^{+\cdot}$	1.0	< 0.0001	7
$Si^{+\cdot} + SO_2$	→	$SO^{+\cdot} + SiO$	1.0	0.81	7
$Si^{+\cdot} + CO$	→	No reaction		< 0.00002	3
$Si^{+\cdot} + CO_2$	→	$SiCO_2^{+\cdot}$	1.0	< 0.00017	7
$Si^{+\cdot} + COS$	→	$SiS^{+\cdot} + CO$	1.0	0.90	7
$Si^{+\cdot} + CS_2$	→	$SiCS_2^{+\cdot}$	1.0	0.066	7
$Si^{+\cdot} + HCN$	→	$CHNSi^{+\cdot}$	0.8	0.0070	5
	→	$CNSi^+ + H^{\cdot}$	0.2		
$Si^{+\cdot} + HCOOH$	→	$SiOH^{+\cdot} + CHO^{\cdot}$	1.0	2.3	3
$Si^{+\cdot} + CH_4$	→	$SiCH_4^{+\cdot}$	1.0	0.0005	8,12
$Si^{+\cdot} + CH_3OH$	→	$SiOH^+ + CH_3^{\cdot}$	0.75	2.2	3
	→	$SiOCH_3^+ + H^{\cdot}$	0.25		
$Si^{+\cdot} + CH_3NH_2$	→	$SiNH_2^+ + CH_3^{\cdot}$	0.55	1.2	4
	→	$CH_2NH_2^+ + SiH^{\cdot}$	0.35		
	→	$SiNHCH_3^+ + H^{\cdot}$	0.10		
$Si^{+\cdot} + C_2N_2$	→	$CNSi^+ + CN^{\cdot}$	0.55	0.15	5
	→	$C_2N_2Si^{+\cdot}$	0.45		
$Si^{+\cdot} + C_2H_2$	→	$SiC_2H^+ + H^{\cdot}$	0.70	0.35	8,12
	→	$SiC_2H_2^{+\cdot}$	0.30		
$Si^{+\cdot} + CH_3CN$	→	$CH_2Si^{+\cdot} + CHN$	0.5	2.4	5
	→	$C_2H_3NSi^{+\cdot}$	0.5		
$Si^{+\cdot} + C_2H_4$	→	$SiC_2H_4^{+\cdot}$	0.60	0.56	12
	→	$SiC_2H_3^+ + H^{\cdot}$	0.40		
$Si^{+\cdot} + CH_3COOH$	→	$SiOH^+ + CH_3CO^{\cdot}$	0.70	3.0	3
	→	$CH_3CO^+ + SiOH^{\cdot}$	0.30		
$Si^{+\cdot} + C_2H_6$	→	$SiCH_3^+ + CH_3^{\cdot}$	0.8	0.80	12
	→	$SiCH_2^{+\cdot} + CH_4$	0.15		
	→	$SiC_2H_4^{+\cdot} + H_2$	0.03		
	→	$SiC_2H_6^{+\cdot}$	0.02		
$Si^{+\cdot} + C_2H_5OH$	→	$SiOH^+ + C_2H_5^{\cdot}$	1.0	2.5	3
$Si^{+\cdot} + (CH_3)_2NH$	→	$CH_2NHCH_3^+ + SiH^{\cdot}$	0.60	1.2	4

TABLE 1

(continued)

Ion/neutral reaction			BR	k_{exp}	Ref.
	→	$(SiNH_2^+ + C_2H_5^{\cdot})$			
	→	$SiNHCH_3^+ + CH_3^{\cdot}$	0.35		
	→	$SiN(CH_3)_2^+ + H^{\cdot}$	0.05		
$Si^{+\cdot} + HC_2CN$	→	$C_2HSi^+ + CN^{\cdot}$	0.7	1.4	5
	→	$C_3HNSi^{+\cdot}$	0.3		
$Si^{+\cdot} + CH_2CCH_2$	→	$SiC_3H_3^+ + H^{\cdot}$	0.70	1.2	12
	→	$SiC_2H^+ + CH_3^{\cdot}$	0.20		
	→	$SiCH_2^{+\cdot} + C_2H_2$	0.10		
$Si^+ + CH_3CCH$	→	$SiC_3H_3^+ + H^{\cdot}$	0.60	1.2	12
	→	$SiC_2H^+ + CH_3^{\cdot}$	0.25		
	→	$SiCH_2^{+\cdot} + C_2H_2$	0.15		
$Si^{+\cdot} + (CH_3)_2CO$	→	$SiOH^+ + C_3H_5^{\cdot}$	0.45	0.28	8
	→	$CH_3CO^+ + SiCH_3^{\cdot}$	0.30		
	→	$C_3H_6^{+\cdot} + SiO$	0.25		
$Si^{+\cdot} + (CH_3)_3N$	→	$CH_2N(CH_3)_2^+ + SiH^{\cdot}$	0.80	0.98	4
	→	$CH_2NHCH_3^+ + SiCH_3^{\cdot}$	0.09		
	→	$(SiNH_2^+ + C_3H_7^{\cdot})$			
	→	$SiN(CH_3)_2^+ + CH_3^{\cdot}$	0.07		
	→	$SiCH_2^{+\cdot} + (CH_3)_2NH$	0.04		
	→	$(CH_3CNH^+ + SiCH_5^{\cdot})$			
$Si^{+\cdot} + C_4H_2$	→	$C_4H^+ + SiH^{\cdot}$	1.0	1.6	8,12
$Si^{+\cdot} + C_6H_6$	→	$(SiC_6H_6)^{+\cdot}$	1.0	Observed	11
$Si^{+\cdot} + C_{10}H_8$	→	$(SiC_{10}H_8)^{+\cdot}$	0.9	Observed	10
	→	$C_{10}H_8^+ + Si$	0.1		
$SiCH_2^{+\cdot} + CH_2CCH$	→	$SiC_3H_3^+ + CH_3^{\cdot}$	0.95	0.61	12
	→	$SiC_4H_5^{+\cdot}$	0.05		
$SiCH_2^{+\cdot} + CH_3CCH$	→	$SiC_3H_3^+ + CH_3^{\cdot}$	0.85	0.91	12
	→	$SiC_4H_5^{+\cdot}$	0.15		
$SiNH_2^+ + H_2$	→	No reaction		< 0.00034	4
$SiNH_2^+ + NH_3$	→	$NH_4^+ + SiNH$	1.0	0.90	4,9
$SiNH_2^+ + CO$	→	No reaction		< 0.0002	4
$SiNH_2^+ + CH_3NH_2$	→	$CH_3NH_3^+ + SiNH$	1.0	1.0	4
$SiNH_2^+ + (CH_3)_2S$	→	$CH_2SCH_3^+ + (SiNH_3)$	0.70	1.5	9
	→	$SiNH_2^+ \cdot (CH_3)_2S$	0.25		
	→	$CH_4NSi^+ + CH_3SH$	0.05		
$SiNH_2^+ + (CH_3)_2CO$	→	$CH_4NSi^+ + (C_2H_4O)$	0.85	2.4	9
	→	$SiNH_2^+ \cdot (CH_3)_2CO$	0.15		
$SiO^{+\cdot} + N_2O$	→	$SiO_2^{+\cdot} + N_2$	1.0	0.48	7
$SiO^{+\cdot} + NO_2^{\cdot}$	→	$NO^+ + SiO_2$	0.63	1.5	7
	→	$NO_2^+ + SiO$	0.35		
	→	$SiO_2^+ + NO^{\cdot}$	0.02		
$SiO^{+\cdot} + O_2$	→	No reaction		< 0.0002	7
$SiOH^+ + H_2$	→	No reaction		< 0.0002	3
$SiOH^+ + H_2O$	→	$SiH_3O_2^+$		0.01	3

TABLE 1

(continued)

Ion/neutral reaction			BR	k_{exp}	Ref.
$SiOH^+ + H_2S$	→	$SiOH^+ \cdot H_2S$	1.0	< 0.001	6
$SiOH^+ + NH_3$	→	$NH_4^+ + SiO$	1.0	2.5	6
$SiOH^+ + CO$	→	$SiOH^+ \cdot CO$	1.0	< 0.0003	3
$SiOH^+ + HCOOH$	→	$SiH_3O_2^+ + CO$	> 0.9	1.0	3
	→	$SiOH^+ \cdot HCOOH$	< 0.1		
$SiOH^+ + CH_3OH$	→	$SiOCH_3^+ + H_2O$	0.90	1.15	3
	→	$SiOH^+ \cdot CH_3OH$	0.10		
$SiOH^+ + CH_3CN$	→	$SiOH^+ \cdot CH_3CN$	0.55	0.48	6
	→	$CH_3CNH^+ + SiO$	0.45		
$SiOH^+ + CH_3COOH$	→	$CH_3CO^+ + (SiH_2O_2)$	0.90	2.3	3
	→	$CH_3COOH_2^+ + SiO$	0.10		
$SiOH^+ + C_2H_5OH$	→	$SiH_3O_2^+ + C_2H_4$	0.60	2.4	3
	→	$SiOC_2H_5^+ + H_2O$	0.30		
	→	$C_2H_5OH_2^+ + SiO$	0.07		
	→	$SiH_3O^+ + C_2H_4O$	0.03		
$SiOH^+ + (CH_3)_2O$	→	$SiOH^+ \cdot (CH_3)_2O$	0.8	0.95	6
	→	$(CH_3)_2OH^+ + SiO$	0.2		
$SiOH^+ + H_2CCCH_2$	→	$SiOH^+ \cdot C_3H_4$	0.8	0.031	6
	→	$C_3H_5^+ + SiO$	0.2		
$SiC_2H^+ + C_2H_2$	→	$SiC_4H_3^+$	0.9	0.2	8
	→	$SiC_4H^+ + H_2$	0.1		
$SiC_2H^+ + CH_2CCH_2$	→	$SiC_5H_5^+$	1.0	0.56	12
$SiC_2H^+ + CH_3CCH$	→	$SiC_5H_5^+$	1.0	0.65	12
$SiNHCH_3^+ + CH_3NH_2$	→	$CH_3NH_3^+ + SiNH$	1.0	1.3	4
$SiNHCH_3^+ + (CH_3)_2NH$	→	$(CH_3)_2NH_2^+ + SiNCH_3$	0.95	0.7	4
	→	$SiNHCH_3^+ \cdot (CH_3)_2NH$	0.05		
$SiC_2H_4^{+\cdot} + C_2H_4$	→	$SiC_2H_3^+ + C_2H_5^{\cdot}$	0.8	0.40	12
	→	$SiC_4H_8^{+\cdot}$	0.2		
$SiC_2H_4^{+\cdot} + C_2H_6$	→	Products		0.077	12
$SiS^{+\cdot} + H_2$	→	No reaction		< 0.00002	7
$SiS^{+\cdot} + O_2$	→	$SO^{+\cdot} + SiO$	0.70	0.089	7
	→	$SiO^{+\cdot} + SO$	0.30		
$SiS^{+\cdot} + CO$	→	No reaction		< 0.00004	7
$SiS^{+\cdot} + COS$	→	$SiS_2^{+\cdot} + CO$	1.0	1.4	7
$SiSH^+ + H_2O$	→	$SiOH^+ + H_2S$	1.0	1.1	6
$SiSH^+ + H_2S$	→	$H_3S^+ + SiS$	1.0	0.29	6
$SiSH^+ + NH_3$	→	$NH_4^+ + SiS$	1.0	0.97	6
$SiSH^+ + HCN$	→	$HCNH^+ + SiS$	1.0	0.61	6
$SiSH^+ + C_2H_4$	→	$SiSH^+ \cdot C_2H_4$	1.0	0.018	6
$SiC_3H_3^+ + NH_3$	→	$SiNH_2^+ + C_3H_4$		0.72 (0.66)	12
	→	$SiC_3H_3^+ \cdot NH_3$			
$SiN(CH_3)_2^+ + (CH_3)_3N$	→	$SiN(CH_3)_2^+ \cdot (CH_3)_3N$	1.0	0.85	4
$SiC_6H_6^{+\cdot} + D_2$	→	No reaction		< 0.0003	11
$SiC_6H_6^{+\cdot} + H_2O$	→	$SiC_6H_6(H_2O)^{+\cdot}$	0.4	0.20	11

TABLE 1
(continued)

Ion/neutral reaction		BR	k_{exp}	Ref.
	→ $C_6H_6^{+\cdot}$ + ($SiOH_2$)	0.35		
	→ $C_6H_7^+$ + $SiOH^\cdot$	0.25		
$SiC_6H_6^{+\cdot}$ + NH_3	→ $SiC_6H_6^{+\cdot}NH_3$	1.0	0.39	11
$SiC_6H_6^{+\cdot}$ + N_2	→ No reaction		< 0.0002	11
$SiC_6H_6^{+\cdot}$ + O_2	→ $C_6H_6^{+\cdot}$ + (SiO_2)	0.9	0.003	11
	→ $C_6H_6O^{+\cdot}$ + SiO	0.1		
$SiC_6H_6^{+\cdot}$ + CO	→ No reactions		< 0.00009	11
$SiC_6H_6^{+\cdot}$ + C_2H_2	→ $SiC_8H_8^{+\cdot}$	0.6	0.06	11
	→ $SiC_8H_7^+$ + $H^\cdot$	0.4		
$SiC_6H_6^{+\cdot}$ + C_4H_2	→ $SiC_4H_2^{+\cdot}$ + C_6H_6	> 0.3	0.70	11
	→ $SiC_6H_6^{+\cdot}\cdot C_4H_2$	< 0.7		
$SiC_{10}H_8^{+\cdot}$ + D_2	→ No reaction		< 0.00035	10
$SiC_{10}H_8^{+\cdot}$ + H_2O	→ $C_{10}H_8^{+\cdot}$ + ($SiOH_2$)	1.0	0.0055	11
$SiC_{10}H_8^{+\cdot}$ + NH_3	→ $SiC_{10}H_8^{+\cdot}\cdot NH_3$	1.0	0.41	11
$SiC_{10}H_8^{+\cdot}$ + N_2	→ No reaction		< 0.0004	10
$SiC_{10}H_8^{+\cdot}$ + O_2	→ $C_{10}H_8^{+\cdot}$ + (SiO_2)	1.0	0.00037	10
$SiC_{10}H_8^{+\cdot}$ + CO	→ No reaction		< 0.00031	11
$SiC_{10}H_8^{+\cdot}$ + C_2H_2	→ $C_{10}H_8^{+\cdot}$ + (SiC_2H_2)	0.9	0.063	10
	→ $SiC_{10}H_8^{+\cdot}\cdot C_2H_2$	0.1		
$SiC_{10}H_8^{+\cdot}$ + C_4H_2	→ $C_{10}H_8^{+\cdot}$ + (SiC_4H_2)	1.0	1.0	10
$SiC_{10}H_8^{+\cdot}$ + C_6H_6	→ No reaction		< 0.0006	10

We have found that molecular hydrogen does not react with ground state Si^+ (^2P) ions but will transfer a hydrogen atom to excited state Si^+ (^4P) ions as shown in reaction (2) with deuterium [3]. These results are not surprising. For X = H, reaction (3) is endothermic by 29 kcal mol^{-1} while reaction (4) is endothermic by 160 kcal mol^{-1} with ground state silicon ions. The excited ^4P state lies 122 kcal mol^{-1} above the ground state.

No hydrogen-atom transfer reactions have been encountered so far with ground state atomic silicon ions, and only a few reactions have been identified and characterized which establish the Si–H bond by hydride transfer. The

TABLE 2
Experimental and computed proton affinities (*PA*) in kcal mol^{-1}

Molecule/Ion	PA_{calc}	PA_{exp}	Ref.
SiNH/$SiNH_2^+$	202.8	203 ± 2	9
SiNH/$HSiNH^+$	149.4		9
SiO/$SiOH^+$	192.4	189.3 ± 2.6	6
SiO/$HSiO^+$	131.8		6
SiS/$SiSH^+$	167.1	170.3 ± 2.0	6
SiS/$HSiS^+$	154.8		6

latter include the reactions with diacetylene and the aliphatic amines $(CH_3)_x NH_{3-x} (x = 1–3)$ which presumably are driven by the stability of X^+, a notion which is reinforced by the observation of an increase in the importance of hydride transfer with the more substituted amines, as discussed later.

Available enthalpies of formation [13] indicate that the proton affinity of silicon is quite high, $PA(\mathrm{Si}) = 200\,\mathrm{kcal\,mol^{-1}}$, so that we can expect facile Si–H bond formation through proton transfer according to reaction (5). Reactions of type (5) have not been measured but the reactivity of SiH^+ is currently being investigated so that we may bracket the proton affinity directly.

$$XH^+ + Si \rightarrow SiH^+ + X \tag{5}$$

Bonding silicon to nitrogen

Ground state silicon ions reacting with ammonia initiate the following reaction sequence which, according to theoretical studies, selectively establishes hydrogen silaisonitrile, Si = N–H; the silicon analogue of CNH [9]:

$$Si^{+\cdot} + NH_3 \rightarrow SiNH_2^+ + H^\cdot \tag{6}$$

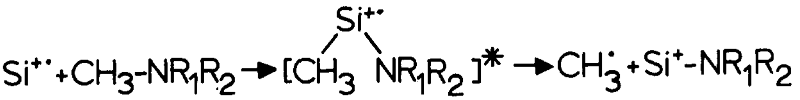
$$SiNH_2^+ + NH_3 \rightarrow SiNH + NH_4^+ \tag{7}$$

Reaction (6) is exothermic only for the formation of the $SiNH_2^+$ isomer which is 53.4 kcal mol^{-1} more stable than the $HSiNH^+$ isomer, while reaction (7) is exothermic only for the formation of SiNH and not the formation of HSiN, which is at least 55 kcal mol^{-1} higher in energy. The H atom eliminated in reaction (6) arises from the N–H bond undergoing insertion [4,9].

Hydrogen silaisonitrile, SiNH, apparently has not yet been observed in the gas phase, but it has been trapped in an argon matrix in an early study of the photolysis of silyl azide, SiH_3N_3, at 4 K [14]. Several interstellar emission lines have been tentatively attributed to HSiN [15] but calculated microwave frequencies for HSiN are not consistent with this assignment. The occurrence of reactions (6) and (7) in interstellar environments will contribute only to the formation of the SiNH isomer.

The proton affinity of silaisonitrile has been calculated at the MP4SDTQ/6-31G**//6-31G** level of theory for protonation at either the Si or N atom [9]. Proton affinities of 202.8 and 149.4 kcal mol^{-1} have been obtained for protonation at N and Si respectively. When combined with a computed enthalpy of formation for SiNH of 50.2 kcal mol^{-1} and an enthalpy of formation for H^+ of 365.7 kcal mol^{-1} [13], these values provide enthalpies of formation at 298 K for $SiNH_2^+$ and $HSiNH^+$ of 213.1 and 266.5 kcal mol^{-1} respectively. An experimental bracketing study with the ion produced in reaction (6) has indicated a proton affinity of 203 ± 2 kcal mol^{-1} which confirms the formation of the $SiNH_2^+$ isomer in reaction (6) [9]. The calculations indicate that the $SiNH_2^+$ isomer is best described as the silene $:Si^+\text{-}NH_2$. The ionic products which were observed for the reactions of $SiNH_2^+$ with $(CH_3)_2CO$ and $(CH_3)_2S$ are consistent with a silene character for $SiNH_2^+$ since they can be formed by carbene-like insertion into C–C and C–S bonds or, in the case of $(CH_3)_2S$, also by H^- transfer to form the aminosilylene $:Si(H)NH_2$[4].

Hydride transfer was not observed to compete with N–H bond insertion in the reaction of $Si^{+\cdot}$ with ammonia but it quickly becomes the predominant channel with increasing methyl substitution as the product immonium ions become increasingly stable. The product distribution measurements for the reactions of $Si^{+\cdot}$ with the methylamines CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ can be understood in terms of $Si^{+\cdot}$ insertion into N–H and/or C–N bonds to form ions of the type $SiNR_1R_2^+$ ($R_1, R_2 = H, CH_3$) proceeding in competition with hydride transfer to form immonium ions of the type $CH_2R_1R_2^+$ according to the reactions (8) and (4):



$$Si^{+\cdot} + CH_3\text{-}NR_1R_2 \rightarrow [CH_3 \overset{Si^{+\cdot}}{\diagup\diagdown} NR_1R_2]^* \rightarrow CH_3^{\cdot} + Si^+\text{-}NR_1R_2 \qquad (8)$$

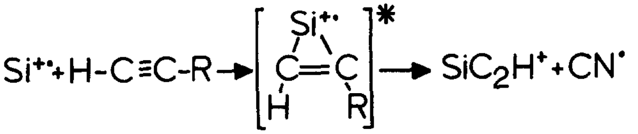
$$Si^{+\cdot} + H\text{-}CH_2\text{-}NR_1R_2 \rightarrow SiH^{\cdot} + CH_2NR_1R_2^+ \qquad (9)$$

C–N bond insertion predominates over N–H bond insertion with methylamine and dimethylamine. The hydride-transfer reaction leads directly to the formation of SiH. The aminosilicon ions $Si^+\text{-}NR_1R_2$ may neutralize by proton or methyl-cation transfer and so provide sources for the doubly bonded silicon/nitrogen molecules $:Si = N\text{-}H$ and $:Si = N\text{-}R$ [4].

The results for the reactions with the methylamines indicate a preference for Si–N and Si–H bond formation over Si–C bond formation. A similar preference appears in the reactions of $Si^{+\cdot}$ with hydrogen cyanide and cyanogen which both form $CNSi^+$ as the bimolecular product ion [5]. Available thermochemical data indicate that formation of the $SiCN^+$ isomer is endothermic with cyanogen and probably also hydrogen cyanide. Calculations at the MP4/6-31G* level indicate that $SiNC^+$ is 10.7 kcal mol^{-1} more stable than the $SiCN^+$ isomer [16]. The $SiNC^+$ isomer can be formed directly if the $Si^{+\cdot}$ approaches these two molecules end-on and attacks the N atom as shown in reaction (10):

$$Si^{+\cdot} + NC\text{-}R \rightarrow [Si^{+\cdot} \cdot\cdot\cdot NC \cdot\cdot\cdot R]^\star \rightarrow SiNC^+ + R \qquad (10)$$

The production of $SiNC^+$ from the reaction of $Si^{+\cdot}$ with HCN is analogous to the exclusive production of CNC^+ from the reaction of $C^{+\cdot}$ with HCN which has been demonstrated experimentally. Also, measurements in our laboratory have shown that $C^{+\cdot}$ reacts with cyanogen to produce C_2N^+ which must be the CNC^+ isomer if the reaction is to be exothermic. The mechanism for the bimolecular production of CH_2Si^+ in the reaction of $Si^{+\cdot}$ with acetonitrile is less certain. A likely structure for CH_2Si^+ is $H_2C = Si^{+\cdot}$ which may be formed directly by C–H bond insertion, for example. Cyanoacetylene reacts with $Si^{+\cdot}$ in a manner characteristic of acetylenes which are thought to lead to cyclic intermediates in a manner shown by Eq. (11) where R = H or CN:



(11)

Adduct formation was a feature common to all the four cyanides studied. For the adduct ion formed with HCN, computations show that the linear $^2\Pi$ species in which Si is bonded to N, $SiNCH^{+\cdot}$, is energetically the most favourable structure of the adduct ion [5]. The Si–N bond in this structure is relatively long (1.944 Å) and only partially covalent since only about 25% of the positive charge on Si is delocalized over the NCH moiety. The calculated Si^+–NCH bond energy is 46.0 kcal mol^{-1}. The corresponding values for the $CNCH^{+\cdot}$ adduct ion calculated at the same level of theory are 54% and 88.9 kcal mol^{-1}, respectively, with a C^+–NCH bond length of 1.275 Å [5].

The ion/molecule reactions of $Si^{+\cdot}$ with cyanide molecules provide interesting opportunities for the synthesis of novel molecules when followed by neutralization. The reactions with HCN and C_2N_2 become sources of CNSi when followed by charge transfer, while the reactions with CH_3CN and cyanoacetylene become sources of CHSi and C_2Si when followed by proton transfer. Given that CN and C_2 have similar electron affinities, we may note that the CNSi molecule is likely to be largely ionic in character ($CN^- Si^+$) in analogy with the $C_2^- Si^+$ electronic structure recently proposed for C_2Si [17]. The $CNSi^+$ ion may play a role as a reactive intermediate in the manner proposed for the carbon analogue CNC^+ [18]. CNC^+ is known to react with molecules of the type HX in a manner similar to C^+ to form C–X bonds. Analogous reactions of $CNSi^+$ would lead to Si–X bond formation.

The adduct ions produced as primary products in the reactions of $Si^{+\cdot}$ with cyanides and as higher-order products of sequential addition reactions, also provide opportunities for interesting synthesis. For example, the $C_3HNSi^{+\cdot}$ adduct formed from cyanoacetylene, the $C_2N_2Si^{+\cdot}$ adduct formed from $CNSi^+$ and HCN, and the $C_5H_2NSi^+$ adduct formed from C_2HSi^+ and cyanoacetylene are possible sources for the molecules $(:SiC_3N)^\cdot$, $:Si(CN)_2$, and $:Si(C_2H)C_3N$, respectively, when they are neutralized by proton transfer, charge transfer or recombination with electrons.

The oxidation and sulphidation of $Si^{+\cdot}$ is of interest in connection with interstellar and circumstellar chemistry in which both SiO and SiS are known to be participants. For example, mm emission from SiO, including maser emission, originates from the outflows of a number of oxygen-rich stars together with emission features indicative of the presence of silicate grains [19]. Emissions from SiO and SiS also originate from dense interstellar clouds such as Sgr B2 [20]. These observations have raised questions about sources and sinks for these molecules as well as their role as intermediates in the gas-phase growth of silicates. The introduction of silicon into the Earth's upper atmosphere by meteor ablation also triggers silicon chemistry, in part through $Si^{+\cdot}$, leading to the formation of silicon oxides. In 1971 a mass spectrometric probe of the upper atmosphere revealed the presence of an ion with a mass-to-charge ratio of 45 which was assigned to $SiOH^+$ [21].

The bimolecular oxidation of atomic silicon ions by molecules of the type XO in the gas phase may occur by O-atom transfer or O^--anion transfer as shown in reactions (12) and (13):

$$Si^{+\cdot} + XO \rightarrow SiO^{+\cdot} + X^{\cdot} \qquad (12)$$

$$Si^{+\cdot} + XO \rightarrow SiO + X^{+\cdot} \qquad (13)$$

Sulphidation can occur in a completely analogous fashion. Systematic measurements have shown that all four of these reactions are thermodynamically controlled at room temperature [7]. The affinities of $Si^{+\cdot}$ for O, O^-, S and S^- are all relatively low. Of the gases CO, O_2, NO, NO_2, N_2O, CO_2, SO_2, COS and CS_2, only NO_2 and N_2O transfer an O atom, only NO_2 and SO_2 transfer an O^- anion and only OCS transfers an S atom to $Si^{+\cdot}$. Otherwise adduct formation occurs, except with CO [7].

The higher-order oxidation of $SiO^{+\cdot}$ and sulphidation of $SiS^{+\cdot}$ has also been investigated [7]. Reactions with NO_2 and N_2O establish SiO_2 and $SiO_2^{+\cdot}$ and further reactions observed with N_2O suggest the occurrence of sequential oxidation by O-atom transfer up to $SiO_4^{+\cdot}$ as in reaction (14):

$$Si^{+\cdot} \rightarrow SiO^{+\cdot} \rightarrow SiO_2^{+\cdot} \rightarrow SiO_3^{+\cdot} \rightarrow SiO_4^{+\cdot} \qquad (14)$$

Also there is evidence to support analogous reactions with COS which may lead to silicon sulphide ions up to $SiS_3^{+\cdot}$. There is essentially no structural or energetic information available for these polyoxide and polysulphide ions.

A very rich chemistry is initiated by $Si^{+\cdot}$ with molecules containing hydroxyl groups. Table 1 shows that $Si^{+\cdot}$ reacts rapidly with H_2O, CH_3OH, C_2H_5OH, HCOOH and CH_3COOH. The latter four reactions occur essentially at every collision. The silene cation, $SiOH^+$, is the predominant product

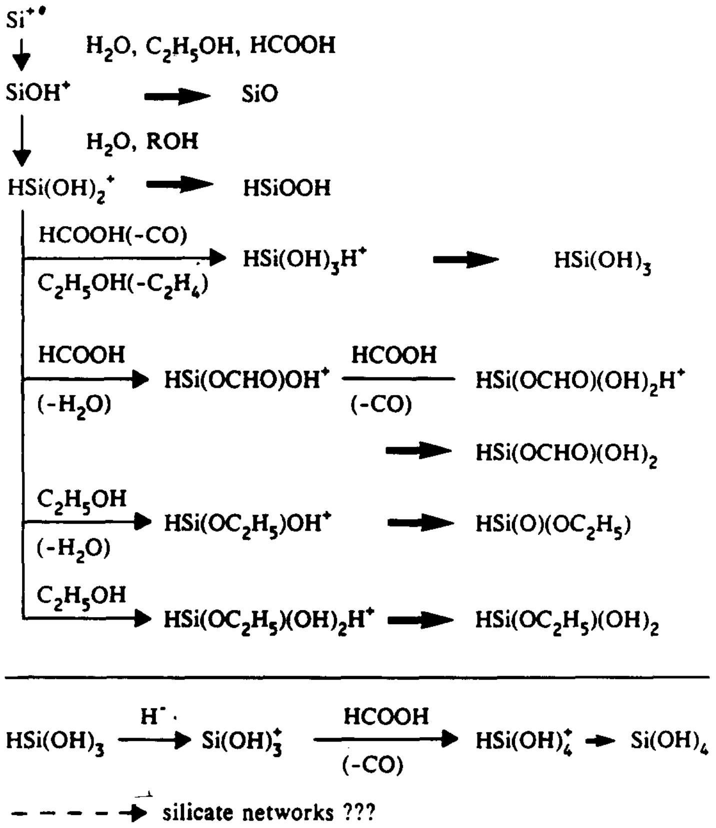


Fig. 1. Limited reaction scheme for the synthesis of silicon oxide, silanoic acid and substituted silanes initiated by atomic silicon ions. The reaction path from trihydroxy to tetrahydroxy silane is speculative. Heavy arrows indicate neutralization reactions such as recombination with electrons and proton transfer.

in all five reactions and may arise from C–OH (H–OH) bond insertion as illustrated in reaction (15):

$$Si^{+\cdot} + R\text{–}OH \rightarrow SiOH^{+} + R^{\cdot} \qquad (15)$$

$SiOH^+$ itself efficiently propagates further chemistry. One overview of the extensive chemistry which has been observed to be initiated by $Si^{+\cdot}$ is given in Fig. 1 which shows that silicon can become increasingly coordinated to oxygen in sequential reactions with oxygen-containing molecules and so form a number of substituted silanes. Indeed, on the basis of the observation of this rich chemistry, we have been tempted to speculate about possible higher-order chemistry which leads to tetrahydroxy silane which is a known building block for silicate networks [3].

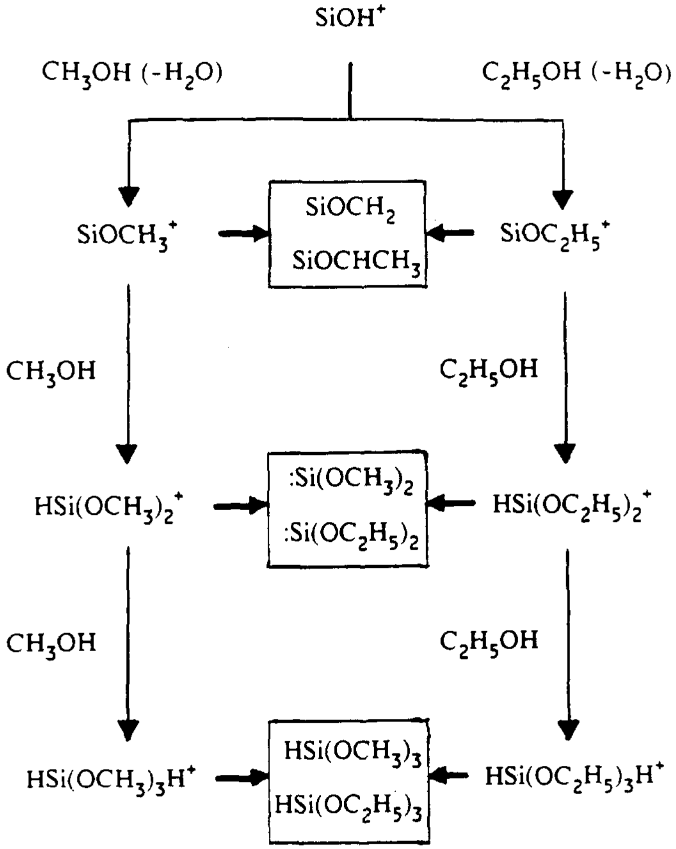


Fig. 2. Limited reaction scheme for the synthesis of Si–O molecules initiated by $SiOH^+$ in methanol and ethanol. Heavy arrows indicate neutralization reactions such as recombination with electrons and proton transfer.

The $SiOH^+$ ion produced in reaction (15) has the silylene character $:Si^+\text{–}OH$. Calculations have shown the $HSiO^+$ isomer to be 60.6 kcal mol^{-1} higher in energy and so inaccessible [6]. In analogy with reactions of carbenes, we can then expect O–H insertion to be preferred in the reactions of $SiOH^+$ with molecules containing hydroxyl groups. Indeed, all the major reactions which have been observed with $SiOH^+$ can be rationalized in terms of this single mechanism. At the helium pressure of the SIFT experiments the intermediate formed by the insertion may also be collisionally stabilized:

$$\mathrm{SiOH^+ + RO\text{–}H \rightarrow [HOSi(H)OR]^{+*} \longrightarrow products} \qquad (16a)$$

$$\xrightarrow{\mathrm{He}} \mathrm{HOSi^+(H)OR} \qquad (16b)$$

Figure 2 shows insertion chemistry of $SiOH^+$ in methanol and ethanol. It is initiated by the bimolecular dehydration of these two alcohols as water molecules are eliminated. Sequential addition reactions lead to ions in which silicon is increasingly coordinated with oxygen. Figure 2 also shows the interesting opportunities for the formation of new oxygen-coordinated silicon molecules upon neutralization by proton transfer or electron/ion recombination.

$SiH_3O_2^+$ is a predominant product ion in the reactions of $SiOH^+$ with water, ethanol and formic acid. Mechanistic considerations suggest that this ion is protonated silanoic acid, $HSi(OH)_2^+$. The observed reactivity of this ion is shown in Fig. 1 together with likely structures of the oxygen-containing product ions and neutral molecules which may be formed on their neutralization.

The ν_1(H–O, D–O) stretches of $SiOH^+$ and $SiOD^+$ have now been observed with a difference-frequency IR-laser system in a hollow cathode discharge [22]. The silene ions were generated by discharging either trimethylsilanol, $(CH_3)_3SiOH$ (or $(CH_3)_3SiOD$) in a buffer containing H_2 (or D_2) and He, or by discharging a mixture of SiH_4 and N_2O in a buffer of H_2 or H_2 and He. The spectroscopic constants which were obtained agree well with theoretical predictions.

Bonding silicon to carbon

The identification of *c*-SiC_2 in the circumstellar envelope of IRC + 10216 several years ago [23] had sparked our interest in ion chemistry leading to Si–C bond formation. A number of reactions of $Si^{+\cdot}$ with interstellar hydrocarbon molecules have now been characterized in our laboratory and the results are beginning to provide insight into the bonding of silicon to carbon. In one case the observed chemistry led to the prediction of a circumstellar molecule which has recently been detected. The studies so far have concentrated on the formation of Si–C bonds which may proceed by C–H and C–C bond insertion.

In sharp contrast to $C^{+\cdot}$, $Si^{+\cdot}$ reacts only slowly with methane to form the adduct ion $SiCH_4^{+\cdot}$. Ab initio calculations provide support for the formation of a loosely bound adduct with a bridged C_{2v} structure ($^2B_1$) with a dissociation energy of only 9.6 kcal mol^{-1} [12]. Computed barriers of 14.0 and 18.6 kcal mol^{-1} are too high for isomerization to take place to the more stable $HSiCH_3^{+\cdot}$ and $H_2SiCH_2^{+\cdot}$ ions respectively. Ethane reacts rapidly to form primarily $SiCH_3^+$ and $SiCH_2^{+\cdot}$, both of which can form by either C–C or C–H bond insertion [12].

Rapid reactions have also been observed with the unsaturated molecules ethylene, acetylene, allene, methylacetylene and diacetylene. Hydrogen atom elimination, presumably arising from C–H bond insertion, is the dominant bimolecular channel with each of these molecules except diacetylene [8,12].

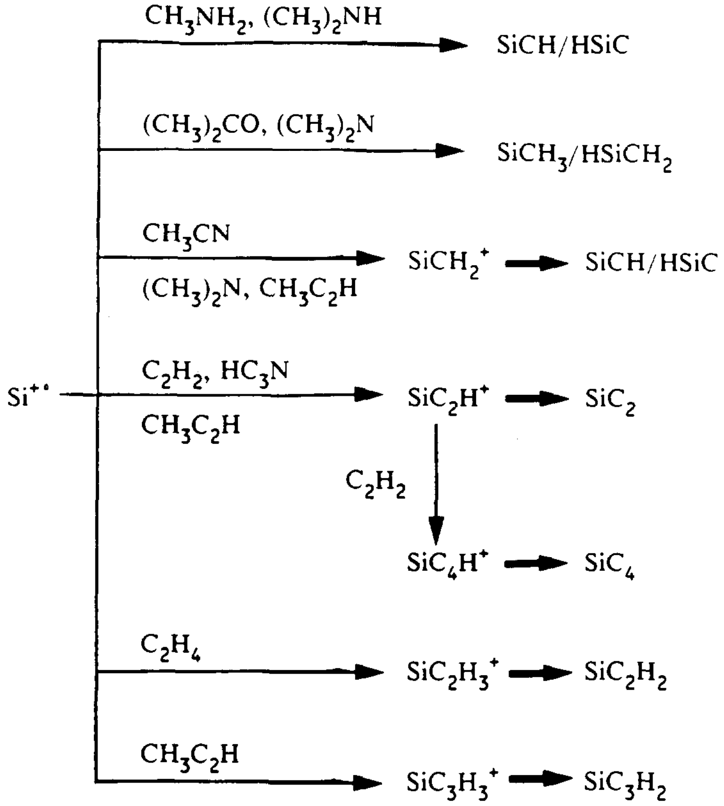


Fig. 3. Limited reaction scheme for the synthesis of Si–C molecules initiated by atomic silicon ions. The heavy arrows indicate neutralization reactions such as recombination with electrons and proton transfer.

Figure 3 summarizes the ion/molecule reaction paths initiated by ground state atomic silicon ions and leading to Si–C bond formation which we have identified so far. In the case of SiCH/HSiC and $SiCH_3/HSiH_2$ the new silicon–carbide molecule appears directly as a neutral product of the ion/molecule reaction. In 1988 we suggested C_4Si, which may be derived from the neutralization of SiC_4H^+, as a likely circumstellar molecule [8]. This molecule has now been detected in the outer envelope of IRC + 10216, which contains the ingredients necessary for the formation of SiC_4H^+ by the sequential reactions initiated by $Si^{+\cdot}$ with acetylene [24].

Bonding silicon to aromatic molecules

Free neutral and positively charged polycyclic aromatic hydrocarbon (PAH) molecules, either completely or partially hydrogenated, have been invoked to account for observed IR emission features in nebulae and observed diffuse interstellar absorption bands [25,26]. The possible presence of these molecules in these environments has led to a strong interest in their physics and chemistry [27]. At York University we have now investigated the capture of atomic silicon ions by naphthalene, the simplest PAH molecule, and benzene, a possible precursor of naphthalene. By studying the reactions of the resulting adduct ions, we have been able to assess the influence of aromatic molecules on the intrinsic chemistry of the isolated atomic silicon ions.

The most striking feature of the results of these studies is that the chemistry of the $SiC_{10}H_8^{+\cdot}$ adduct ion (except for the reaction with ammonia) is dominated by the elimination of ionized naphthalene in reactions of type (17) [10]:

$$SiC_{10}H_8^{+\cdot} + M \rightarrow C_{10}H_8^{+\cdot} + (SiM) \qquad (17)$$

Assuming that $SiC_{10}H_8^{+\cdot}$ is a π complex with the positive charge distributed over the planar naphthalene molecule (charge transfer to naphthalene is exothermic since $IE(\mathrm{Si}) > IE$ (naphthalene)), this reaction may be viewed as a "surface" reaction in which a neutral Si atom interacts with the incoming molecule M above the plane of the charged naphthalene molecule [10]. In the analogous benzene complex the positive charge is expected to remain on the silicon atom since the charge transfer is endothermic. Indeed, the observed reaction of the benzene complex with acetylene mimics that observed with the free $Si^{+\cdot}$ ion which leads to H-atom elimination and formation of the adduct ion $SiC_2H_2^{+\cdot}$ in a branching ratio of 7/3 [8,12].

The identity of the neutral products of the "surface" reactions of the naphthalene complex is intriguing, particularly if SiM leaves as a bound molecule. SiO_2 is well known as a stable molecule in the gas phase. A matrix-isolation study of the reaction of silicon atoms with water has shown that the silicon atom inserts into the O–H bond to form the HSiOH molecule [28]. The gas-phase reaction of silicon with acetylene has been attributed to efficient addition with ring insertion to form 3-silacyclopropenylidene [29] which is then also a plausible product of the "surface" reaction. Ab initio calculations have shown that 3-silacyclopropenylidene is the most stable isomer of SiC_2H_2[30]. In analogy to the reaction with acetylene, the reaction with diacetylene can be expected to lead to the cyclic attachment of Si to one of the triple bonds. The higher PAH molecules have a lower ionization energy so that "surface" reactions similar to that proposed for naphthalene, viz. reactions of type (18), also can be expected to be efficient, at least with molecules containing acetylene units:

$$SiPAH^{+\cdot} + M \rightarrow PAH^{+\cdot} + (SiM) \qquad (18)$$

We have postulated on the basis of our experimental results with naphthalene that PAH molecules may capture atomic silicon ions in interstellar environments (where the capture would need to proceed by radiative stabilization) and promote the synthesis of novel silicon-containing molecules, SiM, where M may be O_2, H_2O, acetylene, polyacetylenes and possibly cyanopolyacetylenes [10]. Furthermore, other atomic cations, $X^{+\cdot}$, may lead to similar capture and chemistry as shown in reactions (19) and (20):

$$X^{+\cdot} + PAH \longrightarrow XPAH^{+\cdot} \tag{19}$$

$$XPAH^{+\cdot} + M \longrightarrow PAH^{+\cdot} + (XM) \tag{20}$$

We note here that the ionization energies (given in parentheses in electronvolts) of the interstellar atoms of S (10.360), Zn (9.394), Fe (7.870) and Mg (7.646) are all larger than that typical for the larger PAH molecules (7.0). The capture and chemistry of the corresponding atomic ions will be the subject of future studies in our laboratory.

SUMMARY

The silicon chemistry studied in our laboratory so far has been restricted to chemistry initiated by ground state atomic silicon ions. Although inert toward H_2 and CO, these ions have been found generally to be quite reactive towards other molecules. Often these reactions lead to the formation of a chemical bond with silicon. We have now identified ion/molecule reactions of Si^+ (^2P) leading to Si–H, Si–C, Si–N, Si–O and Si–S bond formation. Chemical pathways have been reported which lead to the following silicon-bearing molecules:

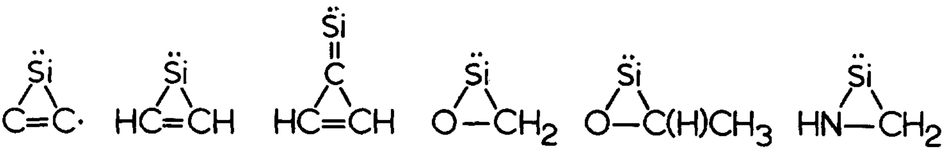
SiH, $SiCH$, $SiCH_3$, SiC_2, SiC_2H_2, SiC_3H_2, SiC_4

SiO, SiO_2, SiS, SiS_2

$HSiOOH$, $SiOCH_2$, $SiOC(H)CH_3$, $HSi(OH)_3$, $HSi(O)(OCHO)$, $HSi(O)(OC_2H_5)$, $HSi(OCHO)(OH)_2$, $Si(OCH_3)_3$, $Si(OC_2H_5)_2$, $HSi(OC_2H_5)_3$

$SiNH$, $SiNCH_3$, H_2SiNH_3

The isomeric structure of the ground states of many of these molecules is uncertain. Little spectroscopic information and few quantum chemical calculations are available to provide insight. Several are likely to be cyclic molecules as shown below. For example, SiC_2 is known to be cyclic. In the case of SiC_2H_2, 3-silacyclopropenylidene has been found to be a global minimum in the singlet potential energy hypersurface [30]. Clearly however, considerable scope remains for further computational, and possibly spectroscopic studies.



The results with aromatic molecules point toward the exciting prospect of studying "surface" chemistry in the gas phase with graphite-like molecules. Experiments are being planned with atomic ions other than silicon and aromatic molecules larger than naphthalene. Current measurements have been extended to silicon-bearing ions other than $Si^{+\cdot}$.

Many of the reactions reported here have recently been incorporated in a pseudo-time-dependent model of the gas-phase chemistry of silicon in dense interstellar clouds [31].

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