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First Kinetic Measurements on SiD_2: Absolute Rate Constant for the Reaction $SiD_2 + H_2$

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SiD_2, generated *via* the laser flash photolysis of phenyl[$^2H_3$]silane, has been detected *via* a ro-vibrational transition in its $\tilde{A}(^1B_1) \leftarrow \tilde{X}(^1A_1)$ absorption band. It has been monitored for the first time in time-resolved studies to give an absolute rate constant of $(3.8 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction $SiD_2 + H_2$. Product SiH_2 from this reaction was also observed.

Silylene, SiH_2, is a key intermediate in the photolytic and thermal decompositions of silanes and plays an important role in the process for chemical vapour deposition of thin films of amorphous silicon. In 1985 Inoue and Suzuki[1] reported the first directly measured rate constants for reactions of SiH_2. Since then the rate constants for several other reactions have been obtained by time-resolved methods.

Kinetic studies of SiD_2 have not previously been carried out although they are of particular interest in two respects, *viz.* (i) a comparison with SiH_2 data will help elucidate reaction mechanisms and (ii) many SiH_2 reactions exhibit pressure dependences often making it problematical to obtain high-pressure limiting rate constants. Isotopic scrambling effects make it possible to circumvent this problem with SiD_2 studies. For example the reaction $SiH_2 + H_2$ can be conveniently described by three elementary steps:

$$SiH_2 + H_2 \rightarrow SiH_4^* \qquad (1)$$

$$SiH_4^* \rightarrow SiH_2 + H_2 \qquad (-1)$$

$$SiH_4^* + M \rightarrow SiH_4 + M \qquad (2)$$

Pressure dependence of this reaction arises from the behaviour of the vibrationally excited molecular product, SiH_4^*, which can either revert back to reactants or be stabilized by a third body. For the analogous SiD_2 reaction the vibrationally excited product is $SiD_2H_2^*$ which can redissociate to $SiHD + HD$ or $SiH_2 + D_2$ as well as reverting to the reactants. Since SiD_2 will only be reformed once in every six times on a statistical basis, following the argument of Jasinski,[2] there should be virtually no pressure effect on its rate of disappearance which will therefore closely approximate the rate of the true insertion reaction.

SiD_2 kinetic studies were carried out using the laser flash–laser absorption technique previously used to study SiH_2 kinetics.[3,4] Transient concentrations of SiD_2 were produced by 193 nm laser flash photolysis of $PhSiD_3$ (synthesized by $LiAlD_4$ deuteriation of $PhSiCl_3$, and of isotopic purity >92.6%). The concentration of SiD_2 was monitored by high-resolution absorption spectroscopy with light from a single-frequency ring-dye laser (linewidth 3×10^{-5} cm^{-1}). Prior to this a high-resolution spectrum of SiD_2 was recorded in order to find a strong characteristic transition for probing. Previously recorded spectra,[5-7] although not sufficiently resolved to reveal a suitable transition, indicated that the $^PQ_1$ bandhead of SiD_2 occurred at 17 385 cm^{-1} for the $\tilde{A}\,^1B_1(0,3,0) \leftarrow \tilde{X}\,^1A_1(0,0,0)$ transitions. Based on this a spectral search was made over the wavenumber range 17 384–17 391 cm^{-1} at intervals of 0.03 cm^{-1}, using a series of one-shot photolysis experiments with gas mixtures consisting of 10 mTorr $PhSiD_3$ in 5 Torr SF_6. The resulting spectrum is shown in Fig. 1, although we have not yet been able to assign the observed transitions. Preliminary calculations of the SiD_2 spectrum confirm the existence of a number of strong ro-vibrational lines in this wavenumber region.[8] A check at 17 259.50 cm^{-1} (the location of a strong SiH_2 transition) suggested a small photolytic yield of SiH_2 from $PhSiD_3$ of *ca.* 10% of the intensity for the equivalent photolysis of $PhSiH_3$. In the latter photolysis we found a weak absorption due to SiH_2 on probing at 17 387.07 cm^{-1} (the location of the strongest SiD_2 transition observed) which was *ca.* 16% of that from $PhSiD_3$ under identical conditions. However these results indicate a less than 2% contribution to the signal at 17 387.07 cm^{-1} from SiH_2 formed from impurity (or by photolytic scrambling) from $PhSiD_3$ and ensure that SiD_2 can be monitored at 17 387.07 cm^{-1} quantitatively to a good approximation.

For kinetic studies SiD_2 was monitored at both 17 387.07 and 17 385.18 cm^{-1}. No detectable difference was observed between results at the two wavelengths. Reaction mixtures generally contained 4 mTorr of $PhSiD_3$, 0–3.2 Torr of hydrogen and added SF_6 buffer gas (total pressure 5 Torr). The temperature was 294 K. First-order decays were averaged for four to ten laser shots at 50 to 140 mJ $pulse^{-1}$. All decays were good-quality single exponentials. The results shown in Fig. 2, confirm that second-order kinetics were obeyed. The slope of this plot yielded a rate constant of $(3.8 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, where the quoted error represents two standard deviations. Variation of the total pressure by a factor of 50 between 2 and 100 Torr indicated that the observed rate was independent of pressure

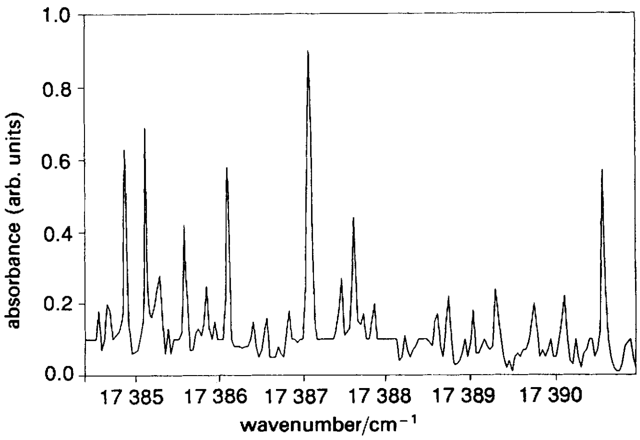

Fig. 1 Observed gas-phase absorption spectrum of SiD_2

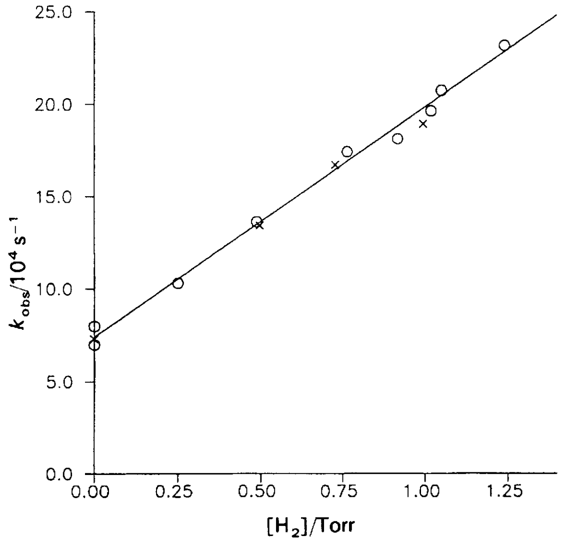

Fig. 2 Second-order plot for reaction of SiD_2 with H_2 at 294 K (total pressure = 5 Torr), SiD_2 detection wavenumber: (○) 17 387.07, (×) 17 385.18 cm^{-1}.

(within ±20%). A comparison of the rate constant reported here for $SiD_2 + H_2$ with the high-pressure limiting rate constant of 3.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} reported for $SiH_2 + H_2$ by Jasinski and Chu[9] and the rate constants of $(2.6 \pm 0.7) \times 10^{-12}$ and $(1.9 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for $SiH_2 + D_2$ reported by Jasinski[2] and Baggott *et al.*[4] respectively, show it to be of a reasonable magnitude. They also indicate the magnitude of the true insertion process isotope effects.

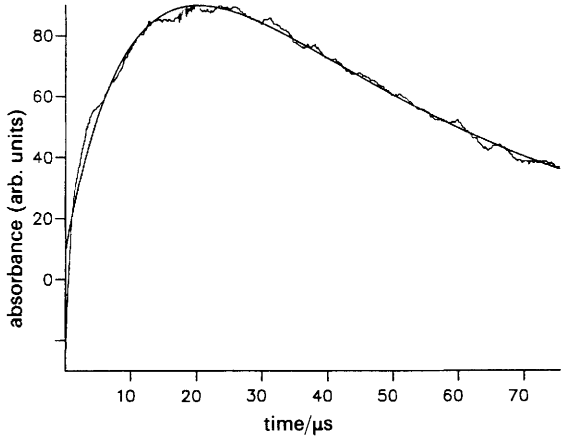

Fig. 3 Time evolution of trace for SiH_2 from the reaction of $SiD_2 + H_2$. $[H_2]$ = 1 Torr. Smooth curve is biexponential best fit.

Table 1 Second-order rate constants found for reaction of SiH_2 with H_2

total pressure/Torr	$k/10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} this paper[a]	$k/10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} Jasinski and Chu[b]
3	1.5 ± 0.3	2.7
5	3.4 ± 0.5	3.9
7	4.5 ± 0.3	5.0
10	4.8 ± 0.5	6.5

[a] Total pressures in H_2. [b] Ref. 9. Total pressures in He.

In addition to monitoring SiD_2 concentration decay curves we have carried out additional experiments where the generation of SiH_2 from isotopic scrambling and its subsequent disappearance by reaction with H_2 were observed. Reaction mixtures containing 2 mTorr of $PhSiD_3$ and made up to total pressures in hydrogen of 1–10 Torr were photolysed and SiH_2 absorption was monitored at 17 259.50 cm^{-1}. Averaged absorption growth–decay traces were obtained by summation of five traces using an excimer laser photolysis energy of 100 mJ $pulse^{-1}$. An example of such a trace is shown in Fig. 3. Although the noise level in these traces was not excessive, the short rise-time (slightly perturbed by the laser pulse) made analysis of the growth part of the curves difficult. Despite this the results obtained from experiments with 1, 3 and 5 Torr of H_2 gave an average growth rate constant of $(4 \pm 2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Although the error limit is large this is the same as the value found by monitoring SiD_2. By contrast there was no time-resolution difficulty in fitting the decay part of the SiH_2 traces and so a set of reasonably precise rate constants for reaction of SiH_2 and H_2 were obtained. These are shown in Table 1 and demonstrate the expected pressure dependence of this reaction. Comparison with the values of Jasinski and Chu[9] for the same reaction in He buffer gas shows reasonable agreement.

The rate constant obtained here for $SiD_2 + H_2$ may be compared with that[9] for $SiH_2 + H_2$, *viz.* 3.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (high-pressure limit). There is thus an inverse isotope effect of *ca.* 0.84. This can be accounted for by transition-state theory.[10] In future publications we will present: (i) a temperature-dependent study of the reaction of SiD_2 with H_2 and (ii) a full experimental and theoretical study of the isotope effects in the SiH_2–SiD_2 + H_2–D_2 reaction systems.

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