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Time resolved spectroscopic investigation of SiD₂ + D₂: kinetic study

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Abstract. Silylenes (silanediyls) have made an important impact on organosilicon chemistry even if it is of more recent foundation than carbenes in organic chemistry and much less complete. These species are highly reactive intermediates. They play a central role in the chemical vapour deposition (CVD) of various silicon-containing thin films which have a technological importance in microelectronics as well as in the dry etching processes of silicon wafers. Spectroscopic methods have been developed to observe these species, a necessary pre-requisite to their direct monitoring. In this work, deuterated phenylsilane precursor, PhSiD₃ was chosen for SiD₂ because its analogue phenylsilane, PhSiH₃ proved to be a good precursor for SiH₂ and the high quality decay signals observed revealed that SiD₂ be readily detected from PhSiD₃ and that if other decomposition pathways (e.g. PhSiD + D₂) are occurring, they do not effect measurements of the rate constants for SiD₂. The absorption spectrum of SiD₂ formed from the flash photolysis of a mixture of PhSiD₃ and SF₆ at 193nm were found in the region 17384-17391 cm⁻¹ with strong band at 17387.07 cm⁻¹. This single rotational line of ^PQ₁ was chosen to monitor SiD₂ removal. Time-resolved studies of SiD₂ have been carried out to obtain rate constants for its bimolecular reactions with D₂. The reactions were studied over the pressure range 5-100 Torr (in SF₆ bath gas) at four temperatures in the range 298-498K. Single decay from 10 photolysis laser shots were averaged and found to give reasonable first-order kinetics fits. Second order kinetics were obtained by pressure dependence of the pseudo first order decay constants and substance D₂ pressures within experimental error. The reaction was found to be weakly pressure dependent at all temperatures, consistent with a third-body mediated association process. In addition, SiH₂+ H₂ reaction is approximately ca. 60% faster than SiD₂+D₂ reaction. Theoretical extrapolations (using Lindemann-Hinshelwood model and Rice, Ramsperger, Kassel and Marcus (RRKM) theory) were also carried out and obtained data fitted the Arrhenius equations.

1 Introduction

The desire to understand the mechanistic details of the reactions of silylene, SiH₂ prompted us to extend our studies to include isotope effect experiments.[1,2]. The only kinetic information available for deuterated silylene, SiD₂ was that for the reaction with H₂. Mason *et al.*[3] reported a rate constant of $3.8 \pm 0.2 \times 10^{-12}$ cm³molecule⁻¹s⁻¹ at 5 Torr total pressure in which the reaction found to be pressure independent in the range 2-100 Torr. The possibility of studies with SiD₂ offers the opportunity to give new insights into reaction system previously studied with SiH₂.

For the reaction of SiH₂ with D₂ at room temperature, Jasinski reported a rate constant of 2.6×10^{-12} cm³molecule⁻¹s⁻¹[4]. This was the first reported measurement for this reaction. It compares with a value of 3.2×10^{-12} cm³molecule⁻¹s⁻¹ for the rate constant for the reaction of SiH₂+H₂ obtained by extrapolation to infinite pressure of a pressure dependent process[5,6]. These high values suggest only a small isotope effect and that the energy barrier to insertion was ≤ 1 kcal mol⁻¹ [4], this provides experimental support for the higher values of

heat of formation at room temperature. This suggestion has been supported by *ab initio* calculations carried out by Gordon and Gano[7]. The calculations for the potential energy surface of the silylene reaction with hydrogen gave an activation energy of 1.7 kcal mol⁻¹.

Subsequently Baggott *et al.*[8] extended Jasinski's room temperature study to cover a range of 298-333K and found k to be in good agreement with Jasinski's reported value[4,5]. The authors found an almost temperature independent rate constants of 1.88×10^{-12} cm³molecule⁻¹s⁻¹. The uncertainties in the rate constants were ca. 7%. This indicated that any activation energy was very small and certainly < 1.57 kcal mol⁻¹. A slightly negative activation energy cannot be ruled out.

In this work we report the first kinetic studies for the reaction of SiD₂ + D₂ at a wide range of pressures and temperatures. Kinetic studies of SiD₂ are of particular interest in two respects, *viz*

- (i) a comparison with SiH₂ data will help elucidate reaction mechanisms,
- (ii) many SiH₂ reactions exhibit pressure dependence often making it problematical to obtain high pressure

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limiting rate constants. Isotopic scrambling effects make it possible to circumvent this problem with SiD₂ studies.

2 SiD₂ precursor and visible absorption spectrum

PhSiD₃ was prepared by reduction of phenyltrichlorosilane (PhSiCl₃) with LiAlD₄ in dry ether [3]. The prepared PhSiD₃ was purified by distillation and found to be 99.8% pure (isotopic purity >92.6%). The PhSiD₃ precursor was chosen because its analogue phenylsilane, PhSiH₃ proved to be a good precursor for SiH₂. Although SiH₂ formation is not the major product of PhSiH₃ photolysis[9], nevertheless, its shown observation, suggest that SiD₂ should be readily detected from PhSiD₃. The high quality decay signals observed in the current work reveals that this is true and that if other decomposition pathways (eg to PhSiD + D₂) are occurring, they do not effect measurements of the rate constants for SiD₂. A typical averaged decay trace is shown in figure 1.

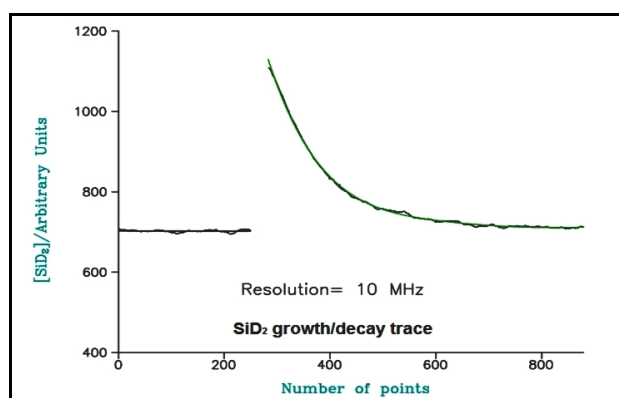


Fig. 1. Typical SiD₂ Absorption trace (3 mTorr of PhSiD₃, 4 Torr D₂ and P_T= 5 Torr in SF₆).

The absorption spectrum of SiD₂, formed from the flash photolysis of a mixture of SiD₄ and D₂, was first investigated by Dubois *et al.* in the region 16175-19200 cm⁻¹ [10]. They recorded a visible spectrum of the (¹B₁)←(¹A₁) band and found the bending vibrational frequency in the excited state to be 610 nm. However a more detailed spectroscopic study of SiD₂ radicals was reported by other researchers such as Fukushima *et al.* and Muramoto *et al.* [11-13]. Fukushima *et al.* [11] photolysed PhSiD₃ at 193nm in the supersonic free jet and observed 11 vibronic bands of the SiD₂ A (¹B₁) ← X (¹A₁) transition in the wavelength region between 21739.13 and 15625 cm⁻¹.

Because little is known about the SiD₂ radical, any fresh spectroscopic data (as well as kinetic data) are of practical and theoretical interest. Laser spectroscopic investigation of SiD₂ at higher resolution than earlier studies has reached similar conclusions in our lab [3]. Mason *et al.*[3] recorded the absorption spectrum of SiD₂ in the gas phase, using the flash photolysis kinetic absorption technique. SiD₂ was generated by photolysing 10mTorr of PhSiD₃ in 5Torr of SF₆ using a series of one-shot photolysis experiments. The authors observed an absorption spectrum in the 17384-17391 cm⁻¹ region (the

laser linewidth was approximately 3×10⁻⁵ cm⁻¹) with a strong band at 17387.07cm⁻¹, which was attributed to an unknown rotational line A(¹B₁)(0,3,0)←X(¹A₁)(0,0,0) vibronic transition of SiD₂. This assignment was based on the original work of Fukushima *et al.*[11]. A 6 cm⁻¹ composite spectrum of vibronic transition of SiD₂ is shown in figure 2 (a). Figure 2 (b) also shows the absorption spectrum of SiH₂ for comparison reason. Approximately 8 peaks were displayed for SiD₂ absorption spectrum. The 17387.07 cm⁻¹ was found to be the most intense peak. Therefore this peak was chosen to observe the SiD₂ species in this kinetic study. It has been estimated that the intensity of this peak is approximately a quarter of that for the transition used to monitor the SiH₂ species in kinetic studies under similar conditions[3].

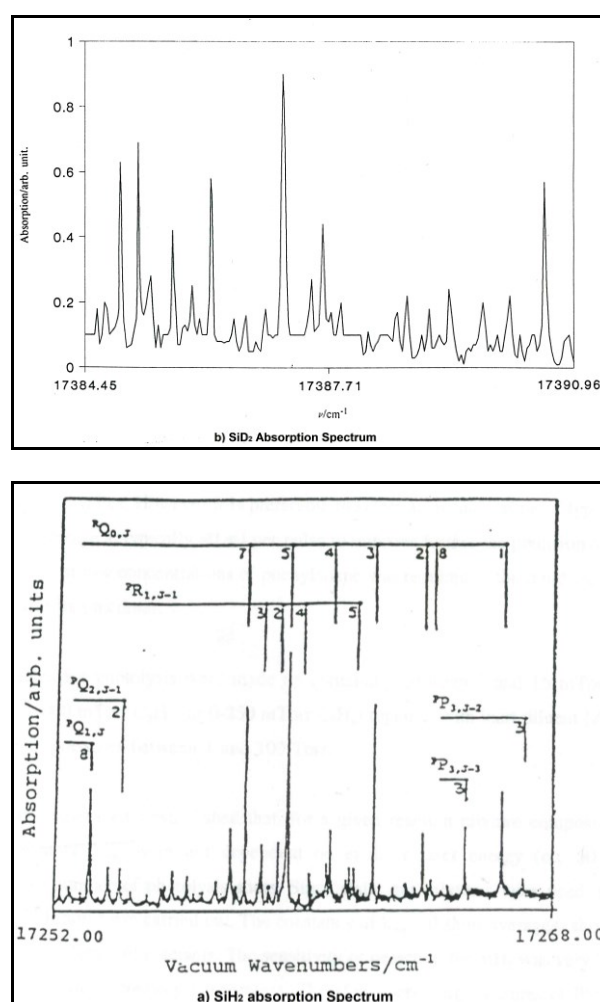


Fig. 2. Absorption spectrum of both a) SiH₂ [4] and b) SiD₂[3].

3 Experimental Setup

Laser flash photolysis/laser absorption apparatus is diagrammatically represented in figure bellow (figure 3).

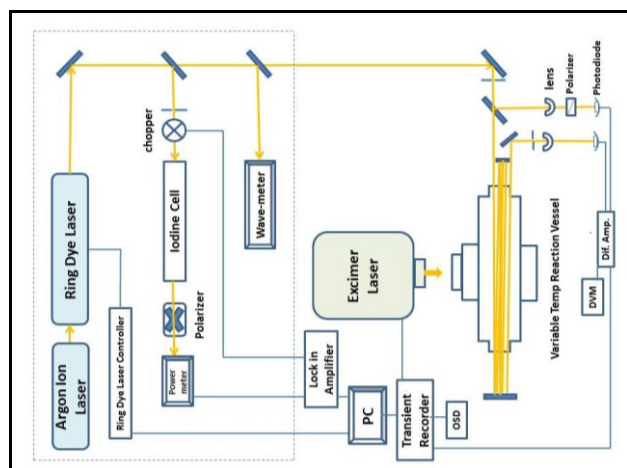


Fig. 3. Schematic diagram of the experimental apparatus.

A mercury-free, glass vacuum line was connected to purpose built variable photolysis cell fitted with a high quality crown glass end windows at Brewster's angle backed by a rotary pump. SiD₂ was produced by the 193 nm flash photolysis of phenylsilane (PhSiD₃) using an Oxford KX2, ArF excimer laser. The emitted pulses have 0.1-1J of energy delivered in a 10 ns light pulse with a repetition rate of 1 Hz. SiD₂ concentrations were monitored in real time by means of a Coherent 699–21 single-mode dye laser pumped by an Innova 90–5 Ar⁺ laser using Rhodamine 6G in solution as an active medium, which provides tunable radiation in the range 560–610nm. The monitoring laser beam was multipassed between 24–48 times through the reaction zone to give an effective path length of between 0.6–6 m. The monitoring laser was tuned to 17387.07 cm⁻¹. A differential amplifier was connected to two photodiodes and then fed into Datalab DI910 transient recorder (20 MHz resolution). The transient recorder's external trigger was activated by radiofrequency noise produced when the excimer laser was fired. Traces were observed during runs and interfaced to a computer via a commercial interface (Camplus) where the signal could be displayed and analyzed.

4 Results

The SiD₂ exponential decay curves were recorded and averaged for 10 excimer laser shots. The degree of depletion of the photolysis mixture was negligible. Experiments were carried out with gas mixtures containing a few mTorr of PhSiD₃, varying quantities of D₂ up to 9.5 Torr, and inert diluent bath gas (SF₆) at total pressures from 5 to 100 Torr to test for pressure dependence. For each pressure, a series of runs (7 points) was performed at different substrate concentrations, as been illustrated in figure 4.

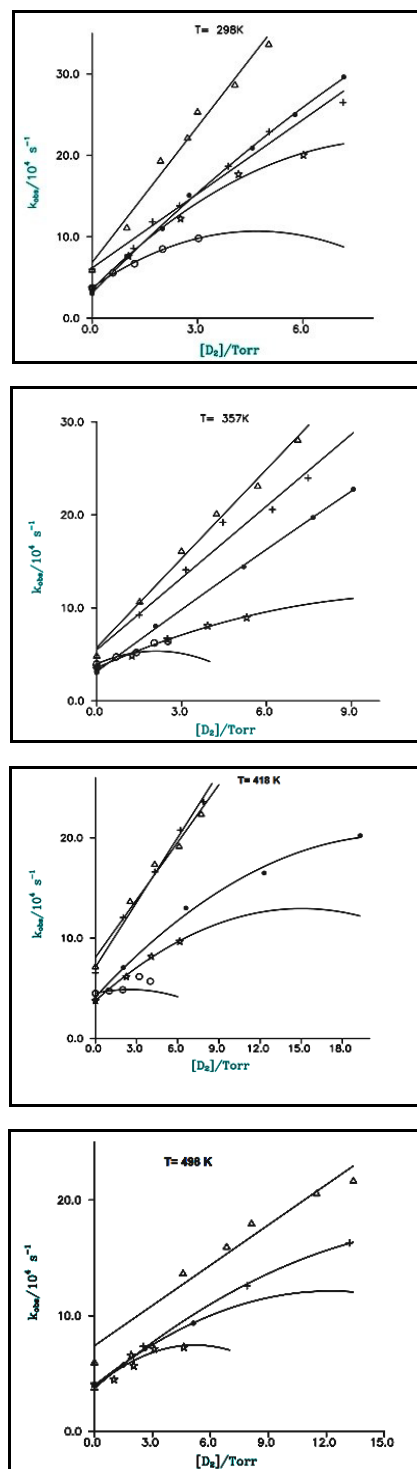


Fig. 4. Second-order plots for the reaction of SiD₂ + D₂ at various total pressures (in SF₆) and Temperatures. ○, 5; ★, 10; •, 20; +, 50; △, 100 Torr.

Only second order plots for data recorded at a total pressure above 20 Torr in SF₆ were linear. Plots for total pressures below this were curved. The quadratic procedure using the polynomial regression was applied for these cases in order to obtain the second order rate constants as gradients of the plots. The intercept corresponds to loss of silylene in the absence of substrate i.e. by reaction with PhSiD₃. The correlation of fitting constants means that the rate constants are somewhat less reliable by this procedure. Second order rate constants were calculated using the following expression:

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = \frac{\text{Gradient}(\text{Torr}^{-1} \text{ s}^{-1}) \times T(\text{K})}{F}$$

The conversion factor, F, was obtained from the ideal gas equation (PV=nRT where R=8.3145 J K⁻¹mol⁻¹). Its value is F= 9.657×10¹⁸.

The second order rate constants for these experiments, representing over 100 measurements of individual rate constants are shown in figure 5 and listed in table 1.

The uncertainties in individual second order rate constants are about *ca.* ± 20% for total pressures <20 Torr and ± 10% for total pressure >20 Torr, but are not shown in the figures to avoid complicating them.

Table.1 Absolute rate constants for the reaction of SiD₂ + D₂

P/Torr	k/10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹			
	298K	357K	418K	498K
5	0.91±0.1	0.45±0.1	0.23±0.1	-
10	1.33±0.1	0.53±0.1	0.53±0.1	-
20	1.35±0.1	0.83±0.1	0.63±0.1	0.69±0.2
50	1.21±0.2	1.16±0.2	1.04±0.1	0.66±0.2
100	1.72±0.2	1.36±0.2	1.00±0.1	0.78±0.2

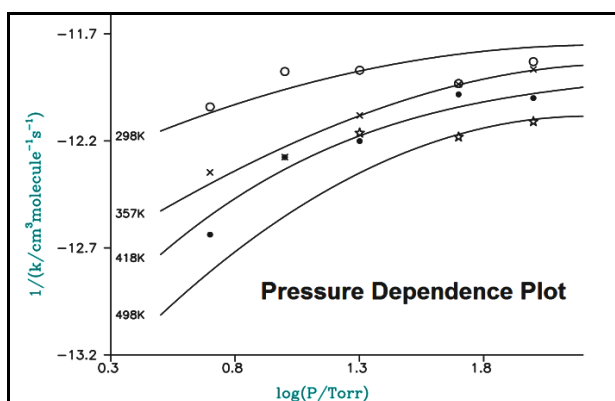


Fig.5. Pressure dependence of second-order rate constants for SiD₂ + D₂ at different temperatures in SF₆ buffer gas.

Comparison of absolute rate constants can only be made at 300K between the reactions of SiH₂+H₂ and SiD₂+D₂ due to big differences of temperatures used in these studies, see figure 6. The graph shows that the SiH₂+ H₂ reaction is approximately *ca.* 60% faster than SiD₂+D₂ reaction at high pressure.

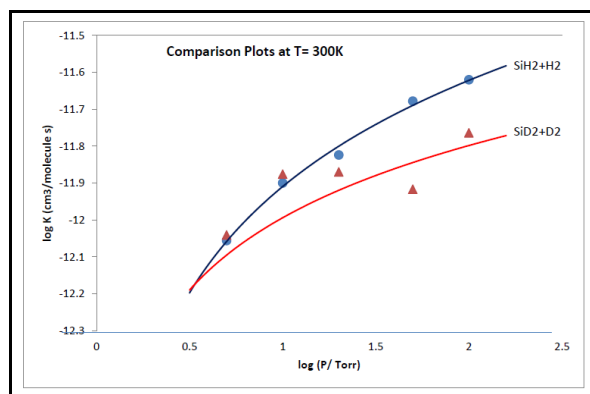


Fig.6. Pressure dependence of second-order rate constants for SiH₂+H₂ and SiD₂+D₂ at T=300K.

The measured rate constants demonstrate the reaction is relatively slow and rate constants are weakly pressure dependent at all temperatures, consistent with a third-body mediated association process. In addition, SiH₂+ H₂ reaction is approximately *ca.* 60-70% faster than SiD₂+D₂ reaction at higher total pressure.

5 Extrapolation by empirical procedures

Since SiD₂+D₂ study lies in the fall-off region at accessible pressures, a reliable method of extrapolation to infinite pressure must be employed. A number of methods have been suggested and used by various workers.

The earliest extrapolation procedure employed plots of k⁻¹ versus P⁻¹. This plot follows from the Hinshelwood-Lindemann model. Recently Oref and Rabinovitch[14] have suggested another empirical procedure which theoretically should yield more accurate infinite pressure rate constants since the precise nature of the extrapolation is determined by the actual data. They suggest a plot of k⁻¹ versus P^α where α lies between 0 and 1 and is optimised to give the best linear plot. Values of α on either side of the optimum value will give curved plots which would lead to an overestimate and underestimate of k[∞] resp. It is important to state that there is no absolute theoretical justification for either of the methods described above. They are simply empirical procedures which have been found to give reasonable linear plots. In the present work the latter method of extrapolation (where α= 0.5 and 1) has been tried and the results are compared.

When data are only available at pressures well into the fall off region it becomes clear that the choice of method of extrapolation becomes crucial, since different methods give different answers. In the current work it was extremely difficult to judge the quality of the fits because of data scatter, values of k[∞] (represented by (intercept)⁻¹) had a large uncertainty. Therefore a modified procedure was adopted here in which a number of points were selected from interpolated curves (drawn by hand). These interpolated fall-off curves were used to represent the data in order to obtain k[∞] with minimum error (see figure 7).

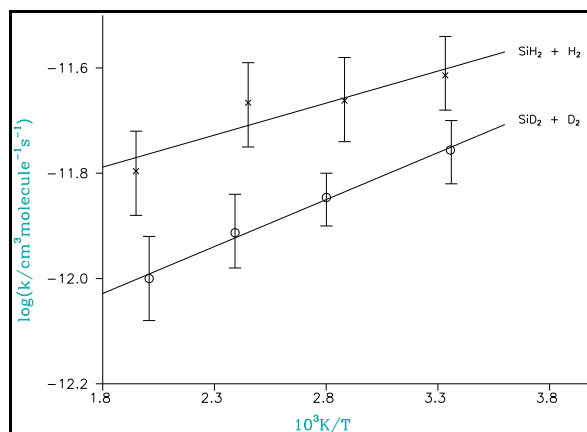
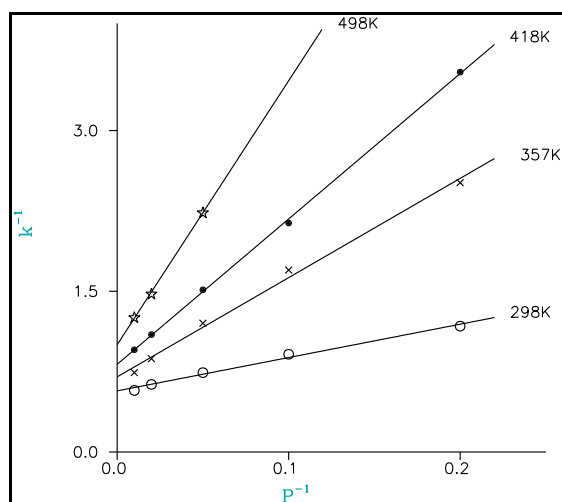
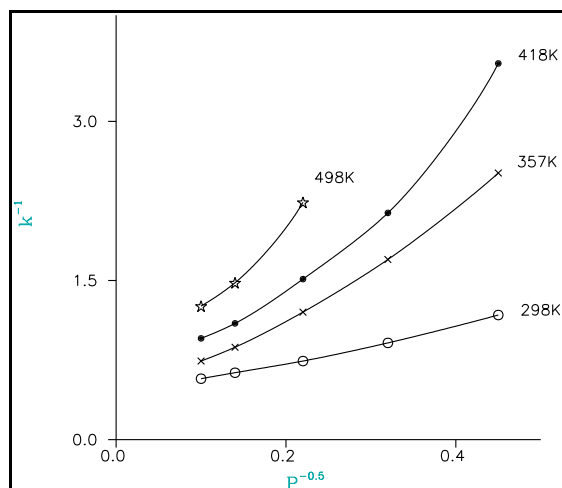


Fig.8. Arrhenius plots for x, SiH₂+H₂ [23]; O, SiD₂+D₂.

6 RRKM modelling of experiments

In order to try to fit the observed pressure dependence of the insertion of SiD₂ + D₂, RRKM calculations were carried out on the pressure dependence of the inverse silane, SiH₄ decomposition in the conventional manner.

$\langle \Delta E \rangle_{\text{down}}$ were based on the assumption of a fixed energy removed on each collision (stepladder model). However we did not include some other correction factors (eg F_{rot}) which could have some effect. For a small molecule like silane (highly excited), the anharmonicity effect was found to be important [16,17]. This correction factor influences the density of states of the reactant at an internal energy equal to the critical energy. The low pressure limiting rate constant is proportional to the anharmonicity factor, by increasing the value of this factor better agreement with the data was obtained [17-19]. It has been suggested that increasing the value of this factor has roughly the same effect as increasing the "looseness" of the transition state.

The fall-off predictions are very sensitive to some of the parameters and not very sensitive to others. The exact assignments of reactant frequencies, transition state frequencies, and reactant path degeneracy are not very important as long as these assignments reproduce the required high pressure A-factor. On the other hand, assignment of bath gas collision efficiencies and their temperature dependencies can be very important, particularly when the reaction is well into its pressure-dependent region and the bath gas molecules are weak colliders.

The effect of varying the energy level grain size (GRAIN) is rather unpredictable and its choice affects the position of the fall-off curves for both strong and weak collision situations. This parameter is used to define the energy gap in the quasi-quantised energy scale covering the energy range of interest. It is clear that the smaller its value, the more closely packed are the levels. Therefore in principle smaller grain sizes are best (although this increases the size of programme storage required and decreases the speed of calculations). However the calculation is also sensitive to the positioning of the critical energy, E_0 with the quantised energy levels. The best situation appears to be when E_0

We find that the plot is not absolutely linear. Consequently some error in the infinite pressure rate constants obtained using a least-squares line must be expected. If we consider the k^{-1} versus $P^{0.5}$ we find that such plots suffer from marked curvature making extrapolation difficult and leading to an underestimated of k^∞ . On the other hand the k^{-1} versus P^{-1} plots are much less curved. It must be noted, however, that scatter in the experimental data can make calculation of an optimum α difficult and may limit the applicability of this method.

The temperature dependence for the reaction may be expressed in Arrhenius form. The derived Arrhenius parameters are shown in table 5. Figure 8 shows a graph of the Arrhenius plot for both SiH₂+H₂ [15] and SiD₂+D₂ reactions. These data show a number of interesting features. First the reaction has a negative activation energies $E = -0.82 \pm 0.05$ kcal mol⁻¹. Secondly there is a significant difference between SiH₂+H₂ and SiD₂+D₂. The former reaction is ca. 60% faster than the latter.

lies in the center of a grain. The choice of minimum energy value, E_{\min} and grain size, determines this. In practice there were chosen to get closer to this condition. The energy range starts from just below the initial energy and goes up to 2-3 times its value. In the present calculation for silylene reaction with hydrogen this parameter was set to be 50 cm^{-1} . The vibration frequencies assigned to the SiD_4 complex were based on those from ab initio calculations of Gordon et al.[20]. The details of the model and parameters used are shown in tables 2, and 3.

Table 2. RRKM parameters for SiD_4 decomposition model, predicted by Gordon *et al.*[20]

	SiD_4	SiD_4^+
	1597(3)	1579(1)
	1558(1)	1551(1)
	701(2)	1488(1)
	681(3)	1163(1)
		721(1)
		681(1)
		528(1)
		498(1)
$I_i/\text{amu \AA}^2$	11.777	13.685
	11.777	11.558
	11.776	9.707
Path degeneracy	12	
Reaction coordinate	681	
$E_o/\text{kcal mol}^{-1}$	56.18 (298K)	
$\log(A/\text{s}^{-1})$	14.38 (298K)	
$Z_{LJ}/10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	4.354 (SF_6 , 298K)	

Table 3. Z_{LJ} for SiD_4 decomposition.

Temperature/K	$Z_{LJ}/10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
298	4.354
357	4.487
418	4.620
498	4.785

The A-factors used here are those obtained using the vibration wavenumbers for both the molecule and the Transition State (employing Smol programme) [15]. Since both SiH_4 and SiD_4 have the same electronic energies, the critical energies can be obtained from the standard formula ($E_o = E_{\text{el}} + \Delta z_{\text{pe}}$). Δz_{pe} is defined as the difference between the zero-point energies of the reactant and activated complex. The activation energies then can be calculated using the equation $E_a = E_o + RT + \langle E^\ddagger \rangle - \langle E \rangle$. The results of these calculations are shown in table 4.

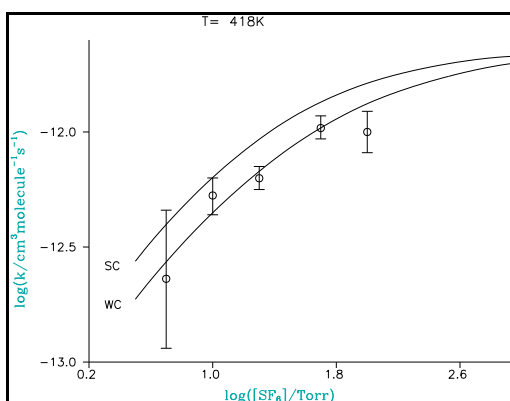
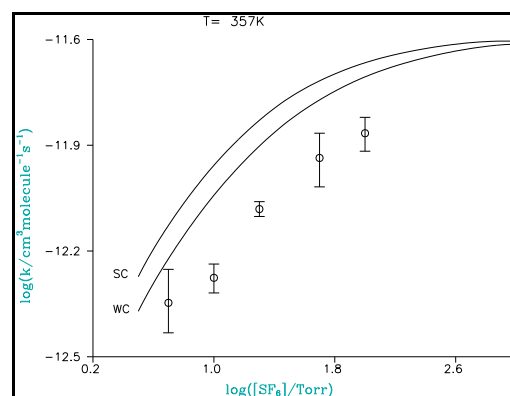
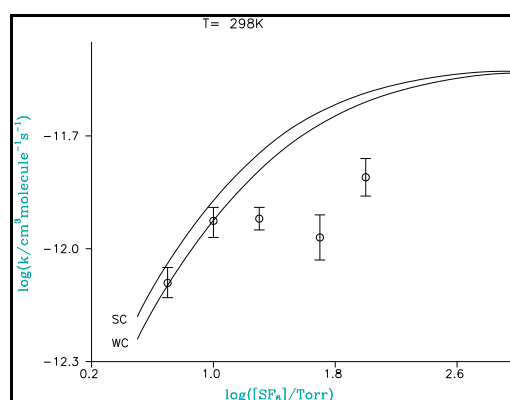
Table 4. Activation energies and A-factors for SiD_4 decomposition.

T/K	$\log(A/\text{s}^{-1})$	$E_a/\text{kcal mol}^{-1}$	$E_o/\text{kcal mol}^{-1}$
298	14.38	56.83	56.18
357	14.45	56.80	56.04
418	14.51	56.74	55.87
498	14.57	56.64	55.65

The calculations were carried out using both a strong and a weak collision model to generate fall-off curves at four different temperatures. A weak collision ($\langle \Delta E \rangle_{\text{down}} = 2.3$

kcal mol^{-1}) was fixed to fit the rate constants at all four temperatures and is reasonably consistent with collisional efficiencies found with similar systems[20]. However these calculations were carried out without including the F_{an} factor which was assumed to have a small effect.

The results are plotted in figure 9 with experimentally determined rate constants. The high pressure limit rate constants were derived from the isotope effect calculations combined with $\text{SiH}_2 + \text{D}_2$ rate data[15]. Reasonable agreement was obtained with the data when compared to that of the previous reaction, except for $T=357\text{K}$ where the theoretical fit and data were in disagreement. However there are probably other choices of parameters that would have produced equally good fits.



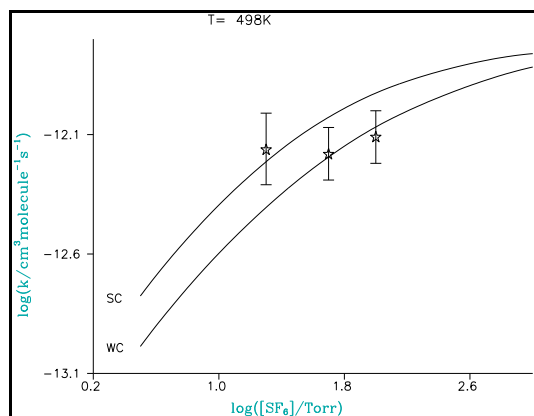


Fig.9. Pressure dependence of second-order rate constants for $\text{SiD}_2 + \text{D}_2$ at different temperatures in SF_6 buffer gas (solid lines are RRKM fits). sc, Strong collision; wc, Weak collision

7 Discussion

These studies proved to be more difficult than earlier ones for silylene with olefins[21]. This arose because the rate constants were smaller and a significant amount of hydrogen was required to observe a reaction. This meant that at low total pressures, reaction of silylene with precursor was always a substantial fraction of the total decay. The magnitude of the intercept of the second order plots were kept as small as possible. This was done by reducing the partial pressure of SiD_4 to the minimum consistent with signal to noise constraints.

This restricted the range of possible substrate pressures and temperatures over which reactions could be studied. At high partial pressures of hydrogen necessary to obtain reaction, SF_6 is present in insufficient quantity to ensure that it is the dominant bath gas collider. This causes curvature in the second order plots (at fixed total pressures). By using a polynomial procedure (quadratic), we are assuming that the slope at $[\text{D}_2/\text{Torr}] = 0$ will provide a reliable estimate of the first-order rate coefficients, k_{obs} , for the removal of SiD_2 in the presence of hydrogen. However this leads to higher uncertainties in this case compared to those of other studies (eg $\text{SiH}_2 + \text{C}_2\text{H}_4$)[21].

A high pressure limit rate comparison is shown in table 5 using different extrapolation procedures.

Table 5. High pressure limit rate comparison for the reaction of $\text{SiD}_2 + \text{D}_2$ using three different procedures.

T/K	$k^\infty/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
	RRKM	Empirical Procedure	Isotope Effect
298	2.24	1.75 ± 0.35	3.38
357	1.78	1.43 ± 0.29	2.54
418	1.58	1.22 ± 0.24	2.23
498	1.41	1.00 ± 0.20	1.92

A comparison is also made for the activation energies and the A-factors for silylene reaction with hydrogen and its isotopic analogues in table 6 (obtained from

extrapolation of experimental data to the high pressure limit using empirical procedure).

Table 6. Arrhenius parameters for $\text{SiH}_2 + \text{H}_2$ and isotopic variants

Reaction	$\log(A/\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$	Activation energy kJ mol^{-1}
$\text{SiH}_2 + \text{H}_2$	-12.01 ^a	-2.34
	-11.75 ^b	-1.84
$\text{SiD}_2 + \text{D}_2$	-12.35 ^a	-3.41
	-12.09 ^b	-3.52
$\text{SiH}_2 + \text{D}_2$	-12.07 ^c	-2.03
$\text{SiD}_2 + \text{H}_2$	-11.87 ^d	-2.54

^a. Obtained by extrapolation (empirical procedure) [15]

^b. Based on isotope effect calculations[15]

^c. $P_T = 10 \text{ Torr}$ [15], ^d. $P_T = 10 \text{ Torr}$ [3]

The following figures can be drawn from this table. Arrhenius parameters of $E_a = -0.48 \pm 0.33 \text{ kcal mol}^{-1}$ and A-factor = $0.80 \pm 0.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can be averaged. The activation energy for the reaction ($\text{SiH}_2 + \text{H}_2$) is approximately a factor of 1.5 smaller than that obtained from reaction ($\text{SiD}_2 + \text{D}_2$) by extrapolation to the high pressure limit.

A reasonable agreement was seen between theory and experiment for SiD_4 decomposition. However there are probably other choices of parameters that would have produced equally good fits. Parameters such as the average energy removal, $\langle \Delta E \rangle_{\text{down}}$, and the high pressure limit rate constant, k^∞ , can be adjusted to obtain a better fit (see table 5).

An example is shown in figure 10 at $T = 357\text{K}$, which shows the fall-off curve when $\langle \Delta E \rangle_{\text{down}} = 2.3 \text{ kcal mol}^{-1}$ and $k^\infty = 1.78 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

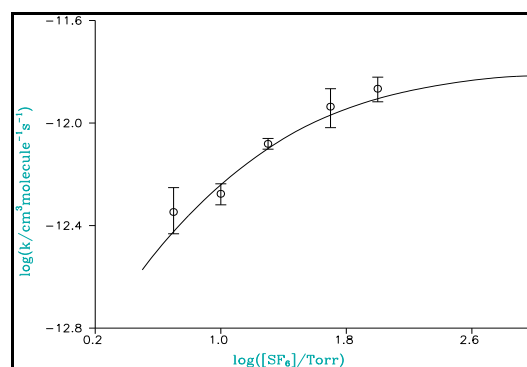


Fig. 10. Pressure dependence of second-order rate constants for $\text{SiD}_2 + \text{D}_2$ at $T = 357\text{K}$ (solid line is RRKM fit)

8 Summary and future work

Time-resolved study of SiD₂ generated by laser flash photolysis of (PhSiD₃) has been carried out to obtain rate constants for its bimolecular reactions with D₂. The reaction was studied over the pressure range 5-100 Torr (in SF₆ bath gas) at four temperatures in the range 298-498K. The reaction was found to be pressure dependent at all temperatures, consistent with a third-body mediated association process. The reactions were modelled using empirical and theoretical procedures to obtain the high pressure limit rate constants. The empirical procedure employed the Hinshelwood-Lindemann model. The data obtained using these extrapolations were fitted to the Arrhenius equation. RRKM modelling, based on the transition states (SiD₄) of Gordon *et al*, gave a reasonable fit to the experiments. Further work is required in the following areas; (i) the RRKM calculation described in this work can be improved by considering some other correction factors in addition to that of F_{an}. (ii) the pressure dependence of the pyrolysis of silane also needs to be reinvestigated over a wider pressure range in order to obtain an improved value for k[∞] for SiD₄ → SiD₂ + D₂. This would then improve the value for the heat of formation of silylene.

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