KINETICS OF THE REACTIONS OF HSiCI WITH SiH4 AND SiH2Cl2

Pauline HO, William G. BREILAND

Sandia National Laboratories, Albuquerque, NM 87185, USA

and

Robert W. CARR

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Received 8 September 1986

Laser-excited fluorescence detection of HSiCl was used to measure the room-temperature kinetics of the reactions of HSiCl with SiH₄ and SiCl₂H₂. An upper bound was also obtained for the HSiCl+H₂ rate coefficient. Rate coefficients for insertion of HSiCl into SiH₄ and SiCl₂H₂ are 3-4 orders of magnitude smaller than rate coefficients for insertion of SiH₂ into Si-H bonds.

1. Introduction

Divalent carbon and silicon species have rich and interesting chemistries that have been the subject of research for years. Recently, silicon chemistry has received increasing emphasis due, at least in part, to its applications to the production of thin silicon films in microelectronics processing.

Chlorosilanes are widely used in the microelectronics industry for the production of silicon thin films, particularly for the deposition of epitaxial silicon films via chemical vapor deposition (CVD). At the temperatures used for epitaxial growth, chlorosilanes are known to decompose in the gas phase. By analogy with silane decomposition $(SiH_4 \rightarrow SiH_2 + H_2)$, chlorosilanes are expected to yield chlorosilylenes. Recent studies have explored the importance of gas-phase chemical kinetics in silane CVD [1-4]. Similar modelling and understanding of chlorosilane CVD will require a knowledge of gas-phase reactions. However, few kinetic data are available for these systems.

Investigations of silylene reactions have been facilitated by direct detection techniques, although the number of such studies is limited. Insertion of SiH₂ into H₂ and Si-H bonds has been studied by

laser-excited fluorescence (LEF) [5] and by laser resonance absorption [6,7]. Safarik et al. [8] used kinetic spectroscopy to investigate rates of SiCl₂ addition to carbon-carbon double bonds. No investigations of insertion rates for chlorosilylenes by direct methods have been reported yet.

Previous workers have obtained general information on relative reactivities of silylenes. The insertion of halosilylenes into Si-H bonds is expected to occur more slowly than insertion of SiH₂. It has been pointed out that during insertion, interaction between silylene σ and p orbitals, and σ and σ^* orbitals of the attacked bond plays an important role, and that reactivity decreases with increasing p-orbital energy [9]. In accord with this, Jenkins et al. [10] have found from product analysis that the order of reactivity for insertion into Si-H bonds is SiH₂>HSiCl> $HSiF \ge SiCl_2$, SiF_2 . Also Doncaster and Walsh [11] were unable to observe reaction of SiCl₂ with HCl and SiCl₄ between 596 and 655 K since the competing reaction with I₂ occurred more rapidly. Furthermore, the ab initio calculations of Sosa and Schlegel [12] predict that the barrier height for insertion into hydrogen increases with fluorine substitution in the order $SiH_2 < HSiF < SiF_2$.

HSiCl is a good candidate for direct detection

0 009-2614/86/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) kinetics experiments. Its spectrum, first identified by Herzberg and Verma [13], consists of widely spaced K subbands that are easily resolved using laserexcited fluorescence [14]. In this paper we report the results of an investigation by LEF of the kinetics of the HSiCl reactions with SiH₄ and SiCl₂H₂. Our measurements confirm that HSiCl is in fact considerably less reactive than SiH₂.

2. Experiment

Although SiCl₂H₂ does not absorb strongly at 193 nm [15], excimer laser photolysis of SiCl₂H₂ (10–15 mJ/pulse) produced sufficient HSiCl for these experiments. HSiCl was identified by comparison of both excitation and fluorescence spectra with the assignments made by Herzberg and Verma [13]. The time dependence of the HSiCl concentration was monitored with LEF by varying the delay between the photolysis laser and a XeCl excimer pumped dye laser (1.5–5 mJ/pulse) tuned to the transition at 482.4 nm of the A ¹A"-X ¹A' system of HSiCl [13].

The reaction cell was constructed of standard 34 mm i.d. stainless-steel vacuum fittings. The gases flowed in at the top of the cell and were pumped out near the bottom. The dye laser beam entered the cell, collinear with the gas flow, through a pyrex window at the top, and was focused to a diameter of less than 0.5 mm at the interaction region. The photolysis laser beam entered the cell orthogonal to the probe beam through a quartz window, and was loosely focused to a height of roughly 1.5 cm and a width of 2.5 mm at the interaction region. The probe beam was kept much smaller than the photolysis beam to reduce possible artifacts caused by diffusion in and out of the probed region.

Fluorescence was collected perpendicular to the laser beams by a pair of 50 mm diameter, 120 mm focal length achromats arranged so that the image of a 1 cm high slit used for spatial filtering overlapped the probe and photolysis lasers. A Schott OG515 glass filter was used to reduce scattered laser light, and the fluorescence was detected with a photomultiplier tube. Signals were processed with a gated integrator/ boxcar (gate width 600 ns), stored and averaged in a small laboratory computer. The photolysis laser was operated at 6.5 Hz and the probe laser at 13 Hz. Digitized signals with and without the photolysis laser were alternately added and subtracted to reduce contributions from scattered dye-laser light and to eliminate baseline problems with instrumental offsets and zero drifts. The delay between the photolysis and dye lasers was controlled by counting pulses from a clock having a period of 150 ns.

The gas flow rates were adjusted to give a linear velocity of 9 cm/s, which roughly changed the gas mixture between every photolysis laser pulse. The total pressure in the system was maintained by an automatic throttle valve located between the cell and the vacuum pump.

3. Results

The SiCl₂H₂ photolysis produced some electronically excited HSiCl, resulting in a prompt fluorescence signal with a lifetime of approximately 100 ns. We therefore used minimum delays of 2.5 μ s in our kinetics measurements to avoid interference from this fluorescence. The photolysis also produced emission between 310 and 410 nm, centered at 350 nm. This spectral feature is similar to that observed and assigned to SiCl₂ by Washida et al. [16], Ruzsicska et al. [17] and Sausa and Ronn [18].

HSiCl decays were measured in SiCl₂H₂/N₂ or SiCl₂H₂/SiH₄/N₂ mixtures at a total pressure of 500 Torr. First-order rate constants were obtained from an unweighted non-linear least-squares fit of the data to a single exponential decay. A sample curve is shown in fig. 1. The experimental error in the firstorder rate constants is roughly 10–20%. Semi-log plots of the decays sometimes showed slight curvature (flattening towards long reaction times), particularly at high SiCl₂H₂ pressures. The low signal-tonoise ratio for the long-time data, however, precludes any detailed investigation of the origin of this curvature.

When the ArF laser beam was focused more tightly to increase the HSiCl concentration, a fast component of the HSiCl decay appeared. This fast decay is probably caused by reactions between HSiCl and itself or other reactive species produced by the photolysis. All data reported in this paper were measured with low enough ArF intensity that the decay appeared first order for about one decade or more.



Fig. 1. HSiCl fluorescence decay. 2 Torr SiCl₂H₂ and 5 Torr SiH₄ in N_2 . 500 Torr total pressure.

As a check for interfering secondary reactions, we varied the linear gas velocity from 9 to 18 cm/s. The decay rate for HSiCl in 5 Torr SiCl₂H₂/495 Torr N₂ was the same within experimental error confirming that a flow rate of 9 cm/s was fast enough to refresh the gas mixture and prevent secondary reactions from interfering with the observed decays.

Fig. 2 shows the dependence of the pseudo-firstorder HSiCl decay rate on SiCl₂H₂ pressure at a total pressure of 500 Torr. The decay rates are linear with SiCl₂H₂ pressure over a twenty-fold range. The slope of this plot yields a rate constant of (4.1 ± 0.3) $\times10^{-15}$ cm³ molecule⁻¹ s⁻¹ for the reaction of HSiCl with SiCl₂H₂. The stated uncertainty was obtained from the scatter in the data. The pseudo-first-order rate constants, however, do not extrapolate to zero at zero SiCl₂H₂ pressure, indicating that an addi-



Fig. 2. Pseudo-first-order decay rate constant as a function of $SiCl_2H_2$ partial pressure in N₂. 500 Torr total pressure.



Fig. 3. Pseudo-first-order decay rate constant as a function of SiH₄ partial pressure. 2 Torr SiCl₂H₂ and SiH₄ in N₂. 500 Torr total pressure.

tional mechanism for HSiCl removal exists.

The reaction of HSiCl with silane was investigated by adding silane to a reaction mixture of 2 Torr SiCl₂H₂ in N₂ at 500 Torr total pressure. Fig. 3 shows the linear dependence of the pseudo-first-order HSiCl decay rate constant for 0-30 Torr of added SiH₄. The slope of this plot yields a rate constant of (5.3 ± 0.1) $\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ for the reaction of HSiCl with silane. The decay rates extrapolate to ≈ 600 s⁻¹ for no added silane, which is consistent with the decay rate for 2 Torr SiCl₂H₂ shown in fig. 2.

We also investigated the HSiCl+H₂ reaction. However, at room temperature the addition of 20 Torr of H₂ had no observable effect on the HSiCl decay rate. By assuming that the HSiCl decay rate with 20 Torr of added H₂ differs by no more than 20% from the decay rate in SiCl₂H₂/N₂, we obtain an upper bound for the HSiCl+H₂ rate coefficient of 3×10^{-16} cm³ molecule⁻¹ s⁻¹.

4. Discussion

The insertion of silylenes into Si-H bonds is a wellknown reaction [19]. Furthermore, HSiCl has been observed to insert into $C_2H_5SiH_3$ forming $C_2H_5SiH_2SiH_2Cl$ [10]. It is virtually certain that the reactions of HSiCl with silane and dichlorosilane are also insertion reactions.

Our measured rate constants for HSiCl insertion reactions are substantially smaller than the corre-

Table 1
Insertion reaction rate constants (in cm ³ molecule ¹ s ⁻¹) for HSiCl
compared with values for SiH ₂ taken from the literature

	H ₂	SiH₄	Ref.
HSiCl	<3 ×10 ⁻¹⁶	5.3×10 ⁻¹⁵	this work
SiH ₂	1.0×10^{-13} 2.6×10^{-12} a)	1.1×10 ⁻¹⁰	[5] [6]
	2.0×10^{-13} 1.1×10^{-12}	8.5×10 ⁻¹¹	[7] [20]
	3.4×10 ⁻¹⁶	5.2×10 ⁻¹³	[21]

a) $SiH_2 + D_2$.

sponding SiH_2 reactions, as shown in table 1. Depending upon the set of SiH₂ data used, HSiCl inserts into silane 2-4 orders of magnitude slower than does SiH₂. Our upper bound for the HSiCl insertion into H_2 is 3-4 orders of magnitude slower than recent measurements of the $SiH_2 + H_2$ reaction [5-7,20]. (These recent results provide growing evidence that the value for the $SiH_2 + H_2$ reaction rate extrapolated from the high-temperature data [21,22] is too low.) Our findings are consistent with the expectation, discussed in section 1, that HSiCl is less reactive than SiH₂ toward insertion into Si-H bonds. The decreased reactivity for the chlorosilylene insertions may be due to an energy barrier. Ab initio calculations indicate that fluorosilylene insertions have significant barriers [12]. In contrast, recent high-level calculations have shown that a barrier of less than 2 kcal/mole exists for insertion of SiH₂ into H₂ [23].

It is reasonable for the insertion of HSiCl into SiH₄ and SiCl₂H₂ to be of the same order of magnitude, with the silane reaction somewhat faster. The divalent silylene species are electrophilic. Replacing hydrogen atoms with electron-withdrawing chlorine atoms removes electron density from the reaction site, slowing the reaction.

The comparisons with SiH_2 reactions also indicate that it is reasonable for $HSiCl+H_2$ to be much slower than $HSiCl+SiH_4$. Although the literature data disagree on the magnitude of the SiH_2 reaction rate constants, they agree that SiH_2 inserts into SiH_4 about 1000 times faster than it inserts into H_2 .

5. Summary

Using laser-excited fluorescence for the direct detection of HSiCl, we have measured the following rate coefficients for HSiCl insertion reactions at 500 Torr total pressure:

$$k(\text{HSiCl}+\text{SiCl}_{2}\text{H}_{2}) = (4.1\pm0.3)\times10^{-15}$$

 $\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$,
 $k(\text{HSiCl}+\text{SiH}_{4}) = (5.3\pm0.1)\times10^{-15}$
 $\text{cm}^{3} \text{ molecule}^{-1}\text{ s}^{-1}$.

We have also obtained an upper bound of 3×10^{-16} cm³ molecule⁻¹ s⁻¹ for the HSiCl+H₂ reaction rate coefficient at room temperature. HSiCl reaction rate coefficients for insertion are 3–4 orders of magnitude smaller than the analogous SiH₂ insertion reactions

Acknowledgement

We thank Michael P. Youngman for his technical assistance with this work. This work was performed at Sandia National Laboratories and supported by the US Department of Energy under contract No. DE-AC04-76DP00789 for the Office of Basic Energy Sciences.

References

- M.E. Coltrin, R.J. Kee and J.A. Miller, J. Electrochem. Soc. 131 (1984) 425.
- [2] M.E. Coltrin, R.J. Kee and J.A. Miller, J. Electrochem. Soc. 133 (1986) 1206.
- [3] W.G. Breiland, M.E. Coltrin and P. Ho, J. Appl. Phys. 59 (1986) 3267.
- [4] W.G. Breiland, P. Ho and M.E. Coltrin, J. Appl. Phys. 60 (1986) 1505.
- [5] G. Inoue and M. Suzuki, Chem. Phys. Letters 122 (1985) 361.
- [6] J.M. Jasinski, J. Phys. Chem. 90 (1986) 555.
- [7] J.M. Jasinski and J.O. Chu, Abstract WED-4, XVII Informal Conference on Photochemistry, Boulder, Colorado, June 23-26, 1986.
- [8] I. Safarik, B.P. Ruzsicska, A. Jodhan, O.P. Strausz and T.N. Bell, Chem. Phys. Letters 113 (1985) 71.

- [9] O.M. Nefedov, S.P. Kolesniskov and A.I. Ioffe, J. Organomet. Chem. Library 5, Organomet. Chem. Rev. (1977) 181.
- [10] R.L. Jenkins, A.J. Vanderwielen, S.P. Ruis, S.R. Gird and M.A. Ring, Inorg. Chem. 12 (1973) 2968.
- [11] A.M. Doncaster and R. Walsh. J. Chem. Soc. Faraday Trans. I 76 (1980) 272.
- [12] C. Sosa and H.B. Schlegel, J. Am. Chem. Soc. 106 (1984) 5847.
- [13] G. Herzberg and R.D. Verma, Can. J. Phys. 42 (1964) 395.
- [14] P. Ho and W.G. Breiland, Appl. Phys. Letters 43 (1983) 125.
- [15] G.C. Causley and B.R. Russell, J. Electron Spectry. 8 (1976) 71.
- [16] N. Washida, Y. Matsumi, T. Hayashi, T. Ibuki, A. Hiraya and K. Shobatake, J. Chem. Phys. 83 (1985) 2769.

- [17] B.P. Ruzsicska, A. Jodhan, I. Safarik, O.P. Strausz and T.N. Bell, Chem. Phys. Letters 113 (1985) 67.
- [18] R.C. Sausa and A.M. Ronn, Chem. Phys. 96 (1985) 183.
- [19] P.P. Gaspar, in: Reactive intermediates, Vol. 3. Silylenes, eds. M. Jones Jr. and R.A. Moss (Wiley, New York, 1985).
- [20] C.D. Eley, M.C.A. Rowe and R. Walsh, Chem. Phys. Letters 126 (1986) 153.
- [21] R.T. White, R.L. Espino-Rios, D.S. Rogers, M.A. Ring and H.E. O'Neal, Intern. J. Chem. Kinetics 17 (1985) 1029.
- [22] P. John and J.H. Purnell, J. Chem. Soc. Faraday Trans. I 69 (1973) 1455.
- [23] M.S. Gordon, D.R. Gano, J.S. Binkley and M.J. Frisch, J. Am. Chem. Soc. 108 (1986) 2191.