J. Phys. Chem. A **2006,** *110,* 13221−13226

Rate Coefficient for the Reaction SiO + Si_2O_2 at $T = 10-1000$ K

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Received: August 23, 2006; In Final Form: October 9, 2006

The reaction paths for the formation of Si_3O_3 molecules have been investigated at high level ab initio quantum chemical calculations by using the QCISD method with the 6-311++G(d,p) basis set. The *cis*-Si_2O_2 isomer does not participate in the chemical mechanism for the formation of Si_3O_3 molecules. Although the SiO + *cis*-Si_2O_2 reaction is exothermic and spontaneous, it is not expected to explain the growth mechanism of Si_3O_3 in the interstellar silicate grains of circumstellar envelopes surrounding M-type giants. The reaction of SiO with cyclic Si_2O_2 molecules is exothermic, is spontaneous, and has a nonplanar transition state. The Gibbs free energy for the transition state formation, ($\Delta G_0^{\#}$), is around 5.5 kcal mol^{-1} at 298 K. The bimolecular rate coefficient for this reaction, k_T, is about 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and in the collision limit, 1.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, at 500 K. The activation energy, E_a, is about 8 kcal mol^{-1}. The enthalpy of Si_3O_3 fragmentation is 53.9 kcal mol^{-1} at 298 K. The SiO + cyclic Si_2O_2 reaction is expected to be the most prominent reaction path for the Si_3O_3 formation in interstellar environment and fabrication of silicon nanowires.

Introduction

Silicon monoxide (SiO) materials are the most abundant constituent on Earth, and SiO itself, one of the most reactive molecular species composed of cosmically abundant mineral forming elements.[1,2] The SiO space density in dust is around 3.0×10^{22} molecules cm^{-3}, and the SiO column density in circumstellar shells is around 4.1×10^{14} molecules cm^{-2}.[3,4] It has been conjectured that the formation of pure oligomeric silicon monoxides ($(SiO)_x$, $x = 2$ to 4) should provide the first surface for the kinetics of condensed phase growth of amorphous interstellar silicate grains in the circumstellar envelopes surrounding M-type giants.[5,6] Furthermore, this growth mechanism seems to involve the formation of silicates through the loss of Si atoms during the nucleation and growth of SiO oligomers.[7,8] They also play a crucial role in many areas of modern technology, including nanotechnology, glass, and fiber optics industries. The most important example for the application of silicon monoxide is the enhancement in the growth of silicon nanowires during the synthesis of these materials, suggesting the importance of the small silicon monoxide clusters studied in this article.[7,8] Therefore, the study of the elementary association reactions underlying the nucleation process of SiO is critical in order to understand the formation process of interstellar silicate grains and growth of silicon nanowires.

Unfortunately, it is difficult to experimentally study the formation of SiO oligomers due to the high SiO reactivity and the unlikely isolation of the target chemical reaction. *Ab initio* quantum chemical calculations may offer an alternative way for the understanding of the chemistry of interstellar silicate grains formation in a wide variety of astronomical regions, and the growth of silicon nanowires in different manufacture conditions. For instance, the temperature in circumstellar shells ranges from 1000 down to 10 K,[3,4] and in the production process of silicon nanowires it is from 300 to 1300 K. The SiO vapor pressure is around 2×10^{-6} Torr at 400 K and evaporates completely at 1400 K. Thus, there is an appreciable SiO concentration in the gas phase of circumstellar shells and the production process of silicon nanowires.

Snyder and Raghavachari (1984)[9] have performed a quantum chemical calculation for the dimerization of silicon monoxide. Using fourth-order Møller−Plesset perturbation theory (MP4), they have found a value of −43.0 kcal mol^{-1} for the heat of formation of the dimer, which is in excellent agreement with the only experimental value, -44.6 ± 3.0 kcal mol^{-1}.[10] They have also calculated the potential energy surface for this reaction and found no evidence for an energy barrier. Schnockel et al. (1989)[11] have investigated the Si_2O_2 dissociation by MP4 and found that it is + 43.7 kcal mol^{-1}. Friesen et al. (1999)[12] have also calculated the oligomerization energies for the SiO species using density functional theory (DFT). They have obtained −48.0 and −57.6 kcal mol^{-1} for the SiO dimerization and trimerization reactions, respectively. Lu et al. (2003)[7] also calculated by DFT that the Si_2O_2 and Si_3O_3 dissociation energies are 46.7 and 54.8 kcal mol^{-1}, respectively. However, using the MP2 theory, they found 41.6 and 50.4 kcal mol^{-1} for the same reactions. Thus, it is very important to apply a higher level of theory to this system in order to achieve a better agreement with this data as indicated by Avromov et al.[8]

Anderson et al. (1968),[13] Anderson and Ogden (1969),[14] and Ogden (1977)[15] have shown by infrared analysis that SiO, cyclic Si_2O_2 and Si_3O_3 molecules are important intermediates in the SiO oligomerization process. Hastie et al. (1969)[16] assigned additional features to pentameric SiO species as well as confirming those features assigned in the literature.[14] Later, Khanna et al. (1981)[17] have also assigned basically the same features using infrared and Raman spectroscopies. However, they have also suggested that the “open” *cis*-Si_2O_2 structure is likely to be generated in the process. In fact, it has a higher reactivity compared with the cyclic structure due to their unpaired electrons. Thus, the *cis*-Si_2O_2 species may readily react with SiO monomeric or dimeric species to form higher SiO

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10.1021/jp065462z CCC: \$33.50

oligomers. It is important to cite that only Khanna et al. (1981)[17] have found some evidence for this intermediate. Recently, Friesen et al. (1999)[12] have also detected the cyclic Si_2O_2 molecule, but not the "open" *cis*-Si_2O_2 one. Furthermore, they have also assigned the features of the Si_4O_4 molecule in addition to those for the Si_2O_2 and Si_3O_3 molecules, which again confirmed the existence of a growth mechanism. They have also supported their infrared analysis using quantum chemical calculations by proposing that the cyclic structures participate in exothermic chemical reactions as shown above.

It is important to point out that the conditions in astrophysical systems where interstellar grain formation occurs differ considerably from those which must be employed in the laboratory, and also from those used in the production process of silicon nanowires, to obtain useful results in a reasonable time. In order to understand why there is such debate regarding the experimental results shown above, the knowledge of a condensation mechanism is required. Under the laboratory conditions previously used in the literature,[12−17] the condensation is extremely fast and, consequently, it is difficult to detect and determine the nature of any intermediate species. Therefore, it is plausible to have such debating in the literature regarding the detection of Si_2O_2 isomers. Indeed, the chemical process involved in the nucleation and growth of SiO oligomers is still not understood, which leave us unclear about the chemical species involved in the formation of higher SiO oligomers.

Little has been done for this class of reactions using high level quantum chemical calculations.[8,9,11] However, to the best of our knowledge, the location of a transition state (TS) for the trimerization reaction was not reported in the literature. In view of the lack of information and systematic theoretical investigations for this system, the purpose of this study is therefore to present high level theoretical characterization of this reactional system. This paper is intended to (1) reliably account for the thermodynamical properties and chemical kinetics of this important chemical reaction; and (2) provide a better description of this important reaction system, e.g., describe the transition states and intermediates.

This paper reports high level *ab initio* quantum chemical calculations to compute the geometries, energies, and frequencies for SiO, Si_2O_2, *cis*-Si_2O_2, and Si_3O_3 species. The reaction path, transition state, and chemical kinetics for the trimerization reaction involved in the conversion of such species are also discussed here. This is the first study to characterize the transition state for the trimerization reaction, which has important implications for the chemistries of interstellar silicate grain formation and silicon nanowire growth. It is not the intention of this paper to propose or study any chemical reaction related to the Si_4O_4 molecule due to its prohibitive computational time. To date, the results of this study represent the best level of theory employed to this system.

Theoretical Methods

Stationary points on the potential energy surface of the reaction system were fully optimized, followed by evaluating harmonic vibration frequencies to characterize their nature as minima or first-order saddle points. The calculations were performed with quadratic configuration interaction with single and double excitations (QCISD).[18] The coupled cluster with single and double excitations (CCSD)[19,20] is only used here to confirm the consistency of the calculation. These methods were applied with the basis sets 6-311++G(d,p), 6-311++G(3df,3pd), cc-pVDZ, and cc-pVTZ. The full active space was employed for all calculations in this study. The electronic structure calculations were carried out with the GAUSSIAN 03 quantum chemistry codes.[21]

The thermodynamical properties calculated are the classical electronic reaction energy (ΔE), the enthalpy of reaction at 0 K (ΔH_0°) (defined as $\Delta E + \Delta$ZPVE, where ZPVE means zero point vibrational energy), the enthalpy of reaction at 298.15 K (ΔH_{298}°), and the Gibbs free energy at 298.15 K (ΔG_{298}°). These thermodynamical properties were also calculated at $T = 10$, 50, 100, 200, 298, 500, and 1000 K. All energy quantities for the reactants, products, and transition state were corrected for the zero-point energies (ZPE). The rate coefficient is calculated by the transition state theory (TST),[22−24] which is given by

$$k(T) = \frac{k_B T}{h}\frac{Q^{\#}}{Q_A Q_B}\exp\left(\frac{-E_0}{k_B T}\right) = \frac{k_B T}{h}\exp\left(\frac{-\Delta G_0^{\#}}{k_B T}\right)$$

where k_B and h are the Boltzmann and Planck constants, respectively; R is the gas constant, $Q^{\#}$ is the equilibrium partition function per unit of volume for the transition state, Q_A and Q_B are the same functions for the reactants, and E_0 is the energy of the lowest level of the transition state relative to that of the lowest level of the reactants. The standard Gibbs free energy, $\Delta G_0^{\#}$, between the transition state and reactants can be calculated by standard methods of statistical mechanics to evaluate the equilibrium partition function. Thus, the rate coefficient, $k(T)$, for the reaction SiO + Si_2O_2 may be calculated over the temperature range of 10−1000 K.

Results and Discussions

The geometry and frequency calculations were in fact initially performed using the second-order Møller−Plesset perturbation theory (MP2),[25] density functional theory (DFT)[26−28] with the hybrid functional B3LYP,[29−30] coupled cluster with single and double excitations (CCSD),[19,20] configuration interaction with single and double excitations (CISD),[31−33] and quadratic configuration interaction with single and double excitations (QCISD)[18] with the large basis set 6-311++G(d,p). However, only the CCSD and QCISD methods gave calculated heat of formation values for the SiO dimerization that were consistent with the experimental value.

Further calculations with the basis sets 6-311++G(3df,3dp), cc-pVDZ, and cc-pVTZ were restricted to the QCISD method, and pertinent results were also obtained with the CCSD method when needed for checking consistency. It is important to mention that, in this case, is desirable to compute reaction energetics with the size-consistent CCSD[19,20] or QCISD[18] methods, since iterative methods can give better estimates of the correlation energy than perturbative methods (MP2 or MP4), especially for these molecules which have large correlation energies. The QCISD method was shown to be less time-consuming than the CCSD method. Thus, it was then indicated to evaluate chemical reactions due to its mathematical properties,[34] and the decision of using it was only based on these facts. However, the results of both methodologies are comparable as the reader can see later on. In the case of the *cis*-Si_2O_2 molecule, the calculations were only performed with the unrestricted CCSD and QCISD/6-311++G(d,p) methods to evaluate the thermodynamics for its formation and the trimerization process (reactions 2 and 4 in Table 5). For the trimerization process (reactions 3 and 4 in Table 5), the Si_3O_3 and transition state optimizations with the largest basis sets extrapolated the memory limit for our software version. Also, the frequency calculations for these species with the largest basis sets were not feasible computationally.

TABLE 1: Bond Length (d, Å) and Vibrational Frequency (ω, cm^{-1}) for the SiO Molecule, $C_{\infty v}$

parameter	basis set	CCSD	QCISD	expt
d Si−O	6-311++G(d,p)	1.5171	1.5246	1.5097[a]
	6-11++G(3df,3pd)	1.5087	1.5143	
	cc-pVDZ	1.5424	1.5530	
	cc-pVTZ	1.5155	1.5213	
ω ($\mathrm{S_g}$)	6-311++G(d,p)	1271.2	1221.2	1223.9[b]
	6-311++G(3df,3pd)	1275.2	1238.2	1224.4[c]
	cc-pVDZ	1216.9	1152.0	
	cc-pVTZ	1278.9	1239.1	

[a] Lovas et al., 1981.[35] [b] Anderson and Ogden, 1969.[14] [c] Khanna et al., 1981.[17]

A. Geometries and Frequencies of the SiO, Cyclic Si_2O_2, *cis*-Si_2O_2, and Si_3O_3 Species. The SiO molecule has symmetry $C_{\infty v}$. Its bond length and harmonic frequency are shown in Table 1. The SiO bond length obtained with CCSD/6-311++G(3df,3pd) is 1.5087 Å, which is in excellent agreement with the experimental value, 1.5097 Å.[35] It should be also noted that the SiO bond length calculated with the double-ζ Dunning basis set is overestimated by nearly 0.04 Å. The harmonic frequency calculated by the QCISD method is in better agreement than the CCSD method compared with the experimental observations.[14,17] An exception for this comparison is again the double-ζ Dunning basis set, which underestimates the SiO frequency by 72 cm^{-1}.

The cyclic Si_2O_2 molecule has the Si and O atoms alternating around the ring with symmetry D_{2h}. The structural parameters and vibrational frequencies for the cyclic Si_2O_2 molecule are presented in Table 2. The SiO bond length calculated by the CCSD and QCISD methods with the double-ζ Dunning basis set is overestimated by nearly 0.03 Å as shown in Table 2. The other basis sets used in this work give good results compared with the experimental value, 1.71 Å.[14] The SiO bond length calculated by the 6-311++G(d,p) basis set and larger ones is about 0.01 Å lower than the experimental value.[14] The Si−O−Si angle is well described with any basis sets used in this work; however, the best results were obtained with the larger basis sets, 6-311++G(3df,3pd) and cc-pVTZ. The QCISD method with the 6-311++G(d,p) basis set gave the highest discrepancy for the harmonic frequencies of the cyclic Si_2O_2 molecule, ω_1 (B_{3u}), ω_4 (B_{2u}), and ω_5 (B_{1u}), when compared with experimental frequencies. The discrepancies for the harmonic frequencies ω_1 (B_{3u}), ω_4 (B_{2u}), and ω_5 (B_{1u}) are about −72, 38, and 65 cm^{-1}, respectively, which are highly acceptable for such a molecule. It is important to note that the torsion mode (B_{3u}) is generally underpredicted. On the other hand, the stretching modes (B_{2u} and B_{1u}) are overpredicted as presented in Table 2. In general, the cyclic Si_2O_2 frequencies are well described using large basis sets.

There are other less stable Si_2O_2 dimers alternating Si and O atoms: linear Si_2O_2, *cis*-Si_2O_2, and *trans*-Si_2O_2. Several other possible structures for the dimer were explored in the literature.[9] Only the *cis*-Si_2O_2 structure was considered in this study because it is the only one with experimental evidence.[16] Furthermore, the *cis*-Si_2O_2 and SiO interaction may have a prospective importance in the trimerization process (reaction 4 in Table 5) as suggested by Khana et al. (1981).[17] The *cis*-Si_2O_2 isomer has symmetry C_s. Table 3 presents the structural parameters and vibrational frequencies of the *cis*-Si_2O_2 molecule using unrestricted methods. The unrestricted CCSD and QCISD methods gave similar results for all structural parameters and frequencies of the *cis*-Si_2O_2 isomer. Unfortunately, there is only an attempt to estimate its structure in the literature.[17] The structure of the *cis*-Si_2O_2 molecule was very different from that estimated by force constant refinement calculation.[17] Indeed, this molecule is very reactive, and its structure is difficult to ascribe in this reactive system. However, the vibrational frequencies are in good agreement when compared with the experimental values.[16,17] The torsion mode ω_2 (A″) was also found in this study assuming the C_s symmetry. It corroborates with the findings of Hastie et al. (1969).[16] However, the mechanism of growth proposed by Khana et al. (1981)[17] where occurs the *cis*-Si_2O_2 and SiO interaction (reaction 4 in Table 5), is ruled out by its energetics as it can be seen later in this text.

TABLE 3: Bond Lengths (d, Å), Angles (∠, deg), and Vibrational Frequencies (ω, cm^{-1}) for the "Open" *cis*-Si_2O_2 Structure, C_s, Calculated by Using the Unrestricted CCSD (UCCSD) and QCISD (UCISD) Methods with the 6-311++G(d,p) Basis Set

parameter	UCCSD	UQCISD	expt[a]
Si−O (Å)	1.6777	1.6788	1.74
O−Si (Å)	1.6264	1.6290	1.74
Si−O (Å)	1.5330	1.5377	1.51
Si−O−Si (deg)	167.6	167.8	109.5
O−Si−O (deg)	127.2	127.1	109.5
ω_1 (A′)	64.0	49.9	
ω_2 (A″)	80.7	80.1	79[b]
ω_3 (A′)	330.2	329.9	
ω_4 (A′)	545.2	541.6	
ω_5 (A′)	1030.3	1023.1	
ω_6 (A′)	1200.7	1187.3	1221.5

[a] Khanna et al., 1981.[17] [b] Hastie et al., 1969.[16]

The cyclic Si_3O_3 has the Si and O atoms alternating around the ring with symmetry D_{3h}. The structural parameters and vibrational frequencies for the cyclic Si_3O_3 molecule are shown in Table 4. Unfortunately, there are no good quality structural

TABLE 2: Bond Length (d, Å), Angles (∠, deg), and Vibrational Frequencies (ω, cm^{-1}) for the Cyclic Si_2O_2 Molecule, D_{2h}

method	d Si−O	∠ Si−O−Si	ω_1 (B_{3u})	ω_2 (B_{3g})	ω_3 (A_g)	ω_4 (B_{2u})	ω_5 (B_{1u})	ω_6 (A_g)
CCSD								
6-311++G(d,p)	1.7041	86.13	216.8	552.0	558.4	776.3	828.8	868.5
6-311++G(3df,3pd)	1.6942	87.1	250.0	567.3	571.4	785.2	826.8	866.9
cc-pVDZ	1.7380	86.5	217.8	529.0	554.5	768.9	808.9	838.6
cc-pVTZ	1.6965	87.2	241.9	571.2	587.9	797.5	842.9	877.5
QCISD								
6-311++G(d,p)	1.6856	85.26	179.7	566.7	606.1	803.4	869.0	913.0
6-311++G(3df,3pd)	1.6955	87.1	246.4	564.6	567.5	779.2	822.0	860.1
cc-pVDZ	1.7406	86.6	212.5	521.1	550.5	759.3	801.9	827.5
cc-pVTZ	1.6989	87.3	239.3	568.1	581.4	789.8	836.3	868.7
expt	1.71[a]	87[a]	252[b]			765.5[b]	804.4[b]	
						766.3[a]	804.7[a]	

[a] Anderson and Ogden, 1969.[14] [b] Khanna et al., 1981.[17]

TABLE 4: Bond Lengths (d, Å), Angles (∠, deg), and Vibrational Frequencies (ω, cm^{-1}) for the Cyclic Si_3O_3 Molecule, D_{3h}

parameter	CCSD	QCISD	expt
Si−O (Å)	1.6790	1.6807	1.70[a]
O−Si (Å)	1.6790	1.6807	1.70[a]
Si−O (Å)	1.6790	1.6807	1.70[a]
Si−O−Si (deg)	139.8	139.9	140[a]
O−Si−O (deg)	100.2	100.2	100[a]
ω_1 (E″)	136.6	113.2	
ω_2 (A_2″)	241.5	225.0	
ω_3 (E′)	333.2	325.3	311[b] 312[a]
ω_4 (A_1′)	576.4	564.4	
ω_5 (A_1′)	600.0	595.6	621[b]
ω_6 (E′)	616.5	619.0	630[b] 631.5[a]
ω_7 (A_2′)	807.2	742.3	
ω_8 (E′)	992.9	991.0	972.2[b] 972.6[a]

[a] Anderson and Ogden, 1969.[14] [b] Khanna et al., 1981.[17]

data for the cyclic Si_3O_3 molecule. Indeed, the only structural data is an estimate from a force constant calculation.[14] The SiO bond lengths in the Si_3O_3 molecule are predicted by both CCSD and QCISD methods to be shorter by 0.02 Å compared with those found in the literature.[14] It is interesting to note that the Si_3O_3 molecule and also the cyclic Si_2O_2 have longer bond lengths than the monomer. The O−Si−O and Si−O−Si angles in the cyclic Si_3O_3 are found in good agreement with the experimental value suggested in the literature.[14] The vibrational frequencies are in excellent agreement compared with those found in the literature.[14,17] Although the doubly degenerated ω_3 and ω_8 (E′) vibration modes are overpredicted by at most 21 cm^{-1}, the nondegenerated ω_5 (A_1′) and the doubly degenerated ω_6 (E′) are underpredicted by at most 21 and 15 cm^{-1}, respectively. The anharmonicity of the Si_3O_3 molecule may explain the discrepancy of these results. Unfortunately, as it was already mentioned, the Si_3O_3 optimization and frequency calculations with the largest basis sets were not feasible computationally. Although we could not achieve better results for this molecule, this work represents the best level of theory ever employed for this system.

B. Energetics and Reaction Paths. The classical electronic energy (ΔE), enthalpies (ΔH_T°), and Gibbs free energies (ΔG_T°) for the SiO dimerization and trimerization processes are presented in Table 5. It is important to mention that these thermodynamical properties were calculated by considering separated molecules using DFT,[26−30] MP2,[25] CISD,[31−33] CCSD,[19,20] and QCISD[18] methodologies, but only the CCSD and QCISD methods are consistent and presented here. The thermodynamical properties calculated with the CCSD and QCISD methods for the SiO dimerization are usually lower by about 10−20% than the previous calculations[9,12] and the only experiment.[10] As discussed previously by Snyder and Raghavachari (1984),[9] their results had considerable oscillation in the convergence of the perturbation theory so that results are not reliable. Our thermodynamical calculations do not critically depend on the quality of basis sets and do not present any oscillation because large basis and a higher level of calculation sets were used here. Thus, our methodology may be applied to the SiO trimerization.

The SiO dimerization forming the cyclic Si_2O_2 is exothermic and spontaneous as presented in Table 5. Snyder and Raghavachari (1984)[9] have observed that small basis sets in the perturbation theory predict the SiO dimerization to be too exothermic. On the other hand, if we consider separated molecules in order to estimate thermodynamical properties, our present work shows that larger basis sets in the CCSD and QCISD level of theories predict smaller enthalpies of reaction for the SiO dimerization than those found in the literature.[9,10,12] This occurs because the larger basis sets for the Si_2O_2 molecule tend to compensate the deficiencies of the basis for the higher electron correlation in this molecule compared to the monomer.

When the potential energy surface is scanned, the enthalpy of reaction for the SiO + SiO reaction to form the cyclic Si_2O_2 molecule is then found to be −47.6 kcal mol^{-1} at 298 K using the QCISD/6-311++G(d,p) level of theory. However, using the QCISD/6-311++G(3df,3pd) and cc-pVTZ levels of theory, we found our best estimates for the enthalpy of reaction, −54.1 and −53.0 kcal mol^{-1}, respectively, which are slightly higher than the experimental enthalpy of reaction found experimentally in the early 1970s, -44.6 ± 3.0 kcal mol^{-1},[10] and the enthalpy of reaction calculated by the MP4 method, −43 kcal mol^{-1}.[9] Our calculated enthalpies of reaction are in better agreement with the most recent calculation, −48 kcal mol^{-1}.[12] We then suggest that the only experiment for the enthalpy of reaction for the dimerization process should be verified to solve this uncertainty.

In addition to this reaction path for the SiO dimerization, Khana et al. (1981)[17] proposed that it may also yield the *cis*-Si_2O_2 molecule. However, it is clear that the reaction path proposed by Khana et al. (1981)[17] does not occur due to its thermodynamics; this reaction path is endothermic and nonspontaneous as presented in Table 5. Furthermore, our findings also corroborate with no evidence of transition state in any of the two reaction paths for the SiO dimerization, which agree with the literature.[9,12]

There are two possibilities for the Si_3O_3 growth mechanism: (1) the SiO + cyclic Si_2O_2 reaction (reaction 3); and (2) the SiO + *cis*-Si_2O_2 reaction (reaction 4). The interaction of SiO with the *cis*-Si_2O_2 isomer may be expected due to the "head to tail" long range interaction. Although the SiO + *cis*-Si_2O_2 reaction is exothermic and spontaneous, as shown in Table 5, this reaction is ruled out by the lack of understanding for a *cis*-Si_2O_2 source since reaction 2 is not spontaneous. From our knowledge, there is not a possible source for this high energetic and reactive isomer. Although Khanna et al. (1981)[17] have observed infrared features of the *cis*-Si_2O_2 isomer, it is not possible yet to indicate reaction 4 as a possibility for a Si_3O_3 growth mechanism. Yet, it is important to comment that we found a planar transition state for the reaction SiO + *cis*-Si_2O_2 with the DFT level of theory (B3LYP/6-311++G(d,p)). The

TABLE 5: Thermodynamical Properties (in kcal mol^{-1}) of the Dimerization and Trimerization Process Calculated by Using the CCSD and QCISD Methods with the Basis Set 6-311++G(d,p) with Zero Point Energy Correction

	ΔE		ΔH_0°		ΔH_{298}°		ΔG_{298}°	
chemical reaction	CCSD	QCISD	CCSD	QCISD	CCSD	QCISD	CCSD	QCISD
(1) SiO + SiO → Si_2O_2	−42.6	−38.9	−40.8	−37.7	−41.9	−38.7	−31.1	−27.9
(2) SiO + SiO → *cis*-Si_2O_2	28.5	30.3	29.6	31.4	29.1	31.0	36.3	38.1
(3) SiO + Si_2O_2 → Si_3O_3	−63.7	−60.4	−59.8	−57.9	−60.4	−58.5	−50.3	−47.4
(4) SiO + *cis*-Si_2O_2 → Si_3O_3	−132.7	−129.5	−130.2	−127.0	−131.4	−128.3	−117.7	−113.4

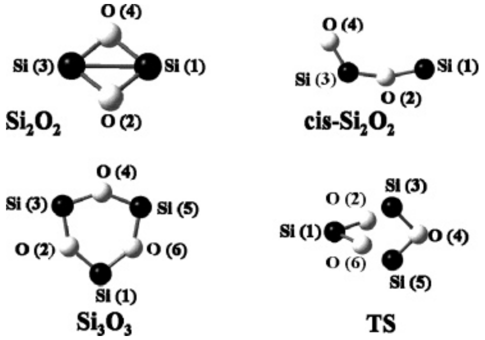

Figure 1. The structures of the Si_2O_2, *cis*-Si_2O_2, and Si_3O_3 molecules and the transition state.

imaginary vibrational frequency of this planar transition state was found to be very low, 69i cm^{-1}, probably not indicating a real transition state. As there should not be a real importance in this reaction path, further calculations with higher level of theory were not performed for the transition state of this reaction path.

The other possibility for the Si_3O_3 growth mechanism is the SiO + cyclic Si_2O_2 reaction, which is exothermic and spontaneous as presented in Table 5. For the trimerization process, we found that the enthalpy of reaction at 298 K is about −58.5 kcal mol^{-1} with the QCISD/6-311++G(d,p) method including the zero point energy correction, which is in excellent agreement with that found in the literature,[12] −58 kcal mol^{-1}.

The proposed mechanism for the trimerization process is then the reaction of SiO with the cyclic Si_2O_2 to form the cyclic Si_3O_3. Avromov et al. (2005)[8] recently performed an extensive work to study this system and found no evidence for a transition state, probably due to the complexity of this system. In an exhaustive investigation of the Si_3O_3 formation, we found a transition state in the reaction path of this reaction. Indeed, it is worthy to emphasize that the mechanism for this reaction is very complex. The reaction path follows a torsion movement to form an out-of-plane transition state as presented in Figure 1. Then, the reaction path passes in a shoulder, which may be an intermediate with a twisted conformation of the Si_3O_3 molecule, just before reaching the planar Si_3O_3 structure. The transition state may thus decay to the product via vibrational relaxation. The transition state for the trimerization process is a coplanar combination between like-SiO_2 and Si_2O groups. The imaginary frequency for this coplanar transition state is 243i cm^{-1}, as calculated by the QCISD/6-311++G(d,p) method. The intrinsic reaction coordinate calculation confirmed that this transition state links the SiO and Si_2O_2 molecules to the Si_3O_3.

The rate coefficient for reaction 3 was calculated by the TST theory[22−24] at temperatures ranging from 10 to 1000 K. In the investigation of the chemical kinetics of this association reaction, it was assumed that the conditions maintain the thermal distribution of reactants, and that reactant equilibrium assumption is then valid, so that the conventional TST approach can be used to calculate the bimolecular rate coefficient. Since only heavy nuclei take part in this reaction and the imaginary frequency is low, tunneling effects are expected to be important only at very low temperatures. The Wigner correction for tunneling effects[24,36] was evaluated at $T = 10-1000$ K and shown to be unimportant (<13%) at temperatures higher than 200 K. The Gibbs free energy for the transition state formation, $\Delta G_0^{\#}$, at 298 K is 4.85 and 5.51 kcal mol^{-1} using the CCSD and QCISD methods with the basis sets 6-311++G(d,p), respectively. Values of the Gibbs free energy for the transition state formation, Wigner correction, and the rate coefficient for the trimerization process calculated by the TST approach at different temperatures of interest are presented in Table 6. Notice, however, that the Gibbs free energy should not be so sensitive to the size of the basis sets because basis set errors tend to be canceled out when the thermodynamical properties are evaluated. However, the larger the basis sets, the better is the Gibbs free energy for the reactant and transition state. Unfortunately, it is not possible to use larger basis sets to calculate the thermodynamical properties for the transition state due to the computational difficulties already explained.

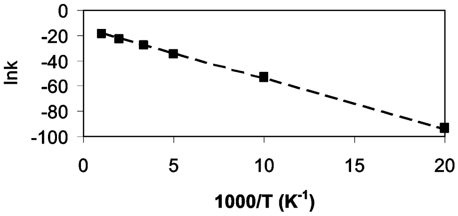

Figure 2. Arrhenius plot of the rate coefficient for the reaction SiO + Si_2O_2 calculated by transition state theory at the QCISD/6-311++G(d,p) level of theory. The units of *k* are cm^3 $molecule^{-1}$ s^{-1}.

TABLE 6: Value of the Gibbs Free Energy $\Delta G_0^{\#}(T)$ (kcal mol^{-1}), Wigner Correction for Tunneling Effect, and Uncorrected and Corrected Bimolecular Rate Constant *k*(*T*) (cm^3 $molecule^{-1}$ s^{-1}) at Different Temperatures of Interest

T (K)	$\Delta G_0^{\#}(T)$ (kcal mol^{-1})	*k*(*T*) (cm^3 $molecule^{-1}$ s^{-1})	Wigner correction	$k_c(T)$ (cm^3 $molecule^{-1}$ s^{-1})
10	7.83	3.02×10^{-181}	51.98	1.57×10^{-179}
50	7.33	1.59×10^{-41}	3.04	4.84×10^{-41}
100	6.74	6.34×10^{-24}	1.51	9.58×10^{-24}
200	6.29	9.17×10^{-16}	1.13	1.03×10^{-15}
298	5.51	9.42×10^{-13}	1.06	9.96×10^{-13}
500	4.76	1.44×10^{-10}	1.02	1.47×10^{-10}
1000	3.69	5.41×10^{-9}	1.01	5.44×10^{-9}

The Gibbs free energy for the transition state and, consequently, the rate coefficient are calculated using the CCSD and QCISD/6-311++G(d,p) levels of theory and presented in Table 6. The Gibbs free energy for the transition state is very consistent when the CCSD and QCISD methodologies are compared. The difference between the Gibbs free energy for the transition state calculated by the two methods is only 12%. The corrected rate coefficient for the SiO + Si_2O_2 reaction (reaction 3) is 3.04×10^{-12} and 9.96×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K with the CCSD/6-311++G(d,p) and QCISD/6-311++G(d,p) methods with the zero point energy correction, respectively. The temperature profile of the rate coefficient is shown in Figure 2. The activation energy for this reaction is estimated to be around 8 kcal mol^{-1}. These rate coefficients are very fast for the environments of interest. The rate coefficient at $T = 500$ K is in the collision limit ($k = 1 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}), where each collision yields the product. However, reaction 3 should be unimportant at lower temperatures ($T < 200$ K). The significance of this reaction should be related to interstellar regions with high temperatures falling into the temperature range of 300 to 1000 K. At the conditions found in the production process of silicon nanowires ($500 < T < 1000$ K), this reaction is also in the collision limit, being very important for this manufacturing process.

Implications for the Chemistries of Interstellar Silicate Grains and Silicon Nanowires

The interstellar implications of this finding mean that this reaction may be very important to the early grain formation process in circumstellar shells as we aimed to demonstrate in

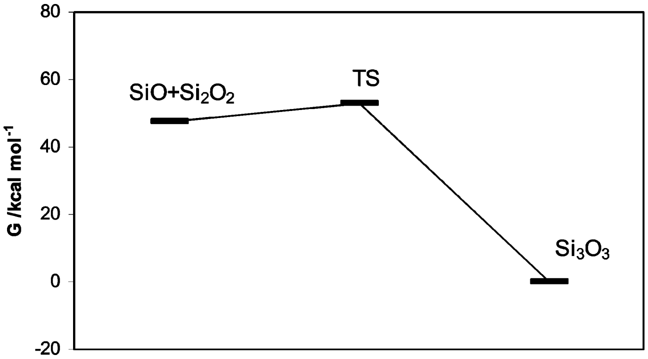

Figure 3. The energetic diagram for the SiO + Si_2O_2 reaction forming Si_3O_3 molecules and the Si_3O_3 fragmentation. The Gibbs free energy, G, is relative to that for the Si_3O_3 molecule.

this paper. The implications for the chemistry of silicon nanowire growth are also very important. Lu et al.[7] and Avromov et al.[8] found no evidence of transition state for the reaction SiO + Si_2O_2. Indeed, they suggested that this reaction is barrierless, which implies that Si_3O_3 fragmentation may be possible. We found that the enthalpy of reaction for the Si_3O_3 fragmentation is 53.9 kcal mol^{-1}. The theoretical enthalpies of Si_3O_3 fragmentation found in the literature are 64.7,[7] 59.6,[7] 50.2,[8] and 56.6[8] kcal mol^{-1}. The latter one is the best level of calculation (CR-CCSD(T)), which is the closest value from the result found in our study. Thus, the Si_3O_3 fragmentation should not occur in these conditions as proposed in the literature[7,8] because it must overcome the transition state barrier mentioned previously. Instead, the very stable Si_3O_3 molecule may participate in the growth mechanism forming Si_3O_3-ring assemblies as suggested by Lu et al.[37] To clarify any misleading interpretation or confusion in the chemical mechanism proposed here, the energetic diagram (ΔG) for the SiO + Si_2O_2 reaction at 298 K is presented in Figure 3.

Conclusion

The SiO + Si_2O_2 reaction path was proposed in this study by finding its transition state for the first time ever. Our work shows that this process is exothermic and spontaneous. The enthalpies of reaction at 298 K for the trimerization and fragmentation processes are -58.5 and 53.9 kcal mol^{-1}, respectively, at the QCISD/6-311++G(d,p) level of theory, which are in excellent agreement with the literature. At this level, the rate coefficient for the SiO + Si_2O_2 reaction is about 1×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and is in the collision limit, 1×10^{-10}, at $T = 500$ K. The activation energy of this reaction is about 8 kcal mol^{-1}. The SiO + Si_2O_2 reaction proposed in this work may be very important for the Si_3O_3 growth in the circumstellar envelopes surrounding M-type giants and in the fabrication of silicon nanowires. Our work gives the first hint for the chemical kinetics of the Si_3O_3 growth in circumstellar shells and in the production process of silicon nanowires. These findings have profound implications in the latter environment because they clarify the chemical mechanism and avoid misleading or confusing about the suggested, but not favorable, Si_3O_3 fragmentation.

Acknowledgment. The authors are grateful to FAPESP for the financial support. A.S.P. also thanks FAPESP for a research fellowship (05/50722-6), and Dr. Ashraf Ali (NASA Goddard Space Flight Center) for bringing the problem to my attention.

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