REACTIONS OF $SiH_2(\tilde{X}\,^1A_1)$ WITH H_2, CH_4, C_2H_4, SiH_4 AND Si_2H_6 AT 298 K

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Reaction rate constants of $SiH_2(\tilde{X}\,^1A_1)$ have been directly measured for the first time using the laser photolysis–laser-induced fluorescence method. The preparation of SiH_2 radical in the laser photolysis (193 nm) of phenylsilane and the concentration of the radical is demonstrated by a dye laser at 580.1 nm ($\tilde{X}\,^1A_1$–$\tilde{A}\,^1B_1$). The reaction rate constants of $SiH_2(\tilde{X}\,^1A_1)$ with H_2, CH_4, C_2H_4, SiH_4 and Si_2H_6 are 0.001, 0.01, 0.97, 1.1 and 5.7×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively. For $SiH_2(\tilde{A}\,^1B_1(0,2,0))$, the collision-free lifetime is 0.6 μs and the quenching rate constant for He is 3.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

1. Introduction

The silylene radical, SiH_2, has been expected to play one of the most important roles in the chemical vapor deposition (CVD) process to form hydrogenated amorphous silicon (a-Si:H) as this radical inserts in the Si—H bond on the surface and forms a new Si—Si bond. In a previous paper [1], we reported the laser-induced fluorescence of the SiH_2 radical, and excitation spectra with tentative rotational assignments and a dispersed fluorescence spectrum were shown. The wavelengths of the vibronic transitions in the 550—650 nm region, which correspond to the $^1B_1(0n'0) \leftarrow {}^1A_1(000)$ transition, agreed well with the values of the absorption measurements [2,3]. The dispersed fluorescence spectrum, $^1B_1(0,2',0) \rightarrow {}^1A_1(0,n'',0)$, also agreed with the hot band absorption [3]. However, the details of the rotational structure did not necessarily agree with the values obtained by Dubois [4]. Nevertheless, the general agreement of the spectra and the observation of identical spectra from different sources, the photolysis of phenylsilane and disilane and the reaction of silane with metastable argon, confirmed it to be fluorescence from the SiH_2 radical.

The reaction rate constants of the SiH_2 radical have been obtained by co-pyrolysis and products analysis. John and Purnell [5] evaluated the rate constants of the following reactions from their co-pyrolysis data of disilane and thermodynamical information:

$$SiH_2 + H_2 \rightarrow SiH_4\,, \qquad (1)$$

$$SiH_2 + SiH_4 \rightarrow Si_2H_6\,, \qquad (2)$$

$$SiH_2 + Si_2H \rightarrow Si_3H_8\,. \qquad (3)$$

The rate constants (in cm^3 $molecule^{-1}$ s^{-1}) extrapolated to 300 K are

$$k_1 = 2.0 \times 10^{-16}, \quad k_2 = 9.5 \times 10^{-13},$$

$$k_3 = 6.1 \times 10^{-12}\,.$$

However, no direct measurement of the rate constants of the SiH_2 radical has yet been reported probably because of the mass-spectrometrically poor detectivity of silicon hydrides.

Here we report reaction rate constants of SiH_2 with H_2, SiH_4, Si_2H_6, CH_4 and C_2H_4, and the collision-free lifetime of the $SiH_2^*(^1B_1)$ state.

2. Experimental

The photolysis and laser-induced fluorescence system was the same as before [6]. Silylene radicals were produced by photolysis of phenylsilane at 193 nm by an ArF excimer laser. The temporal change of silylene radical concentration was detected by a fluorescence intensity measurement excited at 580 nm with different delay times between the photolysis and probe

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laser. The reaction chamber consisted of a stainless steel hexagonal prism of 4 dm^3 volume, which had four side arms with LiF and fused silica windows for the ArF laser and the dye laser beam, respectively. Two other side ports were used as sample gas inlet and pumping port. The fluorescence was detected at the top of the chamber by a photomultiplier (Hamamatsu, R928) through an *f*/2 lens and a filter (Corning 0-53). The phenylsilane pressure was kept at 0.3 mTorr, and the total pressure in the chamber was kept at 1.0 Torr by feedback of the output of the capacitance pressure gauge (MKS) at the reaction chamber to the thermal valve mass flow controller (STEC Co.) at the helium inlet. Another thermal valve mass flow controller was used to keep the flow rate of the reactant at a desired value. The relation between the flow rate and the partial pressure of reactants was calibrated by the observation of the small increase in chamber pressure (keeping the other flow rates constant) at 1.0 Torr for a small amount of reactants (Si_2H_6, SiH_4 and C_2H_4). For other slow reactants such as H_2 and CH_4, the partial pressures of reactant and diluent (He) were calculated from the total pressure, the reads of the mass flow meter at the inlets, and the relative sensitivities of the mass flow meters for the gases. The relative sensitivities of the mass flow meter for sample gases were calibrated by monitoring the pressure decrease in a reservoir with a known volume. This gas flow system kept gas pressures within 1% fluctuation during the experiment.

The reagents, phenylsilane, Shin-Etsu Chemicals Co., monosilane (99.99%) and disilane (99.9%), Mitsui Tohastu Chemicals Co., were used without further purification.

For the fluorescence lifetime measurements at zero pressure, a molecular beam of phenylsilane, injected by an automobile fuel injector valve heated to about 50°C, was photolyzed. In this case, an oil diffusion pump (1500 ℓ s^{-1}) backed up by a rotary pump (1600 ℓ min^{-1}) was used to maintain the vacuum.

3. Results

3.1. *Fluorescence lifetimes*

The fluorescence decay rate was very sensitively dependent on the added gas pressure. Fig. 1 shows that the fluorescence excited at 580.1 nm is effeciently quenched even by helium; the quenching rate constant is (3.8 ± 0.2) × 10^{-10} cm^3 $atom^{-1}$ s^{-1}. The quenching rates and the collision free lifetimes depended very much on the excitation wavelength, and no systematic rotational quantum number dependence was found. Under molecular beam conditions, which were not necessarily collision free conditions, the fluorescence decayed as a double exponential; the weak, fast component had a lifetime around 30–60 ns, and the main, slow component one of 0.6 μs. The latter is just the extrapolated value from the decay rates at various helium pressures.

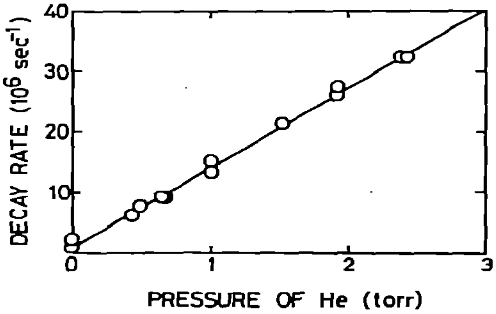

Fig. 1. Helium pressure dependence of the experimental decay rate of the fluorescence from $SiH_2^*(^1B_1)$. The values at zero pressure were obtained from a molecular beam of phenylsilane. The excitation wavelength is 580.1 nm, which corresponds to the $^1B_1(020) \rightarrow {}^1A_1(000)$ transition.

As the bond dissociation energy of HSi–H (76.5 kcal mol^{-1}) [7] is higher than the photon energy at 580 nm (49.3 kcal mol^{-1}) predissociation is energetically impossible. The triplet state is expected to lie about 10 kcal mol^{-1} above the $\tilde{X}\,^1A_1$ state from recent theoretical work [8], or ≤ 14 kcal $mole^{-1}$ from the photodetachment experiment of Lineberger [9] and this triplet state is below the $^1B_1$ state. However, intersystem crossing between $\tilde{A}\,^1B_1$ and $\tilde{a}\,^3B_1$ should not be very efficiently induced by collisions with helium. The remaining and most probable quenching mechanism is to the ground $^1A_1$ state.

3.2. *Reaction rate constants*

The decay rates are plotted against SiH_4 or Si_2H_6 pressure in fig. 2. The decay of the signal against delay time between the photolysis and probe laser in the absence of reactant was single exponential after

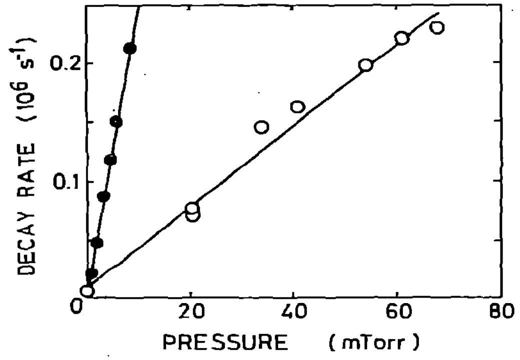

Fig. 2. Plot of reaction rate versus pressure for the reaction of SiH_2 with SiH_4(○) and Si_2H_6(●) using 0.3 mTorr of phenylsilane as a precursor for SiH_2 and He as a buffer gas (P_{tot} = 1.0 Torr). The bimolecular rate constants obtained from the slope of the linear least-squares fits are 1.1 × 10^{-10} and 5.7 × 10^{-10} cm^3 molecule^{-1} s^{-1} for SiH_4 and Si_2H_6, respectively.

30 μs, before 30 μs the observation was disturbed by luminescence caused by the photolysis laser. The rotational and vibrational distribution was thermalized in 30 μs and the laser-induced fluorescence intensity was proportional to the concentration of $SiH_2(\tilde{X}\,^1A_1)$. So the removal rate constant obtained from fig. 2 is the reaction rate constant of $SiH_2(\tilde{X}\,^1A_1)$ reacting with SiH_4 or Si_2H_6. In fig. 3, the decay rates of SiH_2 are plotted against H_2 partial pressure. The zero-pressure intercept of the reactant, about 80 μs, was mainly due to the flow of sample gas out of the viewing spot. All experiments were carried out with 0.3 ± 0.05 mTorr phenylsilane. The typical total pressure in the experiments was 1 Torr except for the experiment with hydrogen, for which a total pressure of 1.8 Torr was chosen because the rate constant was very small and a great amount of hydrogen was required to detect the acceleration of the decay of SiH_2. A relatively small dynamic range of 20 was chosen for the decay measurement because the linearity of the experimental system was limited as the fluorescence lifetime at the pressure used was short; about 50 ns. The adjustment of the probe laser power to keep the fluorescence intensity at an appropriate level makes the dynamic range of the observation wide but this method was not adapted in this case being afraid of the error caused by a limited dynamic range of laser power monitor, though a small correction for laser power fluctuations was made to the signal intensity. The reaction rate constants obtained are summerized in table 1 and the values of $^1CH_2$ are tabulated for comparison [10]. The disappearance rate constants of $^1CH_2$ with SiH_4 were obtained here; $^1CH_2$ was produced by photolysis of ketene by a XeCl excimer laser (308 nm). The removal rate constant of $^1CH_2$ by H_2 was also measured to check our experimental system and the agreement with ref. [10] was within experimental error.

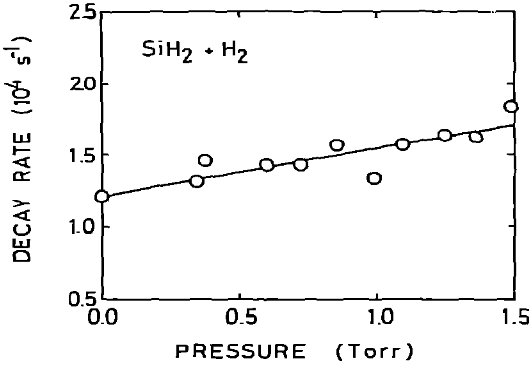

Fig. 3. Plot of reaction rate of SiH_2 with H_2. $P_{phenylsilane}$ = 0.3 mTorr, P_{tot} = 2.0 Torr. The bimolecular rate constant is (1.0 ± 0.4) × 10^{-13} cm^3 molecule^{-1} s^{-1}.

Table 1
Rate constants (cm^3 molecule^{-1} s^{-1}) for the reaction of $SiH_2(\tilde{X}\,^1A_1)$ compared to $CH_2(\tilde{a}\,^1A_1)$ at 298 K

Reactant	SiH_2	$CH_2(\tilde{a}\,^1A_1)$
H_2	(1.0±0.4) × 10^{-13}	(1.3±0.1) × 10^{-10} a)
CH_4	(1.0±0.3) × 10^{-12}	(7.3±0.6) × 10^{-11} a)
C_2H_4	(9.7±1.2) × 10^{-11}	–
SiH_4	(1.1±0.2) × 10^{-10}	(2.4±0.4) × 10^{-10}
Si_2H_6	(5.7±0.2) × 10^{-10}	–
O_2	–	(3.0±0.4) × 10^{-11} a)

a) Values from ref. [10].

4. Discussion

The reaction rate constants of the SiH_2 radical with SiH_4 and Si_2H_6 were obtained to be very large. The reaction mechanism of SiH_2 with SiH_4 is generally accepted to be insertion in the Si—H bond, and the product is the vibrationally excited Si_2H_6 molecule. The fragmentation into two SiH_3 radicals is endothermic [11] by 33 kcal mol^{-1} if we use the ΔH values of

SiH_4, SiH_3 and SiH_2 of 7.3 [11], 49.1 [12] and 57.9 kcal mol^{-1} [5], respectively,

$$SiH_2 + SiH_4 \rightarrow Si_2H_6^{\ddagger} \nrightarrow 2SiH_3 .$$

The rate constant of $^1CH_2$ with SiH_4 was close to be the value of $^1SiH_2$, the mechanism of which is also insertion in the Si–H bond,

$$CH_2 + SiH_4 \rightarrow CH_3SiH_3 .$$

However, their rate constants with molecular hydrogen differ considerably from each other; $^1CH_2$ reacts more than one thousand times faster than SiH_2. The removal rate of $^1CH_2$ includes both chemical reaction and the physical quenching to $^3CH_2$ which lies 9.6–9.1 kcal mol^{-1} below the $\tilde{a}\ ^1A_1$ state. In contrast, the singlet state of SiH_2 is the ground state and no physical quenching is involved in the removal process. However, the physical quenching of $^1CH_2$ by H_2 is expected to be a very small part of the total removal rate, because it is twenty times larger than the value expected from the linear relation between the removal cross sections by M and $E_{MM}^{1/2}$ (the potential energy well depth between pairs of M species) of nonreactive molecules [10].

Ab initio studies of the insertion of CH_2 and SiH_2 in H_2 have been reported by Gordon [13] and more recently by Grev and Schaefer [14]. Their results show that the insertion of CH_2 has no barrier, but the SiH_2 insertion in H_2 has a barrier of 7.1 kcal mol^{-1}. The H–H distance in the transition state of the $SiH_2 + H_2$ reaction, 1.07 Å, is closer to that of the hydrogen molecule, 0.733 Å, than that of the silane molecule, 2.417 Å, and a large strain in the transition state is expected. No ab initio study of SiH_2 or CH_2 insertion in the Si–H bond is reported, but their large reaction rates can be reasonably explained by the qualitative speculation of small strain in the transition state because the final Si–H bond length of SiH_2 insertion, 3.16 Å, is twice that of the initial Si–H bond length of SiH_4, 1.47 Å, and that of $^1CH_2$ insertion, 2.53 Å, is lengthened only 1.7 times.

The reaction rate constants of SiH_2 with H_2, SiH_4 and Si_2H_6 extrapolated from high-temperature measurements by John and Purnell [5] were much smaller than the values obtained here. The upper limit of the extrapolation within experimental error is 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and this is still one order of magnitude smaller than our observation. We believe our direct method is more reliable though the source of this serious discrepancy is not clear.

The reaction rate measurement of SiH_2 with O_2 was unsuccessful because intense chemiluminescence after the excimer irradiation to the phenylsilane and O_2 mixture disturbed the observation of fluorescence. The emission builds up immediately after the excimer irradiation with a time constant of 0.8 μs and it is followed by a decay with a time constant of 2 μs at 200 mTorr of oxygen, for example. The predicted reaction is

$$SiH_2 + O_2 \rightarrow SiO^* + H_2O .$$

The electronic energy that the SiO molecule can carry is 109 kcal mol^{-1}, and the $\tilde{a}\ ^3\Sigma^+$, $\tilde{b}\ ^3\Pi$ and $\tilde{d}\ ^3\Delta$ states can be populated, but the origin of the emission was not studied further at the present stage.

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