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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Time-resolved studies of the title reactions have been carried out over the pressure range 1—100 Torr (in SF$_6$ bath gas) and at temperatures in the range 293—600 K, using laser flash photolysis techniques to generate and monitor the silylenes, SiH$_2$ and 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: SiH$_2$ + C$_3$H$_6$, log(\( \Lambda \)/cm$^3$ molecule$^{-1}$ s$^{-1}$) = $-9.79 \pm 0.03$, $E_a$ (kJ mol$^{-1}$) = $-1.9 \pm 0.3$; SiH$_2$ + C$_4$H$_8$, log(\( \Lambda \)/cm$^3$ molecule$^{-1}$ s$^{-1}$) = $-9.91 \pm 0.04$, $E_a$ (kJ mol$^{-1}$) = $-2.5 \pm 0.3$; SiMe$_2$ + C$_3$H$_6$, log(\( \Lambda \)/cm$^3$ molecule$^{-1}$ s$^{-1}$) = $-12.12 \pm 0.02$, $E_a$ (kJ mol$^{-1}$) = $-8.5 \pm 0.2$. These parameters are consistent with fast, nearly collision-controlled processes for SiH$_2$ but a tighter transition state for 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 kJ mol$^{-1}$ for 2-methyl-, 2,2-dimethyl-, and 1,1-dimethylsilirane, respectively. Compared to the strain enthalpy of 167 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 C=C and C≡C bonds.$^{1,2}$ 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.$^{1-3}$ A significant number of these have been carried out in our own laboratories, among which are the prototype addition reactions:$^{6-9}$

\[ \text{SiH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{Si} + \text{CH}_2 \]  

(1)

\[ \text{SiH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{Si} + \text{CH} \]  

(2)

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, $E_o(\sim 1)$, consistent with $\Delta H^\circ(\sim 201$ kJ mol$^{-1}$), $\Delta H^\circ$(silirane) = 124 ± 12 kJ mol$^{-1}$, and a strain energy$^{10}$ of ca. 167 kJ mol$^{-1}$. These figures are supported by theoretical calculations.$^{11-13}$ 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.$^{14-16}$ There are very few examples of rate studies of decomposition of substituted siliranes,$^{14-17}$ and only one, to our knowledge, for which Arrhenius parameters have been determined. This is the
decomposition of hexamethyldisilirane to give SiMe2 + C2M4, which has a measured activation energy of 130 kJ mol⁻¹ (corresponding to a strain energy of ca. 230 kJ mol⁻¹). 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:

\[
\begin{align*}
\text{SiH}_2 + \text{C}_2\text{H}_6 & \rightarrow \text{H}_2\text{Si} + \text{CHMe} \quad (3) \\
\text{SiH}_2 + \text{iC}_2\text{H}_6 & \rightarrow \text{H}_2\text{Si} + \text{CMe}_2 \quad (4) \\
\text{SiMe}_2 + \text{C}_2\text{H}_4 & \rightarrow \text{Me}_2\text{Si} + \text{CH}_2 \quad (5)
\end{align*}
\]

For the reaction systems investigated here there is very little previous kinetic data. Chu, Beach, and Jasinski obtained a value of \((1.2 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\) for \(k_2\) in 5 Torr He at room temperature and Baggott et al. obtained \((2.21 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\) for \(k_3\), also at room temperature. Unpublished work by Blitz shows that reaction 5 has a negative activation energy. Preliminary reports of the results of the present experimental work have appeared in recent reviews. 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. 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 exciplex 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 spectrosil 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, \(k_{obs}\), for removal of SiH2 and SiMe2 in the presence of known partial pressures of substrate gas.

The photoprecursors for the silylenes were phenylsilane (PhSiH3) for SiH2 and octamethyltrisilirane (OMTS) for SiMe2. The monitoring lasers were a CW argon ion laser (Coherent Innova 90–5) for SiMe2 and a single mode dye laser (Coherent 699-21) pumped by the Ar ion laser for SiH2. Both silylenes were detected via absorption in their strong \(A^1\leftarrow X^1\Pi\) absorption bands, SiMe2 at 457.9 nm and SiH2 at 579.39 nm, a strong vibration–rotation transition.

Gas mixtures for photolysis were made up containing a small pressure of precursor (PhSiH3 between 2 and 15 mTorr; OMTS between 30 and 200 mTorr), varying pressures of substrate (C2H4 up to 250 mTorr; i-C3H8 up to 300 mTorr; C4H4 up to 9.8 Torr) together with inert diluent (sulfur hexafluoride, SF6) 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. PhSiH3 (99.9%) was obtained from Ventron-Alfa (Pettrach). Ethene (99.8%), propene (99.9%), and isobutene (99.9%) were all chemically pure (CP) grade (Matheson). SF6 (no GC-detectable impurities) was from Cambigian Gases.

No attempts were made to search for the silirane products of these reactions by GC, because previous work 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, a refinement of the original G2 method developed by Pople and colleagues. 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, \(k_{obs}\), were not dependent on the exciplex 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 \(k_{obs}\) (10 shot averages) showed no effective depletion of reactants in any of the systems. The sensitivity of detection of SiH2 or SiMe2 was high but decreased with increasing temperature. Therefore, increasing quantities of precursors (PhSiH3 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 \(k_{obs}\) 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 (SF6 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
nature of the kinetics. In addition to these experiments, another set of runs was carried out at each temperature, in which the total pressure (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 $k_{	ext{obs}}$ with substrate pressure. To keep errors to a minimum, sufficient substrate was used to ensure $k_{	ext{obs}}$ values in the range $(2–3) \times 10^5$ 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. For the SiH$_2$ studies, a range of total pressure of 1–100 Torr was possible, but for SiMe$_2$ + C$_2$H$_4$ the pressure range was limited to 3–100 Torr because at least 3 Torr of C$_2$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 SiH$_2$ + C$_3$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. ±10%. Just as with our earlier study$^7$ of SiH$_2$ + C$_2$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 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 SiH$_2$ + i-C$_4$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
shown in the figure, are probably ca. ±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

\[
\log(k_4^\infty) = (-9.91 \pm 0.04) + (2.45 \pm 0.30 \text{ kJ mol}^{-1})/RT \ln 10
\]

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

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

<table>
<thead>
<tr>
<th>( T \text{ (K)} )</th>
<th>( P_T = 10 \text{ Torr} )</th>
<th>( P_T = \infty^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>294</td>
<td>3.09 ± 0.10</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>362</td>
<td>2.40 ± 0.15</td>
<td>2.9 ± 0.25</td>
</tr>
<tr>
<td>414</td>
<td>1.55 ± 0.14</td>
<td>2.5 ± 0.2</td>
</tr>
<tr>
<td>494</td>
<td>0.95 ± 0.15</td>
<td>2.3 ± 0.5</td>
</tr>
<tr>
<td>600</td>
<td>0.36 ± 0.12</td>
<td>1.9 ± 0.4</td>
</tr>
</tbody>
</table>

* Obtained by extrapolation; see text.

---

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

<table>
<thead>
<tr>
<th>( T \text{ (K)} )</th>
<th>( P_T = 10 \text{ Torr} )</th>
<th>( P_T = \infty^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.49 ± 0.16</td>
<td>2.45 ± 0.25</td>
</tr>
<tr>
<td>368</td>
<td>1.36 ± 0.15</td>
<td>1.20 ± 0.18</td>
</tr>
<tr>
<td>426</td>
<td>0.72 ± 0.11</td>
<td>0.81 ± 0.14</td>
</tr>
<tr>
<td>505</td>
<td>0.47 ± 0.10</td>
<td>0.59 ± 0.08</td>
</tr>
<tr>
<td>600</td>
<td>0.21 ± 0.02</td>
<td>0.42 ± 0.12</td>
</tr>
</tbody>
</table>

* Obtained by extrapolation; see text.

**Kinetics of SiMe\(_2\) + C\(_2\)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 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 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. ±10%. Rate constants for reaction 5 were found to be almost pressure independent at
Pressure dependence of second-order rate constants for SiMe₂ + C₂H₆ at different temperatures: (●) 293 K, (○) 368 K, (▲) 426 K, (☐) 505 K, (☒) 600 K. Solid lines are RRKM theoretical fits.

The 10 Torr values of \( k_5^\text{∞} \) 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 as found previously 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 of the pressure dependencies of the unimolecular decompositions of the appropriate silirane molecules, viz 2-methyl-silirane, 2,2-dimethylsilirane, and 1,1-dimethylsilirane.

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( T (\text{K}) )</th>
<th>( \Delta S^\circ (\text{J} \text{K}^{-1} \text{mol}^{-1}) )</th>
<th>( A \text{ factors; } \log(k (\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1})) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(−3,3)</td>
<td>294</td>
<td>17.81</td>
<td>298</td>
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<td></td>
<td>359</td>
<td>17.71</td>
<td>362</td>
</tr>
<tr>
<td></td>
<td>414</td>
<td>17.62</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td>464</td>
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<td>494</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>17.43</td>
<td>600</td>
</tr>
<tr>
<td>(−4,4)</td>
<td>300</td>
<td>159.5</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>159.2</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>157.4</td>
<td>426</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>155.5</td>
<td>505</td>
</tr>
<tr>
<td>(−5,5)</td>
<td>294</td>
<td>159.5</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>359</td>
<td>158.8</td>
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<td>157.4</td>
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<td>464</td>
<td>155.5</td>
<td>505</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>153.8</td>
<td>600</td>
</tr>
</tbody>
</table>

* Standard state = 1 bar. * For derivation see text.

First, \( \Delta S^\circ \) values were estimated for reactions (−3,3), (−4,4), and (−5,5) based on the known \( \Delta S^\circ \) values 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.

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 \( A_d \) and \( A_a \) 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 \( A_d \) 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 \( A_d \) 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, in particular for silirane itself.

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 of reaction (−1,1). At each temperature an initial approximate (eyeball) estimate of the \( k^\circ \) 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 \( k^\circ \) 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 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 for silirane decomposition itself, viz

\[
\text{SiH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{Si} + \text{SiH}_2 \quad (−1,1)
\]
but we believe it will not lead to serious errors. However, we effects (angular momentum conservation problems). This is an changes in overall moments of inertia and adiabatic rotational the decomposing silirane molecules do not lead to significant

The majority are (10% or less, the worst case being

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, treated as low wavenumber vibrations and left unchanged important provided the entropies of activation are matched. 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

estimated uncertainties in $k^*$ values are shown in the tables. The majority are ±10% or less, the worst case being ±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, treated as low wavenumber vibrations and left unchanged important provided the entropies of activation are matched. 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 10: Temperature Dependent Parameters Used in RRKM Calculations for 1,1-dimethylsilirane Decomposition

<table>
<thead>
<tr>
<th>T(K)</th>
<th>293</th>
<th>368</th>
<th>426</th>
<th>505</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>transition state</td>
<td>91 (1)</td>
<td>95 (1)</td>
<td>100 (1)</td>
<td>100 (2)</td>
<td>100 (1)</td>
</tr>
<tr>
<td>wavenumbers (cm⁻¹)</td>
<td>70 (1)</td>
<td>75 (1)</td>
<td>80 (1)</td>
<td>62 (1)</td>
<td>89 (1)</td>
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<tr>
<td></td>
<td>47 (1)</td>
<td>55 (2)</td>
<td>60 (1)</td>
<td>53 (1)</td>
<td>80 (1)</td>
</tr>
<tr>
<td></td>
<td>40 (1)</td>
<td>46 (1)</td>
<td>50 (1)</td>
<td>75 (1)</td>
<td></td>
</tr>
<tr>
<td>E_a (kJ mol⁻¹)</td>
<td>136.1</td>
<td>136.1</td>
<td>136.1</td>
<td>136.1</td>
<td>136.1</td>
</tr>
<tr>
<td>ΔH° (kJ mol⁻¹)</td>
<td>152.1</td>
<td>153.1</td>
<td>153.7</td>
<td>154.4</td>
<td>155.1</td>
</tr>
<tr>
<td>Z_n (10⁻¹⁰ cm⁻¹ molecule⁻¹ s⁻¹)</td>
<td>4.56</td>
<td>4.72</td>
<td>4.83</td>
<td>4.98</td>
<td>5.15</td>
</tr>
</tbody>
</table>

TABLE 11: G2(MP2,SVP) Energies and Enthalpies (kJ mol⁻¹) for Reactions 1 and 3–5

<table>
<thead>
<tr>
<th>reactants</th>
<th>−ΔU° (0 K)</th>
<th>−ΔH° (0 K)</th>
<th>−ΔH° (298 K)</th>
<th>−ΔH° (298 K)</th>
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<tbody>
<tr>
<td>SiH₂ + C₂H₆</td>
<td>213</td>
<td>195</td>
<td>203</td>
<td>201</td>
</tr>
<tr>
<td>SiH₂ + C₃H₆</td>
<td>183</td>
<td>166</td>
<td>173</td>
<td>176</td>
</tr>
<tr>
<td>SiH₂ + C₄H₁₀</td>
<td>179</td>
<td>163</td>
<td>169</td>
<td>165</td>
</tr>
<tr>
<td>SiMe₂ + C₂H₄</td>
<td>192</td>
<td>178</td>
<td>183</td>
<td>152</td>
</tr>
</tbody>
</table>

*Experimental values.

TABLE 12: Arrhenius Parameters for Silylene Addition Reactions

<table>
<thead>
<tr>
<th>reactants</th>
<th>log(A° (cm³ molecule⁻¹ s⁻¹))</th>
<th>E_a (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₂ + C₂H₆</td>
<td>−9.97 ± 0.03</td>
<td>−2.9 ± 0.2</td>
</tr>
<tr>
<td>SiH₂ + C₃H₆</td>
<td>−9.79 ± 0.05</td>
<td>−1.9 ± 0.3</td>
</tr>
<tr>
<td>SiH₂ + C₄H₁₀</td>
<td>−9.91 ± 0.04</td>
<td>−2.45 ± 0.3</td>
</tr>
<tr>
<td>SiMe₂ + C₂H₄</td>
<td>−12.12 ± 0.02</td>
<td>−8.5 ± 0.2</td>
</tr>
</tbody>
</table>

all reactions, by analogy with that found for silirane,⁷ although variations within the range 8.4–12.0 kJ mol⁻¹ 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_a 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_a values were converted to E_a by addition of the thermal energy differences of each molecule and its transition state, and finally into ΔH° via ΔH° = E_a − E_a + RT. The resulting values of ΔH° 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 −ΔU° and −ΔH° 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 SiH₂ + C₂H₆.⁷ 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 SiH₂ addition process, the Arrhenius parameters are all extremely similar and indeed virtually identical within experimental error.

Note that in our review articles⁴,⁵ the cited values for reaction 4 were slightly different (log(A (cm³ molecule⁻¹ s⁻¹)) = −10.38 and E_a = −5.1 kJ mol⁻¹). During preparation of this paper, a check of the data revealed a slightly erroneous extrapolation in the original evaluation.⁴,⁵

Comparison with earlier work shows good consistency. For reaction 3, Chu, Beach, and Jasinski¹⁸ obtained k₄ = [(1.2 ± 0.1) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ in 5 Torr He at room temperature. Our result in 5 Torr SF₆ gives k₄ = [2.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (by interpolation). Because k₄ is into its pressure-dependent region and He is a weaker collision partner than SF₆, this is reasonable agreement. There are no previous studies of reaction 4. For reaction 5, Baggott et al.¹⁹ obtained k₅ = [(2.21 ± 0.12) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at room temperature. This is in reasonable agreement with the value of (2.45 ± 0.25) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ obtained here. The data found by Blitz²⁰ between 295 and 588 K showed a decrease of k₅ 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 SiH₂ addition process (at infinite pressure). Although the rate constants at 298 K follow the trend k₁ > k₂ > k₃, 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 SiH₂ addition process,⁷ supported by theory,³² is of a barrierless reaction involving an initial π attack (“electrophilic phase” donation of C=C π electrons into the Si 3p-orbital), followed by σ attack (“nucleophilic phase” donation of the silicon lone pair electrons into the C=C antibonding π* 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 π 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 SiH₂ additions are consistent with expectations for normal association reactions³³,³⁴ such as those of radical recombination, for which rate constants are often written with a factor of 8.5 kJ mol⁻¹ for SiMe₂ + C₂H₄ allied to the significantly lower A factor (Table 12) suggests a different picture for SiMe₂ additions. As discussed by Baggott et al.,¹⁹ there is strong evidence for steric inhibition by the methyl groups in SiMe₂, in support of the sideways (C₃ symmetry) approach of the silylene to the alkene as indicated by theory.³² There is also positive evidence that for SiMe₂ additions,¹⁸ unlike for SiH₂ additions, the rates are strongly enhanced by methyl substituent effects in the alkene. Such a picture points to a much tighter effective transition state for addition of SiMe₂ than for SiH₂. This may be explicable in terms of an entropy bottleneck as has been proposed for halocarbene addition reactions by Houk and colleagues,³⁵ but it is also suggestive of an intermediate complex involvement as proposed for the silylene Si–H insertion reactions.³² Ab initio theoretical studies are planned to explore this possibility.

In this connection, the study by Berry¹⁷ of the kinetics of decomposition of hexamethylsilirane (giving SiMe₂ + C₃Me₄)
yielded an A factor of 10^{15.7} 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 SiMe_2 + C_2Me_4 the same tighter effective transition state applies as for reaction 5, as we would expect for an SiMe_2 addition process as a result of this and previous work. In addition, the loose transition states found here (even for SiMe_2 addition) are not in conflict with long known, concerted, stereospecific nature of the silylene addition process.6,36

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 SiH_2 + C_2H_4 system.7 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^{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 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 SF_6. 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, (ΔE_o)_down of 9.6 kJ mol^{-1}, was based on previous RRKM fitting to SiH_2 reaction pressure dependencies.7,24 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. ±4 kJ mol^{-1}. Our conclusion is that overall the E_o values, and the consequent ΔH^P values, are unlikely to be in error by more than ±12 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 −ΔH^P with methyl group substitution. It seems, therefore, that there can be little doubt over this finding, which helps significantly to resolve the long-standing, apparent discrepancy between the “low” activation energy (130 kJ mol^{-1}) for hexamethyilsilirane decomposition17 and the “high” value (195 kJ mol^{-1}) for parent silirane itself. 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 ΔH^P of (silylene) were first evaluated via

ΔH^P(silirane) = ΔH^P(silylene) + ΔH^P(alkene) − ΔH^P(reaction)

For this purpose and for simplicity, only the RRKM-derived (“experimental”) values for ΔH^P (reaction) were used. The strain energies were then obtained by comparison with estimates of strain-free ΔH^P values obtained via Benson’s group additivity method.30 The group contributions were taken from Benson’s book29 and our own evaluation of values for organosilicon compounds.37,38 The resulting values from this and our previous work 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 hexamethyilsilirane pyrolysis result17 and yielded a value for the strain energy of ca. 230 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 Nelson39 of the energetics of addition of SiCl_2 and SiF_2 to C_2H_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 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, SiCl_2 and SiF_2. Walsh has quantified this stabilization via the quantity DSSE (divalent state stabilization energy)40 and recently Becerra and Walsh have updated the values for various silylenes.38 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 we37,38,43 and others44 have argued before, methyl

<table>
<thead>
<tr>
<th>silirane</th>
<th>ΔH^P</th>
<th>ΔH^P (est.)</th>
<th>ΔH^P (addy.)</th>
<th>strain energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2Si</td>
<td>201</td>
<td>124</td>
<td>−43</td>
<td>167</td>
</tr>
<tr>
<td>CMe2</td>
<td>176</td>
<td>117</td>
<td>−73</td>
<td>190</td>
</tr>
<tr>
<td>H2Si</td>
<td>165</td>
<td>91</td>
<td>−105</td>
<td>196</td>
</tr>
<tr>
<td>CMe2</td>
<td>152</td>
<td>35</td>
<td>−181</td>
<td>216</td>
</tr>
</tbody>
</table>

* Estimated from the results of this work; see text. \(^a\) Strain-free value; estimated via group additivity.29,30,37,38
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. The small changes that do occur are readily explained by energy changes in the biradical intermediates involved without invoking any change in strain enthalpies. 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, as well as to seek a deeper understanding of it through molecular orbital calculations.

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References and Notes

(10) The term strain energy is used here as is common practice, although strictly it should be strain enthalpy.
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