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Kinetics of the $SiH_3 + H_2O_2$ and $SiH_3 + O_2$ Reactions

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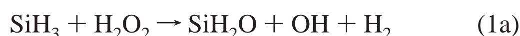
The kinetics of the reaction of silyl radicals (SiH_3) with H_2O_2 and O_2 were studied using time-resolved infrared diode laser absorption spectroscopy. The rate constant $SiH_3 + H_2O_2$ at 298 K was determined to be 9.8×10^{-12} cm^3 molecule^{-1} s^{-1}. This rate constant is independent of temperature over the range 298−573 K. The yield of OH products was quantified by reaction with CO to produce CO_2, which was detected by infrared spectroscopy. The branching ratio of the $SiH_3 + H_2O_2$ reaction into OH product channels was estimated to be <0.05 at 298 K. Similar experiments on the $SiH_3 + O_2$ reaction indicated an OH product branching ratio of 0.076 ± 0.04 at 298 K.

1. Introduction

The kinetics of main group hydride radicals are of interest in the modeling of chemical vapor deposition (CVD) processes for the fabrication of electronic and photovoltaic devices,[1−5] as well as silane combustion.[6,7] The SiH_3 (silyl) radical is believed to be especially important in plasma-enhanced CVD techniques used to deposit thin films of amorphous hydrogenated silicon (a-Si:H).[2−5] As a result, numerous studies of the kinetics of this species have been reported,[8] with published rate constants for reactions of SiH_3 with O_2,[9−12] NO,[10,12−13] NO_2,[12] SiH_3,[14,15] HBr,[16] S_2Cl_2,[17] and several unsaturated hydrocarbons.[15] Recent studies of SiO_2 deposition under photo-CVD conditions included H_2O_2 as one of several possible oxidants.[18,19] Most of the rate constants used in the kinetic model were based on published measurements; however, a major exception was the $SiH_3 + H_2O_2$ reaction, for which an estimated rate constant of 1.2×10^{-10} cm^3 molecule^{-1} s^{-1} was used.[19] No direct measurements of the kinetics of this reaction have been previously reported.

The $SiH_3 + H_2O_2$ reaction has several possible product channels:



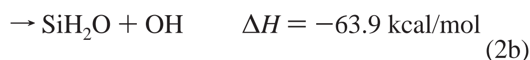
$$SiH_3 + H_2O_2 \rightarrow SiH_2O + OH + H_2 \quad (1a)$$

$$\rightarrow SiH_4 + HO_2 \quad (1b)$$

$$\rightarrow SiH_3O + H_2O \quad (1c)$$

Similarly, the reaction of silyl radical with molecular oxygen has several possible product channels:

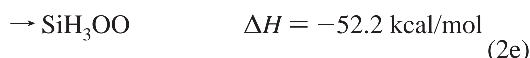
$$SiH_3 + O_2 \rightarrow SiH_3O + O \quad \Delta H = 11.0 \text{ kcal/mol} \quad (2a)$$



$$\rightarrow SiH_2O + OH \quad \Delta H = -63.9 \text{ kcal/mol} \quad (2b)$$

$$\rightarrow HSiOOH + H \quad \Delta H = 2.8 \text{ kcal/mol} \quad (2c)$$

$$\rightarrow HSi(O)OH + H \quad \Delta H = -108.0 \text{ kcal/mol} \quad (2d)$$



$$\rightarrow SiH_3OO \quad \Delta H = -52.2 \text{ kcal/mol} \quad (2e)$$

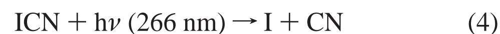
The thermochemical data was taken from the G2 ab initio calculations of Darling and Schlegel.[20] Several other (less likely) product channels were included in their calculations as well. They found a low energy pathway at the G2 level to product channel 2b, suggesting that OH radicals should be a major product in the reaction. Although the literature on total rate constants of reaction 2 is extensive, only one group has previously reported branching ratios. Koshi et al. used time-resolved LIF measurements of H and OH products to estimate $\phi_{2b} = 0.25 \pm 0.05$ and $\phi_{2c} = 0.65 \pm 0.05$ at room temperature.[21] Darling and Schlegel suggested that the observed H atoms originated from secondary chemistry, such as $OH + SiH_2O \rightarrow HSi(O)OH + H$.[20]

We report here measurements of the total rate constant of reaction 1 over the temperature range 298−573 K using laser photolysis/infrared absorption spectroscopy. We also report an estimate for the 298 K branching ratio into the OH-producing channels of both reactions 1 and 2. The total rate constant of reaction 2 has been reported previously by several workers, and such measurements are not repeated here.

SiH_3 was produced in this study by reaction of photolytically generated Cl atoms or CN radicals with silane:

$$S_2Cl_2 + h\nu \text{ (266 nm)} \rightarrow Cl + \text{other products} \quad (3)$$

or



$$ICN + h\nu \text{ (266 nm)} \rightarrow I + CN \quad (4)$$

$$Cl + SiH_4 \rightarrow HCl + SiH_3 \quad (5)$$

or

$$CN + SiH_4 \rightarrow HCN + SiH_3 \quad (6)$$

These reactions are fast, with $k_5 = (3.5-4.5) \times 10^{-10}$ and $k_6 = 2.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.[22−24] SiH_3 radicals formed in reactions 5 or 6 are detected by infrared laser absorption using a lead-salt diode laser at 2200−2230 cm^{-1} corresponding to ^rR branch transitions of the ν_3 stretching mode, which have been spectroscopically characterized.[25]

2. Experimental

The time-resolved infrared diode laser technique has been described previously.[11,26] Continuous, high resolution (0.0003 cm^{-1}) infrared radiation from a lead-salt diode laser (Laser

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Photonics) was made collinear with 266-nm radiation from an Nd:YAG laser (Lumonics) by means of a dichroic mirror. Both laser beams passed through a 6-mm iris in order to precisely define the beam diameter. The beams were then copropagated down a 1.43-m Pyrex absorption cell and passed through a second 6-mm iris. The infrared light then passed through a 0.25-m monochromator and was focused onto an InSb detector (Cincinnati Electronics, ~1 μs response). Transient signals were collected and averaged on a digital oscilloscope and stored on a computer. The HITRAN database[27] and published spectral data[25] for SiH_3 were used as an aid in calibrating laser wavelengths and identifying transitions.

All experiments were performed on static gas mixtures. To ensure complete mixing of reagents, gases were allowed to stand for 5 min in the reaction cell. Typically, only 5–10 laser shots were signal averaged for both the total rate constant and product yield experiments. Under these conditions, only minimal build-up of products or depletion of reactants was observed.

SiH_4 (Matheson), SF_6 (Matheson), and S_2Cl_2 (Aldrich) were purified by freeze–pump–thaw cycles at 77 K. O_2 (Matheson, research grade) was used without further purification. ICN (Fluka) was purified by vacuum sublimation to remove dissolved air. H_2O_2 (Aldrich, 50% in H_2O) was purified by extensive pumping to remove the more volatile water component. After purification, the H_2O_2 solution was estimated to be 95 mol % pure for a vapor phase purity of 63 ± 10% H_2O_2, 37 ± 10% H_2O, assuming Raoult's Law. Vapor phase H_2O_2 pressures reported here include this 0.63 correction factor. The SiH_3 radical does not react with H_2O, so the presence of H_2O does not severely affect these experiments.

3. Results

3.1. Total Rate Constants. Upon photolysis of ICN/SiH_4/SF_6 or S_2Cl_2/SiH_4/SF_6 mixtures, several transient absorptions attributed to SiH_3 radicals were found in the 2200–2230 cm^{-1} region, as predicted by spectroscopic studies. The $^rR_0(1)$ and $^rR_5(3)$ lines at 2201.82 and 2226.26 cm^{-1}, respectively, were chosen for kinetic studies, based on minimal overlap with SiH_4 lines and optimum probe laser intensity. Results obtained using these spectral lines were identical. Using typical photolysis laser energies of ~5–7 mJ/pulse, transient absorptions of ~15% of the probe laser intensity were observed. Small off-resonant background transients (5–20% of the on-resonant transient) were observed when the probe laser was detuned ~0.02 cm^{-1} off the SiH_3 line. These background signals, which are attributed to thermal deflection of the probe laser, were subtracted from the on-resonant signals to obtain SiH_3 time-resolved absorption profiles. A typical SiH_3 signal is shown in Figure 1. These signals display a fast, detector-limited rise followed by a slower decay, consistent with rapid SiH_3 production by reaction 5 or 6, followed by reaction of SiH_3.

Typical reaction conditions were 0.025 Torr of S_2Cl_2 precursor, 0.3 Torr of SiH_4, 0.0–0.4 Torr of H_2O_2, and 0.5 Torr of SF_6 buffer gas. Under these conditions, and at our photolysis laser pulse energies, typical SiH_3 radical densities of ~10^{13} molecule cm^{-3} (~0.3 mTorr) are obtained. Pseudo-first-order conditions of $[SiH_3] \ll [H_2O_2]$ were therefore met whenever H_2O_2 reagent was included. The SF_6 buffer gas was included because it is an efficient collisional relaxer of vibrational excitation of many small molecules. Except for somewhat smaller magnitude, identical results were obtained using ICN as the radical precursor.

The decay portions of the transient signals were fit to single exponential decays to obtain pseudo-first-order rate constants k'. Figure 2 shows a plot of pseudo-first order rate constant vs H_2O_2 pressure. As per standard kinetic treatments, the slope of these plots gives the desired second-order rate constant k_1. The nonzero intercept in Figure 2 is due primarily to the SiH_3 + S_2Cl_2 reaction, which has a rate constant of $(2.4\pm0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[17] Other (minor) contributions to the intercept include SiH_3 + SiH_3 self-reaction (or other radical–radical chemistry) and diffusion of SiH_3 out the probed region in the cell. At the pressures and beam geometries used, diffusion occurs on a ~1 ms time scale, slower than the observed decays. Diffusion therefore does not significantly affect the transient signals. Because S_2Cl_2 is a viscous liquid with a fairly low vapor pressure, it is difficult to precisely control $[S_2Cl_2]$ in these experiments, so the reproducibility of the point at 0.0 Torr H_2O_2 is rather poor. When H_2O_2 reagent is included, most of the pseudo-first-order decay is due to the title reaction, and the reproducibility is better.

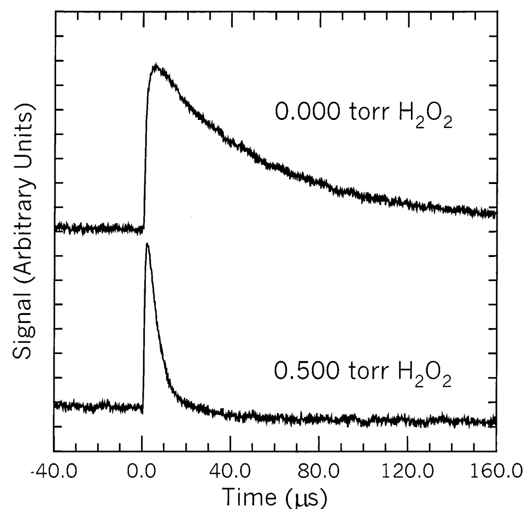


Figure 1. Transient infrared absorption signals of the SiH_3 radical at 2226.26 cm^{-1}. Reaction conditions: $P_{S_2Cl_2}$ = 0.025 Torr, P_{SiH_4} = 0.30 Torr, $P_{H_2O_2}$ = 0.0 Torr (top trace), 0.315 Torr (bottom trace), P_{SF_6} = 0.500 Torr. Each trace is the average of 6 laser shots.

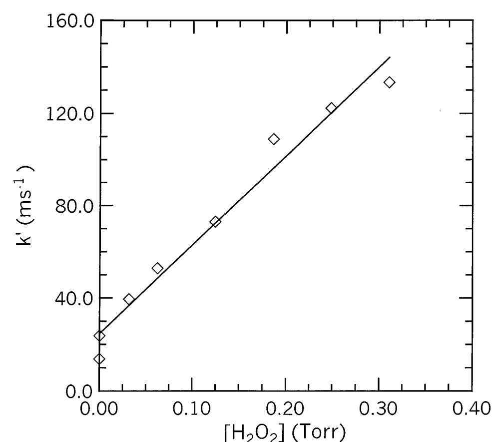


Figure 2. Pseudo-first-order decay rate constant of SiH_3 radical as a function of H_2O_2 pressure. Reaction conditions: $P_{S_2Cl_2}$ = 0.025 Torr, P_{SiH_4} = 0.30, $P_{H_2O_2}$ = variable, P_{SF_6} = 0.500 Torr.

Experiments were conducted over the temperature range 298–573 K. Figure 3 shows an Arrhenius plot of the data. As shown, the rate constant is essentially independent of temperature over this range. The data were fit to the following Arrhenius expression (error bars represent one standard deviation):

$$k_1 = (9.7 \pm 1.8) \times 10^{-12} \exp[(3.2 \pm 61)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

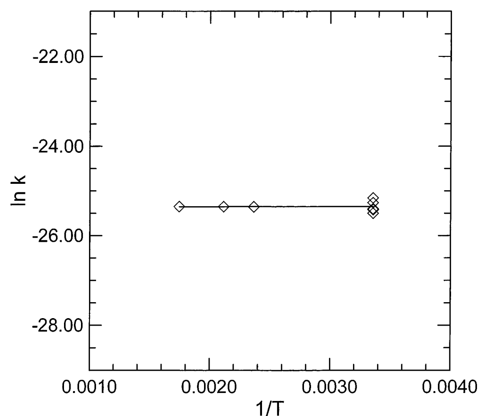


Figure 3. Arrhenius plot of the temperature dependence of the rate constant of the $SiH_3 + H_2O_2$ reaction.

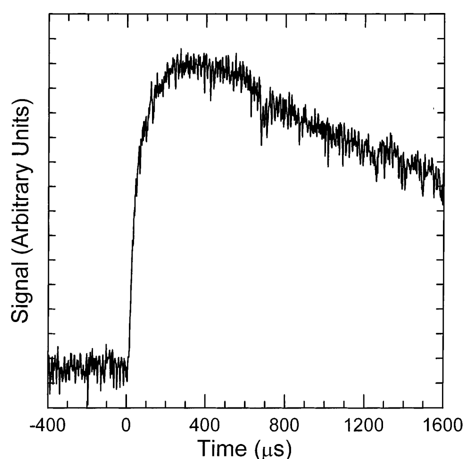
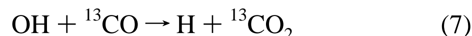


Figure 4. Transient signal (average of 6 laser shots) for $^{13}CO_2$ at 2308.172 cm^{-1} produced in the $SiH_3 + O_2$ reaction, using ^{13}CO to convert OH into $^{13}CO_2$ (see text). Reaction conditions: $P_{ICN} = 0.150$ Torr, $P_{SiH_4} = 0.025$ Torr, $P_{O_2} = 0.300$ Torr, $P_{SF_6} = 0.500$ Torr, $P_{^{13}CO} = 7.35$ Torr.

3.2. Product Channels. No attempt was made to detect SiH_2O or SiH_3O, as there is no available spectroscopic information on these species. The OH radical formed in channel 1a or 2b is readily detectable by laser-induced fluorescence, but calibration of LIF signals to obtain absolute product yields can be difficult. The approach used here is to convert any OH radicals formed in 1a or 2b into CO_2 by reaction with an excess of CO. CO_2 is readily detected and quantified by infrared absorption spectroscopy:



$$OH + {}^{13}CO \rightarrow H + {}^{13}CO_2 \qquad (7)$$

This reaction has a low-pressure rate constant of $k_7 = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[28] Carbon-13 labeled reagents were used because small amounts of CO_2 impurities in the reactants proved difficult to completely remove, resulting in significant static absorptions of $^{12}CO_2$ spectral lines. For detection, we chose the (00°0) R(36) line of $^{13}CO_2$ at 2308.172 cm^{-1}. Figure 4 shows a typical transient signal for $^{13}CO_2$ upon photolysis of an $ICN/SiH_4/O_2/^{13}CO/SF_6$ mixture. Similar looking transient signals were also obtained using an $ICN/SiH_4/H_2O_2/^{13}CO/SF_6$ mixture. As shown, the signal has a rise time of ~150 μs, which is somewhat slower than would be predicted from the rate of reaction 7. We attribute this to the likely formation of vibrationally excited CO_2 molecules, which must be collisionally relaxed to the ground vibrational state. The inclusion of SF_6 buffer gas is primarily designed to accomplish this vibrational relaxation. The slow decay, on a ~1−2 ms time scale, is due to diffusion of CO_2 out of the probed laser beam.

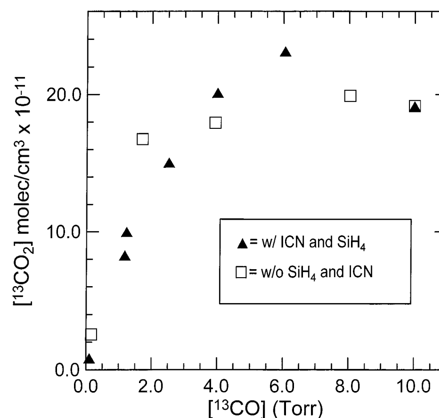


Figure 5. $^{13}CO_2$ product yield in the $SiH_3 + H_2O_2$ reaction, using ^{13}CO to convert OH into $^{13}CO_2$ (see text). Data shown with (triangles) and without (squares) ICN/SiH_4 reactants. Reaction conditions: $P_{ICN} = 0.150$ Torr (triangles), 0.0 Torr (squares), $P_{SiH_4} = 0.05$ Torr (triangles), 0.0 Torr (squares), $P_{H_2O_2} = 0.190$ Torr, $P_{SF_6} = 0.500$ Torr, $P_{^{13}CO}$ = variable.

To quantify the [CO_2] yields, the slow decay portion of the transient $^{13}CO_2$ signals was fit to an exponential decay function. (Diffusion kinetics is not strictly exponential, but the approximation is sufficient for our purposes.) This function was extrapolated back to $t = 0$ to obtain the signal amplitude that would be expected if this decay were not present; this procedure resulted in values only slightly greater than peak-to-peak amplitudes. The amplitude was then converted into absolute number densities using equations described previously,[29] as well as tabulated linestrengths from the HITRAN database.[27] The only modification was that the linestrengths were corrected for isotopic enrichment by dividing by 0.011, which is the natural abundance value of ^{13}C used in the database. Figure 5 shows the resulting $^{13}CO_2$ yield as a function of ^{13}CO pressure for the $SiH_3 + H_2O_2$ reaction, with and without the ICN and SiH_4 reagents. (We prefer the use of ICN rather than S_2Cl_2 precursors in the product yield experiments, because the 266-nm absorption coefficient and photolysis quantum yield are better known for ICN.) The product yield in the absence of ICN and SiH_4 is attributed to formation of OH from direct photolysis of H_2O_2 at 266 nm. The $^{13}CO_2$ yield roughly levels off at high ^{13}CO pressures, indicating that most OH radicals formed are converted into $^{13}CO_2$. When ICN and SiH_4 are included in the reaction, reactions 4 and 6 followed by 1a would be expected to produce additional OH radicals, resulting in an increased yield of $^{13}CO_2$. (Only a small pressure of SiH_4 is used in this experiment, to minimize competition between SiH_4 and CO for OH radicals). As shown, the product yields for H_2O_2/SF_6 and $ICN/SiH_4/H_2O_2/SF_6$ mixtures are virtually the same, indicating that essentially all of the observed product originated from H_2O_2 photolysis. Based on the uncertainties in the measurements, we estimate an upper limit of ~5×10^{11} cm^{-3} for the number density of $^{13}CO_2$ produced by OH from reaction 1a. To obtain a branching ratio ϕ_{1a}, we calculate an initial CN radical density of 2.96×10^{13} cm^{-3} from the initial ICN pressure (0.15 Torr) and measurement of the photolysis laser pulse energy (6.1 mJ) and absorption coefficient of α (266 nm) = 0.0074 cm^{-1} Torr^{-1} for ICN and assuming a quantum yield for CN production of unity. The absorption coefficient was determined by measuring the fraction of 266 nm light transmitted through the cell with varying pressures of ICN. We also measured the magnitude of the SiH_3 transient signal vs SiH_4 pressure, as shown in Figure

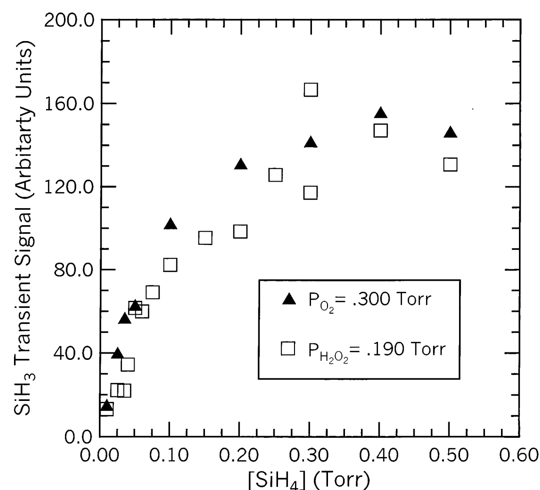


Figure 6. Peak magnitude of SiH_3 transient signal as a function of SiH_4 pressure. Reaction conditions: $P_{ICN} = 0.100$ Torr, P_{SiH_4} = variable, $P_{H_2O_2} = 0.190$ Torr (squares), 0.0 Torr (triangles), $P_{O_2} = 0.300$ Torr (triangles), 0.0 Torr (squares), $P_{SF_6} = 0.500$ Torr.

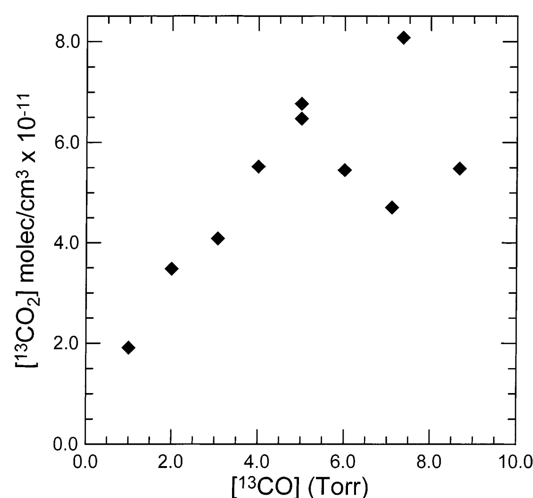


Figure 7. $^{13}CO_2$ product yield in the $SiH_3 + O_2$ reaction as a function of [^{13}CO]. Reaction conditions: $P_{ICN} = 0.150$ Torr, $P_{SiH_4} = 0.025$ Torr, $P_{O_2} = 0.300$ Torr, $P_{SF_6} = 0.500$ Torr, P_{13CO} = variable.

6. This shows that at 0.05 Torr SiH_4 (the conditions used in Figure 5) only approximately 39% of the CN radicals have been converted into SiH_3. The remaining CN radicals are presumably removed by other paths, such as self-reaction, diffusion, reaction with CN + H_2O_2, etc. No literature data on the rate constant of CN with H_2O_2 are available, but it probably produces HCN + HO_2, which are not expected to affect these measurements. We then estimate that about 70% of the SiH_3 radicals reacted with H_2O_2, based on comparison of the intercept of Figure 2 with the k' value at 0.19 Torr H_2O_2 (the pressure used in the experiments of Figure 5). Using these numbers, we estimate an upper limit of the branching ratio $\phi_{1a} < 0.05$.

Similar OH yield experiments were performed for the SiH_3 + O_2 reaction. Figure 7 shows the resulting $^{13}CO_2$ yield as a function of ^{13}CO pressure. In this reaction, there is no direct photolytic source of OH radicals, and the resulting signals are therefore attributed to reaction 2b followed by reaction 7. This assumption was verified by the observation that no $^{13}CO_2$ was formed upon photolysis of $SiH_4/O_2/^{13}CO/SF_6$ mixtures, i.e., in the absence of the ICN precursor. From Figure 6, we estimate that, at 0.025 Torr SiH_4, about 27.5% of the CN radicals were converted into SiH_3. This is roughly consistent with the predicted relative rates of CN + O_2 and CN + SiH_4 under these conditions. By a procedure similar to that described above for $SiH_3 + H_2O_2$, we estimate that about 84% of the SiH_3 radicals reacted with O_2 at $P_{O_2} = 0.300$ Torr. (Because we did not measure SiH_3 pseudo-first-order decay rates in the presence of O_2 in this study, we used our previous study of SiH_3 kinetics.)[12] After averaging several experiments of the type shown in Figure 7, we obtain a branching ratio of $\phi_{2b} = 0.076 \pm 0.04$ for the $SiH_3 + O_2$ reaction.

4. Discussion

Several possible secondary reactions could potentially affect the results. Because H_2O_2 samples, even purified, inevitably contain some water, we considered the $SiH_3 + H_2O$ reaction. The decay rate of transient SiH_3 signals did not increase upon the addition of H_2O over the range 0−0.5 Torr, indicating that this reaction is extremely slow and does not affect the results for k_1 determination. We estimate an upper limit of 3×10^{-13} cm^3 molecule^{-1} s^{-1} for the rate constant of $SiH_3 + H_2O$. The CN + H_2O reaction is very slow, with a measurable rate constant only above 500 K and a large activation energy.[30]

If the radical density is high enough, radical−radical reactions such as $SiH_3 + SiH_3$, SiH_3 + CN, or reaction of SiH_3 with products of reaction 1 could contribute to the observed signal decay rates. These effects are minimized, however, by keeping radical densities as low as possible. Under our typical conditions using ICN precursor, about $\sim 10^{13}$ CN radicals cm^{-3} are initially formed. At these densities, a second-order radical−radical secondary reaction with a gas kinetic rate constant would occur with a half-life of ~ 500 μs, which is far longer than the observed decay rates, even in the absence of added H_2O_2. Radical−radical chemistry therefore has an insignificant effect on the results.

Another potential complication is that H_2O_2 has a small but significant absorption coefficient at 266 nm, producing OH radicals. Using the high [CO] points in Figure 5, we estimate an OH yield from direct H_2O_2 photolysis of $\sim 2 \times 10^{12}$ cm^{-3}. This density is roughly comparable to that calculated by using a measured crude estimate of $\alpha \sim 0.0005 \pm 0.0003$ cm^{-1} Torr^{-1} (base e) for H_2O_2 at 266 nm. Assuming a gas kinetic rate of 2×10^{-10} cm^3 molecule^{-1} s^{-1} for the SiH_3 + OH reaction (probably an overestimate), we predict an SiH_3 lifetime of several milliseconds, an insignificant effect on the measured decay rates.

This work represents the first reported measurement of k_1. The value obtained is significantly lower than the estimate used in the modeling study of photochemical SiO_2 deposition under H_2O_2 oxidant conditions.[18,19] The extent to which this affects the model is not clear, as sensitivity analysis on the kinetic model was not performed. That model, however, considered SiH_2O formed in channel 1a to be the critical intermediate leading to film deposition. Because reaction 1a also forms OH radicals, which react with SiH_4, producing more SiH_3, this channel represents a chain branching step in the overall oxidation mechanism. Our experiments strongly indicate, however, that OH is at most a minor product of the $SiH_3 + H_2O_2$ and SiH_3 + O_2 reactions. This is a quite surprising result, especially for SiH_3 + O_2, for which previous work indicated $\phi_{2b} = 0.25$.[21] Although secondary chemistry involving OH certainly occurs in this system, at the high CO pressures shown in Figures 5 and 7, OH removal should be dominated by reaction 7. For example, OH + SiH_4 has a rate constant of 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.[31] Using 0.025 Torr SiH_4, the pseudo-first-order rates of OH removal by CO and SiH_4 are expected to become equal at 1.25 Torr CO, so that CO_2 formation from reaction 7 should be about half of the amount formed in the high [CO]

limit. This is in approximate agreement with the curve shown in Figure 7. At the highest CO pressures used, a small (∼10%) fraction of OH radicals may still react with SiH_4, but this error is less than the quoted uncertainties in the branching ratios. It is thus very unlikely that we have severely underestimated the amount of OH in our experiments.

5. Conclusions

The reaction of SiH_3 with H_2O_2 was investigated. The total rate constant is 9.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, with no measurable temperature dependence over the range 298−573. By including CO in the reaction mixture to convert OH products into readily detected CO_2 molecules, a branching ratio of <0.05 into OH producing channels was estimated. Similar experiments on the $SiH_3 + O_2$ reaction indicate a branching ratio of 0.076 into OH. At this point, the identity of the major product channel in these reactions is still unknown, but we have demonstrated that OH-producing channels are less important than previously believed.

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