J. Phys. Chem. A **1999,** *103,* 841−846

Laser Flash Photolysis of $SiCl_4$ at High Temperatures Based on Si- and Cl-Concentration Measurements

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Received: July 2, 1998; In Final Form: October 12, 1998

Laser flash photolysis of $SiCl_4$ at 193 nm was studied behind reflected shock waves at temperatures 1000 K $\leq T \leq$ 2050 K and pressures between 1.4 and 1.8 bar. The atomic resonance absorption spectroscopy (ARAS) was applied for time-resolved measurements of Si- and Cl-atom concentrations in gas mixtures containing 10−100 ppm $SiCl_4$ highly diluted in argon. The atoms formed during photolysis of $SiCl_4$ were analyzed in terms of yields, defined as the fractions of the maximum atom concentration to the initial $SiCl_4$ concentration behind the shock wave. At temperatures $1000 \leq T \leq 1510$ K, Cl atoms were detected immediately after the laser flash. The Cl yield was found to be temperature dependent in the range between 0.1 and 2% of the initial $SiCl_4$ concentration. Si atoms first occurred at temperatures $T > 1750$ K, when $SiCl_4$ already has started to decompose. In contrast to Cl, the Si yield obtained correlates with both the temperature and the delay time between the shock-induced gas heating and the laser pulse. This effect was attributed to the photolysis of $SiCl_2$, which is formed during the thermal decomposition of $SiCl_4$. A reaction model including the thermal dissociation of $SiCl_4$ and the photodissociation of $SiCl_2$ is suggested and discussed, in which also reactions of Cl and Si atoms with $SiCl_4$ are considered to describe the measured concentration profiles.

1. Introduction

Kinetic parameters of reactions containing silicon species are of interest in chemical vapor deposition (CVD) as well as for the production of ceramic materials. For a better understanding and modeling of such processes, the knowledge of the reaction behavior at high temperatures is necessary. Elementary reactions of chlorinated silanes, e.g., $SiCl_4$, are of special interest because these species are widely used precursors in high-temperature gas-phase reactors for the synthesis of non-oxide and oxide ceramic powders such as SiC, Si_3N_4,[1−3] and SiO_2.[4] A detailed overview of gas-phase combustion synthesis of particles was recently published by Wooldridge.[5]

Laser-induced gas-phase reactions of chlorinated silanes at various reaction conditions are known to be suitable to produce high-quality ceramic particles,[6,7] which are smaller and more monodisperse compared to particles formed, for example, in flames. However, this technique is not really established, because it is less efficient and the details are not well understood,[2] so that further investigations are needed. On the other hand, photoinitiated reactions are commonly used in CVD reactors to deposit silicon-containing layers of highest quality. Beside SiH_4 and Si_2H_6, chlorinated silanes also are frequently used precursors. In those gas-phase systems $SiCl_2$ is supposed to play an important role as a direct precursor for Si formation and deposition.[8]

The decomposition of $SiCl_4$ into $SiCl_3$ and Cl was recently investigated in our laboratory by indirect kinetic measurements in a $SiCl_4/H_2/Ar$ system by Catoire et al.[9] A simplified mechanism of the thermal dissociation of $SiCl_4$ is given by Kunz and Roth,[10] which is based on direct Si- and Cl-concentration measurements in highly diluted $SiCl_4$/Ar mixtures. In the literature only theoretical considerations of $SiCl_4$ dissociation were found.[11]

Washida et al.[12] have studied the emission spectra of $SiCl_2$ during VUV photolysis of different chlorinated silanes at room temperature. In the case of $SiCl_4$ they could not find any $SiCl_2$ emission at photon energies of 8.44 eV $< E_{\text{photon}} <$ 10.64 eV. Husain et al.[13,14] have generated Si atoms in the ground state and in excited levels by pulsed radiation of $SiCl_4$ at wavelength $\lambda > 165$ nm ($E_{\text{photon}} < 7.51$ eV) and a total energy input of $E = 165$ J in a flow system. They have reported second-order rate coefficients for the reactions of Si atoms with H_2, O_2, and $SiCl_4$ at room temperature. To our knowledge there is no work known, in which the photolysis of $SiCl_4$ was studied at high temperatures.

The present work deals with measurements of Si- and Cl-atom formation in laser flash photolysis experiments of $SiCl_4$ at high temperatures. A reaction model is proposed in which $SiCl_2$ plays an important role for the understanding of the photolytic Si formation.

2. Experimental Section

The experiments were carried out behind reflected shock waves in a stainless steel shock tube of 80 mm internal diameter. The driver section was 3.5 m, the driven section 6.0 m in length, which was specially prepared for ultrahigh-vacuum (UHV) requirements. The driven section can be baked out and pumped down to pressures below 2×10^{-8} mbar by a turbo molecular pump. The gas mixtures used were prepared manometrically in a stainless steel UHV cylinder which can be pumped down by a combination of a chemistry diaphragm pump with a turbo-molecular drag pump. The residual gases in all UHV devices were analyzed by quadrupole mass spectrometers. The gases

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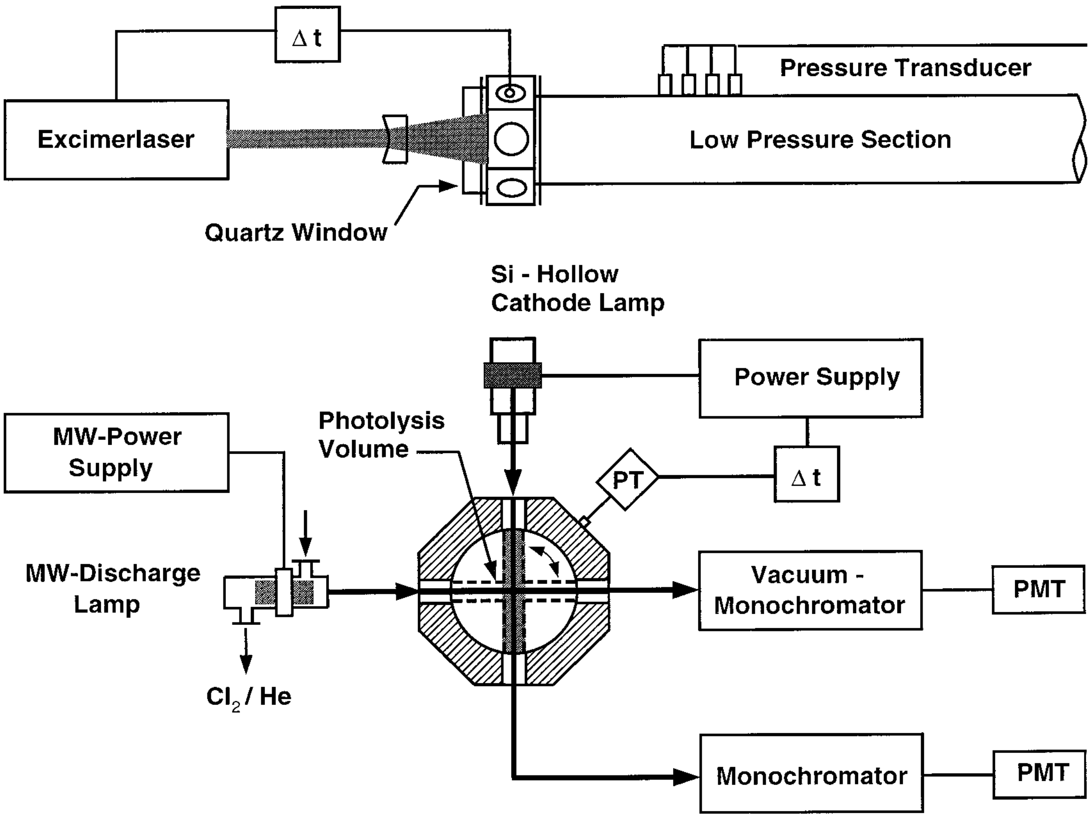

Figure 1. Experimental Setup.

and liquids used were of highest commercial purity: Ar ≥ 99.9999% and $SiCl_4$ ≥ 99.999%. $SiCl_4$, which is liquid at normal conditions, was carefully injected and evaporated in a separated stainless steel vessel. The shock tube was equipped with an ArF-excimer laser (Lambda Physic type EMC 150 MSC) for laser flash photolysis (LFP) experiments at a wavelength of 193 nm ($E_{\text{photon}} = 6.4$ eV $\equiv 148.1$ kcal/mol). A single laser pulse with a duration of about 13 ns was coupled into the measurement plane of the shock tube through the end plate made of quartz glass. The average pulse energy behind the end plate was measured to be 50 ± 7 mJ/pulse, the beam size was 8.0×1.0 cm resulting in an energy density of 6.25 ± 0.9 mJ/cm^2. The laser beam illuminated the whole ARAS absorption pathway located 15 mm apart from the endplate. The laser was electronically triggered after the reflected shock wave has passed the ARAS diagnostic pathway. The delay time was adjustable over the experimental measurement time of 1 ms. A schematic overview of the experimental setup is given in Figure 1.

The Cl-atom ARAS diagnostic system consists of a microwave-excited discharge lamp, the optical absorption path length of the shock tube, a 0.5 m McPherson VUV monochromator, and a solar blind photomultiplier. The microwave lamp was operated with a flowing gas mixture of 0.1% Cl_2 in He maintained at a constant pressure of 6 mbar and a microwave power of about 50 W. Perpendicular to the Cl-detection system, a combination of a pulsed Si hollow cathode lamp, the shock tube absorption path, a 0.25 m Jarrell–Ash monochromator, and a photomultiplier were arranged to detect Si atoms. The spectral shape of both the Cl- and Si-atom resonance lines are not known precisely due to self-absorption and self-reversal in the lamp. Therefore, series of shock wave calibration experiments have been performed to relate the measured absorptions to the corresponding concentrations. Cl-atom calibration was based on the thermal decomposition of CH_3Cl,[15,16] and $SiCl_4$.[10] Shock tube experiments were performed with mixtures of 0.1–5 ppm CH_3Cl and 0.05–5 ppm $SiCl_4$ in Ar at temperatures above 3000 K and pressures around 1.5 bar. Cl-atom absorption was observed at two different Cl-resonance lines: the $[3p^44s(^2P_{3/2}) \leftarrow 3p^5(^2P^0_{3/2})]$ transition at $\lambda = 134.7$ nm and the $[3p^44s(^2P_{3/2}) \leftarrow 3p^5(^2P^0_{1/2})]$ transition at $\lambda = 136.3$ nm. We have monitored two different spin–orbit states, where the $^2P^0_{1/2}$ state is lying 882 cm^{-1} above the $^2P^0_{3/2}$ state. Absorption measurements at 136.3 nm were found to be less sensitive by a factor of 2 compared to the measurements at $\lambda = 134.7$ nm. Therefore, the transition at $\lambda = 134.7$ nm was applied to perform the Cl-calibration procedure. The sensitivity of the Cl calibration does not show any temperature dependence in the investigated temperature range 2500 K $\leq T \leq$ 3800 K and within the experimental uncertainty. Thus, we have extrapolated the validity of the calibration to lower temperatures. Good correspondence between both decomposition systems of CH_3Cl and $SiCl_4$ was found. Si atoms were detected at the $[4s(^3P_2{}^*) \leftarrow 3p^2(^3P_2)]$ transition at $\lambda = 251.6$ nm, which is known to be the most sensitive Si line.[17,18] The calibration was performed on the basis of the dissociation of SiH_4 highly diluted in Ar at temperatures $T > 2000$ K, pressures around 1.6 bar, and mixtures of 0.005–0.5 ppm SiH_4 in Ar, see Mick et al.[19] The results of both calibration series can be expressed by modified Lambert–Beer laws:

$$A = 1 - \exp\left(-\left(\frac{l \times \sigma_\lambda(X)}{\text{cm}^3}\right) \times \left(\frac{[X]}{\text{cm}^{-3}}\right)^n\right) \qquad (1)$$

where l is the absorption length and the concentration exponent n is introduced to describe the nonideal line-emission/line-absorption of ARAS. Best-fit values for σ and n were determined to be

$$\sigma_{134.7}(\mathrm{Cl}) = 9.50 \times 10^{-12}\ \mathrm{cm}^2 \text{ and } n = 0.8$$

$$\sigma_{251.6}(\mathrm{Si}) = 2.75 \times 10^{-11}\ \mathrm{cm}^2 \text{ and } n = 0.8$$

3. Results

Two series of laser flash photolysis experiments have been performed behind reflected shock waves to study the photodissociation of $SiCl_4$ at high temperatures by quantifying the formed Cl and Si atoms.

In the first series of experiments, the concentration of the photolytically generated Cl atoms was measured at temperatures 1000 K $\leq T \leq$ 1510 K. The pressure was around 1.5 bar, the initial $SiCl_4$ concentration highly diluted in Ar varied between 30 and 100 ppm. The time difference between the shock heat-up and the laser pulse was varied between 30 and 600 μs. Figure 2 shows an example of a measured absorption profile at λ = 134.7 nm. A mixture of 100 ppm $SiCl_4$/Ar was heated by the reflected shock (RS) to T = 1113 K and p = 1.8 bar. The sudden increase of absorption at t = 0 to a constant value of 25% is due to the molecular absorption by $SiCl_4$. After a delay time of 175 μs the laser was triggered and the absorption rapidly increases again to a level of about 65% and remains constant until the end of the measurement time. This general behavior was observed for all experiments. The laser-induced absorption level was independent of the delay time, but was found to be dependent on the post-shock temperature.

The absorption cross section of $SiCl_4$ for radiation at λ = 134.7 nm was determined in earlier work by Catoire et al.[9] at temperatures above T = 1100 K, and by Ibuki et al.[20] and Causley and Russel[28] at room temperature. They give a temperature-independent value of $\sigma\,(SiCl_4)_{(134.7\mathrm{nm})} = (3.2 \pm 0.2) \times 10^{-17}$ cm^2 which agrees with our absorption measured behind the reflected shock wave. This temperature-independent cross section is somewhat surprising and might reflect absorption from a low-frequency mode. The instantaneous absorption at λ = 134.7 nm observed after the laser pulse must be attributed to photolytically generated Cl atoms. The molecular absorption by radicals formed during photolysis is expected to be low because their absorption cross sections at the given wavelength can be assumed to be in the range of that of $SiCl_4$ or even smaller. Therefore, all absorption signals were converted into Cl-atom concentration profiles via the calibration relation (eq 1), and were converted in terms of Cl yields, defined as

$$\mathrm{Cl\ yield} = \frac{[\mathrm{Cl}]}{[\mathrm{SiCl_4}]_0} \times 100\% \qquad (2)$$

The Cl yield was found to be temperature dependent with absolute values between 0.1 and 2%. All individual results are shown in the Arrhenius diagram of Figure 3. The temperature dependence of the measured Cl yield can be expressed in the following Arrhenius form:

$$\mathrm{Cl\ yield} = Y_0 \times \exp(-E_A/RT) \qquad (3)$$

The pre-exponential factor is $Y_0 = 68.0^{+34.5}_{-22.91}$%, and the activation energy is E_A = 12.7 ± 1.0 kcal/mol. The line in Figure 3 presents the above expression.

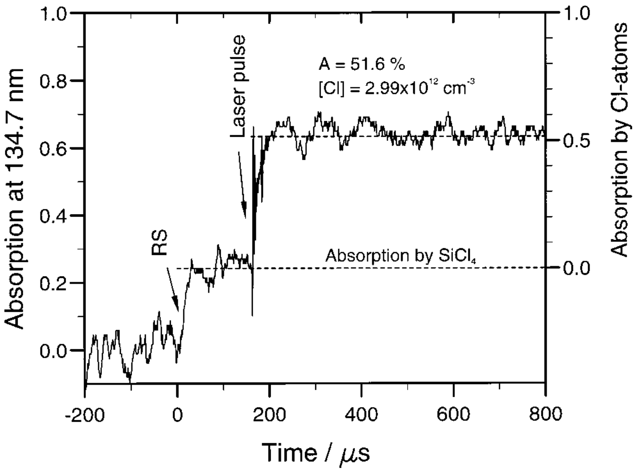

Figure 2. Measured absorption at 134.7 nm during $SiCl_4$ photolysis behind reflected shock wave (RS).

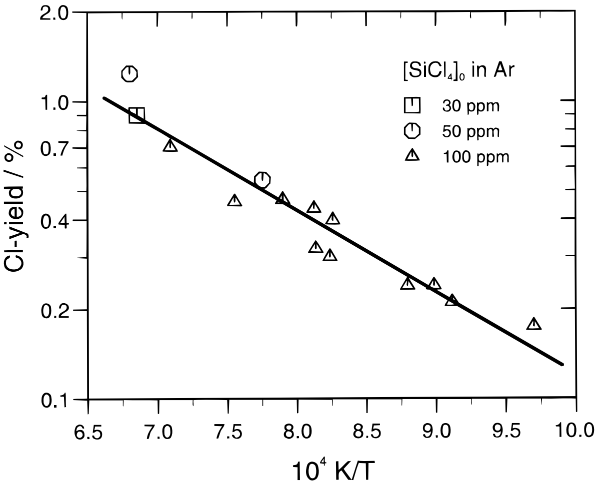

Figure 3. Arrhenius representation of the measured Cl-atom yield.

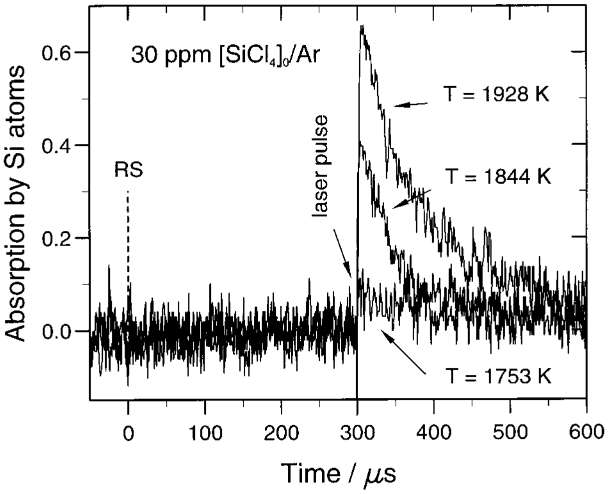

Figure 4. Measured absorption at 251.6 nm during $SiCl_4$ photolysis behind reflected shock wave (RS) at three different temperatures and fixed laser pulse delay time of Δt = 300 μs.

In a second series of experiments, the Si-atom formation in shock-heated mixtures subjected to a laser pulse was measured at temperatures 1750 K $\leq T \leq$ 2050 K. The pressure range used was 1.4−1.8 bar and the $SiCl_4$ content of the gas mixtures was 10−100 ppm highly diluted in argon. At first, the delay time between the arrival of the reflected shock and the laser pulse was kept constant and the gas temperature was varied. Figure 4 shows three absorption profiles measured in a 30 ppm $SiCl_4$/Ar mixture at different temperatures ($p \approx$ 1.7 bar). Time zero is fixed to the arrival of the reflected shock (RS), and the delay time was chosen to be 300 μs. The laser pulse causes an instantaneous increase of absorption followed by a rapid

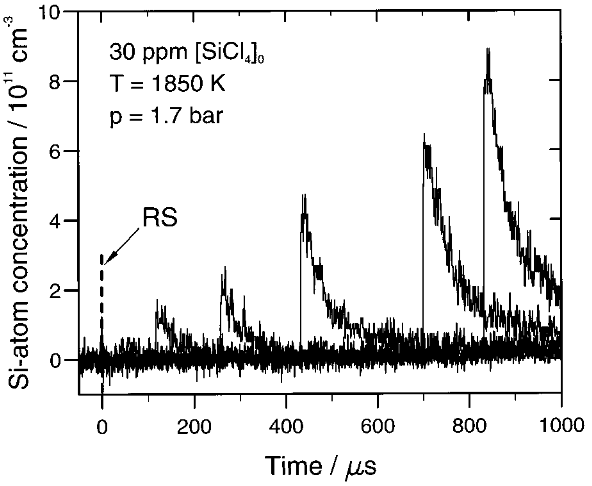

Figure 5. Measured Si-atom concentration profiles for different laser pulse delay times.

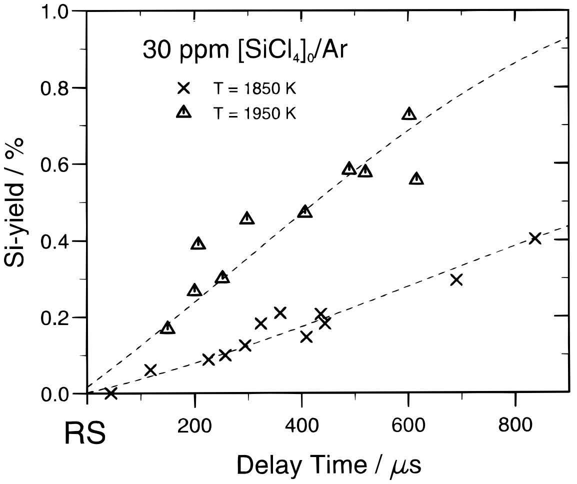

Figure 6. Measured Si yields for different laser pulse delay times.

decrease back to zero within a few hundred microseconds. The absorption peak was found to increase with higher temperatures, whereas the slope of the signal decay depends on the initial $SiCl_4$ concentration. The temperature range of this study was limited at the lower end to $T = 1750$ K, below which no absorption peak could be detected. The upper temperature limit was chosen to be $T = 2100$ K because of the beginning thermal formation of Si atoms. In further experiments the delay time between the reflected shock and the laser pulse was varied for constant temperature. Figure 5 shows five experiments demonstrating the influence of different time delays on Si formation for $T = 1850$ K. The pressure was always about 1.7 bar, and the gas mixture contained 30 ppm $SiCl_4$ in Ar. The absorption signals converted into Si concentrations show increasing peak maxima for longer delay time. All experiments were analyzed in terms of Si-yield defined as

$$\text{Si yield} = \frac{[\text{Si}]}{[\text{SiCl}_4]_0} \times 100\% \tag{4}$$

In Figure 6 the Si yields obtained for two different temperatures are plotted against the delay time. The dashed lines are splines fitted to the experimental points. The increase is nearly linear for both gas temperatures.

4. Discussion

Cl-Atom Measurements. The photoinitiated Cl-atom formation studied over a certain temperature range showed a clear temperature dependence. At those conditions the thermal decomposition of $SiCl_4$ is unimportant,[9,10] which agrees with our observation in cases where the laser was not fired. An ineffective, temperature-dependent, photolytical Cl-atom abstraction from $SiCl_4$ must be proposed. Considering the reaction enthalpies of possible Cl-abstracting photolysis reactions, only reaction P1 has a reaction enthalpy which is below the available photon energy of 148 kcal/mol (≡ 193 nm) for single-photon absorption.

$$\text{SiCl}_4 \xrightleftharpoons{h\nu} \text{SiCl}_3 + \text{Cl}\ \Delta H^R_{298} = 110.4\ \frac{\text{kcal}}{\text{mol}} \tag{P1}$$

$$\text{SiCl}_4 \xrightleftharpoons{h\nu} \text{SiCl}_2 + 2\text{Cl}\ \Delta H^R_{298} = 176.1\ \frac{\text{kcal}}{\text{mol}} \tag{P1a}$$

$$\text{SiCl}_4 \xrightleftharpoons{h\nu} \text{SiCl} + \text{Cl}_2 + \text{Cl}\ \Delta H^R_{298} = 225.3\ \frac{\text{kcal}}{\text{mol}} \tag{P1b}$$

The thermodynamic data used were taken as recommended in ref 21. Su and Schlegel,[22] Ho et al.,[23] and recently Bauschlicher and Partridge[24] calculated the heat of formation of $SiCl_n$ ($n = 1-4$) species by using somewhat different computational ab initio methods, but all results are in good agreement.

A temperature-dependent absorption coefficient of $SiCl_4$ at 193 nm, k_{193} (T) can be estimated, on the basis of the measured Cl yield. According to a simplified theory by Davidson et al.[27] and Dean et al.[26] for a product concentration profile during excimer laser photolysis, an absorption coefficient k_{193} (T) can be expressed:

$$k_{193}(T) = \frac{X_p}{X_0} \times \frac{h\nu}{E} \times \frac{N_A}{RT}(\text{atm}^{-1}\,\text{mol}^{-1}) \tag{5}$$

This equation is based on the assumption of a unity quantum yield and a unity product concentration profile over the photolytic pathway.[26] X_p is the product mol fraction and X_0 is the mole fraction of the absorbing species prior to photolysis. E is the photon energy (J/cm^{-2}), h the Planck constant, ν the frequency, N_A is Avogadro's number (mol^{-1}), and R is the universal gas constant. The following least-squares fit represents our calculated k_{193} data over the range 1000 K ≤ T ≤ 1510 K:

$$k_{193}(T) = 0.045 \pm 0.022 \times \exp(0.0036 \pm 3.5 \times 10^{-4} \times T)\ \text{atm}^{-1}\,\text{mol}^{-1} \tag{6}$$

This value is determined on the basis of the Cl-atom yield measurements and reflects therefore the absorption coefficient for the photolysis reaction (P1) only. Another energetically possible pathway for single-photon dissociation of $SiCl_4$ is the decomposition into $SiCl_2 + Cl_2$ ($\Delta H^R_{298} = 118.1$ kcal/mol) for which no statement can be made here. Overall absorption coefficients for VUV absorption of $SiCl_4$, $SnCl_4$, $GeCl_4$, and CCl_4 at room temperature are given by Causley and Russell.[28] $SiCl_4$ shows no absorption band around 193 nm. This agrees quite well with our low absorption coefficients at higher temperatures (e.g., k_{193} (1200 K) = 3.3 atm^{-1} cm^{-1}). There are no literature data known for the high-temperature absorption coefficient of $SiCl_4$ or other chlorides.

Because of the low photoefficiency we can assume that more than 99% of the initial $SiCl_4$ concentration survives the laser pulse. The Cl atoms formed were found to remain constant in all experiments, which must be expected because of the high

TABLE 1: Simplified Reaction Mechanism of the High-Temperature $SiCl_4$/Ar Pyrolysis/Photolysis System, $k_i = A \times T^n \times exp(-T_A/T)$ cm^3 mol^{-1} s^{-1}

		rate coefficient			
	reaction	A	n	T_A	ref
P1	$SiCl_4 \xrightarrow{h\nu} SiCl_3 + Cl$				this work
P2	$SiCl_2 \xrightarrow{h\nu} Si + Cl_2$				this work
R1	$SiCl_4 + Ar \rightleftharpoons SiCl_3 + Cl + Ar$	6.9×10^{16}		37 760	10
R2	$SiCl_3 + Ar \rightleftharpoons SiCl_2 + Cl + Ar$	4.6×10^{15}		32 815	10
R3	$SiCl_2 + Ar \rightleftharpoons SiCl + Cl + Ar$	1.7×10^{15}		36 865	10
R4	$SiCl + Ar \rightleftharpoons Si + Cl + Ar$	1.4×10^{40}	−7.0	49 315	10
R5	$SiCl_4 + Si \rightleftharpoons SiCl_2 + SiCl_2$	4.0×10^{13}			25
R6	$SiCl_4 + Cl \rightleftharpoons SiCl_3 + Cl_2$	$\leq 1.0 \times 10^{10}$			this work

reaction enthalpy for the reaction between Cl and $SiCl_4$.

$$SiCl_4 + Cl \overset{k_2}{\rightleftharpoons} SiCl_3 + Cl_2 \quad \Delta H^R_{298} = 52.9\ \frac{\text{kcal}}{\text{mol}} \quad \text{(R6)}$$

An upper limit of $k_2 \leq 1 \times 10^{10}$ cm^3 mol^{-1} s^{-1} can be estimated for which no measurable consumption of Cl by reaction with $SiCl_4$ occurs.

Si-Atom Measurements. Si-atoms were measured at temperatures $T \geq 1750$ K where $SiCl_4$ has already started to decompose thermally. The maximum Si concentration was reached immediately after the laser pulse and was strongly dependent on both the delay time between shock heating and laser flash and the post-shock temperature. These observations suggests a direct photolytic dissociation of one of the $SiCl_4$ pyrolysis products. Possible candidates are $SiCl_3$, $SiCl_2$, and SiCl. Regarding the reaction enthalpies, only those of P2 and

$$SiCl_2 \overset{h\nu}{\rightleftharpoons} Si + Cl_2\ \Delta H^R_{298} = 148.0\ \frac{\text{kcal}}{\text{mol}} \quad \text{(P2)}$$

$$SiCl_3 \overset{h\nu}{\rightleftharpoons} Si + Cl_2 + Cl\ \Delta H^R_{298} = 213.2\ \frac{\text{kcal}}{\text{mol}} \quad \text{(P2a)}$$

$$SiCl_2 \overset{h\nu}{\rightleftharpoons} Si + 2Cl\ \Delta H^R_{298} = 206.0\ \frac{\text{kcal}}{\text{mol}} \quad \text{(P2b)}$$

$$SiCl \overset{h\nu}{\rightleftharpoons} Si + Cl\ \Delta H^R_{298} = 98.80\ \frac{\text{kcal}}{\text{mol}} \quad \text{(P2c)}$$

P2c are below the photon energy of 148 kcal/mol, whereby the reaction enthalpy of reaction P2 agrees almost exactly with the energy of a single photon at 193 nm. The supposition that $SiCl_2$ is the most probable candidate for photolytic Si formation is further supported by the kinetics of $SiCl_4$ thermal decomposition. The simplified reaction mechanism listed in Table 1 was used to calculate the concentrations of SiCl, $SiCl_2$, and $SiCl_3$ for the two reaction conditions of Figure 6. Because of the high dilution, only Cl abstraction reactions were considered. The results summarized in Figure 7 clearly indicate that the calculated $SiCl_2$ concentration profiles correlate with the measured Si yield of Figure 6. This is further illustrated in Figure 8, where—in normalized representation—the measured post-flash maximum Si concentration is compared with the calculated $SiCl_2$ profile for the same experimental conditions. The agreement is almost perfect and underlines the supposition of $SiCl_2$ being the precursor for the photolytic generation of Si.

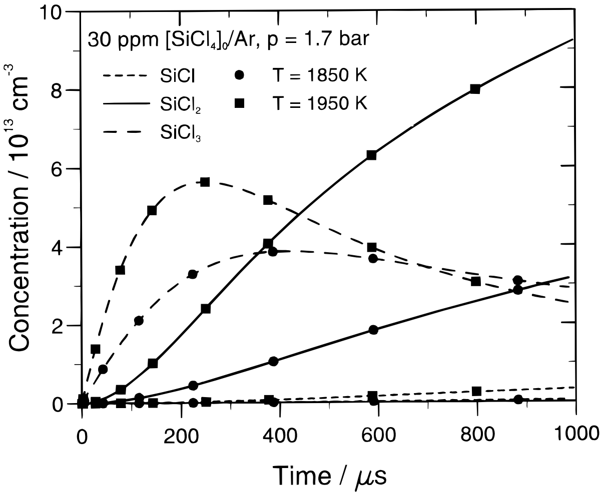

Figure 7. Species concentration profiles calculated during thermal decomposition of $SiCl_4$ with the reaction mechanism of Table 1 for the reaction conditions of Figure 6.

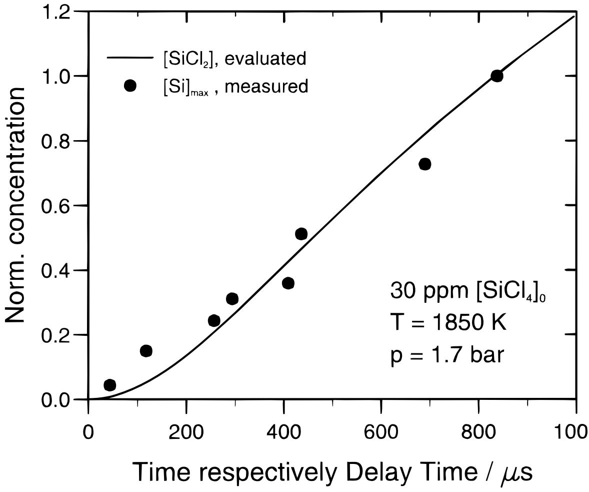

Figure 8. Comparison between $SiCl_2$ concentration calculated on the basis of the mechanism of Table 1 and measured laser flash initiated maximum Si concentration after shock heat-up.

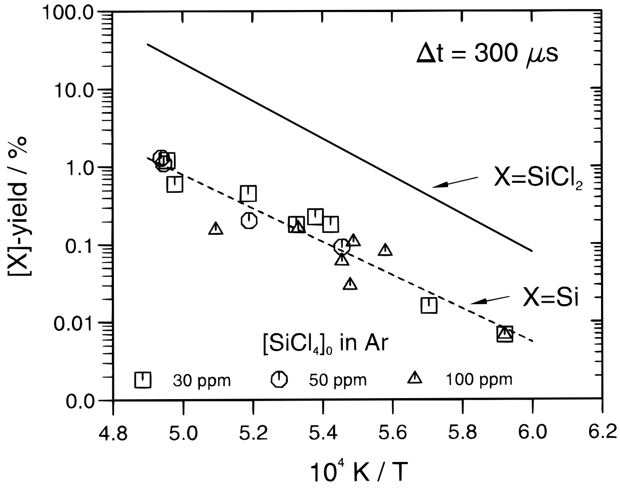

Figure 9. Arrhenius representation of the calculated $SiCl_2$ and measured Si yield.

Considering the temperature dependence of the photolytic Si yield for a fixed delay time, a second similarity with the computed $SiCl_2$ concentration is remarkable. In the Arrhenius diagram of Figure 9 the measured Si yield obtained from three different initial gas mixtures for a laser flash delay time of $\Delta t = 300\ \mu$s is compared with the calculated $SiCl_2$ yield. As expected, both properties disagree significantly in their absolute values, but the temperature dependence is very similar. Both

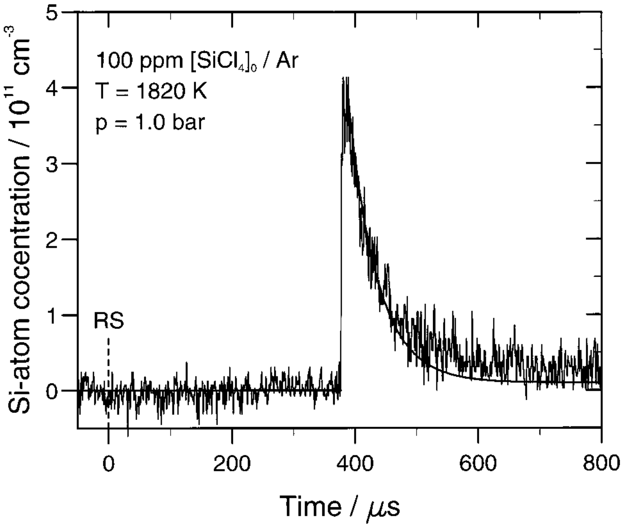

Figure 10. Comparison of measured and calculated Si-concentration profile using the reaction mechanism of Table 1.

yields can be expressed by the following Arrhenius expressions:

$$\text{Si yield} = 3.7 \times 10^{10\pm0.92} \times \exp\left(-97.72 \pm 7.85\frac{\text{kcal}}{\text{mol}}/RT\right)\% \quad (7)$$

$$\text{SiCl}_2\text{ yield} = 3.2 \times 10^{13} \times \exp\left(-111.2\frac{\text{kcal}}{\text{mol}}/RT\right)\% \quad (8)$$

The activation energies agree well within their error limits. The absolute values of the Si yield represents about 3% of the calculated $SiCl_2$ yield.

For the above reasons the photolytic dissociation of $SiCl_2$ via reaction P2 must be proposed for the observed nearly instantaneous formation of Si. The fast decay of the Si-atom concentration is mainly due to the known reaction of Si with $SiCl_4$, see Kunz and Roth.[25] We therefore have tried to compare the measured Si-time behavior with computer simulations on the basis of the simplified kinetic mechanism of Table 1. An example is shown in Figure 10. For the given experimental conditions, the modeling of the $SiCl_4$ thermal decomposition was started at $t = 0$ (arrival of the reflected shock). During the first 300 μs there is nearly no Si formation. At a delay time of $\Delta t = 380$ μs, the laser flash was modeled by interrupting the calculation, converting about 3% of the momentary $SiCl_2$ concentration into Si and Cl_2, and continuing the calculation. According to Figure 10, this results in a Si peak followed by a fast decay. The agreement with the experimental trace (noisy line) is very good, indicating that the model is quite suitable for interpreting all the experimental findings.

5. Conclusion

Laser flash photolysis of $SiCl_4$ at 193 nm has been investigated at high temperatures behind reflected shock waves by ARAS measurements of Cl and Si atoms in highly diluted $SiCl_4$/Ar gas mixtures. The temperature-dependent Cl yield obtained could easily be interpreted by the direct photolytic dissociation of $SiCl_4$. The measured Si yield was strongly dependent on the delay time between shock wave heating and laser pulse and increased with higher temperatures. These observations and energetic considerations led to the assumption that Si is formed by the photolytic dissociation of the $SiCl_4$ pyrolysis product $SiCl_2$. Computer simulations based on a proposed simplified reaction mechanism confirmed the above assumption.

Acknowledgment. The authors thank Mrs. N. Schlösser for her help conducting the experiments. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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