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Direct Kinetic Studies of Silicon Hydride Radicals in the Gas Phase

J. M. Jasinski*

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

R. Becerra

Instituto Quimica Fisica "Rocasolano", C.S.I.C., c/Serrano, 119, 28006, Madrid, Spain

R. Walsh

Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 2AD, U.K.

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Contents

I. Introduction

A predictive understanding of complex, often economically and/or ecologically important, chemical processes requires detailed knowledge of the elementary chemical reactions underlying such processes. Well-known examples include hydrocarbon combustion, atmospheric chemistry, and chemical catalysis. The fundamental understanding of all these processes has benefited enormously from extensive time-resolved chemical kinetics studies of the relevant elementary reactions. In this article, we compile and critically review direct kinetic studies of gas-phase reactions of simple silicon hydride radicals underlying many types of chemical vapor deposition (CVD) processes of importance in the deposition of silicon or silicon-containing thin films which are extensively used in the microelectronics industry.

Unlike processes involving carbon, oxygen, or nitrogen centered radicals, the direct kinetic study of silicon hydride radicals using time-resolved techniques which directly monitor the radical of interest is a relatively new area of kinetics. The first reports of direct kinetic studies of these species in the gas phase appeared in the literature only a decade ago. In the ensuing 10 years, significant progress has been made in understanding the reactions of these simple radicals.

Our goal in this paper is to comprehensively review direct kinetic studies of transient silicon hydride species. In particular we concentrate on gas-phase studies of silylidyne (SiH), silylene (SiH_2), and silyl(SiH_3). These species are of the greatest significance in the breakdown mechanisms of stable silicon hydride molecules such as silane, SiH_4, and disilane, Si_2H_6. We touch briefly on the limited experimental information currently available for the subhydrides of disilane, Si_2H_x. These are of interest because of their potential involvement in gaseous oligomerization processes, but as yet there is little experimental information on the spectroscopy and structure of such species, let alone on the kinetics of their reactions. We also review the small amount of experimental data available on the surface loss kinetics of monosilicon hydride radicals. This information is of great relevance to silicon thin films growth, but direct kinetic studies of these species reacting at characterizable surfaces are in their infancy. We do not discuss CVD mechanisms. This subject has been reviewed for silicon hydrides relatively recently by Jasinski and Gates.[1] Nor do we consider the nonhydride analogues of SiH, SiH_2, and SiH_3. This has been done for silylenes by Strausz *et al.*[2] and by Becerra and Walsh.[3] The history of our knowledge of silane decomposition mechanisms and the role of silicon hydride radicals in these processes extends back to considerably earlier than the time period of direct kinetic studies of silicon hydride radicals. The discussion of this history, which is fascinating in itself, would, we felt, make this article unwieldy. Information on this can be obtained from earlier articles and reviews.[4–8]

Our explicit goal is to provide a comprehensive and exhaustive review of absolute gas-phase rate constants for radical–molecule and radical–radical reactions of silicon hydride radicals through 1994. The mechanisms and products of these reactions are discussed less exhaustively and only when substantial understanding has been achieved. This article is not a review of the structure and spectroscopy of transient silicon hydrides. For practical purposes, we discuss the generation, detection, and monitoring of the transient silicon hydrides as these topics apply to direct kinetic studies. The structures of both ground and excited states are well known and can

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* Author to whom correspondence should be addressed. Electronic mail: JASIN@WATSON.IBM.COM.

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Joseph M. Jasinski received his A.B. from Dartmouth College in Hanover, NH, in 1976. He received a Ph.D. in organic chemistry from Stanford University in 1980, under the direction of Professor John Brauman. Following post-doctoral work at the University of California, Berkeley, in the laboratories of Professor C. B. Moore, he joined the IBM Thomas J. Watson Research Center as a Research Staff Member in 1982. His research interests include the photochemistry, spectroscopy, and kinetics of small inorganic species, particularly silicon hydride radicals, and the detailed understanding of chemical vapor deposition mechanisms. He has held several management positions at IBM and is currently a senior manager in the Physical Sciences department. He is a Fellow of the American Physical Society.

Rosa Becerra obtained her first degree from the University of Santiago de Compostela, Galicia, Spain. For her Ph.D. she moved to Madrid to work at the Instituto de Quimica-Fisica "Rocasolano" of the Consejo Superior de Investigaciones Cientificas (C.S.I.C.), where she carried out research on combustion chemistry. She received her Ph.D. from University Complutense, Madrid. She next joined the research group of Professor Monty Frey at the University of Reading, UK, as a postdoctoral associate, where she worked for several years on the direct and mercury-sensitized photochemistry of small molecules. During this time, she became interested in silicon chemistry and began collaborating with Robin Walsh. In 1987 she returned to C.S.I.C. as a postdoctoral fellow, and in 1988 she became a member of the scientific staff. Her research interests include atmospheric chemistry, silicon chemistry, and kinetic modeling.

Robin Walsh was born in 1939 in London, England. He studied at Cambridge University, where he obtained his B.A. in 1961 and Ph.D. in 1964. After this he held post-doctoral positions with Sidney Benson at Stanford Research Institute and with Monty Frey at the University of Reading where he joined the staff in 1967. His research activities lie in the fields of gas-phase kinetics and mechanisms, photochemistry, and the energetics of chemical reactions. He has particular interests in the measurement of bond dissociation energies, the study of silicon-containing reactive transient species such as silylenes, and of strained ring hydrocarbons like cyclopropene. He has been secretary and chairman of the UK Gas Kinetics Discussion Group. In 1994 he received the Frederic Stanley Kipping Award of the American Chemical Society for Organosilicon Chemistry.

be found in numerous articles. In particular they are discussed by Apeloig[9] in relation to theoretical (*ab initio*) calculations. Such calculations at current state-of-the art levels are capable of reproducing experimental structures well and are approaching the precision and accuracy of experimental values for thermochemical quantities. Grev and Schaefer[10] in particular have performed high-level calculations of this type for the enthalpies of formation of SiH_n ($n = 0-4$) using large atomic orbital basis sets and coupled cluster methods including all single, double, and triple excitations. Although this is not a general review of theoretical calculations, they are nevertheless discussed where relevant to specific reactions and their mechanisms.

Because enthalpies of reaction have always been an important guideline for mechanism we include an evaluation of the enthalpies of formation of SiH_x ($x = 1-3$) in this review. A set of recommended bond dissociation energies is included in the general comments at the end. A comprehensive review of the thermochemistry of these and other silicon containing molecules has appeared.[11]

As an aid to the nonspecialist reader, a list of acronyms and their meaning is given in the Appendix and Conversions section.

2. Silylidyne, SiH

2.1. Sources, Detection and Monitoring

Relatively little direct kinetic information exists for silylidyne, compared to that available on SiH_2 and SiH_3. The first report of a gas phase rate constant was by Schmitt *et al.*[12] who monitored the decay of SiH by laser-induced fluorescence (LIF) following its formation in a pulsed silane discharge. LIF detection, employing the well known $A^2\Delta \leftrightarrow X^2\Pi$ electronic transition[13] has been the preferred monitoring method for subsequent kinetics studies.

Silylidyne has been prepared for kinetics experiments by pulsed discharge methods using silane as the source,[12] and by excimer laser flash photolysis of either phenylsilane[14,15] or disilane[14] at 193 nm. In the case of 193 nm photolysis of either precursor, both ground-state $SiH(^2\Pi)$ and electronically excited-state $SiH(^2\Delta)$ are readily formed at typical excimer laser pulse energies of $\sim$50$-$100 mJ cm^{-2}. The ground-state concentration is linear in excimer laser pulse energy, suggesting formation by a single photon photolysis process, while the excited-state concentration, monitored by emission spectroscopy, is super-

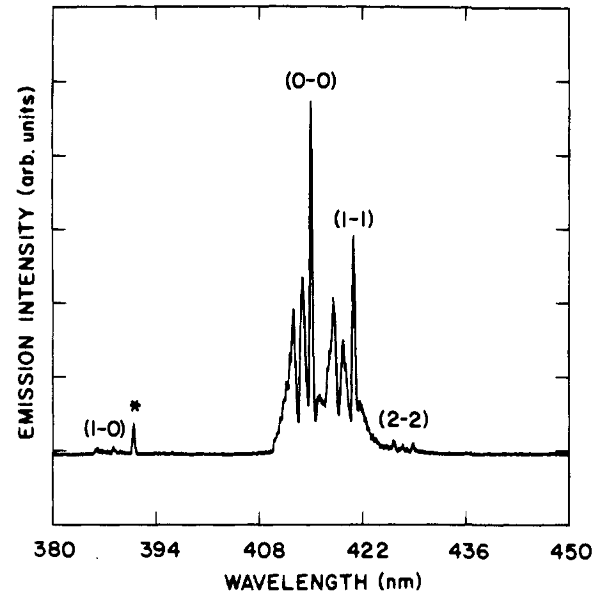


Figure 1. Emission from the SiH $A^2\Delta \rightarrow X^2\Pi$ electronic transition resulting from 193 nm photodissociation of disilane. The asterisk denotes an atomic silicon emission line. Vibronic bands are labeled by their upper and lower state vibrational quantum numbers.

linear in excimer laser pulse energy, suggesting a multiphoton photolysis process. In the case of disilane, at least two photons are energetically required to produce SiH($^2\Delta$). This is also likely to be the case for phenylsilane, although the thermochemistry in this system is less rigorously known.[14-16] The production mechanism for SiH($^2\Delta$) and SiH($^2\Pi$) is not well understood. Begeman *et al.*[14] have noted that while photolysis pulse energy dependencies for production of SiH($^2\Pi$) and SiH($^2\Delta$) make thermochemical sense, the ground-state LIF signal is not "prompt" as would be expected if direct production of SiH in the ground electronic state by a single photon process were the dominant mechanism. Production of SiH($^2\Delta$) by multiphoton processes has also been reported in the 248 nm photolysis of phenylsilane.[15] The facile production of SiH($^2\Delta$) combined with its short radiative lifetime[17] and deep violet emission facilitate detection of SiH by LIF since the detection system can be aligned and tuned without the need for the excitation laser. The emission spectrum from SiH($^2\Delta$) produced by ArF excimer laser photolysis of disilane[16] is shown in Figure 1.

The A ↔ X electronic transition of SiH has been known for over 60 years and has been thoroughly analyzed and assigned.[13,18-21] It consists of a series of rotationally resolved vibronic bands in the region 430–386 nm. A convenient scheme for LIF detection of SiH is excitation of single rotation lines of the $A^2\Delta(v' = 1) \leftarrow X^2\Pi(v'' = 0)$ band and detection of fluorescence from the $A^2\Delta(v' = 1) \rightarrow X^2\Pi(v'' = 1)$ band using appropriate spectral filtering. A portion of this spectrum[14] is shown, with line assignment, in Figure 2.

The high-resolution vibration–rotation spectrum of SiH was first reported in emission from silane discharges and was detected using Fourier transform IR emission spectroscopy.[22,23] The spectrum has also been observed in absorption using infrared diode laser absorption spectroscopy.[24] The (1 ← 0) vibrational band is observed in the range 2094–1838 cm^{-1} which is a convenient region for infrared diode laser work. Time-resolved IR diode laser absorption spectroscopy using this transition has been employed in one kinetic study[25] of SiH.

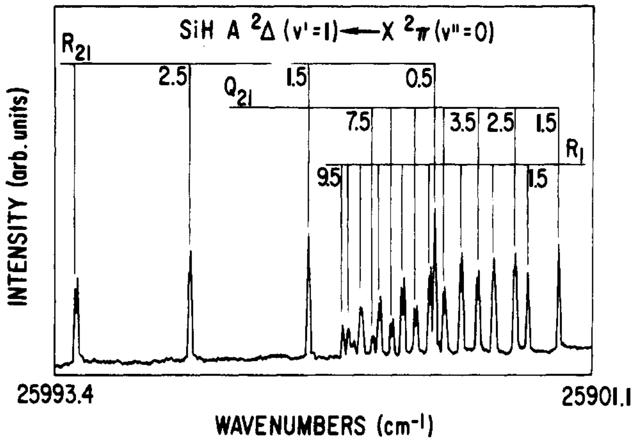


Figure 2. A portion of the LIF spectrum of SiH in a region which is convenient for kinetics studies.

Table 1. Rate Constants for SiH + H_2/D_2 at Room Temperature

reactant	rate constant, cm^3 molecule^{-1} s^{-1}	conditions	ref
H_2	$\leq (1.2 \pm 0.2) \times 10^{-14}$	5 Torr (He)	14
D_2	$\leq (1.8 \pm 0.2) \times 10^{-14}$	5 Torr (He)	14
H_2	$(1.6 \pm 0.1) \times 10^{-11}$	SiH (v'' = 1) 5 Torr (He)	14

Since it is a main group diatomic hydride, SiH has been studied by a variety of other spectroscopic techniques. Far-infrared laser magnetic resonance (LMR) spectra[26] and resonance-enhanced multiphoton ionization (REMPI) spectra[27] have been reported. Silylidyne has also been detected by photoionization mass spectrometry[28] (PIMS) and low-energy electron impact ionization mass spectrometry (EIMS).[29] None of these detection schemes have as yet been applied to direct kinetic studies. For spectroscopic studies, SiH has been formed in discharges of various types,[12,18,19,22,24-26] by broad band flash photolysis of phenylsilane,[21] and by reaction of silane with fluorine atoms.[24,26,27] Silylidyne is also formed in the broad band flash photolysis[30] of SiH_3I and has been shown to be the major product of silane photolysis in the vacuum ultraviolet.[31]

2.2. Reactions of SiH

a. SiH + H_2/D_2

The reaction of SiH with hydrogen has been studied only once, by Begemann *et al.*[14] They used ArF excimer laser photolysis of phenylsilane to generate SiH and LIF to monitor its loss rate. The loss rate for ground vibrational state SiH was measured for reaction with H_2 and D_2 and was found to be slow enough at room temperature that only upper limits could rigorously be reported. Removal of SiH ($v'' = 1$) by H_2 was also studied and was found to be significantly faster. The available data are presented in Table 1.

The only thermochemically feasible reaction channel at room temperature is three-body association to form silyl.

$$SiH + H_2 \rightleftarrows SiH_3^* \qquad (1)$$

$$SiH_3^* + M \rightarrow SiH_3 + M \qquad (2)$$

In (1) and (2) and in all following mechanisms, an asterisk denotes vibrational excitation of a species formed in a chemical activation process, and M is an inert molecule (a "third body") which removes vibrational excitation by collisional energy transfer.

The reaction of SiH with D_2 was studied in an effort to verify this mechanism and obtain an approximation to the high-pressure bimolecular limit, as had been done successfully in the case of SiH_2. Whereas in the case of SiH_2 insertion at similar total pressure,[32,33] substitution of D_2 for H_2 increases the observed loss rate over 1 order of magnitude by opening up isotope-scrambling channels (vide infra), no significant effect was seen in the case of SiH. The small increase in loss rate was attributed to scrambling by reaction (3):

$$SiH + D_2 \rightarrow SiHD_2^* \rightarrow SiD + HD \qquad (3)$$

Since the observed rates were so slow that reaction with impurities could not be ruled out, the result is inconclusive. It does, however, demonstrate that the observed loss rate is slow for reasons other than pressure fall-off effects.

Begemann *et al.*[14] also studied the removal rate for SiH(v'' = 1) by H_2 and observed a much faster process. They argued that the loss process was reaction with H_2 rather than pure vibrational quenching, based on the ~2000 cm^{-1} vibrational frequency mismatch between SiH and H_2. On the basis of this result and the v'' = 0 results they suggested that the reaction probably had an activation barrier on the order of the excess energy available to SiH (v'' = 1), which is ~25 kJ mol^{-1}. This hypothesis has been confirmed by *ab initio* calculations[34] which find a barrier of 23 ± 4 kJ mol^{-1}. Temperature- and pressure-dependent kinetic studies, which are required to confirm the barrier and the insertion mechanism experimentally, have not yet been carried out.

b. SiH + SiH_4 and $C_6H_5SiH_3$

The first report of a direct measurement of any rate constant for an SiH reaction was that of Schmitt *et al.*,[12] who measured the loss rate of SiH following its production in a pulsed silane discharge. They attributed the loss rate to reaction with SiH_4 at a temperature of 500 K and reported a rate constant of 3.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. There have been three subsequent studies of the reaction, two by flash photolysis/LIF[14,15] and one by pulsed-discharge/time-resolved infrared diode laser absorption.[25] The results of all four studies as well as an estimate for the reaction of SiH with its photochemical precursor, phenylsilane, are summarized in Table 2.

The flash kinetic studies give a gas kinetic rate constant (i.e. a rate constant close to the gas-phase collision rate calculated from the kinetic theory of gases) with a pressure dependence, suggesting a barrierless three-body association reaction to form Si_2H_5 as the final product.

$$SiH + SiH_4 \rightleftarrows Si_2H_5^* \qquad (4)$$

$$Si_2H_5^* + M \rightarrow Si_2H_5 + M \qquad (5)$$

Table 2. Rate Constants for Reactions of SiH with Silane and Phenylsilane at Room Temperature

reactant	rate constant, cm^3 $molecule^{-1}$ s^{-1}	conditions[a]	ref
SiH_4	$(4.3 \pm 0.3) \times 10^{-10}$	5 Torr (He)	14
	$(2.7 \pm 0.5) \times 10^{-10}$	2 Torr (He)	14
	$(2.8 \pm 0.6) \times 10^{-10}$	2 Torr (Ar)	15
	$(3.3 \pm 0.5) \times 10^{-12}$	4–50 m Torr, 500 K	12
	$(3.2 \pm 0.9) \times 10^{-12}$	0.5 Torr, 400 K	25
$C_6H_5SiH_3$	$\sim 3 \times 10^{-10}$	2 Torr (Ar)	15

[a] Room temperature unless noted.

Table 3. Rate Constants for Reactions of SiH with NO and O_2 at Room Temperature

reactant	rate constant, cm^3 $molecule^{-1}$ s^{-1}	conditions	ref
NO	$(2.5 \pm 0.3) \times 10^{-10}$	2 Torr (Ar)	15
O_2	$(1.7 \pm 0.2) \times 10^{-10}$	2 Torr (Ar)	15

For the common total pressure of 2 Torr, the flash kinetic results are in excellent agreement, and give rate constants much higher than the pulsed discharge results, which also appear to agree with each other. While one may argue that the pulsed discharge results are subject to some inaccuracy because the silane partial pressure is not known precisely, this cannot explain the 2 order of magnitude difference. A combination of pressure fall-off effects, as suggested by Begemann *et al.*,[14] and a negative activation energy, as suggested by Nemoto *et al.*,[15] can explain the difference. The pressure dependence of the rate constant observed between 2 and 5 Torr is consistent with a three-body reaction and the negative temperature dependence is reasonable, on the basis of experimental results for the analogous SiH_2 reaction (vide infra). The reaction of SiH with phenylsilane is assumed to be insertion into a SiH bond, however reaction with the π-electron system of the phenyl ring cannot be ruled out *a priori*.

c. SiH + NO and O_2

Nemoto *et al.*[15] studied the reaction of SiH with NO and O_2. They observed gas kinetic rate constants, suggesting barrierless reactions. The rate constants are given in Table 3.

On the basis of available thermochemistry they suggest the following reaction chemistry:

$$SiH + NO \rightarrow SiO + NH \qquad (6)$$

$$SiH + O_2 \rightarrow SiO + OH \qquad (7)$$

$$\rightarrow SiO_2 + H \qquad (8)$$

No further information is available on the mechanism or product distributions for these reactions.

2.3. Enthalpy of Formation of SiH

The magnitude of the quantity ΔH_f° (SiH) is apparently reasonably well agreed among experi-

Table 4. Data for ΔH_f° (SiH) (kJ mol^{-1})

year	value	authors	ref
		i.Experimental Values	
1965	369	Verma	21
1971	376	Rao, Lakshman	35
1978	341	Carlson, Duric, Erman, Larsson	36
1987	376 ± 7	Boo, Armentrout	37
1987	376 ± 5	Berkowitz, Greene, Cho, Ruscic	28
1990	382 ± 8	Boo, Elkind, Armentrout	38
		ii.Theoretical Values	
1985−1992	384	Melius *et al.*	39
	385	Melius *et al.*	40
	381	Melius *et al.*	41
	381	Melius *et al.*	42
1985−1991	369	Pople *et al.*	43
	372	Pople *et al.*	44
	366	Pople *et al.*	45
1991	376	Ignacio, Schlegel	46
1991	376	Sax, Kalcher	47
1992	369	Grev, Schaefer	10
1992	375	Grev, Schaefer	10

mentalists, but there is some dispute with the most recent theoretical calculations. The data has been thoroughly reviewed by Grev and Schaefer,[10] and therefore we do not give a detailed history of the measurements.

Data have been obtained via spectroscopic studies[21,35,36] photoionization mass spectrometry[28] and Si$^+$ ion beam reaction thresholds.[37,38] These are listed in Table 4 together with values obtained via *ab initio* theoretical calculations.

A superficial glance at the numbers suggests that in recent years there is reasonable concordance both among experimentalists and theoreticians and between them. However appearances may be deceptive. The calculations of Grev and Schaefer[10] have been carried out at the highest level and do not contain the empirical corrections of some of the other theoretical studies. They have found a discrepancy between their calculated value of the atomization energy of SiH_4 and experiment. Their two values for ΔH_f° (SiH) of 369 and 375 kJ mol^{-1} are relative to ΔH_f° (Si) and ΔH_f° (SiH_4) respectively. Since all the experimental values are relative to ΔH_f° (Si) this indicates that theory is at the extreme error limit of the most recent experimental values. There is clearly a small, but awkward, discrepancy to resolve here.

3. Silylene, SiH2

3.1. Sources, Detection, and Monitoring

Silylene, SiH_2, is one of the most reactive transients known and therefore the study of its reactions by direct monitoring requires appropriate fast response techniques.[48] The most widely applied techniques for study of the kinetics of SiH_2 reactions in the gas phase has been that of laser resonance absorption flash kinetic spectroscopy (LRAFKS) first used by Jasinski[32] and subsequently in the Reading laboratories of Baggott, Frey, and Walsh.[49] The first kinetic study, however, was that of Inoue and Suzuki[33] who used laser-induced fluorescence to detect SiH_2. These techniques have in common the requirements of rapid creation of SiH_2, combined with a fast detection system. The most common source of SiH_2 is the UV 193 nm photolysis of phenylsilane,[32,33] conveniently provided by the ArF line of a rare gas halide excimer laser. With a typical pulse energy of *ca.* 100 mJ cm^{-2} and 10 ns pulsewidth, this UV photodecomposition yields a sufficient concentration of SiH_2 to generate excellent low-noise signals, despite the fact that phenylsilylene, PhSiH, is formed simultaneously and in higher yields.[50] Other UV sources which have been used are the 193 nm photodecompositions of Si_2H_6[51,52] and Si_3H_8[52] and the 248 nm photodecomposition of SiH_3I.[53] The 193 nm radiation most commonly used, means that some substances of potential interest for reactivity studies, which absorb at 193 nm, have not been investigated. There is therefore need and scope for the development of new photochemical sources. Infrared multiphoton decomposition (IRMPD) of SiH_4,[54,55] Si_2H_6,[55] and alkylsilanes[56] has been used to generate SiH_2 but these sources have not found widespread use for kinetic studies.

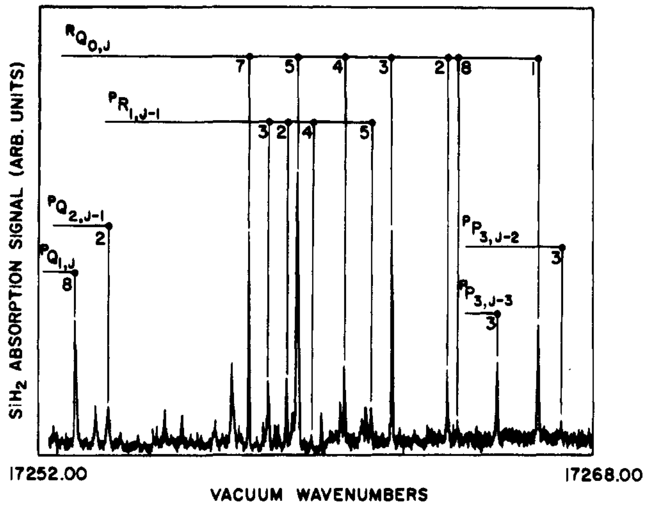


Figure 3. High-resolution absorption spectrum of a portion of the $^1B_1(0,2,0) \leftarrow {}^1A_1(0,0,0)$ spectrum of SiH_2.

Silylenes possesses a strong rovibrational absorption spectrum arising from transitions in the $^1B_1 \leftarrow {}^1A_1$ electronic band. Herzberg and Johns[57] were the first to observe this spectrum in the flash photolysis of $PhSiH_3$. Subsequently, much improved spectra were obtained by Dubois, Herzberg, and Verma[58] in the 480−650 nm region, from silylene produced by the flash discharge of silane in excess hydrogen. The spectrum consisted of seven bands, with the strongest bands at 610.0, 579.6, and 552.6 nm. These correspond to the bending vibrational transitions, $^1B_1$ $(0,n,0) \leftarrow {}^1A_1$ (0,0,0). A detailed rotational analysis of these bands was carried out by Dubois.[59] Jasinski and Chu[51] have recorded the most highly resolved spectrum to date using laser absorption flash kinetic spectroscopy. They scanned the spectral region from 17242 to 17352 cm^{-1}, around the origin of the $^1B_1(0,2,0) \leftarrow {}^1A_1(0,0,0)$ band. Their spectrum consisted of approximately 100 single rotational lines showing that it was considerably richer than previously believed. About half the lines were readily assigned using known SiH_2 transitions.[59] A portion of the spectrum is shown in Figure 3 including the intense $^RQ_{0,J}^{(5)}$ line which has been used by Jasinski and Chu[51] and Baggott *et al.*[49] to monitor

SiH_2. Duxbury *et al.*[60] have performed a recent reanalysis of the SiH_2 spectrum, incorporating all available spectroscopic information.

To detect SiH_2 with good signal-to-noise using this highly resolved narrow line width spectrum a single frequency dye laser is necessary. The chosen absorption line[49,51] occurs at a wavelength of 17259.50 cm^{-1}. Fluorescence from the same vibronic band was used in the LIF experiments.[33] The corresponding high-resolution rovibronic spectrum of SiD_2 has only recently become available.[61] Prior to this Mason *et al.*[62] obtained a crude spectrum by point-by-point scan and were able to use a strong absorption line (unassigned) at 17387.07 cm^{-1} to obtain the first kinetic data for SiD_2 (using flash photolysis of $PhSiD_3$).

Silylene has also been detected[63] by infrared diode laser absorption spectroscopy using the ν_2 (bending) vibration around 998 cm^{-1} and by PIMS[28] and low-energy EIMS.[29] These techniques have, as yet, not been applied to kinetic studies. Robertson and Rossi[64] have also reported a REMPI spectrum for SiH_2 and used this technique to study surface loss kinetics (*vide infra*).

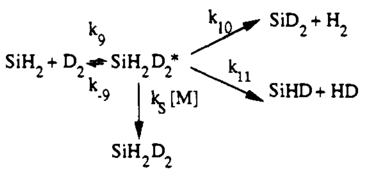
3.2. SiH_2 Insertion Reactions

SiH_2 inserts readily into Si–H bonds and this is one of its characteristic reactions. This section is devoted to this process, but also to the important reaction with H_2 and its isotopic variants. The question of C–H bond insertion is also mentioned.

a. $SiH_2 + H_2/D_2/HD$ (and $SiD_2 + H_2/D_2$)

The first absolute rate constant for the reaction of SiH_2 with H_2 was reported by Inoue and Suzuki[33] using LIF to monitor the concentration of SiH_2. At the total pressure of 1.8 Torr (He) they found a rate constant of $(1.0 \pm 0.4) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Nearly at the same time Jasinski[32] measured the rate constant for SiH_2 with D_2 using the LRAFKS technique. The rate constant obtained at 2–3 Torr total pressure (He) was $(2.7 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. This value is much higher than that obtained by Inoue and Suzuki for reaction with H_2.

Jasinski reasoned that the rate constant for reaction of $SiH_2 + D_2$ more nearly represents the true rate of insertion than that for $SiH_2 + H_2$. The reaction scheme is as follows:



(9-11)

SiH_2D_2*, the vibrationally excited silane formed by the insertion process (9), can react irreversibly by decomposition to SiD_2 (10) or SiHD (11). Assuming no anomalously large isotope effects, only one part in six (on a statistical basis) of the SiH_2D_2* can revert to $SiH_2 + D_2$. This plus collisional stabilization (k_s[M]) renders step (9) almost irreversible and representative of the high-pressure limit of the bimolecular reaction. For $SiH_2 + H_2$, however, SiH_4*, the vibrationally excited silane initially formed, can decompose back to $SiH_2 + H_2$, thus making it a pressure-dependent process, with a significant third-body requirement.

Table 5. Rate Constants for $SiH_2 + H_2$ and Isotopic Variants at Room Temperature

reaction	k, 10^{-12} cm^3 $molecule^{-1}$ s^{-1}	ref
$SiH_2 + H_2$	3.2[a]	51
$SiH_2 + D_2$	2.6 ± 0.7	32
	1.9 ± 0.2	49
$SiH_2 + HD$	2.0 ± 0.4	51
$SiD_2 + H_2$	3.8 ± 0.1	62

[a] Infinite pressure value.

The immediate result of these first direct measurements of this rate constant, was to dispel the view that the reaction of $SiH_2 + H_2$ had a positive activation energy variously estimated at 23.1[65] and 43 kJ mol^{-1}.[66] These values were derived from earlier *relative* rate measurements which were based (in hindsight) on unreliable assumptions. If they had been correct, the room temperature rate constant for $SiH_2 + H_2$ would have had to have been at least 4 orders of magnitude lower than observed. Interestingly at this time theoretical calculations showed a drop in barrier from *ca.* 30[67-70] to 7 kJ mol^{-1}.[71] The first direct measurements of the activation energy gave a value of zero (with an estimated maximum possible value of 1.3 kJ mol^{-1}). This was obtained by Baggott *et al.*[49] who reported a temperature-independent rate constant of $(1.9 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for $SiH_2 + D_2$ over the range 268–330 K (at 5 Torr total pressure in SF_6). More recently the Reading group has extended the temperature range for this reaction up to 553 K and has found a negative activation energy of −2.0 kJ mol^{-1}.

Jasinski and Chu[51] measured absolute rate constants for the $SiH_2 + H_2$ reaction in the 1–100 Torr pressure range (He). The pressure dependence of the rate constants for this reaction was reproduced by RRKM calculations and the high-pressure limiting value derived of $k = 3.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, is in good agreement with the value obtained from the $SiH_2 + D_2$ experiments. The rate constant measured at 2 Torr total pressure was 2.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, in rough agreement with the value obtained at 1.8 Torr by Inoue and Suzuki.[33] These studies also confirmed that the reactions of SiH_2 with HD and D_2 showed much less pressure dependence and the isotope effect appeared to be small.[51] Baggott *et al.*,[49] however, using simple transition-state theory and an activated complex proposed by Roenigk *et al.*,[73] obtained the surprising value of 10.2 for the isotope effect (k_{H_2}/k_{D_2}).

Recently Mason *et al.*[62] have reported the rate constant of 3.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for $SiD_2 + H_2$, the first direct kinetic study of SiD_2. Just as for the $SiH_2 + D_2$ system, this reaction is almost pressure independent and should represent the true rate of insertion (Jasinski's argument). Table 5 summarizes these results.

More recent, unpublished, studies in the Reading laboratories[72] have made a comprehensive survey of kinetics of the four possible SiH_2 (SiD_2) + H_2 (D_2) reactions. Rate constants have been measured over

Table 6. Arrhenius Parameters for $SiH_2 + H_2$ and Isotopic Variants[a]

reaction	T range, K	log A, cm^3 $molecule^{-1}$ s^{-1}	E_a, kJ mol^{-1}
$SiH_2 + D_2$	300−553	−12.07	−2.03
$SiD_2 + H_2$	294−528	−11.87	−2.54
$SiH_2 + H_2$	300−513	−12.01[b]	−2.34[b]
		−11.75[c]	−1.84[c]
$SiD_2 + D_2$	298−498	−12.35[b]	−3.14[b]
		−12.09[c]	−3.52[c]

[a] Data from ref 72. [b] Infinite pressure values obtained from extrapolated rate constants. [c] Values obtained via transition state theory of isotope effects.

more than a 200 K temperature range and 5−100 Torr pressure range ($SiH_2 + H_2$, $SiD_2 + D_2$). The Arrhenius parameters for these processes are listed in Table 6.

Rate constants are consistent with the earlier studies.[32,49,51] The major findings of this work are that the activation energies are all negative, the activated complex for $SiH_2 + H_2$ is fairly tight (corresponding to an A factor for SiH_4 decomposition of *ca.* $10^{14.5}$ s^{-1}) and the isotope effects are small, but not negligible. Simple transition-state theory calculations,[72] not detailed here, reproduce the measured isotope effects reasonably well based on the *ab initio* transition state structure (C_s symmetry) of Gordon *et al.*[71] Calculations based on the semiempirical transition-state structure (C_{2v} symmetry) of Roenigk *et al.*[73] give a poor fit to the isotope effects. These structures are shown in Figure 4.

However, RRKM calculations based on the *ab initio* structure do not reproduce the pressure dependence of the rate constants very well.[72] This contrasts with the calculations of Moffat *et al.*,[74] based on earlier studies of this system. The problem appears to be that the pressure dependencies of both the SiH_2 + H_2 association reaction and the SiH_4 decomposition apparently require a looser transition state (based on A being *ca.* $10^{15.8}$ s^{-1} for the decomposition reaction). Such a transition-state structure, at least for the insertion reaction in the temperature range 300−500 K appears to be incompatible with the data. There are clearly difficulties to be resolved here. Nevertheless the *ab initio* (C_s) structure seems more likely since it represents a geometry of approach of H_2 to SiH_2 in which the electrophilic interaction between the H_2 bonding electrons and empty p orbital of SiH_2 is strongly favored.

b. $SiH_2 + SiH_4$

Insertion of SiH_2 into the Si−H bond is one of the key processes in chemical vapor deposition.[1] Insertion into the Si−H bonds of SiH_4 is the most fundamental of these processes. The reaction is a three-body association:

$$SiH_2 + SiH_4 \rightleftarrows Si_2H_6^* \qquad (12)$$

$$Si_2H_6^* + M \rightarrow Si_2H_6 + M \qquad (13)$$

In the case of reaction with silane, disilane is the only possible product. In reaction with higher silanes, other decomposition channels may be available to the chemically activated polysilane (*vide infra*). Once again direct measurements have supplanted the older, much lower estimates of the rate constant[65,66] on the basis of relative rate measurements. Inoue and Suzuki[33] measured the absolute rate constant, using the LIF technique, for this reaction at 1 Torr total pressure (He) at 298 K. They found a value of (1.1 ± 0.2) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Jasinski and Chu,[51] using the LRAFKS technique, determined the absolute rate constant to be (6.7 ± 0.7) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 1 Torr (He), in reasonable agreement. These authors also studied the effect of pressure up to 95 Torr and performed RRKM calculations to reproduce the observed dependence. This yielded the high-pressure limiting rate constant, $k = 2.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Using the same technique Baggott *et al.*[75] measured absolute rate constants for this reaction and obtained values *ca.* 1.7 times higher over the same pressure range (He bath gas), thus leading to a value for $k = 4.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The cause of the difference with Jasinski and Chu[51] is not obvious. A possible explanation for the discrepancies is that the kinetic measurements were made at significantly different silane number densities, and hence pseudo-first-order decay times, by the two groups. Jasinski and Chu[51] worked at higher silane densities to guard against silylene losses other than by reaction with silane. The resulting more rapid kinetics may have resulted in significant interference from vibrationally excited silylene. Since Jasinski and Chu[51] assumed in their work that the reaction had zero activation energy but in fact it is now known to have a small *negative* activation energy (*vide infra*), the presence of a significant population of vibrationally excited silylene could give rise to slower reported rate constants. This hypothesis remains to be verified experimentally. Another study by Dietrich *et al.*[55] using IRMPD to generate SiH_2 from SiH_4 yields pressure-dependent rate constants leading to $k = (1.1 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. However these experiments were carried out under solid deposition conditions and it is not clear that this corresponds to comparable (298 K) temperatures. In fact the method of formation of SiH_2, IRMPD of silane, could again lead to significant contributions from vibrationally excited species (in this case "hot" silane) and corresponding slower rate constants.

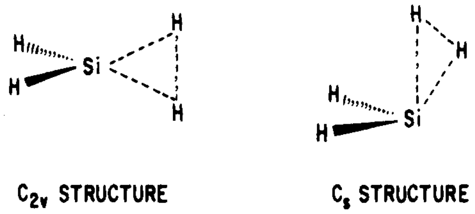


Figure 4. Transition state structures for the reaction of $SiH_2 + H_2$.

A more complete temperature and pressure study (SF_6 bath gas) has been carried out by Becerra *et al.*[52a,76] A selection of the rate constants are shown in Table 7. In this table, k_∞ values were obtained by fitting RRKM calculated fall-off curves as shown in Figure 5. The modeling of these data used a variational transition state. The 298 K value of k_∞ confirmed the earlier measurements[75] and pointed to the high collisional efficiency of this reaction.

Table 7. Rate Constants for SiH_2 + SiH_4 at Two Pressures (SF_6 Bath Gas) and Six Temperatures

	k, 10^{-10} cm^3 molecule^{-1} s^{-1}	
T, K	P = 10 Torr	$P = \infty^a$
296	4.1 ± 0.3	4.6 ± 0.3
363	3.2 ± 0.3	3.9 ± 0.3
432	2.3 ± 0.3	3.2 ± 0.3
488	1.6 ± 0.3	2.6 ± 0.3
578	1.2 ± 0.4	2.6 ± 0.4
658	0.8 ± 0.4	2.2 ± 0.4

[a] Values obtained by extrapolation.

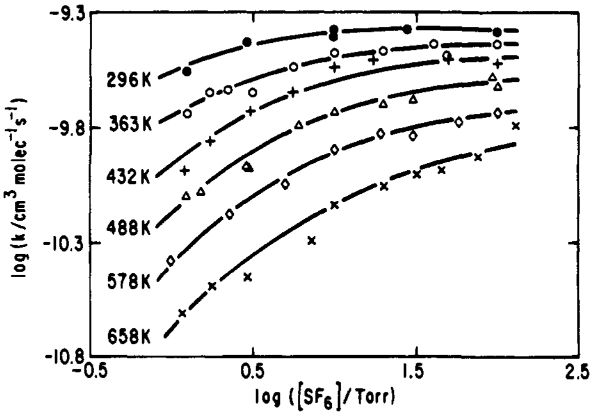


Figure 5. Experimental data and RRKM calculations for SiH_2 + SiH_4 at six temperatures.

Arrhenius treatment of the temperature dependence of k_∞ leads to $A = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $E_a = -3.0$ kJ mol^{-1} although the plot is slightly curved. The negative activation energy is consistent with the idea of a weak intermediate complex on the approach potential for this reaction. *Ab initio* calculations[52a,76] supported the presence of such a complex at *ca.* 52 kJ mol^{-1} below the reaction threshold, although the barrier to rearrangement of this complex to Si_2H_6 was only 6.5 kJ mol^{-1}. The structure of the complex is shown in Figure 6.

The geometry of this complex suggests substantial transfer of H from SiH_4 to SiH_2 again supporting the idea of an electrophilically led insertion process.

This reaction system and its reverse are the basis of the currently most precise value for $\Delta H_f°(SiH_2)$ (*vide infra*).

Table 8. Comparison of Room Temperature Rate Constants for SiH_2 + Si_2H_6

k, 10^{-10} cm^3 molecule^{-1} s^{-1}	P, Torr	ref
5.7 ± 0.2	1 (He)	33
1.5 ± 0.2	1 (He)	51
2.8 ± 0.3	5 (He)	51
3.4 ± 0.3	9.5 (He)	51
4.6 ± 0.7	5 (Ar)	75
5.8 ± 0.6	10 (Ar)	52
6.6 ± 0.3	10 (SF_6)	52
6.4 ± 0.2	10 (C_3H_8)	52

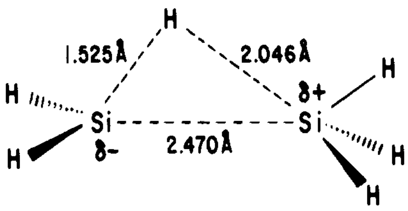


Figure 6. *Ab initio* structure of the intermediate complex formed in the reaction of SiH_2 with SiH_4.

c. SiH_2 + Si_2H_6

Once again direct measurements have supplanted older values[65,66] from relative rate studies. Absolute rate constants have been obtained in the same laboratories as for SiH_2 + SiH_4.[33,51,52a,75,76] Values are shown in Table 8.

A further value of (2.7 ± 0.4) × 10^{-10} cm^3 molecule^{-1} s^{-1} was obtained at an uncertain temperature[55] and is not included in the table. There is a discrepancy here between pressure-dependent rate constants found by Jasinski and Chu[51] and the unpublished pressure-independent values of Becerra *et al.*,[52b] which are close to the value of Inoue and Suzuki.[33] While Jasinski and Chu measure a variation of more than a factor of 2 over a 10-fold pressure range in helium, Becerra *et al.* find higher values, independent of pressure (3–30 Torr, SF_6) and almost independent of bath gas (Ar, C_3H_8, SF_6). Again the reason for these differences is not clear but pressure dependence in this system should not be strong because the initially formed vibrationally excited Si_3H_8 has an alternative, preferred pathway to decomposition,[77] thus making the reaction predominantly irreversible, viz.

$$SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8^* \rightarrow SiH_3SiH + SiH_4 \quad (14)$$

The temperature dependence (295–590 K) of this reaction, studied by Becerra *et al.*,[52b] gives the average Arrhenius parameters $A = 3.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $E_a = -1.9$ kJ mol^{-1}, although the Arrhenius plot is slightly curved. The negative temperature dependence and high collisional efficiency of this reaction suggest that similar considerations determine its mechanism as for SiH_2 + SiH_4.

d. SiH_2 + Si_3H_8

No published kinetic data exists for this reaction. However, in an unpublished study its kinetics have been investigated by Becerra *et al.*,[52b] over a temperature range of 297–595 K in C_3H_8 and Ar buffer gases, and at six temperatures over the range 295–578 K in SF_6. Si_3H_8 was in this case both the precursor of SiH_2 and the substrate for the reaction. The reaction was tested for pressure dependence over the range 1–30 Torr. None was found.

Rate constants at room temperature were (7.8 ± 0.9) × 10^{-10} cm^3 molecule^{-1} s^{-1} in SF_6 and (8.0 ± 0.2) × 10^{-10} cm^3 molecule^{-1} s^{-1} in C_3H_8. In Ar, values were somewhat lower (between 50 and 80% of those in SF_6) over the temperature range but an undetected experimental error was suspected. The increased molecular complexity of this reaction (relative to SiH_2 + SiH_4 and SiH_2 + Si_2H_6) combined with the probability of alternative decomposition pathways from the energized tetrasilane products (both normal and isotetrasilane) explain the lack of a pressure dependence in this reaction. The temperature dependence gives rise to the average Arrhenius parameters, $A = 3.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $E_a = -2.0$ kJ

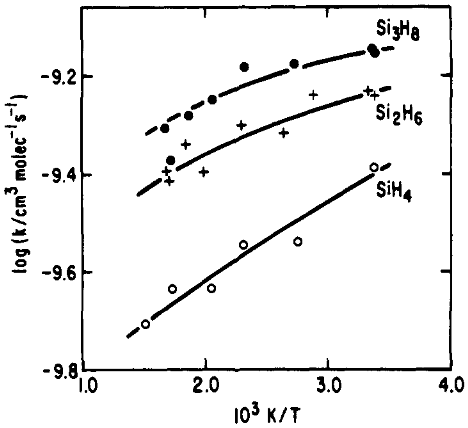


Figure 7. Arrhenius plots for reaction of SiH_2 with a homologous series of silicon hydride molecules.

Table 9. Comparison of Rate Constants for SiH_2 Insertion (per Si−H Bond)

	k, 10^{-10} cm^3 molecule^{-1} s^{-1}	
substrate	$T = 298$ K	$T = 588$ K
SiH_4	1.15	0.59
Si_2H_6	1.08	0.72
Si_3H_8	0.99	0.72

mol^{-1}, although the Arrhenius plot is slightly curved. These curved Arrhenius plots for the reactions of SiH_2 with SiH_4, Si_2H_6 and Si_3H_8 are shown in Figure 7. The magnitude of the rate constants and the almost statistical relationship between them (Table 9) attests to the high collisional efficiency of these reactions, and the looseness of the activated complexes.

e. SiH_2 + Me_nSiH_{4-n} (n = 1–4)

Baggott *et al.*[75] measured the first rate constants for reaction of SiH_2 with the methylsilanes ($MeSiH_3$, Me_2SiH_2, Me_3SiH, and Me_4Si). The study was carried out at room temperature and the results are shown in Table 10. No pressure dependence was found for SiH_2 + $MeSiH_3$, and it was assumed therefore that the other reactions were pressure independent. The unique product[75] of the reactions of silylene with methylsilanes (except tetramethylsilane) is the corresponding disilane:

$$SiH_2 + Me_nSiH_{4-n} \rightarrow Me_nSiH_{3-n}SiH_3 \quad (15)$$

for n = 1−3. In the case of tetramethylsilane only insertion into C−H or Si−C bonds is possible, but is unobserved to date.

Carpenter and Walsh[78] have extended these studies for $MeSiH_3$, Me_2SiH_2, and Me_3SiH over a temperature range of 295−625 K and a pressure range of 3−100 Torr (SF_6). No pressure dependencies were found except for SiH_2 + $MeSiH_3$ at 600 K. The measured Arrhenius parameters can be seen in Table 11.

Again small negative activation energies are found, as for the other Si−H insertion reactions. The study of SiH_2 + Me_4Si has been repeated by Becerra and Walsh[79] giving an (apparent) rate constant of (1.7 ± 0.2) × 10^{-13} cm^3 molecule^{-1} s^{-1}. The rate constant value was shown to reduce with further purification of the already 99.9% pure Me_4Si. However even 0.1% of a remaining reactive impurity would still account for this rate constant. This is consistent with the lack of reactivity of SiH_2 toward C−H bonds compared to its reactivity with Si−H bonds (*vide infra*).

Table 10. Rate Constants for SiH_2 Reactions with the Methylsilanes

species	k, 10^{-10} cm^3 molecule^{-1} s^{-1}
$MeSiH_3$	3.7 ± 0.2
Me_2SiH_2	3.3 ± 0.3
Me_3SiH	2.5 ± 0.1
Me_4Si	0.0027

Table 11. Arrhenius Parameters for SiH_2 Reactions with the Methylsilanes

species	log A, cm^3 molecule^{-1} s^{-1}	E_a, kJ mol^{-1}
$MeSiH_3$	−9.82	−2.39
Me_2SiH_2	−10.00	−3.12
Me_3SiH	−10.14	−3.20

f. SiH_2 + Alkanes

Inoue and Suzuki[33] reported the absolute rate constant, k = (1.0 ± 0.3) × 10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction of SiH_2 with CH_4 measured by the LIF technique at 1 Torr total pressure. Chu *et al.*,[53] using the LRAFKS technique, determined upper limits for the rate constants of the reactions with CH_4 and C_2H_6 at 5 Torr total pressure. They found substantially lower values of (2.5 ± 0.5) × 10^{-14} and (1.2 ± 0.5) × 10^{-14} cm^3 molecule^{-1} s^{-1}, respectively. The authors explained that a 0.01% impurity in the methane or ethane, reacting on every collision with SiH_2, could account for all of the observed silylene removal. This interpretation is also consistent with the observation that ethane appears to react slightly slower even though more CH bonds are available. Eley *et al.*[80] found no observable reaction of silylene with methane in their competitive rate study. The anticipated, but thus far unobserved, reaction is insertion into the C−H bond.

In order to test the reactivity with strained carbon−carbon bonds Chu *et al.*[53] examined the reaction of silylene with cyclopropane. A small rate constant was obtained but this did not signify evidence of the reaction in question because all of the observed reactivity could be accounted for by the 1% propylene impurity (which reacts readily, *vide infra*) in the commercially available sample of cyclopropane.

g. Nature and Mechanism of the Insertion Process

The picture of the insertion process into Si−H bonds that emerges from the kinetic studies with SiH_2 is that of a collisionally controlled process which is almost indiscriminate among different substrate molecules (at the high-pressure limits). Furthermore, the reactions studied so far all appear to possess small negative activation energies in the range −2 to −4 kJ mol^{-1} suggestive of a slight tightening of the activated complex for reaction as the temperature increases (variational character). These findings are consistent with current theoretical ideas of the nature of the insertion process[67,70] which are illustrated in Figure 8.

The insertion process may be viewed as comprising an "electrophilic" stage with transfer of electron density from the Si−H bond into the empty p orbital

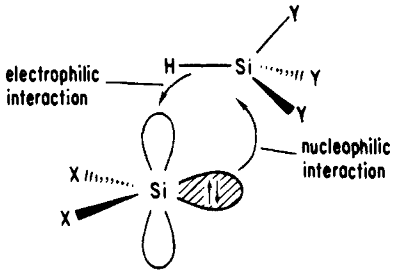


Figure 8. Schematic illustration of the nature of the interaction between a silylene and the Si−H bond of a substrate.

on the silylene and a "nucleophilic" stage with donation of the silylene lone pair to make a new Si−Si bond. Thus potentially the reaction may occur in two steps. From studies of substituent effects in both silylene and substrate a picture has emerged which supports this two-step character and the involvement of an intermediate complex. This picture has been discussed by the Reading group in a number of publications beginning in 1988[81] and most recently in the general review of silylene reactions by Becerra and Walsh.[3] This picture supports the theoretical viewpoint that the electrophilic stage precedes the nucleophilic stage. For SiH_2 reactions, the second, nucleophilic stage appears to occur so fast that the involvement of an intermediate complex has no kinetic consequences under experimental conditions thus far employed (although this is not true for other silylenes, e.g. $SiMe_2$).[3] While the involvement of complexes as intermediates in $SiH_2 + SiH_4$ may not be significant, it is interesting to note the calculations of Trinquier[82] who has found that structures of the type $H_2M-H-MH_3$ become increasingly stable as M changes from C to Pb down group 4 of the periodic table.

As far as insertion of SiH_2 into C−H bonds is concerned, the data suggest little, if any, reaction. These negative results are consistent with a process having a substantial activation barrier. Estimates of the activation energy for reaction of $SiH_2 + CH_4$ based on rate measurements[83,84] of the reverse process (CH_3SiH_3 decomposition) originally gave values of *ca.* 80 kJ mol^{-1}. A more recent evaluation of the thermochemistry by Davidson[85] has reduced this figure to *ca.* 42 kJ mol^{-1}. On the basis of the thermochemistry presented in this review, we estimate a value of 55 ± 12 kJ mol^{-1} in reasonable agreement with Davidson.[85] These values compare with *ab initio* estimates of the barrier by Gordon's group,[67] of 115 and 92 kJ mol^{-1}. Thus, although there are still differences between experimental evaluation and theory, there is agreement that the barrier for this reaction is sizeable. It is worth pointing out that *intramolecular* insertion of silylenes into C−H bonds is a known process.[85]

The difference between the facile insertion into Si−H bonds and the difficult, activated, insertion into C−H bonds is probably related to the differing polarities of the bonds.[3] In the former case the polarization is Si^+-H^- and the electrophilic silylene has no difficulty approaching the negatively charged hydrogen in the initial approach. By contrast the polarization of the carbon−hydrogen bond is C^--H^+ and the silylene access to the desired electron pair is hindered by the positively charged hydrogen.

Table 12. Rate Constants for $SiH_2 + C_2H_4$ in the Presence of Different Bath Gases

	k, 10^{-10} cm^3 molecule^{-1} s^{-1}		
P, Torr	He	Ar[c]	SF$_6$[c]
1	0.97[a] 0.27[b]	0.39	0.67
5	0.55[b]	0.79	1.3
10	0.80[b]	1.3	1.58

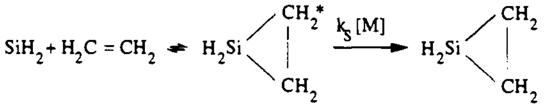
[a] Reference 33. [b] Reference 53. [c] Reference 87.

3.3. SiH_2 π-Type Addition Reactions

SiH_2 adds readily to carbon double and triple bonds. This is another of its most characteristic reactions and, after the Si−H insertion process, the most widely studied.

a. $SiH_2 + C_2H_4/C_2D_4$

Inoue and Suzuki[33] measured the first absolute rate constant for SiH_2 with C_2H_4 at room temperature, using the LIF technique. They found a value of $k = (9.7 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1 Torr total pressure in He. Using the LRAFKS technique, Chu *et al.*[53] obtained a value of $(2.7 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} under the same conditions, and additionally observed a pressure dependence. Al-Rubaiey *et al.*[87] have repeated these measurements in Ar and SF_6 bath gases. The values are compared in Table 12. Al-Rubaiey *et al.*[87] have extended their measurements over the pressure range 1−50 Torr and shown that, apart from the Inoue and Suzuki value,[33] the results can be explained in terms of a third body-assisted association process with differing collisional efficiencies for He, Ar, and SF_6, *viz.*:



(16)

Additionally Al-Rubaiey *et al.*[87] have shown that the pressure dependence can be modeled via an RRKM calculation. To obtain a good fit to the data they required a value for the activation energy for silirane decomposition of *ca.* 197 kJ mol^{-1} consistent with theoretical calculations,[88,89] but in disagreement with a measured value of 130 kJ mol^{-1} for the analogous hexamethylsilirane decomposition[90] (the only silirane decomposition for which at present there is an experimental activation energy). In a more extensive study Al-Rubaiey and Walsh[91] have studied the reaction over the pressure range 1−100 Torr (in SF_6) and at five temperatures in the range 298−595 K. Some of the rate constants are shown in Table 13. The infinite pressure values were found by extrapolation of the pressure-dependent curves with the assistance of RRKM modeling. The temperature-dependent rate constants correspond to Arrhenius parameters of $\log (A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -9.97$ and $E_a = -2.9$ kJ mol^{-1}. These indicated a fast, collisionally controlled association process.

In a disagreement over product formation, Al-Rubaiey and Walsh[91] searched, using GC analysis,

Table 13. Rate Constants for $SiH_2 + C_2H_4$ at Two Pressures (SF_6 Bath Gas) and Five Temperatures

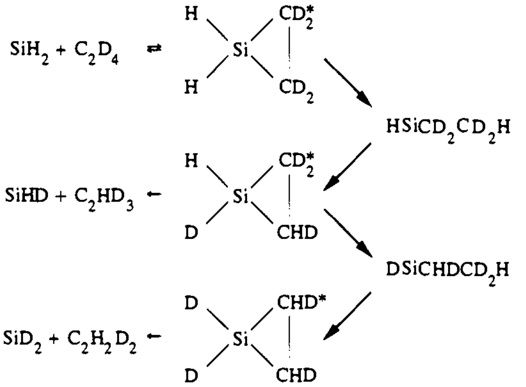
	k, 10^{-10} cm^3 molecule^{-1} s^{-1}	
T, K	P = 10 Torr	$P = \infty^a$
298	1.58 ± 0.03	3.5 ± 1.2
355	1.15 ± 0.02	3.0 ± 1.2
415	0.731 ± 0.017	2.5 ± 1.0
515	0.357 ± 0.005	2.2 ± 0.9
595	0.148 ± 0.007	1.9 ± 0.9

[a] Values obtained by extrapolation.

but found no evidence for vinylsilane formation in this reaction, as claimed by Fisher and Lampe.[92] Other analytical evidence[66,93] is against vinylsilane formation and Al-Rubaiey and Walsh have suggested that Fisher and Lampe may have seen the mass spectrum of silirane. The latter have recently measured relative rate constants[92] for reaction of SiH_2 with C_2H_4 and with SiH_4. It seems as if these are not in good agreement with absolute values.[91] This may be the result of nonthermalized SiH_2 produced by the IR multiphoton method. *Ab initio* theoretical calculations by Anwari and Gordon[94] of the reaction of SiH_2 with C_2H_4 indicate a reaction with no energy barrier, consistent with the high rate constants.

An unpublished study of the reaction of $SiH_2 + C_2D_4$ by Al-Rubaiey and Walsh[95] shows that there is a significant and pressure-dependent isotope effect which is more important at low than high pressures as shown in Figure 9.

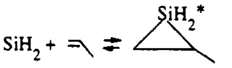
This has been investigated at five temperatures in the range 291–595 K. The high-pressure limiting rate constants are, within experimental error, the same as those for $SiH_2 + C_2H_4$, but RRKM fitting of the fall-off curves on the assumption of involvement of 2,2,3,3-tetradeuteriosilirane alone did not fit the data. At low pressures the reaction was too fast. This suggests the involvement of a rapid isotopic scrambling mechanism as occurs for the $SiH_2 + C_2D_2$ reaction[96,97] (see subsection e). A mechanism for this, based on higher temperature studies,[66,98] plausibly involves the intermediacy of ethylsilylene-d_4, *viz.*:



The propensity for such rapid processes has been documented by Davidson[85] and the energetic considerations are discussed later.

b. $SiH_2 + C_3H_6$

The only published rate constant for this reaction is a value of (1.2 ± 0.1) × 10^{-10} cm^3 molecule^{-1} s^{-1} obtained by Chu *et al.*[53] at room temperature and 5 Torr (He). The expected reaction is addition to form chemically activated 2-methylsilirane:



(17)

which can then be collisionally stabilized.

In an unpublished study, Al-Rubaiey and Walsh[99] have found the reaction to be pressure dependent (1–100 Torr, SF_6) in the temperature range 294–520 K. At 5 Torr (SF_6) and 298 K a rate constant of *ca.* 2.0 × 10^{-10} cm^3 molecule^{-1} s^{-1} can be interpolated in reasonable consistency with value in He,[53] allowing for different collision efficiencies. The high-pressure limiting rate constants give the Arrhenius parameters log(A/cm^3 molecule^{-1} s^{-1}) = −10.38 and E_a = −5.1 kJ mol^{-1}. These rate constants are *ca.* 20% smaller than those for $SiH_2 + C_2H_4$, although because of the extrapolation they could be equal (within error limits). The pressure dependence of this reaction is less than that of $SiH_2 + C_2H_4$. RRKM modeling of the pressure dependence can be made to fit provided the activation energy for decomposition of the product, 2-methylsilirane (back to $SiH_2 + C_3H_6$) is *ca.* 160 kJ mol^{-1}. This is significantly less than the activation energy for decomposition of silirane itself (obtained from the $SiH_2 + C_2H_4$ system). This surprising result is discussed later.

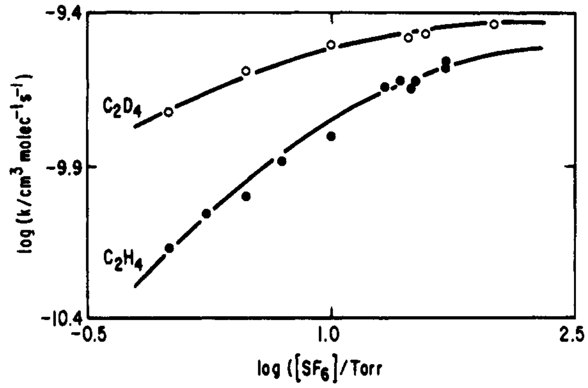
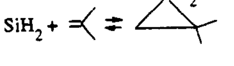


Figure 9. Rate constants and RRKM calculations for the reaction of SiH_2 with C_2H_4 and C_2D_4 at room temperature.

c. $SiH_2 + i\text{-}C_4H_8$

In an unpublished study Carpenter and Walsh[100] have found this reaction to be pressure dependent (1–100 Torr, SF_6) in the temperature range 298–600 K. At 5 Torr (SF_6) and 298 K a rate constant of *ca.* 2.9 × 10^{-10} cm^3 molecule^{-1} s^{-1} has been obtained. The high pressure limiting rate constants give the Arrhenius parameters log(A/cm^3 molecule^{-1} s^{-1}) = −9.89 and E_a = −2.3 kJ mol^{-1}. The rate constants at infinite pressure are very close to those for $SiH_2 + C_3H_6$, however, the pressure dependence is less (and almost nonexistent at 298 K). The expected reaction is again addition to form a chemically activated silirane which can then be collisionally stabilized.



(18)

A preliminary RRKM modeling of the pressure dependence at 600 K can be made to fit provided the

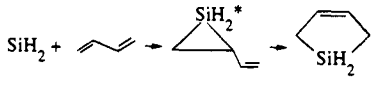
Table 14. Rate Constants (10^{-10} cm^3 molecule^{-1} s^{-1}) for SiH_2 + C_2H_2/C_2D_2 at 10 Torr Total Pressure (SF_6)

T, K	C_2H_2	T, K	C_2D_2
291	3.21 ± 0.33	291	3.74 ± 0.16
346	2.56 ± 0.04	346	2.94 ± 0.07
399	1.99 ± 0.05	395	2.63 ± 0.06
483	1.26 ± 0.04	481	2.02 ± 0.08
613	0.61 ± 0.05	613	1.44 ± 0.06

activation energy for decomposition of the product, 2,2-dimethylsilirane (back to SiH_2 and i-C_4H_8) is *ca.* 146 kJ mol^{-1}. This is again less than the values for both 2-methylsilirane and silirane itself.

d. SiH_2 + C_4H_6

The only published rate constant for this reaction has a value of (1.9 ± 0.2) × 10^{-10} cm^3 molecule^{-1} s^{-1}, obtained by Chu *et al.*[53] at room temperature and 5 Torr (He). This is close to the collisional number and consistent with values for the reactions of SiH_2 with C_2H_4, C_3H_6, and i-C_4H_8. Pressure and temperature variation studies have not yet been carried out. This experimental value is *ca.* 10^5 greater than that proposed by Rogers *et al.*[101] derived from relative rate studies. It is also not very consistent with relative rate studies of Gaspar *et al.*,[102] who found that SiH_2 apparently reacts 13 ± 4 times faster with SiH_4 than C_4H_6 (at 298 K) from chemical product analysis (and 9 ± 1 from nuclear recoil measurements).[103] It is possible that the high values for these ratios arise because of incomplete product recovery from the SiH_2 + C_4H_6 reaction for which only 4-silacyclopentene, the rearranged produce of 2-vinylsilirane, has even been detected, *viz.*:



(19)

e. SiH_2 + C_2H_2/C_2D_2

Chu *et al.*[53] obtained a value of (9.8 ± 1.2) × 10^{-11} cm^3 molecule^{-1} s^{-1} for SiH_2 + C_2H_2 at 298 K and 5 Torr (He). Becerra *et al.*[96,97] have made a comprehensive study of this reaction as well as its isotopic variant, SiH_2 + C_2D_2, over the pressure range 1–100 Torr (SF_6) and temperature range 291–613 K. A selection of rate constants is shown in Table 14.

The room temperature value for SiH_2 + C_2H_2 is consistent with that of Chu *et al.*[53] taking into account pressure and bath gas differences. Just as for the SiH_2 + C_2H_4 reaction, the rate constants show a negative temperature dependence and an isotope effect favoring SiH_2 + C_2D_2. The rate constants also show a pressure dependence as illustrated for SiH_2 + C_2H_2 in Figure 10.

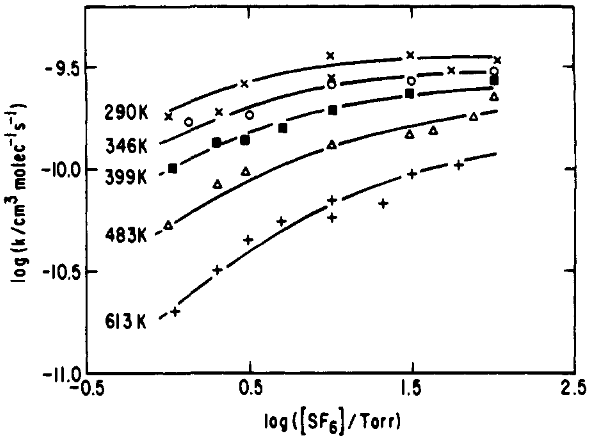
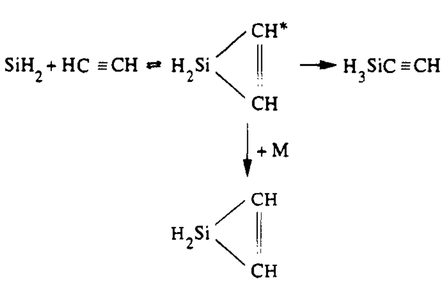


Figure 10. Rate constants and RRKM calculations for the reaction of SiH_2 with C_2H_2 at five temperatures.

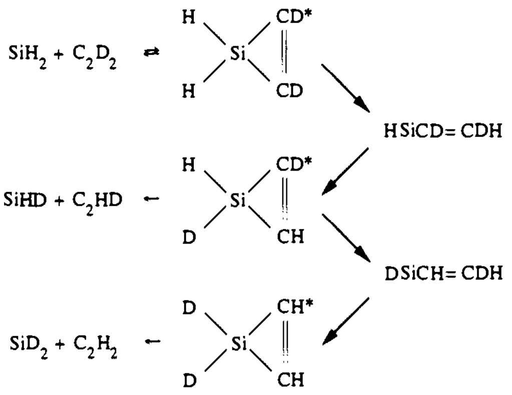
Extrapolation to infinite pressure gives rate constants corresponding to the Arrhenius parameters of log(A/cm^3 molecule^{-1} s^{-1}) = −9.99 and E_a = −3.3 kJ mol^{-1}. The curves for SiH_2 + C_2D_2 converge to the same limit within experimental error. These are again consistent with a fast collision-controlled association process, which is third body assisted at lower pressures. These studies bring together a total of four direct investigations of SiH_2 with $PhSiH_3$,[75] Me_3SiH,[75] C_2H_4,[91] and C_2H_2[97] which have been shown[91] to be consistent with relative rate measurements carried out in the Reading laboratories by Eley *et al.*[80] prior to the first absolute rate measurements. Other estimates of the rate constants for SiH_2 + C_2H_2 based on relative rate constants at higher temperatures[66] are significantly in error.

The direct experimental results are supported by the *ab initio* calculation of Boatz *et al.*[104] which indicates a barrierless reaction. The mechanism of addition is similar to that for SiH_2 + C_2H_4 and is further discussed in section f.

RRKM theoretical attempts to fit the pressure dependence of SiH_2 + C_2H_2, in contrast to the SiH_2 + C_2H_4 reaction, were only successful with an unrealistically high activation energy for decomposition of the supposed silirene product.[96] This led to the suggestion that another product, ethynylsilane (silylacetylene), was probably formed according the scheme:



Subsequent experiments[105] have confirmed the formation of ethynylsilane. Modeling of this system[97] gave a value for the activation energy for the isomerization of silirene to ethynylsilane of *ca.* 156 kJ mol^{-1}, assuming a fairly tight transition state. The isotope effect points to a similar isotopic scrambling mechanism for SiH_2 + C_2D_2 as observed for SiH_2 + C_2D_4, Becerra and Walsh[97] have proposed a mechanism involving vinylsilylene-d_2 *viz.*:



This reaction has been incorporated into the model to fit the pressure dependence of $SiH_2 + C_2D_2$, from which an approximate fit gives an activation energy of *ca.* 151 kJ mol^{-1} for vinylsilylene-d_2 formation from silirene-d_2. This complex mechanism is very similar to that for the $SiH_2 + C_2H_2$ reaction system suggested by Ring, O'Neal, and co-workers[98,101] to operate at the higher temperatures of pyrolysis studies. It appears to occur as low as room temperature.

f. Nature and Mechanism of the Addition Process

The picture of the addition process that emerges from the kinetic studies with SiH_2 is, once again, that of a collisionally controlled process which is almost indiscriminate among the different substrate molecules thus far studied (at the high-pressure limits). Again the reactions all appear to possess small negative activation energies in the range −3 to −5 kJ mol^{-1} suggestive of variational character in the transition states. These findings are consistent with the *ab initio* energy surface for the $SiH_2 + C_2H_4$ reaction.[94]

In similar fashion to the insertion reaction (*vide supra*) the addition may be described as occurring in two stages *viz.* an initial π attack ("electrophilic stage"—donation of C═C π electrons into the Si 3p orbital), follow by σ attack ("nucleophilic stage"—donation of the silicon lone pair electrons into the C═C antibonding π^* orbital). Figure 11 shows these processes and gives an approximate indication of the geometry of the transition state.

Just as for the insertion reaction, if an intermediate complex (π complex) is involved there are no obvious kinetic consequences indicated by the studies undertaken at present.

The growing data base of absolute rate constants for SiH_2 enables us to compare the reactivity of silylene with that of methylene. The values of rate constants for their reactions with selected unsaturated hydrocarbons are shown in Table 15.

It should be noted that the data for $CH_2(^1A_1)$ have been measured and corrected for nonreactive collisionally induced intersystem crossing in the same studies and also that most of the SiH_2 data represent the limiting high-pressure values. So far as is known the reactions of CH_2 are pressure-independent processes. The rate constants for CH_2 and SiH_2 are close to the collisional maximum. SiH_2 is about twice as reactive as CH_2 in accordance with the simple idea of an electrophilic reaction in which the initial interaction is dominated by the size of the receptor orbital (3p for SiH_2, 2p for CH_2).

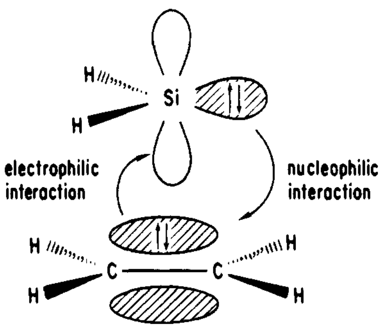


Figure 11. Schematic illustration of the nature of the interaction between silylene and the carbon−carbon double bond of ethylene.

Table 15. Comparison of Rate Constants (k, 10^{-10} cm^3 molecule^{-1} s^{-1}) for Addition Reactions of SiH_2 and CH_2 ($^1A_1$ States) at 298 K

species	SiH_2	ref	CH_2	ref
C_2H_2	4.0[a]	97	2.8	106
C_2H_4	3.5[a]	91	1.9	107
C_3H_6	3.3[a]	99	2.5	107
i-C_4H_8	3.3[a]	100	2.5	107
1,3-C_4H_6	1.9	53	2.6	107

[a] High-pressure limiting values.

Although the rate constants for CH_2 and SiH_2 addition are similar in magnitude, in another important respect the reactions differ. This arises because of the significantly different energies released by the two species in their addition processes. This is considered next.

g. Energy Considerations

Al-Rubaiey *et al.*[87] have shown that the lower energy release in the reaction of $SiH_2 + C_2H_4$ (*ca.* 195 kJ mol^{-1}) compared with the reaction of $CH_2 + C_2H_4$ (*ca.* 429 kJ mol^{-1}) explains why the SiH_2 addition reaction behaves like a third body-assisted association reaction, while the CH_2 addition reaction is a classic example of a chemically activated reaction. More detailed energy surfaces for the prototype π-addition processes have been calculated (from largely experimental sources) by Al-Rubaiey and Walsh[91] ($SiH_2 + C_2H_4$) and Becerra and Walsh[97] ($SiH_2 + C_2H_2$). These are shown in Figures 12 and 13.

Figure 12 shows that silirane formed from $SiH_2 + C_2H_4$ can either revert to $SiH_2 + C_2H_4$ or rearrange to vinylsilane (and other isomers) with approximately equal energies. Since Al-Rubaiey and Walsh[91] found no evidence for isomerization but only for reversion (inferred from the pressure dependence of the kinetics), they suggested that A factors (or relative looseness of transition states) was the explanation for this. The energy of ethylsilylene shows that it is a plausible species to explain the isotopic scrambling mechanism suggested[95] in the $SiH_2 + C_2D_4$ studies. An estimate has been made of the activation barrier to its formation from silirane in higher temperature studies.[108] The value is dependent on the ring strain in silirane but in any case is fairly low. What is clear is that, because ethylsilylene is endothermic relative

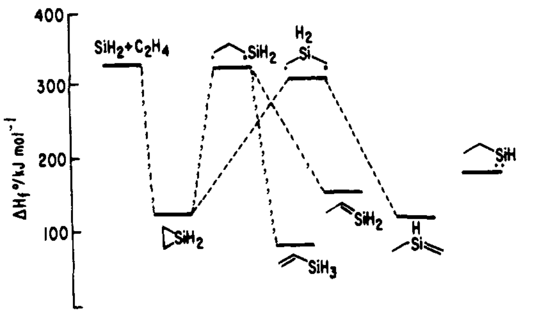


Figure 12. Derived potential surface for the reaction of SiH_2 with ethylene.

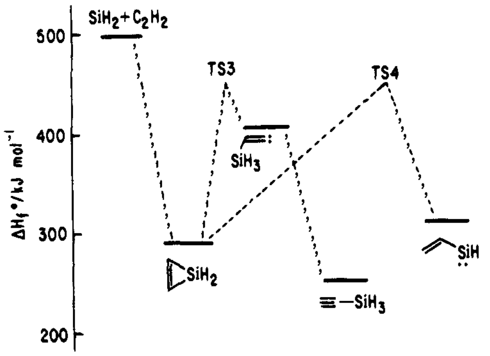


Figure 13. Derived potential surface for the reaction of SiH_2 with acetylene.

to silirane, if ethylsilylene can be readily formed it will rapidly revert to silirane, thus accounting for the proposed label scrambling, in the isotopically substituted silirane species.

Examination of Figure 13 shows that, in the $SiH_2 + C_2H_2$ reaction, silirene (in contrast to silirane) can isomerize more easily than revert to $SiH_2 + C_2H_2$. This can be explained by the low-energy accessibility of the silylvinylidene intermediate leading to ethynylsilane (as found by Becerra and Walsh[105]), so that even if the transition state for its formation is tight, the energetic advantage is sufficient to offset the benefit of the loose transition state for reversion of silirene to $SiH_2 + C_2H_2$. The energies of vinylsilylene and the transition state for its formation show that they can explain the isotopic scrambling mechanism suggested[96,97] in the $SiH_2 + C_2D_2$ studies. Because vinylsilylene is endothermic relative to silirene, when vinylsilylene is formed it will rapidly revert to silirene, again explaining the proposed label scrambling mechanism in the isotopic silirene species.

As explained above, SiH_2 reactions are considerably less exothermic than those of CH_2. The Reading group[87,91,97,105] have explained the underlying differences and characteristics of these energy surfaces in terms of the stabilization energy associated with silylenes.

One other feature of these reactions has recently emerged. In the addition of SiH_2 to alkenes the energy release associated with silirane ring formation appears to be dependent on methyl substitution.[99,100] This suggests the surprising conclusion that the strain energies of silirane rings are substituent dependent. This finding, however, is consistent with the already-noted low activation energy for hexamethylsilirane decomposition.[90] A recent theoretical calculation by Gordon *et al.*[109] has shown that the strain energies of siliranes are dramatically increased by Cl-for-H and F-for-H replacement on the silicon.

3.4. Other Reactions of SiH_2

Silylenes have a high propensity for reaction with lone-pair donor molecules. Matrix isolation studies[110-113] have revealed the existence of molecular complexes, stabilized at low temperatures, between silylenes and a variety of O-, N-, and S-containing molecules. All these complexes, however, are with substituted silylenes: no such complexes with SiH_2 have yet been observed. The formation of such species, however, is strongly supported by theoretical calculations[114] which show the existence of energy minima on the potential surfaces for reactions of SiH_2 with NH_3, H_2O, HF, PH_3, H_2S, and HCl. This is illustrated in Figure 14.

The only reaction of this group for which kinetic data is available is that for SiH_2 + HCl.[115] According to the theory[114] the $H_2Si-ClH$ complex has a significant barrier to rearrangement (via 1,2-H migration) to the final product H_3SiCl, although the experimental result casts some doubt on the actual magnitude.[115] Similar surfaces, but with differing well depths and rearrangement barriers for the donor–acceptor complexes, were calculated for the other reactions. The magnitudes of these energies are given in Table 16. Even if these figures prove not to be precisely correct the surfaces provide a useful framework for mechanistic discussion. Further support for such surfaces and the involvement of complexes comes from studies of $SiMe_2$, particularly with Me_2O,[116,117] which have been reviewed elsewhere.[3] Only one other example for SiH_2 itself falls easily into this category *viz.* the reaction of $SiH_2 + Me_2O$, for which unpublished kinetic data exists.[118,119] However, published kinetic data is available for a number of reactions of SiH_2 with diatomic and triatomic molecules which are discussed below. These reactions belie their apparent simplicity in the variety of secondary chemistry which can arise. For silylenes in general there is a more extensive discussion of these mechanisms in the earlier review by Safarik *et al.*[2]

The kinetics of the reactions of SiH_2 with HCl, Cl_2, NO, O_2, CO, and N_2 have been investigated by Chu *et al.*[115] at 298 K in He (5 Torr). The results are shown in Table 17, alongside those for the analogous reactions of CH_2.

The comparison with CH_2 suggests that, in contrast to the π-type addition reactions to alkenes, methylene reacts 1–2 orders of magnitude faster than silylene. There are however two caveats to be entered. The SiH_2 reactions may be pressure dependent [certainly true for $SiH_2 + O_2$ (see below)] and the CH_2 reactions may involve a contribution from electronic quenching, although this is not thought to be large.[120] Individual reactions are discussed below. The relative rate studies of the group of Lampe, using IRMPD generation of SiH_2, of the reactions of SiH_2 + HCl[121] and SiH_2 + NO[122] in each case relative to $SiH_2 + SiH_4$ do not seem to match the absolute values very closely. However the comparisons are complicated by pressure dependences.

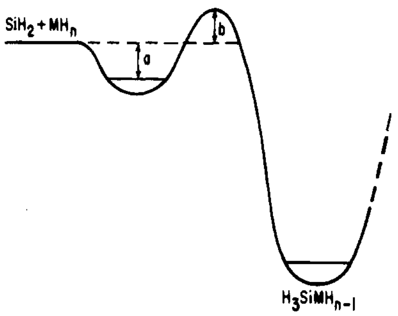


Figure 14. Schematic potential surface for the reaction of SiH_2 with lone pair donor molecules. See Table 16 for values of a and b.

Table 16. Theoretically Calculated Potential Energy Parameters (kJ mol^{-1}) for Reactions of SiH_2 with MH_n Molecules[114]

energy quantity	NH_3	H_2O	HF	PH_3	H_2S	HCl
well depth (a)	105	54	29	75	38	8
activation barrier (b)	54	38	13	8	21	25

[a] See Figure 14.

Table 17. Comparison of Rate Constants (k, 10^{-10} cm^3 molecule^{-1} s^{-1}) for Reactions of SiH_2[a] and CH_2[b] ($^1A_1$ States) with Diatomic Molecules at 298 K

species	SiH_2	ref	CH_2	ref
HCl	0.068 ± 0.010	115		
Cl_2	1.4 ± 0.2	115		
NO	0.17 ± 0.02	115	1.60 ± 0.15	120
O_2	0.077 ± 0.010	115	0.74 ± 0.05	120
CO	<.001	115	0.49 ± 0.04	120
N_2	<.001	115	0.11 ± 0.01	120

[a] Total pressure = 5 Torr (He). [b] Total pressure = 4–6 Torr (He).

a. SiH_2 + HCl

Chu *et al.*[115] found a weak pressure dependence for this reaction with rate constants of $(4.3 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 Torr (He) and $(7.5 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 9.5 Torr (He) as well as the value in Table 17. They suggested the following mechanism:

$$SiH_2 + HCl \rightleftharpoons SiH_3Cl^* \qquad (20)$$

$$SiH_3Cl^* \rightarrow SiHCl + H_2 \qquad (21)$$

$$SiH_3Cl^* + M \rightarrow SiH_3Cl + M \qquad (22)$$

The observed pressure dependence, unless it has another origin, indicates that redissociation of SiH_3Cl^* to SiH_2 + HCl must be competitive with the other channels, so that the overall exothermic pathway to SiHCl + H_2 must have a substantial barrier from SiH_3Cl. There is no clearcut independent evidence for this, but SiH_2Cl_2 and $SiHCl_3$ have been observed as products[121] (the former presumably involving the reaction of SiHCl with HCl). Chu *et al.*[115] have noted that their rate constants are too high to accommodate the theoretically calculated potential energy barrier of 25 kJ mol^{-1} [114] shown above (Figure 14 and Table 16). Using IRMPD to generate SiH_2 from SiH_4, Moore *et al.*[121] found no activation energy difference between the reactions of SiH_2 with HCl and SiH_4. Since the activation energy for SiH_2 + SiH_4 is *ca.* −3 kJ mol^{-1},[76] this implies a similar value for SiH_2 + HCl, although the IRMPD method seems to give rate constant ratios in poor agreement with absolute values.

b. SiH_2 + Cl_2

The measured rate constant is very high (see Table 17). Although the pressure dependence was not studied, Chu *et al.*[115] pointed out that the exothermicity of pathways from initially formed $SiH_2Cl_2^*$ to SiHCl + HCl, or $SiCl_2$ + H_2 was so great that these dissociations were likely to be rapid.

$$SiH_2 + Cl_2 \rightarrow SiH_2Cl_2^* \qquad (23)$$

$$SiH_2Cl_2^* \rightarrow SiHCl + HCl \qquad (24)$$

$$\rightarrow SiCl_2 + H_2 \qquad (25)$$

The high rate constant for reaction is consistent with an electrophilically led process.

c. SiH_2 + NO

Chu *et al.*[115] again found a weak pressure dependence for this reaction with rate constants of $(1.5 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1 Torr (He) and $(2.1 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 9.5 Torr (He) as well as the value in Table 17. The authors point out that a SiH_2NO adduct is likely and that a pathway to SiO + NH_2 would be highly exothermic, although the pressure dependence implies some competition with the reverse dissociation. Although nothing is known about the structure of SiH_2NO, calculations on $SiCl_2NO$[2,123] suggest an Si−O bonded structure. Again relative rate studies with SiH_2 generated by IRMPD[122] lead to rate constant ratios inconsistent with absolute values.

d. SiH_2 + O_2

Chu *et al.*[115] again found a weak pressure dependence for this reaction with rate constants of $(7.5 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 Torr (He) and $(1.4 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 9.5 Torr (He) as well as the value in Table 17. No mechanistic information is available at present, however, the authors point out the extremely exothermic product channel from the adduct $SiH_2O_2^*$ to SiO + H_2O:

$$SiH_2 + O_2 \rightarrow SiH_2O_2^* \qquad (26)$$

$$SiH_2O_2^* \rightarrow SiO + H_2O \qquad (27)$$

Clearly significant intramolecular rearrangement is required if (27) is indeed the product channel. Among the isomers of formula SiH_2O_2 only silanoic acid has been identified in a low-temperature matrix[124] although there is a bit more information about the possible rearrangement pathways for the analogous Me_2SiO_2.[117] Production of electronically excited SiO in the 193 nm photolysis of phenylsilane in the presence of oxygen has been suggested.[33] Competitive studies by Eley *et al.*[80] give a rate constant for SiH_2 + O_2 *ca.* 6 times less than that measured here relative to $SiH_2 + C_2H_4$. The origin of this discrepancy is not clear.

e. SiH_2 + CO, N_2

SiH_2 is unreactive with these molecules.[115] Hamilton and Schaefer[125] have predicted a binding energy of *ca.* 67 kJ mol^{-1} for the SiH_2CO adduct. Lack of reaction may be either due to a third body stabilization requirement or an activation barrier. All possible isomers of SiH_2N_2 are calculated to be unstable with respect to dissociation to $SiH_2 + N_2$.[126]

f. $SiH_2 + N_2O$

Becerra *et al.*[127] obtained a rate constant at 298 K of $(1.90 \pm 0.09) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. In addition they studied the reaction over the temperature range 295–747 K and obtained Arrhenius parameters, $A = (8.1 \pm 0.8) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $E_a = -2.0 \pm 0.3$ kJ mol^{-1}. No pressure dependence [5–50 Torr (Ar)] was found at any temperature.

The kinetic data are consistent with the formation of a short lived $H_2Si{-}ON_2$ complex which decomposes to $H_2SiO + N_2$. The product H_2SiO was not detected but support for its formation comes from detection of Me_2SiO by matrix isolation[128] in the reaction of $SiMe_2 + N_2O$.

g. $SiH_2 + Me_2O$

SiH_2 kinetic studies with the prototype O-donors, H_2O or MeOH have yet to be undertaken. The reaction with Me_2O is the only reaction of SiH_2 with an O-donor for which there are absolute rate constants. King, Lawrance, and Staker[118] have obtained values of between 6.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 3 Torr and 1.25×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 11 Torr (Ar), both at 298 K. Additionally they have studied the temperature dependence from 298–434 K from which they have obtained the Arrhenius parameters (at Ar, 5 Torr) of $\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -13.71$ and $E_a = -15.3$ kJ mol^{-1}. These however do not represent the limiting high-pressure values since the rate constants are clearly pressure dependent.

Becerra, Carpenter, and Walsh[119] have confirmed the pressure dependence of the reaction in SF_6 and obtained values of 1.35, 1.72, 4.80, and 7.54×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at pressure of 3, 5, 20, and 50 Torr. The results are clearly consistent with a third body assisted association reaction with SF_6 a more efficient collider than Ar. The surprise is that this reaction shows no evidence (biexponential decays) of reaching equilibrium as has been observed for $SiMe_2 + Me_2O$.[116] An independent GC search failed to find evidence for $MeSiH_2OMe$.[129] This appears to suggest that the reaction proceeds irreversibly to the association (zwitterionic) complex as shown below, and that there is no further reaction:

$$H_2Si + OMe_2 \rightarrow H_2Si{-}OMe_2 \qquad (28)$$

The implication is that the pressure dependence reflects this association. RRKM calculations (not yet undertaken) should give information about this and also a value for the binding energy. There is already kinetic evidence[116,117] for formation of the analogous complex, $Me_2Si{-}OMe_2$.

Table 18. Recent Values (298 K) for $\Delta H_f°$ (SiH_2) (kJ mol^{-1})

year	value	authors	ref
		i.Experimental Values	
1986	273 ± 6	Frey, Walsh, Watts	131
1986	289 ± 13	Shin, Beauchamp	135
1987	273 ± 3	Berkowitz, Greene, Cho, Ruscic	28
1987	287 ± 6	Boo, Armentrout	37
1987	269 ± 1	Martin, Ring, O'Neal	132
1987	268–287	Roenijk, Jensen, Carr	73
1988	274 ± 7	Van Zoeren, Thomas, Steinfeld, Rainbird	136
1989	267 ± 8	O'Neal, Ring, Richardson, Licciardi	138
1991	274 ± 4	Moffat, Jensen, Carr	74
1991	266 ± 6	Pilcher, Leitâo, Meng-Yan, Walsh	133
1992	273 ± 2	Walsh	130
1992	269 ± 4	Moffat, Jensen, Carr	134
1995	273 ± 2	Becerra, Frey, Mason, Walsh, Gordon	52
		ii.Theoretical Values	
1985	265	Pople, Luke, Frisch, Binkley	43
1985	285	Ho, Coltrin, Binkley, Melius	39
1986	273	Gordon, Gano, Binkley, Frisch	71
1986	287	Ho, Coltrin, Binkley, Melius	40
1988	272	Horowitz, Goddard	137
1988	266	Curtiss, Pople	44
1990	271 ± 9	Ho, Melius	41
1991	275 ± 8	Ignacio, Schlegel	46
1991	277	Sax, Kalcher	47
1992	271 ± 9	Allendorf, Melius	42
1992	273	Grev, Schaefer	10
1992	267	Grev, Schaefer	10

3.5. Enthalpy of Formation of SiH_2

The quantity $\Delta H_f°$ (SiH_2) has become well established in the last few years by a combination of experimental measurement and theoretical calculation. The data was reviewed by Walsh[130] in 1992, and has been considered most recently in some detail by Grev and Schaefer.[10] Because of these reviews we do not give a detailed history of the measurements.

Prior to 1985 the most common quoted figure (298 K value) for $\Delta H_f°$ (SiH_2) was 242 kJ mol^{-1}.[65] This was based on estimated rate constant values for SiH_2 which have subsequently been shown[32,33] to be wrong. The availability of directly measured rate constants for SiH_2 reactions, since 1985, has enabled more reliable values to be obtained from kinetic studies.[52,73,130-134,138] In addition values have been measured during this period by ion cyclotron resonance mass spectrometry,[135] photoionization mass spectrometry,[28] Si^+ ion beam reaction thresholds,[37] and electronic excitation spectroscopy.[136] These are listed in Table 18 together with the values obtained via *ab initio* theoretical calculation.

It is fairly clear that since 1986, there is a reasonable concordance both among experimentalists and theoreticians. Most recently improvements have been made by the refinement of the uncertainty rather than by any dramatic change in the value. In the gas kinetic studies this has been because the new SiH_2 kinetic data,[52,130] discussed in this review, is now extensive enough in its temperature and pressure ranges to be used directly to obtain equilibrium constants for the processes

$$SiH_4 \rightleftharpoons SiH_2 + H_2 \quad (29)$$

$$Si_2H_6 \rightleftharpoons SiH_2 + SiH_4 \quad (30)$$

under common conditions for both forward and reverse processes, without resort to extrapolation of the data. On the theoretical side Grev and Schaefer[10] have found a discrepancy between experiment and calculation of the atomization energy of SiH_4 of *ca.* 6.2 kJ mol^{-1} (theory higher). The possible reasons for this are discussed in detail in the article.[10] The consequence of this is that if $\Delta H_f°$ (SiH_4) or $\Delta H_f°$ (Si) are in error, then values for $\Delta H°_f$ (SiH_2) will depend on which one of these is an anchor point. At present the best value of 273 kJ mol^{-1} rests on the experimental value of $\Delta H_f°$ (SiH_4) determined calorimetrically.[139]

4. Silyl, SiH_3

4.1. Sources, Detection, and Monitoring

In spite of the central role played by the silyl radical in silane discharges[1,29] and its fundamental importance as a main group hydride radical, direct gas-phase studies of silyl kinetics were hindered until 1986 by the lack of any known, unambiguously assigned, optical spectrum. The first report of a gas-phase rate constant for SiH_3, obtained by direct monitoring, was by Krasnoperov *et al.*[140] in 1984. This work was based on LMR detection of silyl, reported in 1981 by the same workers.[141] The LMR assignment was tentative, however, as it was based only on the method of generation of the spectral carrier, reaction of silane with atomic chlorine, and exclusion of known transient silicon species as the carrier, rather than rigorous analysis of the LMR spectrum.

The first high-resolution spectrum attributable to SiH_3 was the infrared spectrum of the ν_2 umbrella vibration in the 14 μm region. The spectrum was recorded and assigned by Yamada and Hirota[142] in 1986. The results confirmed the pyramidal structure of SiH_3,[143,144] provided accurate molecular constants and opened the door for relatively simple optical monitoring of silyl both for kinetic studies[145] and in CVD environments.[146] This transition has now been used successfully by several groups to monitor silyl in direct kinetic studies.[145,147–149] A small region of the Q-branch spectrum is shown in Figure 15. Most recently, the ν_3 band of silyl has been observed and assigned in the 4.5 μm region of the infrared.[150] This band holds considerable promise for monitoring of silyl in kinetic studies owing to the greater experimental ease and flexibility available with the shorter infrared probe wavelength. A transition in this region has been used for one kinetic study, which represents the first detection of silyl in this region of the infrared.[151]

Unlike SiH or SiH_2, for which optical monitoring techniques dominate, nonoptical monitoring of silyl by mass spectrometry has been particularly useful in kinetic studies. Slagle *et al.*[152] pioneered this method using photoionization mass spectrometry (PIMS). Their early study[152] of $SiH_3 + O_2$ by PIMS confirmed the LMR results of Krasnoperov *et al.*[140] within error and added support to the assignment of the LMR signals. Koshi *et al.*[153,154] relied on low-energy electron impact ionization mass spectrometry (EIMS) to detect silyl. This approach was based on the earlier use of low-energy EI to selectively detect silyl and other silicon hydride radicals by Robertson *et al.*[29] Both the PIMS and EIMS methods rely on the ~4 eV difference between the ionization potential of silyl (8 eV) and the dissociative ionization threshold[155] for production of SiH_3^+ from silane (12.3 eV). Silyl is readily detected using 10.2 eV photons for PIMS or ~10 eV electrons in EI with good signal levels, low background and high selectivity against ionization of silane. Figure 16 shows a mass spectrum of silyl detected using EIMS.[156]

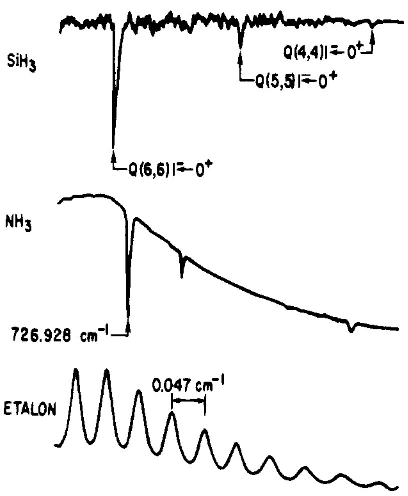


Figure 15. Infrared diode laser absorption spectrum of SiH_3 in the Q-branch region of the ν_2 band.

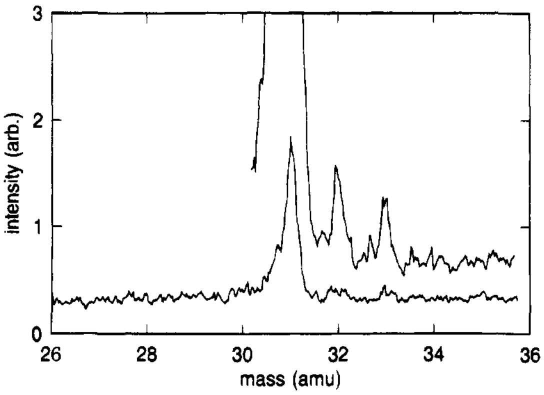


Figure 16. Low-energy EIMS detection of silyl produced in a discharge flow reactor by reaction of silane with atomic chlorine. The expanded spectrum shows the expected isotope peaks due to $^{29}SiH_3$ and $^{30}SiH_3$.

Monitoring of silyl by its single photon electronic absorption, using either direct absorption or LIF, was thwarted for decades by the complete lack of a known A $\leftarrow$ X electronic transition. A significant search for this transition was carried out by the Herzberg group using flash spectroscopic methods.[157] This search yielded electronic spectra of numerous silicon transients, but failed to find evidence for the A $\leftarrow$ X spectrum of SiH_3. Evidence for this transition was finally reported in 1991 by Lightfoot *et al.*[158] They reported a broad featureless absorption spectrum in

Table 19. Schemes for Generation of Silyl by Abstraction

$X + SiH_4 \rightarrow SiH_3 + HX$

source	photolysis wavelength	X	ref
S_2Cl_2	266 nm	Cl	140
CCl_4	193 nm	Cl	152
C_2Cl_4	248 nm	Cl	162
$COCl_2$	248 nm	Cl	163
CCl_3F	9.27 μm (IR multiphoton)	Cl	147
HCl	193 nm	H, Cl	149
ICN	266 nm	CN	151

the region 205–250 nm which was obtained at a dozen discrete probe wavelengths following the reaction of silane with chlorine atoms. Assignment of the spectral carrier as SiH_3 was based upon the method of generation, the formation and decay kinetics, its analogy to spectra of substituted silyl radicals, and the agreement of the observed λ_{max} with that calculated by *ab initio* theory.[159] In addition to the long missing $A \leftarrow X$ transition, higher-lying states of both SiH_3 and SiD_3 have now been observed by REMPI and assigned.[160,161]

Silyl is unique among the monosilicon hydride radicals in its lack of rapid reaction with most closed shell molecules at room temperature. This places more stringent demands on the chemistry used to generate silyl for kinetic studies because parasitic consumption of silyl by other photolysis byproduct radicals limits the meaningful dynamic range for slow radical molecule reactions and introduces added uncertainty into measurements of radical–radical reactions such as silyl recombination. Thus far no ideal source for kinetic studies has been identified.

Virtually all direct kinetic studies of silyl rely on rapid abstraction of hydrogen from silane to produce silyl. The most widely used method[152] of this type employs 193 nm photolysis of CCl_4 to generate Cl. This system is known to generate 1.2 Cl atoms per photon absorbed and produce CCl_3 and CCl_2 radicals.[149] While there is no evidence that the chlorocarbon radicals interfere with silyl kinetic measurements,[149] their fate in these systems is largely unknown. They are of particular concern in studies of the SiH_3 recombination reaction since they are present in concentrations comparable to SiH_3 at zero time. Approaches employing abstraction to generate SiH_3 for direct kinetic studies are summarized in Table 19.

An ideal abstraction system for clean, controlled production of SiH_3 would be photolysis of Cl_2 at a suitable wavelength, such as 351 nm (XeF excimer). This method fails[149] owing to the chain reaction[164]

$$Cl + SiH_4 \rightarrow HCl + SiH_3 \tag{31}$$

$$SiH_3 + Cl_2 \rightarrow SiH_3Cl + Cl \tag{32}$$

which rapidly consumes all available SiH_3 and produces SiH_3Cl.

Silyl has also been generated by direct photolysis of disilane[149] at 193 nm, SiH_3Br at 193 nm[148] and SiH_3I at 248 nm.[149] Loh *et al.*[149] investigated these sources and determined quantum yields for silyl production. The results[149] are summarized in Table 20.

Table 20. Quantum Yields for Photolytic Generation of SiH_3

precursor	photolysis wavelength, nm	quantum yield
SiH_3Br	193	0.1
SiH_3I	248	0.2
Si_2H_6	193	0.05

Table 21. Rate Constants for SiH_3 + SiH_3

authors	rate constant, $cm^3\ molecule^{-1}\ s^{-1}$	conditions[a]	ref
Itabashi *et al.*	$(1.5 \pm 0.6) \times 10^{-10}$	0.9 Torr (H_2)	145
Loh *et al.*	$\leq (6.1 \pm 3.5) \times 10^{-11}$	9.5 Torr (He)	148
Loh and Jasinski	$(7.9 \pm 2.9) \times 10^{-11}$	9.5 Torr (He)	149
Koshi *et al.*	$(1.2 \pm 0.4) \times 10^{-10}$	5 Torr (He)	153
Balklanov and Chichinin	$(1.6 \pm 0.5) \times 10^{-11}$	6–17 Torr (Ar)	163

[a] All determinations are at ambient temperature, 293–298 K, except for the value by Itabashi *et al.*[145] which was determined at 320 K.

While useable quantities of SiH_3 can be generated from photolysis of SiH_3Br and SiH_3I, other species such as Br or I, SiH_2, and SiHX (X = I, Br) are also formed, once again complicating the study of slow radical–molecule reactions and the silyl recombination reaction. In addition, neither SiH_3Br nor SiH_3I are commercially available and both require considerable skill to synthesize and purify.[165] Photolysis of phenylsilane[149] at 193 nm does not yield a detectable quantity of SiH_3.

4.2. Radical Recombination Reactions of SiH_3

One of the most significant silyl loss mechanisms in many systems is radical–radical recombination, especially self-reaction. This reaction, as well as reaction of silyl with atomic H, atomic Cl, and methyl radical have been studied.

a. SiH_3 + SiH_3

The room temperature rate constant for the loss of silyl by self reaction in the gas phase has been measured and reported by four independent groups using four different experimental methods.[145,148,149,153,163] The results, which are independent of total pressure over the range studied, 0.9–17 Torr, are presented in Table 21.

In the first determination of this rate constant, Itabashi *et al.*[145] monitored the decay of SiH_3 by infrared absorption following a pulsed discharge in SiH_4/H_2 mixtures. Unlike the rate constant studies discussed thus far in this review, determination of the silyl recombination requires knowledge of the absolute concentrations of the radical species. Itabashi determined this concentration from the measured Beers law absorption and an absorption coefficient for the transition calculated from an *ab initio* value for the Einstein *A* coefficient.[146]

Loh *et al.*[148] also used time-resolved infrared diode laser absorption spectroscopy of the ν_2 band to monitor SiH_3, but formed the radical via chlorine atom abstraction. Chlorine was generated by photolysis of CCl_4 at 193 nm. In their first report, they estimated the absolute concentration of silyl from the literature values for the quantum yield of Cl formation in CCl_4 photolysis as a function of photolysis wavelength. Because of the co-linear geometry of the experiment and the slight angle of the photolysis beam with respect to the infrared probe beam necessitated by the scheme they devised to allow both 193 nm and 14 μm light into their reaction cell, they were also forced to estimate the actual absorption path length. These considerations led to a large uncertainty in their reported value of $(6.1 \pm 3.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Finally, they reported the value as an upper limit because of uncertainty in the role of chlorocarbon radicals in silyl consumption. Loh and Jasinski[149] improved upon this measurement by measuring the absolute yield of HCl generated and the amount of disilane generated. From the HCl yield, they obtained the absolute silyl concentration and the accurate absorption path length. From the observation that 90 ± 20% of the theoretical maximum yield of disilane was produced, they removed the concern that significant loss of silyl by channels other than recombination occurred. This allowed them to revise their value to $(7.9 \pm 2.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

The third determination of the silyl recombination rate, by Koshi *et al.*,[153] used 193 nm flash photolysis of CCl_4 in SiH_4 to produce silyl and low-energy EIMS to monitor its decay. These workers also calibrated their measurement using the amount of HCl produced and found the same rate constant by silyl loss and disilane rise. Their value, $(1.2 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is in tolerable but not excellent agreement with the results reported by Itabashi *et al.*[145] and by Loh and Jasinski.[149]

The most recent determination of the rate constant, by Baklanov and Chichinin[163] employs photolysis of phosgene at 248 nm to generate chlorine atoms and LMR to monitor silyl. The result is not in good agreement with the previous determinations. Phosgene should be an ideal Cl source, since the photolysis is expected to yield 2Cl atoms and a CO molecule. The CO molecule is unreactive toward SiH_3. This removes the difficulty of accounting for the chlorocarbon radicals when photolysis of CCl_4 is used. The calibration technique used by Baklanov and Chichinin to set the initial SiH_3 concentration was to determine the initial chlorine atom concentration from the rise of the SiH_3 signal and the known rate constant for Cl + SiH_4. This calibration must be performed under conditions where Cl is in excess to SiH_4 while the determination of the SiH_3 recombination rate constant is performed under conditions where $SiH_4 > Cl$. An overestimate of the initial chlorine concentration or loss of Cl by processes which do not form silyl (such as wall loss) would lead to an overestimate of the silyl concentration and a corresponding underestimate of the rate constant. Given the apparent agreement between the three other determinations, one of which does not involve generation of chlorocarbon radicals, it is unlikely that the Baklanov and Chichinin result is correct, even though phosgene photolysis should be a clean method for silyl generation.

While the literature refers to the reaction of silyl with itself as a recombination, the actual mechanism is more complicated than a simple three-body recombination. The preferred mechanism, based on isotope scrambling studies[166] and kinetic modeling results is[167]

$$2SiH_3 \rightarrow SiH_2 + SiH_4 \tag{33}$$

$$2SiH_3 \rightleftarrows Si_2H_6^{**} \tag{34}$$

$$Si_2H_6^{**} \rightarrow SiH_2 + SiH_4 \tag{35}$$

$$Si_2H_6^{**} \rightarrow H_3SiSiH + H_2 \tag{36}$$

$$SiH_2 + SiH_4 \rightleftarrows Si_2H_6^{*} \tag{37}$$

$$Si_2H_6^{*} + M \rightarrow Si_2H_6 + M \tag{38}$$

Reaction 33 is a direct disproportionation reaction,[166] while reactions 34, 35, and 36 represent recombination to form chemically activated disilane which then decomposes irreversibly to products. The species $Si_2H_6^{**}$ is chemically activated disilane formed by (34) and contains more vibrational energy than $Si_2H_6^{*}$ formed by silylene insertion into silane. Under most conditions, with excess silane present, the silylene produced in (33) and (35) is readily converted to disilane. This explains the observed pressure independence of the measured rate constants. The branching between (35) and (36) has not been directly quantified. RRKM modeling and the Loh and Jasinski disilane yield[149] suggest that (35) dominates by ≥90%, but Koshi *et al.*[153] report only 60% production of SiH_2 and 40% production of H_3SiSiH. Becerra and Walsh[167] have estimated that (35) is 84–90% of the total on the basis of product studies in the Hg-sensitized photolysis of silane. This branching fraction cannot be accurately determined without further experimental measurements.

b. SiH_3 + CH_3, H, Cl

Reaction of silyl with CH_3 has been studied under pseudo first order conditions (excess CH_3) using flash photolysis/PIMS by Niiranen and Gutman.[168] From the temperature dependence of the loss rate they determined $k = (5.6 \pm 2.4) \times 10^{-11} \exp(3.0 \pm 1.6\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 $molecule^{-1}$ s^{-1}, independent of pressure. Using this result, they tested the geometric mean rule,[169,170] which is known to work well for cross-combination rate constants involving carbon-centered radicals. Using the known value of 6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for CH_3 + CH_3 and the average value of 1.2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} obtained from the three self-consistent results for SiH_3 + SiH_3 discussed above, they calculate a mean value for SiH_3 + CH_3 of 1.7×10^{-10} cm^3 $molecule^{-1}$ s^{-1} compared to their measured room temperature value of 1.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. This suggests that the geometric mean rule applies to silicon-centered as well as carbon-centered radicals, and may be useful for estimating silicon radical rate constants or checking for consistency among rate constants.

Loh and Jasinski[149] estimated the rate constant for reaction of SiH_3 with H atoms by generating silyl via photolysis of HCl using a variety of ratios of HCl to silane and modeling the system

$$\mathrm{HCl} \rightarrow \mathrm{H} + \mathrm{Cl} \tag{39}$$

$$\mathrm{Cl} + \mathrm{SiH_4} \rightarrow \mathrm{SiH_3} + \mathrm{HCl} \tag{40}$$

$$\mathrm{H} + \mathrm{SiH_4} \rightarrow \mathrm{SiH_3} + \mathrm{H_2} \tag{41}$$

$$\mathrm{H} + \mathrm{SiH_3} \rightarrow \text{products} \tag{42}$$

$$2\mathrm{SiH_3} \rightarrow \text{products} \tag{43}$$

Using their independently measured value for k_{43}, they self-consistently fit the data under conditions where all Cl is consumed rapidly by reaction 40, to give values for k_{41} and k_{42}. They obtained a value of $k_{41} = (2.5 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, in excellent agreement with independent measurements of this rate constant[171,172] which give preferred values in the range (2.0 ± 0.1) to $(2.8 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This procedure gave a value of $k_{42} = (2 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This value is an order of magnitude slower than previous estimates,[173] obtained from modeling steady-state product distributions. The reaction produces chemically activated silane which is expected to decompose quantitatively to $SiH_2 + H_2$ at the pressures employed in the study:

$$\mathrm{SiH_3} + \mathrm{H} \rightarrow \mathrm{SiH_4}^{**} \tag{44}$$

$$\mathrm{SiH_4}^{**} \rightarrow \mathrm{SiH_2} + \mathrm{H_2} \tag{45}$$

The species SiH_4^{**} is silane formed via reaction 44 and has more vibrational energy than silane formed by insertion of silylene into molecular hydrogen, SiH_4^*. Baklanov and Chichinin[163] measured the rate constants for $Cl + SiH_3$ using flash photolysis/LMR. By working under conditions of $[Cl] > [SiH_4]$ they obtained a value of $k = (3.2 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature, independent of pressure. The mechanism of this reaction has not been studied in detail, but likely involves formation of chemically activated monochlorosilane, which decomposes via elimination of H_2 and/or HCl to form the respective silylenes:

$$\mathrm{SiH_3} + \mathrm{Cl} \rightarrow \mathrm{SiH_3Cl}^* \tag{46}$$

$$\mathrm{SiH_3Cl}^* \rightarrow \mathrm{SiH_2} + \mathrm{HCl} \tag{47}$$

$$\rightarrow \mathrm{SiHCl} + \mathrm{H_2} \tag{48}$$

4.3. Oxidation Reactions of SiH_3

A number of groups have reported rate constants for the reaction of SiH_3 with the oxidizers O_2, NO, NO_2, and N_2O. Table 22 summarizes these results at room temperature and a common pressure, for the cases where the rate constant is known to be pressure dependent. The agreement between rate constants measured by different groups using different techniques for this group of reactions is exceptionally good.

Table 22. Rate Constants for Oxidation Reactions of Silyl

reactant	rate constant, cm^3 molecule^{-1} s^{-1}	conditions	ref
O_2	$(9.7 \pm 1.0) \times 10^{-12}$	1–27 Torr (Ar)	174
	$(1.3 \pm 0.4) \times 10^{-11}$	1–6 Torr (He)	152
	$(1.3 \pm 0.3) \times 10^{-11}$	1–10 Torr (N_2)	147
	$(1.26 \pm 0.18) \times 10^{-11}$	5 Torr (He)	154
	$(1.26 \pm 0.20) \times 10^{-11}$	0.2–0.5 Torr	151
NO	$(2.5 \pm 0.3) \times 10^{-12}$	9.5 Torr (N_2)	147
	$(2.5 \pm 0.5) \times 10^{-12}$	9.5 Torr (He)	148
NO_2	$(5.1 \pm 0.9) \times 10^{-11}$	3–10 Torr (N_2)	147
	$(5.6 \pm 0.5) \times 10^{-11}$	0.45 Torr	151
N_2O	$< 5 \times 10^{-15}$		152

a. $SiH_3 + O_2$

The reaction of SiH_3 with O_2 is believed to play a central role in the combustion of silane and has been studied extensively. The first report of a rate constant for this reaction was by Chasnovikov and Krasnoperov.[174] This result was confirmed by Slagle *et al.*,[153] lending credibility to the LMR assignments of Krasnoperov's group and establishing Arrhenius parameters for the reaction. Slagle *et al.*[152] found $k = 4.96 \times 10^{-12} \exp(2.39\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 molecule^{-1} s^{-1} using PIMS. Quandt and Hershberger[151] report $k = (2.07 \pm 0.34) \times 10^{-12} \exp(3.9 \pm 0.5\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 molecule^{-1} s^{-1}. They used infrared diode laser absorption as a probe. While the results of these groups agree well at room temperature, the Arrhenius parameters are significantly different. Quandt and Hershberger[151] suggest the lack of wall loss in the infrared laser absorption experiments as a possible explanation for the discrepancy.

The reaction mechanism is believed to be quite complicated. The most likely processes, based on the results of silane combustion and direct kinetic studies, as discussed by Koshi *et al.*[154,175] are

$$\mathrm{SiH_3} + \mathrm{O_2} \rightarrow \mathrm{SiH_3O_2}^* \tag{49}$$

$$\mathrm{SiH_3O_2}^* \rightarrow \mathrm{SiH_2O} + \mathrm{OH} \tag{50}$$

$$\rightarrow \mathrm{SiH_2O_2} + \mathrm{H} \tag{51}$$

$$\rightarrow \mathrm{HSiO} + \mathrm{H_2O} \tag{52}$$

$$\rightarrow \mathrm{SiH_3O} + \mathrm{O} \tag{53}$$

$$\mathrm{SiH_3O_2}^* + \mathrm{M} \rightarrow \mathrm{SiH_3O_2} + \mathrm{M} \tag{54}$$

with some of the primary products reacting further to regenerate silyl:

$$\mathrm{SiH_4} + \mathrm{O} \rightarrow \mathrm{SiH_3} + \mathrm{OH} \tag{55}$$

$$\mathrm{SiH_4} + \mathrm{OH} \rightarrow \mathrm{SiH_3} + \mathrm{H_2O} \tag{56}$$

$$\mathrm{SiH_4} + \mathrm{H} \rightarrow \mathrm{SiH_3} + \mathrm{H} \tag{57}$$

There are two possible isomers for $SiH_3O_2^*$, which are not indicated in the above scheme. Reaction 50 likely proceeds via unimolecular rearrangement of the initial peroxy radical:[176]

$$\mathrm{SiH_3O_2}^* \rightarrow \mathrm{H_2SiOOH}^* \rightarrow \mathrm{SiH_2O} + \mathrm{OH} \tag{58}$$

Finally, several of the oxidized silicon products may exist in more than one isomeric form,[176] e.g. HSiO or SiOH in (52).

Direct experimental evidence for initial reaction products is scarce. Slagle *et al.*[152] searched for oxidized silicon species by PIMS but found none.

Koshi *et al.*[154] detected SiH_3O^+ in an EIMS experiment, but were unable to determine whether it arose from ionization of SiH_3O[154] or cracking[175] of SiH_3O_2. Koshi *et al.*[175] have also measured the absolute yields of OH and H in this system and have determined branching fraction of 0.25 and 0.65 for (50) and (51), respectively, leaving a total of 0.1 for the combination of (52), (53), and (54).

Darling and Schlegel[176] have studied the potential surface for $SiH_3 + O_2$ using *ab initio* theory. They find rearrangement of the peroxy radical (58) followed by loss of OH to be a facile process. They were, however, unable to identify an energetically feasible unimolecular process leading to the production of H (51) and suggest that the source of H is a reaction of H_2SiO with OH.

$$H_2SiO + OH \rightarrow H_2Si(-O)OH \rightarrow HSi(=O)OH + H \quad (59)$$

The only other energetically feasible pathway for H formation produces the cyclic isomer of H_2SiO_2; however, no transition states for this process could be located.

b. SiH_3 + NO

The reaction of SiH_3 with NO was first studied by Sugawara *et al.*[147] They reported a pressure-dependent rate constant in the low pressure, termolecular limit of $k = (8.2 \pm 0.9) \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} for the pressure range 3–11 Torr (N_2). The result was confirmed at 9.5 Torr (He) by Loh *et al.*[148] While NO has long been used as a scavenger of silyl in steady-state experiments,[177] the detailed reaction mechanism is unknown. Sugawara *et al.*[147] propose

$$SiH_3 + NO \rightleftarrows SiH_3NO^* \quad (60)$$

$$SiH_3NO^* + M \rightarrow SiH_3NO + M \quad (61)$$

and note that this simple mechanism, which adequately explains the observed pressure dependence is different from a mechanism involving formation of SiH_3ON, suggested by Nay *et al.*[178] and Kamaratos and Lampe.[179] Marshall[180] has carried out *ab initio* studies of the potential surface and concluded that while SiH_3NO is not the global minimum, it is the most likely product of the reaction of SiH_3 with NO.

c. SiH_3 + NO_2

The reaction of SiH_3 with NO_2 has been studied by two groups,[147,151] both using time-resolved infrared diode laser absorption spectroscopy, but employing different vibrational transitions of SiH_3. As shown in Table 22, the results agree within error at room temperature. Quandt and Hershberger[151] report the temperature dependence of the rate constant as $k = (2.25 \pm 0.48) \times 10^{-11} \exp(2.19 \pm 0.66 \text{ kJ mol}^{-1}/RT)$ cm^3 molecule^{-1} s^{-1}. Proposed product channels are

$$SiH_3 + NO_2 \rightarrow SiH_2 + HONO \quad (62)$$

$$\rightarrow SiH_3O + NO \quad (63)$$

$$\rightarrow SiH_2O + HNO \quad (64)$$

The intermediacy of vibrationally excited $SiH_3NO_2^*$ has been suggested.[151] No product detection or branching measurements have been reported. Quandt and Hershberger[151] note that NO is produced in their experiments but they cannot unambiguously conclude that it is produced by reaction 63.

d. SiH_3 + N_2O

Slagle *et al.*[152] studied this system up to T = 500 K but were unable to observe a measurable reaction. They placed an upper limit of $k \leq 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} on the rate constant.

4.4. Abstraction Reactions

A number of H-atom abstraction reactions of SiH_3 have been examined, including the nearly thermoneutral reaction with SiD_4 and the mildly exothermic reaction with Si_2H_6. Neither of these reactions was observable at room temperature.[149] Upper limits of $k \leq (4 \pm 2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for SiD_4 and $k \leq (7 \pm 4) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for Si_2H_6 were determined. Studies of SiH_3 + HX have been more successful.

a. SiH_3 + HX, X = Cl, Br, I

Hydrogen abstraction by SiH_3 from three hydrogen halides has been studied. The reaction with HCl is endothermic and unobservably slow. Baklanov and Chichinin[163] give an upper limit of $k \leq (1.8 \pm 0.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Abstraction of H from HBr and HI are mildly exothermic reactions both of which display negative activation energies. Seetula *et al.*[162] report $k = (1.2 \pm 0.4) \times 10^{-12} \exp(0.7 \pm 1.2 \text{ kJ mol}^{-1}/RT)$ cm^3 molecule^{-1} s^{-1} for reaction of SiH_3 with HBr and $k = (7.3 \pm 2.8) \times 10^{-12} \exp(2.0 \pm 1.4 \text{ kJ mol}^{-1}/RT)$ cm^3 molecule^{-1} s^{-1} for reaction of SiH_3 with HI. Room temperature rate coefficients are summarized in Table 23.

Table 23. Rate Constants for H-Abstraction by Silyl

reactant	rate constant, cm^3 molecule^{-1} s^{-1}	ref
HCl	$\leq (1.8 \pm 0.5) \times 10^{-15}$	163
HBr	$(1.77 \pm 0.29) \times 10^{-12}$	162
HI	$(1.79 \pm 0.21) \times 10^{-11}$	162

Based on the surprising lack of a positive activation barrier for the reaction with HBr and HI, Seetula *et al.*[162] propose a mechanism which proceeds via reversible formation of a bound $SiH_3{\cdot}HX$ intermediate rather than simple H-atom metathesis. It is interesting to note that halide abstraction from HX is exothermic for all cases (X = Cl, Br, I) but apparently unobserved. Theoretical exploration of the potential surface for silyl + HX could shed some light on this surprising result.

4.5. Addition to Alkenes and Alkynes

Loh *et al.*[148] studied the addition reactions of SiH_3 with ethylene, propylene, and propyne. With the

Table 24. Rate Constant for Reaction of Silyl with Alkenes and Alkynes

reactant	rate constant, cm^3 $molecule^{-1}$ s^{-1}	condition	ref
C_2H_4	$\leq (3 \pm 3) \times 10^{-15}$	9.5 Torr (He)	149
C_3H_6 (propylene)	$\leq (1.5 \pm 0.5) \times 10^{-14}$	9.5 Torr (He)	149
C_3H_4 (propyne)	$\leq (1.8 \pm 0.4) \times 10^{-14}$	9.5 Torr (He)	149

Table 25. Rate Constants for Miscellaneous Reactions of Silyl

reactant	rate constant, cm^3 $molecule^{-1}$ s^{-1}	conditions	ref
S_2Cl_2	$(2.4 \pm 0.5) \times 10^{-11}$	4–7 Torr (He), 326 K	140
NOCl	$(1.3 \pm 0.3) \times 10^{-11}$	5 Torr (Ar)	174
$COCl_2$	$\leq 5 \times 10^{-15}$		163
NF_3	$\leq 5 \times 10^{-15}$		163
CCl_4	$\leq (5 \pm 2) \times 10^{-14}$	9.5 Torr (He)	149
CO	$\leq 7 \times 10^{-16}$		163

exception of propylene, which gave a measurable rate constant, only upper limits could be determined at room temperature. Reexamination of the anomalous reactivity of propylene using photolysis of SiH_3I at 248 nm instead of photolysis of CCl_4/SiH_4 at 193 nm by Loh and Jasinski[149] demonstrated that the initial observation of reaction with propylene was an artifact, probably caused by removal of SiH_3 by radical photolysis products produced as a result of propylene photodissociation at 193 nm. The upper limits on the rate constants at room temperature are given in Table 24.

4.6. Miscellaneous Reactions

A number of other reactions of SiH_3 with various molecules have been studied, usually as byproducts of the work discussed above. These are reported in Table 25, mostly as upper limits. The rate constant for reaction of SiH_3 with S_2Cl_2 reported by Krasnoperov *et al.*[140] is the first report of a direct measurement of an absolute rate constant for SiH_3. The products and reaction mechanisms for these reactions are unknown.

4.7. Enthalpy of Formation of SiH_3

The quantity $\Delta H_f°$ (SiH_3) has become reasonably well established in the last few years by a combination of experimental measurement and theoretical calculation. The latest experimental data has been discussed by Walsh[130] in 1992 and both theoretical and experimental values have been reviewed by Grev and Schaefer.[10] Because of these reviews the discussion here is not extensive.

On the experimental side the significant recent study is that of Seetula *et al.*[162] of the equilibrium reactions:

$$SiH_3 + HBr \rightleftharpoons SiH_4 + Br \tag{65}$$

$$SiH_3 + HI \rightleftharpoons SiH_4 + I \tag{66}$$

The authors measured the kinetics, and in particular the activation energies, of the forward reactions which were previously unknown (and had been estimated by Walsh, for SiH_3 + HI, at +8 kJ mol^{-1}, in contrast to the new experimental value of −2 kJ mol^{-1}). These studies provide the most reliable estimate of $\Delta H_f°$ (SiH_3) currently available. Other experimental and theoretical values are collected in Table 26.

Table 26. Recent Values for $\Delta H_f°$ (SiH_3) (kJ mol^{-1})

year	value	authors	ref
		i.Experimental Values	
1981	194 ± 6	Doncaster, Walsh	181
		Walsh	182
1987	< 204	Berkowitz, Greene, Cho, Ruscic	28
1987	203 ± 7	Boo, Armentrout	37
1991	200.5 ± 2.5	Seetula, Feng, Gutman, Seakins, Pilling	162
		ii.Theoretical Values	
1985	200	Melius *et al.*	39
1986	200	Melius *et al.*	40
1990	198 ± 4	Melius *et al.*	41
1992	198 ± 4	Melius *et al.*	42
1985	198	Pople *et al.*	43
1988	198	Pople *et al.*	44
1991	200 ± 8	Ignacio, Schlegel	46
1991	199.8	Sax, Kalcher	47
1992	200	Grev, Schaefer	10

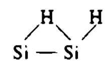
Theoretical values seem to be in good agreement with experiment. The calculations of Grev and Schaefer[10] have been carried out at the highest level. They have pointed out that all values both experimental and theoretical are based on $\Delta H_f°$ (SiH_4) but that, as there is a discrepancy with $\Delta H_f°$ (Si) there may remain a problem over the absolute value of $\Delta H_f°$ (SiH_3).

5. Si_2H_x, $x = 1–5$

5.1. Generation, Detection, and Monitoring

The class of species Si_2H_x, $x = 1–5$, represents a fascinating group of chemical species, all of which are transient. Extensive *ab initio* studies on the structure and ground-state potential surface for these species have been carried out. The major results have been summarized and discussed by Ruscic and Berkowitz[183] and by Jasinski[184] through 1991. Grev and Schaefer have further explored the Si_2H_2 surface.[185] The only members of this group which have been unambiguously characterized (by high-resolution rotational spectroscopy) are two isomeric forms of Si_2H_2, the di-bridged structure (a) and the monobridged structure (b). Both species were generated in a cooled silane discharge.[186,187] No kinetic data are as yet available for these species.

(a)



(b)

One or more isomers of Si_2H_x, $x = 2–5$, have been generated by reaction of fluorine atoms with disilane and characterized by PIMS.[183] While this technique provides accurate ionization potentials, it gives no direct structural or kinetic information.

Jasinski[184] has detected transient absorption in the near-UV region at three probe wavelengths, 363.8, 351.1, and 333.6 nm following flash photolysis of disilane at 193 nm. He has argued that these signals are due to some members of the family Si_2H_x $2 \leq x \leq 4$, but the assignments are highly speculative. The transient absorption at 333.6 nm shows a slow, nonexponential decay. The transient absorption at the two longer wavelengths shows a fast decay riding on top of the slow decay. Jasinski has argued that the slow decay is attributable to the trans-bent isomer of Si_2H_4, on the basis of its lack of reactivity with silane and disilane, its slow removal by NO, its apparent reactivity with silicon radicals, and agreement between a calculated UV absorption spectrum for this species and the region in which the experimental transients are observed.[188] A suggested assignment of the fast transient observed at 363.8 and 351.1 nm was not possible beyond the assertion that it is a silylene or silylidyne isomer from the set Si_2H_x, $x = 2-4$. Jasinski and LeGoues[189] has also shown that these species react further to produce silicon particles, providing a photochemical route to the generation of silicon nanocrystals.

There has been one other report of a transient absorption in the UV which is attributed to Si_2H_x species. Perner and Volz[190] observed a number of bands in the 270−290 nm region following pulsed radiolysis of silane, and suggested that the spectral carrier was an Si_2H_x species. No further assignment was proposed.

Spectroscopic characterization, rational generation, and controlled kinetic studies of the reactivity of this family of transients remain as significant experimental challenges to further advancing our detailed understanding of silicon hydride chemistry.

6. Radical–Surface Kinetics of SiH_x, $x = 1–3$

Because the silicon hydride radicals are reactive species which are generated in silicon CVD environments, they are often proposed as film growth precursors.[1] In order to quantitatively assess the contributions of these species to silicon film growth, direct measurements of the surface reaction kinetics are required. While this field is in its infancy for all radical species of significant chemical complexity and technological interest, some progress has been made in radical surface kinetic studies of SiH, SiH_2, and SiH_3. These studies measure the total surface loss coefficient, β, for a specific radical and cannot yet distinguish sticking from surface reaction with desorption of a different silicon species.

6.1. Generation, Detection, and Monitoring

The generation and monitoring techniques discussed above for gas-phase studies of SiH, SiH_2, and SiH_3 may be applied with equal success to the study of surface loss kinetics, provided that the radical−surface interaction can be distinguished from or made dominant over gas-phase loss mechanisms. Thus far, discharge sources[191,156] and infrared multiphoton dissociation[64,192] have been used to generate the desired radicals. The SiH radical has been monitored using LIF,[191] the SiH_2 radical using REMPI,[64] and the SiH_3 radical has been monitored using low energy EIMS.[156]

Table 27. Best Current Values for Sequential Bond Dissociation Enthalpies of SiH_4 (298 K)

bond	DH°, kJ mol^{-1}	DH°, kcal mol^{-1}
H_3Si-H	384 ± 3	91.8 ± 0.8
H_2Si-H	291 ± 3	69.6 ± 0.8
$HSi-H$	321 ± 6	76.7 ± 1.5
$Si-H$	293 ± 6	70.0 ± 1.5

6.2. Direct Surface Loss Studies for SiH, SiH_2, and SiH_3

Ho *et al.*[191] have measured the surface loss coefficient for the SiH radical using a surface scattering/LIF technique they have developed which they call IRIS (imaging of radicals interacting with surfaces). The method employs spatially resolved LIF of SiH in a molecular beam with and without interaction with a surface. By modeling the expected spatial distribution for trapping/desorption and comparing the observed reflected SiH spatial distribution to the incident distribution, the surface loss coefficient β can be measured. They obtain a value of $\beta \geq 0.94$ for SiH interacting with a hydrogenated silicon film growing on their room temperature surface.

Robertson and Ross[64,192] employed REMPI using the previously unknown REMPI spectrum for SiH_2. The spectrum is observed in the region 480−520 nm and assigned to several REMPI processes. Combining this detection scheme with the technique of very low pressure photolysis, they determine a value of β for SiH_2 on a hydrogenated silicon/carbon film of $\beta = 0.10$. This value increases to $\beta = 0.15$ on a hydrogenated silicon film.

Jasinski[156] has used a discharge flow method to generate SiH_3 and low-energy EIMS to detect this radical. From the measured SiH_3 signal at the end of the flow tube as a function of the flow distance, he was able to determine β for SiH_3 on a halocarbon wax-coated surface and on a hydrogen/chlorine/silicon film surface. He reported values of 0.018 and 0.050, respectively. A similar experiment was performed earlier by Krasnoperov *et al.*,[193] but has not been fully analyzed.[194]

With the exception of the SiH result, which was measured under conditions which are a good approximation to CVD film growth, these data must be used cautiously in drawing conclusions about the role of silicon hydride radicals in film growth, since β is expected to depend, possibly in a very dramatic way, on the nature of the surface or thin film on which the loss is measured. Thus, direct comparison of these surface loss rates with film growth experiments that measure average sticking coefficients[195] for all film growth species cannot yet be meaningfully made.[156]

7. Bond Dissociation Enthalpies

Table 27 gives recommended values of the sequential bond dissociation energies for silane, derived from the thermochemistry discussed above.

8. Conclusions

We have attempted to provide a comprehensive review of the field of absolute rate studies for silicon hydride radicals during its first decade. For the monosilicon species, generation and detection schemes have been worked out and many first reports of rate studies have appeared. Studies of SiH and SiH_3 are still relatively immature, while those of SiH_2 are maturing toward resolving "factor of 2" discrepancies and toward complete pressure and temperature dependencies and the understanding of mechanism and isotope effects. Much work remains. In particular a better understanding of photochemical generation methods and new precursors would be of enormous benefit. The study of transients containing two or more silicon atoms is in its infancy and presents significant experimental and theoretical challenges for the future.

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10. Appendix and Conversions

Acronyms

CVD	chemical vapor deposition
EIMS	electron impact ionization mass spectrometry
IRIS	imaging of radicals interacting with surfaces
IRMPD	infrared multiphoton dissociation
LIF	laser-induced fluorescence
LMR	laser magnetic resonance
LRAFKS	laser resonance absorption flash kinetic spectroscopy
PIMS	photoionization mass spectrometry
REMPI	resonance-enhanced multiphoton ionization
RRKM	Rice Ramsperger Kassel Marcus

Conversion of Units

To obtain bimolecular rate constants in "solution phase" units of $M^{-1}\ s^{-1}$, multiply the values given in cm^3 molecule^{-1} s^{-1} by 6.02×10^{20}.

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