# High-Temperature Kinetics of Si + N<sub>2</sub>O

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In the present study the very fast high-temperature thermal decomposition of silane was used as a Si atom source to initiate its reactions with N<sub>2</sub>O. The experiments were performed behind reflected shock waves in SiH<sub>4</sub>/ N<sub>2</sub>O/Ar systems by applying Atomic Resonance Absorption Spectroscopy (ARAS) for detecting Si and N atoms. Initial mixtures of 0.5–50 ppm SiH<sub>4</sub> and 25–200 ppm N<sub>2</sub>O were used to perform experiments in the temperature range 1780 K  $\leq T \leq 3560$  K at pressures 0.5 bar  $\leq p \leq 1.7$  bar. From the Si atom concentration profiles the overall rate coefficient of the reaction Si + N<sub>2</sub>O  $\rightleftharpoons$  products (R3;  $k_3$ ), was determined by fitting calculated to measured profiles. From energetical reasons reaction R3 can proceed via two exothermic product channels: Si + N<sub>2</sub>O  $\rightleftharpoons$  SiN + NO (R3a;  $k_{3a}$ ) and Si + N<sub>2</sub>O  $\rightleftharpoons$  SiO + N<sub>2</sub> (R3b;  $k_{3b}$ ). To separate both possible channels, N atoms were measured, which are to be expected from secondary reactions including the products of the channel (R3a). Again by computer fittings rate coefficients for  $k_{3a}$  were obtained, which can be summarized by the following Arrhenius expression:  $k_{3a} = 5.0 \times 10^{14} \exp(-8100 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} (\pm 50\%)$ . From the results of both, Si and N atom measurements, a mean value for the remaining rate coefficient  $k_{3b} = 8.0 \times 10^{13}$ cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> ( $\pm 50\%$ ) was obtained. Detailed computer simulations based on a proposed reaction mechanism revealed estimates of further rate coefficients.

### 1. Introduction

In spite of the major role of silane chemistry in chemical vapor deposition and in production of new ceramic materials, the elementary reactions of silane and its fragments are rarely studied. Particularly high-temperature kinetic data of bimolecular reactions including silicon atoms are not available in the literature. Only room-temperature studies were performed by Husain and Norris<sup>1,2</sup> and Swearengen et al.<sup>3</sup> They measured Si atom absorption in numerous reaction systems and determined rate coefficients of elementary reactions of Si atoms with other species. In the present investigation the reaction Si + N<sub>2</sub>O was studied at higher temperatures by measuring the time-dependent Si and N atom concentrations. To our knowledge it is the first time that this reaction was studied at such high temperatures.

#### 2. Experimental Section

The experiments were conducted behind reflected shock waves in a stainless steel shock tube of 79-mm inner diameter. The tube is constructed as heatable ultra-high-vacuum apparatus and can be evacuated through a special end-plate valve using a forepump, a turbo-molecular pump, and a liquid nitrogen-cooled titanium sublimation pump, down to pressures of about  $1 \times 10^{-8}$ mbar. Typical leak-plus-out-gassing rates were  $5 \times 10^{-6}$  mbar/ min. A more detailed description of the apparatus and the experimental procedure is given by Roth and Just<sup>4</sup> and Thielen and Roth.<sup>5</sup>

The gases used were carefully mixed in a stainless steel cylinder by the partial pressure method. The gas mixing setup can be heated and evacuated like the shock tube. Due to the high sensitivity of the ARAS detection technique the test gases were of ultra-high purity: Ar (99.9999%), SiH<sub>4</sub> (99.995%), N<sub>2</sub>O (99.997%). Initial mixtures of 0.5–50 ppm SiH<sub>4</sub> and 25–200 ppm N<sub>2</sub>O diluted in Ar were used. Prior to each run the tube was evacuated to pressures of  $5 \times 10^{-7}$  mbar or lower. Diaphragms made of aluminum, 30 or  $50\,\mu$ m thick, were ruptured by increasing the driver gas (H<sub>2</sub>) pressure. Temperatures and pressures behind the reflected shock waves were calculated from the incident shock speed, which was measured by four thin film gauges, placed along the test section at known intervals. The optical detection technique for measuring Si and N atom absorption is a line emission-line absorption method. In the case of N atoms the arrangement consists of a microwave-excited discharge lamp, the absorption zone in the shock tube separated on both sides by two thin LiF windows, a 1-m McPherson vacuum UV monochromator, and a special solar blind photomultiplier. The spectral NI line at  $\lambda = 119.9$  nm was excited in gas mixtures containing 1% N<sub>2</sub> passing through the lamp at pressures of 6 mbar. In the case of Si atoms the detection system consists of a pulsed hollow-cathode lamp, the shock tube absorption zone, a 0.25-m Jarrel-Ash monochromator, and a photomultiplier. The Si triplet transition [4s(<sup>3</sup>P<sub>J</sub>)  $\leftarrow$  3p<sup>2</sup>(<sup>3</sup>P<sub>J</sub>)] at  $\lambda = 251.6$  nm is known to be the most sensitive line for atomic absorption spectroscopy.<sup>2.6</sup>

The spectral shapes of the lines emitted by the discharge as well as by the hollow-cathode lamp are not known in detail. Hence a simple relation between the directly measured absorption and the atom concentration does not exist. Therefore a series of carefully controlled shock wave calibrations have been done to relate the measured absorptions to the corresponding Si and N atom concentrations. The N atom calibration is based on the NO-N-O quasi-equilibrium at temperatures  $T \ge 5300$  K; see Thielen and Roth.<sup>7</sup> The Si atom calibration is based on the very rapid dissociation of SiH<sub>4</sub> at temperatures above 2000 K; see Mick et al.<sup>8,9</sup> Results of the calibration procedures are represented in Figure 1, where the open symbols correspond to N atom and the closed symbols to Si atom calibration.

### 3. Results and Discussion

Si Atom Measurements. The reaction of Si atoms with N<sub>2</sub>O was studied behind reflected shock waves by Si atom concentration measurements in the temperature range 1780 K  $\leq T \leq 3125$  K at pressures between 0.4 and 1.5 bar. Initial mixtures of 0.5–1.0 ppm SiH<sub>4</sub> and 100–200 ppm N<sub>2</sub>O diluted in Ar were used. The measured light extinction signals can be set equal to the absorption by Si atoms, since no interference absorptions of other species were observed. Thus the transformation to concentration profiles can be done by applying the corresponding calibration curve, which is illustrated in Figure 1.

The Si atom absorption measurements can be grouped according to temperature and reaction time into two parts.

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Figure 1. Calibration curves for Si and N atoms.



Figure 2. Measured and calculated Si atom concentration profile based on reactions R1, R2, R3, and R7 at low temperature.

TABLE 1: Simplified Reaction Mechanism of the SiH<sub>4</sub>/N<sub>2</sub>O System Highly Diluted in Ar  $(k_i = AT^n \exp(-E_a/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ 

no.	reacn	rate coeff			
		A	n	E <sub>a</sub>	ref
1	$SiH_4 + Ar \rightleftharpoons SiH_2 + H_2 + Ar$	9.9 × 10 <sup>15</sup>		24 000	8
2	$SiH_2 + Ar \rightleftharpoons Si + H_2 + Ar$	9.1 × 10 <sup>13</sup>		15 100	8
3a	$Si + N_2O \rightleftharpoons SiN + NO$	$5.0 \times 10^{14}$		8 100	see text
3b	$Si + N_2O \rightleftharpoons SiO + N_2$	$8.0  imes 10^{13}$			see text
4	Si + OH ≠ SiO + H	$2.0  imes 10^{14}$			see text
5	$SiN + O \rightleftharpoons SiO + N$	$4.0  imes 10^{13}$			see text
6	Si + NO ≓ SiO + N	$3.2 \times 10^{13}$		1 775	9
7	$N_2O + Ar \rightleftharpoons N_2 + O + Ar$	$1.8 \times 10^{26}$	-3.1	33 720	10
8	$N + NO \rightleftharpoons N_2 + O$	$2.0 \times 10^{13}$			9
9	$O + H_2 \rightleftharpoons OH + H$	$3.7 \times 10^{6}$	2.3	4 080	11
10	$N + OH \rightleftharpoons NO + H$	$2.0 \times 10^{13}$			10
11	$H_2 + Ar \rightleftharpoons H + H + Ar$	$2.0 \times 10^{14}$		48 360	10
12	$H_2 + N_2 O \Longrightarrow H_2 O + N_2$	$2.0 \times 10^{11}$	0.5		10

Experiments belonging to the first group were performed at temperatures  $T \le 2135$  K. A typical example is illustrated in Figure 2 showing the Si atom concentration versus reaction time. The time zero indicates the arrival of the reflected shock wave in the measurement plane. The Si atoms were generated very rapidly within 20  $\mu$ s and decreased again to zero in a short time period, in this example after about 150  $\mu$ s. This principle behavior was observed in all experiments of this series. The measured Si atom time histories can well be understood by applying the simplified reaction mechanism of Table 1. According to this scheme, the Si atoms were generated via reactions R1 and R2; the corresponding rate coefficients were determined in previous experiments by Mick et al.<sup>8</sup> The well-known thermal decomposition of N<sub>2</sub>O (eq R7) and the overall reaction of Si atoms with



Figure 3. Measured and calculated Si atom concentration profile based on reactions R1, R2, R3, R4, and R7 at high temperature.

 $N_2O$  (eq R3) have the highest sensitivity to the Si atom decay. All other reactions have practically no effect on the Si atom time histories and can therefore be neglected. The only unknown rate parameter in the mechanism of Table 1 is the rate coefficient of reaction

$$Si + N_2O \stackrel{k_3}{\Longrightarrow} products$$
 (R3)

The strong influence of this reaction on the Si atom profiles is also demonstrated in Figure 2 by varying  $k_3$  by factors of 2 and 0.5, respectively; see thin lines. From computer fittings of about 8 Si atom profiles measured in the range 1780 K  $\leq T \leq 2135$ K rate coefficients for  $k_3$  were obtained; see solid points in Figure 4.

The second series of experiments was performed at temperatures  $T \ge 2470$  K. A typical example is illustrated in Figure 3, showing a very rapid increase of the Si atom concentration behind the reflected shock wave followed by a rapid consumption during the first 50  $\mu$ s. The remaining Si atoms decrease slowly during the reaction time of about 800  $\mu$ s. The first part of this profile can be described just like the experiments performed at lower temperatures. The calculated dashed lines in Figure 3 indicate the strong influence of  $k_3$  on the remaining Si atoms after the first consumption. From computer fittings of 11 measured Si atom profiles at short reaction times, rate coefficients for  $k_3$  were determined for conditions 2470 K  $\leq T \leq$  3125 K. The data points obtained are also summarized as solid circles in the Arrhenius diagram of Figure 4. Both groups of Si atom experiments are suited to determine the rate coefficient of the overall reaction  $Si + N_2O$  and are not suited to distinguish between possible reaction product channels. To clarify this situation additional N atom measurements were performed, which will be discussed later.

To understand the high-temperature Si atom profiles at longer reaction times, i.e. the slowly increasing part, an additional Si atom consuming reaction must be considered. As the OH concentration is relatively high at this reaction conditions, the exothermic reaction

Si + OH 
$$\stackrel{k_4}{\rightleftharpoons}$$
 SiO + H  $\Delta^R h_{298} = -88.9 \text{ kcal/mol}$  (R4)

seems to be a good candidate. The influence of this reaction on the Si atom profiles is also shown in Figure 3; see solid thin lines. In that case the rate coefficient  $k_4$  used for the best fit (solid line) was varied by factors of 2 and 0.5, respectively. The results of all fitting procedures to the experimentally observed profiles can be summarized by a temperature-independent rate coefficient of

$$k_4 = 2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The uncertainty due to calibration and experimental scatter is



**Figure 4.** Arrhenius diagram of the overall reaction rate  $k_3$  and the two product channels  $k_{3a}$  and  $k_{3b}$ .

about  $\pm 50\%$ . An alternative description of the Si atom behavior at longer reaction times is possible by considering the recombination reaction Si + O + Ar  $\rightarrow$  SiO + Ar. The measured profiles can also well be fitted by a rate coefficient of  $2 \times 10^{17}$  cm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup>.

N Atom Measurements. The apparent non-Arrhenius behavior of the overall reaction R3 needs a more detailed analysis of possible reaction product channels. From energetic reasons the two exothermic pathways forming SiN and SiO should be considered:

$$\operatorname{Si} + \operatorname{N}_2 O \stackrel{k_{3a}}{\rightleftharpoons} \operatorname{SiN} + \operatorname{NO} \quad \Delta^R h_{298} = -16.0 \text{ kcal/mol} \text{ (R3a)}$$

$$\operatorname{Si} + \operatorname{N}_2 O \rightleftharpoons^{k_{3b}} \operatorname{SiO} + \operatorname{N}_2 \quad \Delta^R h_{298} = -151.3 \text{ kcal/mol} (R3b)$$

The product NO of reaction R3a is known to react with Si to form N atoms and SiO. Also the other reaction product SiN of reaction R3a can in a subsequent reaction be oxidized to form also N atoms. To the contrary, the reaction products of (R3b) are rather stable and are not expected to undergo significant further reactions. It seems therefore useful to perform N atom measurements in the SiH<sub>4</sub>/N<sub>2</sub>O reaction system and to get in this way an insight into the relative importance of the proposed two channels of reaction R3.

The N atom measurements were performed in mixtures containing 15-50 ppm SiH<sub>4</sub> and 25-100 ppm N<sub>2</sub>O diluted in Ar. The temperature range was 1930 K  $\leq T \leq$  3560 K and the pressure 0.8  $\leq p \leq$  1.7 bar. Before the measured light extinction signals are evaluated, the interference absorption of the NI spectral line by the initial reactants or by important intermediates must carefully be measured. From low-temperature shock tube experiments in N<sub>2</sub>O/Ar mixtures the interference absorption of NI radiation by N<sub>2</sub>O was determined to be

$$\sigma_{\rm NI}({\rm N_2O}) = 1.0 \times 10^{-17} \exp(-400 {\rm K}/T) {\rm cm}^2$$

From this data the interference absorption of N<sub>2</sub>O can be estimated to be always below 3% under the experimental conditions of this study and consequently be neglected. The measured NI absorption can directly be related to N atom concentration according to the calibration curve given in Figure 1. A typical N atom concentration profile showing a delayed appearance of N, a maximum value of about  $2.5 \times 10^{12}$  cm<sup>-3</sup> followed by a slight decrease is illustrated in Figure 5. This N atom time history can well be understood by considering reactions R5 and R6 of



Figure 5. Measured and calculated N atom concentration profile based on the reaction scheme of Table 1.

the mechanism given in Table 1. In that case the N atom formation proceeds via reactions of the products of reaction R3a with either Si or O:

$$SiN + O \stackrel{k_5}{\rightleftharpoons} SiO + N \qquad \Delta^R h_{298} = -59.6 \text{ kcal/mol} \quad (R5)$$

$$NO + Si \rightleftharpoons^{k_6} SiO + N \qquad \Delta^R h_{298} = -168.6 \text{ kcal/mol} \quad (R6)$$

The rate coefficient  $k_6$  is known from previous measurements; see Mick et al.<sup>9</sup> The only remaining unknown rate coefficients in the scheme of Table 1 with sensitivity to N atoms are  $k_{3a}$  and  $k_5$ . Their relative influence on calculated N atom profiles is demonstrated in Figure 5. It can be seen that reaction R3a affects the N atom profile strongly during the whole formation process. To the contrary, variations of  $k_5$  have an effect on N at early reaction time. From a total of 13 individual N atom measurements rate parameters for  $k_5$  and  $k_{3a}$  were determined by fitting calculated to measured N atom profiles based on the mechanism given in Table 1. The results can be expressed by

$$k_5 = 4.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
  
 $k_{3a} = 5.0 \times 10^{14} \exp(-8100 \text{K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 

The individual  $k_{3a}$  values obtained from computer fittings are summarized in Figure 4, open circles. The standard deviation due to experimental scatter is about  $\pm 25\%$ . The combined uncertainty from the calibration procedure and the experimental scatter is about  $\pm 50\%$ . From both the overall rate coefficient  $k_3$ obtained from Si atom measurements and  $k_{3a}$  obtained from N atom measurements, the remaining  $k_{3b}$  value can be determined. The evaluation results in a temperature independent value of

$$k_{3b} = 8.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

which is also shown as a dashed line in Figure 4. From Si atom measurements at low temperatures the uncertainty of the rate coefficient due to experimental scatter can be approximated to be  $\pm 20\%$ . The combined uncertainty due to calibration and experimental scatter is about  $\pm 50\%$ . Beside the above given uncertainties the rate coefficients  $k_3$  and  $k_{3a}$  were strongly influenced by the rate coefficient  $k_7$ , especially at temperatures above 3000 K. An uncertainty of  $k_7$  of  $\pm 50\%$  results in the same uncertainty for  $k_3$  and  $k_{3a}$ . This effect decreases with decreasing temperature.

In this study the rate coefficients of the reactions R3a, R3b, R4, and R5 were determined, but to our knowledge only reaction R3b has been discussed in the literature. Husain and Norris<sup>2</sup> determined  $k_{3b}$  from Si atom absorption measurements at room temperature. They found a value of  $k_{3b} = 1.14 \pm 0.12 \times 10^{14}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is about 30% higher than the present value.

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Swearengen et al.<sup>3</sup> studied the same reaction in a flow tube system at T = 350 K. The rate coefficient determined in their study was  $k_{3b} = 4.9 \pm 2.5 \times 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is about 40% lower than the present value. Although the agreement between all three studies is not perfect, the experimental results are all within the uncertainty limit of the present study.

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