

Absolute rate constants for the reaction of silylene with hydrogen, silane, and disilane

Joseph M. Jasinski and Jack O. Chu

Citation: The Journal of Chemical Physics **88**, 1678 (1988); doi: 10.1063/1.454146 View online: http://dx.doi.org/10.1063/1.454146 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/3?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Reply to the "Comment on silane pyrolysis and the insertion of silylene into molecular hydrogen" J. Chem. Phys. **86**, 3059 (1987); 10.1063/1.452016

Reply to the "Comment on silane pyrolysis and the insertion of silylene into molecular hydrogen" J. Chem. Phys. **86**, 3058 (1987); 10.1063/1.452015

Comment on silane pyrolysis and the insertion of silylene into molecular hydrogen J. Chem. Phys. **86**, 3057 (1987); 10.1063/1.452014

Gasphase free radical reactions in the glowdischarge deposition of hydrogenated amorphous silicon from silane and disilane J. Appl. Phys. **57**, 2290 (1985); 10.1063/1.334378

The Absolute Rates of Reaction of Hydrogen with the Halogens J. Chem. Phys. **4**, 178 (1936); 10.1063/1.1749816



Absolute rate constants for the reaction of silylene with hydrogen, silane, and disilane

Joseph M. Jasinski and Jack O. Chu IBM, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 28 July 1987; accepted 14 October 1987)

Absolute rate constants for the reaction of silylene with hydrogen, silane, and disilane have been determined from direct time resolved measurements of silylene removal at room temperature. Silylene was generated and detected using laser resonance absorption flash kinetic spectroscopy. The rate constants are pressure dependent, consistent with expectations for the insertion reactions typical of silylene. The pressure dependence of the overall rate constants has been determined from 1 to 100 Torr for reaction with hydrogen and silane and from 1 to 10 Torr for reaction with disilane. The results for reaction with hydrogen and silane have been successfully modeled using RRKM theory and high pressure bimolecular rate constants have been extracted. The rate constants determined in this work are significantly $(10-10^4 \text{ times})$ faster than those calculated from literature values for the Arrhenius parameters. These findings require a significant upward revision in the heat of formation of silylene, and may require modification of chemical vapor deposition mechanism in which silylene is invoked as a film growth precursor.

INTRODUCTION

Silylene, (SiH_2) is a key reactive intermediate in the mechanistic chemistry of silicon hydride molecules and organosilicon compounds.^{1,2} Silylene is also frequently postulated as an important gas-phase precursor in silicon thin film growth by chemical vapor deposition (CVD).³ An accurate understanding of the spectroscopy, thermochemistry, and reactivity of this simple divalent silicon species is, therefore, crucial to assessing the validity of these mechanisms, and by comparison with results for methylene, to understanding fundamental differences between silicon hydride and hydrocarbon chemistry.

Until recently, the available information on silvlene thermochemistry and reactivity came almost exclusively from classical indirect kinetic studies, such as competitive trapping experiments. In the past several years there has been renewed interest in silicon hydride chemistry, owing largely to an increasing interest in the mechanisms of CVD of electronic materials. As a result, several studies have reported new information on the thermochemistry and reactivity of SiH₂. These include high level ab initio calculations of silylene thermochemistry⁴⁻⁶ and potential energy surfaces for silylene reactions,⁷⁻⁹ measurements of the heat of formation of silylene by ion-molecule^{10,11} and photoionization techniques,¹² and the first direct time resolved measurements of silylene reaction rates by laser flash photolysis techniques.^{13–16} These studies have, in general, produced results which are in serious quantitative disagreement with the conclusions of most previous studies of silylene thermochemistry and reactivity. For example, the most recent values^{5,10-12,14,17} for the heat of formation of silylene are 7-11 kcal/mol higher than the previously accepted value,^{18,19} and the absolute rate constant for the reaction of silylene with hydrogen at room temperature^{13,14} is $\sim 10^4$ times larger than previous estimates.18

Absolute rate constants for the reaction of silylene with hydrogen, silane, and disilane are particularly important to establishing the accuracy and internal consistency of the revised thermochemical and kinetic data, since these reactions are the reverse of the decomposition reactions of the stable silicon hydride molecules silane (SiH₄), disilane (Si₂H₆), and trisilane (Si₃H₈). These rate constants are also particularly important in CVD modeling, since molecules such as hydrogen and silicon hydrides are frequently present in silicon CVD reactors. In this paper we present the results of extensive laser resonance absorption flash kinetic spectroscopy (LRAFKS) measurements of absolute rate constants for these reactions at room temperature. Absolute rate constants for silvlene removal have been measured as a function of total pressure for all three reactions, and RRKM modeling of the pressure dependent three-body rate constants has been carried out for the reactions of silylene with hydrogen and silane.

EXPERIMENTAL

A schematic of the LRAFKS apparatus used in these studies is shown in Fig. 1. The apparatus is similar to that described in a preliminary communication,¹⁴ although several modifications in the flow cell and data acquisition systems have been made. Silylene was generated by excimer laser (Lambda Physik 102E) photolysis of an appropriate precursor molecule, dilute in helium or mixtures of buffer gas and reactant gas, under slowly flowing conditions in a 1 m long by 3.5 cm diameter stainless steel gas cell equipped with Suprasil II windows. Silylene precursor molecules used in this work were phenylsilane and disilane, photolyzed at 193 nm by an ArF excimer laser, and iodosilane, photolyzed at 248 nm by a KrF excimer laser. Silylene was detected by high resolution absorption specroscopy with light from an argon ion pumped single frequency cw ring dye laser (Spec-



FIG. 1. Schematic of the LRAFKS apparatus. BS are beam splitters, DM are dichroic mirrors coated to transmit the dye laser and reflect the excimer laser, POL is a polarizer used to balance the dye laser intensity on the signal and reference photodiodes. The monochromator serves as a bandpass filter to reject stray excimer laser light and, under some experimental conditions, excimer laser induced fluorescence from SiH (see Ref. 15).

tra Physics 380A), tuned to single rotational lines of the ${}^{1}B_{1}(0,2,0) \leftarrow {}^{1}A_{1}(0,0,0)$ electronic transition. The excimer laser beam was unfocused (75–150 mJ/pulse, 0.5×2.5 cm²) and passed once down the length of the cell. The dye laser beam, following wavelength diagnostics and attenuation, was split into signal and reference beams by a variable beam splitter. The signal beam passed collinearly through the photolysis volume three times. The multipass mirrors are not shown in the schematic. Both the signal and reference beams were focused onto fast photodiodes (Hewlett-Packard 5082-4203, -22 V bias, 50- Ω load), equipped with fast preamplifiers (LeCroy VVB100). Light intensity on the signal and reference photodiodes was balanced by a rotatable polarizer, placed in the reference beam. The outputs from the preamplifiers were differentially amplified (Tektronix 7A24) to produce a signal which, for the small ($\leq 10\%$) absorptions of interest, is directly proportional to the SiH₂ concentration. This transient absorption signal was integrated as the dye laser wavelength was scanned for spectroscopic studies, or digitized and signal averaged for kinetic studies.

Gases entered the cell through two symmetrical sets of inlets at the cell ends and were exhausted through a single port in the center of the cell. All gas flows were measured and controlled with calibrated electronic mass flow controllers (Vacuum General UV series, 10, 100, or 1000 sccm), except for phenylsilane and iodosilane, which are liquids at room temperature. Flows of phenylsilane and iodosilane were controlled with a needle valve. Helium and other inert buffer gases entered the cell at the windows, while the silvlene precursor molecule and reactant gases entered the cell, premixed, through inlets located 20 cm downstream from the windows. This arrangement, at buffer gas pressures in excess of ~ 1 Torr, kept the windows well purged. This is necessary in order to acquire significant amounts of data with our experimental geometry, since all three silylene precursors rapidly deposit opaque films on the Suprasil windows when photolyzed under static conditions. In several experiments

with hydrogen, the helium flow as reduced to zero with no noticeable affect on the measured rate constants. An automatic throttle valve (MKS 253A) was attached to the exhaust port of the cell and controlled by the output voltage from the capacitance manometer (MKS 221A, 10 or 100 Torr full scale) which measured the total pressure in the cell. This combination of throttle valve and mass flow controllers allows kinetic studies to be performed under conditions of constant total flow and constant total pressure. Such control is crucial since the rate constants themselves are dependent on total pressure (vide infra) and since the partial pressure of silvlene precursor in the cell is affected by the total flow rate. The cell was pumped by a 13 ℓ /s rotary pump, equipped for corrosive gas operation. The exhaust port and vent line of the pump were continuously purged with a high flow of nitrogen, since silane and disilane are pyrophoric and occasionally explosive in the presence of oxygen.

Transient absorption spectra were recorded with Doppler limited resolution, in overlapping 3 cm⁻¹ segments, using a technique for scanning the Spectra-Physics dye laser described by Petek.²⁰ As the dye laser wavelength was scanned under microcomputer (IBM-PC) control, the integrated (PAR 162/164) transient absorption signal and a fluoresence signal from an iodine reference cell were simultaneously digitized and stored. Silylene line positions in the transient absorption spectrum were determined with the combined use of a wavemeter (Burleigh WA-20) and interpolation between iodine spectral lines.

Kinetic studies were performed under pseudo-first order conditions by adding reactant gases to the cell. The time dependence of the silvlene concentration was measured by tuning the dye laser to a single rotational line of the silvlene absorption spectrum, typically ${}^{R}Q_{0,I}(5)$ at 17 259.50 cm⁻¹, and digitizing and averaging the transient absorption waveform (Tektronix 7912AD interfaced to an IBM-PC) for 64 excimer laser pulses. A background trace was collected by tuning the dye laser ~ 0.15 cm⁻¹ away from the silvlene absorption line. The background trace was subtracted from the transient absorption signal to remove excimer laser pickup and reduce base line fluctuations. The transient digitizer was pretriggered by a pulse generator which also triggered the excimer laser. This allowed an accurate base line to be recorded by the digitizer before the excimer laser fired. The excimer laser repetition rate was typically 2 s⁻¹, although repetition rates as high as 10 s^{-1} were occasionally used. The time resolution of the detection system is ~ 2 ns. although the effective time resolution was limited by the 10-20 ns length of the excimer laser pulse. Silvlene transient absorption waveforms were recorded for a series of added partial pressures of reactant gas at constant total gas flow and constant total pressure. The waveforms were uploaded to a mainframe computer for nonlinear least squares analysis.

Partial pressures of the gases in the flow cell were determined from the known flow rates of each gas, the total flow rate and the total pressure. The estimated absolute uncertainty in the reactant gas partial pressure is $\pm 5\%$. Partial pressures of the silylene precursor molecules were constant throughout a given kinetic experiment, but were less accu-

rately determined because of the small partial pressures and small flow rates. Phenylsilane partial pressures were typically in the 10^{-3} - 10^{-4} Torr range, iodosilane partial pressures were in the 10^{-3} Torr range and disilane partial pressures, when it was used as a silvlene precursor, were in the 10^{-2} - 10^{-3} Torr range. These values reflect, qualitatively, the efficiency of each source in producing silylene. Total flow rates typically ranged from 150 sccm at pressures around 1 Torr to 1000 sccm at pressures near 100 Torr. Average gas residence times in the cell ranged from 0.5 s at 1 Torr to as long as 8 s at 100 Torr, and were typically in the range 1-2 s. Phenylsilane (Petrarch) was degassed prior to use. Silane (Airco C.C.D. grade), disilane (Matheson, 97%), nitrogen (Liquid Carbonic, 99.999%), argon (Liquid Carbonic, 99.999%), and carbon tetrafluoride (Liquid Carbonic, 99.7%) were used as received. The major impurity in silane is hydrogen (~ 200 ppm), and the major impurities in disilane are silane and hydrogen ($\leq 3\%$). Hydrogen (Matheson UHP or Liquid Carbonic 99.9999%) and helium (Liquid Carbonic, 99.999% or Matheson UHP) were passed through cartridge filter purifiers (MG Scientific Gases) to further limit water and oxygen impurities. Iodosilane was prepared by HI cleavage of phenylsilane or chlorophenylsilane.21

RESULTS

1680

Photochemistry

Very little quantitative information is available on the photochemistry of any of the silylene precursor molecules. Phenylsilane absorbs strongly below 220 nm ($\epsilon \sim 10^5$ M^{-1} cm⁻¹ at 193 nm²²) and has a weak, structured absorption band in the range 220–280 nm²³ ($\lambda_{max} \sim 260$ nm, ϵ_{max} $\sim 10^2 \,\mathrm{M^{-1} \, cm^{-1}}$). Disilane absorbs fairly strongly at wavelengths shorter than 200 nm²⁴ ($\epsilon \sim 10^3$ M⁻¹ cm⁻¹ at 193 nm) and is transparent at longer wavelengths. Iodosilane absorbs strongly at wavelengths shorter than 200 nm and has a fairly strong, featureless band in the 205–260 nm range²³ $(\lambda_{\rm max} \sim 220, \epsilon_{\rm max} \sim 10^3 \, {\rm M}^{-1} \, {\rm cm}^{-1})$. Both phenylsilane and disilane produce readily detectable SiH₂ concentrations on photolysis at 193 nm under the conditions given above. Phenylsilane does not produce a detectable amount of silylene on photolysis at 248 nm. Iodosilane produces detectable concentrations of silylene on photolysis at both 193 and 248 nm. The remaining information on the photochemistry of these molecules, including evidence for the formation of other transient products is summarized elsewhere.¹⁵

Spectroscopy

Although it is not the purpose of this work to refine the high resolution spectroscopy^{25,26} of the $\widetilde{A} \leftarrow \widetilde{X}$ transition of SiH₂, it is worth pointing out that the LRAFKS technique has considerable potential in this regard. The inherently high resolution of the ring laser readily provides Doppler limited spectra. Sub-Doppler measurements are also, in principle, possible. The transition is detected in direct absorption, so that accurate line intensities can be determined without considering quantum state dependences of fluorescence lifetimes or collisional quenching. Furthermore, sily-



FIG. 2. Composite spectrum of overlapped 3 cm⁻¹ single frequency dye laser scans of a region near the band center of the ${}^{1}B_{1}(0,2,0) \leftarrow {}^{1}A_{1}(0,0,0)$ vibronic transition of SiH₂ produced in the 193 nm photolysis of phenylsilane. Line assignments are from Ref. 29.

lene is a particuarly advantageous case. The transition of interest originates in the electronic ground state, so that in the absence of reactions, the kinetic lifetime can be quite long, and the major vibronic bands are in a spectral region which is accessible with efficient cw laser dyes. In addition, the oscillator strength for the transition is, apparently, quite large. Peak cross sections for some of the most intense lines are in excess of 10^{-18} cm², possibly by as much as a factor of 10 to 100, depending on the quantum yield for the production of silylene from photolysis of phenylsilane.^{27,28}

A 15 cm⁻¹ composite spectrum of overlapped 3 cm⁻¹ single frequency scans of the transient absorption spectrum produced by 193 nm photolysis of 2 mTorr of phenylsilane in 2 Torr of helium is shown in Fig. 2. Line intensities in this spectrum have not been normalized to the dye laser intensity and are, therefore, only approximate. The spectral region from 17 242 to 17 352 cm^{-1} has been scanned in this manner. This 100 cm^{-1} range is around the origin of the $(0,2,0) \leftarrow (0,0,0)$ vibronic band, and in a region of high line density. Approximately 100 single rotational lines were observed. Of these, 50% were readily assigned to known SiH₂ transitions, using assignments from the original flash spectroscopic studies of Dubois and co-workers.^{25,26,29} The remaining lines, many of which are reasonably intense, are unassigned. Three recent laser spectroscopic investigations of silylene,^{22,27,30} although at somewhat lower resolution than our work, have reached similar conclusions. The spectrum is considerably richer than previously thought. Thoman et al.,27 based on a study of fluorescence lifetimes, have suggested that the excited electronic state is strongly perturbed by the lowest triplet state. This state has not yet been observed spectroscopically in any study.

Kinetics

The silylene reactions of interest are insertion³¹ of the ground electronic single state silylene into the H–H bond of hydrogen, the Si–H bond of silane, and the Si–H and/or Si–Si bond of disilane, reactions (1)-(3):

$$\mathrm{SiH}_2 + \mathrm{H}_2 \rightarrow \mathrm{SiH}_4,\tag{1}$$

$$\mathrm{SiH}_2 + \mathrm{SiH}_4 \to \mathrm{Si}_2\mathrm{H}_6, \tag{2}$$

$$\mathrm{SiH}_2 + \mathrm{Si}_2\mathrm{H}_6 \rightarrow \mathrm{Si}_3\mathrm{H}_8. \tag{3}$$

Insertion into the Si–H or Si–Si bonds of disilane has never been clearly distinguished experimentally. It is well established that silane, disilane, and trisilane are expected stable products of these reactions. 18,31,32

Reactions (1)-(3) are complicated by the fact that they are three-body association reactions, rather than simple bimolecular processes. Collisional stabilization of the nascent, vibrationally excited product is required in order for silylene to be consumed irreversibly, i.e.,

$$\operatorname{SiH}_{2} + \operatorname{XY} \underset{k_{-1}}{\overset{k_{1}}{\rightleftharpoons}} \operatorname{SiH}_{2} \operatorname{XY}^{*}, \tag{5}$$

$$\operatorname{SiH}_2 XY^* \xrightarrow{k_2 M} \operatorname{SiH}_2 XY.$$
 (6)

In the case of reaction with hydrogen and silane, there is considerable experimental^{33–35} and theoretical^{5–9} evidence that no other fragmentation channels are energetically available to the chemically activated molecule SiH₂XY*. This is less well established for the case of reaction with disilane, since there is evidence that pyrolysis of trisilane proceeds by elimination of both silylene and silylsilylene.³⁶ Silylene kinetic studies are necessarily affected by the three-body nature of the reactions, since the rate constants for these processes are expected to be pressure dependent at suitably low total pressure. These effects will be discussed more fully for the specific cases in following sections.

Transient absorption signals for the $5_{0.5}$ rotational level of the (0,0,0) vibrational state, monitored on the ${}^{R}Q_{0,I}(5)$ transition, are shown in Figs. 3 and 4 on two time scales. This rotational line has routinely been used in our kinetic studies since it is one of the most intense lines in the spectrum of the $(0,2,0) \leftarrow (0,0,0)$ band and since the ground state rotational level $5_{0.5}$ is heavily populated at room temperature. Figure 3 shows the rise of the silylene signal from photolysis of phenylsilane dilute in pure helium. The signal consists of two components, a prompt rise and a slower pressure dependent rise. We have attributed the prompt rise to direct formation of silvlene in the quantum state being probed and the slow component to rotational equilibration of the nascent photofragment rotational distribution. From exponential fits to the slow rise component as a function of helium pressure, we have obtained a rate constant of $3.7 \pm 0.4 \times 10^{-11}$ cm³ molecule $^{-1}$ s $^{-1}$ for this process. This means that rotational thermalization of SiH₂ by helium requires ~ 10 gas kinetic collisions.

Pseudo-first order reaction rates have been obtained from single exponential analysis of the decay of the transient absorption signal in the presence of reactant gases, as shown in Fig. 4. Fits were carried out from near the peak of the signal to the base line. The rise and fall components of the signals were suitably different that a biexponential fit was not deemed necessary. Absolute bimolecular rate constants were obtained from plots of the pseudo-first order rates as a function of reactant gas partial pressure at constant total pressure, by linear least squares analysis of the data. Exam-

FIG. 3. Silylene transient absorption signal rise from the photodissociation of phenylsilane in helium at 193 nm, monitored on the ${}^{R}Q_{0,T}(5)$ transition. The solid line is a biexponential fit to the slow component of the rise and the decay.

ples of data for relatively slow and fast rate constants are shown in Figs. 5 and 6. For reaction with hydrogen, which gives relatively slow rate constants, we estimate that the uncertainty in any rate constant is $\pm 20\%$. This estimate is based on typical scatter in the data in pseudo-first order plots and reproducibility of replicate measurements. For the faster rate constants observed in reaction with silane and disilane, we estimate that the error limits are \pm 10%, except in one case noted below. This estimate comes from assuming that the maximum possible error in the absolute pressure scale is twice the estimated error in a single value. Scatter in the data in pseudo-first order plots for these reactions was typically 2%-4%. The intercepts in the plots shown in Figs. 5 and 6 are not zero, but represent all removal processes which are not dependent on the concentration of reactant molecule. These processes are diffusion and reaction of sily-

FIG. 4. Silylene transient absorption signal with hydrogen present. The solid line is a single exponential fit to the decay of the signal.

J. Chem. Phys., Vol. 88, No. 3, 1 February 1988

FIG. 5. Pseudo-first order rate plot for silylene reacting with hydrogen at a total pressure of 8 Torr. The line is a least squares fit to the data. The slope gives the bimolecular rate constant for the reaction. The intercept represents all removal processes which do not depend on the hydrogen concentration.

lene with unphotolyzed precursor molecules or photoproducts from photolysis of precursor molecules. The magnitude of the intercept was made as small as possible, by reducing the partial pressure of silylene precursor, consistent with signal to noise constraints. The lowest precursor partial pressures were necessarily used in measuring the slowest rate constants. The magnitude of the intercept was only significant compared to the magnitude of the change in removal rate for the case of hydrogen at low total pressures. Typically, the value of the intercept was less than 10% of the maximum pseudo-first order rate in any rate constant deter-

FIG. 6. Pseudo-first order rate plots for silylene reacting with silane (\bullet) and disilane (\circ) at a total pressure of 8 Torr. The lines are least squares fits to the data.

mination. The minimum intercept value at which useful data could be obtained was $\sim 3000 \text{ s}^{-1}$, at which point diffusion out of the photolysis volume begins to dominate reactive removal.

Major concerns in any kinetic study which extracts rate constants from removal rates of transient species monitored by quantum state specific techniques are whether, in fact, the measured removal rates correspond to removal by chemical reaction, and if so whether the decay of a given quantum level is representative of the thermal reaction rate. These questions deserve particular consideration in this case, since the rate constants reported below are considerably faster than values derived by indirect methods. Artifacts related to diffusion, experimental geometry, or gas handling techniques can immediately be ruled out as contributing to anomalously fast silvlene removal rates, since we have demonstrated that we can measure removal rate constants which are at least one order of magnitude slower than the slowest rate constant reported below and at least four orders of magnitude slower than the fastest rate constant reported below, using the identical experimental arrangement.^{15,16} Likewise, purely physical quenching phenomena can be ruled out. We are probing the electronic and vibrational ground state of silylene and a rotational level which is near the maximum of a room temperature Boltzmann distribution. Furthermore, we can observe rapid collisional population of that rotational level in pure helium. These facts and a substantial database¹⁶ of rate constants for a number of other reactions, which give rate constants that vary over four orders of magnitude and in a manner which is consistent with qualitative expectations for silylene reactivity, lead us to conclude that we are measuring silylene removal rates which are due only to chemical reaction.

There is also considerable evidence which demonstrates that the removal rate constants are appropriate values for the thermal rate constants at room temperature. Heating of the gas by absorption of the excimer laser beam should be negligible. Under typical experimental conditions, the temperature rise in the cell is estimated to be 5 K or less. Total pressures were always sufficiently high (1 to 100 Torr) that nascent silvlene translational distributions should always be relaxed rapidly compared to the rate of reaction. In most data sets, helium is present in sufficient excess that rotational equilibration rates, calculated using the rate constant reported above, were at least ten times faster than reaction rates. This was not always possible, particularly at low total pressures. Even in these cases, pseudo-first order decay rates determined over the full range of concentrations from 100% helium to 100% hydrogen show no anomalous behavior. Furthermore, no significant change in removal rate constant for the reaction of silylene with deuterium was observed when rotational levels 100 cm^{-1} higher or 50 cm^{-1} lower in energy than $5_{0,5}$ were probed.¹⁴ Finally, in several cases, we have compared rate constants for the same reaction measured using different silylene precursors and have seen no significant differences.^{15,16} It is extremely unlikely that photodissociation of phenylsilane and disilane at 193 nm and iodosilane at 248 nm produce identical nonthermal nascent silylene distributions.

J. Chem. Phys., Vol. 88, No. 3, 1 February 1988

Vibrational equilibration of silylene cannot be guaranteed. However, we probe only the (0,0,0) level. The lowest excited vibrational level is $\sim 1000 \text{ cm}^{-1}$ higher in energy and has a negligible population at room temperature. If excited vibrational levels are formed, it is reasonable to assume that they react rapidly without influencing the ground state kinetics and/or, possibly, that they are efficiently equilibrated by the three-body nature of the reactions. Possible evidence for this type of relaxation mechanism can be seen in the transient absorption signals when reactant gases are present. The rise time of the signal becomes faster and the peak amplitude of the signal increases significantly compared to the values in pure helium. This effect is especially noticeable when hydrogen is added to the cell. Further evidence that excited vibrational levels do not affect our rate constants is that in one experiment with hydrogen, CF₄ was used as a buffer gas. This molecule should allow for rapid V-V relaxation of silvlene, but does not yield a rate constant which is significantly different from those obtained using other buffer gases.

Hydrogen

A plot of absolute rate constants for reaction of silylene with hydrogen as a function of total pressure is shown in Fig. 7. Data points in the range 1-11 Torr were obtained with phenylsilane as the silylene precursor. Data points at higher pressures were obtained with disilane as the silylene precursor, owing to the 20 Torr room temperature vapor pressure of phenylsilane. Internal consistency of the data was checked at 5 Torr in helium buffer gas. The rate constants measured using phenylsilane (average of two separate experiments) and disilane as silylene sources were $4.9 \pm 1.0 \times 10^{-13}$ $4.4 \pm 0.8 \times 10^{-13}$ cm³ moleand cule⁻¹ s⁻¹, respectively. A comparison of different buffer gases was also made at 5 Torr total pressure. Measured rate

FIG. 7. Absolute rate constants for the reaction of silylene with hydrogen as a function of total pressure. The solid line is a result of an RRKM analysis of the three-body association reaction, described in the text.

TABLE I. RRKM parameters for three-body association rate constant calculations.

	SiH ₄	SiH₄*	Si ₂ H ₆	Si ₂ H ₆ *
$\overline{\nu_i \ (\mathrm{cm}^{-1})^{\mathrm{b}}}$	2187 (1)	2108 (1)	2179 (2)	2181 (1)
	2183 (3)	2103 (1)	2163 (1)	2169 (2)
	978 (2)	1328 (1)	2155 (1)	2105 (1)
	910 (3)	993 (1)	2154 (1)	2087 (1)
		839 (2)	941 (2)	1585 (1)
		523 (2)	940 (2)	960 (1)
			920 (1)	949 (1)
			844 (1)	927 (1)
			628 (2)	925 (3)
			432 (1)	155 (2)
			379 (2)	128 (1)
			128 (1)	94 (2)
I_i (amu Å ²)	5.7	2.8	11.8	11.8
	5.7	7.6	97.7	101.7
	5.7	9.5	97.7	101.7
Average bond energy (kcal/mol)	90	90	••••	
E_0 (kcal/mol)		55	50)
k_1 (cm ³ molecule ⁻¹ s ⁻¹)		3.2×10	2.2×10^{-10} 5.2×10^{-10}	
$k_2 ({\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1})^{\rm b}$		4.1×10		
Collision		1.0	0.19	
efficiency (λ)				
Reaction path		6	18	3
degeneracy				
Temperature (K)		300	300)

^aTransition state parameters.

^b Numbers in parentheses are degeneracies.

^c Lennard-Jones collision rate constant, evaluated using approximations given in J. Troe, J. Chem. Phys. **66**, 4758 (1977). Lennard-Jones parameters for silane and disilane are given in Ref. 39.

constants with argon, nitrogen, and carbon tetrafluoride as buffer gases were 4.2 ± 0.8 , 4.2 ± 0.8 , and $4.8 \pm 1.0 \times 10^{-13}$ cm³ molecules⁻¹ s⁻¹, respectively. This observation also provides further assurance that our rate constant studies are representative of thermal values, since rotational and vibrational energy transfer rates for silylene should vary considerably over this range of buffer gases.

The observed pressure dependence of the rate constants confirms the three-body association behavior discussed above. The line in Fig. 7 was calcualted using RRKM theory to model the process in a straightforward manner.^{37,38} The input parameters for the calculation are given in Table I. The transition state parameters were taken from a recent RRKM study of the thermal decomposition of silane and disilane by Roenigk et al.³⁹ Strong collisions were assumed, based on the absence of any observable dependence of the association rate constant on the buffer gas used. Both sums and densities of states were evaluated by direct count procedures and an anharmonic correction was made, since silane is a relatively small molecule with only high frequency vibrational modes. The only parameter which was freely adjusted to fit the data was the high pressure limiting bimolecular rate constant. The fit shown in Fig. 7 was obtained with a value for this rate constant of 3.2×10^{-12} cm³ molecule⁻¹ s⁻¹.

The high pressure rate constant extracted from the data for H_2 is in excellent agreement with our previous estimate¹⁴ for this value, based on a study of the reaction with D_2 $(2.6 \pm 0.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$. The rate constant we measure at 2 Torr total pressure is $2.6 \pm 0.6 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. This value is in reasonable, but not quantitative, agreement with the value of $1.0 \pm 0.4 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at a pressure of 1.8 Torr reported by Inoue and Suzuki in their laser induced fluorescence study (LIF).¹³

The pressure dependences of the rate constants for reaction of SiH₂ with D₂ and HD have also been examined. As expected, they are much less severe than for H₂. The rate constant for reaction with D₂ changes from $1.6 \pm 0.3 \times 10^{-12}$ to 2.7×10^{-12} cm³ molecule⁻¹ s⁻¹ over the range 1–95 Torr. Any isotope effects appear to be small. A full analysis of the isotopic reactions below the high pressure limit is complicated by the possibility of isotope effects on the insertion reaction and the multichannel decomposition of the isotopically substituted, chemically activated silanes. Such an analysis is beyond the scope of this paper.

Silane

A plot of absolute rate constants for the reaction of silylene with silane as a function of total pressure is shown in Fig. 8. As in the case of hydrogen, low pressure data points were obtained using phenylsilane as the silylene source and higher pressure points were obtained using disilane as the silylene source. All data were obtained with helium buffer gas. The line in Fig. 8 was calculated using RRKM theory with transition state parameters again taken from work by Roenigk *et al.*³⁹ and tabulated in Table I. In this case the density of states was evaluated semiclassically and no anharmonic correction was made. Furthermore, the pressure dependence of the data could be fit only by assuming less than unit collisional efficiency. The high pressure limiting rate constant obtained from this analysis is 2.2×10^{-10} cm³ molecule⁻¹ s⁻¹. Our value for the reaction rate constant at 1

FIG. 8. Absolute rate constants for the reaction of silylene with silane as a function of total pressure. The line is the result of a RRKM analysis of the three-body association reaction, described in the text.

FIG. 9. Absolute rate constants for the reaction of silylene with disilane as a function of total pressure.

Torr is $6.7 \pm 0.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Inoue and Suzuki report a rate constant of $1.1 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 1 Torr total pressure in helium.¹³

Disilane

A plot of absolute rate constants for the reaction of silylene with disilane as a function of total pressure from 1 to 10 Torr is shown in Fig. 9. The data in Fig. 9 were obtained using phenylsilane as the silylene source and helium as the buffer gas. As discussed above, however, disilane is not transparent at 193 nm, although it is less strongly absorbing than phenylsilane. In order to check for possible artifacts owing to excitation or depletion of disilane, one experiment was carried out using photolysis of iodosilane at 248 nm as the silvlene source. This experiment, at 5 Torr total pressure, produced a rate constant of $2.1 \pm 0.5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. This is in good agreement with the result of $2.8 \pm 0.3 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, obtained with photolysis of phenylsilane at 193 nm. The larger error limits on the data obtained at 248 nm reflect the fact that fewer data points than usual were taken and less time was available to optimize conditions since only a limited supply of iodosilane was available. Nonetheless, the agreement is satisfactory and there do not appear to be any serious complications with the data taken at a photolysis wavelength of 193 nm. No RRKM modeling of the observed pressure dependence has been carried out, since experimental fall off data and RRKM models for trisilane pyrolysis are not yet available. Although data were obtained only up to 10 Torr total pressure, the rate constant measured at 10 Torr should be much less than a factor of 2 from the high pressure limiting value. This estimate is based on the observed behavior for silane and the fact that trisilane is a larger molecule than disilane with more degrees of freedom and, therefore, a longer statistical lifetime when chemically activated. This conclusion ignores possible effects of a lower energy but entropically less favorable decomposition to silvisilylene and silane, a channel

J. Chem. Phys., Vol. 88, No. 3, 1 February 1988

which has been proposed in the pyrolysis mechanism for trisilane.³⁶ Our value for the reaction rate constant of silylene with disilane at 1 Torr total pressure is $1.5 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, and is significantly lower than Inoue and Suzuki's reported value¹³ of $5.7 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

DISCUSSION

Our results are the most extensive set of kinetic data presently available for any bimolecular reaction of silylene. Qualitatively, we have shown that silvlene reacts nearly gas kinetically with silane and disilane and somewhat less efficiently with hydrogen. We have also demonstrated that the reaction rate constants are pressure dependent in the manner expected for three-body association reactions. This observation is particularly important for the case of reaction with hydrogen. It provides direct support for the three center elimination of molecular hydrogen as the lowest energy dissociation pathway for silane in the gas phase. This point has had a long and controversial history.^{33,34} If some other channel for silane decomposition were available at lower energy, e.g., dissociation to silvl radicals and hydrogen atoms, then the overall reaction of silylene with hydrogen would exhibit bimolecular reaction kinetics rather than three-body kinetics.

More quantitatively, we have succeeded in modeling the observed kinetic behavior for the reaction of silvlene with hydrogen and silane using RRKM theory with a minimal number of adjustable parameters. The significance of the different energy transfer parameters required to fit the observed pressure dependences in the hydrogen and silane data is not clear. Our results are, however, consistent with the modeling studies of Roenigk et al.39 who also consistently found that collision efficiency parameters for disilane decomposition were lower than those for silane decomposition. The implication of these observations is that energy transfer parameters do have non-negligible effects on the overall kinetics of silane and disilane decomposition reactions. Strong collision calculations cannot necessarily be expected to give accurate results. Compared to hydrocarbon systems, very little is known about energy transfer in silicon hydride molecules. Since trends in energy transfer for different substrate moelcules with the same set of bath gases cannot yet be accu-

FIG. 10. Calculated three-body association rate constants for the reaction of silylene with hydrogen (\bullet) and silane (\bigcirc) as a function of total pressure in helium buffer gas at 300 K.

rately predicted *a priori*, more experimental data on energy transfer in silicon hydride systems is clearly required. It is somewhat surprising that we are unable to observe a difference in collisional stabilization efficiencies for chemically activated silane using helium, argon, nitrogen, and carbon tetrafluoride, although the data may be close enough to the high pressure limit that such effects are minimal and would only be discernable by comparison of full pressure dependences for each bath gas. In order to aid in assessing the magnitude of pressure dependent effects on silylene reactions with hydrogen and silane in other reaction environments, we present the calculated three-body association rate constants as a function of pressure over an extended range in Fig. 10.

Table II provides a comparison of our rate constants and Inoue and Suzuki's LIF results¹³ with values calculated from Arrhenius parameters originally suggested by John and Purnell.¹⁸ It is clear that there are enormous discrepancies between the directly measured rate constants and the estimates of John and Purnell, especially in the case of reaction with hydrogen. Taken together, the LRAFKS and LIF studies leave no doubt that previous estimates of silylene reactivity with hydrogen, silane, and disilane give rate constants which are much too low.

TABLE II. Comparison of silviene reaction rate co	constants.°
----------------------------------------------------------	-------------

			This work			<u></u>
Reactant	John and Purnell ^b	Inoue and Suzuki ^c	1 Torr	20 Torr	High pressure limit	
H ₂ SiH ₄ Si ₂ H ₆	$2.0 \times 10^{-16} 9.4 \times 10^{-13} 7.6 \times 10^{-12} $	$1.0 \times 10^{-13} d$ 1.1×10^{-10} 5.7×10^{-10}	$\begin{array}{c} 2.6 \times 10^{-13} \text{ d} \\ 6.7 \times 10^{-11} \\ 1.5 \times 10^{-10} \end{array}$	$ \begin{array}{c} 1.3 \times 10^{-12} \\ 1.8 \times 10^{-10} \\ 3.4 \times 10^{-10} \\ \end{array} $	$3.2 \times 10^{-12} \\ 2.2 \times 10^{-10}$	

^aRate constants are in cm³ molecule⁻¹ s⁻¹ at 300 K.

^bCalculated from Arrhenius parameters estimated from kinetic data in the range 20-70 Torr, 578-608 K (Ref. 17).

° Values from Ref. 13 at 1 Torr in helium, except as noted.

^d Rate constant at 2 Torr total pressure.

°Rate constant at 9.5 Torr total pressure.

The disagreement between our rate constants for reaction with hydrogen and silane and those determined in Inoue and Suzuki's LIF study¹³ are relatively small, and not unusual even in direct kinetic studies of complicated chemical systems. The disagreement in the case of reaction with disilane is, however, well outside of experimental uncertainty. We can offer only limited insight into possible reasons for the discrepany. The measurements differ significantly in two regards, the silvlene detection scheme and the design and operation of the flow cells. It is possible that LIF detection may be complicated by the flurorescence behavior of the \tilde{A} state of silylene,²⁷ while the absorption technique is not. It seems more likely that difficulties in handling reactive gases at small concentrations in flow reactors are responsible. Reactant purity is unlikely to be an issue, since the rate constants are so near gas kinetic that enormous impurity levels would be required to account for a factor of 3.8.

These results have important consequences for silvlene thermochemistry. In our original study of the reaction of silylene with deuterium, we suggested that the rate constant for that reaction was a good approximation to the high pressure limiting value for $SiH_2 + H_2$ and that the observed rate constant strongly supported the claims of ab initio calculations^{4,5} that the heat of formation of silvlene was too low.¹⁴ Our present data for the reaction of SiH₂ with hydrogen clearly prove this contention. Since Arrhenius parameters are known for the thermal decomposition of silane,⁴⁰ disilane,⁴¹ and trisilane,³⁶ we can now estimate the heat of formation of silvlene from three independent sets of data, using known heats of formation and third law entropies.⁴² Using rate constants for the decomposition of silane, disilane, and trisilane at 300 K, calculated from the Arrhenius parameters, and our measured high pressure rate constants, we calculate heats of formation for silylene of 65.1, 64.6, and 64.1 kcal/mol, based on the equilibria $SiH_4 \neq SiH_2 + H_2$, $Si_2H_6 \rightleftharpoons SiH_2 + SiH_4$, and $Si_3H_8 \rightleftharpoons SiH_2 + Si_2H_6$, respectively. The uncertainties in these values are $\sim \pm 2$ kcal/mol. A difficulty with the thermochemistry of the decomposition of disilane, discussed in our initial communication,¹⁴ has been removed by a recent reinvestigation of disilane pyrolysis and an upward revision of the activation energy for this reaction.^{17,41} The calculated heats of formation show excellent internal consistency and agree well with a similar recent evaluation by Martin et al.41 The consistency of the kinetic analysis, combined with ion-molecule derived values^{10,11} of 69 ± 3 and 68.5 ± 1.5 , photoionization derived values^{11,12} of 65.2 \pm 0.7 or 68.2 \pm 0.8, and *ab initio* values^{4,5} of 63.4 and 68.1 kcal/mol, leave no doubt that the previously accepted value of 58 kcal/mol for the heat of formation of silylene requires revision. The kinetic results appear to support the lower of the two values arrived at in the photoionization study, while ion-molecule data appears to support the higher value. However, reevaluation⁴³ of Boo and Armentrout's ion beam data¹¹ using a heat of formation of 278.0 ± 1.4 kcal/mol for SiH_2^+ and an ionization potential for silylene of 9.15 ± 0.02 eV, the higher of the two values suggested in the photoionization study,¹² gives a value for the heat of formation of silylene of 65.5 \pm 1.5 kcal/mol, in agreement with the kinetically derived values presented above.

Uncertainties in the thermochemistry, even as small as 2 kcal/mol, make meaningful estimates of activation energies for the insertion reactions difficult, since the activation energies are almost certainly smaller than this. Any activation energy for the reaction of silvlene with silane or disilane is very small, and we have previously estimated¹⁴ that the activation energy for the insertion of silylene into hydrogen was less than 1 kcal/mol. The thermochemistry presented above is consistent with an activation energy of 1.7 kcal/mol for this reaction. Temperature dependent studies over a substantial temperature range will be required to make any further progress in this area. It is clear that the previously accepted¹⁸ activation energy of 5.5 kcal/mol for the reaction of silylene with hydrogen, as well as a number of ab initio values⁴⁴⁻⁴⁸ are too high. Our rate constants are, however, in excellent agreement with the most recent ab initio calculations by Gordon et al.8

The rate constants presented above also provide a new insight into mechanistic models of silicon CVD from silane. The results are particularly applicable to low temperature deposition processes, such as glow discharge deposition of amorphous hydrogenated silicon. Silylene has very often been postulated as a film growth precursor in this deposition process, yet several direct studies of silylene concentrations in silane glow discharges find remarkably little silylene present.^{49,50} The explanation for this result is now straightforward. Silylene is almost certainly formed efficiently in glow discharge decomposition of silane, but it is also consumed rapidly to produce higher silanes. Therefore, the steady state concentration is low, as is the direct flux of silylene to the film growth surface. This suggests that higher silanes may be much more important in silicon CVD mechanisms than previously suspected, especially under low temperature conditions.⁵¹ It is also clear that any equilibrium or kinetic model for silicon CVD which has been evaluated using data from the existing silvlene literature overestimates the concentration of silylene.

CONCLUSIONS

We have investigated the kinetics of silylene reactions with hydrogen, silane, and disilane in some detail. The results require substantial revision in accepted values for the absolute rate constants for these reactions and in the heat of formation of silylene. The kinetic data presented in this study, when combined with *ab initio* calculations, mass spectrometric studies, and reevaluation of silicon hydride pyrolysis kinetics, provide a remarkably consistent, quantitatively new picture of the chemistry of silicon hydrides. This information, in turn, should provide new insight into modeling of silicon CVD processes at increasingly sophisticated and accurate levels.

ACKNOWLEDGMENTS

We would like to thank Dr. David Beach for providing a sample of iodosilane, Mr. Richard Estes for technical assistance, Dr. Bruce Scott for numerous discussions on the role of silylene in silicon hydride chemistry and CVD processes, Professor Peter Armentrout for helpful discussions on the heat of formation of silylene, and Dr. Robin Walsh for helpful comments on the RRKM calculations.

- ¹P. P. Gaspar, *Silylenes, Reactive Intermediates*, edited by M. Jones and R. A. Moss (Wiley, New York, 1985), Vol. 3.
- ²I. M. Davidson, Annu. Rep. Prog. Chem. Sect. C 82, 47 (1985).
- ³J. M. Jasinski, B. S. Meyerson, and B. A. Scott, Annu. Rev. Phys. Chem. **38**, 109 (1987).
- ⁴J. A. Pople, B. T. Luke, M. J. Frisch, and J. S. Binkley, J. Phys. Chem. **89**, 2198 (1985).
- ⁵P. Ho, M. E. Coltrin, J. S. Binkley, and C. F. Melius, J. Phys. Chem. 89, 4647 (1985).
- ⁶P. Ho, M. E. Coltrin, J. S. Binkley, and C. F. Melius, J. Phys. Chem. **90**, 3399 (1986).
- ⁷M. S. Gordon and D. R. Gano, J. Am. Chem. Soc. 106, 5421 (1984).
- ⁸M. S. Gordon, D. R. Gano, J. S. Binkley, and M. J. Frisch, J. Am. Chem. Soc. **108**, 2191 (1986).
- ⁹M. S. Gordon, T. N. Truong, and E. K. Bonderson, J. Am. Chem. Soc. 108, 1421 (1986).
- ¹⁰S. K. Shin and J. L. Beauchamp, J. Phys. Chem. 90, 1507 (1986).
- ¹¹B. H. Boo and P. B. Armentrout, J. Am. Chem. Soc. 109, 3549 (1987).
 ¹²J. Berkowitz, J. P. Greene, H. Cho, and B. Rusic, J. Chem. Phys. 86, 1235 (1987).
- ¹³G. Inoue and M. Suzuki, Chem. Phys. Lett. 122, 361 (1985).
- ¹⁴J. M. Jasinski, J. Phys. Chem. 90, 555 (1986).
- ¹⁵J. O. Chu, D. B. Beach, and J. M. Jasinski, J. Phys. Chem. **91**, 5340 (1987).
- ¹⁶J. O. Chu and J. M. Jasinski, Pure Appl. Chem. (in press).
- ¹⁷H. M. Frey, R. Walsh, and I. M. Watts, J. Chem. Soc. Chem. Commun. **1986**, 1189.
- ¹⁸P. John and J. H. Purnell, Faraday Trans. I 69, 1455 (1973).
- ¹⁹R. Walsh, Acc. Chem. Res. 14, 246 (1981).
- ²⁰H. Petek, Ph.D. thesis, University of California, Berkeley, California, 1985.
- ²¹G. L. Ward, Inorg. Synth. 11, 159 (1968).
- ²²G. Inoue and M. Suzuki, Chem. Phys. Lett. 105, 641 (1984).
- ²³R. D. Estes, D. B. Beach, and J. M. Jasinski (unpublished).
- ²⁴U. Itoh, Y. Toyoshima, H. Onuki, N. Washida, and T. Ibuki, J. Chem.
- Phys. 85, 4867 (1986). ²⁵I. Dubois, G. Herzberg, and R. D. Verma, J. Chem. Phys. 47, 4262 (1967).
- ²⁶I. Dubois, Can. J. Phys. 46, 2485 (1968).
- ²⁷J. W. Thoman, J. I. Steinfeld, R. I. McKay, and A. E. W. Knight, J. Chem. Phys. 86, 5909 (1987).
- ²⁸J. E. Baggott, H. M. Frey, P. D. Lightfoot, and R. Walsh, Chem. Phys. Lett. **125**, 22 (1986).
- ²⁹I. Dubois, Depository for Unpublished Data, National Science Library, Ottawa, Canada.
- ³⁰J. J. O'Brien and G. H. Atkinson, Chem. Phys. Lett. 130, 321 (1986).

- ³¹Y. N. Tang, Reactions of Silicon Atoms and Silylenes, Reactive Intermediates, edited by R. A. Abramovitch (Plenum, New York, 1982), Vol. 2.
- ³²R. T. White, R. L. Espinos-Rios, D. S. Rogers, M. A. Ring, and H. E. O'Neal, Int. J. Chem. Kinet. 17, 1029 (1985).
- ³³J. H. Purnell and R. Walsh, Proc. R. Soc. London Ser. A 293, 543 (1966).
- ³⁴J. M. Jasinski and R. D. Estes, Chem. Phys. Lett. 117, 495 (1985), and references therein.
- ³⁵M. Bowery and J. H. Purnell, Proc. R. Soc. London Ser. A **321**, 341 (1971).
- ³⁶A. J. Vanderwielen, M. A. Ring, and H. E. O'Neal, J. Am. Chem. Soc. 97, 993 (1975).
- ³⁷R. J. Robinson and K. A. Holbrook, *Theory of Unimolecular Reactions* (Academic, New York, 1973).
- ³⁸W. L. Hase and D. L. Bunker, QCPE 11, 234 (1973). The program was modified to compute chemical activation rate constants for the case where the activating reaction is the reverse of the decomposition reaction as described in Ref. 31, Chap. 8.
- ³⁹K. F. Roenigk, K. F. Jensen, and R. W. Carr, J. Phys. Chem. **91**, 5732 (1987).
- ⁴⁰C. G. Newman, H. E. O'Neal, M. A. Ring, F. Leska, and N. Shipley, Int. J. Chem. Kinet. **11**, 1167 (1979).
- ⁴¹J. G. Martin, M. A. Ring, and H. E. O'Neal, Int. J. Chem. Kinet. 19, 715 (1987).
- ⁴²Thermochemical values used in this evaluation were taken from (a) Ref. 18; (b) Ref. 34; (c) S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976); (d) L. Fredin, R. H. Hauge, Z. H. Kafafi, and J. L. Margrave, J. Chem. Phys. 82, 3542 (1985). Values for the silicon hydride species are: molecule $\Delta H_{f,300}^{\circ}$ kcal/mol, S_{300}° e.u.; SiH₂, evaluated in the text, 49.6; SiH₄, 8.2, 49.0; Si₂H₆, 19.1, 65.6; Si₃H₈, 28.9, 84.5. Arrhenius parameters for silane, disilane, and trisilane pyrolysis were taken as: $\log_{10}k = 15.5-58\ 000/\Theta$; $\log_{10}k = 15.75-52\ 200/\Theta$; $\log_{10}k = 15.69-52\ 990/\theta$, respectively, where $\Theta = 2.303$ RT.
- ⁴³P. B. Armentrout (personal communication).
- ⁴⁴T. N. Bell, K. A. Perkins, and P. G. Perkins, J. Chem. Soc. Chem. Commun. 1980, 1046.
- ⁴⁵M. S. Gordon, J. Chem. Soc. Chem. Commun. 1981, 890.
- ⁴⁶R. S. Grev and H. F. Schaefer III, J. Chem. Soc. Chem. Commun. 1983, 785.
- ⁴⁷T. N. Bell, K. A. Perkins, and P. G. Perkins, J. Phys. Chem. 88, 116 (1984).
- ⁴⁸A. Sax and G. Olbrich, J. Am. Chem. Soc. 107, 4868 (1985).
- ⁴⁹J. M. Jasinski, E. A. Whittaker, G. C. Bjorklund, R. W. Dreyfus, R. D. Estes, and R. E. Walkup, Appl. Phys. Lett. 44, 1155 (1984).
- ⁵⁰R. Robertson, D. Hils, H. Chatham, and A. Gallagher, Appl. Phys. Lett. 43, 544 (1983).
- ⁵¹B. A. Scott, R. D. Estes, and D. B. Beach, Pure Appl. Chem. (in press).