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Unimolecular Decomposition of Silane in Shock Waves

Hitoshi Tanaka, Mitsuo Koshi,* and Hiroyuki Matsui
Department of Reaction Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Thermal decomposition of silane highly diluted in argon was studied behind incident shock waves at the temperatures ranging from 1250 to 1600 K. The decomposition course was followed by monitoring the infrared emission of silane at 4.4 μm. It was confirmed that the effects of consecutive reactions on the decay rate of silane were negligible under our experimental conditions. The unimolecular rate constants obtained directly from the decay curve of silane were found to be smaller than previous experimental values but consistent with the result of the recent trajectory-RRK calculation. It was also found that the addition of molecular hydrogen or nitrogen monoxide to the reactant mixtures had no effect on the decomposition rate of silane.

The homogeneous gas-phase decomposition of silane has already been investigated by several groups of workers. Various methods including static pyrolysis,[1-4] single pulse shock tube technique[5,6] and IR laser powered homogeneous pyrolysis[7,8] have been used to investigate the mechanistic detail of silane pyrolysis. Although some ambiguities on the role of the inhomogeneous production of hydrogen atoms are still remained,[9,10] the primary step of the homogeneous gas-phase decomposition has been now well established. At low temperature this step is the elimination of molecular hydrogen to form silylene.

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

The homolytic cleavage of one SiH bond only becomes important at internal silane energies in excess of about 106 kcal mol^{-1} [11] (1 cal=4.184J). The conclusion has been supported by a consideration of symmetry of the reaction,[12] a calculation of the potential energy surface[13] and a trajectory-RRK calculation.[11]

Rate constants for the unimolecular decomposition of the Reaction 1 have already been measured by several investigators[1,2,5,6] and it was found that the reaction was in its pressure fall-off region at the atmospheric pressure and below. Purnell and Walsh[1] found that the rate constant of Reaction 1 was proportional to the square root of the total pressure. White et al.[3] observed the same pressure dependence in the similar pressure and temperature range and this pressure dependence was well explained by their RRKM calculations. However, the mechanism of the consecutive reactions of silylene is rather complex. Rate inhibition of the silane decay by molecular hydrogen which was attributed to the reverse process of the Reaction 1 was observed.[3] Also the reaction of silylene with silane would play a significant role on the silane loss rate.

It should be noted that all of these previous studies were based on the products analysis. If the decomposition process of silane has the induction period, as suggested by Newman et al.,[6] it might be difficult to get precise rate constant for the initiation reaction by the products analysis only. Time resolved measurement of silane concentration is desirable to investigate the mechanism of silane decomposition in details. Moreover, the published experimental works have been done for relatively high concentrations of silane, which made the roles of the consecutive reactions unclear, and the temperatures covered in these works have been limited to a relatively low range.

In the present study, we derived the unimolecular rate constant for the Reaction 1 directly from the time history of silane highly diluted in argon by monitoring infrared emission. The present study was performed for high temperatures up to 1600 K. The results were compared with those of the previous experimental and theoretical studies.

Experimental

A diaphragmless stainless-steel shock tube of 5 cm diameter was used. The driven section was 4 m in length and was evacuated to less than 2×10^{-6} Torr (1 Torr=133.322Pa) before charging it with a sample gas. The shock tube window (CaF_2) was located at 3.0 m downstream from the driver section. Highly diluted mixtures of silane (500 ppm) in argon were heated behind incident shock waves. The temperature, pressure and density of shocked gas were calculated from the shock velocity measured by piezo electric pressure gauges. The temperature and pressure of the reaction zone varied from 1250 to 1600 K and from 0.25 to 1.3 atm, respectively.

The intensity of the infrared emission at 4.4 μm, which could be attributed to the ν_3 fundamental band of silane, was monitored by an interference band pass filter (0.19 μm FWHM) and an InSb detector. The time response of the detection system was estimated to be less than 8 μs.

The gas mixtures were prepared manometrically with a calibrated diaphragm-type pressure gauge. Commercially available ultra-high purity gases (SiH_4: 99.9999%, Ar: 99.9995%, H_2: 99.9999%, and NO: 99.8%) were used without further purification.

Results and Discussion

An example of the time profile of 4.4 μm emission intensity is shown in Fig. 1. The intensity decreases exponentially behind the shock front and increases slowly near the contact surface of the shock wave. According to the recent ab initio calculation on the Si-containing species,[14] many of Si_2H_x and Si_3H_x

molecules have fundamental vibration-rotation bands in 4.5—4.7 μm region. For example, SiH_4, Si_2H_4, Si_2H_6, and Si_3H_8 have the fundamental bands at 4.56, 4.5, 4.63—4.66, and 4.63—4.69 μm respectively. Therefore it is possible that the observed emission is caused by not only SiH_4 but also other species like Si_2H_4. However, for the IR emission at initial decay this possibility is rejected by the following observations. 1) The decay of the emission intensity is described by a single exponential function as shown in Fig. 1. This implies that any product species which increase with time may not have significant contributions to the emission intensity, since the intensity goes down to the ground line before it shows gradual increase near the contact surface. 2) The solution of the simultaneous kinetic equations, which is discussed later in detail, predicts that the main reaction intermediates or products during the course of the silane decomposition under our experimental conditions are H_2, Si_2, Si, Si_2H_2, Si_3, and SiH_2. These species do not emit at 4.4 μm. 3) We also observed the emission at 4.87 μm with an interference band pass filter. The time profile of 4.87 μm emission intensity was the same as that of 4.4 μm intensity. No emission was observed at 5.22 μm. Therefore there is no significant contribution of the emission from SiH (4.88 μm), SiH_3 (5.0 μm), and SiH_2 (4.95 μm) to the emission at 4.4 μm.

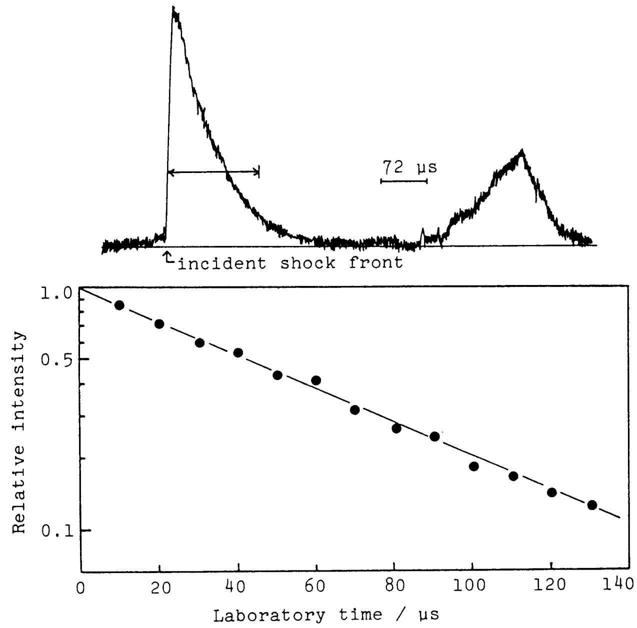

Fig. 1. Time history of the emission intensity at 4.4 μm. Upper panel: An example of the oscillogram trace. Lower panel: A log plot of the normarized intensity. T=1380 K, P=0.28 atm, 500 ppm SiH_4 in Ar. The region indicated by an arrow in the upper panel is plotted in the lower panel.

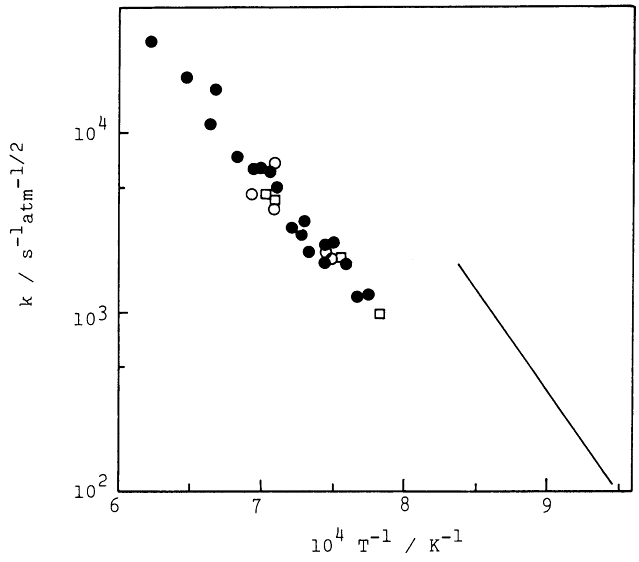

Fig. 2. Arrhenius plots of the pressure independent rate constants for the unimolecular decomposition of silane. k is defined by Eq. I in the text. Pressures of the experimental data are in the range of 0.25—1.2 atm. Closed circle: 500 ppm SiH_4 in Ar, open circle: 500 ppm SiH_4 in Ar with 1.1% H_2, open square: 500 ppm SiH_4 in Ar with 0.31% NO, line: from Ref. 6 (P=5.26 atm, 0.96% SiH_4 in Ar).

The origin of the slowly rising part of the emission profile near the contact surface is not clear. Only the decaying part of the emission intensity which was concluded to be proportional to the concentration of silane is analyzed in the present study. It was found that the first-order rate constants for the silane decay, k_{obs}, were proportional to a square root of the total pressure. Figure 2 shows Arrhenius plots of the pressure independent rate constants, k, which are defined by

$$k = k_{obs} P^{-1/2}, \qquad \text{(I)}$$

where P is the total pressure. Irrespective of the total pressure ranging from 0.25 to 1.3 atm, all the experimental points can be very well represented by a single straight line. The least-squares analysis of the data gave the following Arrhenius expression:

$$k = 10^{11.1\pm0.8} \exp(-(48.1 \pm 0.7)\ \text{kcal mol}^{-1}/RT)\ \text{atm}^{-1/2}\ \text{s}^{-1} \qquad \text{(II)}$$

A square root pressure dependence of the rate of molecular hydrogen production and of silane decay was also found in static pyrolysis studies at low temperatures.[1,6] This pressure dependence has been well explained by the pressure fall-off behavior of the Reaction 1.[6] However, it is not obvious if the measured rate constants in the present study can be attributed to the rate constant of Reaction 1, because the overall reaction mechanism of the silane decomposition is rather complicated. White et al.[3] proposed the following reaction mechanism for the consecutive reactions of the homogeneous decomposition of silane at static system reaction temperatures.

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

$$Si_2H_6 \rightarrow Si_2H_4 + H_2 \qquad (4)$$

Table 1. Reaction Mechanism

	Reaction				log A[a)]	E[a)]	Reference
1.	SiH_4		$=SiH_2$	$+H_2$	11.1[b)]	48.1	This work
2.	SiH_2	$+SiH_4$	$=Si_2H_6$		12.45	1.3	3
3.	SiH_2	$+SiH_2$	$=Si_2H_4$		11.2	0.0	3
4.	Si_2H_6		$=Si_2H_4$	$+H_2$	14.4	52.2	3
5.	SiH_2	$+Si_2H_6$	$=Si_3H_8$		12.61	0.4	3
6.	Si_3H_8		$=SiH_3SiH$	$+SiH_4$	14.68	49.24	3
7.	Si_2H_4		$=Si_2H_2$	$+H_2$	14.50	53.0	3
8.	SiH_3SiH		$=Si_2H_4$		12.80	29.2	3
9.	Si	$+H_2$	$=SiH_2$		14.06	2.0	15
10.	SiH_2	$+Si_2$	$=Si_3$	$+H_2$	11.55	2.0	15
11.	SiH_2	$+Si_3$	$=Si_2H_2$	$+Si_2$	11.16	18.8	15
12.	Si_2	$+H_2$	$=Si_2H_2$		13.19	2.0	15
13.	Si_2	$+H_2$	$=SiH$	$+SiH$	13.19	40.0	15
14.	Si_3	$+H_2$	$=Si_2H_2$	$+Si$	12.99	42.6	15

a) Arrhenius parameters for the rate constants in the forward direction written in the form $k=A\exp(-E/RT)$. The units of A depend on the reaction order, but are given in terms of moles, cubic centimeters and seconds. E is in kcal mol^{-1}. b) See text for discussion of the pressure dependence. Listed value is for $P=1$ atm.

They suggested that the rate acceleration by these reactions might occur when silane conversion was less than 30%. Consequently the induction period on the silane loss was expected. At conversions greater than 40%, a gradual rate deceleration with increasing deviations from first-order kinetics was observed.[3)] This rate inhibition was attributed to the contribution of the back reaction of hydrogen and silylene.

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

White et al.[3)] further suggested that the silylene dimerization-decomposition reactions, 3, −3, and 7, might play a significant role on the silane decay rate over the temperature range of the single pulse shock tube experiments by Newman et al.[5,6)]

$$SiH_2+SiH_2 \rightarrow Si_2H_4 \qquad (3)$$

$$Si_2H_4 \rightarrow Si_2H_2+H_2 \qquad (7)$$

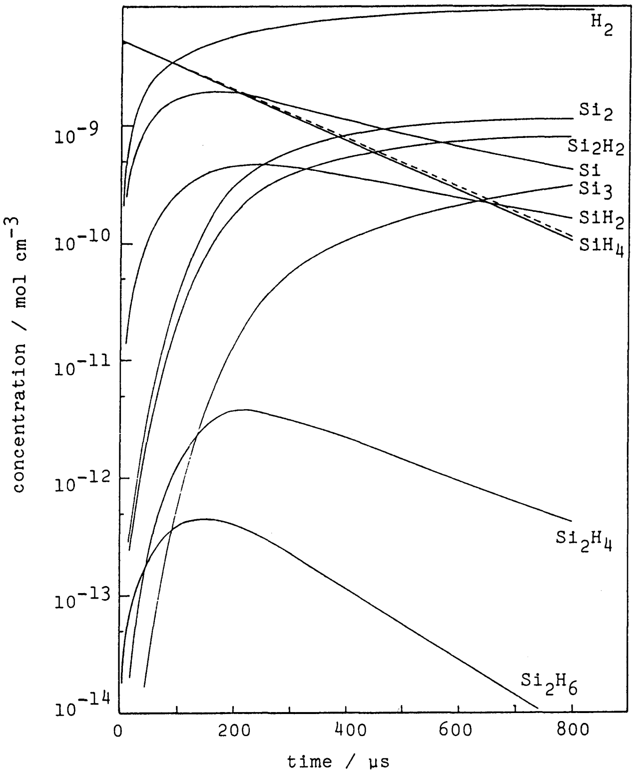

Fig. 3. Calculated concentrations for the mixture of 500 ppm SiH_4 in Ar at $T=1400$ K and $P=1.24$ atm.

In the present study, the induction period on the silane decay was not observed. Moreover, no effect of the addition of molecular hydrogen to the reactant mixtures was observed. This is evident in Fig. 2 in which the pressure independent rate constants obtained with the addition of 1.1% molecular hydrogen are shown. This is consistent with the single exponential decay of sliane during the entire course of the decomposition. This behavior of the silane decay can be explained if the Reaction 3 is much faster than the Reactions 2 and −1 in our experimental conditions. If this is the case, the rate constants for the initial decay observed in the present study correspond directly to the rate constants for the Reaction 1 only. In order to confirm the validity of this prediction, the simultaneous kinetic equations for the various species were numerically solved based on the reaction mechanism and the rate constants listed in Table 1. Each of the reactions listed in the table is reversible. The rate constants for the reverse reactions can be obtained from the reaction thermochemistry. Thermochemical data for each species involved in the reaction mechanism are taken from the work by Coltrin et al.[15)] Although there are no reliable data for the Reactions 9 through 14, these reactions have no sensitivity for the silane loss rate. The rate constants estimated by Coltrin et al.[15)] were used for these reactions. An example of the calculated time-concentration profiles of the various species involved in the model is shown in Fig. 3. The dashed curve in the figure represents the analytical solution for the silane concentration calculated by using Reaction 1 only. This curve agrees very well with that obtained by the numerical integrations of the full kinetic equations. Therefore it is confirmed that the silane decay rate in our experimental conditions is determined by the unimolecular decomposition of silane without any significant contribution of other consecutive reactions.

Another possible silane loss mechanism that is not involved in our model is Si-chain mechanism:

$$SiH_2\,(+M) \rightarrow Si + H_2\,(+M) \qquad (-9)$$

$$Si + SiH_4 \rightarrow SiH_2 + SiH_2 \qquad (15)$$

There have been no experimental and theoretical works on the Reaction 15. If we include this reaction with the rate constant estimated by Coltrin et al.[15] in our model, the rate of the silane loss is greatly accelerated and a single exponential decay of silane is no longer obtained. To clarify the contribution of the Si-chain reactions to the rate of the silane decay, nitrogen monoxide was added to the mixtures. Because of the extremely fast reaction between nitrogen monoxide and silicon atom,[16] the silane loss rate might be considerably decelerated if the Si-chain reactions could play an important role. The pressure independent rate constants with the addition of 0.31% nitrogen monoxide are also included in Fig. 2. It was found that the single exponential decay of the silane concentration was not affected by the addition of nitrogen monoxide. No significant deviation of the rate constants from those obtained without the addition of nitrogen monoxide is evident in the figure. The absence of an induction period and the fact that the addition of nitrogen monoxide has no effect on the silane decay provide good evidence that the Si-chain reactions are not responsible for the rate of the silane decay.

The unimolecular rate constants obtained by the single pulse shock tube experiments of Newman et al.[6] are also shown in Fig. 2, where the square root dependence of the rate constants on the total pressure is assumed. The extrapolation of their values to our experimental temperatures gives much higher values than those obtained in this work. Under the conditions of their single pulse shock tube experiments (T=1000—1200 K, P=5.25 atm with 0.96—0.12% SiH_4 in argon), the rate of Reaction 1 is slower than the rates of Reactions 2 and 3. As a result, the decay rate of silane can be accelerated by these consecutive reactions even in a very early stage of the decomposition. If we consider only Reactions 1—3 with an assumption of the steady state concentration of silylene, the following expressions for the initial decay rate of silane are obtained.

$$-\mathrm{d}[SiH_4]/\mathrm{d}t = k_1[SiH_4]\,(1+F) \qquad (III)$$

$$F = g(1+2/g)^{1/2},\; g = (k_2^2/4k_1k_3)\,[SiH_4] \qquad (IV)$$

Using the rate constants listed in Table 1, the value of F is estimated to be equal to 4.2 at T=1100 K and P=5.26 atm for 0.96% SiH_4 in argon. In contrast, F-values in our experimental conditions are always less than 0.14. Although the realistic reaction mechanism is much more complicated because of the reverse process of Reaction 2 and other consecutive reactions, the discrepancy shown in Fig. 2 is caused by the contributions of the consecutive reactions of silylene in the single pulse shock tube experiment.

Recently the rate constant of Reaction 1 has been calculated by Viswanathan et al.[11] They obtained the dissociation rate coefficient at internal energy E, $k(E)$, by means of the Monte-Carlo trajectory calculations. The values of $k(E)$ were fitted to a RRK form:

$$k(E) = \nu[(E-E_0)/E]^{s-1} \qquad (V)$$

The values of the RRK parameters obtained by Viswanathan et al. were $\nu = 1.08\times10^{13}\ s^{-1}$, E_0=49.6 kcal mol^{-1} and s=2.7. It is interesting to compare the results of their calculations with those of this study. The unimolecular rate coefficient was calculated with the following classical RRK formula.

$$k_1 = \int_{E_0}^{\infty}[f(E)k_\mathrm{d}k(E)]\,\mathrm{d}E/[k_\mathrm{d}+k(E)], \qquad (VI)$$

$$k_\mathrm{d} = \lambda z p,$$

$$f(E) = (kT)^{-s}E^{s-1}\exp(-E/kT)/\Gamma(s),$$

where z is the hard-sphere collision frequency, p is the pressure, λ is the deactivation probability upon collision and $\Gamma(s)$ is the Gamma function. In the calculation, hard-sphere collision diameters of 5.76 Å for silane and 3.47 Å for argon were used with a strong collision assumption (λ=1). The pressure dependence of the rate coefficients is compared in Fig. 4. The calculated rate constants with parameters given by Viswanathan et al. show steeper pressure dependence (curve A in Fig. 4) compared with the experimental values. We have searched a new set of RRK parameters

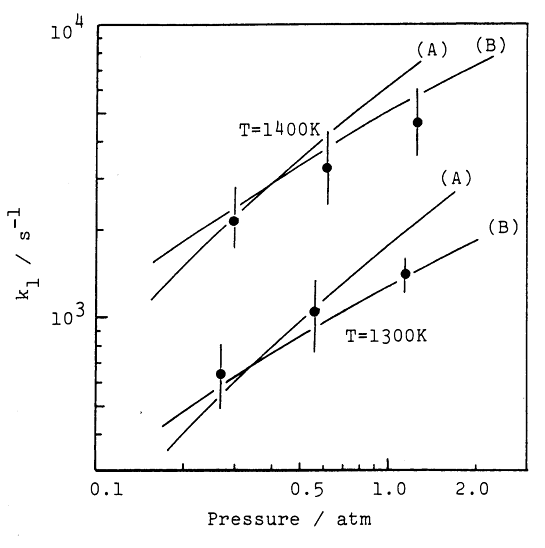

Fig. 4. Pressure dependence of the unimolecular decomposition of silane. Shaded circle with an error bar: Present experimental value, curves A and B: RRK calculations. See text for the RRK parameters used.

which can give better agreement with our experimental results. Although the limited range of the pressure and rather large scatter of the data points prevent the precise determination of parameters, the following set of parameters seems to be reasonable; E_0=55 kcal mol^{-1}, ν=1×10^{13} s^{-1}, and s=4.2. The calculated rate constants with these parameters are shown in Fig. 4 (curve B). The new value for a critical threshold energy is in good agreement with the result of the recent ab initio calculation.[13)] The activation energy, E_a, of the unimolecular reaction in the low pressure region will be given by the following equation.[17)]

$$E_a = E_0 - (s - 1.5)RT \qquad \text{(VII)}$$

Using the RRK parameters obtained in this work, the values of E_a were estimated to be equal to 49.6 kcal mol^{-1} at T=1000 K and 46.7 kcal mol^{-1} at T=1500 K. The observed activation energy in Eq. II agrees well with these estimated values.

Conclusion

In order to obtain the unimolecular rate coefficient for the silane decomposition without any effect of the consecutive reactions, highly diluted silane in argon was decomposed behind shock waves at the temperatures ranging from 1250—1600 K and the intensity of the infrared emission at 4.4 μm which was proportional to the concentration of silane was monitored. The conclusions obtained in the present study are summarized as follows.

(1) In our experimental conditions, the decay of silane is exclusively caused by the unimolocular decomposition of silane. The rate constants for this reaction were determined directly from the time resolved measurements on the silane concentration. (2) No effect on the silane decay rate was observed with the addition of molecular hydrogen nor nitrogen monoxide. (3) The observed pressure fall-off behavior of the rate constant for the silane decomposition is reasonably well explained by a RRK theory with appropriate parameters.

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