# Kinetics of the SiH<sub>3</sub> + O<sub>2</sub> Reaction: A New Transition State for SiO Production

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The mechanism of SiO formation in the laser photolysis of SiH<sub>4</sub>/O<sub>2</sub>/CCl<sub>4</sub> mixtures was investigated using a laser-induced fluorescence method. Measured rates for the SiO production corresponded to the decay rates of SiH<sub>3</sub> radical and depended linearly on the O<sub>2</sub> concentration. The yield of SiO was estimated on the basis of LIF intensity, and it was found that SiO was one of the major products in the SiH<sub>3</sub> + O<sub>2</sub> reaction. The bimolecular rate constant for the SiO production was determined to be  $(1.14 \pm 0.18) \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>. *Ab initio* molecular orbital calculations were performed for various pathways of the SiH<sub>3</sub> + O<sub>2</sub> reaction. Geometries were optimized at the MP2(full)/6-31G(d) level of theory, and relative energies and barrier heights were calculated at the G2(MP2) level of theory. Silyl radical and O<sub>2</sub> react to form SiH<sub>3</sub>OO, which irreversibly decomposes to various excited products. A new transition state for the production of cyclic H<sub>2</sub>SiO<sub>2</sub> (siladioxirane) + H from SiH<sub>3</sub>OO adduct was found. Possible decomposition channels of the vibrationally excited products of the SiH<sub>3</sub> + O<sub>2</sub> reaction to produce SiO are discussed.

#### Introduction

The oxidation mechanism of gaseous silicon hydride continues to be of considerable interest because of its importance in many practical applications including chemical vapor deposition (CVD) processes in the semiconductor industry<sup>1,2</sup> and in the SiH<sub>4</sub>/O<sub>2</sub> combustion/explosion systems.<sup>3–8</sup> However, the chemical kinetic mechanism of silane combustion is complex and not fully understood. For example, the chemical kinetic mechanism for SiO formation in fuel-rich flame is unknown.<sup>5</sup> One of the primary purposes of the present study is to understand the mechanism of SiO formation in the silane oxidation process.

It is generally agreed that the first step in silane combustion is generation of SiH<sub>3</sub> radicals followed by the reaction of SiH<sub>3</sub> +  $O_2$ .<sup>8,9</sup> SiO is expected to be produced by consecutive reactions among the products of this reaction. Therefore, identification of the main product channels of the SiH<sub>3</sub> +  $O_2$ reaction is important to understand the mechanism of SiO formation in silane oxidation.

Rate constants for the reaction of SiH<sub>3</sub> with O<sub>2</sub> have been determined by several groups.<sup>10-13</sup> Their values at room temperature agree quite well with each other despite the different experimental techniques used in these studies. Slagle et al.<sup>10</sup> measured the rate constant over the range 296–500 K using time-resolved mass spectrometry and found a slight negative temperature dependence ( $E_a = -0.5$  kcal/mol). Quandt et al.<sup>13</sup> also observed this negative temperature dependence of the rate constants ( $E_a = -0.9$  kcal/mol) by means of time-resolved infrared diode laser absorption spectroscopy. The rate constant was found to be independent of pressure in the range 0.9–5.4 Torr with He buffer<sup>10</sup> or in the range 1–10 Torr with N<sub>2</sub>

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buffer.<sup>11</sup> The observed negative temperature dependence and the pressure independence of the rate constants are consistent with an addition—elimination mechanism proposed by Hartman et al.<sup>8</sup> They postulated the following mechanism based on the empirical estimation of the heats of formation for silicon—oxygen compounds:

 $SiH_3 + O_2 \rightarrow SiH_3OO^* \tag{1}$ 

$$SiH_3OO^* \rightarrow SiH_3O + O$$
 (1a)

$$SiH_3OO^* \rightarrow SiH_2O + OH$$
 (1b)

$$SiH_3OO^* \rightarrow SiH_2O_2 + H$$
 (1c)

$$SiH_3OO^* + M \rightarrow SiH_3OO + M$$
 (1d)

Competition between the collisional deactivation of the vibrationally excited adduct SiH<sub>3</sub>OO\* (reaction 1d) and irreversible decomposition of SiH<sub>3</sub>OO\* (reactions 1a-1c) determines the second explosion limit of the SiH<sub>4</sub>/O<sub>2</sub> mixtures, but reaction 1d is not important at pressures below several hundred Torr at low temperatures.<sup>8</sup> Britten et al.<sup>9</sup> developed the kinetic model for the silane combustion including the above reactions. They could explain both high-temperature shock tube ignition delay times and nonlinear variation of autoignition time with initial pressures at near-ambient temperatures. On the basis of their kinetic simulations of silane combustion, they concluded that the favored pathway for the SiH<sub>3</sub>OO\* decomposition was reaction 1b. The branching ratios for reactions 1b and 1c can be determined directly by measuring the absolute concentrations of H atoms and OH radicals. Such measurements have been performed by Koshi et al.14 using laser-induced fluorescence detection of H atoms (at 121.6 nm) and OH radicals (at 308 nm), and values of 0.25 and 0.65 were obtained for the product branching ratios of the reactions 1b and 1c, respectively.

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Experimental determination of the branching ratios by Koshi et al.<sup>12,14</sup> indicated that the main reaction channel is reaction 1c at low pressures. Darling et al.<sup>15</sup> have performed *ab initio* molecular orbital calculations for the SiH<sub>3</sub> + O<sub>2</sub> reaction at the G2 level of theory. They found that OH radicals were produced by breaking the O–O bond after the 1,3 hydrogen shift in SiH<sub>3</sub>OO, but they could not find the direct pathway for the H atom production and suggested that H atoms were formed by the reaction of SiH<sub>2</sub>O with OH. This mechanism, however, cannot explain the time profiles of H and OH observed by Koshi et al.

In this work, SiO was detected in the laser photolysis of SiH<sub>4</sub>/ $O_2/CCl_4$  mixtures by using a laser-induced fluorescence method. It is shown that SiO is one of the major products in the SiH<sub>3</sub> +  $O_2$  reaction. *Ab initio* molecular orbital calculations were also conducted to confirm the main product channel of the SiH<sub>3</sub> +  $O_2$  reaction, and the possible pathways for the SiO production are discussed.

### **Experimental Section**

The apparatus used for the laser-induced fluorescence (LIF) studies is identical to the system used for the previous work.<sup>14,16</sup> Sample gas mixtures of CCl<sub>4</sub>, SiH<sub>4</sub>, and O<sub>2</sub> diluted in He were slowly flowed in the Pyrex reaction cell at a typical pressure of 20 Torr. The total pressure was measured with a capacitance manometer (MKS Baratron 112A), and the partial pressures of each reactant were determined from the corresponding flow rates. The partial pressures of CCl<sub>4</sub>, SiH<sub>4</sub>, and O<sub>2</sub> were in the rang 1–3, 1–5, and 0–3 mTorr, respectively.

Cl atoms generated by the photolysis of CCl<sub>4</sub> at 193 nm (5– 10 mJ) rapidly react with SiH<sub>4</sub> to produce SiH<sub>3</sub> by very fast reaction of Cl + SiH<sub>4</sub>  $\rightarrow$  HCl + SiH<sub>3</sub>. Initial concentrations of SiH<sub>3</sub> were less than 5 × 10<sup>11</sup> molecules cm<sup>-3</sup>; radical-radical and radical-atom reactions were kept negligible compared to the rate of the SiH<sub>3</sub> + O<sub>2</sub> reaction. This has been confirmed by kinetic simulations which included several consecutive reactions.<sup>14</sup>

The SiO(X<sup>1</sup> $\Sigma$ , $\nu''=0,1,2$ ) produced in this reaction system is probed by monitoring the fluorescence on the A–X transition at the wavelength range 225–240 nm.<sup>17</sup> The probe laser radiation is generated by frequency doubling in the  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystal and counterpropagated to the photolysis ArF laser beam in the reaction cell. The fundamental light is obtained by a dye laser (PRA-DL14P) excited by a XeCl excimer laser (Lambda Physik LPX110i). The laser-induced fluorescence signal was detected with a photomultiplier (Hamamastu R106U) at a right angle to probe the photolysis laser beams. The signal was normalized with the intensity of probe laser radiation monitored by a photodiode (Hamamatsu S1772-02). Signals from the photomultiplier and the photodiode were averaged with boxcar integrators (Stanford Research SR250) and stored in a microcomputer.

He (Nippon Sanso, 99.9999%), SiH<sub>4</sub> (Mistui-Toastu, electronic grade), and O<sub>2</sub> (Nippon Sanso, 99.99%) were used without further purification.  $CCl_4$  (Wako, research grade) was degassed by multiple freeze-pump-thaw cycles.

# **Results and Discussion**

A. SiO Production in the SiH<sub>3</sub> + O<sub>2</sub> Reaction. Figure 1 shows an example of the SiO excitation spectrum observed in the laser photolysis of CCl<sub>4</sub>/SiH<sub>4</sub>/O<sub>2</sub>/He mixture. This spectrum was obtained with a 500  $\mu$ s time delay between photolysis and probe laser. It was confirmed that no SiO signal was detected when CCl<sub>4</sub> was not present. As can be seen in Figure 1, the (3–2) band of the A–X transition, as well as (0–0) band, was



**Figure 1.** LIF spectrum of the SiO produced in the SiH<sub>3</sub> + O<sub>2</sub> reaction. Experimental conditions are as follows: partial pressures of CCl<sub>4</sub>/SiH<sub>4</sub>/ $O_2 = 3/10/1$  mTorr; total pressure = 30 Torr. Delay time between photolysis ArF and probe dye lasers is set to 500  $\mu$ s.



**Figure 2.** Time profiles of the LIF signal intensity of SiO(v'' = 0) and SiO(v'' = 1). The solid circles are obtained without the addition of CF<sub>4</sub>, and open circles are taken with the addition of 21 mTorr of CF4. Experimental conditions are as follows: partial pressures of CCl<sub>4</sub>/SiH<sub>4</sub>/O<sub>2</sub> = 3.3/3.8/2 mTorr; total pressure = 20 Torr.

observed. This indicated that vibrationally excited SiO was also produced in this reaction system. To avoid the complex influences of the vibrational relaxation on the measurement of the total production rates of SiO, CF4 was added as an efficient collider for the vibrational relaxation. Because of the nearresonant V–V energy transfer between the  $v_3$  mode of CF<sub>4</sub>  $(1265 \text{ cm}^{-1})^{18}$  and the SiO fundamental vibration  $(1241 \text{ cm}^{-1})^{19}$ fast vibrational relaxation of SiO with the addition of CF4 is expected. This was confirmed experimentally by comparing time profiles of the LIF intensities for SiO with and without CF<sub>4</sub> at the same experimental conditions. Typical examples of the time profiles for SiO (v''=0 and 1) are shown in Figure 2. After the ArF laser radiation, the LIF intensity of SiO(v''=0)increased with time and reached the steady state value, whereas the intensity of SiO(v''=1) shows rise and decay caused by the vibrational relaxation. With the addition of 21 mTorr of CF<sub>4</sub>, SiO in the v''=1 state rapidly relaxed to the v''=0 state, and accordingly the rise rate of v''=0 increased. This indicated that the production rate of total SiO (=sum of all the vibrational states) can be derived from measurements of the rise rate of



Figure 3. First-order production rates of SiO as a function of  $O_2$  pressures: total pressure = 20 Torr,  $CCl_4/SiH_4/CF_4 = 3.3/3.8/21$  mTorr.

SiO( $\nu''=0$ ) with the addition of CF<sub>4</sub>. The pseudo-first-order rate constant for SiO production was analyzed by a nonlinear least squares fit of the time profiles of SiO( $\nu''=0$ ). Resulting first-order rate constants are plotted in Figure 3 as a function of O<sub>2</sub> concentration. The rise rates for the total SiO linearly depend on O<sub>2</sub> concentration, and the bimolecular rate constant was determined to be  $(1.14 \pm 0.18) \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>. This value is comparable to the rate constant for the reaction of SiH<sub>3</sub> with O<sub>2</sub> ((1.26 ± 0.18) × 10<sup>-11</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>).<sup>12</sup> Experimental results on SiO formation are summarized as follows.

(1) The production rate of SiO is proportional to  $O_2$  concentration, but is independent of the concentrations of SiH<sub>4</sub> and CCl<sub>4</sub>. Under pseudo-first-order conditions (i.e.,  $[O_2] \gg$  [SiH<sub>3</sub>]), the production rate should be proportional to  $[O_2]$  but is independent of the concentrations of other species.

(2) The bimolecular rate constant for SiO production is almost the same as the rate constant for  $SiH_3$  decay.

(3) Under the constant dissociation laser power, the amount of SiO produced is proportional to the concentration of CCl<sub>4</sub> (and therefore proportional to the concentration of SiH<sub>3</sub>) and is independent of the concentration of SiH<sub>4</sub>. Since present measurements were performed under pseudo-first-order conditions of  $[O_2]_0 > [SiH_3]_0$ , one would expect that the yield of SiO is also independent of  $[O_2]_0$ . However, the yields of SiO slightly decrease with decreasing the initial concentration of  $O_2$ . This behavior of SiO production was found to be well explained by the loss of SiH<sub>3</sub> at the cell wall.

All these results indicated that SiO is directly produced by the SiH<sub>3</sub> +  $O_2$  reaction.

**B.** Yield of SiO in the SiH<sub>3</sub> + O<sub>2</sub> Reaction. It is important to clarify whether or not SiO is a major product. To estimate the SiO yield, initial concentrations of SiH<sub>3</sub> are calculated from the absorption cross section of CCl<sub>4</sub> at 193 nm ( $\sigma$ (CCl<sub>4</sub>,193nm) =  $1.0 \times 10^{18}$  cm<sup>2</sup>)<sup>20</sup> and the quantum yield of Cl atom formation ( $\Phi$ (Cl) = 1.2)<sup>20</sup> by ArF laser photolysis. For a typical example, [SiH<sub>3</sub>]<sub>0</sub> =  $6.6 \times 10^{10}$  molecules/cm<sup>3</sup> is obtained with [CCl<sub>4</sub>] =  $2.7 \times 10^{13}$  molecules/cm<sup>3</sup> and a laser fluence of 2.12 mJ/cm<sup>2</sup>.



**Figure 4.** LIF spectrum of the NO A–X (0–0) band and SiO A–X (2–0) band. Upper trace, SiO taken with a mixture of CCl<sub>4</sub>/SiH<sub>4</sub>/O<sub>2</sub>/CF<sub>4</sub> = 0.83/0.83/3.2/30 mTorr diluted in 10 Torr of He. Delay time between photolysis and probe laser beam is 500  $\mu$ s. Lower trace: 0.047 mTorr NO in 10 Torr of He.

The absolute concentrations of SiO are estimated from the LIF intensity. Conversion of the LIF intensity to the absolute concentration requires a calibration procedure: a comparative method has been employed, i.e., the LIF intensity of the NO  $X^2\Pi(v''=0) \rightarrow A^2\Sigma(v'=0)$  transition at the wavelength region 225.5-227.1 nm and the LIF signal of the SiO  $X^{1}\Sigma(v''=0) \rightarrow$  $A^{1}\Pi(v'=2)$  transition at almost the same wavelength region were repeatedly monitored. Figure 4 shows examples of the NO and SiO spectra in this wavelength region. Measurements of the SiO LIF signal for the A-X (2-0) band were performed with the addition of CF<sub>4</sub> in order to ensure complete vibrational relaxation, and the integrated signal intensity over all rotational lines was calculated to obtain the total concentration. The integrated LIF intensity over all rotational lines in the given vibrational band system is approximately proportional to the product of the oscillator strength f for the given vibrational band system and the total concentration:  $I_{\rm NO} = C({\rm NO})f_{\rm NO}$  and  $I_{\rm SiO}$ =  $C(SiO)f_{SiO}$ . Here,  $I_{NO}$  and  $I_{SiO}$  are the LIF intensities integrated over all rotational lines and C is the proportionality constant. The value of C is determined by measuring  $I_{NO}$  with the known concentration of NO. Once the value of C is known, the concentration of SiO can be estimated. It is confirmed that the LIF intensity is proportional to the intensity of the probe laser, and therefore the saturation effect is negligible under the present experimental conditions. The collisional quenching (both for SiO and NO) is also confirmed to be negligible by the fact that the LIF intensities after the complete vibrational relaxation do not change by changing the total pressure (in the range 10-30 Torr).

The oscillator strength of the NO A-X(0,0) band has been measured by several groups<sup>21,22</sup> and is well established ( $f_{NO} =$  $4.0 \times 10^{-4}$ ). On the other hand, there is disagreement between the reported magnitudes of  $f_{SiO}$  for the SiO A-X (2,0) band. The value reported by Smith and Lifszt<sup>23</sup> is  $f_{SiO} = 3.6 \times 10^{-2}$ for the A-X (2,0) band. Oddershede and Elander<sup>24</sup> determined  $f_{\rm SiO}$  for the A-X (0,0) band to be  $1.02 \times 10^{-2}$ . By using the Franck-Condon factors derived by Weijer and Zwerver,<sup>25</sup> the oscillator strength for the A-X(2,0) band was calculated to be  $1.66 \times 10^{-2}$ , which is about half of the value of Smith and Lifszt. This value of  $f_{\rm SiO} = 1.66 \times 10^{-2}$  for the (2,0) band is consistent with the radiative lifetimes of this band system measured by the LIF method.<sup>26</sup> The yield of SiO was estimated to be  $[SiO]_{\infty}/[SiH_3]_0 = 0.71 \pm 0.04$  (with the value of  $f_{SiO} =$  $1.66 \times 10^{-2}$ ) or 0.33 ( $f_{SiO} = 3.6 \times 10^{-2}$ ) as an average over four independent measurements. Although estimation of the



Optimized geometry of transition strucuture SiH\_3O2 <-> SiH\_2O2 + H HF/6-31G(d) ( MP2(full)/6-31G(d) )

**Figure 5.** Geometry of the transition state (TS1) for SiH<sub>3</sub>OO  $\rightarrow$  H + cyclic H<sub>2</sub>SiO<sub>2</sub> optimized at HF/6-31G(d). Values in parentheses were obtained by calculations at the MP2(full)/6-31G(d) level of theory.

yield depends largely on the magnitude of the oscillator strength for the SiO A–X (2,0) band, it is clear that SiO is one of the major products in the SiH<sub>3</sub> + O<sub>2</sub> reaction.

C. Ab Initio Calculations of the Reaction Pathways of the  $SiH_3 + O_2$  Reaction. The identification of the product channels in the  $SiH_3 + O_2$  reaction is essential for understanding the mechanism of SiO formation. There is a discrepancy between experimental and theoretical investigations for the product channels of this reaction. On the basis of their experimental results on VUV (vacuum ultraviolet)-LIF detection of H atoms, Koshi et al.<sup>14</sup> concluded that the reaction pathway to produce H atoms was one of the direct and main channels in the  $SiH_3 + O_2$  reaction. On the other hand, the transition state for the reaction of H atom production has not been found in the recent *ab initio* molecular orbital calculations.<sup>15</sup> However, the channel to produce  $H + cyclic H_2SiO_2$  (siladioxirane) is energetically possible. In the present study, the ab initio calculations have been conducted to find the transition state for the channel producing H atoms.

The present calculations were carried out by using the GAUSSIAN 92 and 94 series of programs.<sup>27</sup> It is found that cyclic H<sub>2</sub>SiO<sub>2</sub> has considerable singlet biradical character, and the energies of this species cannot be treated satisfactorily by the single-determinant Hartree–Fock (HF) theory. Second-order Møller–Plesset perturbation (MP2) theory was employed to optimize the equilibrium geometries. The transition states were searched at the MP2(full)/6-31G(d) level of theory, and the vibrational frequencies were calculated by numerical differentiation of the analytic energy gradients. After optimizing the geometries, single-point calculations were carried out by using G2(MP2) method.<sup>28</sup> It is found that the energies of the species relevant to the SiH<sub>3</sub> + O<sub>2</sub> reaction obtained by the G2(MP2) method agreed well (within 2 kcal/mol) with those of Daring and Schlegel<sup>15</sup> calculated by the G2(full) method.

The transition state for the channel to form  $H + cyclic H_2SiO_2$  (TS1) was found in the present calculation. The structure optimized at the MP2(full)/6-31G(d) level is shown in Figure 5. The transition state TS1 is in  $C_1$  symmetry, and it has the pyramidalized siladioxirane structure with elongating one of the three Si-H bonds. The barrier height relative to that of SiH<sub>3</sub> + O<sub>2</sub> calculated by the G2(MP2) method was -19.98 kcal/

mol, which is lower than the barrier for the isomerization from  $SiH_3OO^*$  to form  $H_2SiOOH$  (TS6 in Figure 6b). It is noted that the transition state TS6 calculated by Darling and Schlegel<sup>15</sup> is in  $C_s$  symmetry, while the present TS6 has  $C_1$  symmetry. This isomerization pathway was previously thought to be the lowest energy unimolecular process for SiH<sub>3</sub>OO\* decomposition. The G2(MP2) energy for the transition state TS2 is calculated to be -17.27 kcal/mol (relative to SiH<sub>3</sub> + O<sub>2</sub>), which is in good agreement with the G2(full) value of -17.50 kcal/ mol by Darling and Schlegel. The energies and vibrational frequencies for these transition states are summarized in Table 1, and the energy diagram is shown in Figure 6a,b. SiH<sub>3</sub> radical reacts with oxygen to form a stable adduct SiH<sub>3</sub>OO of  $C_S$ symmetry. Since this adduct has an excess energy of 51.5 kcal/ mol (by G2(MP2) calculation), various products can be formed by the irreversible unimolecular decomposition reactions. Present calculations predict that the main reaction pathway is the decomposition channel to form  $H + cyclic H_2SiO_2$  through the transition state TS1 (Figure 6a). Another major channel is the isomerization of SiH<sub>3</sub>OO\* adduct to form H<sub>2</sub>SiOOH following OH elimination to form  $SiH_2O + OH$  (Figure 6b). These predictions are in good agreement with the experimental observations that H and OH were the dominant and direct products of the  $SiH_3 + O_2$  reaction.<sup>14</sup>

**D.** Mechanism of SiO Formation. There are two plausible explanations for rapid formation (as fast as the decay rate of SiH<sub>3</sub>) of SiO with a large yield. One is SiO formation by consecutive reactions of major products of the unimolecular decomposition, i.e., reactions of cyclic H<sub>2</sub>SiO<sub>2</sub> or SiH<sub>2</sub>O. Since the concentrations of radicals or products were always kept low enough to prevent the secondary processes by keeping the initial concentrations of SiH<sub>3</sub> below  $5 \times 10^{11}$  molecules/cm<sup>3</sup>, reactions with these radicals or products could not be responsible for the fast SiO formation. Although reactivity of cyclic H<sub>2</sub>SiO<sub>2</sub> or SiH<sub>2</sub>O is not well-known, their reactions with SiH<sub>4</sub> or O<sub>2</sub> are not expected to produce SiO directly. Therefore, bimolecular reactions of cyclic H<sub>2</sub>SiO<sub>2</sub> or SiH<sub>2</sub>O are excluded as a source of SiO.

Another possibility is the unimolecular decomposition of cyclic H<sub>2</sub>SiO<sub>2</sub> or SiH<sub>2</sub>O. Maximum excess energies for cyclic H<sub>2</sub>SiO<sub>2</sub> and SiH<sub>2</sub>O are 26.6 and 65.5 kcal/mol, respectively. The unimolecular decomposition of SiH<sub>2</sub>O has been studied by Kudo and Nagase.<sup>29,30</sup> More recently, extensive calculations of the various reaction pathways for  $Si_xH_yO_z$  species have been performed by Zachariah and Tsang<sup>31</sup> using the BAC-MP4 procedures. They also calculated the barrier height for the unimolecular decomposition and isomerization reactions of SiH<sub>2</sub>O. The direct decomposition of SiH<sub>2</sub>O to form SiO +  $H_2$ has an energy barrier of 13.8 kcal/mol (relative to  $SiH_3 + O_2$ ), which is higher than the maximum excess energy of SiH<sub>2</sub>O. The barrier height for the isomerization to HSiOH is -11.0and -26.8 kcal/mol for HSiOH  $\rightarrow$  SiO + H<sub>2</sub>. These values of barrier height are considerably lower than the previously reported values.<sup>30,32</sup> This process,  $SiH_2O \rightarrow HSiOH \rightarrow SiO +$ H<sub>2</sub>, is energetically possible, and one of the candidates for the SiO formation route (see Figure 6b). It is noted that a part of the reaction exothermicity for  $SiH_3OO^* \rightarrow SiH_2O + OH$  has to be partitioned in the relative translational energy and the internal energy of OH. Therefore, the available energy of SiH<sub>2</sub>O can be smaller than the maximum excess energy. In addition, vibrationally excited OH is produced in the SiH<sub>3</sub> + O<sub>2</sub> reaction.<sup>14</sup> Such vibrational excitation in the OH fragment from H<sub>2</sub>SiOOH will further reduce the energy available to SiH<sub>2</sub>O decomposition.



**Figure 6.** Estimates of the relative energies for the SiH<sub>3</sub> +  $O_2$  reaction. Energies for TS8, TS9, and TS10 in part b are taken from ref 31. Energies for cyclic H<sub>2</sub>SiO<sub>2</sub> and TS2 are estimated at the CASSCF(6/6)/6-31G(d) level of theory. All other energies are obtained at the G2(MP2) level of theory.

 TABLE 1: Calculated Energies and Vibrational Frequencies

 for the Transition States

TS	energy <sup>a</sup> / kcal mol <sup>-1</sup>	frequencies <sup>b</sup> /cm <sup>-1</sup>
TS1: $H_3SiOO \rightarrow H + OSiH_2O$	-19.98	638i, 317, 641, 658 758, 846, 981, 1109
TS6: H <sub>3</sub> SiOO → H <sub>2</sub> SiOOH	-17.27	1279, 2210, 2400, 2682 1894i, 120, 461, 683 766, 819, 891, 998, 1729 1896, 2336, 2378

<sup>*a*</sup> Calculated at the G2(MP2) level, relative to  $SiH_3 + O_2$ . <sup>*b*</sup> Calculated at the MP2/6-31G(d) level; frequencies are unscaled.

The unimolecular process of cyclic  $H_2SiO_2$  seems to be the other possible channel for SiO formation. Attempts to follow the reaction coordinates for the unimolecular decomposition of cyclic  $H_2SiO_2$  at the MP2(full)/6-31G(d) level of theory were not successful because of the very complicated electronic structure of cyclic  $H_2SiO_2$ . There are several singlet and triplet energy surfaces that are located very close to the ground state surface. As the singlet states show strong biradical character, any calculation based on single-determinant zeroth-order wave function was not successful. However the transition state for the unimolecular isomerization, cyclic  $H_2SiO_2 \rightarrow HSiO(OH)$ , could be found by the CASSCF(6 electrons in 6 active orbitals)/6-31G(d) calculations. We choose active orbitals according to the calculations on  $CH_2O_2$  of Dupuis et al.<sup>33</sup> The barrier height of this transition state (TS2 in Figure 6a) is estimated to be

only 6.4 kcal/mol above the energy of  $H_2SiO_2 + H$ , that is, about 20 kcal/mol below  $SiH_3 + O_2$ . The product of this isomerization, HSiO(OH), can have large excess energy (the exothermicity for  $SiH_3 + O_2 \rightarrow HSiO(OH)$  is -109.9 kcal/ mol). By analogy to the thermal decomposition of formic acid,<sup>34,35</sup> it is expected that SiO and  $H_2O$  are produced by the unimolecular decomposition of the highly excited HSiO(OH). This is confirmed by the present G2(MP2) calculations, and results are shown in Figure 6a. This is also consistent with the BAC-MP4 calculations of Zachariah and Tsang.<sup>31</sup> There are two decomposition channels of HSiO(OH) to form SiO: HSiO(OH)  $\rightarrow$  TS3  $\rightarrow$  SiO + H<sub>2</sub>O and HSiO(OH)  $\rightarrow$  TS4  $\rightarrow$ Si(OH)<sub>2</sub>  $\rightarrow$  TS5  $\rightarrow$  SiO + H<sub>2</sub>O. Both are energetically possible, but the latter path has a lower energy barrier.

Another channel to form  $\text{SiO}_2 + \text{H}_2$  is also energetically possible (which is not shown in the figure), but multichannel RRKM calculations for the unimolecular decomposition of HSiO(OH) performed by Zachariah and Tsang<sup>31</sup> indicated that channels to form SiO + H<sub>2</sub>O dominated at low pressures. Present calculations indicate that SiO, as well as H and OH, is the major product of the multistep unimolecular decomposition of SiH<sub>3</sub>OO\*.

### **Concluding Remarks**

A laser-induced fluorescence method has been employed to detect SiO in the ArF laser photolysis of SiH<sub>4</sub>/O<sub>2</sub>/CCl<sub>4</sub> mixtures.

It has been shown that SiO is one of the major products of the  $SiH_3 + O_2$  reaction. *Ab initio* molecular orbital calculations have been conducted to investigate the mechanism of SiO formation. Present G2(MP2) calculations with geometry optimization at the MP2(full)/6-31G(d) level of theory indicated that the H + cyclic H<sub>2</sub>SiO<sub>2</sub> channel is one of the major pathways for unimolecular decomposition of the vibrationally excited adduct, SiH<sub>3</sub>OO\*. Combining present results with results of previous *ab initio* calculations by Darling and Schlegel,<sup>15</sup> and Zacharish and Tsang,<sup>33</sup> it is suggested that one of the possible routes for SiO formation is sequential unimolecular decomposition of SiH<sub>3</sub>OO\*:

$$SiH_{3}OO^{*} \rightarrow cyclic H_{2}SiO_{2} + H \rightarrow$$

$$HSiO(OH) + H \rightarrow SiO + H_{2}O + H$$

Another sequential unimolecular decomposition route through the isomerization of SiH<sub>2</sub>O intermediate is also possible:

$$SiH_3OO^* \rightarrow H_2SiOOH \rightarrow SiH_2O + OH \rightarrow$$
  
HSiOH + OH  $\rightarrow$  SiO + H<sub>2</sub> + OH

The latter processes have a higher overall energy barrier and seem to be less probable than the former route.

It is noted that the mechanism of silane combustion has to be reconsidered by taking into account these experimental and theoretical results. The reaction of  $SiH_3 + O_2 \rightarrow SiH_3O + O$ (1a) is postulated in the mechanism proposed by Hartman et al.<sup>8</sup> and by Britton et al.<sup>9</sup> to explain the low-temperature explosion of  $SiH_4/O_2$  mixtures. This reaction initiates the important chain branching step,  $O + SiH_4 \rightarrow SiH_3 + OH$ . However, present and recent studies of the  $SiH_3 + O_2$  reaction<sup>14,15</sup> indicate that reaction 1a is of minor importance at low temperatures. Exclusion of the reaction 1a from the existing  $SiH_4$  combustion mechanism results in the failure of the ignition of  $SiH_4/O_2$  mixtures at low temperatures. Construction of the new mechanism for the low-temperature combustion of silane is open for further investigations.

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