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Gas-phase Oxidation and Sulphidation of $Si^+(^2P)$, SiO^+ and SiS^+

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Experimental results are presented for a selected-ion flow tube (SIFT) study of the kinetics of oxidation and sulphidation of $Si^+(^2P)$, SiO^+ and SiS^+ with the molecules O_2, NO, CO_2, NO_2, N_2O, COS, CS_2 and SO_2 at 294 ± 2 K. Both adduct ions and bimolecular products were identified. The bimolecular oxidation and sulphidation reactions of $Si^+(^2P)$ which were observed to form SiO^+, SiO, SiS^+ or SiS by atom or atomic anion transfer are shown to be thermodynamically controlled. Adduct formation is viewed in terms of a model involving O-atom transfer within the intermediate complex. The same model also provides reasonable mechanisms for the bimolecular oxidation and sulphidation reactions of Si^+, SiO^+ and SiS^+ which were observed. The implications of the results are discussed for the oxidation and sulphidation of silicon ions in general, and in the interstellar medium in particular.

Oxides of silicon are ubiquitous both in terrestrial and extraterrestrial environments. For example, it is common knowledge that silicon dioxide is the main component of the earth's crust. Less well known is the presence of oxides of silicon in extraterrestrial environments. We note here that mm emission from SiO, including maser emission, has been observed to originate from the outflows of a number of oxygen-rich stars together with emission features indicative of the presence of silicate grains.[1] Also, emissions from the molecules SiO and SiS have been observed to originate from dense interstellar gas clouds such as Sgr B2.[2,3] These observations have raised questions about the extraterrestrial chemical sources and sinks of these molecules, as well as their role as intermediates in the gas-phase formation of silicate grains. Both neutral and ionic reactions of silicon are expected to be important as sources and sinks since these extraterrestrial environments are partially ionized, either thermally or chemically, or by u.v. photons and cosmic rays. An understanding of the homogeneous nucleation of silicon oxides is also of practical importance in the formation of particles and thin films of silicon oxides. These are being studied with suitably designed flames,[4] shock-tube and plasma devices,[5,6] or with direct vaporization techniques.[7]

The growth of oxides of silicon may be initiated by reactions either of silicon atoms or of atomic silicon ions. The chemistry of isolated silicon atoms has been difficult to investigate in the laboratory. Nevertheless, some experimental studies of the kinetics for reactions of silicon atoms with simple oxygen-containing molecules have been reported in which these atoms are prepared by the pulsed irradiation of $SiCl_4$ and monitored by atomic absorption spectroscopy.[8] Here we present experimental results for reactions with atomic silicon ions in their ground electronic ^2P state. In contrast to neutral atoms of silicon, silicon ions are readily produced in isolation in the gas phase by selection with a mass spectrometer from a mixture of ions produced by electron impact of a suitable parent molecule such as $Si(CH_3)_4$. Such a technique for producing silicon ions has been adopted in this study performed with a selected-ion flow tube or SIFT mass spectrometer.[9,10] The SIFT instrument has the additional advantage that ionized compounds of silicon which may be produced as reaction products when neutral reactants are added into the flow tube can be monitored with a second mass spectrometer.

Table 1. Thermodynamic affinities or bond dissociation enthalpies (in kcal mol^{-1})^a for atomic oxygen, atomic sulphur, the oxide anion and the sulphide anion at 298 K

O, S atom affinities		O^-, S^- anion affinities	
C—O	257.3	C^+—O^-	483.2
C^+—O	195 ± 2	N^+—O^-	452.5
Si—O	192 ± 4	OC^+—O^-	415 ± 2
SC—O	160 ± 6	O^+—O^-	399.3
N—O	151.0	SC^+—O^-	389 ± 3
OS—O	131.7	NN^+—O^-	365.5
OC—O	127.3	OC^+—S^-	347 ± 3
O—O	119.2	Si^+—O^-	345 ± 3
Si^+—O	114 ± 5	OSi^+—O^-	340 ± 12
OSi^+—O	111 ± 24	OS^+—O^-	337 ± 2
SC—S	105 ± 6	SC^+—S^-	320 ± 2
Si^+—S	101 ± 4	Si^+—S^-	289 ± 4
ON—O	73.3	ON^+—O^-	253.1
OC—S	72.9		
NN—O	40.0		

[a] Unless indicated otherwise, the uncertainty is <1.0 kcal mol^{-1}. All enthalpies of formation were taken from the JANAF tables[11] except those for CO^+, CS^+ and OS^+ which were estimated to be 297 ± 2, 331 ± 3 and 242 ± 2 kcal mol^{-1} at 298 K from the compilation of Rosenstock *et al.*[12] Also, the enthalpies of formation for SiO^+, SiS^+ and SiO_2^+ were estimated from reported ionization energies of 11.58 ± 0.10 eV[13], 10.26 eV[14] and 11.5 ± 0.5 eV[15] to be 243 ± 4, 262 ± 3 and 192 ± 20 kcal mol^{-1}, respectively.

A variety of diatomic and triatomic molecules were chosen as neutral reactants including CO, O_2, NO, NO_2, N_2O, CO_2, SO_2, COS and CS_2. These molecules are all potential donors of oxygen or sulphur and many of them have been identified in extraterrestrial environments.

With molecules of the type XO, bimolecular oxidation of atomic silicon ions may occur by O-atom transfer:

$$Si^+ + XO \rightarrow SiO^+ + X \tag{1}$$

or by O^--anion transfer:

$$Si^+ + XO \rightarrow SiO + X^+. \tag{2}$$

Sulphidation may occur in a completely analogous fashion with molecules of the type XS. The standard enthalpy change of reaction (1) will be determined by the relative O atom affinity (henceforth referred to as A_O) of Si^+ and X, while that of reaction (2) will be governed by the relative O^--anion affinity (henceforth referred to as A_{O^-}) of Si^+ and X^+. The analogous reactions involving S are governed by differences in A_S and A_{S^-}. Table 1 summarizes values for the O, O^-, S and S^- affinities for a number of the molecules of interest. Perhaps surprisingly, the atomic silicon ion is seen to have relatively low affinities for O, O^-, S and S^-. For the molecules listed in table 1, O-atom transfer with Si^+ is thermodynamically allowed only for NO_2 and N_2O, O^--anion transfer is possible only for SO_2 and NO_2, and S-atom transfer is possible only for COS. Indeed, we shall see that only these heavy-atom or anion transfer reactions occur in the gas phase at

294 K and that similar higher-order reactions are possible with NO_2, N_2O and COS. The remaining molecules are constrained to undergo association reactions.

Experimental

All measurements of rate constants and product distributions were performed with the selected-ion flow tube (SIFT) apparatus which has been described in detail elsewhere.[9,10] Atomic silicon ions in their ground electronic ^2P state were derived from 3-7 mol% mixtures of tetramethylsilane in deuterium by electron impact at 45-100 eV. The deuterium was added to scavenge metastable $Si^+(^4P)$ ions in the source with the following reaction:[16]

$$Si^+(^4P) + D_2 \rightarrow SiD^+ + D. \tag{3}$$

Metastable atomic silicon ions are also depleted at the higher additions of tetramethylsilane probably due indirectly to the partial degradation of the initial kinetic energy distribution of the electrons and directly to selective ion/molecule reactions such as the charge-transfer reaction:

$$Si^+(^4P) + Si(CH_3)_4 \rightarrow Si(CH_3)_4{}^+ + Si. \tag{4}$$

This charge transfer is endothermic relative to ground-state atomic silicon ions by 1.7 eV.

Only the isotope of Si^+ at $m/z = 28$ was selected and introduced upstream into the helium buffer gas at 0.34 ± 0.02 Torr.† Neutral reactants were added downstream. Primary and secondary ions were monitored as a function of the added neutral reagents. Rate constants and product distributions were determined in the usual manner. They were observed to be independent of the mode of formation of the ground-state Si^+ ions and the initial electron energy. No attempt was made to investigate the pressure dependence of rate constants and product distributions. Traces of water vapour in the helium buffer gas were removed by passing the buffer gas through a zeolite molecular sieve at 77 K. The reactant gases NO, CO_2, SO_2 and COS were reagent grade (Matheson) while N_2O and O_2 were used as ultra-high purity gases. The CS_2 was of spectroquality (Matheson, Coleman & Bell) while the NO_2 had a purity of 99.5% (Union Carbide).

Results

Reactions with $Si^+(^2P)$

Table 2 provides a summary of the rate constants, products, and product distributions which have been determined in this laboratory for reactions of gound-state $Si^+(^2P)$ ions with CO, O_2, NO, CO_2, N_2O, NO_2, SO_2, COS and CS_2. We have reported previously that $Si^+(^2P)$ does not react with CO.[16] Two types of reaction were observed with the remaining molecules: the formation of adduct ions and the formation of bimolecular products. Adduct formation occurred most rapidly, and exclusively, with CS_2 and was also observed with O_2, NO and CO_2, but it was much slower with these latter molecules. In the reaction with NO_2 adduct formation was observed to compete with O-atom and O^--anion transfer. The reactions with COS and SO_2 formed only bimolecular products.

Only upper limits to the rate constants could be determined from the observed decays of Si^+ for O_2, CO_2 and NO. The presence of impurities allowed only a moderately high upper limit to be set to the rate constant for the reaction with NO since they contributed to the observed decay which an effective rate constant of 1.0×10^{-11} cm^3 molecule^{-1} s^{-1}. Possible impurities are nitrogen compounds such as NO_2 and N_2O_3 and possibly HNO_2 and HNO_3 initially present and/or produced by oxidation of NO with traces of O_2 and

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† 1 Torr = 101 325/760 Pa.

Table 2. Rate constants (in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}) and product distributions for reactions of Si^2 (^2P) with molecules of the type MX (X = O, S) at 294 ± 2 K

MX	products	product distribution[a]	k_{exptl}[b]	k/k_c[c]	ΔH°_{298}[d]
CO	no reaction		<0.0002	<0.000 02	
O_2	SiO_2^+		<0.001	<0.000 13	−105 ± 21
NO	$SiNO^+$		<0.1	<0.012	
NO_2	$SiO^+ + NO$	0.68	8.6	0.83	−41 ± 5
	$NO^+ + SiO$	0.30			−92 ± 3
	$SiNO_2^+$	0.02			
N_2O	$SiO^+ + N_2$		4.0	0.40	−74 ± 5
CO_2	$SiCO_2^+$		<0.0017	<0.000 19	
SO_2	$SO^+ + SiO$		8.1	0.41	−8 ± 5
COS	$SiS^+ + CO$		9.0	0.63	−28 ± 4
CS_2	$SiCS_2^+$		0.66	0.045	

[a] Product distributions are estimated from experimental repetition to have a relative accuracy of within ±30%. [b] The effective bimolecular rate constant is given at a total helium pressure of 0.34 ± 0.02 Torr and density of 1.1×10^{16} atoms cm^{-3}. The accuracy is estimated to be better than ±30%. [c] k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition-state theory/classical trajectory study of Su and Chesnavich.[17] [d] Changes in enthalpy are based on values given in table 1 and references cited therein.

H_2O present in the buffer gas and adsorbed on the walls of the storage bulb. Fitting the appearance of the $SiNO^+$ and $SiCO_2{}^+$ adduct ions provided values of $(1.5 \pm 0.8) \times 10^{-14}$ and $(2.2 \pm 1.1) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, for the apparent bimolecular rate constants for their formation in helium at 0.35 Torr and 1.1×10^{-16} He atoms cm^{-3}. The uncertainties of ±50% are valid if there are no rapid secondary reactions of the adduct ions, as is expected.

The reactions with O_2 and NO were investigated previously by Fahey *et al.*[18] who reported a value of $(1.0 \pm 0.4) \times 10^{29}$ cm^6 $molecule^{-2}$ s^{-1} for the three-body rate constant for the reaction with O_2 in helium at 0.5 Torr. This translates to an apparent bimolecular rate constant of *ca.* 1.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 0.5 Torr which is in agreement with our limiting value at 0.35 Torr. These authors also reported the same upper limit for the rate constant at room temperature for the addition reaction with NO but not the observation of the adduct ion $SiNO^+$.

Bimolecular products were observed to predominate in the reactions of Si^+ with NO_2, N_2O, SO_2 and COS which were all observed to be rapid. Both O-atom and O^--anion transfer occurred with NO_2, O-atom transfer occurred with N_2O and O^- transfer occurred with SO_2. For the reaction with N_2O, charge transfer had to be considered as a possible product channel since the mass spectrometer could not distinguish between SiO^+ and N_2O^+. However, charge transfer could be excluded on energetic grounds since it is endothermic by 109 kcal mol^{-1}. Only S-atom transfer occurred with COS. In this case the SiS^+ product could not be distinguished from COS^+ with our mass spectrometer, but charge transfer could again be excluded on energetic grounds since it is endothermic by 70 kcal mol^{-1}.

The reaction of Si^+ with N_2O has been observed previously by Creasy *et al.*[19] in their Fourier-transform mass spectrometry (FTMS) experiments with silicon cation clusters. Their reported rate constant of $(8.2 \pm 0.9) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is twice as large as that determined in our study. This discrepancy may be attributed to the non-thermal conditions of the FTMS measurements if the rate constant for this reaction has a kinetic energy dependence.

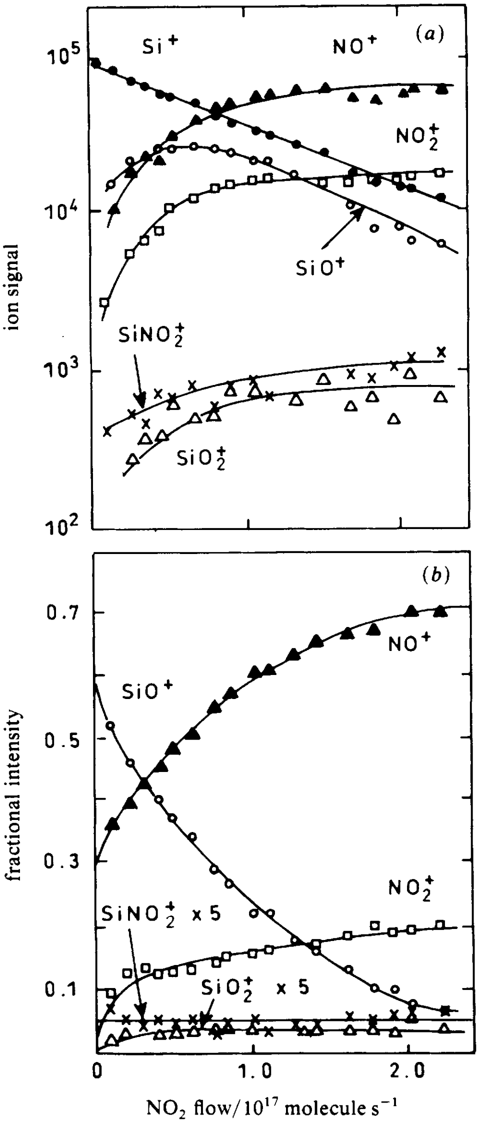

Fig. 1. (*a*) Observed variations in the ion signals recorded for the addition of NO_2 into the reaction region of the SIFT apparatus in which Si^+ is initially established as the dominant ion in helium buffer gas. $P = 0.35$ Torr, $\bar{v} = 6.7 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 292$ K. (*b*) The fractional abundance of the product ions observed in (*a*). The intercepts at zero flow of nitrogen dioxide provide a measure of the primary product distribution and the profiles at high flows provide insight into the secondary reaction of SiO^+ and its product distribution.

Reactions with SiO^+ and SiS^+

The SiO^+ and SiS^+ product ions of the reactions of Si^+ with NO_2, N_2O and COS were observed to undergo further oxidation or sulphidation reactions. This is illustrated in fig. 1(*a*) in which the ion evolution following injection of Si^+ into the flow tube is presented as a function of the NO_2 flow rate. The rate constants for the secondary reactions of SiO^+ and SiS^+ with NO_2, O_2 and COS were derived by fitting the entire SiO^+ or SiS^+ ion profiles with double exponentials. For the reaction of SiO^+ with N_2O

Table 3. Rate constants (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}) and product distributions for reactions of SiO^+ and SiS^+ at 294±2 K

reaction	product distribution[a]	k_{exptl}[b]	k/k_c[c]	ΔH°_{298}[d]
$SiO^+ + O_2 \rightarrow$ no reaction		<0.002	<0.0003	
$SiO^+ + NO_2 \rightarrow NO^+ + SiO_2$	0.63	15	1.6	−87±12
$\rightarrow NO_2^+ + SiO$	0.35			−42±6
$\rightarrow SiO_2^+ + NO$	0.02			−37±24
$SiO^+ + N_2O \rightarrow SiO_2^+ + N_2$		4.8	0.56	−71±24
$SiS^+ + H_2 \rightarrow$ no reaction		< 0.0002		
$SiS^+ + CO \rightarrow$ no reaction		<0.0004		
$SiS^+ + O_2 \rightarrow SO^+ + SiO$	0.70	0.89	0.14	−44±5
$\rightarrow SiO^+ + SO$	0.30			−18±7
$SiS^+ + COS \rightarrow SiS_2^+ + CO$		14	1.2	

[a] Product distributions are estimated from experimental repetition to have a relative accuracy within ±30%. [b] The effective bimolecular rate constant is given at a total helium pressure of 0.34±0.02 Torr and density of 1.1×10^{16} atoms cm^{-3}. The accuracy is estimated to be better than ±30%. [c] k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c, are derived from the classical variational transition-state theory/classical trajectory study of Su and Chesnavich.[17] [d] Changes in enthalpy are based on values given in table 1 and references cited therein.

this fitting procedure was confined to the initial portion of the profile (the first eight flows of N_2O) because of the possible tertiary production of SiO^+ from SiO_2^+. Table 3 provides a summary of the rate constants and product distributions. The product distributions were determined from plots of the type shown in fig. 1(*b*).

The secondary reaction of SiO^+ with NO_2 produced three ions in the distribution indicated by reaction (5). The relative importance of the reaction channels

$$SiO^+ + NO_2 \xrightarrow{0.63} NO^+ + SiO_2 \qquad (5a)$$

$$\xrightarrow{0.35} NO_2^+ + SiO \qquad (5b)$$

$$\xrightarrow{0.02} SiO_2^+ + NO \qquad (5c)$$

appears to follow their exothermicities which are −87±12, −42±6 and −37±24 kcal mol^{-1}, respectively. Channel (5*b*) corresponds to charge transfer. The predominant channel (5*a*) formally corresponds to O^- transfer but may proceed instead by O-atom transfer followed by charge transfer before separation into products. This latter mechanism is suggested by the observation of channel (5*c*) which corresponds to O-atom transfer only.

An extensive secondary chemistry was initated in N_2O by the SiO^+ formed from Si^+. This may be appreciated from the data shown in fig. 2. The analysis of these data is complicated by the mass coincidence of Si and N_2. Sequential ions were observed with masses consistent with the sequential O-atom transfer steps:

$$Si^+ \rightarrow SiO^+ \rightarrow SiO_2^+ \rightarrow SiO_3^+ \rightarrow SiO_4^+. \qquad (6)$$

However, the mass coincidence of Si and N_2 leaves ambiguous the products of:

$$SiO_n^+ + N_2O \rightarrow SiO_{n+1}^+(N_2O_{n+1}^+) + N_2(Si) \qquad (n > 1). \qquad (7)$$

Furthermore, the O_2^+ ions produced in the secondary chemistry are known to add N_2O molecules to form the ions $O_2^+ \cdot N_2O$ and $O_2^+ \cdot (N_2O)_2$, which are mass coincident with SiO_3^+ and $SiO_3^+ \cdot N_2O$, respectively.[20]

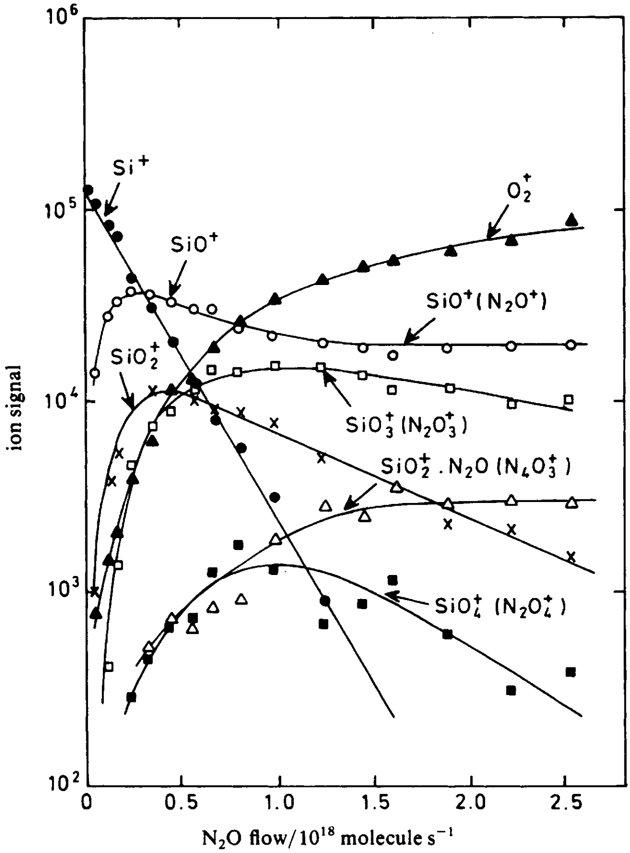

Fig. 2. Observed variation in the ion signals recorded for the addition of N_2O into the reaction region of the SIFT apparatus in which Si^+ is initially established as the dominant ion in helium buffer gas. $P = 0.35$ Torr, $\bar{v} = 6.5 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 294$ K.

We claim here that SiO^+ reacts with N_2O by O-atom transfer to produce SiO_2^+, which is exothermic by 71 ± 24 kcal mol^{-1}, and not by O^+ transfer to form an ion of the type $N_2O_2^+$. Formation of $O_2^+ \cdot N_2$, which is known to be formed from the addition reaction between O_2^+ and N_2,[20] would be endothermic by more than 100 kcal mol^{-1}, and other more stable isomers of $N_2O_2^+$ are not known. The ensuing reaction of SiO_2^+ with N_2O yields O_2^+ and, according to a careful analysis of the early rise in the ion at $m/z = 76$, some SiO_3^+. Formation of O_2^+ (+SiO + N_2) requires excitation of the SiO_2^+ ion since it is endothermic by 42 ±22 kcal mol^{-1} for ground state SiO_2^+ and so implies that most of the 71 kcal mol^{-1} of exothermicity of the reaction of SiO^+ with N_2O appears as excitation of the SiO_2^+. The SiO_2^+ will then also be sufficiently excited to charge-transfer with N_2O to form N_2O^+ which is endothermic by only 32 ± 12 kcal mol^{-1}. This would explain the flat component of the mass 44 peak decay at higher flows of N_2O in fig. 2 (the reaction of N_2O^+ with N_2O is relatively slow).[20] A third channel which becomes possible as a result of the exitation of SiO_2^+ is the production of SiO^+ and this also complicates the derivation of a rate constant for the reaction of SiO^+ with N_2O.

Further evidence for the excitation of SiO_2^+ formed from SiO^+ and N_2O came from separate measurements of its reaction with O_2, which indicated charge transfer with a rate constant of $(7.8 \pm 2.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for a large reactive component of the signal (>90%). Charge transfer is endothermic by 0.6 ± 0.5 eV for ground-state reactants. There also appeared to be a small (<10%) unreactive component to the signal at $m/z = 60$ with $k < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. These observations are very reminiscent of those reported by Fahey *et al.* for the behaviour of SiO_2^+ generated from the addition reaction of Si^+ with O_2, which is exothermic by 105 ± 21 kcal mol^{-1}.[18] The production of SiO_2^+ from SiO^+ and of SiO_3^+ from SiO_2^+ in reactions with N_2O has been observed previously by Creasy *et al.*[19] in their FTMS experiments, but no mention was made by these authors of the mass coincidence. They reported a rate constant of $(2.3 \pm 0.09) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction of SiO^+ and $(3.1 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction of SiO_2^+ to form SiO_3^+ and SiO^+.[19]

An ion with a mass corresponding to SiS_2^+ was observed to be produced in the reaction of SiS^+ with COS for which the rate constant was obtained from a double-exponential fit to the SiS^+ data points. Mass coincidence does not allow us to exclude COS_2^+ as a possible product but S-atom transfer to form SiS_2^+ (in analogy with the reaction of Si^+ with COS) is intuitively preferable to the transfer of S^+ to COS to form COS_2^+. We cannot distinguish between the two possibilities on energetic grounds since enthalpies of formation for SiS_2^+ and COS_2^+ are not available. The SiS_2^+ (COS_2^+) ion did not rapidly react further, $k < 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, but small amounts of an ion with a mass corresponding to SiS_3^+ (or COS_3^+) were observed to be formed.

Separate measurements were performed of the reactions of SiO^+ and SiS^+ with O_2, CO and H_2 in which these ions were produced from the reactions of Si^+ with N_2O and COS, respectively. Their results are included in table 3. For the most part these are non-reactions. The SiO^+ did not react with O_2, $k < 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Both SiS^+ and SiS_2^+ (COS_2^+) were observed to be unreactive toward H_2, $k < 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and toward CO, $k < 4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Also SiS_2^+ (COS_2^+) did not react with O_2, but SiS^+ reacted with O_2 in an interesting fashion:

$$SiS^+ + O_2 \xrightarrow{0.70} SO^+ + SiO \qquad (8a)$$

$$\xrightarrow{0.30} SiO^+ + SO \qquad (8b)$$

The two channels which were observed are exothermic by 44 ± 5 and 18 ± 7 kcal mol^{-1}, respecitively.

$D(Si^+—S)$ and $E_i(SiS)$

Whereas the O-atom affinity of Si^+, $D(Si^+—O) = 114 \pm 5$ kcal mol^{-1}, can be based completely on experimental thermochemical values, *viz.* enthalpies of formation for Si, SiO and O and ionization energies for Si and SiO, this is not the case for the S-atom affinity of Si^+. No experimental determinations of E_i(SiS) or the enthalpy of formation of SiS^+ have been reported, to the best of our knowledge. There has been only one report of E_i(SiS) derived from theory.[14]

Two reactions investigated in this study provide an experimental window for the enthalpy of formation of SiS^+. Failure to observe the formation of SiS^+ by the S-atom transfer reaction:

$$Si^+ + CS_2 \rightarrow SiS^+ + CS \qquad (9)$$

the analogue of the S-atom transfer reaction with COS which was observed, provides a lower limit of 258 ± 7 kcal mol^{-1} for $\Delta H^\circ_{f,298}$ (SiS^+), while the failure to observe the H-atom transfer reaction:

$$SiS^+ + H_2 \rightarrow SiSH^+ + H \qquad (10)$$

the analogue of the H-atom transfer with SiO^+ which has been observed,[18] leads to an upper limit of 273 ± 5 kcal mol^{-1} (the standard enthalpy of formation of $SiSH^+$ has recently been reported to be 220.8 ± 5.0 kcal mol^{-1}).[21] These determinations allow us to report a value of 265 ± 13 kcal mol^{-1} for $\Delta H^{\circ}_{f,298}$ (SiS^+), which can be used to derive value of 91 ± 15 kcal mol^{-1} for $D(Si^+—S)$ and 10.4 ± 0.7 eV for $E_i(SiS)$. The theoretical value reported for $E_i(SiS)$ is 10.26 eV[14] which translates to values for $D(Si^+—S) =$ 101 ± 4 kcal mol^{-1} and for $\Delta H^{\circ}_{f,298}$ (SiS^+) = 262 ± 3 kcal mol^{-1}. The agreement between theory and experiment is fair.

Discussion and Conclusions

The results of the measurements clearly indicate that the gas-phase bimolecular oxidation and sulphidation of atomic silicon ions to form SiO^+, SiO, SiS^+ or SiS is thermodynamically controlled, *i.e.* it is fast when exothermic and slow when endothermic. $Si^+(^2P)$ is not oxidized to SiO^+ or SiO by molecules with more tightly bound O atoms or O^- anions such as O_2, CO_2, CO, NO and OCS, or to SiS^+ by molecules with more tightly bound S atoms such as CS_2, or to SiS by molecules with more tightly bound S^- anions such as OCS and CS_2. $Si^+(^2P)$ is oxidized to SiO^+ by molecules with less tightly bound O atoms such as NO_2 and N_2O, and to SiO by molecules with less tightly bound O^- anions such as NO_2 and SO_2, and to SiS^+ by molecules with less tightly bound S atoms such as OCS. All the thermodynamically allowed reactions were observed to be rapid, $k > 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Reaction efficiencies for these reactions were calculated to be >0.4.

The O-atom affinity of the neutral silicon atom is much higher than that of its atomic ion, $A_O(Si) - A_O(Si^+) = 78 \pm 9$ kcal mol^{-1}, so that O-atom transfer to neutral silicon atoms is exothermic with all the molecules listed in table 1, except CO. Indeed O-atom transfer has been reported for the reactions of ground-state silicon atoms with N_2O, NO_2, OCS, CO_2, NO and O_2, and found not to occur with CO.[8] A comparison of the oxidation of atomic silicon ions with the oxidation of atomic carbon ions shows that the O-atom affinity of atomic carbon ions is much higher, $A_O(C^+) - A_O(Si^+) = 81 \pm 7$ kcal mol^{-1}. A survey of the reaction products observed previously for gas-phase reactions of C^+ with the molecules in table 1 indicates the occurrence of O-atom, O^--anion and S-atom transfer.[20] However, for the reactions with the molecules NO, NO_2 and OCS the electron-recombination energy of C^+ is sufficiently high, 11.26 eV, to allow charge transfer to compete as a reaction channel. This competition is not possible for the reactions with ground-state Si^+, which has a much lower electron recombination energy (8.15 eV).

Adduct formation with $Si^+(^2P)$ was observed for all the molecules which could not lead to exothermic bimolecular oxidation, except CO, but with a range of rate constants and efficiencies. If this adduct formation proceeds by collisional stabilization of an initial energized adduct

$$Si^+ + XO \rightleftharpoons [Si\cdots OX^+]^* \xrightarrow{He} SiOX^+ \qquad (11)$$

the magnitude of the rate constant for association will be determined by the lifetime of the initial energized adduct $(SiXO^+)^*$ against dissociation back to reactants. Both $(SiOX^+)^*$ and $(SiXO^+)^*$ are possible intermediates but the Si^+ will preferentially align with the electronegative end of the XO molecule because of the electrostatic ion–dipole interaction. The lifetime of $(SiOX^+)^*$ will depend on the molecular complexity of $SiOX^+$ and the well-depth of $SiOX^+$ relative to the reactants Si^+ and XO.

According to a qualitative model recently proposed by Ferguson *et al.*,[22] an addition reaction of type (11) can become more efficient when O-atom transfer becomes energetically accessible within the intermediate complex $[SiOX^+]^*$

$$Si^+ + XO \rightleftharpoons [Si\cdots OX^+ \rightleftharpoons SiO^+\cdots X \rightleftharpoons X\cdots SiO^+]^* \xrightarrow{He} SiOX^+, XSiO^+ \quad (12)$$

The increased efficiency is thought to arise from the increase in lifetime which results from the partial conversion of relative kinetic energy into the isomerization energy of the intermediate complex. In other words, the motion of the intermediate complex along the double (or muliple)-minimum potential-energy surface is expected to lead to a decrease in the probability for dissociation back to reactants. Ferguson *et al.* suggest that reaction (12) is energetically possible when the ion-neutral impact energy is comparable to, or greater than, the endothermicity of the corresponding bimolecular O-atom transfer reaction.[22] We note here that reaction (12) accounts for the formation of the isomeric form $XSiO^+$ of the aduct ion through the migration of X in the intermediate complex to the Si end of the SiO molecule.

For the addition reactions of Si^+ with CO, NO, CO_2 and O_2 the corresponding O-atom transfer reactions are endothermic by 143 ± 5, 37 ± 5, 13 ± 5, and 5 ± 5 kcal mol^{-1}, respectively. For available impact energies of *ca.* 10-15 kcal mol^{-1}, which might be typical electrostatic interaction energies for these reactions, the model of Ferguson *et al.* predicts efficient association for the reactions of Si^+ with CO_2 and O_2 which is consistent with our observations since both were observed to occur, albeit with non-measurable rates. The model of Ferguson *et al.* also provides a suitable mechanism for the formation of the chemically bound $(O{-}Si{-}O)^+$ molecule which has been shown to occur in the earlier experiments of Fahey *et al.*[18] Formation of $(O{-}Si{-}O)^+$ can occur *via* the loosely bound $[SiO^+\cdots O]^*$ intermediate if this intermediate has a lifetime sufficiently long for the O atom to migrate to the other side of the SiO molecule and thus for the intermediate to explore the potential well of $(O{-}Si{-}O)^+$.[21] By analogy, in the case of CO_2, the intermediate complex $[SiO^+\cdots CO]^*$ might be sufficiently long lived to explore the potential well of the $(OC{-}SiO)^+$ ion if this ion is stable.

In contrast to the situation with O_2 and CO_2, the immeasurably small rate constant for the association reaction with CO together with the very large endothermicity (143 kcal mol^{-1}) of the corresponding bimolecular oxidation reaction suggest the formation, at best, of a weakly bound adduct ion held together electrostatically by ion-induced dipole and ion-dipole interaction, *viz.* $Si^+\cdot CO$.

The reaction with NO lies intermediate between the two extremes. The association reaction is still relatively fast but the reaction endothermicity of 37 ± 5 kcal mol^{-1} for the corresponding O-atom transfer reaction is high relative to the endothermicities of the analogous reactions with O_2 and CO_2. It appears that in this case isomerization of the intermediate complex through O-atom transfer is not possible and that the observations must be attributed to the direct formation of a relatively stable adduct ion of Si^+ and NO. Preliminary *ab initio* molecular orbital calculations performed at the MP4SDTQ/6-31G*//6-31G* level with the use of the GAUSSIAN 82 program[23] indicate that the linear triplet $^+Si{-}N{=}O$ $(^3\Sigma^-)$ adduct ion is stable by 42 kcal mol^{-1} with respect to Si^+ and NO and that the triplet $SiON^+$ isomer which may be formed preferentially due to the small dipole moment of NO (0.16 D†) is less stable by only 7.5 kcal mol^{-1}.

The model of Ferguson *et al.*[22] could account for the very fast association reaction of Si^+ with CS_2. The bimolecular S-atom transfer reaction which corresponds to this association is only 4 ± 10 kcal mol^{-1} endothermic. This means that the intermediate complex $[SiS^+\cdots CS]^*$ may be formed which may have a long lifetime to explore the formation of several isomers, including $(SCSiS)^+$ and $(CSSiS)^+$ as well as $(SiSCS)^+$.

Similar mechanisms may apply to the higher-order oxidation reactions of SiO^+. For example, the intermediates $[OSiO^+\cdots N_2]^*$ and $[SSiS^+\cdots CO]^*$ in the reactions of SiO^+ with NNO and SiS^+ with OCS would allow the formation of the molecular ions of OSiO and SSiS, respectively. The reaction of SiO^+ with NO_2 provides an example in which electron transfer, O-atom transfer and O^--transfer compete for SiO^+ in the reaction intermediate. If the intermediate ion $[SSiO^+\cdots O]^*$ in the reaction of SiS^+ with O_2 has a long lifetime it should explore the potential wells of $[O\cdots SSiO^+]^*$ and $[OS\cdots SiO^+]^*$ and finally decompose into the observed products $SO^+ + SiO$ and SiO^+ and SO. Another

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† 1 D ≈ $3.335\,64 \times 10^{-30}$ C m.

alternative, which might be more consistent with the relatively small rate constant which was determined for this reaction, would be a four-centred intermediate which ruptures the O—O bond and forms the Si—O and S—O bonds in a concerted fashion. We should note also from table 1 that the O-atom affinity of SiO^+, which is 111 ± 24 kcal mol^{-1}, is similar to that of Si^+ so that we can expect similar correlations for the rate constants of collisional association reactions of SiO^+ and Si^+.

CO, O_2, CO_2, SO_2 and OCS are all known interstellar molecules. Our experimental results indicate that their roles in the oxidation or sulphidation of Si^+ in interstellar clouds are varied. Because of the low pressures in these regions, the molecules CO, O_2, and CO_2 can only contribute to the oxidation of Si^+ by radiative recombination. The model analysis given above indicates that the radiative recombination of Si^+ with O_2 or CO_2 might be more efficient because of the longer lifetimes against dissociation of the corresponding intermediate complexes. Successive S-atom transfer reactions of Si^+ with OCS can lead to SiS^+ and SiS_2^+. Charge transfer is required to neutralize these ions to SiS and SiS_2. Our results indicate that the reaction sequence

$$SiS^+ \xrightarrow{H_2} SiSH^+ \xrightarrow{e} SiS + H \qquad (13)$$

cannot be invoked for the production of SiS from SiS^+ as has been done in the past.[24] The first step in sequence (13) is also endothermic by 12 ± 8 kcal mol^{-1}. In contrast, the analogous sequence for the production of SiO from $SiOH^+$ given in the reaction

$$SiO^+ \xrightarrow{H_2} SiOH^+ \xrightarrow{e} SiO + H \qquad (14)$$

is possible. The first step in this sequence is exothermic by 39 ± 9 kcal mol^{-1} and relatively efficient ($k = 3.2 \pm 1.0 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$).[18] Also, the reaction of Si^+ with SO_2 can lead directly to neutral SiO as one of its bimolecular products as can the reaction of SiS^+ with O_2.

Oxidation can be more extensive with NO_2 and N_2O, which have not yet been identified as interstellar molecules. Sequential reactions with these two molecules can establish SiO_2 or SiO_2^+. There is also some evidence from our experiments that further O-atom transfer reactions in N_2O may eventually produce SiO_3^+ and SiO_4^+ and that analogous reactions in COS may lead to SiS_2^+ and SiS_3^+. These silicon polyoxide and polysulphide ions deserve further investigation, both experimental and theoretical, to confirm their formation and to elucidate their energies and structures.

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