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Absolute Rate Constant for the Reaction $SiH_2 + D_2$

Joseph M. Jasinski

IBM, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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An absolute rate constant for the reaction of silylene with molecular deuterium at room temperature has been measured by laser resonance absorption flash kinetic spectroscopy. The rate constant is four orders of magnitude larger than previous data suggest and provides experimental support for recent ab initio theoretical results.

Silylene, SiH_2, has often been invoked as an important reactive intermediate in the thermal,[1-6] photochemical,[7,8] and glow discharge[9,10] decomposition of silicon hydrides such as silane and disilane. Its intermediacy in these processes has generally been inferred indirectly on the basis of reaction product analysis, thermochemical arguments, isotope scrambling experiments, or chemical scavenging experiments. It has, however, occasionally been directly observed by optical spectroscopy or mass spectrometry in flash spectroscopy,[11-13] matrix isolation,[14,15] and glow discharge[16,17] studies. Because of its small size and structural relationship to its lighter congener methylene, silylene has also been the subject of a number of theoretical studies, concerned both with its electronic structure[18-21] and with potential surfaces for some of its simple bimolecular reactions.[22-30]

As a consequence of the experimental and theoretical evidence for the importance of SiH_2 in silicon hydride chemistry, silylene has also been discussed as an important film growth precursor in the chemical vapor deposition (CVD) of various silicon-containing thin films of technological importance in microelectronics.[31-34] The desire to understand the mechanistic details of these CVD processes has led to a recent effort to assess existing chemical information and to provide new experimental and theoretical thermodynamic, spectroscopic, and kinetic data on silylene and other reactive silicon-containing species. This Letter reports a measurement of the absolute rate coefficient for the reaction of silylene with molecular deuterium. While a number of relative rate measurements for silylene reactions have been reported,[35] this work represents the first direct measurement of a gas-phase rate constant for any bimolecular reaction of SiH_2. The results demonstrate that silylene is much more reactive than previous studies suggest and provide experimental evidence which supports a recently proposed revision in the heat of formation of silylene. Direct measurements of several rate constants for reactions of the related divalent silicon species SiF_2 and $SiCl_2$ have recently appeared.[36,37]

Experiments were performed in a slowly flowing gas cell using laser resonance absorption flash kinetic spectroscopy[38] (LRAFKS) to generate SiH_2 and monitor its concentration in real time. A schematic of the apparatus is shown in Figure 1. The cell is 1 m long and 3.5 cm in diameter. Helium and deuterium, metered with mass flow controllers, enter the cell at each window. Phenylsilane, the photochemical precursor for SiH_2, enters the cell through two inlets positioned 20 cm downstream from the windows. The phenylsilane flow is controlled with a needle valve. Gases are pumped out through a single port at the center of the cell with a mechanical pump. This arrangement, with total pressures of helium and deuterium kept at or above 1 torr, effectively prevents photochemical deposition of opaque organosilicon films on the windows. Such films form rapidly in static systems, even at very low partial pressures of phenylsilane. Silylene is generated by photolysis of phenylsilane with an ArF excimer laser

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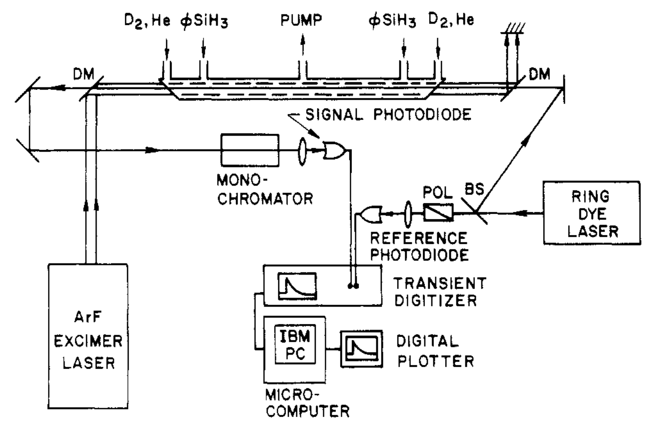

Figure 1. Schematic of the LRAFKS apparatus. The dye laser is multipassed three times through the cell by using additional mirrors (not shown). The monochromator serves as a band-pass filter to reject stray excimer laser light. DM are dichroic mirrors, BS is a variable beam splitter, POL is a polarizer used to balance the dye laser intensities incident on the signal and reference photodiodes. The transient digitizer is triggered by a trigger pulse from the excimer laser.

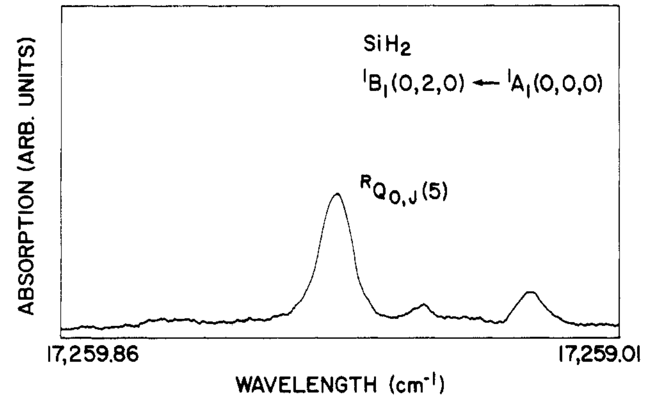

Figure 2. Spectral scan through the $^rQ_{0,J}(5)$ line of the $^1B_1$ (0,2,0) ← $^1A_1$ (0,0,0) transition of SiH_2. The spectrum was obtained by integrating the first 15 μs of the transient absorption signal as the dye laser frequency was scanned.

(Lambda Physik 102E, 50–75 mJ, 10-ns pulse, 193 nm). Transient absorption from single rotational lines of the $^1B_1 \leftarrow {}^1A_1$ transition is observed by using a single-frequency CW ring dye laser (Spectra Physics 380A, Rhodamine 6G dye). The dye laser beam passes through the cell three times before being focussed onto a PIN photodiode (H.P. 5082-4203, -22-V bias, 2-kΩ load). The absorption signal and a reference signal from an identical photodiode are fed into a differential amplifier (Tektronix 7A26). In order to obtain kinetic data, the resulting waveform is digitized (Tektronix 7912AD), averaged, and output to a microcomputer (IBM PC) for further analysis. To obtain spectral scans, the output from the differential amplifier is averaged by a boxcar integrator (PAR 162/164) and recorded on a strip chart recorder as the dye laser wavelength is scanned.

The photochemistry of phenylsilane has not been systematically studied. The molecule has, however, been demonstrated as a photochemical source of ground singlet-state silylene both in the original flash spectroscopic work of Dubois, Herzberg, and Verma[11] and in a laser-induced fluorescence study by Inoue and Suzuki.[13] It is possible, and indeed likely, that other reactive species are also generated in the photolysis. The only stable photoproduct observed in the present study was a yellow-white polymeric deposit which builds up on the walls of the cell. Identification of transient absorption features as single rotational lines of the $^1B_1 \leftarrow {}^1A_1$ silylene transition was made on the basis of line positions, obtained with the aid of a wavemeter (Burleigh WA-20). The small number of lines which have been searched for and detected thus far are in excellent agreement with those obseved earlier in this laboratory during a study of SiH_2 in silane glow discharges,[16] and with an extensive tabulation of line positions prepared by Dubois.[39] A spectral scan through the strong $^rQ_{0,J}(5)$ line of the (0,2,0)–(0,0,0) vibronic band is shown in Figure 2. The two weaker features in the spectrum have not been assigned.

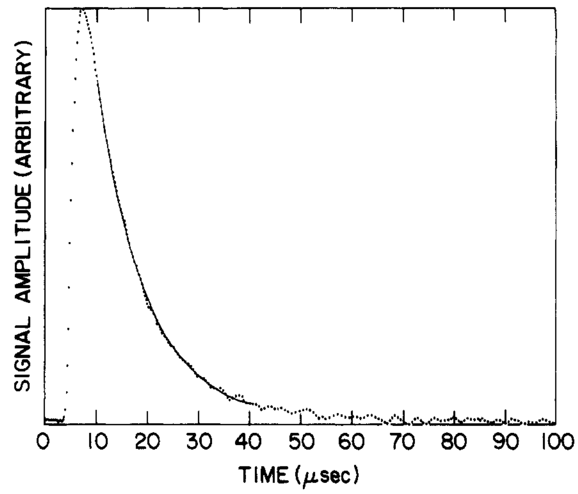

Figure 3. Transient absorption signal for the $^rQ_{0,J}(5)$ transition. The peak corresponds to ~10% absorption. The waveform is the average of 64 shots. The solid line is a least-squares fit to a single-exponential decay.

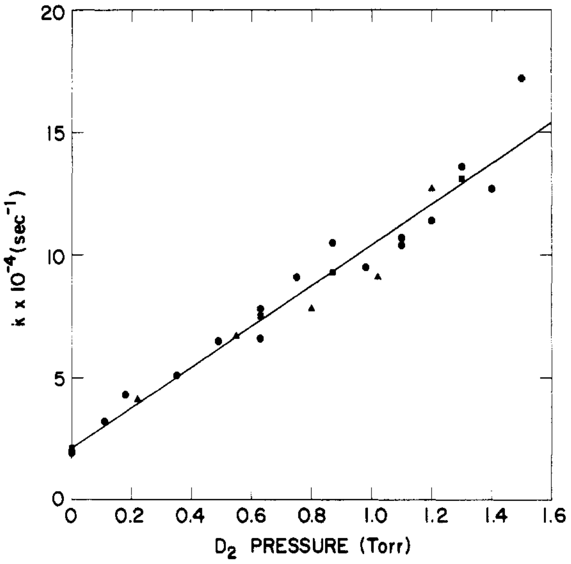

Figure 4. Plot of pseudo-first-order rate constants for silylene removal vs. deuterium pressure: squares, $^rQ_{0,J}(3)$; circles, $^rQ_{0,J}(5)$; triangles, $^rQ_{0,J}(7)$. The line is a least-squares fit to the data and gives a bimolecular rate constant of $(2.6 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The error limits are ±1 standard deviation in the slope.

Pseudo-first-order rate constants for loss of SiH_2 were obtained from single exponential analysis of the decay of the SiH_2 absorption signal. A typical transient absorption waveform is shown in Figure 3. Bimolecular rate constants were obtained from a plot of pseudo-first-order rate constants as a function of reactant gas pressure. In a typical experiment, helium and phenylsilane flows were established at 50 and 0.04 sccm, respectively, and decay rates for a given SiH_2 rotational line were then measured as a function of an added flow of deuterium. The deuterium flow rates ranged from 0 to 80 sccm. The partial pressure of deuterium was calculated from the total pressure, measured with a capacitance manometer, and the known flow rates of helium and deuterium. The flow of phenylsilane was negligible in all cases and the partial pressure of phenylsilane was ~1 mTorr or less. The total pressure was not constant, but rose from 2 Torr in the absence of deuterium to ~3 Torr at the maximum deuterium flow. A plot of pseudo-first-order rate constants vs. deuterium pressure is shown in Figure 4. The data were obtained by using three SiH_2 transitions

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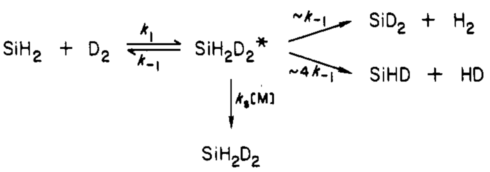
[39] I. Dubois, Depository for Unpublished Data, National Science Library, NRC, Ottawa, Canada.

SCHEME I



originating from three different rotational levels of the ground state, $3_{0,3}$, $5_{0,5}$, and $7_{0,7}$. These lines all give the same decay rates within the scatter in the data shown in Figure 4. In addition, the decay of the SiH_2 signal is a constant, independent of helium pressure (from 1 to 5 Torr), in the absence of deuterium. These observations rule out rotational relaxation as a contribution to the observed decay rate. Identical results are obtained at excimer laser repetition rates of 5 and 10 Hz. This observation rules out reaction with accumulated product molecules as a contribution to the observed decay rates. The bimolecular rate constant, obtained from the slope of a least-squares fit to the data, is $(2.6 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. All experiments were performed at an ambient temperature of ~300 K.

The only available exothermic channel for the reaction of silylene with hydrogen or deuterium is insertion to form a silane, SiH_4 or SiH_2D_2. Previous experimental and theoretical studies have been carried out on the reaction of silylene with hydrogen. The reaction of silylene with deuterium has been studied in this preliminary work in order to avoid the experimental complications associated with studying a three-body association reaction at pressures which are below the high-pressure bimolecular limit. The reaction of silylene with deuterium can be described by the mechanism shown in Scheme I. In Scheme I, $SiH_2D_2^*$ is the vibrationally excited silane formed by the insertion reaction. This species is either collisionally stabilized by a third body, with rate constant $k_s[M]$, or decomposes unimolecularly by one of the three paths shown. In the bimolecular limit, the rate constant for loss of SiH_2 is simply k_1. This rate constant provides information on the potential surface for the interaction of silylene with hydrogen or deuterium and is the value which can most readily be compared with previous experimental and theoretical results. In the absence of anomalously large isotope effects, the rate constant for the loss of SiH_2 by reaction with D_2 provides a good approximation to k_1, even at pressures where collisional stabilization is not rapid compared to unimolecular decay of $SiH_2D_2^*$. Of the six possible channels for decomposition of $SiH_2D_2^*$, only one leads back to SiH_2. The other channels lead to formation of deuterated silylenes, which have absorption bands that are shifted from those of SiH_2 because of differences in the rotational constants and bending frequencies. Formation of deuterated silylenes, therefore, is detected as reaction in an experiment which monitors only loss of SiH_2.

For purposes of discussion, it is most convenient to view the rate constant reported above as a good approximation to the rate constant for the reaction of SiH_2 with H_2 in the bimolecular limit. This is justified by the previous discussion of the mechanism presented in Scheme I. The further assumption that any isotope effect on the insertion reaction is small and normal (i.e. $k_H > k_D$) results in the value for the rate constant reported above being a *lower limit* to the rate constant for $SiH_2 + H_2$ in the high-pressure, bimolecular limit. Arrhenius parameters for the insertion of SiH_2 into H_2 have been determined from a combination of relative rate measurements and an estimate of the heat of formation of SiH_2 by John and Purnell.[40] They find an activation energy of 5.5 kcal mol^{-1} and a preexponential factor of $10^{-11.6}$ cm^3 molecule^{-1} s^{-1}. At room temperature, these Arrhenius parameters correspond to a rate constant of 2×10^{-16} cm^3 molecule^{-1} s^{-1}, a value *four orders of magnitude smaller* than the rate constant reported above. None of the assumptions made in claiming that the rate constant for the reaction $SiH_2 + D_2$ is an approximation to the rate constant for $SiH_2 + H_2$ can account for a discrepancy of this magnitude. The magnitude of the preexponential factor reported by John and Purnell is reasonable for an association reaction.[41] Therefore, the most likely source of the discrepancy is the activation energy.

The magnitude of the activation energy reported by John and Purnell is supported by a number of ab initio theoretical results.[22-25,29] A more recent calculation[30] on $SiH_2 + H_2$, however, suggests a barrier closer to 1 kcal mol^{-1}, as does a calculation of the heat of formation[42] of SiH_2, when combined with the activation energy for the reverse reaction, decomposition of silane to silylene and hydrogen. The Arrhenius parameters for the decomposition of silane in the high-pressure limit have been revised significantly[2] from the values used by John and Purnell, and a spectroscopic determination of the entropy of formation of SiH_2 has recently become available.[15] These values make possible a calculation of the preexponential factor for the $SiH_2 + H_2$ reaction, using the relationship $A_1/A_{-1} = \exp(\Delta S/R)$. Using $A_{-1} = 10^{15.5}$ s^{-1} as the preexponential factor for the dissociation of silane[2] and $\Delta S = -25.4$ eu (concentration units)[43] leads to a value of $10^{-10.9}$ cm^3 molecule^{-1} s^{-1} for A_1. Combining this value for A_1 with the value of $k_1 \geq 2.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} gives an activation energy of $E_1 \leq 1.0$ kcal mol^{-1}. The rate data determined in the present study, therefore, support the proposed revision[42] in the heat of formation of SiH_2 from 58.0 to 68.1 kcal mol^{-1}. This revision provides an internally consistent set of thermodynamic and kinetic data for $SiH_2 + H_2 \rightleftarrows SiH_4$. However, revision of the heat of formation of SiH_2 to 68.1 kcal mol^{-1} opens new inconsistencies in data for $SiH_2 + SiH_4 \rightleftarrows Si_2H_6$, since the decomposition of disilane now becomes ~10 kcal mol^{-1} more endothermic than the measured activation energy.[3,4]

In conclusion, the utility of LRAFKS for direct measurements of SiH_2 removal rates has been demonstrated. A measurement of the rate constant for the reaction of SiH_2 with D_2 has been made. The reaction is found to be much faster than previous experimental studies suggest, and the rate constant provides experimental support for a revision in the heat of formation of SiH_2 which has recently been made on a theoretical basis. More extensive studies of the reaction of silylene with deuterium, hydrogen, silane, and a variety of other molecules using LRAFKS are currently in progress.

Note Added in Proof. While this manuscript was in press, an independent report of direct measurements with absolute rate constants for several silylene reactions appeared.[44]

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(43) The following values for $S°_{300}$ were used: H_2, 31.2 eu (ref 41); SiH_4, 49.0 eu (ref 41); SiH_2, 49.587 eu (ref 15). The value of $S°_{300}$ for SiH_2 calculated in ref 15 from revised vibrational frequencies is only slightly different from a value calculated earlier (P. John and J. H. Purnell, *J. Organometal. Chem.*, **29**, 233 (1971)) from vibrational frequencies given in ref 14. A correction term appropriate for conversion from a standard state of 1 atm to concentration units was used as described in ref 41, p 160.

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