THE $SiH_4+O(^1D)$ REACTION STUDIED BY INFRARED DIODE LASER KINETIC SPECTROSCOPY

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The reaction of $O(^1D)+SiH_4$ was studied by means of infrared diode laser kinetic spectroscopy, where $O(^1D)$ was prepared by ArF excimer laser irradiation of N_2O. Vibrationally ground state silyl radicals and $v=2$ OH radicals were identified, and their time profiles were discussed on the basis of an appropriate reaction mechanism.

1. Introduction

Oxygen atoms in the first electronically excited state, $O(^1D)$, are known to insert in various X–H bonds such as C–H and N–H, and dissociation products due to the large excess energy are frequently observed [1–4]. For example, one of the main products from the $CH_4+O(^1D)$ reaction is highly vibrationally excited OH [4]. A similar reaction is expected to proceed in the case of silane, but the reaction, $SiH_4+O(^1D)$, has not been studied until now, while the corresponding reaction of $O(^3P)$ has been investigated by several researchers [5–9]. The kinetic study of these oxygen atom reactions is also important for analyzing various CVD and combustion systems [10–13].

Assuming that $O(^1D)$ inserts to the Si–H bond initially, the product silanol may decompose "instantaneously" under reduced pressure. The possible reaction products on the basis of thermochemistry are shown below[#1] (ΔH_r^0 given in kJ mol^{-1} throughout this paper),

$$SiH_4+O(^1D)\rightarrow SiH_3+OH \quad \Delta H_r^0=-231, \quad (1a)$$

$$\rightarrow SiH_3O+H \quad \Delta H_r^0=-349, \quad (1b)$$

$$\rightarrow SiH_2+H_2O \quad \Delta H_r^0=-427, \quad (1c)$$

$$\rightarrow SiH_2O+H_2 \quad \Delta H_r^0=-556. \quad (1d)$$

Some of these products still possess large amounts of excess energy which allow their subsequent unimolecular dissociations. For example, the following reaction:

$$SiH_3\rightarrow SiH+H_2\,, \quad \Delta H_r^0=174 \quad (2)$$

though endothermic, may proceed to some extent as a successive reaction following (1a) on energetic considerations. Here, however, we will not tabulate all of the possible subsequent reactions of (1a)–(1d).

The present study, as our first study on the $O(^1D)$

[#1] Necessary heat of formation data are taken from standard tables for ordinary species. Data for SiH_3 ($\Delta H_f^0=203$ kJ mol^{-1}), SiH_2(289), and SiH(377) are taken from ref. [14]. Data for SiH_3O (−94) is taken from ref. [11], and the value of SiH_2O (as trans-HSiOH, −82) has been estimated based on ref. [15].

reaction with silane, is intended to evidence production of the silyl radical in situ by means of the infrared diode laser kinetic absorption spectroscopic technique developed in the Institute for Molecular Science [16–18]. Indeed the ν_2 mode of silyl radical has already been analysed spectroscopically [19]. $O(^1D)$ atoms were prepared via ArF excimer laser irradiation of N_2O at 193 nm [20] and the time profiles of the above radicals produced through the reaction with silane were pursued and simulated on the basis of an appropriate reaction mechanism. Besides silyl radicals, rovibrationally excited OH radicals could be also detected. Investigation of the kinetic behavior of the silyl radical is an important first step for discussing the detailed reaction mechanism of the $O(^1D)$ reaction with silane.

2. Experimental

The experimental set-up was almost the same as the system employed for studying SO_2 photolysis by ArF excimer laser light [16,17]. That is, the reaction cell was a cylinder of Pyrex glass (length 2 m, the inner diameter 10 cm), which was equipped at the tube ends with a White-type multireflection mirror system for the diode laser light beam. The inlet window for the excimer laser light was also fixed at one tube end, off-axis from the two windows for the diode laser light.

The gases, SiH_4(10% in Ar), N_2O and He(as a balance gas) from commercial cylinders, were flowed through calibrated flow meters before being introduced to the cell. Although the balance gas, He, was introduced from the window side, other gases were introduced from an inlet nozzle at the side wall. They flowed along the cell and were pumped out from a branch at the side wall. The total cell pressure (typically, 1.0–1.5 Torr) was measured by a capacitance manometer, and the partial pressures of individual gases were estimated from the corresponding flow rates. The pressures of silane and N_2O were varied between 50–200 mTorr. The residence length of the sample mixture was around 1 m in the central part of the cell, and the residence time, around 1.5 s, where the excimer and the diode laser light beams merged to each other.

The ArF excimer laser light beam at 193 nm came from a Lambda Physik 201 MSC excimer laser apparatus (employed pulse energy, 50–100 mJ pulse^{-1}), whose cross section in the cell was around 25 mm × 10 mm. The laser fluence was calculated from the measured laser pulse energy at the outlet of the laser apparatus and by use of the geometry as well as the absorption loss through the air and the window material. The absorption cross section of N_2O at 193 nm was taken to be 8.95×10^{-20} cm^2 from the literature [20]. The excimer laser was repeatedly fired usually at 18 Hz, because it was confirmed in advance that the obtained results were not dependent on the laser repetition rate between 4–20 Hz.

The diode laser beam was passed 16 times through the White-type multireflection system, and the effective overlap length between the excimer and the diode laser light was roughly estimated to be 1.5–3.0 m. The system for detection of the diode laser absorption after the excimer laser shot, and that for data acquisition were almost the same as those previously described [16,17]. For measuring the time profile of radical concentrations, the transient absorption signal was stored for 1024 time points in a transient memory by using a sampling interval of 50 or 200 ns. Usually more than 100 of the time profile data as mentioned above were accumulated by using a personal computer in order to increase the S/N ratio. The diode laser intensity without absorption (I_0) was also measured and used for calculating the absorbance. In the case of spectrum measurements, the time gate was fixed at an appropriate time position, and the diode laser was scanned. The time resolution of the system was found to be about 0.5 μs, which was mainly determined by the response of the IR detector.

3. Results and discussion

Fig. 1 shows typical absorption spectra obtained by using three different time gates, 2–12, 12–22, and 22–46 μs after the excimer laser shot. Two different types of absorption signals are easily recognized; one type increases gradually with time and the other appears only in the initial stage. The former signals are ascribed to silyl radical (ν_2 mode, Q lines from the $v=0^+$ state), consulting the previous analysis [19]. The individual rotational assignments are given in

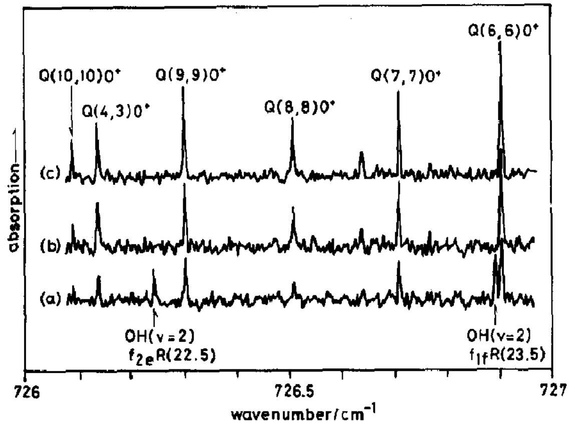

Fig. 1. Absorption spectra observed under typical reaction conditions. Mixture condition: SiH_4 65 mTorr, N_2O 200 mTorr, total pressure 1 Torr (Ar, He balance), output excimer laser power: 100 mJ pulse^{-1}, time gate: (a) 2–12 μs, (b) 12–24 μs, (c) 24–46 μs.

the figure. The relative absorption intensities for different rotational transitions show that the silyl radicals are in rotational equilibrium. The latter short-lived signals are assigned to pure rotational transitions of OH in the $v=2$ state on the basis of the comprehensive analysis by Coxon [21]. One line is the $f_{1f}R(23.5)$ transition (calculated 726.916 and observed 726.887 cm^{-1}), and the other, the $f_{2e}R(22.5)$ transition (calculated 726.289 and observed 726.313 cm^{-1}).

Time profiles of the silyl ($Q(6,6)0^+$ line) and OH($v=2$, $f_{1f}R(23.5)$ line) radicals under typical conditions are shown in fig. 2 for two different time bases ((a) and (b)). The profiles observed with a different gaseous mixture and those under a weaker laser irradiation are also shown ((c), (d) respectively). The concentration of radicals could not be estimated precisely, due to the difficulties of estimating the effective optical length of the diode laser light beam in the excimer laser irradiation region and of estimating the absolute absorption coefficient. However, according to the method described in the previous literature [22], the concentration of silyl radical corresponding to the observed absorbance ($\ln(I_0/I))=0.01$ at $Q(6,6)0^+$ line is considered to be between 1.0×10^{12} and 2.0×10^{12} molecule cm^{-3}.

The time profiles of OH($v=2$, $f_{1f}R(23.5)$ line) and silyl radicals have been simulated on the basis of the proposed mechanism (table 1) which will be described later, and the results are shown in fig. 2. Simulations have been performed by integrating kinetic differential equations on a personal computer. In the mechanism, among possible Si-containing radicals only silyl radical is taken into account, because it is indeed a main Si-containing radical as will be shown later. Even if other Si-containing radicals exist to some extent, they are considered not to affect appreciably the reactions relevant to silyl radicals.

The very rapid rise of the OH($v=2$) radical is determined by the lifetime of O(^{1}D) due to the reactions,

$$O(^1D)+SiH_4\rightarrow\text{products}\,, \tag{2}$$

and

$$O(^1D)+N_2O\rightarrow\text{products}\ (NO, N_2, O_2)\,. \tag{3}$$

The rate constant of (3) is established to be $(1.2\pm0.5)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} [20]. The rising curve of the OH signal can be reasonably simulated when the rate constant of (1) is assumed to be 5.0×10^{-11} cm^3 molecule^{-1} s^{-1}. This rate constant also explains the relative yields of silyl radicals under different mixture conditions fairly well. The OH signals decay exponentially at a rate of 2.8×10^5 s^{-1} in most experiments, probably via rotational relaxation,

$$OH^{\neq}\rightarrow OH\,, \tag{4}$$

where ≠ means rovibrational excitation. Because the absolute intensity of these weak, transient signals could not be determined precisely, only the relative time profiles have been discussed at present.

The signals of silyl radical increase very slowly compared to the fast rise and decay of the OH($v=2$) radical. A preliminary analysis of the initial stage with assuming a first-order rise suggested that the silyl radical increases via a certain bimolecular process with silane at a rate of the order of 1×10^{-11} cm^3 molecule^{-1} s^{-1}. There are two possible mechanisms. One mechanism is that the silyl radicals are initially produced vibrationally excited through (1a), and then they relax to the $v=0$ state observable by means of the present absorption spectroscopy, being principally controlled by collisions with silane via,

$$SiH_3^{\neq}+SiH_4\rightarrow SiH_3+SiH_4\,. \tag{5}$$

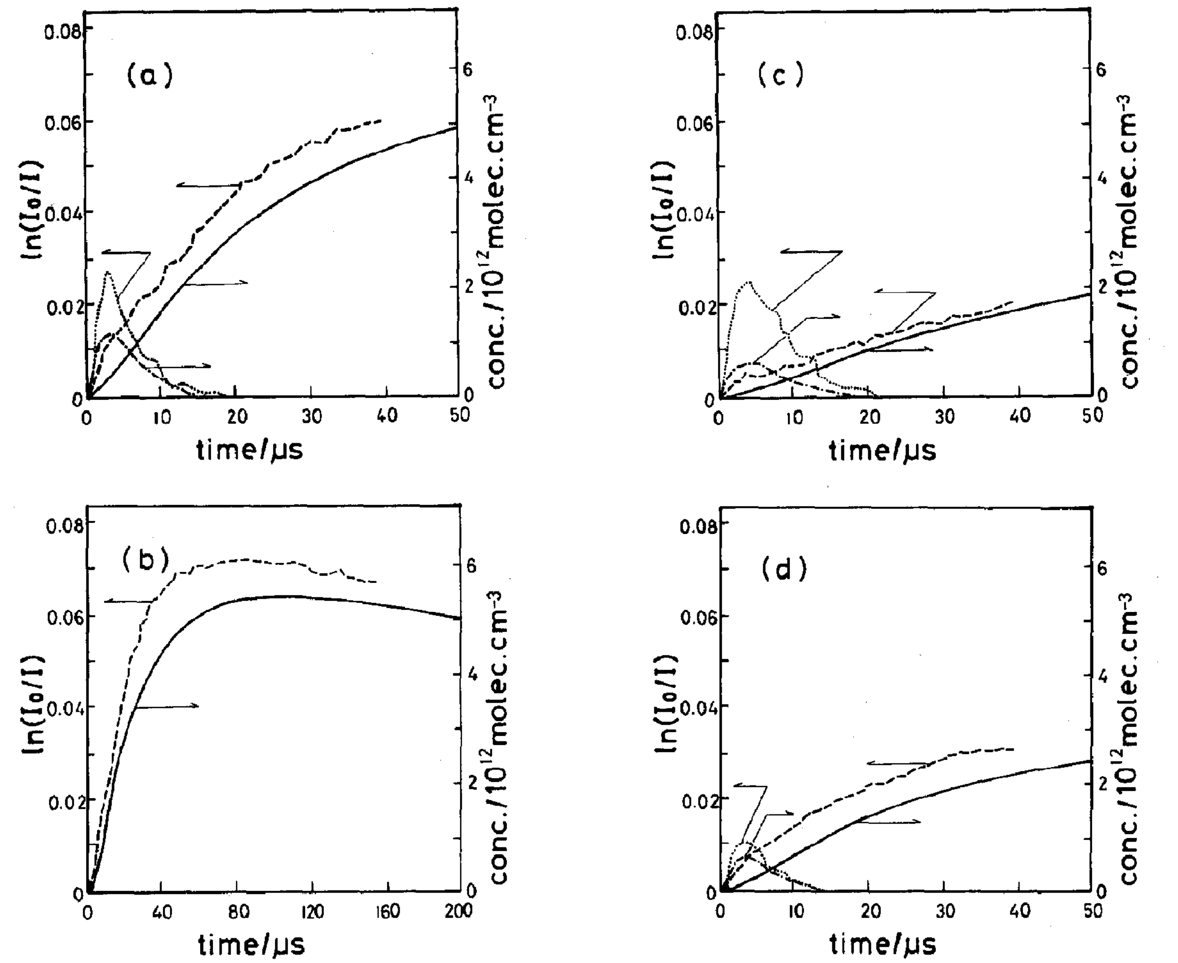

Fig. 2. Time profiles of silyl and OH radicals: (---) SiH_3 (experiments), (—) SiH_3 (simulation), (...) OH^* (experiments), (-·-·-) OH^* (simulation). Mixture condition: (a), (b) SiH_4 110 mTorr, N_2O 60 mTorr, total pressure 1.5 Torr (Ar, He balance), (c) SiH_4 50 mTorr, N_2O 50 mTorr, total pressure 1.5 Torr, (d) SiH_4 110 mTorr, N_2O 60 mTorr, total pressure 1.5 Torr, output excimer laser power: (a)–(c) 100 mJ pulse^{-1}, (d) 50 mJ pulse^{-1}.

As a comparison, the vibrational relaxation of methyl radical is reported to proceed through collisions with methane with a rate constant of the order of 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} [24,25]. Thus the analogous rate constant between the silyl radical and silane is acceptable. It is plausible that some of the silyl radicals produced through (1a) dissociate along (2), but the fraction of such dissociation should be small, considering from the exo- and endo-thermicity of (1a) and (2), respectively. Thus the secondary dissociation has been neglected in order to simplify the simulation procedure.

The other mechanism for the formation of silyl radical is a secondary reaction between silane and the primarily produced OH radical,

$$OH+SiH_4 \rightarrow SiH_3+H_2O\,. \qquad (6)$$

Atkinson and Pitts reported $(1.2\pm0.2)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} as the rate constant of (6) [5]. Thus reaction (6) should contribute to the production of silyl radical. In the following simulation, we employ a mechanism where (5) and (6) altogether contribute to the production of the observed silyl radicals.

A small rapid initial rise seems to exist in the experimental silyl radical time profiles, which causes the small apparent disagreement between the exper-

Table 1
Reaction mechanism and adopted rate constants

Reaction		Rate constant (cm^3, molecule, s base)	Ref.
(0)	$N_2O+h\nu \rightarrow N_2+O(^1D)$	–	[20]
(1a)	$O(^1D)+SiH_4 \rightarrow SiH_3^{\ddagger}+OH^{+}$	5.0×10^{-11}	see text
(3)	$O(^1D)+N_2O \rightarrow$ products (NO, N_2, O_2)	1.2×10^{-10}	[20]
(4)	$OH^{*} \rightarrow OH$	2.8×10^{5}	see text
(5)	$SiH_3^{\ddagger}+SiH_4 \rightarrow SiH_3+SiH_4$	1.0×10^{-11}	see text
(6)	$OH(OH^{*})+SiH_4 \rightarrow SiH_3+H_2O$	1.2×10^{-11}	[6]
(7)	$SiH_3(SiH_3^{\ddagger})+SiH_3(SiH_3^{\ddagger}) \rightarrow$ products	1.5×10^{-10}	[23]
(8)	$SiH_3(SiH_3^{\ddagger})+OH(OH^{*}) \rightarrow$ products	1.5×10^{-10}	see text
(9)	radicals → first-order decay	2.0×10^{2}	see text

imental and simulated time profiles. The initial rapid rise may imply that the ground vibrational state is also populated, though to a small extent.

Radical–radical reactions should be also taken into consideration. Relevant reactions are,

$$SiH_3(SiH_3^{\ddagger})+SiH_3(SiH_3^{\ddagger}) \rightarrow \text{products}\,, \qquad (7)$$

and

$$SiH_3(SiH_3^{\ddagger})+OH(OH^{*}) \rightarrow \text{products}\,. \qquad (8)$$

In these equations, we do not discriminate the reactivity of rovibrationally excited and normal radicals for simplicity. The rate constant of reaction (7) was once supposed to be 8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [26], and very recently Itabashi et al. [23] estimated it to be $(1.5\pm0.6)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, which we adopt in the present simulation. The products may be SiH_2+SiH_4 [23,26], but we do not take into account of their subsequent reactions. The rate constant of (8) seems not to have been studied until now. Therefore, we rather arbitrarily adopt a value of 1.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Again, subsequent reactions are not taken into consideration. The silyl radical concentration may decrease due to a diffusion loss process, whose first order rate constant is evaluated to be around 2×10^2 s^{-1}. For the evaluation, the diffusion constant D of 150 cm^2 s^{-1} at 1 Torr, assuming that the diffusion is comparable to the diffusion of methane, and the diffusion equation,

$$\bar{x}^2=2Dt\,,$$

have been employed, equating $\bar{x}$ to the half-width of the excimer laser beam cross section.

The proposed mechanism with adopted rate constants is shown in table 1. Here (1a) is assumed to be the exclusive channel of the reaction, $SiH_4+O(^1D)$. The simulated results are already shown in fig. 2, where they are drawn with the scale which relates the absorbance 0.01 to the concentration 0.84×10^{12} molecule cm^{-3}. On the other hand, the previous estimation has indicated that absorbance 0.01 corresponds to the concentration $(1.0–2.0)\times10^{12}$ molecule cm^{-3} in experiments. The fair agreement of the above two relationships between the absorbance and the concentration shows that the branching ratio of (1a) should be close to unity. Thus it is concluded that (1a) is a major channel as assumed in the reaction mechanism tabulated in table 1.

4. Concluding remarks

(1) The reaction between $O(^1D)$ and SiH_4 proceeds to yield silyl radical $+OH$ (1a) as a major channel.

(2) Most of the initial silyl radicals are vibrationally excited, and some of them relax and are detected by the present infrared diode laser kinetic absorption spectroscopy. Comparable amounts of silyl radical may be also produced via the secondary reaction of silane with the primarily produced OH.

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