



## Isotope Effects in the Gas Phase Reaction of $\text{SiH}_2 + \text{D}_2$

Najem Al-Rubaiey<sup>1,\*</sup> and Robin Walsh<sup>2</sup>

<sup>1</sup>Petroleum Technology Department, University of Technology-Iraq, Baghdad, Iraq.

<sup>2</sup>Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK.

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#### \*Corresponding Author:

Najem Al-Rubaiey

[100108@uotechnology.edu.iq](mailto:100108@uotechnology.edu.iq)

### Abstract

Time-resolved studies of silylene,  $\text{SiH}_2$ , generated by laser flash photolysis of phenylsilane,  $\text{PhSiH}_3$  were employed to obtain rate constants for its bimolecular reaction with deuterated hydrogen,  $\text{D}_2$ . The monitoring laser was tuned to  $17259.50 \text{ cm}^{-1}$ , corresponding to a known strong vibration-rotation transition,  $A (^1B_1) \leftarrow X (^1A_1)$ , in the  $\text{SiH}_2$  absorption band. The  $\text{SiH}_2$  concentration-time profiles were recorded for mixtures of phenylsilane and various partial pressures of  $\text{D}_2$  at temperatures in the range 300-553K. At three different temperatures, data were recorded in a series of runs for second order plots at 10 Torr total pressure. In addition to those experiments, another set of runs was carried out at each temperature, in which the total pressure ( $\text{SF}_6$ ) was varied in the range 1 to 100 Torr in order to test the pressure dependence of the second order rate constants. In these runs, second order kinetic behaviour was observed. The rate constants were found to be pressure independent. The following Arrhenius equation was obtained:

$$\log(k/\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}) = \frac{0.48 \pm 0.04 \text{ kcal mol}^{-1}}{RT \ln 10} - 12.07 \pm 0.03$$

The isotopic ratios obtained from experimental data for  $\text{SiH}_2/\text{SiD}_2 + \text{D}_2/\text{H}_2$  were compared with those of Transition State Theory and found to be in reasonable agreement when the Transition State structure of Gordon et al was used.

## 1. Introduction

The insertion reaction of silylene with molecular hydrogen is one of the key reactions with great mechanistic importance in organosilicon chemistry. This reaction is of particular interest because of the central role played by SiH<sub>2</sub> in the mechanism of silane pyrolysis [1-4] and in the modern method of vapour decomposition of thin films of amorphous silicon [5]. Available kinetic data on this reaction came from studies of the thermal decomposition of silane and disilane [6,7] in the presence of hydrogen besides the more recent time resolved spectroscopic measurements [8-11].

This study is an essential one in both experimental and theoretical silicon chemistry. This reaction was originally investigated by competitive rate measurements in the 1960s by pyrolysis of silane or disilane in the presence of hydrogen. The decomposition of silane is the reverse of the SiH<sub>2</sub>+H<sub>2</sub> reaction. Subsequent to the original pyrolysis study a significant barrier for this back reaction was claimed in other pyrolysis studies [6,7].

Inoue and Suzuki [8] (IS) published the first directly measured rate constant for the reaction of SiH<sub>2</sub> with H<sub>2</sub> using a laser-induced fluorescence technique (LIF) to detect the transient concentration of SiH<sub>2</sub> in the presence of H<sub>2</sub>. A rate constant of  $1.0 \pm 0.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was reported at a total pressure of 1.8 Torr. Subsequently the rate constant for the reaction of SiH<sub>2</sub> with D<sub>2</sub> was measured by Jasinski [9], using the laser resonance absorption flash kinetic spectroscopy (LRAFKS) method. A second order rate constant at a total pressure of 2.3 Torr was found to be  $2.60 \pm 0.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is significantly higher than the value obtained by IS for SiH<sub>2</sub> + H<sub>2</sub>.

Jasinski and Chu [12] subsequently investigated the reaction of SiH<sub>2</sub> with H<sub>2</sub> at total pressures of 1 to 100 Torr. The authors fitted their data to the fall-off curve using RRKM calculations in order to obtain the high pressure limiting value. The resulting number,  $k_{\infty} = 3.14 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is close to that for the SiH<sub>2</sub>+D<sub>2</sub> experiment. Employing the same technique in our labs, Baggott et al. [13] measured the rate constants of the reaction of SiH<sub>2</sub> in the presence of D<sub>2</sub> over a temperature range of 268-330K at total pressure of 5 Torr. The reaction appeared to be temperature independent with  $k = 1.88 \pm 0.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range studied. An upper limit to the magnitude of the activation energy of 1.57 kcal mol<sup>-1</sup> was in reasonable agreement with Jasinski's estimate of 1.0 kcal mol<sup>-1</sup>. The values obtained by these direct measurements are approximately 2-4 orders of magnitude faster than that obtained using competitive methods. A very recent study carried out in our labs [11] on SiH<sub>2</sub>/SiD<sub>2</sub>+H<sub>2</sub>/D<sub>2</sub> showed that the reaction was weakly pressure dependent at all temperatures (298-498K). In addition, the SiH<sub>2</sub>+ H<sub>2</sub> reaction is approximately ca. 60% faster than the SiD<sub>2</sub>+D<sub>2</sub> reaction.

Recent ab initio calculations [14] on the potential energy surface for this reaction yielded an activation energy of 1.7 kcal mol<sup>-1</sup> which is in close agreement with both Baggott et al's [13] and Jasinski's [12] estimate.

Previous studies had only carried out a limited investigation into the temperature dependence of this reaction, therefore this study was undertaken in order to obtain a more accurate value for the activation energy [15-20].

## 2. Methods and Materials

Several attempts have been made in the past years to record the spectrum of SiH<sub>2</sub>. Seven bands were found in the range 650-480nm, all of them firmly established to occur from a lower (<sup>1</sup>A<sub>1</sub>) ground state to an excited (<sup>1</sup>B<sub>1</sub>) state with

the strongest bands at 610.0, 579.6 and 552.6 nm[21-23]. A band range of 550-650nm ( ${}^1B_1(0,n',0)\rightarrow({}^1A_1)(0,0,0)$  transition was also recorded for the excitation spectrum of  $\text{SiH}_2$ [24]. The further work of Jasinski *et al.*[25] generated absorption around the spectral region from 579.98 nm ( $17242\text{ cm}^{-1}$ ) to 576.3 nm ( $17352\text{ cm}^{-1}$ ). The  $100\text{ cm}^{-1}$  range is located in the  $(0,2,0)\leftarrow(0,0,0)$  vibronic band and around a high line-density region. An estimated 100 single rotational lines were observed in which 50% of them could be assigned to the declared  $\text{SiH}_2$  transition based on original studies. The typical single rotational line of ( ${}^RQ_{0,J}$ ) at 579.39 nm ( $17259.5\text{ cm}^{-1}$ ) was used in this work to monitor  $\text{SiH}_2$  removal in the presence of  $\text{D}_2$ .

The apparatus, equipment and chemicals for this study have been described in detail elsewhere<sup>[26-29]</sup>. The apparatus is shown in Figure 1.

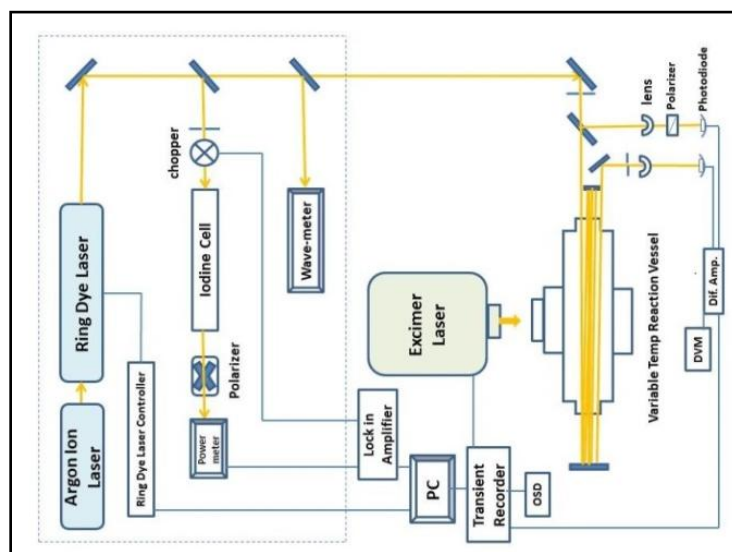


Figure 1. Schematic diagram of the experimental apparatus.

Good initial concentrations of  $\text{SiH}_2$  have been obtained from the 193 nm photolysis of  $\text{PhSiH}_3$ .  $\text{PhSiH}_3$  has an extinction coefficient of  $10^5\text{ M}^{-1}\text{ cm}^{-1}$ . Phenylsilane absorbs strongly below 220nm and has a weak structured absorption band in the range 220-280 nm. The high extinction coefficient for  $\text{SiH}_2$  absorption for the selected rotational line together with the multipass arrangement of the probe dye laser beam provided a good sensitivity for species detection and a high signal/noise ratio. In this set of experiments, one shot was enough to allow analysis of silylene concentration profiles. However it is preferable to select an accumulation of typically 5-15 shots average at typically 80 mJ per pulse to improve further the precision of the data. The use of low concentrations of precursor was required to minimise reaction of  $\text{SiH}_2$  with  $\text{PhSiH}_3$ .

Gas mixtures for photolysis were made up containing between 2 and 15 mTorr of  $\text{PhSiH}_3$ , 0-1000 mTorr  $\text{D}_2$  together with inert diluent ( $\text{SF}_6$ ) at total pressures between 1 and 100 Torr.

Preliminary experiments established that, for a given reaction mixture composition, decay constants,  $k_{\text{obs}}$ , were not dependent on excimer laser energy (*ca.* 50-200 mJ/pulse) or number of photolysis shots. Since static gas mixtures were used, tests with up to 30 shots were carried out. The constancy of  $k_{\text{obs}}$  (10 shots averages) showed no effective depletion of reactants. The sensitivity of detection for  $\text{SiH}_2$  was very high but decreased with increasing temperature.

Therefore increasing pressures of  $\text{PhSiH}_3$  precursor were required at higher temperatures. At any given temperature  $\text{PhSiH}_3$  pressures were kept fixed, in order to provide a fixed reference for rate constant measurement.

### 3. Results and Discussions

#### 3.1 Pressure and temperature dependence study

A series of experiments was carried out at each of three temperatures in the range 300-553K as follows. At 10 Torr total pressure, between five and ten runs (of 5 to 15 laser shots each) at different hydrogen partial pressures were carried out at each temperature. A selection of second order plots are shown in figure 2.

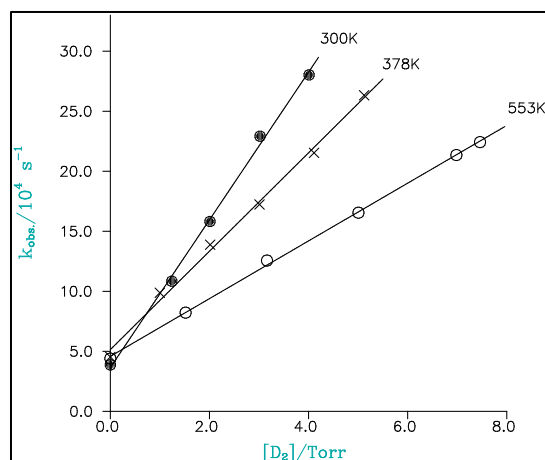


Figure 2. Examples of second-order plots for the reaction of  $\text{SiH}_2 + \text{D}_2$  at different temperatures and  $P_T = 10$  Torr.

These plots show good linearity, and the rate constants obtained by least-mean-squares fitting procedure are shown in table 1.

Table 1. Absolute rate constants for the reaction of  $\text{SiH}_2 + \text{D}_2$ .

$P_T/\text{Torr}$	$k/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
	300K	373K	553K
1	$1.54 \pm 0.30$	$1.10 \pm 0.22$	$1.00 \pm 0.20$
3	$1.83 \pm 0.37$	$1.57 \pm 0.31$	$1.43 \pm 0.29$
10	$1.91 \pm 0.11$	$1.65 \pm 0.12$	$1.33 \pm 0.10$
30	$1.79 \pm 0.27$	$1.57 \pm 0.24$	$1.50 \pm 0.23$
100	$1.84 \pm 0.28$	$1.78 \pm 0.21$	$1.30 \pm 0.20$

The data were displayed in an Arrhenius plot in figure 3 together with previous kinetic studies on the same reaction.

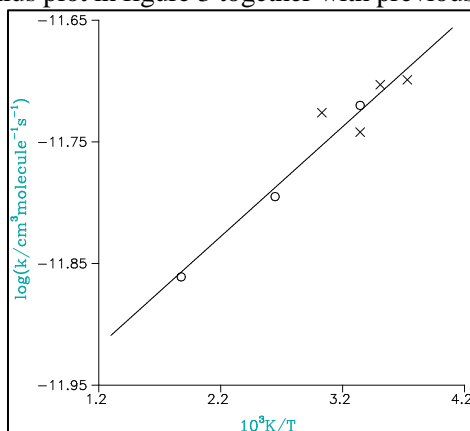


Figure 3. Arrhenius plot for  $\text{SiH}_2 + \text{D}_2$  reaction, (o, this work, x, Ref. [13]).

The data can be represented by the following equation;

$$\log(k/cm^3molec^{-1}s^{-1}) = -12.07 \pm 0.03 + \frac{0.48 \pm 0.04 \text{ kcal mol}^{-1}}{R T \ln 10}$$

The much lesser pressure dependence of this reaction compare to  $\text{SiH}_2 + \text{H}_2$  arises from the different behaviour of the vibrationally excited molecule,  $\text{SiH}_2\text{D}_2^*$ , compared with  $\text{SiH}_4^*$ . Whereas the latter can only either decay back to reactants or be stabilized by a third body,  $\text{SiH}_2\text{D}_2^*$  can additionally redissociate to  $\text{SiHD} + \text{HD}$  or  $\text{SiD}_2 + \text{H}_2$  as shown in figure 4. As can be seen, the redissociation of  $\text{SiH}_2\text{D}_2^*$  to  $\text{SiH}_2 + \text{D}_2$  only occurs once in 6 times on a statistical basis. This scrambling mechanism explains the lower pressure dependence for  $\text{SiH}_2 + \text{D}_2$ .

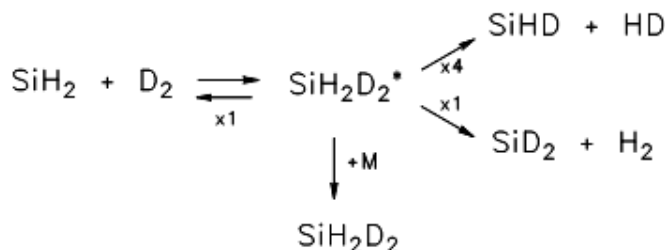


Figure 4. The scrambling mechanism suggested for the reaction of  $\text{SiH}_2 + \text{D}_2$ .

### 3.2 Comparison and Reactivity

The absolute rate coefficients we have obtained are compared with those of other studies in table 2.

Table 2. Absolute rate comparison for the reaction of silylene with some substrates at 298K and  $P^\infty$ .

Silylene	$k/10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
	$\text{H}_2$	$\text{D}_2$
$\text{SiH}_2$	0.24 <sup>[10]</sup>	0.19
$\text{SiD}_2$	0.38 <sup>[30]</sup>	0.17 <sup>[11]</sup>

Some important implications can be drawn from the numbers in this table. For example, it's quite clear that for the same  $\text{SiD}_2$  substrate the rate constants are very close to the  $\text{SiH}_2$  rate constants at the high pressure limit.

In table 3 our results are compared with other available direct kinetic data for the reactions of  $\text{SiH}_2 + \text{D}_2$  and  $\text{SiH}_2 + \text{H}_2$  at room temperature.

Table 3 Absolute rate comparison for the reaction of  $\text{SiH}_2 + \text{H}_2/\text{D}_2$  at 298K and  $P^\infty$ .

Reaction	$k/10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$			
	BFKLWW	JC	This work	IS
$\text{SiH}_2 + \text{D}_2$	0.188 <sup>[13]</sup>	0.26 <sup>[9]</sup>	0.19	-
$\text{SiH}_2 + \text{H}_2$	-	0.32 <sup>[12]</sup>	0.24 <sup>[10]</sup>	0.01 <sup>[8]</sup>

There is good agreement with both Jasinski *et al.*[9] and Baggott *et al.*[13]. However Baggott *et al.* also reported a zero activation energy in the temperature range 268-330K. This apparently disagrees with the current investigation in which a negative activation energy of  $-0.48 \pm 0.04 \text{ kcal mol}^{-1}$  has been observed over an extended temperature range of 300 to 553K. Nevertheless the error bars quoted in Baggott's Arrhenius plot would not rule

out a similar activation energy to our reported value. This negative activation energy together with *ab initio* calculations of the potential energy surface for  $\text{SiH}_2 + \text{H}_2$  indicates that the transition state (TS1) leading from reactants forms a weakly bound complex. The transition state (TS2) leading from complex to products however is both tighter and lower in energy when compared to TS1.

In addition, Mason *et al.*[30] carried out the only available kinetic data on  $\text{SiD}_2 + \text{H}_2$ . He observed a negative activation energy of  $-0.6 \text{ kcal mol}^{-1}$  in tolerable agreement with our value for  $\text{SiH}_2 + \text{D}_2$ .

### 3.3 Isotope effects

In reactions which may occur either by simple abstraction or a more complicated mechanism, such as complex formation followed by dissociation, isotopic substitution may help discriminate between pathways. The replacement of an atom in a reactant molecule may cause a modification to the rate of the reaction.

There are several contributions to this effect. In order to describe these we start from the transition state theory (TST) expression for an isotope effect:

$$\frac{(k_{\infty})_H}{(k_{\infty})_D} = \frac{(q^+)_H (q)_D}{(q^+)_D (q)_H} \text{Exp}\left(-\frac{\Delta\epsilon_H - \Delta\epsilon_D}{kT}\right)$$

The partition functions  $q_H$  and  $q_D$  are related to the two reactants,  $q_H^+$ ,  $q_D^+$  are the partition functions at the transition state, and  $\Delta\epsilon_H$ ,  $\Delta\epsilon_D$  are the activation barrier for the reaction of  $\text{SiH}_2(\text{SiD}_2)$  in question.

Isotope effects arise from,

- i) differences in partition functions.
- ii) differences in zero point energies.

The zero point energy (ZPE) is given by the following expression;

$$\Delta(\text{ZPE}) = \frac{1}{2} (\sum h\nu^+ - \sum h\nu_{\text{rea}})$$

$$\text{Isotope effect} = \Delta(\text{ZPE})_D - \Delta(\text{ZPE})_H$$

Where  $h$  = Planck's constant and  $\nu$  = vibration frequency.

The isotope effect arises because of differences in vibrational frequencies due to the substitution of an H atom by a D atom. The change in mass affects the translation and rotational partition functions ( $q_{\text{tran}}$  and  $q_{\text{rot}}$ ), whereas the change in vibration frequencies only affects the vibrational partition function ( $q_{\text{vib}}$ ).

Most of the studies of isotope effects in bimolecular reactions have focused on H/D substitution. Walsh[31] estimated the isotope effect for the reaction of  $\text{SiH}_2/\text{SiD}_2$  with  $\text{H}_2/\text{D}_2$  using the TST equation at room temperature. The calculation of partition functions based on molecular information (bond lengths, bond angles, vibrational frequencies, *etc.*) is straightforward using standard techniques. This information is readily available for  $\text{SiH}_2 + \text{H}_2$  and its isotopic variants and so reaction partition are easily calculated. For the transition state a structure has to be assumed before the partition functions can be calculated. The geometries and vibration wavenumbers of both Gordon *et al.*[14] (GGBF) and Carr *et al.*[26] (RJC) have been employed to calculate the isotope effects. The transition states put forward by RJC and GGBF are illustrated in figure 5.

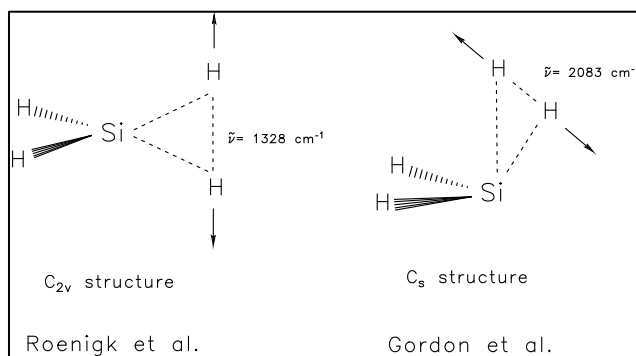


Figure 5. Silane Transition State and bending vibration.

RJC assumed that the H-Si-H angle in the TS was similar to that of silylene. The bond length-bond order correlation technique was partly employed to assign the frequencies of the SiH<sub>4</sub> transition state. Walsh [25] has used the same technique to assign the frequencies of SiH<sub>2</sub>D<sub>2</sub> transition state. This method is rather more arbitrary in estimating the frequencies compared to the *ab initio* calculations employed by GGBF [14<sup>l</sup> to obtain the frequencies of SiH<sub>4</sub><sup>+</sup>, SiH<sub>2</sub>D<sub>2</sub><sup>+</sup> (two alternatives), and SiD<sub>4</sub><sup>+</sup>.

Thus for the reaction pair;



TST gives the expression:

$$\frac{(k_\infty)_1}{(k_\infty)_2} = \frac{(q^+)_{\text{SiH}_4} (q)_{\text{D}_2}}{(q^+)_{\text{SiH}_2\text{D}_2} (q)_{\text{H}_2}} \text{Exp}\left(-\frac{\Delta E_{\text{H}_2} - \Delta E_{\text{D}_2}}{kT}\right)$$

The terms in the above expression were evaluated at 298K. The solution of the TST equation can be divided into three parts:

First the estimation of  $q_{\text{D}_2}/q_{\text{H}_2}$ :

$$\text{The translation partition function} = q_{\text{trans.}} = \left(\frac{2\pi m k T}{h^2}\right)^{3/2}$$

$$\text{The rotation partition function} = q_{\text{rotat.}} = \left(\frac{8\pi I k T}{\sigma h^2}\right)$$

$$q_{\text{rotat.}} = \left(\frac{8\pi I k T}{\sigma h^2}\right)$$

$$\text{The vibration partition function} = q_{\text{vib.}} = \left(\frac{1}{1 - e^{-h\nu/kT}}\right)$$

Where  $m$ = mass of molecule.

$I$ =moment of inertia for linear molecule.

$\nu$ =normal mode vibrational frequency.

$k$ =Boltzmann constant.

$T$ =absolute temperature.

$h$ =Planck's constant.

$\sigma$ =symmetry number.

These values were calculated and listed in table 4.

Table 4. shows the values of partition functions for different motions.

Motion	$q_{\text{D}_2}/q_{\text{H}_2}$	
Translation	$(m_{\text{D}_2}/m_{\text{H}_2})^{3/2}$	= 2 <sup>3/2</sup>
Rotation	$\mu_{\text{D}_2}/\mu_{\text{H}_2}$	=1/(1/2)
Vibration	$\frac{[(1 - e^{-u})^{-1}]_{\text{D}_2}}{[(1 - e^{-u})^{-1}]_{\text{H}_2}}$	=1
Total		=5.66

where  $u=h\nu/kT$

Next  $q_{SiH_4^+}/q_{SiH_2D_2^+}$  has to be evaluated. The masses of the activated complexes are:  $(SiH_4^+)=32$  and for  $(SiH_2D_2^+)=34$  and thus the translational contribution to the partition function is:

$$\left(\frac{q^+SiH_4}{q^+SiH_2D_2}\right)_{tran.} = \left(\frac{32}{34}\right)^{3/2} = 0.913$$

For this example, the structure of GGBF[14] was chosen to calculate the moments of inertia of the activated complex. A computer program written by Professor Ian Mills from Reading University was used to evaluate  $I_A I_B I_C$  for both activated complexes. The rotational partition function ratio for the activate complexes is:

$$\left(\frac{q^+SiH_4}{q^+SiH_2D_2}\right)_{rot.} = \left(\frac{(I_A I_B I_C)H}{(I_A I_B I_C)D}\right)^{1/2} = 0.913$$

$$\left(\frac{q^+SiH_4}{q^+SiH_2D_2}\right)_{rot.} = \left(\frac{7.05 \times 6.07 \times 4.94}{10.66 \times 10.32 \times 5.58}\right)^{1/2} = 0.587$$

The vibrational partition functions corresponding to the low vibrational frequencies of the activated complex chosen to do the calculations are presented in table 5 as follows:

Table 5. The vibrational partition functions corresponding to the low vibrational frequencies of the activated complex

$\nu/cm^{-1}$	$SiH_4^+$ $(1-e^{-h\nu/kT})^{-1}$	$\nu/cm^{-1}$	$SiH_2D_2^+$ $(1-e^{-h\nu/kT})^{-1}$
691	1.037	615	1.054
739	1.029	632	1.050
945	1.011	798	1.022
	935		1.011

This leads to:

$$\left(\frac{q^+SiH_4}{q^+SiH_2D_2}\right)_{vib.} = \left(\frac{1.073 \times 1.029 \times 1.011}{1.054 \times 2.050 \times 1.022 \times 1.011}\right) = 0.947$$

Higher frequencies make no contribution and so are neglected.

Thus, the complete partition function ratio for the activated complex is;

$$\left(\frac{q^+SiH_4}{q^+SiH_2D_2}\right) = 0.931 \times 0.587 \times 0.947 = 0.507$$

In order to calculate the zero point energy differences, the vibrational frequencies of both the activated complex and the reactants are needed. The vibrational frequencies of GGBF [14] are listed in table 6 for  $SiH_4^+$ ,  $SiH_2D_2^+$ ,  $SiD_2H_2^+$ , and  $SiD_4^+$ .

Table 6 Vibrational wavenumbers for  $SiH_4$ ,  $SiH_2D_2$ ,  $SiD_2H_2$  and  $SiD_4$  decomposition predicted by Gordon *et al.*[14] to calculate the isotope effect.

<u>Vibrational Wavenumbers</u>			
$SiH_4^+$	$SiH_2D_2^+$	$SiD_2H_2^+$	$SiD_4^+$
2182	2182	2083	1579
2164	2164	1618	1551
2083	1492	1550	1488
1616	1165	1544	1163
1011	935	965	721
945	798	689	687
739	632	632	528
691	615	571	498

The zero point energy differences is;

$$\Delta\epsilon_o(H_2) = 1/2 \left\{ \sum (h\nu)_{SiH_4} - \sum (h\nu)_{H_2} \right\}$$

$$\Delta\epsilon_o(H_2) = 1/2 (11431 - 4401) = 3515 \text{ cm}^{-1}$$



$$\Delta\varepsilon_o(D_2) = 1/2 (9983 - 3116) = 3433.5 \text{ cm}^{-1}$$

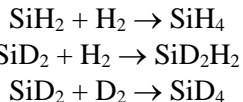
$$\Delta\varepsilon_o = \Delta\varepsilon_o(H_2) - \Delta\varepsilon_o(D_2) = 81.5 \text{ cm}^{-1}$$

$$e^{-\frac{\Delta E}{kT}} = e^{-1.435 \frac{w/cm^{-1}}{T/K}} = 0.675$$

Finally, the combination of all these terms results the value of  $(k_\infty)_1/(k_\infty)_2$ ;

$$\frac{(k_\infty)_1}{(k_\infty)_2} = 5.66 \times 0.507 \times 0.675 = 1.94$$

The same procedure was used to calculate isotope effects involving the following reactions:



The resulting partition function contributions are shown in table 7 below.

Table 7. shows the resulting partition function using different system.

<b>SiH<sub>2</sub> + H<sub>2</sub> → SiH<sub>4</sub><sup>+</sup> ....(1)</b>	<b>GGBF</b>	<b>RJC</b>
<b>SiH<sub>2</sub> + D<sub>2</sub> → SiH<sub>2</sub>D<sub>2</sub><sup>+</sup> ....(2)</b>		
$q_{D_2}/q_{H_2}$	5.66	5.66
$q_{SiH_4^+}/q_{SiH_2D_2^+}$	0.507	0.487
$EXP((\Delta E_{H_2} - \Delta E_{D_2})/kT)$	0.675	3.70
$(k_\infty)_1/(k_\infty)_2$	1.94	10.20
<b>SiH<sub>2</sub> + H<sub>2</sub> → SiH<sub>4</sub><sup>+</sup> .....(1)</b>	<b>GGBF</b>	<b>RJC</b>
<b>SiD<sub>2</sub> + H<sub>2</sub> → SiH<sub>2</sub>D<sub>2</sub><sup>+</sup> .....(2)</b>		
$q_{SiD_2}/q_{SiH_2}$	3.04	3.04
$q_{SiH_4^+}/q_{SiH_2D_2^+}$	0.478	0.437
$EXP((\Delta E_{H_2} - \Delta E_{D_2})/kT)$	0.352	0.336
$(k_\infty)_1/(k_\infty)_2$	0.511	0.447
<b>SiH<sub>2</sub> + H<sub>2</sub> → SiH<sub>4</sub><sup>+</sup> → SiH<sub>4</sub> .....(1)</b>		<b>GGBF</b>
<b>SiD<sub>2</sub> + D<sub>2</sub> → SiD<sub>4</sub><sup>+</sup> → SiD<sub>4</sub> .....(2)</b>		
$q_{D_2}/q_{H_2}$		5.660
$q_{SiD_2}/q_{SiH_2}$		3.040
$q_{SiH_4^+}/q_{SiD_4^+}$		0.263
$EXP((\Delta E_{H_2} - \Delta E_{D_2})/kT)$		0.240
$(k_\infty)_1/(k_\infty)_2$		1.090
<b>SiH<sub>2</sub> + H<sub>2</sub> → SiH<sub>4</sub><sup>+</sup> .....(1)</b>		<b>RJC</b>
<b>SiH<sub>2</sub> + HD → SiH<sub>3</sub>D<sup>+</sup> .....(2)</b>		
$q_{HD}/q_{H_2}$		2.45
$q_{SiH_4^+}/q_{SiH_3D^+}$		0.688
$EXP((\Delta E_{H_2} - \Delta E_{HD})/kT)$		1.29
$(k_\infty)_1/(k_\infty)_2$		2.17

Four different rate constants ratio measurements and room temperature are shown in table 8.

Table 8 Comparison of isotope ratios for silylene reaction with hydrogen at room temperature.

<b>Isotope Ratio</b>	<b>Theory</b>	<b>Experiment</b>
$k(\text{SiH}_2 + \text{H}_2)$	10.20 <sup>a</sup>	1.27 ± 0.26
$k(\text{SiH}_2 + \text{D}_2)$	1.94 <sup>b</sup>	1.52 <sup>c</sup>
$k(\text{SiH}_2 + \text{H}_2)$	0.45 <sup>a</sup>	0.64 ± 0.13
$k(\text{SiD}_2 + \text{H}_2)$	0.51 <sup>b</sup>	
$k(\text{SiH}_2 + \text{H}_2)$	1.09 <sup>b</sup>	1.39 ± 0.39
$k(\text{SiD}_2 + \text{D}_2)$		
$k(\text{SiH}_2 + \text{D}_2)$	0.04 <sup>a</sup>	0.50 ± 0.10
$k(\text{SiD}_2 + \text{H}_2)$	0.26 <sup>b</sup>	

<sup>a</sup>. RJC TS, <sup>b</sup>. GGBF's TS and <sup>c</sup>. JC's experimental values

The comparison between the theory and experiment is clearly dependent on the transition state assumption. GGBF's TS[14<sup>1</sup>] structure gave results in reasonable agreement with our experimental values. A surprisingly strong isotope effect in the case of SiH<sub>2</sub> with H<sub>2</sub> and D<sub>2</sub> was predicted using RJC's structure[31<sup>1</sup>]. This is in disagreement with our experimental value as shown in table 8. The term  $\Delta E_0(\text{H}_2) - \Delta E_0(\text{D}_2)$  (*ie.* the difference between the zero-point energies) is the predominant factor behind the disagreement between GGBF's isotopic ratio and RJC's. Examination of both transition states shows that the significant change in frequencies on going from reactant to transition state will be the H<sub>a</sub>-H<sub>b</sub> stretch mode (see figure 5). This will influence the zero-point energy term which has been found to be significantly different between the two transition states.

#### 4. Conclusion

SiH<sub>2</sub>, generated *via* the laser flash photolysis of phenylsilane, PhSiH<sub>3</sub>, has been detected *via* a rotational transition in its A (<sup>1</sup>B<sub>1</sub>) ← X (<sup>1</sup>A<sub>1</sub>) absorption band. Rate constants were obtained over a wide range of temperature for the reactions of SiH<sub>2</sub> with D<sub>2</sub> in the range 1-100 Torr in SF<sub>6</sub> and found to be pressure independent. The following Arrhenius equation was obtained.

$$\log(k/\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}) = -12.07 \pm 0.03 + \frac{0.48 \pm 0.04 \text{ kcal mol}^{-1}}{R T \ln 10}$$

The isotopic ratios obtained from experimental data for SiH<sub>2</sub>/SiD<sub>2</sub> + D<sub>2</sub>/H<sub>2</sub> were compared with those of TST and found to be in reasonable agreement when the TS structure of Gordon *et al* was applied but in disagreement with that of Carr *et al*.

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