Time-resolved gas-phase kinetic studies of the reactions of silylene with disilane and trisilane [1]

Rosa Becerra [a], H. Monty Frey [b], Ben P. Mason [b], Robin Walsh [b,*]

[a] *Instituto de Quimica-Fisica "Rocasolano", C.S.I.C., C / Serrano 119, 28006 Madrid, Spain*
[b] *Department of Chemistry, University of Reading, Whiteknights, PO Box 224, Reading RG6 6AD, UK*

Abstract

Absolute rate constants for the reactions of SiH_2 with Si_2H_6 and Si_3H_8 have been determined over the temperature range 295–595 K by means of laser flash photolysis. The 193 nm UV photolyses of di- and trisilane were themselves used as the sources of SiH_2. Rate constants were independent of total pressure (1–30 Torr) and inert buffer gas (C_3H_8 or SF_6). Arrhenius plots of the rate constants were slightly curved but gave the following average parameters: Si_2H_6, $\log(A/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.51 \pm 0.04$, $E_a = -1.9 \pm 0.3$ kJ mol^{-1}; Si_3H_8, $\log(A/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.43 \pm 0.06$, $E_a = -2.0 \pm 0.4$ kJ mol^{-1}. These values show both reactions to be rapid, collisional association processes. The results are consistent with Si–H bond insertion processes led by the electrophilic interaction between the bonding electron pair and the SiH_2 empty p orbital.

Keywords: Silylene; Disilane; Trisilane; Flash photolysis; Kinetics; Mechanism

1. Introduction

The reactions of silylene, SiH_2, are of interest both because of their involvement in the breakdown mechanisms of silanes leading to solid silicon and amorphous silicon hydrides (chemical vapour deposition) and also because they serve as a model for gas-phase acid/base chemistry [1,2]. We recently carried out a comprehensive study of the gas-phase kinetics of the prototype Si–H insertion reaction of SiH_2 with monosilane, SiH_4 [3]. This showed that the reaction proceeds at close to the collision rate, on a potential energy surface with no activation barrier, but with the intermediacy of two possible weakly bound complexes preceding the formation of disilane, Si_2H_6. The reaction showed the characteristic pressure dependence of a third-body assisted association process. We now turn our attention to the reactions of SiH_2 with Si_2H_6 and Si_3H_8, reactions which lead to the formation of the higher hydrides Si_3H_8 and Si_4H_{10} in the pyrolysis of SiH_4 [4,5].

Room temperature studies of the reaction of SiH_2 + Si_2H_6 show it to be a fast reaction. Inoue and Suzuki [6] obtained the first absolute value for the rate constant of 5.7×10^{-10} cm^3 molecule^{-1} s^{-1} in 1 Torr of helium using laser-induced fluorescence (LIF) to detect SiH_2. Jasinski and Chu [7], using laser absorption to monitor SiH_2, obtained a value of 1.5×10^{-10} cm^3 molecule^{-1} s^{-1} at 1 Torr (He), but additionally found the reaction to be pressure dependent. Measurements in our own laboratory [8], using the same method, gave a value of 4.6×10^{-10} cm^3 molecule^{-1} s^{-1} at 5 Torr (Ar). Another study by Dietrich et al. [9], using IRMPD to generate SiH_2, gave a value of 2.7×10^{-10} cm^3 molecule^{-1} s^{-1}, but this measurement was made under solid deposition conditions and it is not clear that this corresponds to room temperature.

There are no previous absolute rate constant values for the reaction SiH_2 + Si_3H_8. A summary of the findings of this work has appeared in recent reviews [1,2].

2. Experimental

The apparatus, procedures, data acquisition and analysis method have been described in general [10] and in

their application to silylene kinetic studies in particular [8,11,12]. Only essential and brief details are therefore included here.

SiH_2 was produced by the 193 nm flash photolysis of phenylsilane ($PhSiH_3$), disilane or trisilane using an Oxford Lasers KX2 ArF exciplex laser. SiH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with rhodamine 6G. Experiments were carried out in a variable temperature stainless steel reaction vessel with demountable windows [13]. The monitoring laser beam was multipassed between 32 and 48 times through the reaction zone to give an effective path length of up to 1.8 m. The laser wavelength was set by reference to a known coincident transition in the visible spectrum of I_2 vapour and was checked at frequent intervals during the experiments.

The monitoring laser was tuned to 17259.50 cm^{-1} corresponding to the strong $^RQ_{0J}$ (5) vibration–rotation transition [7,11] in the SiH_2 $A^1B_1(0, 2, 0) \leftarrow X^1A_1(0, 0, 0)$ absorption band. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of up to 25 laser shots (at a repetition rate of 1 or 2 Hz).

The average decay traces were processed by fitting the data to an exponential form using a non-linear least-squares package. This analysis provided the values for the first-order rate coefficients k_{obs} for removal of SiH_2 in the presence of known partial pressures of the Si_2H_6 or Si_3H_8 substrate gases.

Static gas mixtures were used and the optics were cleaned regularly. Previously it was shown that the same results were obtained from experiments performed with both static and slowly flowing gas samples [8]. The photolysis mixtures generally consisted of either Si_2H_6 (up to 35 mTorr) or Si_3H_8 (up to 25 mTorr) and inert diluent bath gas (Ar, C_3H_8 or SF_6) at a total pressure of 10 Torr. In these studies the silane served as both the silylene precursor and the reaction substrate. In some experiments $PhSiH_3$ (up to 12 mTorr) was added to verify that use of an additional silylene source made no difference. Also in some experiments the total pressure was varied (between 1 and 30 Torr). Pressures were measured by a capacitance manometer (MKS, Baratron). These experiments generated a considerable amount of gas-borne dust, and although this did not seriously interfere with the decay traces, regular cleaning of the cell, in particular the windows, was necessary to maintain good signals.

Phenylsilane (99.8%) was obtained from Ventron-Alpha (Petrarch). Si_2H_6 was supplied by BOC special gases (Electra grade II, > 99.995%). Si_3H_8 was a gift from L'Air Liquide, and was found to be > 96% pure by GC analysis (main impurities n- and i-Si_4H_{10}). Ar

was supplied by BOC (Electra grade II, > 99% pure). C_3H_8 was obtained from Cambrian Chemicals (> 99.5%). SF_6 (no GC detectable impurities) was obtained from ICI. All reagents with the exception of Ar were thoroughly degassed before use. Argon was purified by passage through a deoxo-unit.

3. Results

3.1. Preliminary experiments

Preliminary experiments established that, for a given reaction mixture, decomposition rate constants k_{obs} were not dependent on exciplex laser energy (60–140 mJ $pulse^{-1}$) or the number of photolysis shots. Since static gas mixtures were used, tests with up to 25 shots were carried out. The constancy of k_{obs} values (five shot averages) showed no effective depletion of reactants. The original intention of this work was to investigate the kinetics over as wide a range of temperature and pressure as possible using both strong (SF_6) and weak (Ar) collider gases as diluents, just as in our study [3] of the kinetics of SiH_2 + SiH_4. However, the studies in Ar proved problematical, producing both greater scatter in the data and unreasonable apparent pressure effects (rate constants decreasing with increasing pressure). Moreover, the rate constants were consistently less, except at room temperature, than those obtained with the other bath gases. While we cannot be sure of the reason for this we suspect small quantities of remaining impurity oxygen in the argon (in spite of the filter), which had the effect of consuming a part of the substrate silane in the cell at elevated temperatures prior to photolysis. There was no evidence of such an effect in our previous studies [3] of SiH_2 + SiH_4, however it is plausible that di- and trisilanes should be more sensitive to adventitious oxygen than monosilane. We therefore substituted propane as an alternative inert diluent (it is known that SiH_2 does not react with alkanes [1,2]).

Since the the UV (193 nm) photolysis of Si_3H_8 has not previously been used as a source of SiH_2, we undertook a check of the rate constants for SiH_2 + SiH_4 at 295 K in argon. The rate constants were in complete agreement with those reported previously using $PhSiH_3$ photolysis as the SiH_2 source [3] over the pressure range 1–40 Torr.

3.2. Rate measurements

A series of experiments was carried out at each of several temperatures in the range 295–595 K for each substrate gas. At 5 or 10 Torr total pressure (C_3H_8 or SF_6 diluent) and at each temperature, four to ten runs (of five to ten laser shots each) at different substrate

partial pressures were carried out. Additionally, at several temperatures the total pressure was varied in some runs.

The results of a selection of these experiments are shown in the plots of Fig. 1 for $SiH_2 + Si_2H_6$ and Fig. 2 for $SiH_2 + Si_3H_8$, which demonstrate the linear dependence of k_{obs} on substrate pressure, as expected for second-order kinetics. These plots also show the generally negligible effects on the values of k_{obs} of overall pressure changes in the range 1–30 Torr. The only possible systematic variation, beyond experimental er-

ror, would appear to be for Si_2H_6 at 584 K, but it is small anyway. It is noteworthy that the best fit lines, obtained via linear least-squares fitting, pass very close to the graph origins as expected for substrates which are themselves the SiH_2 precursors. The second-order rate constants, obtained from the slopes of these lines, are given in Tables 1 and 2. The error limits are single standard deviations, and are generally well within the ±10% thought to be reasonable for this type of measurement. Apart from the data in these tables, the only reliable rate data obtained using argon as the inert
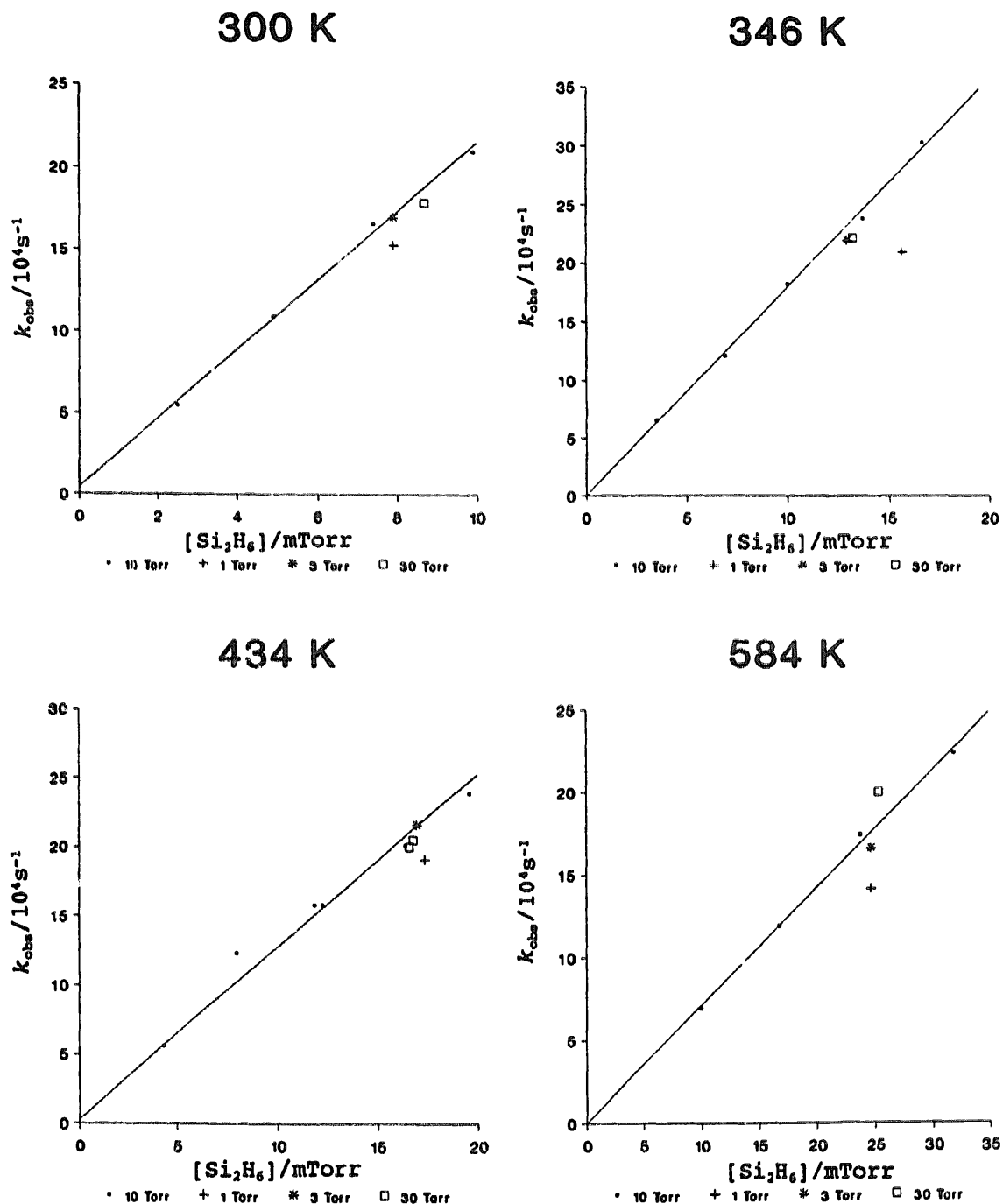

Fig. 1. Examples of second-order plots for reaction of SiH_2 with Si_2H_6 in SF_6 buffer gas.

diluent gave a rate constant value for $SiH_2 + Si_2H_6$ (Ar 10 Torr) at 298 K of $(5.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Arrhenius plots of the rate constants of Tables 1 and 2 are shown in Fig. 3, which also includes that for the reaction of $SiH_2 + SiH_4$ (high pressure limiting rate constants) for reference. The plots can be seen to be slightly curved, which may be real or arising from small systematic errors. Linear least-squares fitting to the Arrhenius equation gives the following (average) parameters. For $SiH_2 + Si_2H_6$: $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.51 \pm 0.04$, $E_a = -1.9 \pm 0.3$ kJ mol^{-1}; for

$SiH_2 + Si_3H_8$: $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.43 \pm 0.06$, $E_a = -2.0 \pm 0.4$ kJ mol^{-1}. The negative activation energies reflect the common observation for SiH_2 reactions [1,2] of rate constants which diminish with increasing temperature.

4. Discussion

4.1. Comparison with previous work

The results obtained in this work represent the first direct measurements of (i) rate constants for the reaction
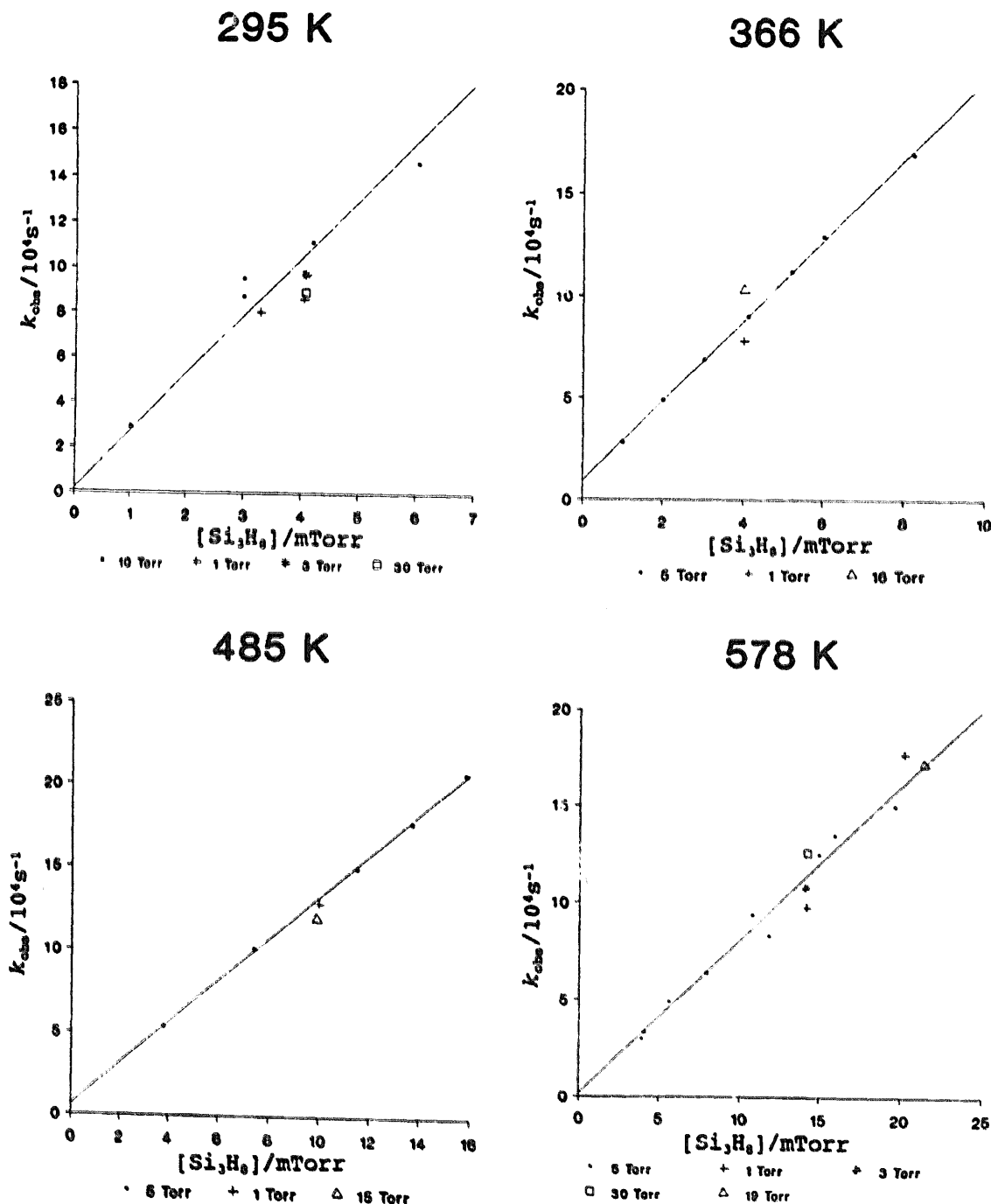

Fig. 2. Examples of second-order plots for reaction of SiH_2 with Si_3H_8 in SF_6 buffer gas.

Table 1
Second-order rate constants for the reaction of SiH_2 with Si_2H_6

T (K)	k (10^{-10} cm^3 molecule^{-1} s^{-1})	Buffer gas
295	6.41 ± 0.24	C_3H_8
300	6.56 ± 0.27	SF_6
346	6.44 ± 0.20	SF_6
378	5.40 ± 0.29	C_3H_8
434	5.60 ± 0.40	SF_6
502	4.50 ± 0.52	C_3H_8
540	5.13 ± 0.26	C_3H_8
584	4.32 ± 0.16	SF_6
590	4.52 ± 0.22	C_3H_8

Table 2
Second-order rate constants for the reaction of SiH_2 with Si_3H_8

T (K)	k (10^{-10} cm^3 molecule^{-1} s^{-1})	Buffer gas
295	7.79 ± 0.86	SF_6
297	7.96 ± 0.22	C_3H_8
366	7.43 ± 0.07	SF_6
430	7.34 ± 0.06	SF_6
485	6.30 ± 0.09	SF_6
534	5.87 ± 0.21	SF_6
578	4.75 ± 0.21	SF_6
595	5.52 ± 0.52	C_3H_8

Table 3
Comparison of room temperature rate constants for $SiH_2 + Si_2H_6$

k (10^{-10} cm^3 molecule^{-1} s^{-1})	P (Torr) (buffer)	Ref.
5.7 ± 0.2	1 (He)	[6]
1.5 ± 0.2	1 (He)	[7]
2.8 ± 0.3	5 (He)	[7]
3.4 ± 0.3	9.5 (He)	[7]
4.6 ± 0.7	5 (Ar)	[8]
5.7 ± 0.3	10 (Ar)	This work
6.6 ± 0.3	10 (SF_6)	This work
6.4 ± 0.2	10 (C_3H_8)	This work

of $SiH_2 + Si_3H_8$ and (ii) temperature dependences of rate constants for reactions of SiH_2 with both Si_2H_6 and Si_3H_8. Comparisons with previous data are only possible for $SiH_2 + Si_2H_6$ at room temperature. Such a comparison is shown in Table 3. The table does not include the value obtained by Dietrich et al. [9], because for the reasons already given (see Introduction) it is not obviously a room temperature value (see Appendix).

The comparison shows that our results are consistent for the three inert diluent gases used in this work, and
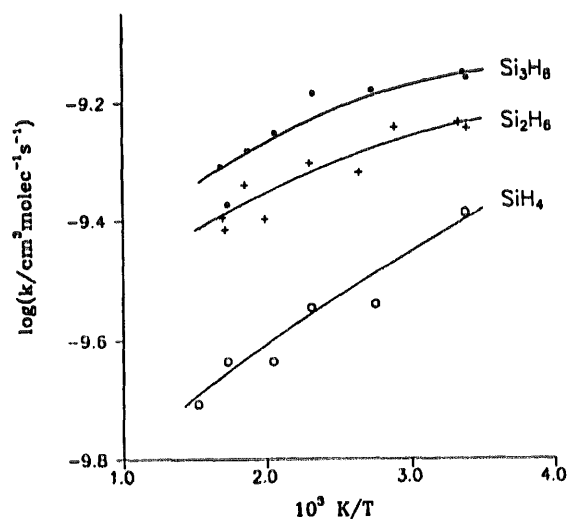

Fig. 3. Arrhenius plots for the reactions of SiH_2 with SiH_4 (Ref. [3]), Si_2H_6 and Si_3H_8.

are in best agreement with those of Inoue and Suzuki [6]. These results are slightly higher than those reported earlier [8] from our laboratories, but apparently larger by a factor of between 2 and 4 than those of Jasinski and Chu [7]. However, an extrapolation of the latters' values to higher pressures would clearly be in better agreement with the other figures. Thus the main disagreement between our results and those of Jasinski and Chu is over the question of pressure dependence. This is discussed further below.

There exist in the older literature [14,15] other reported values for the rate constants and also Arrhenius parameters for the reaction of $SiH_2 + Si_2H_6$. These values were estimates based on relative rate studies, incorporating additional assumptions which are now known to be erroneous.

4.2. The nature of the insertion process

The high magnitudes of the rate constants and the similarity of the Arrhenius parameters for the reactions of SiH_2 with SiH_4, Si_2H_6 and Si_3H_8 suggests a similarity of the mechanism. The reaction of $SiH_2 + SiH_4$ is an Si–H bond insertion process. If the measured rate constants for these reactions are divided by the number of available Si–H bonds, the figures shown in Table 4 are obtained, which demonstrate the essentially statistical nature of the reaction. The rate constants at room temperature are indeed all close, if not equal, to the collision magnitude, which attests to the looseness of the activated complexes for this reaction. Although potential energy surfaces for these reactions are not available, it seems extremely likely that they would show similar features to those of the $SiH_2 + SiH_4$ reac-

Table 4
Comparison of per Si–H insertion rate constants (10^{-10} cm^3 molecule^{-1} s^{-1})

Substrate	$T \approx 298$ K	$T \approx 588$ K	Ref.
SiH_4	1.15	0.59	[3]
Si_2H_6	1.08	0.72	This work
Si_3H_8	0.99	0.72	This work

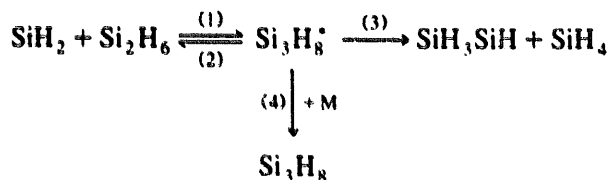tion which proceeds via the initial intermediacy of weakly bound complexes prior to formation of Si_2H_6. Thus for the reactions of SiH_2 with Si_2H_6 and Si_3H_8, weakly bound association complexes would probably also exist close to the reaction entrance channel due the favourable electrophilic interaction of any of the Si–H bonding electron pairs and the empty p orbital of SiH_2. It is these features of such surfaces which give rise to the negative activation energies observed [1].

It is worth adding that since the extremely high collisional efficiency of these reactions can be understood in terms of the Si–H bond insertion, it therefore seems unlikely that Si–Si bond insertion (which would lead to the same products) is occuring. It is known that $SiMe_2$, which is much less reactive than SiH_2 [1], does not insert in Si–Si bonds [16].

4.3. Overall products and the lack of pressure dependence

The overall products of reaction of SiH_2 with Si_2H_6 and Si_3H_8 are known to be Si_3H_8 and the two tetrasilanes $n-Si_4H_{10}$ and $i-Si_4H_{10}$ respectively [4,5]. However, the formation of these products in the gas-phase is accompanied by an energy release of ca. 230 kJ mol^{-1}. Therefore the initial product is vibrationally excited and requires collisional stabilisation. Thus these reactions are potentially third-body assisted association reactions like that of $SiH_2 + SiH_4$. Two factors militate against observation of pressure dependence. First, the vibrationally excited products $Si_3H_8^*$ and $Si_4H_{10}^*$ are larger, possess more vibrational modes, and will therefore have longer lifetimes than the $Si_2H_6^*$ formed from $SiH_2 + SiH_4$. Second, the vibrationally excited higher silanes possess alternative decomposition pathways not available to $Si_2H_6^*$.

The probable mechanism for reaction of SiH_2 with Si_2H_6 is as follows:

$$SiH_2 + Si_2H_6 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} Si_3H_8^* \overset{(3)}{\longrightarrow} SiH_3SiH + SiH_4$$

$$(4) \downarrow + M$$

$$Si_3H_8$$

From the published rate constants of Ring, O'Neal and coworkers [17,18] for the thermal decomposition of Si_3H_8, the ratio k_1/k_2 was found to be 3.18 at 558 K (temperature of study) and is calculated to be 15.8 at 298 K. Even allowing for some error in the extrapolation of this ratio to room temperature it seems as if the fate of $Si_3H_8^*$ formed here must be predominantly decomposition via step (3), if it is not stabilised via step (4). Only decomposition via step (2) can give rise to an apparent overall pressure dependence for this reaction, and therefore this seems likely to be small. Our own

measurements show a slight hint of a rate reduction at the lowest pressure of SF_6 (1 Torr). It is possible that the apparently low values of the rate constants in Ar (Table 3) reflect a small pressure dependence in this weaker collider gas. However, these results appear to be in disagreement with those of Jasinski and Chu [7], who found a more significant pressure dependence in He (factor of more than 2 between 1 and 9.5 Torr). It is true that He is a weaker collider gas than SF_6 or C_3H_8 used in this study, and is therefore more likely to show any pressure dependence. Nevertheless the measurements of Jasinski and Chu imply that at low pressures step (3) can have only a minor significance. Dietrich et al. [9] also find a strong pressure dependence for this reaction, which they interpret in terms of lifetimes of the initially formed vibrationally excited $Si_3H_8^*$. However, for the reasons of temperature uncertainty, we are cautious about commenting on their findings in this respect.

The reactions of the two vibrationally excited $Si_4H_{10}^*$ molecules formed from $SiH_2 + Si_3H_8$ are potentially more complex still, but are even less likely to lead to the reversion to SiH_2 needed to give rise to a pressure dependence.

Thus for both reactions our observations of little or no pressure effect are consistent with expectations based on the known chemistry.

Appendix (added during review)

A referee claims that the experimental conditions of Dietrich et al. [9] are obviously at room temperature. In Ref. [9] it is stated that "The kinetic studies are carried out under film-formation conditions, which allows one to measure the deposition rates in comparable experiments." The film-formation conditions are stated as a "pressure of 2.4 Torr and a constant substrate temperature of 550 K". Under these conditions there must be temperature gradients in the gas flowing over the substrate. Without a complete description, this means that the temperature of the gas probed by the laser which initiates deposition must depend on the precise beam

position relative to the substrate. It is not obvious to us that the kinetic studies under these conditions are at room temperature.

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