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The chemistry of silicon in dense interstellar clouds

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Summary. The gas phase chemistry of silicon in dense interstellar clouds has been investigated using a pseudo-time-dependent model. Based on new ion-molecule reaction studies as well as on improvements in the knowledge of the thermochemistry of silicon-bearing species, our model contains approximately 300 gas phase reactions involving such species. Calculated abundances are presented for a number of silicon-containing molecules including those with carbon-silicon bonds. Our results for a dark cloud with $T = 10$ K and $n(H_2) = 10^4$ cm^{-3} show that unless a very large depletion for silicon in the gas phase is assumed, the predicted SiO abundance is much larger than observed in such sources.

Key words: interstellar medium: molecules – chemical reactions

1. Introduction

Despite having a cosmic abundance approximately twice that of sulphur, the element silicon does not appear to form molecules readily in interstellar clouds. It is known from observations of diffuse interstellar clouds that silicon is depleted from the gas phase by a factor of ten due to its incorporation into silicate grains (Van Steenberg and Shull, 1988) but it is unclear what fraction of silicon remains in the gas within more dense clouds. While thirteen sulphur-bearing molecules have been detected so far, SiO and SiS are the only interstellar silicon-bearing molecules to be observed (Downes et al., 1982; Dickinson and Rodriguez Kuiper, 1981), although SiC_2 and possibly $HSiC_2$ have been detected in the envelope surrounding IRC+10216 (Thaddeus et al., 1984; Guélin et al., 1986). Observations of thermal SiO and of SiS suggest that these molecules exist in hot material surrounding star-forming regions, possibly associated with shocks (Downes et al., 1982; Wright et al., 1983; Ziurys and Friberg, 1987; Ziurys, 1988) but not in cold clouds such as TMC-1 in which an upper limit for the fractional abundance of SiO of $2.4\ 10^{-12}$ has been deduced (Ziurys et al., 1985, 1989). However, a weak detection of SiO at a position in Orion away from any star-forming activity has recently been reported (Ziurys et al., 1989). In a paper containing a summary of these and additional observations, Ziurys et al. (1989) demonstrate a correlation between SiO abundance and temperature; indeed these authors have been able to obtain an effective activation energy for the (unknown) process of formation of ≈ 90 K by plotting $\ln\{[SiO]/[HCN]\}$ vs. $1/T$. On the other hand, White (1988) has reported evidence for SiO seen in absorption in Sgr B2 which may be the first evidence for cold gaseous SiO in the interstellar medium. A previous observation of SiO in this complex source (Irvine et al., 1987) may not have sampled a low temperature region.

Turner and Dalgarno (1977), Millar (1980), and Prasad and Huntress (1980) have discussed the gas phase chemistry of silicon but quantitative information on abundances were affected severely by the almost total lack of laboratory information available at that time. The high temperature shock chemistry has been discussed by Hartquist et al. (1980). In recent years, Bohme and co-workers have made an extensive study of the reactions of silicon-bearing ions and neutral molecules (Wlodek et al., 1987; Bohme et al., 1988; Wlodek and Bohme, 1988, 1989). In addition, a variety of theoretical studies have determined the thermodynamics of important silicon-bearing species (see e.g. Qi et al., 1984; Flores and Largo-Cabrerizo, 1987; Wong et al., 1988). The experimentally determined rate coefficients and standard enthalpies of formation for many silicon-bearing species have been summarized in a compilation by Wlodek and Bohme (private communication; available from these authors). These new data have encouraged us to explore in detail the gas phase chemistry of silicon in dense interstellar clouds. A salient feature of the laboratory data is that Si^+ ions, in analogy with C^+ and S^+ ions, can insert into hydrocarbon neutrals and drive a chemistry similar to that which is believed to form the organo-sulphur species C_2S and C_3S (Smith et al., 1988; Wlodek et al., 1988) which have recently been detected in interstellar and circumstellar clouds (Saito et al., 1987; Yamamoto et al., 1987; Cernicharo et al., 1987). The tentative identification of $HSiC_2$ in IRC+10216 (Guélin et al., 1986) also suggests the possibility of a rich organo-silicon chemistry.

We have therefore extended the dense cloud chemical kinetic model of Millar et al. (1987) and Millar et al. (1988) to include the Si-bearing species listed in Table 1. This model is of the pseudo-time-dependent variety, in which chemical abundances evolve from initial values under fixed physical conditions. The important reactions included in our model that have been newly measured are listed in Table 2 along with previously studied systems. In addition, approximately 280 unstudied ion-molecule, dissociative recombination, and neutral-neutral reactions have been included based on new thermodynamic information, previous work, and analogy with other studied reactions. A list of these

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Table 1. Silicon-bearing species in model

A. NEUTRAL SPECIES (21)

Si	SiH	SiH_2	SiH_3	SiH_4
	SiO	HCSi	$SiCH_2$	$SiCH_3$
	SiC	HNSi	$HSiC_2$	SiC_2H_2
	SiN	SiNC	SiC_3	SiC_3H
		SiC_2	H_2SiO	SiC_4
		SiO_2		

B. IONIC SPECIES (30)

Si^+	SiH^+	SiH_2^+	SiH_3^+	SiH_4^+	SiH_5^+
	SiC^+	$HCSi^+$	$SiCH_2^+$	$SiCH_3^+$	$SiCH_4^+$
	SiO^+	SiC_2^+	SiC_2H^+	$SiC_2H_2^+$	$SiC_2H_3^+$
	SiN^+	$SiOH^+$	SiC_3^+	SiC_3H^+	$SiC_3H_2^+$
		$HNSi^+$	$SiNH_2^+$	SiC_4^+	SiC_4H^+
		$SiNC^+$	$SiNCH^+$	H_3SiO^+	
			H_2SiO^+		
			$HSiO_2^+$		

Table 2. Experimentally studied reactions of silicon species in model[a]

Reaction	k ($cm^3 s^{-1}$)	Reference
$Si^+ + H_2O \longrightarrow SiOH^+ + H$	2.3(-10)	WFB; FFFV
$Si^+ + HCN \longrightarrow SiNC^+ + H$	1.4(-12)	BWF
$Si^+ + C_2H_2 \longrightarrow SiC_2H^+ + H$	2.5(-10)	BWF
$Si^+ + NH_3 \longrightarrow SiNH_2^+ + H$	6.4(-10)	WB
$Si^+ + C_4H_2 \longrightarrow C_4H^+ + SiH$	1.6(-9)	BWF
$SiH^+ + H_2 \longrightarrow$ Products	no reaction	this work
$SiO^+ + H_2 \longrightarrow SiOH^+ + H$	3.2(-10)	FFFV
$SiO^+ + O \longrightarrow Si^+ + O_2$	2.0(-10)	F
$SiH_2^+ + O_2 \longrightarrow SiOH^+ + OH$	2.4(-11)	AH
$SiH_3^+ + O_2 \longrightarrow H_3SiO^+ + O$	2.9(-12)	AH
$SiC_2H^+ + C_2H_2 \longrightarrow SiC_4H^+ + H_2$	2.0(-11)	BWF
$Si + O_2 \longrightarrow SiO + O$	2.7(-10)	HN
	9.8(-12)	SDN

Note: a(-b) refers to a 10^{-b}.

[a] all rates measured at room temperature.

References: WFB, Wlodek et al. 1987; FFFV, Fahey et al. 1981; BWF, Bohme et al. 1988; WB, Wlodek and Bohme 1988; F, Fehsenfeld 1969; AH, Anicich and Huntress 1986; HN, Husain and Norris 1979; SDN, Swearengen et al. 1978.

latter reactions is available from E.H. or T.J.M. One reaction listed as occurring in the literature (Anicich and Huntress, 1986)

$$SiH^+ + H_2 \rightarrow SiH_2^+ + H \tag{1}$$

has been found not to proceed at all by measurements at York University, in agreement with our current knowledge of the heats of formation of silicon-containing ions.

In previous pseudo-time-dependent models (e.g. Millar et al., 1988), the abundances of most organic molecules peak at a so-called "early time" before declining to their steady-state values. The abundances calculated at this "early time" for a variety of recent models are in much better agreement with observation for sources such as TMC-1; this is seen dramatically in the recent model of Herbst and Leung (1989) which considers some of the most complex molecules yet detected unambiguously. In addition, the "early-time" abundances are insensitive to a lot of uncertainties afflicting steady-state abundances such as dissociative recombination branching ratios (Millar et al., 1988), cosmic ray-induced photodissociation (Gredel et al., 1989), and adsorption on to the dust grains. For these reasons, we shall emphasize our "early-time" results.

The remainder of the paper is organized as follows. In Sect. 2, we discuss some particular reactions of importance and give an overview of the chemistry of silicon. Our detailed numerical results are presented and discussed in Sect. 3, while our conclusions are given in Sect. 4.

2. The chemical model

2.1. *Changes to the basic chemistry*

For the purposes of the calculations presented here, we have used the standard dense cloud model developed for dark clouds such as TMC-1 and described by Millar et al. (1987, 1988). The temperature is taken to be 10 K and $n(H_2) = 10^4\,cm^{-3}$. To account for recent theoretical and experimental results, we have updated the rate coefficients of several important reactions. In particular, we have set the rate coefficient of the $N^+ + H_2 \rightarrow NH^+ + H$ reaction to $3\,10^{-14}\,cm^3 s^{-1}$ (Herbst et al., 1987; Marquette et al., 1988; Galloway and Herbst, 1989) and included the reaction $C_4H^+ + H_2 \rightarrow C_4H_2{}^+ + H$ (Giles et al., 1989) which greatly enhances the formation of C_4H. We have also used the recent results of Smith and Adams (in preparation) which give a branching ratio of 80% for the production of OH in the dissociative recombination of H_3O^+. Other dissociative recombination branching ratios are treated by the "standard" approximation (Millar et al., 1988). We note that the current debate over the value for the $H_3{}^+$ dissociative recombination rate coefficient (Smith and Adams, 1984; Amano, 1988) is irrelevant in this context since $H_3{}^+$ is lost in reactions with atoms and molecules such as CO rather than with electrons.

2.2. *Radiative association involving silicon*

Seven radiative association reactions involving silicon-bearing ions have been included in our model. None of these has been studied directly in the laboratory although the analogous ternary association reactions have been investigated for some. The individual reactions are discussed below.

The reaction

$$Si^+ + H_2 \rightarrow SiH_2^+ + h\nu \tag{2}$$

has been included in previous treatments but at much too high a rate (Prasad and Huntress, 1980). The exothermicity is only ~ 1 eV which is much less than in the corresponding association involving C^+. The theoretical results obtained for $C^+ + H_2$ (Herbst, 1982) can be scaled by the appropriate vibrational density of states ratio (Bates and Herbst, 1988) to get a result for reaction (2) with the added proviso that the actual radiative stabilization rate for the SiH_2^{+*} complex cannot be as rapid as that for CH_2^{+*}. We estimate that $k_2 \sim 3\,10^{-18}\,\mathrm{cm^3\,s^{-1}}$ independent of temperature in the $10-70$ K range, a range used for all other results as well. This is over two orders of magnitude smaller than the rate coefficient of the important radiative association between C^+ and H_2.

The rate coefficient for the reaction

$$SiH^+ + H_2 \rightarrow SiH_3^+ + h\nu \qquad (3)$$

has been calculated using the modified thermal approach of Bates (1980; see also Bates and Herbst, 1988). We obtain that $k_3 \approx 3\,10^{-17}\,(T/300)^{-1.0}\,\mathrm{cm^3\,s^{-1}}$, where T is the temperature in K. At 10 K, the rate coefficient is only $9\,10^{-16}\,\mathrm{cm^3\,s^{-1}}$ due principally to a moderate reaction exothermicity of ~ 2 eV. Once produced the SiH_3^+ can associate slowly with H_2 to form SiH_5^+:

$$SiH_3^+ + H_2 \rightarrow SiH_5^+ + h\nu \qquad (4)$$

but the very low reaction exothermicity of ≤ 0.5 eV compared with the analogous reaction involving CH_3^+ leads to a much smaller rate. By suitable scaling of the $CH_3^+ + H_2$ theoretical results (Bates and Herbst, 1988), we obtain that $k_4 \sim 1.0\,10^{-18}\,(T/300)^{-0.5}\,\mathrm{cm^3\,s^{-1}}$.

The association reactions

$$Si^+ + HCN \rightarrow SiNCH^+ \qquad (5)$$

$$Si^+ + CH_4 \rightarrow SiCH_4^+ \qquad (6)$$

$$Si^+ + C_2H_2 \rightarrow SiC_2H_2^+ \qquad (7)$$

have been studied by Bohme et al. (1988) under high pressure ternary conditions at 300 K in a SIFT apparatus. Using theory to deduce the corresponding radiative association rate coefficients at 300 K and then the appropriate temperature dependence (Bates and Herbst, 1988), we obtain for the radiative association rate coefficients $k_5 = 6.0\,10^{-15}(T/300)^{-1.5}\,\mathrm{cm^3\,s^{-1}}$, $k_6 = 4.0\,10^{-16}\,(T/300)^{-1.5}\,\mathrm{cm^3\,s^{-1}}$, and $k_7 = 1.0\,10^{-13}\,(T/300)^{-1.0}\,\mathrm{cm^3\,s^{-1}}$. For reactions (5) and (7), the existence of competing exothermic channels has been ignored since their inclusion in the theoretical treatment (Herbst, 1987) requires detailed knowledge of potential surfaces which is currently unavailable.

Finally, the rate coefficient for the reaction

$$SiC_2H^+ + H_2 \rightarrow SiC_2H_3^+ + h\nu \qquad (8)$$

has been crudely estimated to be $k_8 \sim 3.0\,10^{-16}\,(T/300)^{-1.0}\,\mathrm{cm^3\,s^{-1}}$.

2.3. *The silicon chemistry*

In the discussion below, most of the reactions have not been studied and their existence and rates have been estimated based on thermochemical considerations and analogous reactions that have been studied. Reactions actually measured in the laboratory contain an asterisk next to their number.

Because the reaction

$$Si^+ + H_2 \rightarrow SiH_2^+ + h\nu \qquad (9)$$

is estimated to be so slow, the ion-molecule silicon chemistry is initiated by the proton transfer reaction

$$H_3^+ + Si \rightarrow SiH^+ + H_2. \qquad (10)$$

At early times, loss of SiH^+ occurs predominantly through reactions with atoms (rather than through association with H_2); viz.,

$$SiH^+ + O \rightarrow SiO^+ + H \qquad (11)$$

$$SiH^+ + C \rightarrow SiC^+ + H \qquad (12)$$

$$SiH^+ + N \rightarrow SiN^+ + H \qquad (13)$$

$$SiH^+ + M \rightarrow SiH + M^+ \qquad (14)$$

in which M represents a metal with a low ionisation potential. The hydrogenation of SiH^+ into SiH_5^+ and subsequently to silane (SiH_4) is very inefficient since it proceeds via the slow radiative association reactions $SiH^+ + H_2 \rightarrow SiH_3^+$ (reaction 3) followed by $SiH_3^+ + H_2 \rightarrow SiH_5^+$ (reaction 4). Unlike SiN^+, both SiO^+ and SiC^+ can react with H_2 to form SiO, SiC, and HCSi in a sequence of reactions terminated by dissociative recombination processes:

$$SiO^+ + H_2 \rightarrow SiOH^+ + H \qquad {*}(15)$$

$$SiC^+ + H_2 \rightarrow HCSi^+ + H \qquad (16)$$

$$HCSi^+ + H_2 \rightarrow SiCH_2^+ + H \qquad (17)$$

$$SiOH^+ + e \rightarrow SiO + H;\ Si + OH \qquad (18)$$

$$SiCH_2^+ + e \rightarrow HCSi + H;\ SiC + H_2(2H). \qquad (19)$$

The SiO^+ ion also forms through the reaction

$$Si^+ + OH \rightarrow SiO^+ + H \qquad (20)$$

which, followed by reaction (15), together with the reaction

$$Si^+ + H_2O \rightarrow SiOH^+ + H \qquad {*}(21)$$

subsequently lead to SiO production via dissociative recombination (reaction 18). In analogy to the $C + O_2$ reaction, atomic silicon is also converted into SiO via

$$Si + O_2 \rightarrow SiO + O, \qquad {*}(22)$$

a process studied by two groups in the laboratory (Swearengen et al., 1978; Husain and Norris, 1979). Again in analogy with the carbon case, reactive neutral diatomics such as SiH, SiC, and SiN react exothermically with atomic oxygen to produce SiO which possesses a stronger chemical bond. The dominant chemical pathway followed through these reactions is the conversion of Si and Si^+ into SiO. Once SiO is produced, it can be used to produce SiO_2 via the reaction

$$SiO + OH \rightarrow SiO_2 + H. \qquad (23)$$

In addition to reaction (12), silicon-carbon bonds are formed in a number of reactions involving Si^+, Si, C^+, and C. Since Si^+ reacts slowly with both H_2 and electrons as well as with abundant species such as CO and O_2 (Bohme et al., 1988; Fahey et al., 1981), its insertion reactions with hydrocarbons are of some importance. These include

$$Si^+ + C_2H_2 \rightarrow SiC_2H^+ + H \qquad {*}(24)$$

$$Si^+ + C_3H_2 \rightarrow SiC_3H^+ + H. \qquad (25)$$

The radiative association reactions between Si^+ and the hydrocarbons CH_4 and C_2H_2 (reactions 6 and 7) are also of some importance in this regard. In addition to insertion reactions involving Si^+, reactions involving Si occur, for example

$$Si + CH_5^+ \rightarrow SiCH_3^+ + H_2. \qquad (26)$$

Insertion reactions between C^+ and neutral organo-silicon compounds and between C and organo-silicon ions also play a role in the formation of complex organo-silicon species. Finally, the condensation reaction

$$SiC_2H^+ + C_2H_2 \rightarrow SiC_4H^+ + H_2 \qquad {}^*(27)$$

occurs, in analogy with hydrocarbon chemistry. All of these types of reactions lead to complex species such as $SiCH_2$, $SiCH_3$, SiC_2, $HSiC_2$, SiC_2H_2, SiC_3, SiC_3H, and SiC_4. As in the case of organic molecules, reactions between unsaturated organo-silicon ions and H_2 are often endothermic leading to unsaturated rather than saturated organo-silicon neutral species.

Silicon-nitrogen chemistry stems from reactions involving *N* atoms (e.g. reaction 13) or NH_3. The SiH_3^+ ion reacts with atomic nitrogen to form $HNSi^+$ and $SiNH_2^+$:

$$SiH_3^+ + N \rightarrow HNSi^+ + H_2;\ SiNH_2^+ + H. \qquad (28)$$

Since $HNSi^+$ is thought to react with H_2, essentially all reactions of SiH_3^+ with N produce $SiNH_2^+$. This ion is also formed via

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \qquad {}^*(29)$$

and recombines to form SiN and HNSi:

$$SiNH_2^+ + e \rightarrow SiN + H_2(2H);\ HNSi + H. \qquad (30)$$

Table 3. Fractional abundances with respect to H_2 at early time ($3\,10^5$ yr)

Species	Model Number 1	2	3	4
Si	1.5(-09)	8.2(-09)	1.4(-10)	7.9(-11)
SiH	1.7(-12)	7.9(-12)	1.8(-13)	2.5(-14)
SiO	3.7(-08)	1.8(-07)	3.7(-09)	3.9(-08)
SiC	1.8(-11)	8.9(-11)	1.8(-12)	1.1(-12)
SiN	1.8(-12)	8.7(-12)	1.8(-13)	9.2(-14)
SiH_2	1.3(-14)	6.4(-14)	1.3(-15)	2.3(-17)
HCSi	3.4(-13)	1.7(-12)	3.4(-14)	7.8(-15)
HNSi	4.4(-12)	2.4(-11)	4.3(-13)	9.7(-13)
SiNC	1.3(-16)	7.9(-16)	1.3(-17)	5.8(-19)
SiC_2	4.4(-12)	2.1(-11)	4.4(-13)	7.6(-13)
SiO_2	8.4(-10)	4.1(-09)	8.4(-11)	3.2(-10)
SiH_3	1.9(-17)	5.3(-17)	2.2(-18)	4.8(-20)
$SiCH_2$	1.6(-10)	8.3(-10)	1.6(-11)	7.1(-12)
$HSiC_2$	2.4(-10)	1.3(-09)	2.3(-11)	1.7(-10)
SiC_3	1.6(-12)	7.5(-12)	1.6(-13)	1.5(-13)
H_2SiO	3.9(-15)	1.2(-14)	4.4(-16)	8.6(-17)
SiH_4	4.3(-16)	2.0(-15)	4.5(-17)	1.9(-18)
$SiCH_3$	3.7(-11)	2.0(-10)	3.6(-12)	4.0(-13)
SiC_2H_2	7.0(-11)	3.2(-10)	7.1(-12)	3.3(-12)
SiC_3H	2.5(-11)	1.1(-10)	2.6(-12)	8.1(-12)
SiC_4	7.9(-15)	3.4(-14)	8.2(-16)	1.6(-16)
Si^+	2.5(-11)	1.3(-10)	2.5(-12)	8.3(-12)
SiH^+	3.3(-13)	1.5(-12)	3.4(-14)	1.4(-14)
SiH_2^+	5.4(-16)	2.5(-15)	5.6(-17)	1.9(-16)
$SiOH^+$	2.3(-11)	8.6(-11)	2.5(-12)	3.3(-11)

Notes: a(-b) refers to a 10^{-b} Models 1, 2, and 3 have $n(H_2) = 10^4\ cm^{-3}$ and $T = 10$ K, while model 4 has $n(H_2) = 10^5\ cm^{-3}$ and $T = 70$ K. The total silicon abundances with respect to H_2 used in these models are $4\,10^{-8}$, $2\,10^{-7}$, $4\,10^{-9}$, and $4\,10^{-8}$, respectively.

3. Results and discussion

In Tables 3 and 4 we present the fractional abundances (with respect to H_2) of various silicon-bearing species at early time ($3.16\,10^5$ yr) and steady state ($\sim 10^7$ yr) respectively. Model 1, our standard model, is that used to simulate TMC-1 and has an adopted elemental silicon fractional abundance of $4\,10^{-8}$, which is roughly 10^3 times below its cosmic abundance. Models 2 and 3 have been used to study the effects of varying the depletion of silicon; in model 2 the elemental silicon fractional abundance has been increased by a factor of 5 whereas in model 3 it has been decreased by a factor of 10. Model 4 has been run with physical conditions typical of the Orion ridge clouds $-n(H_2) = 10^5\ cm^{-3}$ and $T = 70$ K.

As can be seen from the results listed in Table 3, silicon should exist mainly in the forms of Si and SiO in cold dense clouds with appreciable fractional abundances ($\geq 10^{-10}$) of SiO_2, $SiCH_2$, $HSiC_2$, and SiC_2H_2 also predicted at early time by our standard (TMC-1) model. All other species, including SiC_2, which has been detected in IRC+10216 but not interstellar clouds, have abundances which are predicted to be too small to be detected with present techniques. The small abundances of SiC_2, SiC_3, and SiC_4 result from our assumption that O atoms destroy these species in analogy with previous assumptions concerning the reactions of O atoms with C_n molecules (Millar et al., 1987; Herbst and Leung, 1989). If the silicon-carbon radicals are not destroyed by reactions with O atoms, then we predict appreciable early-time fractional abundances of $3.9\,10^{-9}$, $2.0\,10^{-9}$, and $7.1\,10^{-12}$ for SiC_2, SiC_3, and SiC_4 respectively. In IRC+10216, of course, the reaction of SiC_2 with O atoms is negligible because of the low abundance of O atoms. The predicted abundance of the SiN molecule is less than the observed upper limit (Ziurys et al., 1984).

The calculated abundance for SiO of $\sim 4\,10^{-8}$ in our standard model is much larger than the upper limit of $2\,10^{-12}$ in TMC-1 (Ziurys et al., 1989) and suggests that either our adopted chemistry is incorrect or that silicon is much more depleted than we have assumed. The result of models 2 and 3 show that the fractional abundances of silicon-bearing molecules are directly proportional to the adopted elemental silicon abundance. In order to reduce the SiO abundance to less than $2\,10^{-12}$, we would therefore require a depletion factor of $\sim 10^7$; that is, only one silicon atoms in 10 million is in the gas phase. If, instead, the adopted chemistry is in error, then the upper limit in TMC-1 may be satisfied without the need for such an enormous depletion factor. The dominant reactions in the production of SiO are $Si^+ + H_2O \rightarrow SiOH^+ + H$ (reaction 21) followed by dissociative recombination and $Si + O_2 \rightarrow SiO + O$ (reaction 22). The rate coefficient of reaction (21) has been measured at 296 K to be $2.3\,10^{-10}\ cm^3\,s^{-1}$ (Wlodek et al., 1987), a factor of 12 less than the collisional rate coefficient. This may indicate the presence of a small energy barrier in reaction (21) although some theoretical calculations argue against this (Yanqui et al., 1984; S. Wlodek,

Table 4. Fractional abundances with respect to H_2 at steady state

Species	Model Number 1	2	3	4
Si	1.1(−10)	5.1(−10)	1.1(−11)	2.0(−11)
SiH	5.3(−13)	2.4(−12)	5.6(−14)	4.4(−14)
SiO	3.7(−08)	1.8(−07)	3.7(−09)	3.9(−08)
SiC	3.7(−12)	1.7(−11)	3.8(−13)	2.3(−13)
SiN	4.0(−12)	2.1(−11)	4.0(−13)	2.4(−13)
SiH_2	8.9(−14)	3.7(−13)	9.6(−15)	7.6(−16)
HCSi	7.5(−14)	3.4(−13)	7.8(−15)	1.7(−15)
HNSi	3.5(−11)	2.0(−10)	3.3(−12)	8.3(−12)
SiNC	7.7(−18)	4.4(−17)	7.2(−19)	2.8(−20)
SiC_2	8.4(−13)	3.7(−12)	8.8(−14)	1.4(−13)
SiO_2	2.9(−09)	1.6(−08)	2.8(−10)	4.5(−10)
SiH_3	9.1(−17)	2.6(−16)	1.1(−17)	1.4(−18)
$SiCH_2$	5.8(−14)	2.8(−13)	5.8(−15)	3.2(−15)
$HSiC_2$	2.6(−11)	1.2(−10)	2.7(−12)	8.1(−12)
SiC_3	1.9(−14)	9.9(−14)	1.9(−15)	2.1(−16)
H_2SiO	9.2(−15)	3.5(−14)	1.0(−15)	9.0(−16)
SiH_4	2.4(−16)	9.2(−16)	2.6(−17)	6.5(−18)
$SiCH_3$	1.9(−14)	9.3(−14)	1.9(−15)	1.4(−15)
SiC_2H_2	1.6(−12)	7.5(−12)	1.7(−13)	6.8(−14)
SiC_3H	2.2(−14)	1.0(−13)	2.3(−15)	7.7(−15)
SiC_4	1.5(−18)	6.4(−18)	1.6(−19)	8.1(−21)
Si^+	6.4(−11)	3.2(−10)	6.4(−12)	5.4(−11)
SiH^+	8.9(−14)	3.6(−13)	9.8(−15)	1.8(−14)
SiH_2^+	3.0(−15)	1.4(−14)	3.1(−16)	4.4(−15)
$SiOH^+$	2.1(−11)	8.7(−11)	2.3(−12)	3.5(−11)

Notes: as for Table 3

private communication). If the difference between the measured and collisional rate coefficient is due to a barrier, it is ~740 K in size and would make reaction (21) unimportant for cold interstellar gas. While the possibility of activation energy for reaction (22) is left uncertain by laboratory studies (see Table 2), it is entirely possible that this reaction also has a barrier. We have therefore repeated our Model 1 calculation but with reactions (21) and (22) excluded. At early time, the SiO abundance decreases, but only by ~25% because reactions (11) and (20) followed by (15) now drive the SiO chemistry. Reaction (15) has a measured rate coefficient of $3.2\,10^{-10}$ $cm^3\,s^{-1}$ at 300 K (Fahey et al., 1981) which may indicate a small activation energy barrier. Even if this reaction is excluded, we find the fractional abundance of SiO at early time to still be large ($1.7\,10^{-8}$) because the neutral-neutral reactions SiC + O and SiH + O now form SiO. A similar conclusion is reached if reaction (18) is assumed to produce no SiO. Clearly, our calculations show that SiO is formed by many different exothermic reactions so that its non-observation in TMC-1 is unlikely to be due to activation energy barriers. What about a more rapid destruction step than the processes assumed in our model? Hartquist et al. (1980) speculate that the reaction

$$\mathrm{SiO + C \rightarrow CO + Si} \tag{31}$$

may destroy SiO in shocks. Although it is exceedingly likely that this reaction possesses activation energy and therefore is unimportant for cold gas its inclusion in our model would deplete the SiO approximately two orders of magnitude more rapidly than do ion-molecule reactions and reaction (23). A discrepancy of two orders of magnitude between the calculated and observed TMC-1 abundance would remain. Yet another possibility is that a high carbon-to-oxygen abundance ratio might drive the calculated abundance of SiO down. Using a C/O ratio of 1.3, we find only a slight reduction in the SiO abundance from our oxygen-rich models.

If depletion is the cause of the non-observation of SiO in cold clouds, then our results make it clear that no other Si-bearing molecules will be detectable under these conditions if they are produced by gas phase reactions. Observation of thermal SiO emission from warm gas then implies that either shocks (Hartquist et al., 1980) for some other cause of warm temperatures such as photodissociation regions (Stutzki et al., 1988) are needed to maintain silicon in the gas phase where it can undergo reaction. Since larger shock velocities result in a greater degree of grain destruction (Seab, 1987), it would be instructive to look for a correlation between SiO abundances and shock velocities. We note that only a small fraction of the grain need be destroyed in order to return silicon in appreciable quantities to the gas. In diffuse clouds, only 10% of the cosmic abundance of silicon remains in the gas phase and will be incorporated, presumably, into icy molecular mantles in dense clouds, a senario consistent with the recent identification of the 4.6 micron absorption feature in W33A as an Si-H vibrational transition (Nuth and Moore, 1988). If this silicon is distributed isotropically throughout the mantle, then the removal of only 0.1% of the mantle will result in an elemental silicon fractional abundance of $\sim 4\,10^{-9}$. A fractional abundance of this size will lead to a comparable SiO fractional abundance via gas phase reactions (Table 3). Large shock velocities of 30–40 $km\,s^{-1}$, required to remove silicon from refractory particles, are not required to release silicon from icy mantles.

The 90 K "activation energy" found by Ziurys et al., (1989) might reflect a barrier against thermal desorption of silicon from an icy mantle. Such desorption could occur in the warm regions near photodissociation zones (Stutzki et al., 1988). Ziurys, et al. (1989) argue against this on the grounds that mantle removal should result in a gas rich in species such as NH_3 and H_2O, but this will not be the case if only a small fraction of the mantle is removed. For example, if 10% of the cosmic abundance of nitrogen ($2\,10^{-4}$ with respect to H_2) is in the form of ammonia in grain mantles, then release of 0.1% of the mantle results in a gaseous ammonia fractional abundance of only $2\,10^{-8}$, which is not in conflict with observations.

If the gas phase formation of SiO is hindered by activation energy barriers of ~90 K in the gas phase reactions themselves, then cold clouds such as TMC-1 may contain observable amounts of organo-silicon molecules with fractional abundances up to a few times 10^{-10}. Some of these species will also be present in warmer sources. Our Orion model shows that at higher temperatures only some of the organo-silicon species are reduced in abundance since the radiative association reactions which are crucial in their formation, are less rapid. Other organo-silicon species such as $HSiC_2$, and SiC_3H do not show much of a temperature variation in their calculated abundances. Warmer clouds are the most likely sources for searches directed towards these species.

4. Conclusions

At both early time and steady state, the major Si-bearing molecule is calculated to be SiO which typically takes up more than

50% of the available silicon. For a depletion factor of $\sim 10^3$, the calculated SiO abundance is much larger than its upper limit in TMC-1. Although it is possible that energy barriers exist in several of the important reactions involved in the synthesis of SiO, the multitude of reactions which form the Si-O bond ensures that the calculated SiO abundance is fairly insensitive to these barriers. In the unlikely event that energy barriers exist in most if not all of the reactions producing SiO, we calculate that some organo-silicon species will be abundant in cold clouds. If the non-detection of SiO in TMC-1 is due to a low abundance of gas phase silicon, then the depletion must be so large ($>10^6$) that no silicon-bearing molecules will be detectable in such clouds unless they are formed mainly on grain surfaces and preferentially desorbed.

The existence of silicon in the gas phase due to thermal grain desorption or following the shock destruction of interstellar grains will lead to the subsequent formation of SiO via gas phase reactions, a scenario consistent with the observations (Downes et al., 1982; Wright et al., 1983; Ziurys et al., 1989). If SiO is formed by the grain disruption itself, the subsequent gas phase chemistry will preserve its high abundance. Although SiO is the major repository of silicon even at early time, several other species including SiO_2, SiC, and organo-silicon species have appreciable calculated abundances if silicon can be maintained in the gas phase.

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