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# Direct Gas-Phase Kinetic Studies of Silylene Addition Reactions: $\text{SiH}_2 + \text{C}_3\text{H}_6$ , $\text{SiH}_2 + i\text{-C}_4\text{H}_8$ , and $\text{SiMe}_2 + \text{C}_2\text{H}_4$ . The Effects of Methyl Substitution on Strain Energies in Siliranes

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# Direct Gas-Phase Kinetic Studies of Silylene Addition Reactions: SiH<sub>2</sub> + C<sub>3</sub>H<sub>6</sub>, SiH<sub>2</sub> + *i*-C<sub>4</sub>H<sub>8</sub>, and SiMe<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>. The Effects of Methyl Substitution on Strain Energies in Siliranes

## Abstract

Time-resolved studies of the title reactions have been carried out over the pressure range 1–100 Torr (in SF<sub>6</sub> bath gas) and at temperatures in the range 293–600 K, using laser flash photolysis techniques to generate and monitor the silylenes, SiH<sub>2</sub> and SiMe<sub>2</sub>. All three reactions showed evidence of pressure dependence, consistent with third-body assisted association reactions to form silirane products. Extrapolation of the pressure-dependent rate constants gave the following Arrhenius parameters: SiH<sub>2</sub> + C<sub>3</sub>H<sub>6</sub>,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.79 \pm 0.03$ ,  $E_a$  (kJ mol<sup>-1</sup>) =  $-1.9 \pm 0.3$ ; SiH<sub>2</sub> + C<sub>4</sub>H<sub>8</sub>,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.91 \pm 0.04$ ,  $E_a$  (kJ mol<sup>-1</sup>) =  $-2.5 \pm 0.3$ ; SiMe<sub>2</sub> + C<sub>4</sub>H<sub>8</sub>,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -12.12 \pm 0.02$ ,  $E_a$  (kJ mol<sup>-1</sup>) =  $-8.5 \pm 0.2$ . These parameters are consistent with fast, nearly collision-controlled processes for SiH<sub>2</sub> but a tighter transition state for SiMe<sub>2</sub>. Rice, Ramsperger, Kassel, Marcus theory (RRKM) modeling, based on consistent transition states for silirane decomposition, and employing a weak collisional deactivation model, gave good fits to the pressure-dependent curves for each system, provided an appropriate value of  $E_0$  (fitting parameter) was used for each reaction. The kinetic results are consistent with an electrophilically led addition mechanism, although methyl substitution in the alkene hardly affects the rate constants. The RRKM-derived  $E_0$  values have been used to derive reaction enthalpies which are in reasonable agreement with values obtained by ab initio calculations at the G2 (MP2,SVP) level. The experimental  $\Delta H^\circ$  values yield strain energies of 190, 196, and 216 kJ mol<sup>-1</sup> for 2-methyl-, 2,2-dimethyl-, and 1,1-dimethylsilirane, respectively. Compared to the strain enthalpy of 167 kJ mol<sup>-1</sup> for silirane itself, this shows that methyl substituents in the silirane products substantially increase the strain energies. Theory supports this.

## Disciplines

Chemistry

## Comments

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# Direct Gas-Phase Kinetic Studies of Silylene Addition Reactions: $\text{SiH}_2 + \text{C}_3\text{H}_6$ , $\text{SiH}_2 + i\text{-C}_4\text{H}_8$ , and $\text{SiMe}_2 + \text{C}_2\text{H}_4$ . The Effects of Methyl Substitution on Strain Energies in Siliranes

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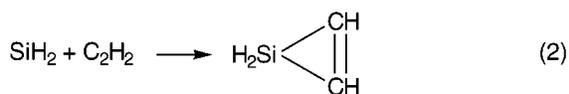
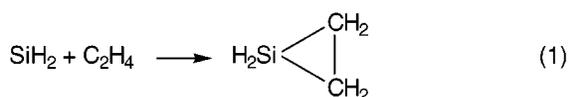
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Time-resolved studies of the title reactions have been carried out over the pressure range 1–100 Torr (in  $\text{SF}_6$  bath gas) and at temperatures in the range 293–600 K, using laser flash photolysis techniques to generate and monitor the silylenes,  $\text{SiH}_2$  and  $\text{SiMe}_2$ . All three reactions showed evidence of pressure dependence, consistent with third-body assisted association reactions to form silirane products. Extrapolation of the pressure-dependent rate constants gave the following Arrhenius parameters:  $\text{SiH}_2 + \text{C}_3\text{H}_6$ ,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.79 \pm 0.03$ ,  $E_a$  ( $\text{kJ mol}^{-1}$ ) =  $-1.9 \pm 0.3$ ;  $\text{SiH}_2 + \text{C}_4\text{H}_8$ ,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.91 \pm 0.04$ ,  $E_a$  ( $\text{kJ mol}^{-1}$ ) =  $-2.5 \pm 0.3$ ;  $\text{SiMe}_2 + \text{C}_4\text{H}_8$ ,  $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -12.12 \pm 0.02$ ,  $E_a$  ( $\text{kJ mol}^{-1}$ ) =  $-8.5 \pm 0.2$ . These parameters are consistent with fast, nearly collision-controlled processes for  $\text{SiH}_2$  but a tighter transition state for  $\text{SiMe}_2$ . Rice, Ramsperger, Kassel, Marcus theory (RRKM) modeling, based on consistent transition states for silirane decomposition, and employing a weak collisional deactivation model, gave good fits to the pressure-dependent curves for each system, provided an appropriate value of  $E_o$  (fitting parameter) was used for each reaction. The kinetic results are consistent with an electrophilically led addition mechanism, although methyl substitution in the alkene hardly affects the rate constants. The RRKM-derived  $E_o$  values have been used to derive reaction enthalpies which are in reasonable agreement with values obtained by ab initio calculations at the G2 (MP2,SVP) level. The experimental  $\Delta H^\circ$  values yield strain energies of 190, 196, and 216  $\text{kJ mol}^{-1}$  for 2-methyl-, 2,2-dimethyl-, and 1,1-dimethylsilirane, respectively. Compared to the strain enthalpy of 167  $\text{kJ mol}^{-1}$  for silirane itself, this shows that methyl substituents in the silirane products substantially increase the strain energies. Theory supports this.

## Introduction

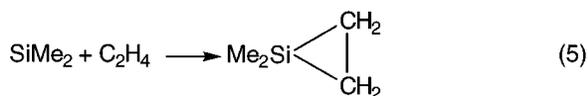
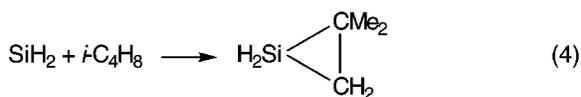
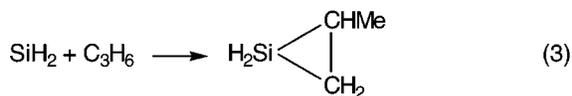
Silylenes are widely recognized as important intermediates in silicon hydride and organosilicon chemistry. They exist as ground-state singlets, and their characteristic reactions include insertions into Si–H, Si–OR, and O–H bonds and  $\pi$ -type additions across  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  bonds.<sup>1,2</sup> Although early work (pre-1985) concentrated on product identification and mechanisms, in recent years there has been an increasing number of direct, time-resolved kinetic studies of silylene reactions leading to a steadily accumulating database of absolute rate constants.<sup>3–5</sup> A significant number of these have been carried out in our own laboratories, among which are the prototype addition reactions:<sup>6–9</sup>



Reactions 1 and 2 have pressure-dependent second-order rate constants close to the collision value (at the high-pressure limit), together with small negative activation energies, consistent with third-body assisted association mechanisms.

Rice, Ramsperger, Kassel, Marcus Theory (RRKM) modeling of reaction 1, based on a consistent transition state for silirane decomposition, gave a good fit to the experimental pressure dependence using a critical energy,  $E_o(-1)$ , consistent with  $\Delta H^\circ(-1) = 201 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{silirane}) = 124 \pm 12 \text{ kJ mol}^{-1}$ , and a strain energy<sup>10</sup> of ca. 167  $\text{kJ mol}^{-1}$ . These figures are supported by theoretical calculations.<sup>11–13</sup> This approach of combining kinetic measurements with RRKM modeling appears to be the only viable "experimental" approach available for determining the strain energy of silirane, because the obvious alternative of direct kinetic measurement of its activation energy of decomposition is ruled out by its unavailability. Siliranes, in general, are fairly labile compounds and appear to require a high degree of substitution to be stabilized.<sup>14–16</sup> There are very few examples of rate studies of decomposition of substituted siliranes,<sup>14–17</sup> and only one, to our knowledge, for which Arrhenius parameters have been determined. This is the

decomposition of hexamethylsilirane<sup>17</sup> to give SiMe<sub>2</sub> + C<sub>2</sub>Me<sub>4</sub>, which has a measured activation energy of 130 kJ mol<sup>-1</sup> (corresponding to a strain energy of ca. 230 kJ mol<sup>-1</sup>). This is sufficiently different from silirane itself to suggest a conflict of information. One possible resolution of this apparent difference is the existence of a methyl substituent effect which *destabilizes* the more substituted siliranes. Thus, the present investigation was undertaken with two objectives in mind: first, to reveal methyl substituent effects on the kinetics of addition of silylenes and second, to see whether, via RRKM modeling studies, information on the stabilities and strain energies of several methyl-substituted siliranes could be obtained. To this end the following reactions were selected for study:



For the reaction systems investigated here there is very little previous kinetic data. Chu, Beach, and Jasinski<sup>18</sup> obtained a value of  $(1.2 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $k_3$  in 5 Torr He at room temperature and Baggott et al.<sup>19</sup> obtained  $(2.21 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $k_5$ , also at room temperature. Unpublished work by Blitz<sup>20</sup> shows that reaction 5 has a negative activation energy. Preliminary reports of the results of the present experimental work have appeared in recent reviews.<sup>4,5</sup> To back up the strain energy measurements, theoretical (ab initio) calculations were also undertaken for reactions 3–5. No previous theoretical studies exist for these reactions.

## Experimental Section

The apparatus and equipment for these studies have been described in detail previously.<sup>21–24</sup> Only essential and brief details are included here. Silylenes were produced by the 193 nm flash photolysis of gaseous mixtures containing suitable precursors using an Oxford Lasers KX2 ArF excimer laser. Photolysis pulses were fired into a variable temperature reaction vessel with demountable windows, at right angles to its main axis. At different times vessels of spectroil quartz and stainless steel were used but there was no effect of vessel material on the kinetic observations. The monitoring laser beam was multipassed between 32 and 48 times along the vessel axis, through the reaction zone, to give an effective path length of up to 1.8 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. Light signals were measured by a dual photodiode/differential amplifier combination and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of up to 30 photolysis laser shots (at a repetition rate of 1 or 2 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a nonlinear least-squares package. This analysis provided the values for first-order rate coefficients,  $k_{\text{obs}}$ , for removal of SiH<sub>2</sub> and SiMe<sub>2</sub> in the presence of known partial pressures of substrate gas.

The photoprecursors for the silylenes were phenylsilane (PhSiH<sub>3</sub>) for SiH<sub>2</sub> and octamethyltrisilane (OMTS) for SiMe<sub>2</sub>. The monitoring lasers were a CW argon ion laser (Coherent Innova 90–5) for SiMe<sub>2</sub> and a single mode dye laser (Coherent 699–21) pumped by the Ar ion laser for SiH<sub>2</sub>. Both silylenes were detected via absorption in their strong  $\tilde{A}(^1B_1) \leftarrow \tilde{X}(^1A_1)$  absorption bands, SiMe<sub>2</sub> at 457.9 nm<sup>21,22</sup> and SiH<sub>2</sub> at 579.39 nm (17259.50 cm<sup>-1</sup>), a strong vibration–rotation transition.<sup>23–25</sup>

Gas mixtures for photolysis were made up containing a small pressure of precursor (PhSiH<sub>3</sub> between 2 and 15 mTorr; OMTS between 30 and 200 mTorr), varying pressures of substrate (C<sub>3</sub>H<sub>6</sub> up to 250 mTorr; *i*-C<sub>4</sub>H<sub>8</sub> up to 300 mTorr; C<sub>2</sub>H<sub>4</sub> up to 9.8 Torr) together with inert diluent (sulfur hexafluoride, SF<sub>6</sub>) at total pressures between 1 and 100 Torr. Pressures were measured by capacitance manometers (MKS, Baratron).

All gases used in this work were thoroughly degassed prior to use. PhSiH<sub>3</sub> (99.9%) was obtained from Ventron-Alfa (Petrarch). Ethene (99.8%), propene (99.9%), and isobutene (99.9%) were all chemically pure (CP) grade (Matheson). SF<sub>6</sub> (no GC-detectable impurities) was from Cambrian Gases.

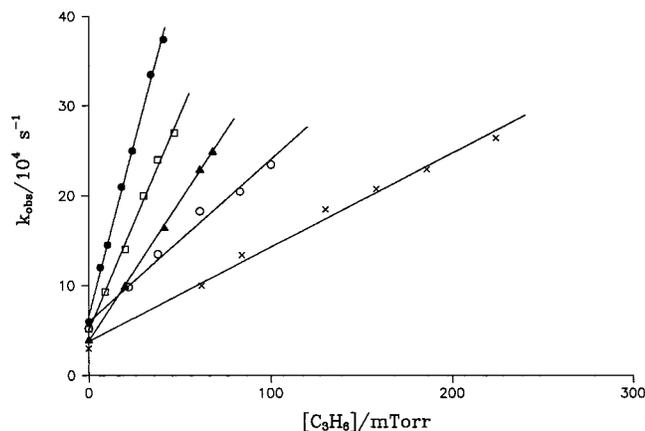
No attempts were made to search for the silirane products of these reactions by GC, because previous work<sup>7,19</sup> has shown that, although the products are almost certainly formed, they do not survive passage through normal GC columns.

**Ab Initio Calculations.** The ab initio calculations of the energy (and enthalpy) changes for the reactions of interest here were carried out using the G2(MP2,SVP) method,<sup>26</sup> a refinement of the original G2 method developed by Pople and colleagues.<sup>27</sup> Briefly, this is as follows. Geometries and frequencies of all species were calculated using MP2/6-31G(d) and the frequencies were scaled to match known experimental averages (factor of 0.9427). Next, single point energies were calculated at the MP2 geometries using (a) MP2/6-311+(3df,2p) and (b) QCISD(T)/6-31G(d). Energies at QCISD(T)/6-311+(3df,2p) were estimated from (a) and (b) assuming that the basis set and configuration interaction refinements are independent and therefore additive. Reaction 1 was investigated for reference purposes as well as reactions 3–5. Because all reactions involve only closed shell species, no further higher level corrections were made. For each reaction electronic energies were obtained and corrected for vibrational zero point energy differences to give  $\Delta H^\circ$  (0 K) and then adjusted for thermal energy to give  $\Delta H^\circ$  (298 K).

## Results

**(i) General Considerations.** In each reaction system, it was independently verified during preliminary experiments that, for a given reaction mixture, decomposition decay constants,  $k_{\text{obs}}$ , were not dependent on the excimer laser energy or number of photolysis shots. Because static gas mixtures were used, tests with up to 30 shots were carried out. The constancy of  $k_{\text{obs}}$  (10 shot averages) showed no effective depletion of reactants in any of the systems. The sensitivity of detection of SiH<sub>2</sub> or SiMe<sub>2</sub> was high but decreased with increasing temperature. Therefore, increasing quantities of precursors (PhSiH<sub>3</sub> or OMTS) were required at higher temperatures. However, at any given temperature precursor pressures were kept fixed, to ensure a constant (but always small) contribution to  $k_{\text{obs}}$  values.

For each substrate a series of experiments was carried out at each of five temperatures in the range from room temperature up to ca. 600 K. At 10 Torr total pressure (SF<sub>6</sub> diluent), five or six runs (of 10–20 laser shots each) at different substrate partial pressures were carried out at each temperature. The purpose of these experiments was to establish the second-order



**Figure 1.** Second-order plots for reaction 3,  $\text{SiH}_2 + \text{C}_3\text{H}_6$ : (●) 294 K, (□) 359 K, (▲) 414 K, (○) 464 K, (×) 520 K.

**TABLE 1: Experimental Second-Order Rate Constants for  $\text{SiH}_2 + \text{C}_3\text{H}_6$  at Different Pressures ( $\text{SF}_6$ )**

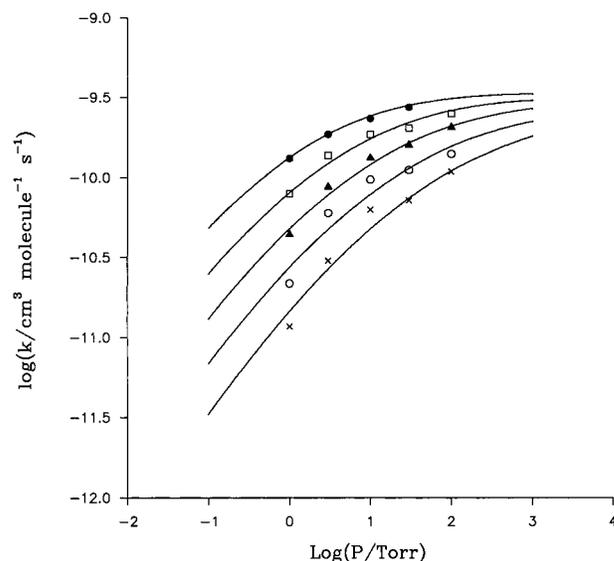
$T$ (K)	$k$ ( $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	
	$P_T = 10 \text{ Torr}$	$P_T = \infty^a$
294	$2.34 \pm 0.06$	$3.4 \pm 0.2$
359	$1.86 \pm 0.07$	$3.2 \pm 0.3$
414	$1.35 \pm 0.03$	$3.0 \pm 0.3$
464	$0.977 \pm 0.096$	$2.6 \pm 0.4$
520	$0.631 \pm 0.054$	$2.4 \pm 0.3$

<sup>a</sup> Obtained by extrapolation; see text.

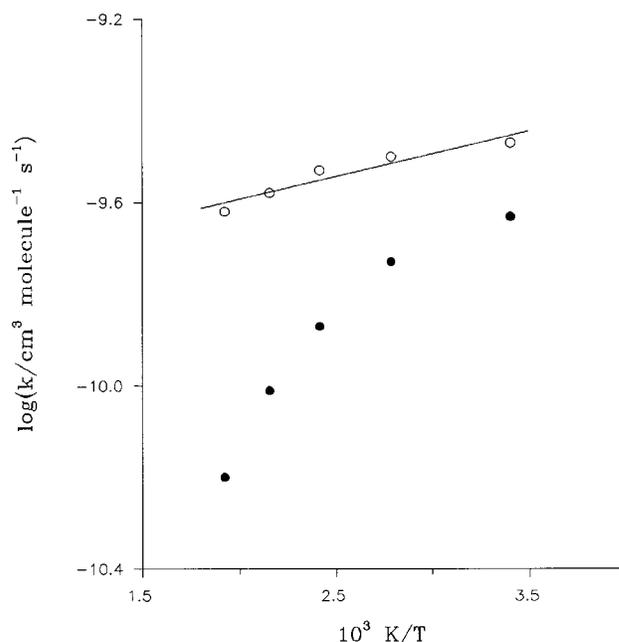
nature of the kinetics. In addition to these experiments, another set of runs was carried out at each temperature, in which the total pressure ( $\text{SF}_6$ ) was varied in the range 1–100 Torr to test the pressure dependence of the second-order rate constants. In these runs, the full second-order plot was not obtained, but second-order behavior was assumed, and the constants were obtained by assuming linear dependence of  $k_{\text{obs}}$  with substrate pressure. To keep errors to a minimum, sufficient substrate was used to ensure  $k_{\text{obs}}$  values in the range  $(2\text{--}3) \times 10^5 \text{ s}^{-1}$  where reaction with substrate was at least 75% of total reaction. Allowance was made for reaction of the silylene with precursor (measured directly for each pressure, but found to be pressure independent). The total pressure range was dictated by practical considerations.<sup>7</sup> For the  $\text{SiH}_2$  studies, a range of total pressure of 1–100 Torr was possible, but for  $\text{SiMe}_2 + \text{C}_2\text{H}_4$  the pressure range was limited to 3–100 Torr because at least 3 Torr of  $\text{C}_2\text{H}_4$  was needed in some of the kinetic experiments. The results of the work described here represent measurements of some 300 decay constants ( $k_{\text{obs}}$  values) overall.

(ii) **Kinetics of  $\text{SiH}_2 + \text{C}_3\text{H}_6$ .** This reaction was investigated over the temperature range 294–520 K. The second-order rate plots at 10 Torr total pressure are shown in Figure 1 for the five temperatures studied. Good linear fits were obtained as can be clearly seen. The second-order rate constants, obtained by linear least-squares fitting to these plots are collected in Table 1. The error limits are single standard deviations. The rate constants clearly decrease with increasing temperature.

The pressure dependence of these rate constants is shown in Figure 2. The uncertainties in individual rate constants, not shown in the figure, are probably ca.  $\pm 10\%$ . Just as with our earlier study<sup>7</sup> of  $\text{SiH}_2 + \text{C}_2\text{H}_4$ , rate constants were found to be pressure dependent over the whole range of study. Infinite pressure values,  $k_3^\infty$ , were obtained by extrapolation with the aid of RRKM theory (see next section) and these are also included in Table 1. An Arrhenius plot of  $k_3^\infty$  values, shown in Figure 3, gives a reasonably linear fit, bearing in mind the



**Figure 2.** Pressure dependence of second-order rate constants for  $\text{SiH}_2 + \text{C}_3\text{H}_6$  at different temperatures: (●) 294 K, (□) 359 K, (▲) 414 K, (○) 464 K, (×) 520 K. Solid lines are RRKM theoretical fits.



**Figure 3.** Arrhenius plots of rate constants for  $\text{SiH}_2 + \text{C}_3\text{H}_6$ : (●),  $p = 10 \text{ Torr}$ ; (○), extrapolated to  $p = \infty$ .

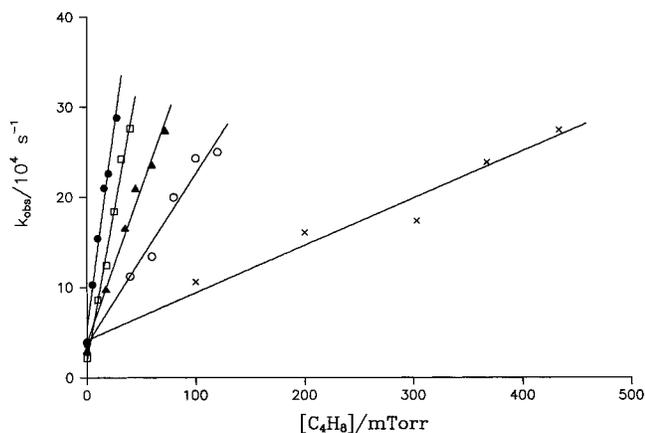
uncertainties. The resulting Arrhenius equation is

$$\log(k_3^\infty (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})) = (-9.79 \pm 0.05) + (1.90 \pm 0.34 \text{ kJ mol}^{-1})/RT \ln 10$$

The 10 Torr values of  $k_3$  clearly give rise to a curved Arrhenius plot.

(iii) **Kinetics of  $\text{SiH}_2 + i\text{-C}_4\text{H}_8$ .** This reaction was investigated over the temperature range 294–600 K. The second-order rate plots at 10 Torr total pressure are shown in Figure 4 for the five temperatures studied. Good linear fits were obtained as can be clearly seen. The second-order rate constants, obtained by linear least-squares fitting to these plots are collected in Table 2. The error limits are single standard deviations. The rate constants clearly decrease with increasing temperature.

The pressure dependence of these rate constants is shown in Figure 5. The uncertainties in individual rate constants, not

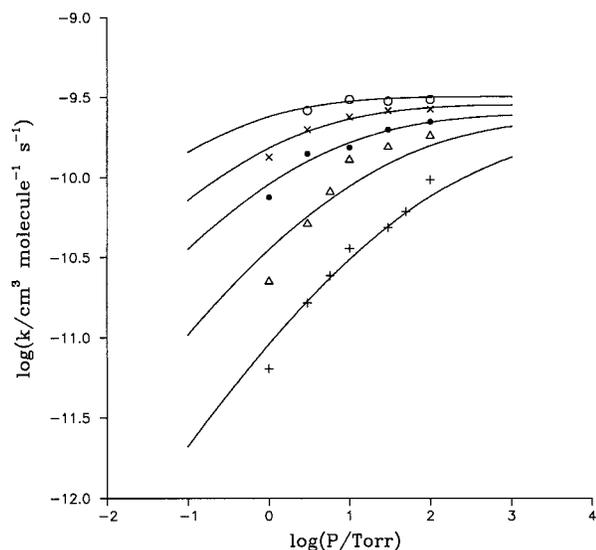


**Figure 4.** Second-order plots for reaction 4,  $\text{SiH}_2 + i\text{-C}_4\text{H}_8$ : (●) 294 K, (□) 362 K, (▲) 414 K, (○) 494 K, (×) 600 K.

**TABLE 2: Experimental Second-Order Rate Constants for  $\text{SiH}_2 + i\text{-C}_4\text{H}_8$  at Different Pressures ( $\text{SF}_6$ )**

T (K)	$k$ ( $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	
	$P_T = 10 \text{ Torr}$	$P_T = \infty^a$
294	$3.09 \pm 0.10$	$3.2 \pm 0.2$
362	$2.40 \pm 0.15$	$2.9 \pm 0.25$
414	$1.55 \pm 0.14$	$2.5 \pm 0.2$
494	$0.95 \pm 0.15$	$2.3 \pm 0.5$
600	$0.36 \pm 0.12$	$1.9 \pm 0.4$

<sup>a</sup> Obtained by extrapolation; see text.

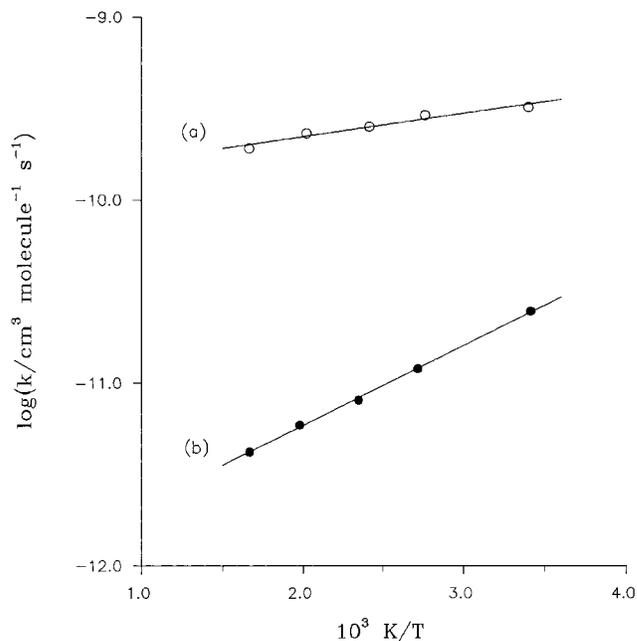


**Figure 5.** Pressure dependence of second-order rate constants for  $\text{SiH}_2 + i\text{-C}_4\text{H}_8$  at different temperatures: (○) 294 K, (×) 362 K, (●) 414 K, (△) 494 K, (+) 600 K. Solid lines are RRKM theoretical fits.

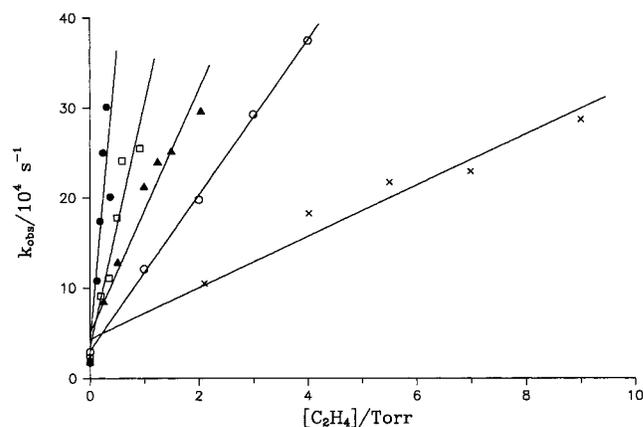
shown in the figure, are probably ca.  $\pm 10\%$ . In contrast to reaction 3, rate constants for this reaction were found to be much less pressure dependent. Infinite pressure values,  $k_4^\infty$ , were obtained by extrapolation with the aid of RRKM theory (see next section) and these are also included in Table 2. An Arrhenius plot of  $k_4^\infty$  values, shown in Figure 6, gives a reasonably linear fit, bearing in mind the uncertainties. The resulting Arrhenius equation is

$$\log(k_4^\infty (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})) = (-9.91 \pm 0.04) + (2.45 \pm 0.30 \text{ kJ mol}^{-1})/RT \ln 10$$

The 10 Torr values of  $k_4$  give rise to a curved Arrhenius plot, but are not shown in the figure, for simplicity.



**Figure 6.** Arrhenius plots of extrapolated ( $p = \infty$ ) rate constants for reactions 4 and 5: (a)  $\text{SiH}_2 + i\text{-C}_4\text{H}_8$ , (b)  $\text{SiMe}_2 + \text{C}_2\text{H}_4$ .



**Figure 7.** Second-order plots for reaction 5,  $\text{SiMe}_2 + \text{C}_2\text{H}_4$ : (●) 293 K, (□) 368 K, (▲) 426 K, (○) 505 K, (×) 600 K.

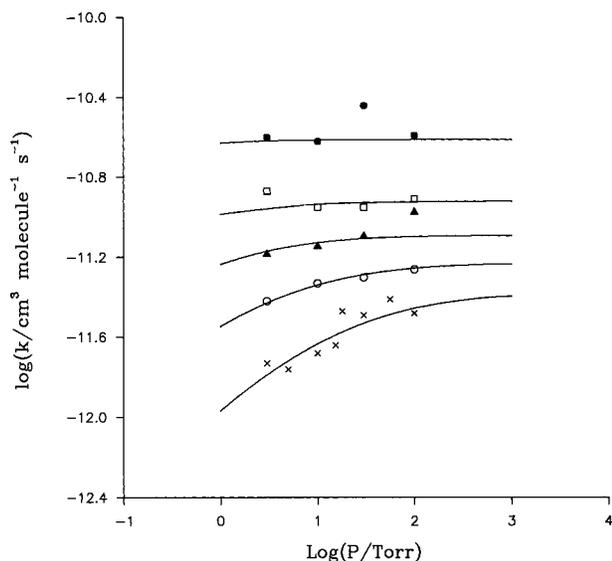
**TABLE 3: Experimental Second-Order Rate Constants for  $\text{SiMe}_2 + \text{C}_2\text{H}_4$  at Different Pressures ( $\text{SF}_6$ )**

T (K)	$k$ ( $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	
	$P_T = 10 \text{ Torr}$	$P_T = \infty^a$
293	$2.49 \pm 0.16$	$2.45 \pm 0.25$
368	$1.36 \pm 0.15$	$1.20 \pm 0.18$
426	$0.72 \pm 0.11$	$0.81 \pm 0.14$
505	$0.47 \pm 0.10$	$0.59 \pm 0.08$
600	$0.21 \pm 0.02$	$0.42 \pm 0.12$

<sup>a</sup> Obtained by extrapolation; see text.

**Kinetics of  $\text{SiMe}_2 + \text{C}_2\text{H}_4$ .** This reaction was investigated over the temperature range 293–600 K. The second-order rate plots at 10 Torr total pressure are shown in Figure 7 for the five temperatures studied. Good linear fits can be clearly seen. The second-order rate constants, obtained by linear least-squares fitting to these plots are collected in Table 3. The error limits are single standard deviations. The rate constants clearly decrease with increasing temperature.

The pressure dependence of these rate constants is shown in Figure 8. The uncertainties in individual rate constants, not shown in the figure are probably ca.  $\pm 10\%$ . Rate constants for reaction 5 were found to be almost pressure independent at



**Figure 8.** Pressure dependence of second-order rate constants for  $\text{SiMe}_2 + \text{C}_3\text{H}_6$  at different temperatures: (●) 293 K, (□) 368 K, (▲) 426 K, (○) 505 K, (×) 600 K. Solid lines are RRKM theoretical fits.

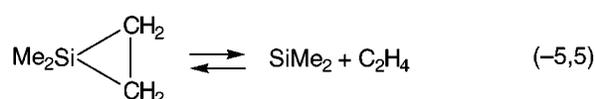
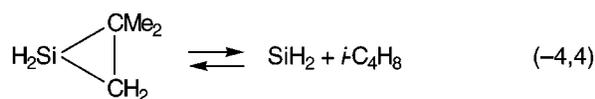
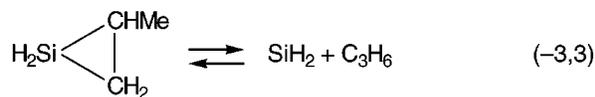
the lower temperatures and only clearly pressure dependent at 600 K. Where necessary infinite pressure values,  $k_5^\infty$ , were obtained by extrapolation with the aid of RRKM theory (see next section) and these are also included in Table 3. An Arrhenius plot of  $k_5^\infty$  values, also shown in Figure 6, gives a reasonably linear fit, bearing in mind the uncertainties. The resulting Arrhenius equation is

$$\log(k_5^\infty (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})) = (-12.12 \pm 0.02) + (8.48 \pm 0.15 \text{ kJ mol}^{-1})/RT \ln 10$$

The 10 Torr values of  $k_5$  give rise to a curved Arrhenius plot, but are not shown in the figure, for simplicity.

All three of these reactions show the temperature and pressure dependencies characteristic of a third-body assisted association reaction<sup>28</sup> as found previously<sup>6,7</sup> for reaction 1. To model these pressure dependencies, we have carried out RRKM modeling calculations, described in the next section.

**RRKM Calculations.** The pressure dependence of an association reaction corresponds exactly to that of the reverse unimolecular dissociation process provided there are no other perturbing reaction channels. Therefore, we have carried out RRKM calculations<sup>28</sup> of the pressure dependencies of the unimolecular decompositions of the appropriate silirane molecules, viz 2-methyl-silirane, 2,2-dimethylsilirane, and 1,1-dimethylsilirane



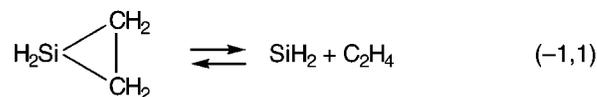
Just as for the parent silirane, these methyl-substituted siliranes have never been isolated and therefore their decomposition kinetics are unknown. However, there is sufficient

**TABLE 4: Some Calculated Thermodynamic and Kinetic Quantities for Reactions (-3,3), (-4,4), and (-5,5)**

Entropy changes; $\Delta S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) <sup>a</sup>					
<i>T</i> (K)	reaction				
	(-3,3)	(-4,4)	(-5,5)		
300	165.2	159.5	159.5		
400	164.9	159.2	159.2		
500	163.2	157.4	157.4		
600	161.3	155.5	155.5		
A factors; $\log(A \text{ (s}^{-1}))$ <sup>b</sup>					
<i>T</i> (K)	reaction (-3,3)	<i>T</i> (K)	reaction (-4,4)	<i>T</i> (K)	reaction (-5,5)
294	17.81	298	17.40	293	15.28
359	17.71	362	17.31	368	15.18
414	17.62	414	17.22	426	15.09
464	17.53	494	17.08	505	14.97
520	17.43	600	16.88	600	14.77

<sup>a</sup> Standard state = 1 bar. <sup>b</sup> For derivation see text.

available information to make good estimates of all the necessary parameters for these calculations apart from the critical energies for the reactions which were therefore used as fitting parameters in each case. The approach adopted was adapted from that used earlier<sup>7</sup> for silirane decomposition itself, viz



First,  $\Delta S^\circ$  values were estimated for reactions (-3,3), (-4,4), and (-5,5) based on the known  $\Delta S^\circ$  values<sup>7</sup> for reaction (-1,1). These are shown in Table 4. The assumption here is that methyl substitution affects the entropies of both reactants and products equally in each of these reactions (apart from symmetry considerations). This assumption is known to work well for many reaction systems and is one of Benson's many contributions.<sup>29,30</sup> The  $\Delta S^\circ$  values are then combined with the measured *A* factors for reactions 3–5 to yield the *A* factors for the decompositions via  $\ln(A_d/A_a) = \Delta S^\circ/R$ , where *A<sub>d</sub>* and *A<sub>a</sub>* are the *A* factors for the decomposition and association processes, respectively, for each reaction pair. Standard state conversions are required in these calculations, and the necessary interpolations have been carried out to obtain the *A<sub>d</sub>* values at all experimental temperatures for each reaction. These are shown in Table 4. Because of the temperature (*T*)-dependence of  $\Delta S^\circ$ , the *A<sub>d</sub>* values all show small but significant variation with *T*. This implies a slight curvature in the Arrhenius plots for decomposition of the siliranes over the ca. 300 K temperature range of these studies. Although this behavior cannot be independently verified, we believe it reflects the variational character of the transition states for many of the decomposition reactions which result in silylene formation,<sup>4</sup> in particular for silirane itself.<sup>7</sup>

The only problem in this procedure is the extrapolation of the pressure-dependent rate constants. We have adopted a theoretically assisted procedure for this just as for our study<sup>7</sup> of reaction (-1,1). At each temperature an initial approximate (eyeball) estimate of the  $k^\infty$  value was obtained, to provide the basis for a first attempt at the RRKM calculation for each system. The pressure-dependent ("falloff") curves generated were then used to refine  $k^\infty$  values to the ones shown in Tables 1–3. Fortunately the extrapolations were relatively short compared to the range of falloff values. The curvatures for reactions (-4,4) and (-5,5) were also quite small. The

**TABLE 5: Molecular and Transition-State Parameters for RRKM Calculations for 2-methylsilirane Decomposition at 294 K**

	2-methylsilirane	2-methylsilirane <sup>‡</sup>
$\nu$ (cm <sup>-1</sup> )	2960 (6) 2135 (2) 1450 (3) 1410 (1) 1150 (1) 1120 (2) 1000 (2) 955 (1) 935 (1) 875 (1) 740 (2) 676 (1) 620 (2) 473 (1) 420 (2) 392 (1) 174 (1)	2960 (6) 2135 (2) 1450 (3) 1410 (1) 1150 (1) 1120 (2) 1000 (2) 1500 (1) 935 (1) 875 (1) 740 (2) 57 (1) 40 (2) 30 (1) 420 (2) 174 (1)
reaction coordinate	620 cm <sup>-1</sup>	
$I^{\ddagger}/I$	1	
path degeneracy	1	
$E_o$ (critical energy)	162.8 kJ mol <sup>-1</sup> (38.9 kcal mol <sup>-1</sup> )	
collision number, $Z_{LJ}$	$4.58 \times 10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> (SF <sub>6</sub> )	

**TABLE 6: Temperature Dependent Parameters Used in RRKM Calculations for 2-methylsilirane Decomposition**

$T$ (K)	294	359	414	464	520
transition state wavenumbers (cm <sup>-1</sup> )	38 (1) 30 (1) 25 (1) 20 (1)	41 (1) 33 (1) 30 (1) 25 (1)	45 (1) 40 (1) 33 (1) 25 (1)	48 (1) 40 (1) 35 (1) 30 (1)	57 (1) 40 (2) 30 (1)
$E_o$ (kJ mol <sup>-1</sup> )	162.8	162.8	162.8	162.8	162.8
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	176.1	177.4	178.4	179.1	179.8
$Z_{LJ}$ (10 <sup>-10</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	4.64	4.67	4.89	5.09	5.24

estimated uncertainties in  $k^\infty$  values are shown in the tables. The majority are  $\pm 10\%$  or less, the worst case being  $\pm 30\%$ .

The next stage was to assign the vibrational wavenumbers of the molecule and activated complex for each reaction at each temperature of study. This was done first for the molecules, by taking the assignment for silirane itself<sup>7</sup> and making additions to incorporate the average wavenumber values for CH<sub>3</sub> group modes according to Benson.<sup>29</sup> The activated complexes were assigned by adjusting the wavenumbers, principally of the ring modes and SiH<sub>2</sub> group vibrations of the molecules, until a match was obtained with the entropy of activation and the  $A$  factor for each one in the usual way.<sup>28</sup> Values for other modes were left unchanged except for the C–C stretch. Internal rotors were treated as low wavenumber vibrations and left unchanged between molecule and activated complex. Whether precise values of all vibrational wavenumbers are correct is not important provided the entropies of activation are matched. Because of the apparent decrease in values of the  $A$  factors with temperature, which we believe to be correct, we have modified the activated complex wavenumbers at each temperature in order to build in variational character, rather than use a temperature-averaged, fixed-wavenumber, complex. The details are shown in Tables 5–10. We have assumed that geometry changes in the decomposing silirane molecules do not lead to significant changes in overall moments of inertia and adiabatic rotational effects (angular momentum conservation problems). This is an approximation, in view of the loose activated complex structures, but we believe it will not lead to serious errors. However, we

**TABLE 7: Molecular and Transition-State Parameters for RRKM Calculations for 2,2-Dimethylsilirane Decomposition at 294 K**

	2,2-dimethylsilirane	2,2-dimethylsilirane <sup>‡</sup>
$\nu$ (cm <sup>-1</sup> )	2960 (8) 2135 (2) 1450 (6) 1410 (1) 1150 (2) 1120 (1) 1000 (4) 955 (1) 935 (1) 875 (1) 740 (1) 676 (1) 620 (2) 473 (1) 420 (4) 392 (1) 174 (2)	2960 (8) 2135 (2) 1450 (6) 1410 (1) 1150 (2) 1120 (1) 1000 (4) 1500 (1) 935 (1) 875 (1) 740 (1) 50 (1) 40 (1) 30 (1) 25 (1) 420 (4) 174 (2)
reaction coordinate	620 cm <sup>-1</sup>	
$I^{\ddagger}/I$	1	
path degeneracy	1	
$E_o$ (critical energy)	151.0 kJ mol <sup>-1</sup> (36.1 kcal mol <sup>-1</sup> )	
collision number, $Z_{LJ}$	$4.57 \times 10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> (SF <sub>6</sub> )	

**TABLE 8: Temperature-Dependent Parameters Used in RRKM Calculations for 2,2-Dimethylsilirane Decomposition**

$T$ (K)	294	362	414	494	600
transition state wavenumbers (cm <sup>-1</sup> )	50 (1) 40 (1) 30 (1) 25 (1)	53 (1) 40 (1) 35 (2) 25 (1)	50 (2) 40 (1) 37 (1)	55 (1) 50 (1) 48 (1) 45 (1)	69 (1) 56 (1) 55 (1) 49 (1)
$E_o$ (kJ mol <sup>-1</sup> )	151.0	149.3	148.5	146.8	144.4
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	164.8	164.4	164.4	164.0	162.8
$Z_{LJ}$ (10 <sup>-10</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	4.57	4.69	4.79	5.12	5.15

**TABLE 9: Molecular and Transition-state Parameters for RRKM Calculations for 1,1-Dimethylsilirane Decomposition at 293 K**

	1,1-dimethylsilirane	1,1-dimethylsilirane <sup>‡</sup>
$\nu$ (cm <sup>-1</sup> )	2960 (10) 1450 (6) 1410 (2) 1150 (2) 1120 (2) 1000 (2) 955 (1) 935 (2) 740 (2) 700 (2) 620 (2) 185 (2) 150 (2) 147 (2)	2960 (10) 1450 (6) 1410 (2) 1150 (2) 1120 (2) 1000 (2) 1500 (1) 935 (2) 740 (2) 700 (2) 185 (1) 147 (2) 91 (1) 70 (1) 47 (1) 40 (1)
reaction coordinate	620 cm <sup>-1</sup>	
$I^{\ddagger}/I$	1	
path degeneracy	1	
$E_o$ (critical energy)	136.1 kJ mol <sup>-1</sup> (32.5 kcal mol <sup>-1</sup> )	
collision number, $Z_{LJ}$	$4.56 \times 10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> (SF <sub>6</sub> )	

have used a weak collisional (stepladder) model for collisional deactivation,<sup>28</sup> because there is considerable evidence against the strong collision assumption.<sup>31</sup> The average energy removal parameter,  $\langle \Delta E \rangle_{\text{down}}$ , was taken as 9.6 kJ mol<sup>-1</sup> (800 cm<sup>-1</sup>) for

**TABLE 10: Temperature Dependent Parameters Used in RRKM Calculations for 1,1-dimethylsilirane Decomposition**

<i>T</i> (K)	293	368	426	505	600
transition state	91 (1)	95 (1)	100 (1)	100 (2)	100 (1)
wavenumbers (cm <sup>-1</sup> )	70 (1)	75 (1)	80 (1)	62 (1)	89 (1)
	47 (1)	55 (2)	60 (1)	53 (1)	80 (1)
	40 (1)	46 (1)	50 (1)		75 (1)
<i>E</i> <sub>0</sub> (kJ mol <sup>-1</sup> )	136.1	136.1	136.1	136.1	136.1
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	152.1	153.1	153.7	154.4	155.1
<i>Z</i> <sub>LJ</sub> (10 <sup>-10</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	4.56	4.72	4.83	4.98	5.15

**TABLE 11: G2(MP2,SVP) Energies and Enthalpies (kJ mol<sup>-1</sup>) for Reactions 1 and 3–5**

reactants	$-\Delta U^\circ$ (0 K)	$-\Delta H^\circ$ (0 K)	$-\Delta H^\circ$ (298 K)	$-\Delta H^\circ$ (298 K) <sup>a</sup>
SiH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	213	195	203	201
SiH <sub>2</sub> + C <sub>3</sub> H <sub>6</sub>	183	166	173	176
SiH <sub>2</sub> + <i>i</i> -C <sub>4</sub> H <sub>8</sub>	179	163	169	165
SiMe <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	192	178	183	152

<sup>a</sup> Experimental values.**TABLE 12: Arrhenius Parameters for Silylene Addition Reactions**

reactants	log( <i>A</i> <sup>∞</sup> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ))	<i>E</i> <sub>a</sub> (kJ mol <sup>-1</sup> )
SiH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	-9.97 ± 0.03	-2.9 ± 0.2
SiH <sub>2</sub> + C <sub>3</sub> H <sub>6</sub>	-9.79 ± 0.05	-1.9 ± 0.3
SiH <sub>2</sub> + <i>i</i> -C <sub>4</sub> H <sub>8</sub>	-9.91 ± 0.04	-2.45 ± 0.3
SiMe <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	-12.12 ± 0.02	-8.5 ± 0.2

all reactions, by analogy with that found for silirane,<sup>7</sup> although variations within the range 8.4–12.0 kJ mol<sup>-1</sup> had little effect on the fitting.

The critical energies were obtained by trial and error until the degree of falloff was matched. For each reaction this was done first at the highest temperature, where falloff was greatest. The *E*<sub>0</sub> value obtained was then either kept fixed or adjusted only slightly at other temperatures to make a slight allowance for variational character. Once obtained, *E*<sub>0</sub> values were converted to *E*<sub>a</sub> by addition of the thermal energy differences of each molecule and its transition state, and finally into  $\Delta H^\circ$  via  $\Delta H^\circ = E_{-a} - E_a + RT$ . The resulting values of  $\Delta H^\circ$  are shown in Tables 6, 8, and 10.

The results of our final calculations are shown as the full curves in Figures 2, 5, and 8.

**Ab initio Calculations.** The outcome of these calculations for the reactions studied here is shown in Table 11. There are clearly significant reductions in  $-\Delta U^\circ$  (and  $-\Delta H^\circ$ ) for reactions 3–5 compared with reaction 1.

## Discussion

**General Comments, Comparisons, and Nature of the Reaction Process.** The results reported here represent a systematic extension of our earlier study of SiH<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>.<sup>7</sup> Pressure dependencies have been found in all three reaction systems investigated although the effect is negligible at the lower two temperatures for reaction 5 and small at the lower temperatures for reaction 4. Extrapolation to the high-pressure limits yields rate constants which show a decrease in value as temperature is increased for all three reactions. This is similar to the findings for reaction 1 in the earlier study. For comparison purposes the Arrhenius parameters for all of these addition reactions are shown in Table 12. Clearly, for the SiH<sub>2</sub> addition process, the Arrhenius parameters are all extremely similar and indeed virtually identical within experimental error.

Note that in our review articles<sup>4,5</sup> the cited values for reaction 4 were slightly different (log(*A* (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)) = -10.38 and *E*<sub>a</sub> = -5.1 kJ mol<sup>-1</sup>). During preparation of this paper, a check of the data revealed a slightly erroneous extrapolation in the original evaluation.<sup>4,5</sup>

Comparison with earlier work shows good consistency. For reaction 3, Chu, Beach, and Jasinski<sup>18</sup> obtained *k*<sub>3</sub> = (1.2 ± 0.1) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in 5 Torr He at room temperature. Our result in 5 Torr SF<sub>6</sub> gives *k*<sub>3</sub> = 2.0 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (by interpolation). Because *k*<sub>3</sub> is into its pressure-dependent region and He is a weaker collision partner than SF<sub>6</sub>, this is reasonable agreement. There are no previous studies of reaction 4. For reaction 5, Baggott et al.<sup>19</sup> obtained *k*<sub>5</sub> = (2.21 ± 0.12) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature. This is in reasonable agreement with the value of (2.45 ± 0.25) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained here. The data found by Blitz<sup>20</sup> between 295 and 588 K showed a decrease of *k*<sub>5</sub> with increasing temperature at total pressures of 5 Torr (Ar buffer gas). The data are closely consistent with that presented here although pressure dependence was not investigated (i.e., it was assumed to be negligible).

It is virtually impossible to discern an alkene methyl substituent effect on the kinetics of the SiH<sub>2</sub> addition process (at infinite pressure). Although the rate constants at 298 K follow the trend *k*<sub>1</sub> > *k*<sub>3</sub> > *k*<sub>4</sub>, they are in fact equal within experimental error (see Tables 1 and 2 of this paper and Table 1 of ref 7). The present view of the nature of the SiH<sub>2</sub> addition process,<sup>7</sup> supported by theory,<sup>32</sup> is of a barrierless reaction involving an initial  $\pi$  attack ("electrophilic phase" donation of C=C  $\pi$  electrons into the Si 3p-orbital), followed by  $\sigma$  attack ("nucleophilic phase" donation of the silicon lone pair electrons into the C=C antibonding  $\pi^*$  orbital). Methyl substituents on the alkene are normally expected to enhance the rates of electrophilic processes, by making easier the transfer of the C=C  $\pi$  electrons. However, in this case the reaction rate constants are all virtually at their upper collisional limits. Thus, the lack of a methyl effect is not in conflict with this view.

The small negative activation energies for the SiH<sub>2</sub> additions are consistent with expectations for normal association reactions<sup>33,34</sup> such as those of radical recombination, for which rate constants are often written with a *T*<sup>-*n*</sup> temperature dependence. In this work *n* would have values of ca. 0.6 (reaction 3), 0.7 (reaction 4) and 0.8 (reaction 1), which are within the normal range. Thus, they do not need to imply the intermediacy of a complex such as that thought to be involved in the SiH<sub>2</sub> + SiH<sub>4</sub> reaction.<sup>24</sup> However, the much more negative activation energy (-8.5 kJ mol<sup>-1</sup>) for SiMe<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> allied to the significantly lower *A* factor (Table 12) suggests a different picture for SiMe<sub>2</sub> additions. As discussed by Baggott et al.,<sup>19</sup> there is strong evidence for steric inhibition by the methyl groups in SiMe<sub>2</sub>, in support of the sideways (C<sub>s</sub> symmetry) approach of the silylene to the alkene as indicated by theory.<sup>32</sup> There is also positive evidence that for SiMe<sub>2</sub> additions,<sup>19</sup> unlike for SiH<sub>2</sub> additions, the rates are strongly enhanced by methyl substituent effects in the alkenes. Such a picture points to a much tighter effective transition state for addition of SiMe<sub>2</sub> than for SiH<sub>2</sub>. This may be explicable in terms of an entropy bottleneck as has been proposed for halocarbene addition reactions by Houk and colleagues,<sup>35</sup> but it is also suggestive of an intermediate complex involvement as proposed for the silylene Si-H insertion reactions.<sup>22</sup> Ab initio theoretical studies are planned to explore this possibility.

In this connection, the study by Berry<sup>17</sup> of the kinetics of decomposition of hexamethylsilirane (giving SiMe<sub>2</sub> + C<sub>2</sub>Me<sub>4</sub>)

yielded an  $A$  factor of  $10^{15.7} \text{ s}^{-1}$ . This is quite close to the value estimated for reaction  $-5$  in Table 4, and by the principle of microscopic reversibility, indicates that for the addition reaction of  $\text{SiMe}_2 + \text{C}_2\text{Me}_4$  the same tighter effective transition state applies as for reaction 5, as we would expect for an  $\text{SiMe}_2$  addition process as a result of this and previous work.<sup>19</sup> In addition, the loose transition states found here (even for  $\text{SiMe}_2$  addition) are not in conflict with long known, concerted, stereospecific nature of the silylene addition process.<sup>16,36</sup>

**RRKM Calculations, Ab Initio Calculations, and Silirane Strain Energies.** The reasonable fit of the RRKM calculations to the pressure dependencies of the experimental rate constants lends weight to the conclusion that the addition reactions 3, 4, and 5 investigated here are all straightforward third-body assisted association processes. The occurrence of side reactions, such as those leading to alkenylsilane formation, would have altered the shapes of the observed pressure-dependence curves and thus worsened the fitting, although a small contribution of side reaction might pass unnoticed. This is consistent with our earlier finding of the absence of vinylsilane as a product in the  $\text{SiH}_2 + \text{C}_2\text{H}_4$  system.<sup>7</sup> To judge arguments based on the energetics of these reactions, the question of uncertainties arising from other causes needs some consideration. The  $A$  factors for the silirane decompositions are almost certainly reliable within a factor of  $10^{\pm 0.5}$ , because they depend on reliable entropy estimates and the measured addition  $A$  factors of this study with their very small uncertainties. A check showed that an error of  $10^{0.5}$  in  $A$  factor, translated into an appropriately modified transition state vibrational assignment, could be approximately compensated for by an alteration of  $E_o$  by ca.  $10 \text{ kJ mol}^{-1}$ . The incorporation of variational character into the modeling of the transition state reflects the need for transition state “tightening” as the temperature is increased, which arises naturally from the parametrization of the model. Uncertainties over this are not a major source of error and are anyway incorporated in those of the  $A$  factors employed. The remaining uncertainty is that of the weak collisional stabilization model. This is based on reasonable average energy removal parameters for  $\text{SF}_6$ .  $\text{SF}_6$  was in fact chosen as the bath gas because of its relatively efficient collider characteristics (thus keeping this source of uncertainty to a minimum). Our use of a stepladder model with an average energy removal value,  $\langle \Delta E \rangle_{\text{down}}$  of  $9.6 \text{ kJ mol}^{-1}$ , was based on previous RRKM fitting to  $\text{SiH}_2$  reaction pressure dependencies.<sup>7,24</sup> Although this cannot be independently verified here, variation within a reasonable range only affects the choice of the  $E_o$  value used for fitting by ca.  $\pm 4 \text{ kJ mol}^{-1}$ . Our conclusion is that overall the  $E_o$  values, and the consequent  $\Delta H^\circ$  values, are unlikely to be in error by more than  $\pm 12 \text{ kJ mol}^{-1}$  and because the  $E_o$  value for each reaction is common to all temperatures, i.e., the fits are based on 5 temperatures together and not just one, the probable error is less than this. The greatest uncertainty attaches to reaction 5 because it has the least pressure dependence.

It is clear then, that the present modeling exercise yields values for the enthalpies of extrusion of silylenes which are dependent on the degree and position of methyl substitution. It was because of this rather unexpected variation that we undertook the ab initio calculations, the results of which are compared with the RRKM-derived values in Table 11. The agreement is excellent for reactions 1, 3, and 4, but not so good for reaction 5, but nevertheless the G2(MP2,SVP) values support the general trend of reduction in  $-\Delta H^\circ$  with methyl group substitution. It seems, therefore, that there can be little doubt over this finding, which helps significantly to resolve the long-

**TABLE 13: Enthalpies of Formation and Strain Energies of Siliranes ( $\text{kJ mol}^{-1}$ )**

silirane	$\Delta H^\circ$	$\Delta H_f^\circ$ (est.) <sup>a</sup>	$\Delta H_f^\circ$ (addy.) <sup>b</sup>	strain energy
	201	124	-43	167
	176	117	-73	190
	165	91	-105	196
	152	35	-181	216

<sup>a</sup> Estimated from the results of this work; see text. <sup>b</sup> Strain-free value; estimated via group additivity.<sup>29,30,37,38</sup>

standing, apparent discrepancy between the “low” activation energy ( $130 \text{ kJ mol}^{-1}$ ) for hexamethylsilirane decomposition<sup>17</sup> and the “high” value ( $195 \text{ kJ mol}^{-1}$ ) for parent silirane itself.<sup>7</sup> It is evidently an effect of methyl substitution. This origin of this effect must be a variation of strain energy within the various siliranes. To work out the strain energies the values of  $\Delta H_f^\circ$ - (silirane) were first evaluated via

$$\Delta H_f^\circ(\text{silirane}) = \Delta H_f^\circ(\text{silylene}) + \Delta H_f^\circ(\text{alkene}) - \Delta H^\circ(\text{reaction})$$

For this purpose and for simplicity, only the RRKM-derived (“experimental”) values for  $\Delta H^\circ$  (reaction) were used. The strain energies were then obtained by comparison with estimates of strain-free  $\Delta H_f^\circ$  values obtained via Benson’s group additivity method.<sup>30</sup> The group contributions were taken from Benson’s book<sup>29</sup> and our own evaluation of values for organosilicon compounds.<sup>37,38</sup> The resulting values from this and our previous work<sup>7</sup> are shown in Table 13. This clearly shows the trend of increasing ring strain with methyl substitution which is significant even allowing for some uncertainties deriving from the RRKM calculations. This analysis was also applied (with approximations) to the hexamethylsilirane pyrolysis result<sup>17</sup> and yielded a value for the strain energy of ca.  $230 \text{ kJ mol}^{-1}$ , even larger than any of the values in Table 13. Other work which indirectly adds support is the theoretical study by Gordon and Nelson<sup>39</sup> of the energetics of addition of  $\text{SiCl}_2$  and  $\text{SiF}_2$  to  $\text{C}_2\text{H}_4$ . The calculations indicate, among other things, that the two ring products, 1,1-dichlorosilirane, and 1,1-difluorosilirane, possess ring strain energies of ca.  $230$  and ca.  $250 \text{ kJ mol}^{-1}$ , respectively, indicating that electronegative substituents on the silicon atom increase the strain of the silirane ring.

It is not difficult to understand that these latter siliranes should be more strained because they involve the addition to the alkene of the highly stabilized silylenes,  $\text{SiCl}_2$  and  $\text{SiF}_2$ . Walsh has quantified this stabilization via the quantity DSSE (divalent state stabilization energy)<sup>40–42</sup> and recently Becerra and Walsh have updated the values for various silylenes.<sup>38</sup> The values of relevance to this work are shown in Table 14. It can be seen that there is a reasonable correlation between DSSE and the related silirane ring strain. This is an easily rationalized result, because clearly in order for the silylene to form the two Si–C ring bonds during addition it has to overcome the DSSE to be in a state ready for bonding. It is understandable, therefore, that methyl groups at the silicon position should increase strain, because, as we<sup>37,38,43</sup> and others<sup>44</sup> have argued before, methyl

**TABLE 14: Enthalpies of Formation and DSSE Values<sup>a</sup> for Silylenes<sup>b</sup> (kJ mol<sup>-1</sup>)**

silylene	$\Delta H_f^\circ$	DSSE
SiH <sub>2</sub>	273 ± 2	94 ± 4
SiMe <sub>2</sub>	135 ± 8	128 ± 11
SiCl <sub>2</sub>	-169 ± 3	188 ± 10
SiF <sub>2</sub>	-638 ± 6	259 ± 8

<sup>a</sup> Divalent state stabilization energy. <sup>b</sup> From ref 38.

acts as an electronegative (electron-withdrawing) substituent. What is less easy to see is why methyl groups at the carbon positions should increase strain in siliranes. It is generally accepted that ring strain enthalpies in cyclopropanes are little affected by methyl substitution as evidenced by the very minor changes in activation energies for thermal isomerization.<sup>45,46</sup> The small changes that do occur are readily explained by energy changes in the biradical intermediates involved without invoking any change in strain enthalpies.<sup>47</sup> Clearly, the presence of a silicon atom in a three-membered ring can perturb substituents at positions other than that of the silicon in unexpected ways. We are continuing to investigate this phenomenon experimentally with both siliranes and silirenes,<sup>48</sup> as well as to seek a deeper understanding of it through molecular orbital calculations.<sup>49</sup>

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