KINETICS OF THE REACTIONS OF SiH_3 WITH O_2 AND N_2O

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The kinetics of the reactions SiH_3+O_2 and SiH_3+N_2O have been investigated using time-resolved photoionization mass spectrometric detection of SiH_3. Rate constants for the SiH_3+O_2 reaction were determined from 296 to 500 K ($k=4.96\times10^{-12}\exp(275/T)$ cm^3 molecule^{-1} s^{-1}). An upper limit for the SiH_3+N_2O rate constant at 500 K was also established (5×10^{-15} cm^3 molecule^{-1} s^{-1}).

1. Introduction

In spite of the widespread interest in the chemically induced vapor deposition of SiO_2 (using SiH_4 as the silicon source), little is known about the chemical reactions which are responsible for transforming the gaseous silicon hydride into the solid oxide [1,2]. Such processes are initiated by decomposing SiH_4 (usually with an electric discharge) or by reacting the hydride with transient species which are capable of removing a hydrogen atom. In both cases the initial silicon-containing free radical produced is largely SiH_3. This radical has been found to be by far the most abundant Si_1 intermediate produced when SiH_4 is flowed through a dc electric discharge [3,4].

Very little is known about the kinetics of the SiH_3 radical. This is, in part, due to the lack of a convenient spectroscopic property of SiH_3 which can be used to monitor its concentration under conditions which are suitable for obtaining knowledge of the kinetics of its elementary reactions. Recently time-resolved laser magnetic resonance detection has been employed to monitor SiH_3 in kinetic studies. Chasovnikov and Krasnoperov (CK) [5] have used this method to monitor SiH_3 and have determined rate constants at ambient temperature for two reactions, SiH_3+O_2 and SiH_3+NOCl. Earlier, Krasnoperov et al. [6] reported an upper limit for the $SiH_3+S_2Cl_2$ rate constant determined using the same diagnostic method.

To gain additional knowledge of the reactivity of the SiH_3 radical, we have begun a series of studies of the kinetics of its reactions using photoionization mass spectrometry to detect SiH_3. The first reactions studied have been those with O_2 and N_2O [#1]:

$$SiH_3+O_2\rightarrow SiH_3O_2\,,\quad \Delta H=-72\text{ kcal mol}^{-1}\,, \tag{1}$$

$$SiH_3+N_2O\rightarrow SiH_3O+N_2\,,\quad \Delta H=-88\text{ kcal mol}^{-1}\,. \tag{2}$$

Reaction (1) is clearly an important step in the conversion of SiH_4 to SiO_2. Its rate constant has been determined only once before, in the prior investigation discussed above [5].

Films of SiO_2 can be deposited when N_2O is photodecomposed (at 193 nm) in the presence of SiH_4 over a suitable substrate [9]. The oxygen atoms produced by the N_2O photolysis react with SiH_4 yielding SiH_3 (and OH) [10]. Because of the unusual strength of the Si–O bond [7], the O atom transfer in reaction (2) is highly exothermic, and hence this reaction is potentially an important rapid step in the chain of events leading to the deposition of SiO_2 under these conditions. There is no prior information available on the kinetics of reaction (2). The first results of our investigation of the kinetics of SiH_3 re-

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[#1] The heats of formation for silicon-containing free radicals were taken from ref. [7], others from ref. [8].

actions using photoionization mass spectrometric detection of the radical are reported here.

2. Experimental

The apparatus and experimental procedures used have been described previously [11,12]. Briefly, gas flowing through the 1.05 cm inner diameter Pyrex tubular reactor contains the SiH_3 source (see below), the second reactant in varying amounts, and an inert carrier gas in large excess (He, >99%). Reaction is initiated by laser photolysis, which results in the rapid production of SiH_3. Gas flowing from a small sampling orifice in the wall of the reactor is formed into a molecular beam and analyzed continuously using a photoionization mass spectrometer (PIMS). SiH_3 was monitored using 10.2 eV ionizing radiation in the PIMS. The decay of this radical was monitored in time-resolved experiments in the absence and presence of the second reactant (whose concentration was varied) to obtain the reaction rate constant. Experiments were conducted under pseudo-first-order conditions (O_2 or N_2O in large excess). Initial conditions were chosen to essentially isolate the reaction of interest. By keeping the initial concentration of SiH_3 low ($< 1 \times 10^{10}$ molecules cm^{-3}), radical–radical and radical–atom reactions had negligible rates compared to the one of interest.

SiH_3 was prepared in a two-step process. Pulsed, unfocused radiation from a Lambda Physik 201 MSC laser was directed along the axis of the tubular reactor and was used to photodecompose CCl_4. The chlorine atoms produced rapidly reacted with SiH_4 to produce SiH_3:

$$CCl_4 \rightarrow CCl_3 + Cl\,, \qquad (3)$$

$$Cl + SiH_4 \rightarrow SiH_3 + HCl\,. \qquad (4)$$

The CCl_4 decomposed only slightly, ≈0.1%. Comparable use of reaction (4) has been made to produce SiH_3 for kinetic studies [5,6,13] (no direct photolytic source of SiH_3 has yet been identified). Adequate SiH_4 concentrations were used to complete the production of SiH_3 in a time (<1 ms) which is short compared to the half-life of its subsequent reaction (typically 10–20 ms).

For the experimental conditions used, SiH_3 was lost in only two reactions, the one of interest and a heterogeneous loss process which was kinetically first order,

$$SiH_3 \rightarrow \text{heterogeneous loss}\,. \qquad (5)$$

Measurements of the SiH_3 exponential decay constant as a function of the concentration of the second reactant yielded the rate constant of interest. A sample measured decay of SiH_3 and a plot of the decay constants versus $[O_2]$ from one set of experiments to measure k_1 are shown in fig. 1.

Heterogeneous loss of SiH_3 was a significant process in these experiments. A coating on the wall of the Pyrex reactor was essential to partially control this loss. Two different coatings were employed, halocarbon wax and polytetrafluoroethylene (PTFE). Use of either yielded essentially the same results. The decay constant (k_5) with either coating was typically 150 s^{-1}. Without a coating, it was too high to measure, > 1000 s^{-1}. The importance of this competing process lowered the accuracy of the measured rate constants to ±30% (from the more typical ±15%).

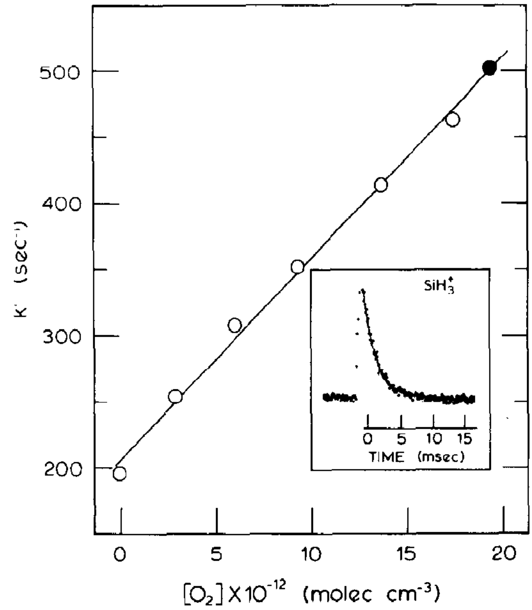

Fig. 1. Plot of SiH_3 exponential decay constants versus $[O_2]$ from a set of experiments to measure k_1 at 296 K. $[M] = 1.2 \times 10^{17}$ molecules cm^{-3}. Insert gives data from experiment conducted at $[O_2] = 1.96 \times 10^{13}$ molecules cm^{-3} (filled circle on plot). Decay constant = 502 s^{-1}.

2.1. Study of reaction (1)

Reaction (1) was studied at five temperatures between 296 and 500 K. Rate constants were determined as a function of density at each temperature (typically 6×10^{16} and 12×10^{16} molecules cm^{-3} but $(3-18)\times10^{16}$ molecules cm^{-3} at 296 K). Both wall coatings were used only at 296 K. At the higher temperatures, only PTFE was used. The measured rate constants for reaction (1) were independent of gas density and the wall coating material as well as independent of [SiH_3] and [CCl_4] as expected by the mechanism for SiH_3 loss. The range of conditions used and a summary of the results obtained are presented in table 1.

An unsuccessful search was conducted to identify the products of reaction (1). Experiments were conducted to detect the likely (and unlikely) reaction products: SiH_3O_2, SiH_2O_2, $SiHO_2$, SiH_3O, SiH_2O, SiO_2, SiHO, SiO, and SiH_2. None was detected, i.e. none was observed to appear as SiH_3 reacted with O_2. Detection of the first six of the possible products listed was partially obscured by additional ion signals at the corresponding mass numbers from photolysis products of the CCl_4/SiH_4 system. This interference reduced the detection sensitivity for these possible products.

The highest two available photoionizing energies were used in the PIMS in this search, 10.2 and 11.6 eV. Failure to detect these products could have been due to their absence but could also have been caused by other factors including the poor detection sensitivity discussed above, instability of the product's ion or a product ionization potential which is higher than 11.6 eV. Unfortunately, the relevant properties of most of the ions of these potential products are not known, and hence the failure to detect a product in the current investigation cannot be used as evidence to exclude it as a possible reaction product of reaction (1).

2.2. Study of reaction (2)

No measurable reaction between SiH_3 and N_2O was observed. When N_2O was present, it also photodecomposed (to $O+N_2$) to a limited degree. The oxygen atoms produced by the photolysis of N_2O rapidly reacted with SiH_4 to produce SiH_3+OH [10]. This alternate source of SiH_3 was used in a determination of the upper limit of k_2 at the highest temperature at which the PTFE-coated reactor could be used, 500 K. A gas mixture containing SiH_4 (1.16×10^{14} molecules cm^{-3}), N_2O (1.58×10^{15} molecules cm^{-3}), and He (balance) was photolyzed at 193 nm and SiH_3 decays monitored. No difference was observed between the SiH_3 decay constants measured when N_2O was present and those measured when N_2O was absent (and CCl_4 substituted for N_2O to provide a source of SiH_3). From the magnitudes and uncertainties of the measured decay constants, an upper limit of 5×10^{-15} cm^3 molecule^{-1} s^{-1} was established for k_2 at 500 K.

Table 1
Range of conditions and results of experiments to measure k_1 [a]

T (K)	10^{-16} [M] range [c]	10^{-12} [CCl_4] range [c]	10^{-13} [SiH_4] typical [c]	10^{-13} [O_2] range [c]	k_5 typical [d]	$10^{12}k_1$ average [e]
296 [b]	3.0–18	0.71–1.5	1.1	0.34–3.3	137	12
296	6.0–12	1.3 –1.6	1.2	0.29–2.8	186	15
328	6.0–12	0.93–3.3	9.6	0.30–3.3	185	13
370	6.0–12	3.1 –6.3	13	0.43–4.1	160	8.9
426	6.0–12	6.1 –6.6	13	0.50–3.2	188	9.4
500	6.0–12	6.2 –6.7	13	0.56–3.3	177	9.2

[a] Table presents summary of multiple experiments performed at each temperature: two experiments at 296, 370, 426, and 500 K; three experiments at 328 K; four experiments at 296 K.

[b] Experiments conducted using reactor coated with halocarbon wax. All other experiments conducted with PTFE-coated reactor.

[c] In molecules cm^{-3}. [d] In s^{-1}. [e] In cm^3 molecule^{-1} s^{-1}.

3. Discussion

3.1. *Kinetics of reaction (1)*

The measured values of k_1 display a small decrease with increasing temperature characteristic of an association reaction proceeding along an attractive reaction coordinate. Fit to an Arrhenius equation, these values yield the expression

$$k_1 = 4.96\times10^{-12}\exp(275/T)\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}\,.$$

It is likely that the SiH_3+O_2 reaction begins as a simple association process. The fact that no density dependence was detected in k_1 (both in the current study and the prior one by CK [5]) strongly suggests that once formed, the SiH_3O_2 adduct irreversibly decomposes by a second route (other than back to reactants) or isomerizes (and perhaps then decomposes). The likely decomposition and isomerization routes for reaction (1) as well as the associated thermochemistry of each channel have been discussed by Hartman et al. [7] and will not be reviewed here, particularly since none of the likely products was detected in the current study.

There is reasonably good agreement between the average of the values of k_1 determined at 296 K in the current investigation (1.3×10^{-11} cm^3 molecule^{-1} s^{-1}) and the value reported by CK [5] (0.97×10^{-11} cm^3 molecule^{-1} s^{-1}). The difference is within the ±30% uncertainty in the current value and the ±10% probable error indicated by CK for their value.

Ruiz and Bayes [14] have demonstrated that a linear correlation exists between the logarithm of $R+O_2$ association rate constants (R = alkyl radical) and the ionization potential of R. This correlation has been accounted for by using a model reaction potential which is highly attractive, one which approaches $-\infty$ at the classical crossing distance between the ionic ($R^+ + O_2^-$) and covalent potential curves. The SiH_3+O_2 rate constant complies very closely with this correlation for $R+O_2$ reactions (see fig. 2). While this compliance may be fortuitous, it is worth noting. If it is not fortuitous, it supports the claim of Ruiz and Bayes [14] that the portion of the long-range potential which affects the association rate constant is determined largely by one-electron properties of the reactants rather than reaction thermochemistry. The thermochemistry of reaction (1) is entirely different from that of the $R+O_2$ reactions, the former being 72 kcal exothermic [7] and the latter group ≈35 kcal exothermic [15].

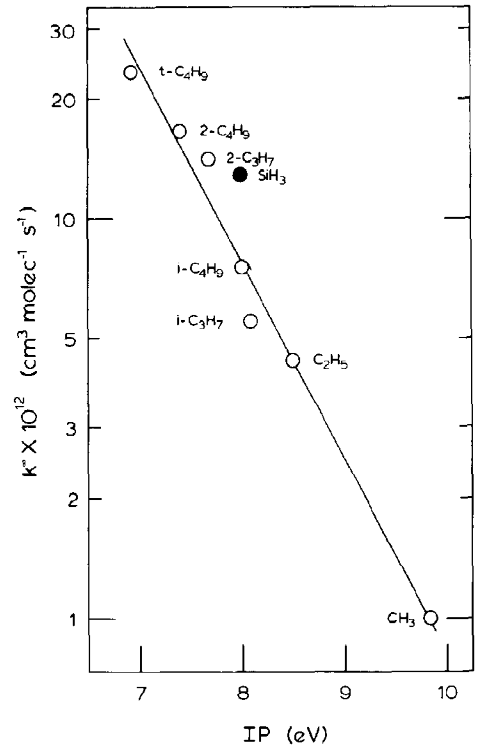

Fig. 2. Semilog plot of high-pressure limit $R+O_2$ rate constants (k^∞) versus ionization potential of R. (Data for alkyl radicals taken from ref. [14].)

Further studies are planned of the kinetics of SiH_3 and other silicon-centered free radicals to gain additional knowledge of their kinetic behavior and the factors controlling their reactivity.

3.2. *Kinetics of reaction (2)*

The low value of the upper limit of k_2 at 500 K (and a likely still lower upper limit for k_2 at ambient temperature) excludes this elementary reaction from having any significant role in the photo-induced deposition of SiO_2 from mixtures of SiH_4 and N_2O at ambient temperatures [9]. It is still possible that other silicon-centered radicals formed in this system do react rapidly with N_2O. The search for evidence of such reactions will continue.

3.3. Photoionization mass spectrometric detection of SiH_3

The experimental apparatus and procedure described here provide the most sensitive method yet reported for monitoring SiH_3 concentrations in the gas phase. Initial concentrations of SiH_3 as low as 1×10^9 molecules cm^{-3} were employed without experimental difficulty in the current investigation (implying an effective detection sensitivity of $\approx1\times10^8$ molecules cm^{-3}). The time-resolved LMR method of CK is reported to have a detection sensitivity about 1000 times poorer, $\approx1\times10^{11}$ molecules cm^{-3} [6]. The unusually high sensitivity of the PIMS for detecting such a relatively small free radical is due in part to the fact that there is no fragmentation of SiH_4 at the SiH_3 mass number even when 10.2 eV radiation (the most intense of the available ionizing energies) is used in the PIMS to ionize SiH_3, an energy which is over 2 eV above the ionization potential of SiH_3 (which is 8.0 eV [16]). The appearance potential of SiH_3^+ from SiH_4 is ≈12 eV [16].

The PIMS detector will continue to be used in future studies of the kinetics of SiH_3 reactions, and its potential use for monitoring the concentrations of other silicon-centered free radicals in reacting systems will also be explored.

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References

[1] J.M. Jasinski, B.S. Meyerson and B.A. Scott, Ann. Rev. Phys. Chem. 38 (1987) 109.
[2] Plasma, Ion and Laser Assisted Chemical Processing of Electronic Materials, Report of the NSF Workshop, San Diego (February 1987).
[3] R. Robertson, D. Hils, H. Chatham and A. Gallagher, Appl. Phys. Letters 43 (1983) 544.
[4] R. Robertson and A. Gallagher, J. Appl. Phys. 59 (1986) 3402.
[5] S.A. Chasovnikov and L.N. Krasnoperov, Khim. Fiz. 6 (1987) 956.
[6] L.N. Krasnoperov, E.N. Chesnokov and V.N. Panfilov, Chem. Phys. 89 (1984) 297.
[7] J.R. Hartman, J. Famil-Ghiriha, M.A. Ring and H.F. O'Neal, Combustion Flame 68 (1987) 43.
[8] S.W. Benson, Thermochemical kinetics, 2nd Ed. (Wiley-Interscience, New York, 1976).
[9] P.K. Boyer, C.A. Moore, R. Solanki, W.K. Ritchie, G.A. Roche and G.J. Collins, in: Laser diagnostics and photochemical processing for semiconductor devices, eds. R.M. Osgood, S.R.J. Brueck and H.R. Schlossberg (North-Holland, Amsterdam, 1983) p. 119.
[10] B.S. Agrawalla and D.W. Setser, J.Chem. Phys. 86 (1987) 5421.
[11] I.R. Slagle and D. Gutman, J. Am. Chem. Soc. 107 (1985) 5342.
[12] R.S. Timonen and D. Gutman, J. Phys. Chem. 90 (1986) 2987.
[13] H. Niki, P.D. Maker, C.M. Savage and L.P. Breitenbach, J. Phys. Chem. 89 (1985) 1752.
[14] R.P. Ruiz and K.D. Bayes, J. Phys. Chem. 88 (1984) 2592.
[15] I.R. Slagle, E. Ratajczak and D. Gutman, J. Phys. Chem. 90 (1986) 402.
[16] J. Berkowitz, J.P. Greene, H. Cho and B. Ruščič, J. Chem. Phys. 86 (1987) 1235.