Notes

Determination of the Rate Constants for Bimolecular Reactions of O(^{3}P) Atom with SiH$_4$ and SiHCl$_3$

Jee-Yon Lee, Hee-Soo Yoo,[*] **and Jin Seog Kim**[†]

*Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea. *E-mail: shyoo@chungbuk.ac.kr*
[†]*Division of Metrology for Quality Life, Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-600, Korea*
Received April 27, 2007

The reaction of silanes with oxygen atom is very important because of the roles in semiconductor fabrication such as chemical vapor deposition (CVD) processes, as well as in the study of unstable nature under oxygen atmosphere including combustion and explosion processes. However, experimental kinetic data for the reaction of oxygen atom with silanes are not well documented and are very limited, compare to the data for the reaction with olefins.[1-3] The O(^{3}P) atom reactions with SiHCl$_3$ and SiH$_4$ were theoretically studied by Q. Zhang *et al.*[4] They calculated the rate constants with the Arrhenius expression over a wide temperature range of 200-3000 K, specifically on the hydrogen abstraction channel, optimizing geometrical parameters of reactants at saddle point by *ab initio* method. Buchta *et al.* reported the experimental work on the reaction of O(^{3}P) with silanes by discharge flow method and mass spectrometry.[5,6] The rate constant for the reaction of O(^{3}P) with SiHCl$_3$ was given as a function of temperature, $k = (1.41 \pm 0.28) \times 10^{-11}$ cm^{3}molcule^{-1}s^{-1} exp$[-(13.5 \pm 2.7)$ kJmol^{-1}/RT] in the range of 298-773 K, however, the rate expression considered only hydrogen abstraction channel rather than total reaction pathways.[5]

In this note, we report kinetic data on the measurements of total reaction pathways for reaction of O(^{3}P) with SiHCl$_3$ and SiH$_4$, by using discharge flow/chemiluminescence imaging technique. The rate constants were obtained to be $(1.38 \pm 0.06) \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} for SiH$_4$ and $(1.74 \pm 0.13) \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} for SiHCl$_3$ at 298 K. The NO$_2$ chemiluminescence was observed and analyzing second order rate equations, which provides apparently much information at an initial reaction zone.[3,7]

Experimental Section

The discharge flow/chemiluminescence imaging system is well described in the previously reported articles.[3,7,8] The flow velocity was controlled by the total amount of gas injected and the inner diameter of reaction tube. During the experiment, the flow velocity was controlled to be 86 cms^{-1} in borosilicate reaction tube (inner diameter = 30 mm) by

mass flow controllers (MKS, 1179A). A capacitance gauge (MKS 626) was used to monitor the pressure in the reaction zone. The reaction tube was replaced after a set of measurements, considering a possible contamination of reaction products on the wall.

The ground state oxygen atom, O(^{3}P), was generated by using microwave (Opthos, MPG-4M) discharge of 1% O$_2$ balanced in He. The concentrations of O(^{3}P) are proportional to the intensity of chemiluminescence from the following reactions (1) and (2).

$$O(^3P) + NO + M \rightarrow NO_2^* + M \qquad (1)$$

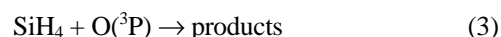$$NO_2^* \rightarrow NO_2 + h\nu \qquad (2)$$

The chemiluminescence was monitored by a charge coupled device (CCD) camera (Princeton Instrument, CCD-763) equipped with a personal computer for data acquisition. The exposure time was 0.5 s for a single shot and the signals were accumulated by 50 times.

The C$_2$H$_4$ (Aldrich, 99%) and SiH$_3$Cl (Aldrich, 99%) were purified by freeze-thaw method and diluted by He (Praxair Korea, 99.9995%) to 5% and 1.4%, respectively. The gas mixtures, O$_2$ (0.98% in He, Praxair Korea), NO (1.0% in He, Praxair Korea), and SiH$_4$ (1.32%, Korea Research Institute of Standards and Science) were used without any further purification.

Results and Discussion

The following reactions were examined to obtain their rate constants at 298 K by using the initial rate method.

$$SiH_4 + O(^3P) \rightarrow products \qquad (3)$$

$$SiHCl_3 + O(^3P) \rightarrow products \qquad (4)$$

The reaction rates are determined from the decay rate of oxygen atom concentration during the reaction in the flow reaction tube. The oxygen atoms are consumed by the reaction with silanes, as well as the wall of reaction tube by the collision, as given in equations (5) and (6), respectively.

$$O + A \xrightarrow{k_{bi}} \text{products} \qquad (5)$$

$$O + \text{wall} \xrightarrow{k_{w}} \text{products} \qquad (6)$$

where, k_{bi} is the rate constant of bimolecular reaction; k_w is the first order rate constant for wall effect regarding the consumption due to O_2 and also reaction products. Near the injection point, the rate equation for the consumption of oxygen atom is described by the equation (I) since the reaction (5) is major process.

$$-\frac{d[O]}{dt} = k_w[O] + k_{bi}[O][A]$$
$$= k_w[O] + k_{bi}[O]\,([O] + [A]_o - [O]_o) \qquad (I)$$

By solving the equation (I) we could get the integrated rate expression as follows

$$\ln\frac{[O]_t}{[O]_0} = -(k_w + k_{bi}a)t + \ln\frac{[A]_t + k_w/k_{bi}}{[A]_0 + k_w/k_{bi}} \qquad (II)$$

where, $a = [A]_0 - [O]_0$; $[A]_0$ and $[O]_0$ are the initial concentrations for the sample and O(^{3}P) atom, respectively; $[A]_t$ and $[O]_t$ represent their concentrations at specific reaction time, t. Because $[A]_t$ comes to $[A]_0$ as t is close to 0, the equation (II) is approximated to the equation (III).

$$\ln\frac{[O]_t}{[O]_0} = \ln\frac{I_t}{I_0} = -(k_w + k_{bi}a)t \qquad (III)$$

where, I_t and I_0 indicate the intensities of chemiluminescence at specific time and $t = 0$, respectively. The initial concentration of oxygen atom, $[O]_0$, can be determined by the equation (IV).
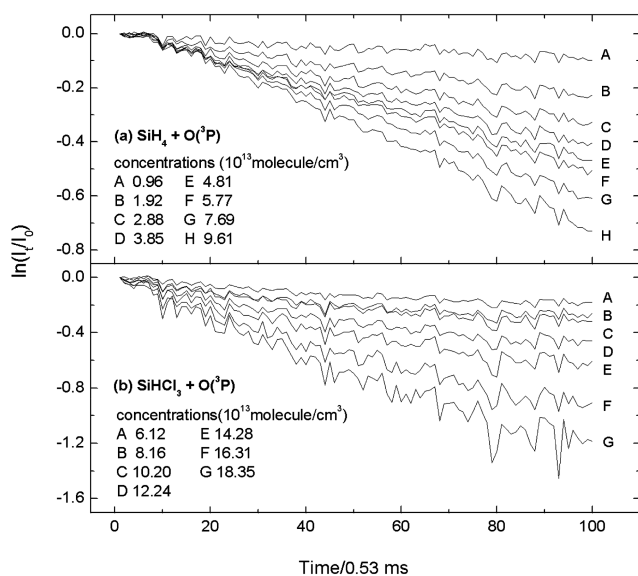

Figure 1. The $\ln(I/I_0)$ versus reaction time are plotted for different concentrations of (a) SiH$_4$ and (b) SiHCl$_3$ at 298 K. The O(^{3}P) atom decay rates, k_{decay}, were obtained from the slope of this plot.

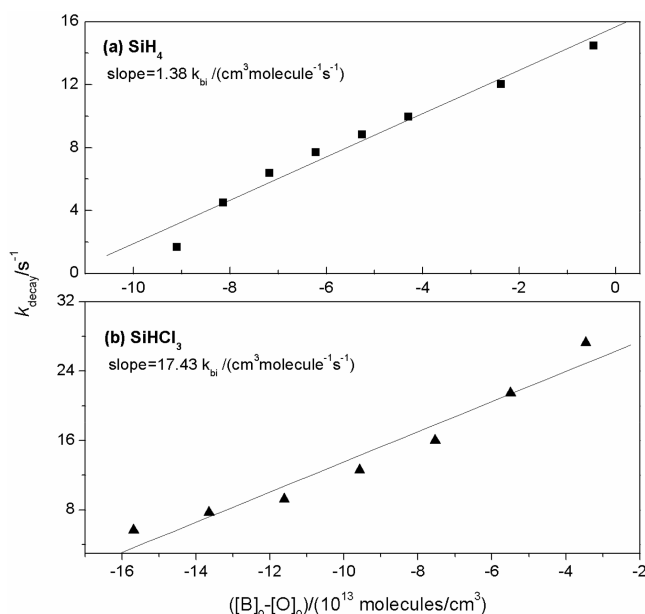**Figure 2**. The second-order decay rate coefficient, k_{decay}, are plotted versus (a) [SiH$_4$]$_0$-[O]$_0$; (b) [SiHCl$_3$]$_0$-[O]$_0$ at 298 K.

$$[O]_0 = \frac{[A]_0}{1 - [O]_\infty/[O]_0} \qquad (IV)$$

where, $[O]_\infty$ represents the concentration of remaining O(^{3}P) when the samples are completely consumed.[7]

We observed the decay signal of the NO$_2$ chemiluminescence derived from the reactions of O(^{3}P) atom with samples SiH$_4$ and SiHCl$_3$. Data from the first 100 pixels ($\sim5.34 \times 10^{-2}$ s) are considered as for the reaction near $t = 0$ and are used to plot $\ln(I_t/I_0)$ versus reaction time as shown in Figure 1. The slope from this correlation determines a decay constant, $k_{decay} = -(k_w + k_{bi}a)$. Figure 2 shows the plot of $-(k_w + k_{bi}a)$ versus $[A]_0 - [O]_0$ at different concentrations of initially injected sample in the reaction tube to determine the bimolecular rate constant k_{bi}. The measured bimolecular rate constants are summarized in Table 1.

In earlier work,[7] we have confirmed reliability of our measuring method showing a good agreement with previously reported rate constants for the reactions of O(^{3}P) with C$_2$H$_4$ (7.3×10^{-13} cm^{3}molecule^{-1}s^{-1}),[1] CF$_3$I (4.5×10^{-12}

Table 1. Bimolecular rate constants for SiH$_4$ and SiHCl$_3$. All data are obtained at room temperature

sample	rate constant, k_{bi}/ (cm^{3}molecule^{-1}s^{-1})	
	this work	reported value
SiH$_4$	$(1.38 \pm 0.06) \times 10^{-13}$	$4.8 \times 10^{-13\,a}$
		$2.8 \times 10^{-13\,b}$
		$3.5 \times 10^{-13\,c}$
SiHCl$_3$	$(1.74 \pm 0.13) \times 10^{-13}$	$5.94 \times 10^{-14\,d}$

[a]flashphotolysis with O/NO chemiluminescence detection[10]; [b]discharge-flow method with ESP detection of O atoms (DF-ESR)[11]; [c]flashphotolysis resonance-fluorescence technique[12]; [d]discharge-mass spectrometry[5]

cm^3molecule^{-1}s^{-1}),[9] and CH$_3$I (1.8 × 10^{-11} cm^3molecule^{-1} s^{-1}).[9] The rate constants for the reaction of O(^{3}P) with SiH$_4$ and SiHCl$_3$ were determined to be (1.38 ± 0.06) × 10^{-13} and (1.74 ± 0.13) × 10^{-13} cm^3molecule^{-1}s^{-1}, respectively. For the reaction of SiH$_4$, our rate constant is smaller than the previously reported data (see Table 1).[10-12] They produce O(^{3}P) by flash photolysis of O$_2$ and NO in metallic reaction cell, the chemiluminescence signal is decayed by the reaction of O(^{3}P) atoms as well as by the diffusion from observing zone. In our system, O(^{3}P) concentrations are uniform over a full reaction cell until the sample is injected. Moreover, a sufficient amount of chemiluminescence intensity provides a high signal to noise ratio (S/N) under second order reaction condition. In contrast, under pseudo-first order condition, the S/N of chemiluminescence is relatively small due to the weak chemiluminescence intensities obtained from a low concentration of O(^{3}P) atom. Obtained rate constant for SiHCl$_3$, (1.74 ± 0.13) × 10^{-13} cm^3molecule^{-1}s^{-1}, indicates total consumption of SiHCl$_3$ and shows to be larger than reported value (k = 5.94 × 10^{-14} cm^3molecule^{-1}s^{-1}).[5] Note that their measurement was carried out using excess O(^{3}P) concentration with moving sample injector system under pseudo-first order condition.[5,6]

References

1. Cvetanovic, R. J. *J. Phys. Chem. Ref. Data* **1987**, *16*, 261.
2. Teruel, M.; Taccone, R.; Lane, S. I. *Int. J. Chem. Kinet.* **2001**, *33*, 415 (see also references therein).
3. Lee, S. Y.; Yoo, H. S.; Kang, W. K.; Jung, K.-H. *Chem. Phys. Lett.* **1996**, *257*, 415.
4. (a) Zhang, Q.; Gu, Y.; Wang, S. *Chem. Phys. Lett.* **2004**, *383*, 16. (b) Zhang, Q.; Wang, S.; Zhou, J.; Gu, Y. *J. Phys. Chem. A* **2002**, *106*, 115.
5. Buchta, C.; Stucken, D.-V.; Vollmer, J.-T.; Wagner, H. G. *Z. Phys. Chem. (Munich)* **1994**, *185*, 153.
6. Mirsa, A.; Ding, L.; Marshall, P.; Buchta, C.; Stucken, D.-V.; Vollmer, J.-T.; Wagner, H. Gg. *J. Phys. Chem.* **1994**, *98*, 4020.
7. Lee, J.-Y.; Yoo, H.-S. *Bull. Korean Chem. Soc.* **2002**, *23*, 291.
8. Choi, G. H.; Yoo, H. S. *Bull. Korean Chem. Soc.* **2000**, *21*, 1149.
9. Gilles, M. K.; Turnipseed, A. A.; Talukdar, R. K.; Villalta, Y. R. P. W.; Huey, L. G.; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1996**, *100*, 14005.
10. Atkinson, R.; Pitts, Jr. J. N. *Int. J. Chem. Kinet.* **1978**, *10*, 1151.
11. Kharutunyan, S. A.; Mkryan, T. G.; Sarkisyan, E. N. *Oxid. Commun.* **1984**, *7*, 49.
12. Ding, L.; Marshall, O. *J. Chem. Phys.* **1993**, *98*, 8545.