# Thermochemistry and Thermal Decomposition of the Chlorinated Disilanes $\left(\mathrm{Si}_{2} \mathbf{H}_{n} \mathbf{C l}_{6-n}, n=\right.$ 0-6) Studied by ab Initio Molecular Orbital Methods 

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#### Abstract

The thermochemistry and thermal unimolecular decomposition reactions of the chlorinated disilanes have been characterized using ab initio molecular orbital techniques. Silylene, chlorosilylene, dichlorosilylene, and hydrogen elimination reactions and their reverse insertions were considered. Reactant, product, and transition-state geometries and vibrational frequencies were calculated at the MP2/6-31G(d,p) level. Energetics were obtained at the MP2/6-31+G(2df,p), MP4/6-31+G(2df,p), G2(MP2), and/or G2 levels of theory, depending on the number of chlorine atoms in the molecule. In addition to the expected insertion reactions, direct reaction paths for $\mathrm{SiHCl}+\mathrm{SiH}_{n} \mathrm{Cl}_{4-n} \rightleftharpoons \mathrm{SiH}_{2}+\mathrm{SiH}_{n-1} \mathrm{Cl}_{5-n}$ and $\mathrm{SiHCl}+\mathrm{SiH}_{n} \mathrm{Cl}_{4-n} \rightleftharpoons \mathrm{SiCl}_{2}+$ $\mathrm{SiH}_{n+1} \mathrm{Cl}_{3-\mathrm{n}}$ were observed, with energetic barriers lying a few $\mathrm{kcal} / \mathrm{mol}$ above the insertion reactions. To our knowledge, these concerted, two-atom exchange reactions have not previously been observed or predicted. They appear to represent a new type of elementary reaction for these compounds. Heats of formation for the chlorinated disilane reactants and chlorinated silylsilylene products of hydrogen elimination were calculated using isodesmic reactions. Energy barriers and conventional transition state theory rate constants for all of the reactions are presented. These can provide a basis for the construction of a detailed mechanism for the multistep thermal decomposition of the chlorinated silanes, which plays an important role in the chemical vapor deposition of epitaxial silicon from the chlorinated silanes.


## Introduction

The chlorinated silanes, particularly dichlorosilane and trichlorosilane, are used as precursors for the chemical vapor deposition (CVD) of epitaxial silicon. At the high temperatures where this process is carried out, homogeneous decomposition of the precursor molecules can play an important role by generating reactive species that lead to film growth. Secondary reactions can both accelerate the decomposition of the precursor and consume reactive intermediates that could otherwise lead to film growth. SiHCl and $\mathrm{SiCl}_{2}$, products of direct decomposition of the chlorinated silanes, can insert into the parent molecules to give chlorinated disilanes, which then decompose very quickly. This makes possible complex secondary chemistry involving the chlorinated disilanes. For example, dichlorosilane could decompose in a silylene- or chlorosilylene-catalyzed cycle such as

$$
\begin{gathered}
\mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \\
\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2} \\
\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{SiHCl}+\mathrm{H}_{2}
\end{gathered}
$$

This cycle of reactions, and others like it, provide lower energy paths for dichlorosilane decomposition than the corresponding direct reaction $\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SiCl}_{2}+\mathrm{H}_{2}$, which has a significant activation barrier. To understand the importance of such reactions and develop detailed kinetic models for the decomposition of chlorinated silanes, we need rates for the thermal decomposition reactions of the chlorinated disilanes and their reverse reactions, the insertion of $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, and $\mathrm{SiCl}_{2}$ into the chlorinated silanes.

[^0]Theoretical investigations of the thermochemistry and thermal decomposition of silanes and halosilanes have been reviewed by Gordon et al. ${ }^{1}$ The kinetics and mechanisms of silylene reactions have been reviewed by Becerra et al. ${ }^{2}$ and Jasinski et al. ${ }^{3}$ Elimination of silylene from disilane and the reverse insertion reaction have been well studied both experimentally ${ }^{4-9}$ and theoretically. ${ }^{4,5,10-13}$ The insertion reaction is effectively barrierless and exothermic by about $54 \mathrm{kcal} / \mathrm{mol}$. Thermal decomposition reactions of the chlorinated silanes were studied theoretically by Su and Schlegel. ${ }^{14,15}$ In this work we use the same levels of calculation and basis sets as those used by Su and Schlegel, so that consistent thermochemical and kinetic parameters can be obtained. Wittbrodt and Schlegel have recently published higher level calculations for dichlorosilane decomposition. ${ }^{16}$ These results differed only slightly from the previous study. Hay ${ }^{17}$ has recently assessed the use of density functional methods for calculating the thermochemistry of $\mathrm{Si}-$ $\mathrm{H}-\mathrm{Cl}$ compounds and found that while DFT methods were promising, they did not do as well as the high-level conventional methods used here. Ignacio and Schlegel ${ }^{18}$ performed calculations similar to those presented here for the fluorinated disilanes with up to two fluorine atoms. McKean et al. ${ }^{19,20}$ have calculated structures and vibrational frequencies for the chlorinated disilanes with up to three chlorine atoms in conjunction with an experimental study of the infrared spectra of these compounds, but they did not present calculated energies. To our knowledge, there have been no previously published theoretical studies of either the thermochemistry or reactions of the chlorinated disilanes. There is experimental information for the insertion of SiHCl into $\mathrm{SiH}_{4}$ and $\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ at room temperature. ${ }^{21}$ The insertion rate was roughly the same for both reactions and indicated that there is a significant barrier to this insertion. Jenkins et al. ${ }^{22}$ measured relative rates of $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, and $\mathrm{SiCl}_{2}$ elimination from $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ and $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$. They observed comparable rates for competing elimination reactions.

Doncaster and Walsh ${ }^{23}$ investigated the thermal decomposition of $\mathrm{Si}_{2} \mathrm{Cl}_{6}$ and found an activation energy of $49 \mathrm{kcal} / \mathrm{mol}$ for $\mathrm{SiCl}_{2}$ elimination near 600 K .

Based on our knowledge of disilane decomposition, chlorinated silane decomposition, and estimates of the thermochemistry from the sources cited above, there are four possible reactions for the decomposition of a chlorinated disilane. These are elimination of $\mathrm{SiH}_{2}$, elimination of SiHCl , elimination of $\mathrm{SiCl}_{2}$, and 1,1 elimination of $\mathrm{H}_{2}$. Direct cleavage of any of the bonds would be too endothermic to be competitive with these channels, as would elimination of HCl or $\mathrm{Cl}_{2}$. 1,2-Hydrogen elimination from disilane was found to have a high barrier ${ }^{11}$ and be unimportant compared to 1,1 -elimination. This is expected to be true for the chlorinated disilanes as well, so the 1,2 -elimination is not considered here. Preliminary estimates of the thermochemistry were made by assuming that each chlorine substitution results in a constant increment of the heats of formation. In the decomposition direction, $\mathrm{SiH}_{2}$ elimination and $\mathrm{H}_{2}$ elimination are roughly $55 \mathrm{kcal} / \mathrm{mol}$ endothermic, SiHCl elimination is roughly $44 \mathrm{kcal} / \mathrm{mol}$ endothermic, and $\mathrm{SiCl}_{2}$ elimination is roughly $33 \mathrm{kcal} / \mathrm{mol}$ endothermic. However, the order of reactivity of the silylenes is well established as $\mathrm{SiH}_{2}$ $>\mathrm{SiHCl}>\mathrm{SiCl}_{2}$, so we expect the barriers for the reverse reactions to increase from $\mathrm{SiH}_{2}$, which has no barrier for insertion into silane, ${ }^{4}$ to SiHCl , which has a barrier for insertion into silane and dichlorosilane, ${ }^{21}$ to $\mathrm{SiCl}_{2}$. The insertion of $\mathrm{H}_{3} \mathrm{SiSiH}$ into $\mathrm{H}_{2}$ has almost no barrier, so we might expect the corresponding insertions of chlorinated silylsilylenes into hydrogen, the reverse of 1,1 -hydrogen elimination, to also have small barriers. Thus, these four primary decomposition paths could all be competitive with one another, and we investigate all of them, realizing that different reactions could dominate for the different chlorinated disilanes.

## Computational Method

The ab initio molecular orbital calculations presented here were carried out using the GAUSSIAN 94 series of programs. ${ }^{24}$ Geometries were fully optimized using the "tight" convergence criteria at the MP2(full)/6-31G(d,p) level using analytical gradients. Vibrational frequencies were obtained at this same level using analytical second derivatives. The frequency calculations verified that the points located were indeed minima or first-order saddle points with zero or one imaginary frequency, respectively. Energies were calculated using a larger basis set and second-order Møller-Plesset perturbation theory (MP2/6-31+G(2df,p), frozen core) for all of the species considered. For molecules and transition states with three or fewer chlorine atoms, energies were also calculated using fourthorder Møller-Plesset theory (MP4SDTQ/6-31+G(2df,p),frozen core) and at the G2(MP2) ${ }^{25}$ level. Full G2 ${ }^{26}$ energy calculations were performed for those molecules with two or fewer chlorines. The G2 methods approximate a quadratic configuration interaction ${ }^{27}$ calculation at the $\operatorname{QCISD}(\mathrm{T}) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ level by applying basis set corrections additively to a $\operatorname{QCISD}(\mathrm{T}) / 6-$ $311 \mathrm{G}(\mathrm{d}, \mathrm{p})$ calculation. ${ }^{26}$ In the original G2 method, some of these corrections are calculated at the MP4 level, whereas in the modified G2(MP2) method, all of the corrections are calculated at the MP2 level. ${ }^{25}$ In both cases, zero-point energy based on the HF/6-31G(d) frequencies, scaled by 0.8929 , is added to the energy, as is an empirical correction based on the number of paired and unpaired electrons in the molecule. Note that in all of the reactions considered here, all of the electrons remain formally paired, so that this empirical correction in the G2 methods cancels when taking energy differences between reactants and products or transition states.

## Results and Discussion

The total energies for reactants, products, and transition states calculated in this work are given in Table 1. The energies of the chlorinated silanes and silylenes at these levels have been previously published by Su and Schlegel. ${ }^{14}$ Our calculated results are identical with theirs and are presented here only for convenience. We have added the G2(MP2) calculations for these species and the G2 calculations for $\mathrm{SiHCl}_{3}$ and $\mathrm{SiCl}_{4}$. G2 energies for disilane and silylsilylene have also been previously published. ${ }^{28}$ Again, our results are identical. The zero-point energies and thermal energies are calculated from the geometries and unscaled frequencies at the MP2(full)/6-31G(d,p) level in the rigid rotor, harmonic oscillator approximations.

Geometries and Frequencies. Generic representations of a chlorinated silylsilylene and a chlorinated disilane are presented in Figure 1, parts a and b, respectively. The atoms numbered 1 and 2 are silicon for all of the structures considered, whereas those numbered 3 and higher can be either chlorine or hydrogen. The geometric parameters for these structures are given in Table 2. The atom labeling in Table 2 corresponds to the numbering in Figure 1. The geometries are described by bond lengths, bond angles, all relative to the $\mathrm{Si}-\mathrm{Si}$ bond, and dihedral angles about the $\mathrm{Si}-\mathrm{Si}$ bond, relative to the atom numbered 3 in the figure. In all cases, the structure given is that believed to be the lowest energy rotamer, although the other rotamers may be very close in energy to the one shown. There is little change in the geometries with chlorine substitution.

Figure 2 gives generic representations of the four types of transition-state structures considered here. The geometric parameters for these structures are presented in Table 3 and are the same bond lengths and angles used to describe the chlorinated disilanes. Figure 2 a is the transition state for elimination of $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, or $\mathrm{SiCl}_{2}$. The atoms numbered 3-8 can be either hydrogen or chlorine. For some reactions there are multiple rotamers of this structure, obtained by interchanging atoms 3,4 , and 5 . In those cases, only the structure believed to be the lowest energy rotamer is given. Note that there are some reactions where the transition state has $C_{s}$ symmetry. However, there are others where $C_{s}$ symmetry would be possible, including $\mathrm{SiH}_{2}$ elimination from $\mathrm{H}_{3} \mathrm{SiSiH}_{3}$ and $\mathrm{SiCl}_{2}$ elimination from $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$, that have transition states which distort to $C_{1}$ symmetry. There is little change in the geometry of these structures with chlorine substitution. The $\mathrm{Si}-\mathrm{Si}$ distance in the transition state tends to be longest for $\mathrm{SiH}_{2}$ elimination and shortest for $\mathrm{SiCl}_{2}$ elimination. This can be explained by the fact that the reaction endothermicity increases from $\mathrm{SiCl}_{2}$ to SiHCl to $\mathrm{SiH}_{2}$, while the height of the barrier to reaction changes very little. This would lead us to expect that the transition-state location would move closer to the products as we go from $\mathrm{SiCl}_{2}$ to SiHCl to $\mathrm{SiH}_{2}$, and this is what is observed. It is expected that for each of the structures such as Figure 2a, there is a corresponding potential minimum with similar geometry but with the inserting chlorinated silylene further removed from the chlorinated silane. These clusters are known to exist for $\mathrm{SiH}_{2}$ insertion into $\mathrm{SiH}_{4}{ }^{4}$ and for $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, and $\mathrm{SiCl}_{2}$ insertions into $\mathrm{H}_{2}, \mathrm{HCl}$, and $\mathrm{Cl}_{2} .{ }^{15}$ We located such clusters for the insertions of SiHCl into $\mathrm{SiH}_{4}$ and $\mathrm{SiH}_{2}$ into $\mathrm{SiH}_{3} \mathrm{Cl}$, but to conserve limited computational resources did not characterize them with higher level energy calculations. We did not attempt to locate the clusters for reactions with more than one chlorine.

Figure 2b shows the generic geometry for $\mathrm{H}_{2}$ elimination. Atoms 3-6 can be hydrogen or chlorine, but atoms 7 and 8 are always hydrogen. Again, only the lowest energy rotamer is given. The transition-state geometry is almost unaffected by

TABLE 1: Total Energies ${ }^{a}$

|  | $\begin{gathered} \text { MP2 } \\ 6-31 G(\mathrm{~d}, \mathrm{p}) \end{gathered}$ | $\begin{gathered} \text { MP2 } \\ 6-31+\mathrm{G}(2 \mathrm{df}, \mathrm{p}) \end{gathered}$ | MP4 $6-31+G(2 d f, p)$ | G2(MP2) | G2 | ZPE | thermal + ZPE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Stable Molecules |  |  |  |  |  |  |  |
| $\mathrm{H}_{2}$ | $-1.15766$ | -1.157 66 | -1.164 56 | -1.166 36 | $-1.16636$ | 6.589 | 8.070 |
| HCl | -460.215 62 | -460.257 26 | -460.284 61 | -460.331 62 | -460.340 17 | 4.471 | 5.952 |
| $\mathrm{Cl}_{2}$ | -919.19122 | -919.284 23 | -919.334 12 | -919.425 73 | -919.442 21 | 0.781 | 2.383 |
| $\mathrm{SiH}_{2}$ | -290.093 98 | -290.106 22 | -290.134 49 | -290.164 26 | -290.167 71 | 7.763 | 9.558 |
| SiHCl | -749.195 37 | -749.255 01 | -749.300 33 | -749.375 27 | -749.38596 | 5.098 | 7.036 |
| $\mathrm{SiCl}_{2}$ | -1208.301 79 | -1208.409 87 | -1208.472 01 | -1208.592 40 | -1208.610 39 | 1.842 | 4.210 |
| $\mathrm{SiH}_{4}$ | -291.349 86 | -291.36478 | -291.39656 | -291.415 55 | -291.419 07 | 20.565 | 22.462 |
| $\mathrm{SiH}_{3} \mathrm{Cl}$ | -750.434 14 | -750.496 47 | -750.545 32 | -750.610 44 | -750.62181 | 17.307 | 19.408 |
| $\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ | -1209.520 71 | -1209.630 82 | -1209.69686 | -1209.808 94 | $-1209.82818$ | 13.536 | 16.092 |
| $\mathrm{SiHCl}_{3}$ | -1668.60726 | -1668.765 26 | -1668.848 59 | -1669.008 35 | -1669.035 48 | 9.313 | 12.529 |
| $\mathrm{SiCl}_{4}$ | -2127.691 64 | -2127.89726 | -2127.997 99 | -2128.206 00 | -2128.241 13 | 4.809 | 8.794 |
| H3SiSiH | -580.280 05 | -580.308 69 | -580.36181 | -580.410 77 | -580.417 83 | 20.161 | 23.087 |
| $\mathrm{H}_{3} \mathrm{SiSiCl}$ | -1039.378 02 | -1039.455 17 | -1039.525 29 | -1039.620 09 | $-1039.63433$ | 17.024 | 20.429 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}$ | -1039.365 67 | -1039.44196 | -1039.512 03 | -1039.607 87 | -1039.622 54 | 16.582 | 19.915 |
| $\mathrm{H}_{2} \mathrm{ClSiSiCl}$ | -1498.463 66 | -1498.588 52 | -1498.675 58 | -1498.81756 | -1498.839 37 | 13.387 | 17.328 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}$ | -1498.454 22 | -1498.579 31 | -1498.666 04 | -1498.809 38 | -1498.831 50 | 12.877 | 16.822 |
| $\mathrm{HCl}_{2} \mathrm{SiSiCl}$ | -1957.55162 | -1957.724 47 | -1957.828 47 | -1958.018 08 |  | 9.477 | 14.112 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}$ | -1957.543 67 | -1957.715 13 | -1957.819 12 | -1958.010 25 |  | 8.529 | 13.308 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}$ | -2416.640 66 | -2416.860 96 |  |  |  | 5.165 | 10.600 |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3}$ | -581.53462 | -581.564 54 | $-581.62123$ | -581.660 95 | -581.668 09 | 32.245 | 35.314 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ | -1040.61861 | -1040.696 08 | -1040.769 76 | -1040.856 25 | $-1040.87116$ | 28.629 | 32.188 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | -1499.706 11 | -1499.831 29 | -1499.922 00 | -1500.055 98 | $-1500.07868$ | 24.613 | 28.839 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}$ | -1499.702 51 | -1499.827 57 | -1499.918 26 | -1500.05181 | -1500.074 50 | 24.943 | 29.073 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | -1958.789 19 | -1958.962 22 | -1959.069 99 | -1959.25126 |  | 20.884 | 25.697 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$ | -1958.795 11 | -1958.967 73 | -1959.075 52 | -1959.25766 |  | 20.289 | 25.286 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2}$ | -2417.875 77 | -2418.096 92 |  |  |  | 16.765 | 22.305 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | -2417.877 76 | -2418.098 32 |  |  |  | 16.560 | 22.148 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2}$ | -2876.964 23 | -2877.23289 |  |  |  | 12.454 | 18.761 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3}$ | -3336.052 76 | -3336.368 86 |  |  |  | 8.095 | 15.199 |
| Transition States with Structure of Figure 2a |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | -581.454 40 | -581.489 51 | -581.547 61 | -581.590 53 | -581.597 04 | 31.196 | 33.995 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {b }}$ | -1040.535 82 | -1040.61768 | -1040.693 57 | -1040.784 38 | -1040.798 70 | 27.693 | 31.033 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {c }}$ | -1040.524 54 | -1040.61174 | -1040.686 15 | -1040.77520 | -1040.78953 | 27.728 | 31.057 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiHCl}$ | -1040.534 76 | -1040.61784 | -1040.693 09 | -1040.783 30 | -1040.79731 | 27.632 | 30.917 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | -1499.617 37 | -1499.753 08 | -1499.844 16 | -1499.980 03 | -1500.00220 | 23.899 | 27.775 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | -1499.624 42 | -1499.755 17 | -1499.847 12 | -1499.984 36 | -1500.00628 | 23.866 | 27.647 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | -1499.61919 | -1499.749 41 | -1499.842 51 | -1499.98140 | -1500.003 46 | 23.489 | 27.512 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | -1499.614 76 | -1499.750 34 | -1499.841 77 | -1499.977 74 | -1499.999 65 | 23.975 | 27.972 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiCl}_{2}$ | -1499.613 54 | -1499.744 47 | -1499.837 06 | -1499.975 09 | -1499.996 73 | 23.734 | 27.638 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | -1958.697 73 | -1958.881 93 | -1958.990 66 | -1959.175 07 |  | 19.477 | 24.113 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{b}$ | -1958.706 93 | -1958.886 40 | -1958.995 57 | -1959.180 42 |  | 19.761 | 24.276 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{c}$ | -1958.705 78 | -1958.889 97 | -1958.998 02 | -1959.181 17 |  | 20.052 | 24.626 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | -1958.703 66 | -1958.882 31 | -1958.991 56 | -1959.176 90 |  | 19.868 | 24.329 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | -1958.705 17 | -1958.882 81 | -1958.993 25 | -1959.180 27 |  | 19.124 | 23.914 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | -1958.706 86 | -1958.890 69 | -1958.999 12 | -1959.182 76 |  | 19.851 | 24.647 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | -2417.788 11 | -2418.020 74 |  |  |  | 15.698 | 21.037 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | -2417.786 94 | -2418.013 90 |  |  |  | 15.864 | 21.027 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiH}_{2}$ | -2417.777 13 | -2418.009 12 |  |  |  | 14.930 | 20.378 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | -2417.790 73 | -2418.018 11 |  |  |  | 15.455 | 20.747 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | -2417.795 59 | -2418.027 85 |  |  |  | 15.882 | 21.255 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiHCl}$ | -2876.868 88 | -2877.149 21 |  |  |  | 11.153 | 17.317 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{\text {b }}$ | -2876.870 11 | -2877.145 53 |  |  |  | 11.357 | 17.348 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{c}$ | -2876.880 58 | -2877.159 90 |  |  |  | 11.821 | 18.003 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiCl}_{2}$ | -3335.962 19 | -3336.291 02 |  |  |  | 7.187 | 14.110 |
| Transition States with Structure of Figure 2b |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{H}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | -581.440 97 | -581.475 63 | -581.53294 | -581.578 69 | -581.58504 | 29.919 | 32.925 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{H}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | -1040.520 68 | -1040.604 87 | -1040.67899 | -1040.77149 | -1040.785 04 | 26.220 | 29.754 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}+\mathrm{H}_{2}$ | -1040.526 29 | -1040.609 20 | -1040.683 35 | -1040.77596 | -1040.790 00 | 26.164 | 29.697 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{H}_{2} \mathrm{ClSiSiCl}+\mathrm{H}_{2}$ | -1499.605 73 | -1499.738 06 | -1499.828 98 | -1499.96852 | -1499.989 84 | 22.527 | 26.608 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}+\mathrm{H}_{2}$ | -1499.614 25 | -1499.745 24 | -1499.836 26 | -1499.976 57 | -1499.998 26 | 22.121 | 26.317 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{HCl}_{2} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | -1958.69261 | -1958.873 11 | -1958.980 94 | -1959.168 67 |  | 18.318 | 23.138 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | -1958.702 42 | -1958.880 62 | -1958.988 74 | -1959.177 31 |  | 17.782 | 22.730 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{Cl}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | -2417.780 08 | $-2418.00840$ |  |  |  | 14.028 | 19.596 |
| Transition States with Structure of Figure 2c |  |  |  |  |  |  |  |
| $\mathrm{SiH}_{4}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}$ | -1040.509 58 | -1040.59782 | -1040.673 12 | -1040.763 69 | -1040.777 38 | 28.071 | 31.279 |
| $\mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | -1499.599 87 | -1499.73572 | -1499.828 02 | -1499.965 43 | -1499.98686 | 24.547 | 28.191 |
| $\mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiCl}_{2}$ | -1499.604 33 | -1499.74178 | -1499.833 99 | -1499.971 62 | $-1499.99262$ | 24.072 | 28.054 |
| $\mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | -1958.686 48 | -1958.871 41 | -1958.980 80 | -1959.165 17 |  | 20.406 | 24.777 |
| $\mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | -1958.69488 | -1958.879 63 | -1958.988 90 | -1959.173 67 |  | 20.490 | 24.928 |
| $\mathrm{SiHCl}_{3}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiH}_{2}$ | -2417.766 13 | -2418.000 84 |  |  |  | 15.935 | 20.976 |
| $\mathrm{SiHCl}_{3}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | -2417.780 94 | -2418.014 18 |  |  |  | 16.196 | 21.466 |
| $\mathrm{SiCl}_{4}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}$ | $-2876.85891$ | -2877.141 64 |  |  |  | 11.594 | 17.622 |

TABLE 1 (Continued)

|  | $\begin{gathered} \text { MP2 } \\ 6-31 G(\mathrm{~d}, \mathrm{p}) \end{gathered}$ | $\begin{gathered} \text { MP2 } \\ 6-31+\mathrm{G}(2 \mathrm{df}, \mathrm{p}) \\ \hline \end{gathered}$ | MP4 $6-31+G(2 d f, p)$ | G2(MP2) | G2 | ZPE | thermal + ZPE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Transition States with Structure of Figure 2d |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | -581.456 76 | -581.49138 | -581.549 63 | -581.59366 | -581.599 77 | 31.485 | 34.329 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}$ | -1040.53790 | -1040.61944 | -1040.695 23 | -1040.786 60 | -1040.800 66 | 27.827 | 31.109 |

[^1]

Figure 1. Generic molecular geometries. Atoms 1 and 2 are silicon: atoms 3-8 may be hydrogen or chlorine. Bond lengths and angles are given in Table 2.
chlorine substitution. Potential minima with the $\mathrm{H}_{2}$ molecule further removed from the chlorinated silylsilylene are expected to be present for these reactions, analogous to those for insertion of $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, and $\mathrm{SiCl}_{2}$ into $\mathrm{H}_{2}{ }^{15}$ These were located for $\mathrm{H}_{3} \mathrm{SiSiCl}$ and $\mathrm{H}_{2} \mathrm{ClSiSiH}$ insertions into $\mathrm{H}_{2}$. We did not attempt to locate them for the reactions where more than one chlorine atom is present.

Figure 2d shows an alternative geometry for the elimination and insertion of $\mathrm{SiH}_{2}$. For $\mathrm{SiH}_{2}$ insertion into $\mathrm{SiH}_{4}$, this type of geometry has been presented and discussed by several authors. ${ }^{4,5,12}$ It lies approximately $8 \mathrm{kcal} / \mathrm{mol}$ below the separated $\mathrm{SiH}_{2}$ and $\mathrm{SiH}_{4}$. We found that following the minimum energy path from this point toward $\mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ (at the MP2/ 6-31G(d,p) level) leads to a potential minimum of similar geometry but with $\mathrm{SiH}_{2}$ further removed from $\mathrm{SiH}_{4}$. This cluster can presumably form from $\mathrm{SiH}_{2}$ and $\mathrm{SiH}_{4}$ with no barrier. Following the minimum energy path toward disilane leads to another minimum in energy which has $C_{3 v}$ symmetry and corresponds to a complex between a normal $\mathrm{SiH}_{3}$ group and an inverted $\mathrm{SiH}_{3}$ group. This is the structure presented by Becerra et al., ${ }^{4}$ who showed that it can convert to disilane with a very small barrier. Thus, it appears that the insertion of $\mathrm{SiH}_{2}$ into $\mathrm{SiH}_{4}$ proceeding along this path would go first through a structure like that of Figure 2d, then through the $C_{3 v}$ structure and on to disilane. It should be kept in mind that the potential surface in this region is quite flat and the barriers are small, so that the insertion is not tightly constrained to this path, and there may be completely barrierless paths that have not been discovered. With this in mind, we located transition states with structures such as Figure 2d for insertion of $\mathrm{SiH}_{2}$ into the $\mathrm{Si}-\mathrm{H}$
bonds of $\mathrm{SiH}_{4}$ and $\mathrm{SiH}_{3} \mathrm{Cl}$. We were unable to locate corresponding structures for insertion of $\mathrm{SiH}_{2}$ into the $\mathrm{Si}-\mathrm{H}$ bonds of $\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ and $\mathrm{SiHCl}_{3}$. In these cases the potential surface is still very flat near the expected geometry for this structure, but appears not to have a saddle point.

Attempts to locate a structure like that of Figure 2d for insertions of SiHCl and $\mathrm{SiCl}_{2}$ into $\mathrm{Si}-\mathrm{H}$ and $\mathrm{Si}-\mathrm{Cl}$ bonds and for insertions of $\mathrm{SiH}_{2}$ into $\mathrm{Si}-\mathrm{Cl}$ bonds led instead to the structure shown in Figure 2c. In this structure, atom 6 is chlorine and atom 7 is hydrogen. Reaction paths passing through this transition state do not lead to insertion, but instead lead to the concerted four-centered exchange of a hydrogen atom for a chlorine atom between the two silicon centers. This exchange motion is shown clearly when one looks at the normal mode corresponding to the imaginary vibrational frequency of this structure. For the reaction

$$
\mathrm{SiHCl}+\mathrm{SiH}_{4} \rightleftharpoons \mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl}
$$

we followed the minimum energy path at the HF/6-31G(d) level from the structure of Figure 2c in both directions. This path connected to a cluster of SiHCl and $\mathrm{SiH}_{4}$ in one direction and a cluster of $\mathrm{SiH}_{2}$ and $\mathrm{SiH}_{3} \mathrm{Cl}$ in the other, confirming the path of this exchange reaction through the transition structure of Figure 2c. To our knowledge, these concerted, two-atom exchange reactions have not previously been observed or predicted for these compounds. Geometric parameters for the transition states for the eight possible reactions of this type are given in Table 3. Only the lowest energy rotamer of each structure is given. Based on the $\mathrm{Si}-\mathrm{H}$ and $\mathrm{Si}-\mathrm{Cl}$ distances, these appear to be genuinely four-centered structures. Both the hydrogen atom (7) and the chlorine atom (6) are approximately equidistant from the two silicon atoms in this structure. The distances $R(2-6)$ and $R(2-7)$ are given in Table 3 and range from 2.29 to $2.35 \AA$ and 1.58 to $1.66 \AA$, respectively. The corresponding distances to the other silicon atom, $R(1-6)$ and $R(1-7)$, range from 2.28 to $2.41 \AA$ and 1.60 to $1.73 \AA$, respectively. For all of the structures of type 2c the difference between the two $\mathrm{Si}-\mathrm{Cl}$ distances is $0.12 \AA$ or less, and the difference between the two $\mathrm{Si}-\mathrm{H}$ distances is $0.14 \AA$ or less.

Computed vibrational frequencies for the chlorinated disilanes, chlorinated silylsilylenes, and transition states are given in Table 4. There is limited experimental information on these compounds that can be used to estimate a scaling factor for the frequencies. Matching the calculated frequencies to experimental anharmonic frequencies for disilane ${ }^{29}$ requires a mean scaling factor of 0.938 . The $\mathrm{Si}-\mathrm{H}$ stretching frequencies of $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3}, \mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}, \mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$, and $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ would require scaling by a factor of 0.928 to match those measured by McKean et al. ${ }^{19,20}$ Schlegel ${ }^{14}$ suggested a scaling factor of 0.945 for the frequencies of $\mathrm{SiH}_{m} \mathrm{Cl}_{n}$ calculated at the same level, for which a number of comparisons with experimental frequencies were possible. Thus it appears that a factor of $0.93-0.94$ is probably appropriate.
TABLE 2: Parameters of MP2/6-31G(d,p) Optimized Molecular Geometries ${ }^{a}$
 and atoms 4 and 8 are Cl in Figure 1b.


Figure 2. Generic geometries for the four types of transition states considered in this paper. Atoms 1 and 2 are silicon: atoms 3-8 may be hydrogen or chlorine. Bond lengths and angles are given in Table 3.

Heats of Formation. Heats of formation for the chlorinated disilanes and chlorinated silylsilylenes were calculated from the energies given in Table 1 and are presented in Table 5. The heats of formation of the chlorinated disilanes were calculated using the isodesmic reaction

$$
\mathrm{Si}_{2} \mathrm{H}_{6}+\frac{n}{4} \mathrm{SiCl}_{4} \rightarrow \mathrm{Si}_{2} \mathrm{H}_{6-n} \mathrm{Cl}_{n}+\frac{n}{4} \mathrm{SiH}_{4}
$$

For the chlorinated silylsilylenes, the reaction

$$
\mathrm{SiH}_{2}+\mathrm{Si}_{2} \mathrm{H}_{6}+\frac{n}{4} \mathrm{SiCl}_{4} \rightarrow \mathrm{Si}_{2} \mathrm{H}_{4-n} \mathrm{Cl}_{n}+\left(1+\frac{n}{4}\right) \mathrm{SiH}_{4}
$$

was used to compute the heats of formation. Experimental heats of formation for $\mathrm{SiH}_{4},{ }^{30} \mathrm{SiCl}_{4},{ }^{30} \mathrm{Si}_{2} \mathrm{H}_{6},{ }^{31}$ and $\mathrm{SiH}_{2}{ }^{4}$ were used as references. For the results in Table 5, there is very good agreement among all of the levels of theory used, including MP2/6-31G(d,p). This increases our confidence in the results for the more chlorinated species for which MP2/6-31+G(2df,p) calculations were the highest level that could be performed. The heats of formation of $\mathrm{SiH}_{4}$ and $\mathrm{SiCl}_{4}$ are well established and show good agreement between experiment and theory. The heat of formation used for $\mathrm{Si}_{2} \mathrm{H}_{6}(19.1 \mathrm{kcal} / \mathrm{mol})$ is from the CATCH tables. ${ }^{31}$ This differs somewhat from the best theoretical estimates for $\mathrm{Si}_{2} \mathrm{H}_{6},{ }^{28}$ which predict a heat of formation of 16 $\mathrm{kcal} / \mathrm{mol}$. However, the $\Delta H_{\mathrm{f}}{ }^{\circ}$ of $\mathrm{SiH}_{2}$ used as a reference here
TABLE 3：Parameters of MP2／6－31G（d，p）Optimized Transition State Geometries ${ }^{a}$


Transition States with Structure of Figure 2a びひびひびひびひひひひひひびびひびひびひひびび

| iH H H H |
| :---: |
|  |
| H |
| SiSiH H H H ClH |
| SiSiClH H ClH H |
| SiSiClH H H ClH |
| SiSiH ClClH H H |
| SiH H H ClClH |
| SiSiH H H H ClCl |
| iSiClClH ClH |
| SiSiClH ClH ClH |
| SiSiClH H ClClH |
| SiSiClH H H ClCl |
| SiClClClH H H |
| SiH H H ClClCl |
| SiSiClH ClClClH |
| SiSiClClH H ClCl |
| SiSiClClClClH H |
| SiSiClClClH ClH |
| SiSiClH H ClClCl |
| SiSiClClClClClH |
| SiSiClClClH ClCl |
| SiSiH ClClClClCl |
| SiClClClClClCl | $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}{ }^{2}$ $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{b}{ }^{c}{ }^{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{c}$ $\mathrm{H}_{2} \mathrm{CISiSiH} \mathrm{H}_{3} \rightarrow \mathrm{SiH}_{4}+\mathrm{SiHCl}$ $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}_{2} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$

 $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}_{1} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{c}$
 $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ $\xrightarrow{\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}_{2}} \mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$


 $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiHCl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{b}$ $\stackrel{\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{c}}{\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiCl}_{2}}$





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 | Transition States with Structure of Figure 2 b |  |  |  |  |
| :--- | :--- | :--- | :--- | :---: |
| 1.475 | 1.477 | 1.481 | 1.634 | 1.537 | ovion No omo on o jo 엉



 | $\infty$ |
| :--- | :--- |
| + |
| 0 |
| $i$ |
|  |



$$
\begin{array}{ll}
2.690 & 1.464 \\
2.813 & 2.038
\end{array}
$$

## 




TABLE 4: Unscaled MP2/6-31G(d,p) Vibrational Frequencies ${ }^{a}$

| Stable Molecules |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}_{3} \mathrm{SiSiH}$ | 95 | 402 | 409 | 455 | 755 | 925 | 974 | 998 | 2163 | 2293 | 2306 | 2328 |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiCl}$ | 70 | 144 | 397 | 416 | 509 | 547 | 918 | 972 | 986 | 2303 | 2322 | 2324 |  |  |  |  |  |  |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}$ | 136 | 183 | 322 | 391 | 565 | 667 | 739 | 867 | 958 | 2148 | 2304 | 2320 |  |  |  |  |  |  |
| $\mathrm{H}_{2} \mathrm{ClSiSiCl}$ | 44 | 88 | 168 | 356 | 438 | 528 | 563 | 716 | 846 | 968 | 2315 | 2335 |  |  |  |  |  |  |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}$ | 42 | 144 | 190 | 292 | 411 | 526 | 595 | 683 | 763 | 848 | 2165 | 2348 |  |  |  |  |  |  |
| $\mathrm{HCl}_{2} \mathrm{SiSiCl}$ | 22 | 82 | 112 | 142 | 217 | 443 | 535 | 549 | 588 | 773 | 819 | 2348 |  |  |  |  |  |  |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}$ | 30 | 109 | 184 | 184 | 209 | 233 | 365 | 563 | 593 | 600 | 712 | 2185 |  |  |  |  |  |  |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}$ | 11 | 75 | 85 | 141 | 180 | 188 | 236 | 366 | 544 | 573 | 599 | 614 |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3}$ | 144 | 384 | 384 | 460 | 667 | 667 | 901 | 980 | 985 | 985 | 1002 | 1002 | 2318 | 2328 | 2333 | 2333 | 2341 | 2341 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ | 115 | 128 | 372 | 436 | 542 | 571 | 627 | 742 | 861 | 943 | 987 | 988 | 1005 | 2325 | 2339 | 2345 | 2347 | 2355 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | 109 | 121 | 152 | 201 | 414 | 534 | 550 | 567 | 607 | 809 | 841 | 939 | 984 | 987 | 2333 | 2353 | 2356 | 2361 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}$ | 47 | 81 | 165 | 367 | 468 | 560 | 573 | 598 | 712 | 745 | 810 | 913 | 991 | 998 | 2345 | 2349 | 2359 | 2367 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | 39 | 71 | 146 | 156 | 211 | 428 | 517 | 552 | 584 | 607 | 717 | 780 | 838 | 893 | 985 | 2349 | 2365 | 2370 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$ | 109 | 109 | 124 | 188 | 188 | 211 | 383 | 539 | 539 | 592 | 625 | 625 | 927 | 983 | 983 | 2340 | 2363 | 2363 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2}$ | 23 | 64 | 125 | 130 | 165 | 194 | 241 | 455 | 532 | 591 | 602 | 617 | 728 | 826 | 829 | 863 | 2371 | 2372 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | 39 | 66 | 110 | 142 | 186 | 195 | 234 | 386 | 509 | 554 | 604 | 624 | 626 | 727 | 871 | 982 | 2353 | 2373 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2}$ | 27 | 66 | 77 | 132 | 141 | 183 | 210 | 211 | 262 | 388 | 521 | 610 | 613 | 628 | 636 | 806 | 830 | 2372 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3}$ | 28 | 68 | 68 | 130 | 130 | 136 | 184 | 184 | 225 | 225 | 254 | 368 | 484 | 625 | 625 | 637 | 637 | 656 |
| Transition States with Structure of Figure 2a |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | 192i | 197 | 361 | 519 | 617 | 692 | 827 | 911 | 974 | 1018 | 1051 | 1456 | 1652 | 2247 | 2268 | 2296 | 2353 | 2382 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {b }}$ | 64i | 109 | 163 | 403 | 520 | 593 | 620 | 704 | 787 | 942 | 997 | 1026 | 1299 | 2045 | 2179 | 2199 | 2366 | 2418 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{c}$ | 271i | 195 | 250 | 278 | 395 | 608 | 644 | 664 | 763 | 898 | 1017 | 1057 | 1101 | 2253 | 2274 | 2281 | 2341 | 2378 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiHCl}$ | 470i | 112 | 178 | 405 | 550 | 569 | 652 | 765 | 832 | 934 | 967 | 1059 | 1319 | 1673 | 2291 | 2313 | 2333 | 2375 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | 120 i | 76 | 154 | 237 | 432 | 487 | 573 | 605 | 712 | 814 | 900 | 970 | 1075 | 1290 | 1958 | 2029 | 2349 | 2356 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | 332 i | 71 | 114 | 269 | 396 | 479 | 534 | 596 | 732 | 817 | 837 | 900 | 939 | 1243 | 1702 | 2317 | 2357 | 2393 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | 122i | 77 | 164 | 165 | 209 | 506 | 536 | 593 | 648 | 731 | 742 | 905 | 1024 | 1268 | 2086 | 2185 | 2198 | 2392 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | 284i | 70 | 135 | 215 | 271 | 384 | 552 | 622 | 642 | 739 | 831 | 900 | 1044 | 1100 | 2268 | 2294 | 2333 | 2369 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiCl}_{2}$ | 488i | 105 | 155 | 168 | 310 | 443 | 539 | 579 | 612 | 788 | 939 | 961 | 1060 | 1264 | 1658 | 2314 | 2320 | 2388 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | 185i | 89 | 133 | 179 | 222 | 270 | 304 | 441 | 516 | 577 | 580 | 690 | 730 | 909 | 1037 | 2253 | 2276 | 2418 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{b}$ | $254 i$ | 55 | 69 | 163 | 200 | 281 | 477 | 530 | 567 | 612 | 700 | 757 | 826 | 918 | 1361 | 1628 | 2301 | 2379 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{c}$ | 187i | 54 | 122 | 159 | 204 | 279 | 400 | 478 | 501 | 575 | 676 | 817 | 829 | 932 | 962 | 2301 | 2344 | 2393 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | 373 i | 54 | 107 | 123 | 185 | 346 | 462 | 522 | 606 | 627 | 694 | 815 | 897 | 922 | 1069 | 1719 | 2350 | 2399 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | $106 i$ | 76 | 106 | 156 | 187 | 195 | 242 | 479 | 520 | 616 | 627 | 660 | 767 | 1026 | 1217 | 2115 | 2188 | 2201 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | 290i | 61 | 125 | 151 | 179 | 186 | 285 | 378 | 561 | 569 | 642 | 715 | 895 | 1036 | 1093 | 2312 | 2332 | 2368 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | 155i | 47 | 82 | 119 | 164 | 196 | 256 | 264 | 426 | 506 | 556 | 570 | 640 | 708 | 816 | 960 | 2283 | 2388 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | 256 i | 46 | 69 | 110 | 150 | 213 | 250 | 332 | 518 | 562 | 598 | 615 | 652 | 821 | 871 | 1246 | 1643 | 2401 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiH}_{2}$ | $218 i$ | 86 | 112 | 120 | 194 | 223 | 224 | 267 | 288 | 390 | 535 | 558 | 578 | 654 | 682 | 1032 | 2239 | 2261 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | 153i | 54 | 64 | 135 | 169 | 198 | 222 | 260 | 445 | 542 | 570 | 584 | 649 | 737 | 827 | 1460 | 1630 | 2266 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | $224 i$ | 45 | 105 | 138 | 147 | 167 | 224 | 287 | 391 | 462 | 511 | 597 | 605 | 830 | 920 | 949 | 2342 | 2389 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiHCl}$ | 195i | 46 | 64 | 102 | 125 | 172 | 203 | 229 | 232 | 259 | 385 | 524 | 550 | 569 | 614 | 643 | 829 | 2254 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{\text {b }}$ | $263 i$ | 26 | 68 | 98 | 135 | 164 | 185 | 218 | 232 | 326 | 484 | 564 | 602 | 617 | 635 | 743 | 1214 | 1634 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{c}$ | 179i | 52 | 58 | 90 | 120 | 131 | 166 | 177 | 240 | 293 | 393 | 537 | 576 | 596 | 620 | 921 | 928 | 2373 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiCl}_{2}$ | 153 i | 48 | 55 | 84 | 118 | 134 | 159 | 180 | 229 | 230 | 248 | 274 | 375 | 509 | 557 | 593 | 602 | 631 |
| Transition States with Structure of Figure 2b |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{H}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | 1021i | 170 | 358 | 430 | 463 | 617 | 728 | 874 | 945 | 978 | 1017 | 1078 | 1812 | 2167 | 2298 | 2322 | 2334 | 2338 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{H}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | 1041i | 102 | 150 | 321 | 474 | 519 | 570 | 630 | 708 | 940 | 966 | 1012 | 1156 | 1769 | 2020 | 2323 | 2337 | 2345 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}+\mathrm{H}_{2}$ | 982i | 120 | 169 | 357 | 394 | 470 | 562 | 671 | 799 | 875 | 892 | 969 | 1072 | 1818 | 2151 | 2297 | 2334 | 2353 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{H}_{2} \mathrm{ClSiSiCl}+\mathrm{H}_{2}$ | 1048i | 61 | 89 | 200 | 324 | 448 | 523 | 551 | 583 | 704 | 769 | 882 | 967 | 1156 | 1780 | 2025 | 2336 | 2358 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}+\mathrm{H}_{2}$ | 1067i | 116 | 137 | 176 | 220 | 348 | 451 | 558 | 581 | 629 | 819 | 853 | 872 | 1055 | 1817 | 2174 | 2303 | 2363 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{HCl}_{2} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | 1061i | 48 | 76 | 151 | 176 | 223 | 302 | 502 | 525 | 576 | 607 | 699 | 779 | 870 | 1106 | 1750 | 2062 | 2364 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | 1088i | 107 | 129 | 169 | 195 | 203 | 221 | 362 | 397 | 581 | 582 | 603 | 660 | 857 | 1045 | 1822 | 2188 | 2319 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \leftrightarrow \mathrm{Cl}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | 1035i | 41 | 65 | 142 | 150 | 199 | 204 | 227 | 311 | 471 | 534 | 590 | 601 | 632 | 735 | 1103 | 1743 | 2064 |
| Transition States with Structure of Figure 2c |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $\mathrm{SiH}_{4}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}$ | 389i | 178 | 248 | 357 | 361 | 684 | 703 | 752 | 916 | 975 | 1022 | 1125 | 1167 | 1937 | 2187 | 2293 | 2329 | 2401 |
| $\mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | 161 i | 139 | 200 | 272 | 348 | 426 | 533 | 636 | 746 | 788 | 963 | 1023 | 1038 | 1197 | 1919 | 2191 | 2354 | 2399 |
| $\mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiCl}_{2}$ | 380i | 61 | 156 | 183 | 323 | 351 | 494 | 532 | 678 | 908 | 961 | 993 | 1122 | 1185 | 1857 | 2310 | 2341 | 2384 |
| $\mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | 113 i | 87 | 113 | 171 | 216 | 343 | 373 | 507 | 550 | 612 | 766 | 833 | 978 | 993 | 1285 | 1868 | 2205 | 2378 |
| $\mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | $168 i$ | 85 | 107 | 166 | 196 | 328 | 353 | 514 | 531 | 561 | 776 | 887 | 1008 | 1018 | 1250 | 1801 | 2360 | 2392 |
| $\mathrm{SiHCl}_{3}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiCl}_{4}+\mathrm{SiH}_{2}$ | 85 i | 115 | 141 | 166 | 199 | 220 | 238 | 305 | 369 | 495 | 532 | 594 | 629 | 778 | 1027 | 1231 | 1906 | 2199 |
| $\mathrm{SiHCl}_{3}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | 171i | 35 | 53 | 124 | 157 | 174 | 230 | 350 | 380 | 500 | 537 | 622 | 859 | 910 | 943 | 1330 | 1732 | 2392 |
| $\mathrm{SiCl}_{4}+\mathrm{SiHCl} \leftrightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}$ | 156 i | 32 | 55 | 128 | 152 | 167 | 207 | 227 | 232 | 316 | 371 | 490 | 534 | 582 | 636 | 865 | 1345 | 1772 |
| Transition States with Structure of Figure 2d |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \leftrightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | 144i | 105 | 359 | 560 | 665 | 694 | 949 | 965 | 1001 | 1011 | 1077 | 1325 | 1854 | 2160 | 2177 | 2351 | 2375 | 2396 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \leftrightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}$ | 137i | 143 | 222 | 271 | 568 | 582 | 661 | 746 | 862 | 944 | 999 | 1035 | 1443 | 1862 | 2154 | 2193 | 2368 | 2410 |

[^2]was derived from the experimentally established heat of reaction for $\mathrm{Si}_{2} \mathrm{H}_{6}$ decomposition and referenced to the value of 19.1 $\mathrm{kcal} / \mathrm{mol}$ for $\mathrm{Si}_{2} \mathrm{H}_{6} .{ }^{4}$ So, if we changed the value of $\Delta H_{\mathrm{f}}{ }^{\circ}$ for $\mathrm{Si}_{2} \mathrm{H}_{6}$, we would need to make a corresponding change in $\Delta H_{\mathrm{f}}{ }^{\circ}$ for $\mathrm{SiH}_{2}$. The result of this is that the heat of reaction for all
of the reactions considered here is unaffected by the value of $\Delta H_{\mathrm{f}}{ }^{\circ}$ for $\mathrm{Si}_{2} \mathrm{H}_{6}$, provided that the value used for $\mathrm{SiH}_{2}$ is consistent with it.

The heats of formation in Table 5 can be reasonably reproduced by a bond additivity scheme. We can write the heats

TABLE 5: Heats of Formation Calculated Using Isodesmic Reactions ${ }^{a}$

|  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| molecule | MP2 <br> $6-31 G(d, p)$ | MP2 <br> $6-31+G(2 d f, p)$ | MP4 <br> $6-31+G(2 d f, p)$ | G2(MP2) | G2 |

[^3]of formation for the $\mathrm{Si}-\mathrm{H}-\mathrm{Cl}$ compounds as
\[

$$
\begin{aligned}
& \Delta H_{\mathrm{f}}^{\circ}=\Delta H_{\mathrm{Si}-\mathrm{Si}} n_{\mathrm{Si}-\mathrm{Si}}+\Delta H_{\mathrm{Si}-\mathrm{H}} n_{\mathrm{Si}-\mathrm{H}}+\Delta H_{\mathrm{Si}-\mathrm{Cl}} n_{\mathrm{Si}-\mathrm{Cl}}+ \\
& \quad \Delta H_{\mathrm{Si}(\mathrm{~d})-\mathrm{Si}} n_{\mathrm{Si}(\mathrm{~d})-\mathrm{Si}}+\Delta H_{\mathrm{Si}(\mathrm{~d})-\mathrm{H}} n_{\mathrm{Si}(\mathrm{~d})-\mathrm{H}}+\Delta H_{\mathrm{Si}(\mathrm{~d})-\mathrm{Cl}} n_{\mathrm{Si}(\mathrm{~d})-\mathrm{Cl}}
\end{aligned}
$$
\]

where $n_{\mathrm{Si}-\mathrm{Si}}$ is the number of $\mathrm{Si}-\mathrm{Si}$ bonds, $n_{\mathrm{Si}-\mathrm{H}}$ is the number of $\mathrm{Si}-\mathrm{H}$ bonds, $n_{\mathrm{Si}-\mathrm{Cl}}$ is the number of $\mathrm{Si}-\mathrm{Cl}$ bonds, $n_{\mathrm{Si}(\mathrm{d})-\mathrm{Si}}$ is the number of $\mathrm{Si}-\mathrm{Si}$ bonds where one of the silicon atoms is divalent, $n_{\mathrm{Si}(\mathrm{d})-\mathrm{H}}$ is the number of $\mathrm{Si}-\mathrm{H}$ bonds where the silicon atom is divalent, and $n_{\mathrm{Si}(\mathrm{d})-\mathrm{Cl}}$ is the number of $\mathrm{Si}-\mathrm{Cl}$ bonds where the silicon atom is divalent. The $\Delta H$ values are the corresponding increments to the heat of formation. Values of $\Delta H_{\mathrm{Si}-\mathrm{Si}}=6.23 \mathrm{kcal} / \mathrm{mol}, \Delta H_{\mathrm{Si}-\mathrm{H}}=2.50 \mathrm{kcal} / \mathrm{mol}, \Delta H_{\mathrm{Si}-\mathrm{Cl}}$ $=-39.84, \Delta H_{\mathrm{Si}(\mathrm{d})-\mathrm{S}}=29.95 \mathrm{kcal} / \mathrm{mol}, \Delta H_{\mathrm{Si}(\mathrm{d})-\mathrm{H}}=29.67 \mathrm{kcal} /$ mol , and $\Delta H_{\mathrm{Si}(\mathrm{d})-\mathrm{Cl}}=21.66 \mathrm{kcal} / \mathrm{mol}$ were obtained by a leastsquares fit of the above expression to the heats of formation of the compounds in Table 5, plus disilane, the chlorinated silanes $\mathrm{SiH}_{n} \mathrm{Cl}_{4-n}$, and the chlorinated silylenes $\mathrm{SiH}_{n} \mathrm{Cl}_{2-n}$. These parameters fit the heats of formation of the 26 compounds considered to within an average absolute error of $1.1 \mathrm{kcal} / \mathrm{mol}$ and a maximum absolute error of $2.3 \mathrm{kcal} / \mathrm{mol}$. This forms a reasonable basis for a bond additivity scheme that could be used to predict heats of formation for larger $\mathrm{Si}-\mathrm{H}-\mathrm{Cl}$ compounds.

Decomposition Reaction Energetics and Kinetics. The heats of reaction, forward and reverse reaction barriers, and estimated rate parameters at 1000 K for all of the thermal decomposition reactions considered are presented in Table 6. The reverse barriers are obtained by subtracting the calculated energy, including zero-point energy, of the products from that of the transition state. A negative barrier means that the transition structure is lower in energy than the separated products. It is still, of course, higher in energy than the minimum energy cluster between the products. The forward barrier is obtained by adding the reverse barrier to the overall energy change for reaction. This was obtained from the energies of formation of reactants and products at 0 K using the isodesmic reactions presented above. The insertion barriers were more sensitive to the level of calculation than the heats of formation, but are still reasonably consistent from the MP2/6-31+G(2df,p) to the G2 levels. The barriers increase by an average of 0.3 $\mathrm{kcal} / \mathrm{mol}$ from the G2(MP2) to the G2 level, decreasing in only one case. Likewise, the barriers increase by an average of 0.5 $\mathrm{kcal} / \mathrm{mol}$ from the MP4/6-31+G(2df,p) level to the G2 level,
decreasing in only three cases. The barriers increase in all cases from the MP2/6-31+G(2df,p) level to the G2 level, by an average of $1.8 \mathrm{kcal} / \mathrm{mol}$, with the increases ranging from 0.3 to $3.5 \mathrm{kcal} / \mathrm{mol}$. For estimating rate parameters, the barriers at the G2 level were used for compounds with two or fewer chlorines, and the barriers at the G2(MP2) level were used for the compounds with three chlorines. For those with four or more chlorines, the average increase of $1.8 \mathrm{kcal} / \mathrm{mol}$ was added to the barriers at the MP2/6-31+G(2df,p) level. These are the barriers given in the column labeled "best value" in Table 6.

The estimated rate constants, activation energies, and preexponential factors were obtained from conventional transition state theory calculations ${ }^{32}$ treating all vibrations as harmonic oscillators and all rotations as rigid rotors. Improved treatment of internal rotations and low vibrational frequencies, as well as a variational treatment for those reactions with negative calculated barriers, would be required to make more accurate estimates of rate constants, but would go beyond the scope of this paper. Note that ratios of rates of competing reactions, i.e., different decomposition reactions of a single reactant, depend only on the energies and partition functions of the transition states for the competing paths and not those of the reacting molecules. Many of these reactions are likely to be in the pressure dependent falloff regime at conditions of practical interest, so unimolecular rate theory calculations of the pressure and temperature dependence of the reactions are needed to fully characterize them. This also falls outside the scope of this work. Figure 3 gives a diagram of the energetics for the $\mathrm{Si}_{2} \mathrm{H}_{3} \mathrm{Cl}_{3}$ system to illustrate typical results for the various possible reaction paths. Note that for this system, as well as most of the others, the energetic barriers for different reaction paths lie quite close together. The observations below are based on the energetics as presented in Table 5, realizing that relative changes of a few $\mathrm{kcal} / \mathrm{mol}$ in the energetics would change the results significantly. However, these observations still represent the best information that is available at this time for the reactions considered.
$\mathbf{H}_{3} \mathbf{S i S i H}_{3}$ Decomposition. The results for disilane decomposition agree well with the previous studies cited above. Silylene elimination from disilane is predicted to occur via a loose transition state. The saddle points located for both $\mathrm{SiH}_{2}$ elimination geometries lie well below the separated products. The rate parameters in Table 5 are those obtained with the

TABLE 6: Thermal Decomposition Barriers and Rate Parameters ${ }^{a}$

| reaction | $\begin{aligned} & \mathrm{TS} \\ & \text { type } \end{aligned}$ | $\Delta H_{\text {rxn }}$ | reverse barrier |  |  |  |  |  | forward barrier | $k(1000 \mathrm{~K})$ | $\begin{gathered} \log \\ \mathrm{A} \end{gathered}$ | $E_{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\begin{gathered} \text { MP2 } \\ 6-31 G(d, p) \end{gathered}$ | $\begin{gathered} \text { MP2 } \\ 6-31+\mathrm{G}(2 \mathrm{df}, \mathrm{p}) \end{gathered}$ | $\begin{gathered} \text { MP4 } \\ 6-31+\mathrm{G}(2 \mathrm{df}, \mathrm{p}) \end{gathered}$ | G2(MP2) | G2 | best <br> value |  |  |  |  |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | a | 54.3 | -3.8 | -8.8 | -7.5 | -6.7 | -6.4 | -6.44 | 46.7 | 7537 | 14.2 | 47.1 |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{4}+\mathrm{SiH}_{2}$ | d | 54.3 | -5.0 | -9.6 | -8.5 | -8.7 | -8.2 | -8.2 | 44.9 | 28740 | 14.4 | 45.3 |
| $\mathrm{H}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{H}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | b | 56.3 | 1.1 | -2.7 | -1.0 | -1.0 | -0.5 | -0.5 | 53.8 | 430 | 14.7 | 55.0 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {b }}$ | a | 54.2 | -2.2 | -6.8 | -6.0 | -6.1 | -5.8 | -5.8 | 47.5 | 3351 | 14.0 | 48.0 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {c }}$ | a | 54.2 | 4.9 | -3.0 | -1.3 | -0.3 | 0.0 | 0.0 | 53.3 | 32 | 13.3 | 53.9 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiH}_{2}{ }^{\text {b }}$ | d | 54.2 | -3.4 | -7.8 | -6.9 | -7.5 | -7.0 | -7.0 | 46.3 | 4226 | 13.8 | 46.6 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{SiH}_{4}+\mathrm{SiHCl}$ | a | 44.4 | 8.5 | 3.2 | 4.4 | 4.7 | 4.8 | 4.8 | 48.4 | 505 | 13.4 | 48.8 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{H}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | b | 47.8 | 12.0 | 7.6 | 9.4 | 9.4 | 9.8 | 9.8 | 55.7 | 33 | 14.0 | 57.0 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}+\mathrm{H}_{2}$ | b | 55.2 | 1.1 | -3.0 | -1.3 | -1.1 | -0.7 | -0.7 | 52.6 | 396 | 14.4 | 53.9 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | a | 52.2 | 0.9 | -7.5 | -5.4 | -4.3 | -3.9 | -4.0 | 47.4 | 457 | 13.1 | 47.6 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | a | 44.4 | 4.7 | -0.9 | 0.5 | 0.9 | 0.9 | 0.9 | 44.9 | 7737 | 13.8 | 45.3 |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiCl}+\mathrm{H}_{2}$ | b | 46.7 | 12.3 | 7.7 | 9.6 | 9.7 | 10.0 | 10.0 | 54.8 | 81 | 14.2 | 56.0 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiH}_{2}$ | a | 54.7 | -0.6 | -5.6 | -4.8 | -5.2 | -4.8 | -4.8 | 49.3 | 1503 | 14.1 | 49.8 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiHCl}$ | a | 47.0 | 10.8 | 2.3 | 4.0 | 5.0 | 5.1 | 5.1 | 51.7 | 226 | 13.8 | 52.1 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{4}+\mathrm{SiCl}_{2}$ | a | 33.6 | 25.2 | 20.3 | 21.1 | 20.6 | 20.5 | 20.5 | 53.5 | 33 | 13.3 | 53.8 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{3} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}+\mathrm{H}_{2}$ | b | 54.2 | 1.1 | -2.6 | -1.0 | -0.5 | -0.3 | -0.3 | 52.2 | 485 | 14.4 | 53.5 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | a | 52.3 | 4.6 | -4.2 | -2.4 | -1.5 |  | -1.5 | 50.0 | 83 | 13.1 | 50.9 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{b}$ | a | 44.5 | 6.9 | 0.8 | 2.1 | 2.4 |  | 2.4 | 46.6 | 903 | 13.3 | 47.1 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiHCl}^{c}$ | a | 44.5 | 7.9 | -1.2 | 0.9 | 1.9 |  | 2.0 | 46.2 | 1530 | 13.4 | 46.8 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | a | 32.8 | 21.0 | 15.8 | 16.9 | 16.3 |  | 16.3 | 48.8 | 238 | 13.1 | 49.3 |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | b | 45.6 | 12.7 | 7.9 | 9.8 | 9.9 |  | 9.9 | 53.6 | 80 | 13.9 | 54.9 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiH}_{2}$ | a | 56.1 | -0.4 | -5.1 | -4.3 | -4.8 |  | -4.8 | 50.7 | 773 | 14.1 | 51.3 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{SiH}_{3} \mathrm{Cl}+\mathrm{SiCl}_{2}$ | a | 36.6 | 18.9 | 10.5 | 12.1 | 12.6 |  | 12.6 | 49.2 | 1656 | 14.1 | 49.6 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}+\mathrm{H}_{2}$ | b | 54.5 | 2.0 | -2.3 | -0.5 | -0.4 |  | -0.4 | 52.2 | 421 | 14.3 | 53.5 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | a | 44.3 | 10.4 | 1.0 |  |  |  | 2.8 | 46.9 | 2124 | 13.7 | 47.7 |
| $\mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | a | 32.2 | 22.8 | 17.30 |  |  |  | 19.1 | 51.3 | 92 | 13.3 | 51.7 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiCl}_{4}+\mathrm{SiH}_{2}$ | a | 54.6 | 7.7 | -1.2 |  |  |  | 0.7 | 54.5 | 10 | 13.2 | 55.5 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiHCl}$ | a | 45.3 | 8.5 | 2.4 |  |  |  | 4.2 | 49.4 | 420 | 13.5 | 49.8 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{SiH}_{2} \mathrm{Cl}_{2}+\mathrm{SiCl}_{2}$ | a | 33.2 | 17.4 | 8.6 |  |  |  | 10.4 | 43.7 | 12587 | 13.8 | 44.3 |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2}$ | b | 45.1 | 13.7 | 8.7 |  |  |  | 10.5 | 53.7 | 228 | 14.4 | 55.0 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \rightarrow \mathrm{SiCl}_{4}+\mathrm{SiHCl}$ | a | 46.6 | 12.6 | 3.2 |  |  |  | 5.0 | 51.3 | 180 | 13.7 | 52.3 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{\text {b }}$ | a | 33.1 | 24.6 | 18.8 |  |  |  | 20.6 | 53.9 | 27 | 13.3 | 54.3 |
| $\mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2} \rightarrow \mathrm{SiHCl}_{3}+\mathrm{SiCl}_{2}{ }^{\text {c }}$ | a | 33.1 | 18.5 | 10.2 |  |  |  | 12.1 | 45.3 | 7756 | 13.9 | 45.9 |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3} \rightarrow \mathrm{SiCl}_{4}+\mathrm{SiCl}_{2}$ | a | 35.4 | 20.1 | 10.7 |  |  |  | 12.5 | 48.1 | 3095 | 14.2 | 48.8 |

${ }^{a}$ Energies are in $\mathrm{kcal} / \mathrm{mol} . \Delta H_{\mathrm{rxn}}$ is the standard heat of reaction at 298 K calculated from the heats of formation in Table 4 . Forward and reverse reaction barriers at 0 K , including zero-point energy, calculated as described in the text. Transition-state type refers to the structures of Figure 2. Estimated rate parameters are at $1000 \mathrm{~K} . k$ and $A$ are in $\mathrm{s}^{-1}, E_{\mathrm{a}}$ is in $\mathrm{kcal} / \mathrm{mol}$. Entries left blank were not calculated due to computational expense. ${ }^{b}$ Transition state corresponding to insertion into a $\mathrm{Si}-\mathrm{H}$ bond. ${ }^{c}$ Transition state corresponding to insertion into a $\mathrm{Si}-\mathrm{Cl}$ bond.
transition states located at the saddle points. A variational treatment with the transition state located closer to the separated products would be needed to make reasonable rate constant predictions for this reaction over wide temperature ranges. ${ }^{4}$ However, at high enough temperatures, the transition state will tighten until it lies at or near the saddle points located on the potential surface. At sufficiently high temperatures, greater than around 1000 K in this case, tight transition state calculations will then provide reasonable estimates of the rate parameters. The transition state for $\mathrm{H}_{2}$ elimination is predicted to lie 0.5 $\mathrm{kcal} / \mathrm{mol}$ below the separated products, giving an activation energy of about $55 \mathrm{kcal} / \mathrm{mol}$, consistent with shock tube measurements of this reaction. ${ }^{33}$ This reaction is slower than the silylene elimination, but is known to play a role in the mechanism of thermal decomposition of silane. ${ }^{34}$
$\mathbf{H}_{2} \mathbf{C l S i S i H} 3 \mathbf{~ D e c o m p o s i t i o n . ~ C h l o r o d i s i l a n e ~ i s ~ p r e d i c t e d ~ t o ~}$ decompose by $\mathrm{SiH}_{2}$ and SiHCl elimination, with $\mathrm{SiH}_{2}$ elimination being faster. As was the case for disilane, the saddle point on the path for $\mathrm{SiH}_{2}$ elimination via an H atom shift lies below the separated products. At low temperatures, this reaction should occur via a loose transition state with an activation energy near the heat of reaction. At higher temperatures, the transition state will tighten until the activation energy is near $48 \mathrm{kcal} /$ mol and the preexponential drops to near $10^{14} \mathrm{~s}^{-1}$, as predicted by the tight transition state calculations. By contrast, the barrier for $\mathrm{SiH}_{2}$ elimination via a Cl atom shift is essentially isoenergetic with the products. That reaction would therefore proceed through a tight transition state and would be much slower than
the path involving transfer of an H atom. SiHCl elimination is predicted to have an activation energy comparable to the hightemperature activation energy for silylene elimination. Jenkins et al. ${ }^{22}$ found that the ratio of $\mathrm{SiH}_{2}$ elimination to SiHCl elimination was 0.8 at 663 K , based on an analysis of the final products of $\mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ decomposition and reasonable mechanistic assumptions. This is inconsistent with our results, which predict $\mathrm{SiH}_{2}$ elimination to be faster by a factor of at least 5, depending how the loose transition state for $\mathrm{SiH}_{2}$ elimination is treated. An increase of $2-3 \mathrm{kcal} / \mathrm{mol}$ in the activation energy for $\mathrm{SiH}_{2}$ elimination relative to SiHCl elimination would be required to bring our results into agreement with the branching ratio observed by Jenkins et al. It should be noted that their experiments were carried out at reduced pressure and were probably in the unimolecular falloff regime, which may have affected the observed branching ratio. Their pyrolysis experiments also took place in the presence of hot walls, which may have catalyzed reactions that would change the branching ratio or observed final products. Hydrogen elimination is predicted to be slightly slower than SiHCl elimination, with production of $\mathrm{H}_{2} \mathrm{ClSiSiH}$ strongly favored over production of $\mathrm{H}_{3} \mathrm{SiSiCl}$.
$\mathbf{H}_{2} \mathrm{ClSiSiH} \mathbf{2} \mathbf{C l}$ Decomposition. For 1,2-dichlorodisilane, SiHCl elimination is predicted to have an activation energy of $45 \mathrm{kcal} / \mathrm{mol}$ and be faster than $\mathrm{SiH}_{2}$ elimination. Silylene elimination again will be governed by a loose transition state and should show a decreasing activation energy with increasing temperature. $\mathrm{H}_{2}$ elimination is predicted to have an activation


Figure 3. Diagram of energies of $\mathrm{SiH}_{3} \mathrm{Cl}_{3}$ species and saddle points on the paths connecting them. Energies are in $\mathrm{kcal} / \mathrm{mol}$ at 0 K relative to $\mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$. Energies of reaction and barrier heights were calculated as described in the text from the G2(MP2) energies. Transition-state labels (a, b, c) correspond to the transition-state types illustrated in Figure 2.
energy of $56 \mathrm{kcal} / \mathrm{mol}$, making it much slower than the other reactions.
$\mathbf{H C l}_{2} \mathbf{S i S i H}_{3}$ Decomposition. Silylene elimination is predicted to be the fastest reaction, again proceeding through a loose transition state with an activation energy decreasing from nearly the heat of reaction down to $50 \mathrm{kcal} / \mathrm{mol}$ as the temperature is increased. SiHCl and $\mathrm{H}_{2}$ elimination proceed at comparable rates with activation energies of 52 and $53 \mathrm{kcal} /$ mol , respectively. $\mathrm{SiCl}_{2}$ elimination is predicted to be the slowest reaction, with an activation energy near $54 \mathrm{kcal} / \mathrm{mol}$ and a relatively low preexponential factor. These predictions disagree with the observation of Jenkins et al. ${ }^{22}$ that $\mathrm{SiH}_{2}$ and $\mathrm{SiCl}_{2}$ elimination proceeded at the same rate while SiHCl and $\mathrm{H}_{2}$ elimination were not observed. Again, the experimental results were obtained in the presence of hot walls and at reduced pressure, and the branching ratio is based on final product analysis with assumptions about the mechanism of product production. Reconciling our results with the observation of Jenkins et al. would require at least a $4 \mathrm{kcal} / \mathrm{mol}$ reduction in the activation barrier for $\mathrm{SiCl}_{2}$ elimination relative to that for $\mathrm{SiH}_{2}$ elimination.
$\mathbf{H C l}_{2} \mathbf{S i S i H}_{2} \mathbf{C l}$ Decomposition. The energetics of these reactions are illustrated in Figure 3. SiHCl elimination is predicted to be the fastest decomposition route, with $1,2 \mathrm{H}$ atom transfer and $1,2 \mathrm{Cl}$ atom transfer contributing nearly equally. The predicted activation energy is $47 \mathrm{kcal} / \mathrm{mol}$. $\mathrm{SiCl}_{2}$ elimination is the next fastest process, with an activation energy of 49 $\mathrm{kcal} / \mathrm{mol}$. Silylene elimination in this molecule can only occur via a $1,2 \mathrm{Cl}$ atom transfer and is substantially slower. $\mathrm{H}_{2}$ elimination is also slower, with a rate comparable to the silylene elimination rate at 1000 K .
$\mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$ Decomposition. The energetics of this reaction are also illustrated in Figure 3. $\mathrm{SiCl}_{2}$ elimination, passing through a tight transition state with an activation energy of 50 $\mathrm{kcal} / \mathrm{mol}$, is predicted to be faster than silylene elimination, which goes through a loose transition state but has a higher
activation energy. $\mathrm{H}_{2}$ elimination is slower yet, with an activation barrier $3 \mathrm{kcal} / \mathrm{mol}$ higher than $\mathrm{SiCl}_{2}$ elimination.
$\mathbf{H C l}_{2} \mathbf{S i S i H C l}_{2}$ Decomposition. The only possible reactions are SiHCl elimination and $\mathrm{SiCl}_{2}$ elimination. The SiHCl elimination is predicted to be faster, with an activation energy of $48 \mathrm{kcal} / \mathrm{mol}$, compared to $52 \mathrm{kcal} / \mathrm{mol}$ for $\mathrm{SiCl}_{2}$.
$\mathbf{C l}_{3} \mathbf{S i S i H}_{2} \mathbf{C l}$ Decomposition. $\mathrm{SiCl}_{2}$ elimination is fastest, followed by SiHCl elimination, $\mathrm{H}_{2}$ elimination, and $\mathrm{SiH}_{2}$ elimination. $\mathrm{SiCl}_{2}$ elimination is predicted to have an activation energy of only $44 \mathrm{kcal} / \mathrm{mol}$.
$\mathbf{C l}_{3} \mathbf{S i S i H C l} \mathbf{2}_{2}$ Decomposition. $\mathrm{SiCl}_{2}$ elimination is much faster than SiHCl elimination. These reactions have activation energies of 46 and $52 \mathrm{kcal} / \mathrm{mol}$, respectively. The $\mathrm{SiCl}_{2}$ elimination occurs almost entirely by Cl atom transfer. Elimination via H atom transfer is predicted to have a barrier that is $8 \mathrm{kcal} / \mathrm{mol}$ higher than Cl atom transfer. Thus, Cl atom transfer is preferred to H atom transfer for $\mathrm{SiCl}_{2}$ elimination, in contrast to $\mathrm{SiH}_{2}$ elimination, where H atom transfer was preferred.
$\mathrm{Cl}_{3} \mathrm{SiSiCl}_{3}$ Decomposition. The only possible reaction is $\mathrm{SiCl}_{2}$ elimination, which is predicted to occur with an activation energy of $49 \mathrm{kcal} / \mathrm{mol}$. This is in good agreement with the value of $49.2 \mathrm{kcal} / \mathrm{mol}$ measured by Doncaster and Walsh near 600 K. ${ }^{23}$

Insertion and Exchange Reaction Energetics and Kinetics. Table 7 presents energetic and kinetic results for the insertion reactions which are the reverse of the thermal decomposition reactions and direct exchange reactions between chlorinated silylenes and chlorinated silanes. The barriers and rate constants are determined by the same methods as for the thermal decomposition reactions. Direct exchange reactions in which a hydrogen atom and a chlorine atom are simultaneously transferred in opposite directions between a silylene and a silane are considered along with the insertion reactions. These proceed through the four centered transition state illustrated in Figure 2 c , and have higher barriers than the insertions. Since these direct reactions would have different pressure dependence than

TABLE 7: Energetics and Rate Constants for Insertion and Exchange Reactions

| reaction | TS | barrier | $k(298)$ | $k(1000)$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{4} \rightarrow \mathrm{H}_{3} \mathrm{SiSiH}_{3}$ | a | -6.4 |  | $2.1 \mathrm{E}-11$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{4} \rightarrow \mathrm{H}_{3} \mathrm{SiSiH}_{3}$ | d | -8.2 |  | $8.0 \mathrm{E}-11$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}{ }^{\text {b }}$ | a | -5.8 |  | $4.1 \mathrm{E}-12$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}{ }^{\text {b }}$ | d | -7.0 |  | $5.2 \mathrm{E}-12$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}{ }^{\text {c }}$ | a | 0.0 |  | $2.3 \mathrm{E}-13$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{SiHCl}+\mathrm{SiH}_{4}$ | c | 7.6 |  | $1.9 \mathrm{E}-15$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | a | -4.8 |  | $1.5 \mathrm{E}-12$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}$ | a | -4.0 |  | $2.3 \mathrm{E}-13$ |
| $\mathrm{SiH}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl}$ | c | 5.7 |  | $1.2 \mathrm{E}-15$ |
| $\mathrm{SiH}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{H}_{3} \mathrm{SiSiCl}_{3}$ | a | -4.8 |  | $2.1 \mathrm{E}-12$ |
| $\mathrm{SiH}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | a | -1.5 |  | $1.5 \mathrm{E}-13$ |
| $\mathrm{SiH}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ | c | 4.7 |  | $3.2 \mathrm{E}-15$ |
| $\mathrm{SiH}_{2}+\mathrm{SiCl}_{4} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | a | 0.7 |  | $2.1 \mathrm{E}-13$ |
| $\mathrm{SiH}_{2}+\mathrm{SiCl}_{4} \rightarrow \mathrm{SiHCl}+\mathrm{SiHCl}_{3}$ | c | 7.0 |  | $1.6 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{4} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ | a | 4.8 | $1.8 \mathrm{E}-17$ | $2.0 \mathrm{E}-14$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{4} \rightarrow \mathrm{SiH}_{2}+\mathrm{SiH}_{3} \mathrm{Cl}$ | c | 17.4 | $7.7 \mathrm{E}-27$ | $2.0 \mathrm{E}-17$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}$ | a | 0.9 | $1.1 \mathrm{E}-15$ | $1.9 \mathrm{E}-14$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | a | 5.1 | $9.6 \mathrm{E}-19$ | $3.1 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{SiH}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ | c | 13.1 | $4.7 \mathrm{E}-25$ | $1.1 \mathrm{E}-17$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{SiCl}_{2}+\mathrm{SiH}_{4}$ | c | 9.5 | $6.1 \mathrm{E}-22$ | $3.3 \mathrm{E}-16$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}^{b}$ | a | 2.4 | $4.1 \mathrm{E}-17$ | $5.4 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}^{c}$ | a | 1.9 | $5.2 \mathrm{E}-17$ | $4.6 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SiH}_{2}+\mathrm{SiHCl}_{3}$ | c | 12.0 | $1.3 \mathrm{E}-24$ | $1.1 \mathrm{E}-17$ |
| $\mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SiCl}_{2}+\mathrm{SiH}_{3} \mathrm{Cl}$ | c | 6.6 | $1.5 \mathrm{E}-20$ | $2.4 \mathrm{E}-16$ |
| $\mathrm{SiHCl}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | a | 4.2 | $1.6 \mathrm{E}-18$ | $2.2 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2}$ | a | 2.8 | $1.6 \mathrm{E}-17$ | $5.0 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{SiH}_{2}+\mathrm{SiCl}_{4}$ | c | 15.6 | $1.3 \mathrm{E}-27$ | $8.6 \mathrm{E}-19$ |
| $\mathrm{SiHCl}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{SiCl}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ | c | 7.4 | $1.2 \mathrm{E}-20$ | $6.4 \mathrm{E}-16$ |
| $\mathrm{SiHCl}+\mathrm{SiCl}_{4} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiHCl}_{2}$ | a | 5.0 | $1.8 \mathrm{E}-18$ | $7.5 \mathrm{E}-15$ |
| $\mathrm{SiHCl}+\mathrm{SiCl}_{4} \rightarrow \mathrm{SiCl}_{2}+\mathrm{SiHCl}_{3}$ | c | 10.2 | $3.0 \mathrm{E}-22$ | $4.1 \mathrm{E}-16$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{4} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | a | 20.5 | $3.8 \mathrm{E}-29$ | $7.0 \mathrm{E}-18$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{4} \rightarrow \mathrm{SiHCl}+\mathrm{SiH}_{3} \mathrm{Cl}$ | c | 23.1 | $6.2 \mathrm{E}-31$ | $2.5 \mathrm{E}-18$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | a | 16.3 | $4.3 \mathrm{E}-27$ | $8.4 \mathrm{E}-18$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$ | a | 12.6 | $2.1 \mathrm{E}-24$ | $8.9 \mathrm{E}-17$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{3} \mathrm{Cl} \rightarrow \mathrm{SiHCl}+\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ | c | 18.3 | $7.5 \mathrm{E}-29$ | $1.4 \mathrm{E}-18$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiHCl}_{2}$ | a | 19.1 | $9.9 \mathrm{E}-30$ | $7.7 \mathrm{E}-19$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | a | 10.4 | $2.1 \mathrm{E}-23$ | $7.9 \mathrm{E}-17$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiH}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SiHCl}+\mathrm{SiHCl}_{3}$ | c | 19.3 | $1.2 \mathrm{E}-29$ | $1.2 \mathrm{E}-18$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiCl}_{3}{ }^{\text {b }}$ | a | 20.6 | $1.1 \mathrm{E}-30$ | $6.4 \mathrm{E}-19$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiCl}_{3}{ }^{\text {c }}$ | a | 12.0 | $2.1 \mathrm{E}-24$ | $6.3 \mathrm{E}-17$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiHCl}_{3} \rightarrow \mathrm{SiHCl}+\mathrm{SiCl}_{4}$ | c | 23.3 | $8.4 \mathrm{E}-33$ | $1.2 \mathrm{E}-19$ |
| $\mathrm{SiCl}_{2}+\mathrm{SiCl}_{4} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiCl}_{3}$ | a | 12.5 | $2.6 \mathrm{E}-24$ | $1.3 \mathrm{E}-16$ |
| $\mathrm{H}_{3} \mathrm{SiSiH}+\mathrm{H}_{2} \rightarrow \mathrm{H}_{3} \mathrm{SiSiH}_{3}$ | b | -0.5 | $3.2 \mathrm{E}-12$ | $7.9 \mathrm{E}-13$ |
| $\mathrm{H}_{2} \mathrm{ClSiSiH}+\mathrm{H}_{2} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ | b | -0.7 | $6.0 \mathrm{E}-12$ | $1.4 \mathrm{E}-12$ |
| $\mathrm{HCl}_{2} \mathrm{SiSiH}+\mathrm{H}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{3}$ | b | -0.3 | $1.5 \mathrm{E}-12$ | $6.9 \mathrm{E}-13$ |
| $\mathrm{Cl}_{3} \mathrm{SiSiH}+\mathrm{H}_{2} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{3}$ | b | -0.4 | $1.1 \mathrm{E}-12$ | $3.8 \mathrm{E}-13$ |
| $\mathrm{H}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{3}$ | b | 9.8 | $7.8 \mathrm{E}-20$ | $4.6 \mathrm{E}-15$ |
| $\mathrm{H}_{2} \mathrm{ClSiSiCl}+\mathrm{H}_{2} \rightarrow \mathrm{H}_{2} \mathrm{ClSiSiH}_{2} \mathrm{Cl}$ | b | 10.0 | $6.3 \mathrm{E}-20$ | $4.5 \mathrm{E}-15$ |
| $\mathrm{HCl}_{2} \mathrm{SiSiCl}+\mathrm{H}_{2} \rightarrow \mathrm{HCl}_{2} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | b | 9.9 | $3.6 \mathrm{E}-20$ | $2.7 \mathrm{E}-15$ |
| $\mathrm{Cl}_{3} \mathrm{SiSiCl}+\mathrm{H}_{2} \rightarrow \mathrm{Cl}_{3} \mathrm{SiSiH}_{2} \mathrm{Cl}$ | b | 10.5 | $6.6 \mathrm{E}-21$ | $9.6 \mathrm{E}-16$ |

into $\mathrm{Si}-\mathrm{Cl}$ bonds have higher barriers than insertions into $\mathrm{Si}-\mathrm{H}$ bonds, but the saddle points are still at or slightly below the energy of the separated reactants. The rate constants in Table 7 are calculated assuming a tight transition state at the location of the saddle point on the potential surface. This results in overestimates of the rate constants, especially at low temperatures, where the transition state should be much closer to the products, and therefore at higher energy. No room-temperature rate constants are presented for the silylene reactions because calculations using a tight transition state do not give reasonable results for many of the insertions. At 1000 K the predicted rate constant for silylene insertion into silane is in reasonable agreement with experimental results. ${ }^{4}$ Transition states for direct exchange of a hydrogen atom for a chlorine atom to give SiHCl were located and have barriers which are $5-7 \mathrm{kcal} / \mathrm{mol}$ above the separated reactants. Due to the relatively high barriers, these paths are not expected to be observed except at very high temperatures or at low pressures, where falloff effects have reduced the rate of the insertion reactions.

SiHCl Insertion and Exchange Reactions. Barriers for insertion of SiHCl into $\mathrm{Si}-\mathrm{H}$ bonds are predicted to range from 1 to $5 \mathrm{kcal} / \mathrm{mol}$, with no clear trend with increasing chlorination of the silane into which it is inserting. Likewise, barriers for insertion of SiHCl into $\mathrm{Si}-\mathrm{Cl}$ bonds range from 2 to $5 \mathrm{kcal} /$ mol, again with no clear trend observed as the silane is chlorinated. However, for the three cases where there is competition between the two processes, there is a relative trend. For reaction with $\mathrm{SiH}_{3} \mathrm{Cl}$, insertion into the $\mathrm{Si}-\mathrm{H}$ bond is faster. For reaction with $\mathrm{SiH}_{2} \mathrm{Cl}_{2}$ the rates are nearly the same. Finally, for reaction with $\mathrm{SiHCl}_{3}$, insertion into the $\mathrm{Si}-\mathrm{Cl}$ bond is faster. The insertion barriers are smaller than for SiHCl insertion into diatomics. Insertions of SiHCl into $\mathrm{H}_{2}$ and HCl were predicted to have barriers of 7 and $20 \mathrm{kcal} / \mathrm{mol}$, respectively. ${ }^{15}$ Exothermic exchange reactions that convert SiHCl to $\mathrm{SiCl}_{2}$ have barriers of $7-10 \mathrm{kcal} / \mathrm{mol}$, lying $5-8 \mathrm{kcal} / \mathrm{mol}$ above the lowest energy insertion barrier. Again these might become competitive at high temperatures and low pressures. The endothermic exchange reactions which convert SiHCl to $\mathrm{SiH}_{2}$ have barriers of 12-17 $\mathrm{kcal} / \mathrm{mol}$ and are therefore not likely to be important.

Ho et al. ${ }^{21}$ measured room-temperature rates of insertion of SiHCl into $\mathrm{SiH}_{4}$ and $\mathrm{SiH}_{2} \mathrm{Cl}_{2}$. Consistent with our results, they found that the rates were roughly the same. However, our predicted rates at room temperature are nearly 2 orders of magnitude smaller than what they observed. This is not as bad a disagreement as it might first appear, since these roomtemperature rates are very sensitive to the activation barrier. Lowering the barriers by about $2-3 \mathrm{kcal} / \mathrm{mol}$ would bring our estimates in line with the experimental observations. Additionally, our treatment of the low-frequency modes of the transition state as harmonic vibrations likely results in somewhat of an underestimate of the preexponential factor. Loosening of the transition structure by treating these modes anharmonically would also bring our estimates closer to the observations of Ho et al.
$\mathbf{S i C l}_{\mathbf{2}}$ Insertion and Exchange Reactions. Barriers for insertion of $\mathrm{SiCl}_{2}$ into $\mathrm{Si}-\mathrm{H}$ bonds range from 16 to $21 \mathrm{kcal} /$ mol, while barriers for insertion into $\mathrm{Si}-\mathrm{Cl}$ bonds are only $10-$ $13 \mathrm{kcal} / \mathrm{mol}$. We see that $\mathrm{SiCl}_{2}$ preferentially reacts with $\mathrm{Si}-$ Cl bonds, whereas $\mathrm{SiH}_{2}$ preferentially reacted with $\mathrm{Si}-\mathrm{H}$ bonds, and SiHCl exhibited no clear preference. Consistent with previous studies, $\mathrm{SiCl}_{2}$ is predicted to be much less reactive than $\mathrm{SiH}_{2}$ or SiHCl . For comparison, the barriers for insertion into HCl and $\mathrm{H}_{2}$ were predicted to be 16 and $40 \mathrm{kcal} / \mathrm{mol}$, respectively. ${ }^{15}$ The exchange reactions that convert $\mathrm{SiCl}_{2}$ to SiHCl have barriers of $18-23 \mathrm{kcal} / \mathrm{mol}$. Thus, they are
consistently slower than than the insertion reactions, having barriers that are $3-11 \mathrm{kcal} / \mathrm{mol}$ higher than the lowest energy insertion channel.

Chlorinated Silylsilylene Insertions into $\mathbf{H}_{\mathbf{2}}$. Insertions of $\mathrm{H}_{n} \mathrm{Cl}_{3-n} \mathrm{SiSiH}$ into $\mathrm{H}_{2}$ all have transition states that are essentially isoenergetic with the separated reactants, ranging from 0.3 to $0.7 \mathrm{kcal} / \mathrm{mol}$ below the reactants. Chlorine substitution on the tetravalent silicon is predicted to have almost no effect. Insertions of $\mathrm{H}_{n} \mathrm{Cl}_{3-n} \mathrm{SiSiCl}$ into $\mathrm{H}_{2}$ have barriers near $10 \mathrm{kcal} /$ mol. Again, chlorine substitution on the tetravalent silicon has almost no effect. However, chlorine substitution on the divalent silicon raises the insertion barrier by $10 \mathrm{kcal} / \mathrm{mol}$. This is a smaller effect than is seen for chlorine substitution on silylene. $\mathrm{SiH}_{2}, \mathrm{SiHCl}$, and $\mathrm{SiCl}_{2}$ have insertion barriers for reaction with hydrogen of 2,20 , and $40 \mathrm{kcal} / \mathrm{mol}$, respectively. Thus, chlorine substitution on the divalent silicon of the silylsilylenes raises the insertion barrier only about half as much as is observed for chlorine substitution on the silylenes.

## Summary and Conclusions

The thermochemistry and reaction kinetics of the thermal decomposition of the chlorinated disilanes have been explored using high-level ab initio calculations. These results provide a basis for the modeling of multistep homogeneous decomposition of chlorinated silanes and a basis for predicting the reactivity of the compounds considered. Comparable energy barriers were found for the different possible elimination reactions, with different reactions dominating for different chlorinated disilanes. In addition to the insertion reactions, which are the reverse of the thermal decomposition reactions, new reaction paths were found where a hydrogen and chlorine atom are simultaneously exchanged between a chlorinated silane and a chlorinated silylene in a concerted four-centered process. These paths may become important at high temperatures and low pressures, where the insertion reactions exhibit falloff effects.

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[^0]:    ${ }^{\otimes}$ Abstract published in Advance ACS Abstracts, September 15, 1997

[^1]:    ${ }^{a}$ Total energies in hartrees ( 1 hartree $=627.51 \mathrm{kcal} / \mathrm{mol}$ ), zero-point energies (ZPE), and thermal energy in $\mathrm{kcal} / \mathrm{mol}$ at 298 K and 1 atm using geometry and unscaled frequencies at the MP2/6-31G(d,p) level. MP2/6-31+G(2df,p) and MP4/6-31+G(2df,p) energies are at MP2/6-31G(d,p) geometry. Note that G2 and G2(MP2) energies include zero-point energy calculated using scaled HF/6-31G(d) frequencies. Entries left blank were not calculated due to computational expense. ${ }^{b}$ Transition state corresponding to insertion into $\mathrm{Si}-\mathrm{H}$ bond. ${ }^{c}$ Transition state corresponding to insertion into $\mathrm{Si}-\mathrm{Cl}$ bond.

[^2]:    ${ }^{a}$ Frequencies are in units of $\mathrm{cm}^{-1}$ and are unscaled. Degenerate frequencies are simply repeated an appropriate number of times. ${ }^{b}$ Transition state corresponding to insertion into $\mathrm{Si}-\mathrm{H}$ bond. ${ }^{c}$ Transition state corresponding to insertion into $\mathrm{Si}-\mathrm{Cl}$ bond.

[^3]:    ${ }^{a}$ Heats of formation in $\mathrm{kcal} / \mathrm{mol}$ at 298.15 K and 1 atm calculated using isodesmic reactions given in text and total energies, thermal, and zero-point energies from Table 1 . Entropies are in $\mathrm{cal} /(\mathrm{mol} / \mathrm{K})$ calculated using the unscaled MP2/6-31G(d,p) vibrational frequencies. Reference values for calculating heats of formation were $\Delta H_{\mathrm{f}}\left(\mathrm{SiH}_{4}\right)=8.2 \mathrm{kcal} / \mathrm{mol},{ }^{30} \Delta H_{\mathrm{f}}\left(\mathrm{SiCl}_{4}\right)=-158.4 \mathrm{kcal} / \mathrm{mol}^{30} \Delta H_{\mathrm{f}}\left(\mathrm{SiH}_{2}\right)=65.2 \mathrm{kcal} / \mathrm{mol},{ }^{4}$ and $\Delta H_{\mathrm{f}}\left(\mathrm{Si}_{2} \mathrm{H}_{6}\right)=19.1 \mathrm{kcal} / \mathrm{mol} .{ }^{31}$ Entries left blank were not calculated due to computational expense.

