A High Temperature Study of the Reaction $SiH_4+H \leftrightharpoons SiH_3+H_2$

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The reaction of silane with H atoms

$$SiH_4+H \overset{k_5}{\rightleftharpoons} SiH_3+H_2 \qquad (R5)$$

was studied behind reflected shock waves at temperatures between 998 K and 1273 K and pressures around 1.5 bar. The thermal decomposition of a few ppm ethyl iodide (C_2H_5I) was used as a well known H-atom source. The atomic resonance absorption spectroscopy (ARAS) was applied for time resolved and simultaneous measurements of H- and Si-atom concentrations. The presence of an excess of SiH_4 causes a fast consumption of H atoms according to reaction (R5). The signals obtained were kinetically evaluated by computer simulations based on a simplified reaction mechanism. The rate coefficient for reaction (R5) was found to be:

$$k_5 = 7.8\times10^{14} \exp(-2260/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

1. Introduction

Kinetic parameters of gas-phase reactions of silicon-containing species are of high interest because of their importance in chemical vapour deposition (CVD) processes as well as for the production of ceramic materials. For the modelling of such processes, the knowledge of various kinetic parameters is needed. Especially reactions of H atoms are of general interest in the silane chemistry, because of their known high reactivity towards silane and its derivatives. Also silyl radicals (SiH_3) play an important role in photo-CVD and plasma-CVD processes [1, 2]. It is therefore of general interest to study the hydrogen abstraction from SiH_4 by the reaction:

$$SiH_4 + H \overset{k_5}{\rightleftharpoons} SiH_3 + H_2 \qquad (R5)$$

Rate constants for (R5) have been determined in the past by several groups, mostly at room temperature. Cowfer et al. [3] and Austin and Lampe [4] applied a time of flight mass spectrometer in discharge [3] or photolysis [4] flow reactors. A flow technique combined with L_α absorption spectroscopy was used by Choo et al. [5], Wörsdorfer et al. [6], and Arthur et al. [7]. Reaction (R5) was also studied by Johnson et al. [8] in a remote plasma reactor applying electron spin resonance (ESR). Loh and Jasinski [9] observed silyl radicals by diode laser absorption in a flow reactor. They used a limited reaction mechanism involving (R5) to model the measured SiH_3 signals in a HCl/SiH_4 reaction system. VUV-LiF was employed by Koshi et al. [10] in a flow reactor to measure the rate coefficient k_5. An extensive literature review is given by Arthur and Bell [11]. Matsui et al. [12] used a theoretical study to determine k_5. The conditions and rate coefficients obtained in the above mentioned works are listed in Table 1.

All previous studies on the rate coefficient k_5 are restricted to temperatures $T<400$ K. It is the aim of the present work to enlarge the temperature range to about 1300 K. In the shock tube experiments, ethyl iodide was used as a well known H-atom source [13], and its reaction with silane was measured by H-atom ARAS (Atomic Resonance Absorption Spectroscopy). A temperature dependent rate constant could be determined which is in good agreement with earlier studies when extrapolated to lower temperatures.

2. Experiment

The experiments were carried out behind reflected shock waves in a stainless steel shock tube of 79 mm internal diameter. The driver section was 3.5 m, the driven section 5.7 m in length, which was specially prepared for ultra-high-vacuum (UHV) requirements. The driver section can be baked out and pumped down to pressures below 5×10^{-8} mbar. The residual gases in all UHV devices were analysed by quadrupole mass-spectrometers, and were found to be practically free of hydrocarbons. More details of the experimental setup and the experimental procedure are given elsewhere [14]. The gas mixtures were prepared manometrically in a stainless steel UHV cylinder. All gases used were of highest commercial purity: Ar≥99.9999%, SiH_4≥99.995%, C_2H_5I≥99%. Ethyl iodide which is liquid at normal conditions was carefully injected and evaporated in a separated stainless steel vessel.

The H-atom ARAS diagnostic system consists of a microwave excited discharge lamp, the optical path length, a 1 m McPherson VUV monochromator, and a solar blind photomultiplier. The lamp was operated with a flowing gas mixture of 1% H_2 in He maintained at a constant pressure of 6 mbar and a microwave power of about 50 W. Si atoms were detected at the $[4\,s^3P_2^* \leftarrow 3p_2\,{}^3P_2]$-transition at $\lambda=251.6$ nm, which is known to be the most sensitive Si-line [15, 16]. A combination of a pulsed Si hollow cathode lamp, a 0.25 m Jarrell Ash monochromator, and a photomultiplier was used. The spectral shape of both the H- and Si-atom resonance lines are not known

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Table 1
Overview of experimental studies on the reaction SiH_4+H

Exp. System	T/K	p/bar	k/cm^3 mol^{-1} s^{-1}	Ref.
Flow/H_2-discharge/Mass Spec.	298	0.004	1.57×10^{11}	[3]
Flow/H_2-Hg phot./Mass Spec.	305	0.0267–0.08	2.59×10^{11}	[4]
Flow/H_2-discharge/L_α	300	0.0267	5.12×10^{12}	[5]
Flow/H_2-phot./L_α	298	0.65	2.65×10^{11}	[6]
Flow/H_2-phot./L_α	294–487	1	1.39×10^{13} exp (−1400/T)	[7]
Flow/H_2-discharge/ESR	298	0.00267	2.4×10^{11}	[8]
Flow/H_2-phot./Kin. Modell	298	0.0127	1.51×10^{11}	[9]
Static/Radiolytic Exp./L_α	300	1.07–2.27	2.77×10^{11}	[26]
Theoretical Study	290–306	–	1.7×10^{13} exp (−1260/T)	[12]
Reevaluated Data	298	0.267–2.27	2.14×10^{11}	[11]
Shock Tube/C_2H_5I/L_α	998–1273	1.5	7.8×10^{14} exp (−2260/T)	t.w.

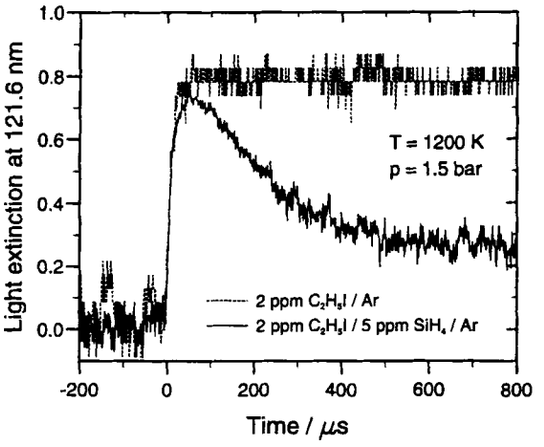

Fig. 1
Measured light extinctions at $\lambda=121.6$ nm behind the reflected shock wave in a C_2H_5I/Argon mixture without and with addition of SiH_4

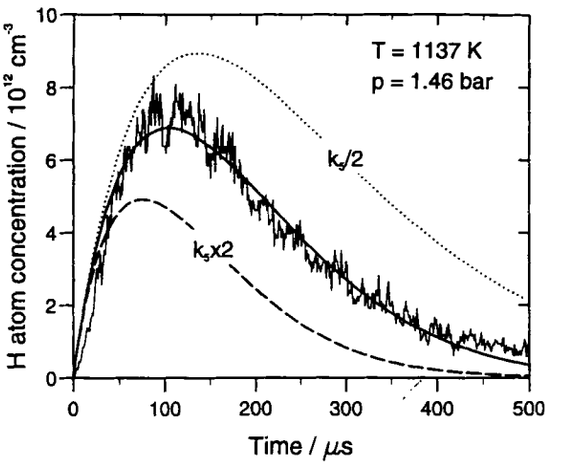

Fig. 2
H-atom concentration profile measured behind the reflected shock wave in comparison with calculated profiles. Experimental conditions: 2 ppm C_2H_5I/5 ppm SiH_4/Ar

precisely due to self absorption and self reversal. Therefore, series of shock wave calibration experiments have been performed to relate the measured absorptions to the corresponding concentrations. H-atom calibration was made with N_2O/H_2 systems by comparing measured absorptions with calculated H profiles ($1500\,K \le T \le 2000\,K$, $p \sim 1.4$ bar), see Roth and Just [17] and Just [18]. The Si-atom calibration was performed based on the dissociation of SiH_4 highly diluted in Argon at temperatures $T>2000$ K, pressures around 1.1 bar and mixtures of 0.05 to 1 ppm SiH_4 in Argon, See Mick et al. [19]. Based on experiments by Koshi et al. [10] for the absorption cross section of SiH_4 at 121.6 nm and our own experiments, the absorption of H- and Si-resonance radiation by molecular species is negligible for our experimental conditions. Thus, the measured extinction signals are equal to the absorption by H and Si, respectively.

The kinetic behaviour of the H-atom source C_2H_5I was studied in a few separate experiments in mixtures of 0.5 to 2 ppm C_2H_5I diluted in Argon at similar experimental conditions. The H-atom yield obtained was $[H]_\infty/[C_2H_5I]_0=0.76\pm0.07$. It agrees with values measured by Kumaran et al. [20] with 0.87 ± 0.11, Lim et al. [21] with 0.80 ± 0.03 and Takahashi [22] with 0.73. This yield is known to be due to both the dissociation pathways of C_2H_5I via I- and HI-fission (see Table 3). Branching ratios for the rate coefficients k_2/k_1 are given by [20] to be 0.15 and by [13] with ≤ 0.2, respectively. Both have observed H- and I-atom concentrations in C_2H_5I pyrolysis experiments. Apart from the branching ratio, effects of wall adsorption have also been reported [23], which might slightly affect the H-atom yield.

3. Results

The experiments were performed behind reflected shock waves in the temperature range of $998\,K \le T \le 1273$ K at pressures around 1.5 bar in gas mixtures of 5 to 10 ppm SiH_4 and 2 ppm C_2H_5I diluted in Argon. H- and Si-atom absorptions were simultaneously measured. The range of experimental conditions was chosen such that secondary reactions of reaction products of (R 5) are of minor importance.

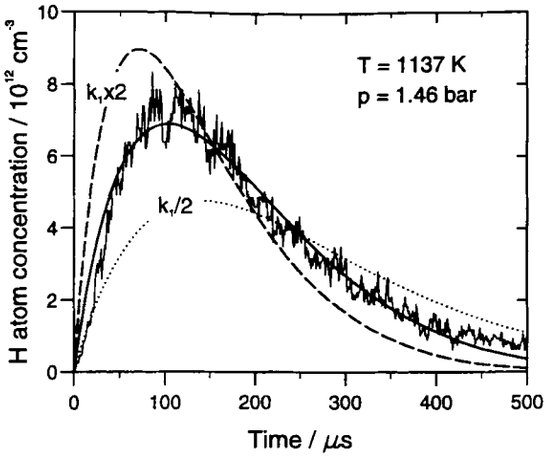

Fig. 3
Sensitivity of k_1 on the calculated H-atom concentration profile for the experiment of Fig. 2

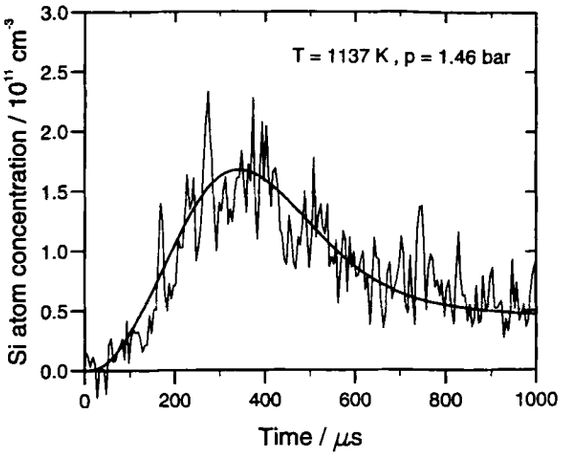

Fig. 4
Measured and calculated Si-atom concentration profiles for the experiment of Fig. 2

Table 2
Experimental conditions and kinetic parameters obtained

T K	p bar	$[C_2H_5I]_0$ ppm	$[SiH_4]_0$ ppm	k_1 s^{-1}	k_5 $cm^3\ mol^{-1}\ s^{-1}$
1137	1.46	2	5	9.35×10^3	1.11×10^{14}
1208	1.52	2	5	2.09×10^4	1.17×10^{14}
1273	1.55	2	5	3.97×10^4	1.41×10^{14}
1105	1.56	2	5	5.50×10^3	1.06×10^{14}
1139	1.55	2	5	9.47×10^3	9.94×10^{13}
1243	1.27	2	5	2.84×10^4	1.18×10^{14}
998	1.32	2	5	1.00×10^3	8.39×10^{13}
1131	1.27	2	5	7.20×10^3	1.25×10^{14}
1162	1.61	2	10	1.13×10^4	1.08×10^{14}
1159	1.51	2	10	1.12×10^4	1.09×10^{14}
1169	1.43	2	10	1.48×10^4	1.12×10^{14}
1254	1.50	2	10	3.57×10^4	1.28×10^{14}
1122	1.61	2	10	7.05×10^3	9.73×10^{13}
1132	1.40	2	10	8.85×10^3	1.08×10^{14}
1048	1.51	2	10	2.84×10^3	9.08×10^{13}
1089	1.53	2	10	5.31×10^3	9.22×10^{13}
1155	1.59	2	10	1.27×10^4	1.05×10^{14}
1175	1.54	2	10	1.50×10^4	1.21×10^{14}
1225	1.51	2	10	2.79×10^4	1.35×10^{14}

A typical example illustrating both the formation of H atoms by the decomposition of C_2H_5I and their perturbation by the reaction with SiH_4 is shown in Fig. 1. The dotted line represents the H-atom formation during C_2H_5I pyrolysis and the solid line shows the influence of the SiH_4 addition on the H absorption. The signal decrease depends strongly on the temperature and the SiH_4 concentration. According to the work of Mick et al. [19, 24] the expected loss of silane by thermal decomposition is only between 0.2 and 0.5% under the present experimental conditions. Thus it can be assumed that the consumption of H atoms is primarily caused by the reaction with silane.

The Si-atom absorption measurements at $\lambda=251.6$ nm were performed to validate the current reaction mechanism used to analyse the H-measurements. A typical example of both a H- and a Si-concentration profile measured in one shock tube experiment is shown in Figs. 2 and 4. After the reflected shock wave has reached the measurement plane, the H-atom concentration rises up to a maximum within 100 μs followed by a slower decrease. The measured Si atom concentration reaches a maximum within 300 μs and decreases again. The experimental conditions and the kinetic parameters (see later) obtained from all H-atom measurements are summarized in Table 2.

4. Discussion

Based on the thermal decomposition mechanism of C_2H_5I given in a recent study by Kumaran et al. [20] and the exothermic reaction

Table 3
Simplified reaction mechanism of the C_2H_5I/SiH_4 system highly diluted in Argon $k_i = A \times \exp(-T_A/T)$ cm^3 mol^{-1} s^{-1}, s^{-1}

	Reaction				Rate coefficient		Ref.
					A	T_A	
1	C_2H_5I		$\rightarrow C_2H_5$	$+I$	2.19×10^{10}	16728	[20], see text
2	C_2H_5I		$\rightarrow C_2H_4$	$+HI$	$0.15\times k_1$		[20]
3	C_2H_5		$\rightarrow C_2H_4$	$+H$	$\rightarrow\infty$		[20]
4	H	$+HI$	$\rightarrow H_2$	$+I$	4.74×10^{13}	330	[20]
5	SiH_4	$+H$	$\rightleftharpoons SiH_3$	$+H_2$	7.80×10^{14}	2260	this study
6	SiH_4	$+SiH_2$	$\rightleftharpoons H_3SiSiH$	$+H_2$	1.30×10^{13}	0	[27]
7	SiH_4	$+SiH$	$\rightleftharpoons SiH_3$	$+SiH_2$	2.90×10^{14}	0	[28]
8	SiH_4		$\rightleftharpoons SiH_2$	$+H_2$	1.90×10^{10}	22550	[19, 24]
9	SiH_3	$+SiH_3$	$\rightleftharpoons SiH_2$	$+SiH_4$	6.26×10^{13}	0	[25]
10	SiH_3	$+SiH_3$	$\rightleftharpoons H_3SiSiH$	$+H_2$	7.00×10^{12}	0	[25]
11a	SiH_3		$\rightleftharpoons SiH$	$+H_2$	$<1.00\times10^{10}$	22290	see text
12	SiH_2	$+Ar$	$\rightleftharpoons Si$	$+H_2+Ar$	9.10×10^{13}	15100	[19]
13	SiH_2	$+SiH_2$	$\rightleftharpoons Si_2H_2$	$+H_2$	6.50×10^{14}	0	[27]
14	SiH_2	$+C_2H_4$	$\rightleftharpoons SiC_2H_6$		6.44×10^{13}	348	[29]
15	SiH	$+H_2$	$\rightleftharpoons SiH_2$	$+H$	4.80×10^{14}	11900	[30]
16	Si	$+SiH_4$	$\rightleftharpoons Si_2H_2$	$+H_2$	4.00×10^{14}	0	[31]
17	Si	$+H_2$	$\rightleftharpoons SiH$	$+H$	1.50×10^{15}	16000	[30]
18	Si	$+C_2H_4$	$\rightarrow SiC_2H_4$		5.30×10^{13}	0	[32]
19	H_2	$+Ar$	$\rightleftharpoons H$	$+H+Ar$	2.20×10^{14}	48300	[33]

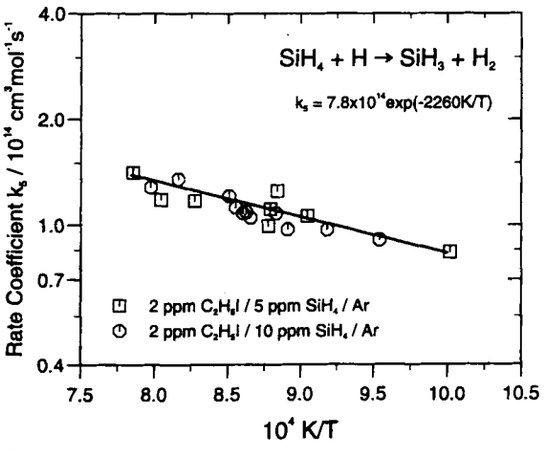

Fig. 5
Arrhenius representation of the rate coefficient k_5

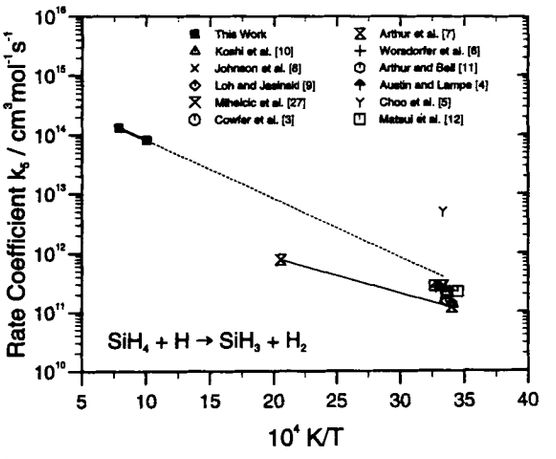

Fig. 6
Literature values of k_5 compared to the results of the present study

$$SiH_4 + H \xrightarrow{k_5} SiH_3 + H_2 \quad \Delta H^0_{298} = -53.4\ \text{kJ/mol} \tag{R5}$$

a reaction mechanism involving additional 14 reactions was proposed to analyse the measured H and Si concentration profiles, see Table 3.

The dissociation kinetics of C_2H_5I must be considered for our experimental conditions because it is sensitive to the H-atom profiles at temperatures below 1200 K. We have successfully included a mechanism which was recently proposed by [20] to describe the pyrolysis of C_2H_5I. The rate coefficient of reaction (R1) given in [20] was slightly increased by a factor of about 1.6 to get the best agreement between measured and calculated H-atom concentration profiles of C_2H_5I decomposition experiments and also to match the initial slope of the H-atom profiles of the $SiH_4/C_2H_5I/Ar$ experiments. This adjustment seems to be justified due to the fact that compared to [20] our study was performed at pressures being a factor of 4 higher and the usage of Argon instead of Krypton.

The further evaluation of the measured Si- and the full H-concentration profiles was performed by varying the rate coefficient k_5 to achieve best fits of the calculated to the measured H- and Si-atom profiles. The best fit parameter k_5 and the rate coefficient k_1 obtained are summarized in Table 2. In Fig. 2 the calculated H atom concentration is compared with the measured one showing quite

good agreement. A variation of the rate coefficient k_5 by factors of 0.5 and 2 demonstrates the sensitivity of reaction (R5) to the measured H atoms, whereas, for the same low temperature experiment, the sensitivity of reaction (R1) to the measured H-atom profile is shown in Fig. 3 by variations of k_1. Reaction (R1) strongly influences the initial slope of the H-atom concentration profile, whilst after about 100 µs the decay in the concentration is mainly affected by reaction (R5). The validity of our overall model is supported by the calculated Si-atom concentration profiles matching the measured ones quite well. The example shown in Fig. 4 illustrates this good agreement. All individual values of the rate coefficient k_5 obtained from the fitting procedure are shown in the Arrhenius diagram of Fig. 5. The points scatter around a straight line, which was obtained by a least-square-fit calculation and lead to following Arrhenius expression:

$$k_5 = 7.8^{+2.22}_{-1.73} \times 10^{14} \exp(-2260(\pm 288)\mathrm{K}/T) \cdot \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

Due to the fast formation of SiH_3 via reaction (R5), secondary reactions involving the silyl radical must be taken into account, although their sensitivity to the calculated H-atom and Si-atom concentrations is very limited. Arrhenius expressions for reaction

$$SiH_3 + SiH_3 \rightarrow \text{products}$$

were recently determined by Matsumoto et al. [25] and were successfully integrated in our reaction mechanism. Another reaction, which has to be considered is the decomposition of SiH_3:

$$SiH_3 \overset{k_{11a}}{\rightleftharpoons} SiH + H_2 \quad \Delta H^0_{298} = 185.3\ \mathrm{kJ/mol} \qquad (R11a)$$

$$\overset{k_{11b}}{\rightleftharpoons} SiH_2 + H \quad \Delta H^0_{298} = 290.7\ \mathrm{kJ/mol} \qquad (R11b)$$

We have included reaction (R11a) in our mechanism because of the lower reaction enthalpy. In [24] a first-order rate coefficient for $k_{11\alpha}$ at atmospheric pressure is suggested which was obtained by RRKM calculations. This value leads to slightly higher Si concentrations compared to the experiments when inserted in our simplified mechanism, whereas the calculated H concentration profiles are not sensitive. Best fits for all measured Si concentrations were possible with a rate coefficient $k_{11\alpha} < 1.0 \times 10^{10} \exp(-22\,290\ \mathrm{K}/T)\ \mathrm{s^{-1}}$ for the high pressure decomposition, which is a factor of 28 smaller than the one calculated by [24].

Fig. 6 compares our high temperature Arrhenius expression for reaction (R5) with rate coefficients obtained in previous works at lower temperatures. An extrapolation – represented by a dashed line – shows good agreement with most of the room temperature results. In contrast to the work of Arthur et al. [7] which was limited to temperature ranges of $294\ \mathrm{K} \leq T \leq 487\ \mathrm{K}$, our activation energy is about 8.0 kJ/mol higher.

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References

[1] J.M. Jasinski, B.S. Meyerson, and B.A. Scott, Mechanistic studies of chemical vapor deposition, Ann. Rev. Phys. Chem. *38*, 109–140 (1987).
[2] J.M. Jasinski and S.M. Gates, Silicon chemical vapor deposition one step at a time: Fundamental studies of silicon hydride chemistry, Acc. Chem. Res. *24*, 9–15 (1991).
[3] J.A. Cowfer, K.P. Lynch, and J.V. Michael, Reactions of hydrogen and deuterium with silane and mono-, di-, and trimethylsilanes at room temperature, J. Phys. Chem. *79* (12), 1139–1147 (1975).
[4] E.R. Austin and F.W. Lampe, Rate constants for the reactions of hydrogen atoms with some silanes and germanes, J. Phys. Chem. *81* (12), 1134–1138 (1977).
[5] K.Y. Choo, P.P. Gaspar, and A.P. Wolf, Rates of reaction of hydrogen atoms with silane and germane, J. Phys. Chem. *79* (17), 1752–1758 (1975).
[6] K. Worsdorfer, B. Reimann, and P. Potzinger, The reaction of hydrogen atoms with silyl radicals; the decomposition pathways of chemically activated silanes, Z. Naturforsch. *38a*, 896–908 (1983).
[7] N.L. Arthur, P. Potzinger, B. Reimann, and H.P. Steenbergen, Reaction of H atoms with some silanes and disilanes, J. Chem. Soc. Faraday Trans. 2, *85* (9), 1447–1463 (1989).
[8] N.M. Johnson, J. Walker, and K.S. Stevens, Characterisation of a remote hydrogen plasma reactor with electron spin resonance, J. Appl. Phys. *69* (4), 2631–2634 (1991).
[9] S.K. Loh and J.M. Jasinski, Direct kinetic studies of SiH_3+SiH_3, H, CCl_4, Si_2H_6, and C_3H_6 by tunable infrared diode laser spectroscopy, J. Chem. Phys. *95* (7), 4914–4926 (1991).
[10] M. Koshi, F. Tamura, and H. Matsui, Rate constants for the reactions of hydrogen atoms with SiH_nF_{4-n} (n=4,3,2), Chem. Phys. Let. *173* (2, 3), 235–240 (1990).
[11] N.L. Arthur and T.N. Bell, An evaluation of the kinetic data for hydrogen abstraction from silanes in the gas phase, Rev. Chem. Intermed. *2*, 37–74 (1978).
[12] Y. Matsui, A. Yuuki, N. Morita, and K. Tachibana, On the reaction kinetics in a mercury photosensitized CVD of a-Si:H films, Jpn. J. Appl. Phys. *26* (9), 1571–1581 (1987).
[13] J. Herzler and P. Frank, High temperature reactions of phenylacethylene, Ber. Bunsenges. Phys. Chem. *96* (10), 1333–1338 (1992).
[14] P. Roth and Th. Just, Atomabsorptionsmessungen zur Kinetik der Reaktion $CH_4+O \rightarrow CH_3+OH$ im Temperaturbereich $1500 \leq T \leq 2250$ K, Ber. Bunsenges. Phys. Chem. *81* (6), 572–577 (1977).
[15] L.A. Dean and T.C. Rains, Flame emission and atomic absorption spectrometry, volume 3, Marcel Dekker, Inc., New York, 1975.
[16] D. Husain and P.E. Norris, Kinetic study of reactions of ground state silicon atoms, $Si[3p^2(^3P_J)]$, by atomic absorption spectroscopy, J. Chem. Soc. Faraday 2, *74*, 106–114 (1978).
[17] P. Roth and Th. Just, Messungen zur Hochtemperaturpyrolyse von Äthan, Ber. Bunsenges. Phys. Chem. *88*, 577–583 (1979).
[18] Th. Just, Atomic Resonance Absorption Spectrometry in Shock Tubes, Marcel Dekker, Inc., New York and Basel, 1981.

[19] H.J. Mick, V.N. Smirnov, and P. Roth, ARAS measurements on the thermal decomposition of silane, Ber. Bunsenges. Phys. Chem. *97* (6), 793–798 (1993).

[20] S.S. Kumaran, M.C. Su, K.P. Lim, and J.V. Michael, Thermal decomposition of C_2H_5I. In 26th Symp. (Int.) On Comb., The Combustion Institute, 605–611 (1996).

[21] K.P. Lim and J.V. Michael, The thermal reaction of CH_3, 25th Symp. (Int.) Comb., [Proc.] *25*, 713–719 (1994).

[22] K. Takahashi, Department of Chemistry, Sophia University, Tokyo, Japan, private communications.

[23] K. Wintergerst, Reaktionskinetische Untersuchungen von verbrennungsrelevanten Methan- und Methylreaktionen, PhD thesis, Universität Stuttgart, 1993.

[24] H.J. Mick, P. Roth, V.N. Smirnov, and I.S. Zaslonko, Formation of H atoms in silane pyrolysis behind shock waves. Kinetics and thermochemistry of SiH_4, SiH_3, and SiH_2 dissociation, Kinetics and Catalysis *35* (4), 439–451 (1994).

[25] K. Matsumoto, M. Koshi, K. Okawa, and H. Matsui, Mechanism and product branching ratios of the SiH_3+SiH_3 reaction, J. Phys. Chem. *100*, 8796–8801 (1996).

[26] D. Mihelcic, V. Schubert, R.N. Schindler, and P. Potzinger, Rate constants for the reaction of hydrogen and deuterium atoms with silane, J. Phys. Chem. *81* (16), 1543–1545 (1977).

[27] H.J. Mick, M.W. Markus, P. Roth, and V.N. Smirnov, A shock tube study of the thermal decomposition of Si_2H_6 based on Si and SiH_2 measurements, Ber. Bunsenges. Phys. Chem. *99* (6), 880–890 (1995).

[28] M. Nemoto, A. Suzuki, H. Nakamura, K. Shibuya, and K. Obi, Electronic quenching and chemical reactions of SiH radicals in the gas phase, Chem. Phys. Lett. *162* (6), 467–471 (1989).

[29] N. Al-Rubaiey and R. Walsh, Gas-phase kinetic study of the prototype silylene addition reaction $SiH_2+C_2H_4$ over the temperature range 298–595 K. An example of third body mediated association, J. Phys. Chem. *98*, 5303–5309 (1994).

[30] H.-J. Mick, T. Kruse, and P. Roth, A shock-tube study of the reaction $Si+H_2 \rightleftharpoons SiH+H$, Proc. 20th Int. Symp., On Shock Waves, Volume II, 875–880 (1995).

[31] D. Woiki, A. Kunz, and P. Roth, Laser flash photolysis of SiH_4 and Si_2H_6 behind reflected shock waves, 21st Int. Symp., On Shock Waves, 1997, accepted for publication.

[32] S.C. Basu and D. Husain, Absolute rate data for the reaction of ground state atomic silicon, Si (3^3P_J), with olefins determined by time-resolved atomic resonance absorption spectroscopy, Z. Phys. Chem. (Munich) *158*, 1–13 (1988).

[33] D.L. Baulch, D.D. Drysdale, D.G. Horne, and A.C. Lloyd, Homogeneous gas phase reactions of the H_2-O_2 system, volume 1 of Evaluated Kinetic Data for High Temperature Reactions, Butterworth, London, 1 edition, 1972.

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