THEORETICAL INVESTIGATIONS
OF THE THERMOCHEMISTRY
AND THERMAL DECOMPOSITION
OF SILANES, HALOSILANES,
AND ALKYLSILANES

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1. INTRODUCTION

1.1. Preliminary Remarks

Research activity in silicon chemistry has exploded in the past ten years. This is particularly true of the quality and quantity of theoretical predictions of the energetics of chemical reactions for compounds containing silicon. Ten years ago, most of the few theoretical papers that dealt with silicon chemistry made use of minimal basis set \textit{ab initio} or semi-empirical self-consistent field (SCF) calculations. Most of these papers dealt with predictions of molecular and electronic structures, primarily of compounds containing multiple bonds to silicon or their isomers. Very few dealt with energetics of reactions and fewer still made use of second derivative calculations to characterize stationary points on a potential energy surface. Most previous reviews have reflected this early orientation toward structure, rather than energetics."

During the past 10 years, great advances have been made both in the methods that can be brought to bear on the prediction of reaction energetics and the computer technology that makes use of those methods. Consequently, it is possible to predict from first principles the energetics related to reactions of molecules of small to medium size. Of particular interest to us are the applications of these advances to silicon chemistry. Since a great many papers dealing with the energetics of molecules containing silicon have now appeared, it seems timely to review that body of literature. That is the goal of this work.

It is necessary in any review to define its limits. In the following, we review two main aspects of silicon chemistry energetics: predictions of heats of formation of silicon-containing compounds (Section 2) and predictions of reaction energetics containing those compounds (Section 3). Since most of the latter works address unimolecular reactions (isomerizations and decompositions), Section 3 focuses on these reactions, but not exclusively. While there has been some excellent work in this area using semi-empirical methods, the present effort addresses only \textit{ab initio}, or \textit{ab initio}, electronic structure calculations. Similarly, the many excellent papers on the dynamics of gas-phase or surface silicon chemistry, using semiclassical dynamics techniques are beyond the scope of this work. Finally, since the most systematic and extensive energetics calculations have been performed for silanes, alkylsilanes, and halosilanes, the focus of the review is on these classes of compounds.
1.2. Terminology

It is inevitable that as the tools available to a field increase, the complexity of the terminology follows suit. While it is not intended to provide an exhaustive compilation of terminology here, a brief summary will aid the readability of the following sections. For more detailed accounting, the reader is referred to several excellent works.\footnote{1}

The two essential ingredients in an \textit{ab initio} electronic structure calculation are the basis set and the level of theory used in the calculation. For the prediction of energetic properties of molecules and reactions, high quality basis sets and correlation corrections to the Hartree-Fock (HF) self-consistent field (SCF) molecular orbitals are both essential. The basis sets must be of at least double zeta plus polarization (DZP) quality. Such basis sets contain two functions for each formal atomic orbital (e.g., 1s, 3d, etc.) on each atom plus one set of functions (polarization functions) on each atom with 1 quantum number one higher than required in the isolated atoms. Commonly used basis sets at this level are those due to Dunning and Hay\footnote{2} and the well-known 6-31G(d) and 6-31G(d,p) basis sets developed by Pople and co-workers\footnote{3}. Note that we will use 6-31G(d) and the older 6-31G* notation interchangeably. Similarly, 6-31G(d,p) and 6-31G** are equivalent. These two basis sets are the ones most commonly used for the predictions of molecular geometries and vibrational frequencies. For the prediction of energetic properties, much larger basis sets are required, with at least triple zeta plus polarization quality (TZP). Examples are 6-311G(d,p) and larger basis sets such as 6-311G(3df,3pd).\footnote{4} The latter basis set includes three sets of d functions and one set of f functions on each heavy atom and three sets of p functions and one set of d functions on each hydrogen. Additionally, a proper treatment of anions requires diffuse functions on each atom, usually indicated by a plus in the basis set notation.

There are several ways in which correlation corrections can be added into an electronic structure calculation. At present, the most popular approaches are:

1. Many body perturbation theory, most commonly as popularized by Pople and co-workers within the Møller-Plesset (MP) formalism.\footnote{5} To second, third, and fourth order, these are referred to as MP2, MP3, and MP4, respectively. MP4 calculations can be performed with (SDTQ) or without (SDQ) the inclusion of...
triple excitations. Triples can be quite important for the prediction of energetics, but they are also quite computationally expensive.

2. Coupled cluster theory is closely related to many body perturbation theory and has become increasingly popular recently. It is commonly formulated with the inclusion of single and double excitations (CCSD), single, double and triple excitations (CCSDT), or through quadruples (CCSDTQ).

3. Multi-reference configuration interaction (MRCI) calculations are particularly important when there is significant diradical character at important points on a potential energy surface. In such cases, MP and CC approaches frequently break down. A common approach to MRCI calculations is to first perform a fully optimized reaction space (FORS) SCF (or CASSCF) calculation, followed by a singles and doubles CI from all the FORS reference configurations. All three of these approaches are commonly used to predict energetic properties.

2. THERMOCHEMISTRY OF SILICON CENTERS

The thermochemistry of small silicon compounds is one of the success stories of the interplay between experiment and theory. Some of the silicon containing molecules of interest to experimental chemists are small enough to allow very high level calculations to be carried out, so that the accuracy of the calculations can be tested against reliable experimental results. On the other hand, some of the interesting molecules are highly reactive making them difficult to study experimentally, and theoretical calculations of the energetics and structure can provide a guide to experiment. In this section we will examine the calculation of heats of formation by theoretical means and compare the results of systematic computational studies with experiment.

2.1. Computational Procedures for Predicting Reliable Heats of Formation

Theoretical heats of formation can be obtained from calculated bond dissociation energies, total atomization energies and heats of reactions. Semi-empirical molecular orbital calculations provide useful insights, but they are often not sufficiently reliable for accurate estimates of the heats of formation. A detailed discussion of the performance of ab
Silanes, Halo-silanes, and Alkyldilanes

initio molecular orbital theory can be found in the book by Hehre et al.7 Even high level ab initio calculations can be inadequate if measures have not been taken to control the systematic errors. Unless reactions are chosen carefully to cancel errors, the various levels of ab initio theory that are currently practical all require some degree of empirical correction in order to achieve chemical accuracy (± 1 kcal/mol).

Two factors determine the quality of a given level of ab initio molecular orbital calculation:7 the basis set and the treatment of electron correlation. However, increasing the size of the basis set or improving the treatment of correlation is expensive (computational cost is proportional to n to the 4th power, where n is the number of basis functions). For most work, the basis set must be at least double zeta plus polarization or 6-31G** quality, preferably triple zeta plus polarization or 6-311G**. Depending on the reaction, it is often necessary to add extra polarization functions and diffuse functions (e.g., 6-311+G(3df,3pd)). Electron correlation energy should be calculated at an appropriately high level, such as fourth order perturbation theory (including triple excitations, e.g., MP4SDTQ) or by an iterative method like CISD (with corrections for higher excitations), QCISD or CCSD (with corrections for triples). Even at the MP4SDTQ/6-31G** level, direct calculations of bond dissociation energies can be in error by as much as 10-20 kcal/mol.

One method to control the errors arising from basis set deficiencies and inadequacies in the treatment of electron correlation energy is to choose reactions so that the systematic errors tend to cancel. A class of reactions of this type is the isodesmic reaction; that is, a reaction in which the number of bonds of each type is conserved:

\[
\begin{align*}
\sum_i n_i \text{SiX}_4 + \sum_j n_j \text{Si} & \rightarrow \sum_i n_i \text{SiX}_4 \\
\sum_i n_i \text{SiX}_4 + \sum_j n_j \text{SiH}_4 & \rightarrow \sum_i n_i \text{SiH}_4 + \sum_j n_j \text{SiX}_4 \\
\sum_i n_i \text{SiX}_n + \sum_j n_j \text{SiH}_m & \rightarrow \sum_i n_i \text{SiH}_m + \sum_j n_j \text{SiX}_n
\end{align*}
\]  

(1)  

(2)  

(3)

Depending on how carefully the bonding environments are preserved in an isodesmic reaction, the errors in the computed heats of reaction can range from ±1 to ±5 kcal/mol at the MP4SDTQ/6-31G** level. The cancellation of errors is particularly good in reaction (3). A homodesmic reaction takes this idea one step further by conserving not just bonds but entire groups and bonding environments:

\[
\text{SiH}_2\text{CH}_3 + \text{CH}_2\text{SiCH}_3 \rightarrow \text{SiH}_2\text{CH}_4\text{CH}_3 + \text{CH}_2\text{CH}_3
\]

(4)
Errors in homodesmic reactions can be $\pm 1$ kcal/mol at the MP4SDTQ/6-31G** level.

For open shell systems, unrestricted Hartree–Fock and Møller–Plesset perturbation theory are often used to calculate energy differences. These methods can suffer from spin contamination that can cause errors of $\pm 1$ kcal/mol in heats of reaction for systems where the contamination is small to errors of 15 kcal/mol in activation energies if the spin contamination is large. An isogamic reaction is one that conserves spin and eliminates a substantial fraction of the spin contamination error, provided the contamination is small:

$$\text{SiH}_4 + a \text{H} \rightarrow \text{Si} + a \text{H}_2 + (a-4) \text{H}$$  (5)

When perturbative methods are used for systems with substantial spin contamination, spin projection can be used to remove most of the error. Iterative methods that include single excitations, such as UCISD, UQCISD and UCQSD are less susceptible to spin contamination. Alternatively, spin restricted, multireference CI methods can be used to avoid the problem entirely.

To compute the heat of formation of a particular compound via an isodesmic or homodesmic reaction requires the heats of formation of all the other compounds in the reaction. As an alternative to building a specific isodesmic reaction for each compound of interest, one can devise a correction factor for each bond made or broken in a reaction. The bond additivity correction method$$^{16,41}$$ (BAC) assumes that a certain level of theory underestimates the dissociation energy of a given bond (e.g., S–H) by a specific amount. The needed correction factor can be obtained by comparing the calculated and experimental dissociation or atomization energies for a reference compound (e.g., SiH$_4$):

$$\text{BAC(Si–H)} = \frac{1}{4} (\Delta H_{\text{calc}} - \Delta H_{\text{theor}})$$ for $\text{SiH}_4 \rightarrow \text{Si} + 4 \text{H}$  (6)

This bond additivity correction is assumed to be constant (or have a simple bond length dependence$$^4$$) and is added to the calculated dissociation energy of each bond broken to obtain a corrected atomization energy that can be used to compute a theoretical heat of formation. With energies computed at the MP4SDTQ/6-31G** level, the bond additivity scheme (denoted BAC-MP4) has a mean absolute error of about 3 kcal/mol.
be $\pm 1$ kcal/mol at the Hartree–Fock and Møller–Plesset Hamiltonian. The calculation was performed with Gaussian 16 at the MP2/6-31G* level using the 6-311G** basis set. The calculations were done at the B3LYP/6-311G* level using the same basis set. The results are in good agreement with the experimental data. The authors also performed calculations at the G-1 and G-2 levels of theory. The G-1 level of theory is accurate to $\pm 2$ kcal/mol for first and second row hydrides, and for singly bonded two heavy atom systems. The mean absolute deviation for the G-2 level is 1.2 kcal/mol for a set of 125 molecules that includes multiply bonded systems.

2.2. Heats of Formation of Silicon Centers: Some Important Examples

The experimental work on heats of formation of small silicon compounds has been reviewed extensively by Walsh. The values recommended by these reviews are generally more reliable than some of the values in earlier collections. A number of experimental deter-
minations of $\Delta H_{298}^\circ$ of small silicon compounds have been reported recently and are included in the discussion below in conjunction with the theoretical calculations of the heats of formation. The survey of theoretical work in this section is limited to calculations of the heats of formation carried out within the last six to eight years by methods that are expected to be accurate to ±5 kcal/mol or better. Only the energetics of ground state silicon compounds ( neutrals, cations and anions) containing carbon, hydrogen, and halogens are discussed. Structures, properties, excited states, etc. are considered outside the scope of this section. Despite this narrow focus, there is a substantial body of literature to review.

2.2.1. SiH₆

The calculated and experimental heats of formation for SiH₆ neutrals and cations are compared in Table 1. The experimental heat of formation of SiH₆ is well established at $\Delta H_{298}^\circ = 8.2 \pm 0.5$ kcal/mol obtained from the decomposition of SiH₆ into Si and H₂. A number of groups have reported values for SiH₆. The most recent determination is based on a careful analysis of the forward and reverse rates for SiH₆ + HX → SiH₅ + X (X = Br, I) and recommends $\Delta H_{298}^\circ = 47.9 \pm 0.6$ kcal/mol. Only 10 years ago, the accepted value for the heat of formation of SiH₆ was about 38 kcal/mol. However, theoretical studies indicated that the value should be 63–68 kcal/mol. In the meantime there have been quite a number of experimental studies using a variety of techniques to determine the heat of formation of SiH₆. A recent re-analysis of the rate data for SiH₆ + H₂ from a number of different authors recommends 65.5 ± 1.0 kcal/mol. This agrees very well with what is mass spectrometry, proton affinity measurements and photoelectron studies (65.6 ± 0.7, 65.5 ± 1.3, 65.4 ± 1.6, 66 ± 3.6, 63.6 ± 2.8). For SiH₆, spectroscopic studies give $\Delta H_{298}^\circ = 90 \pm 2$ kcal/mol and photoionization experiments yield 89.6 ± 1.2 kcal/mol.

Hö, Melius and co-workers have calculated the heats of formation of SiH₆ using the bond additivity correction (BAC) approach based on the MP4/6-31G**//HF/6-31G** level with and without bond length dependence, with and without a correction for spin contamination. Horowitz and Goddard applied a 1.5 kcal/mol correction to the Si-H, SiH-H and SiH₂-H bond dissociation energies obtained from GVB-CI calculations. Sax and Kalcher used the BAC approach with CISO.
Table 1. Theoretical and Experimental $\Delta H^\circ_{f,exp}$ for SiH$_i$, and SiH$_i^+$ (n = 1-4) (kcal/mol)

<table>
<thead>
<tr>
<th>Level</th>
<th>Ref.</th>
<th>SiH$_1$</th>
<th>SiH$_2$</th>
<th>SiH$_3$</th>
<th>SiH$_4$</th>
</tr>
</thead>
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<tr>
<td>Neutral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAC-MPSI</td>
<td>[17]</td>
<td>91.7</td>
<td>68.1</td>
<td>47.8</td>
<td>8.2*</td>
</tr>
<tr>
<td>BAC-MPSI</td>
<td>[18]</td>
<td>92.0</td>
<td>68.7</td>
<td>47.8</td>
<td>8.2*</td>
</tr>
<tr>
<td>BAC-MPSI</td>
<td>[19]</td>
<td>91.0</td>
<td>64.8</td>
<td>47.4</td>
<td>8.2*</td>
</tr>
<tr>
<td>BAC-CISD</td>
<td>[21]</td>
<td>90.0</td>
<td>66.2</td>
<td>47.8</td>
<td>8.2*</td>
</tr>
<tr>
<td>BAC-GVB</td>
<td>[20]</td>
<td>90.1</td>
<td>66.6</td>
<td>47.7</td>
<td>8.2*</td>
</tr>
<tr>
<td>atomization</td>
<td>[20]</td>
<td>88.3</td>
<td>63.4</td>
<td>47.3</td>
<td>6.3</td>
</tr>
<tr>
<td>atomization</td>
<td>[21]</td>
<td>88.8</td>
<td>63.5</td>
<td>47.4</td>
<td>6.3</td>
</tr>
<tr>
<td>atomization</td>
<td>[22]</td>
<td>87.7</td>
<td>62.4</td>
<td>46.7</td>
<td>5.2</td>
</tr>
<tr>
<td>G1</td>
<td>[23]</td>
<td>88.0</td>
<td>62.6</td>
<td>47.1</td>
<td>6.4</td>
</tr>
<tr>
<td>G2</td>
<td>[24]</td>
<td>87.8</td>
<td>62.4</td>
<td>46.7</td>
<td>6.0</td>
</tr>
<tr>
<td>G2</td>
<td>[25]</td>
<td>88.2</td>
<td>63.3</td>
<td>48.1</td>
<td>8.0</td>
</tr>
<tr>
<td>isodimetric</td>
<td>[26]</td>
<td>89.9</td>
<td>65.7</td>
<td>47.7</td>
<td>8.2*</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>89.6 $\pm$ 1.2*</td>
<td>65.5 $\pm$ 1.0*</td>
<td>47.9 $\pm$ 0.6*</td>
<td>8.2 $\pm$ 0.5*</td>
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<td>276.6</td>
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<td>264.9</td>
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<tr>
<td>BAC-MPSI</td>
<td>[55]</td>
<td>273.0</td>
<td>274.1</td>
<td>232.4*</td>
<td>265.6</td>
</tr>
<tr>
<td>isodimetric</td>
<td>[55]</td>
<td>273.6</td>
<td>276.7</td>
<td>235.2</td>
<td>266.1</td>
</tr>
<tr>
<td>G1</td>
<td>[2]</td>
<td>268.8</td>
<td>274.1</td>
<td>232.8</td>
<td>261.1</td>
</tr>
<tr>
<td>G2</td>
<td>[3]</td>
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<td>273.9</td>
<td>222.3</td>
<td>260.5</td>
</tr>
<tr>
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<td>276.6*</td>
<td>232.4*</td>
<td>264.2*</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isodimetric</td>
<td>[56]</td>
<td>65.0</td>
<td>47.4</td>
<td>24.2</td>
<td></td>
</tr>
<tr>
<td>G-1</td>
<td>[23]</td>
<td>61.5</td>
<td>40.5</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>G-2</td>
<td>[24]</td>
<td>60.6</td>
<td>39.6</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>G-2</td>
<td>[25]</td>
<td>60.9</td>
<td>40.5</td>
<td>15.4</td>
<td></td>
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<tr>
<td>Experiment</td>
<td></td>
<td>60.2*</td>
<td>39.6*</td>
<td>15.5*</td>
<td></td>
</tr>
</tbody>
</table>

*reference value *ref. [35] *ref. [38] *ref. [37] *ref. [29] *ref. [34] *ref. [36] *ref. [37]

$^{a}$calculations plus Davidson's correction (single reference and, where necessary, MCSCPF reference); and a TZ+ d + p basis set to obtain their estimates of the heats of formation of SiH$_i^+$. All of the BAC approaches give very good results for SiH$_i$, but tend to be 1-2 kcal/mol too high for SiH$_2$ and SiH. Pople, Curiss, Radom and co-workers have computed atomization energies using isogyric reactions. Similar results are found with and without basis set additivity assumptions and with 6-31G** or 6-311G** basis sets. The calculated heats of

f formation for SiH$_i$, neutrals experimental heat of formation $\Delta H^\circ_{f,exp}$ = 8.2 ± 0.5 kcal/mol into Si and H$_2$. A number of The most recent determinations and reverse rates for and recommends $\Delta H^\circ_{f,exp}$, the accepted value for the unfortunately could be 63-68 kcal/mol. In number of experimental studies the heat of formation of the, for SiH$_4$ → SiH$_3$ + H$_2$ omissions 65.5 ± 1.0 kcal/mol. 1 from mass spectrometry, excitation studies (65.5 ± 3%). For $\geq 90$ ± 2 kcal/mol and ± 1.2 kcal/mol, the heats of formation of the (BAC) approach based on the and without a bond length estimation for spin contamination. $\uparrow$modification to the Si-H, gies obtained from GVB-Cl BAC approach with CISD

$^{a}$ Refs. 35, 38, 37, 29, 34, 36.

$^{b}$ Ref. 37.
formation tend to be 0 to 2 kcal/mol below the experimental values. Similar agreement is found for the G-1 and G-2 values. Isodesmic reactions such as eq. (3) have also been used to estimate \( \Delta H_{298}^{\text{f}} \) of SiH\(_4\) based on the experimental heat of formation of SiH\(_4\). At the MP4/6-311+ + G(3df,3p) level, these calculations\(^b\) give heats of formation that are within 0.5 kcal/mol of experiment.

### 2.2.2. SiH\(_4\)\(^+\)

Berkowitz et al.\(^{10}\) have used photoionization mass-spectroscopy studies to examine the thermochemistry of the SiH\(_4\) and SiH\(_4\)\(^+\) systems. The heats of formation of SiH\(_4\)\(^+\) were obtained from the adiabatic ionization threshold for SiH\(_4\) and SiH\(_4\)\(^+\), the appearance potential of SiH\(_4\)\(^+\) from SiH\(_4\) and the Rydberg spectrum of SiH. Shin and Beauchamp\(^{10}\) have determined the proton affinity of SiH\(_4\). Boo and Armentrout\(^{10}\) have measured thresholds for Si\(^+\) + SiH\(_4\) \rightarrow SiH\(_4\)\(^+\) + SiH\(_2\), Si\(^+\) + SiH\(_4\) + SiH\(_2\), Si\(^+\) + SiH\(_4\)\(^+\) + SiH and have derived heats of formation for SiH\(_4\)\(^+\).

The total atomization energies for the neutrals\(^b\) have been combined with isogonic ionization reactions to yield calculated heats of formation of the cations\(^b\). Theoretical heats of formation of SiH\(_4\)\(^+\) have been obtained\(^b\) by combining the results from the BAC calculations (based on the observed \( \Delta H_{298}^{\text{f}} \) for SiH\(_4\)\(^+\)), computed proton affinities and isogonic ionization potential calculations at the MP4/6-31G** level. The \( \Delta H_{298}^{\text{f}} \) of the cations have also been calculated by the G-1 and G-2 levels of theory. The G-1 theory supports the lower of the two values for SiH\(_4\)\(^+\), whereas lower level calculations tend to be somewhat higher. For SiH\(_4\)\(^+\) and SiH\(_4\)\(^+\), the other calculations agree well with the experimental numbers, but G-1 seems to be about 3 kcal/mol lower. Nevertheless, the mean absolute difference between theory and experiment is only 1.6 kcal/mol.

### 2.2.3. SiH\(_4\)\(^-\)

Lineberger et al.\(^{10}\) have determined the electron affinities of SiH and SiH\(_4\) by photoelectron spectroscopy of the anions. Silyl radical and anion are pyramidal, and determining the electron affinity is complicated by inversion potential for both species. Analysis of the vibrational structure of the photoelectron spectra of SiH\(_4\)\(^-\) and SiH\(_4\)\(^-\) by Ellison and Nimlos\(^{10}\) yielded the electron affinity, as well as an estimate of
the inversion barriers. Heats of formation derived from isodesmic reactions at the MP4/6-311G(d,p)/MP2/6-31G(d,p) level\(^{15}\) differ from the experimental values by 5–10 kcal/mol, but calculations by G-1 and G-2 theory\(^{20,21,25,26}\) are within 1 kcal/mol of experiment. Related to the foregoing calculations are the predictions of the gas-phase acidities of silanes by Gordon et al.\(^{23,24}\) At the MP4(SDQ)/6-311 + + G(3df,2pd)//HF/6-31G(d) level of theory, these authors predict the 0\(^{°}\)K enthalpy for the reaction XSiH\(_4\) → XSiH\(_4^+\) + H\(^+\) to be 16.15 eV, compared with the experimental value of 16.23 eV, when X = H. Third period substituents X tend to increase the gas-phase acidity, while second period substituents have the opposite effect.

2.2.4. \(\text{Si}_2\text{H}_4\)

The experimental thermochemistry of di-, tri- and tetrasilanes has been discussed by Becerra and Walsh\(^{26}\) and by Ring and co-workers.\(^{73}\) The energetics of the Si\(_2\)H\(_4\) neutrals and cations have recently been studied by Berkowitz and Rusci\(^{14}\) using photoionization/mass spectroscopy methods. A comprehensive theoretical study of the heats of formation and adiabatic ionization potentials of Si\(_2\)H\(_4\) has also been completed recently by Curtiss et al. using the G-2 level of theory.\(^{27}\) Boatz and Gordon\(^{26}\) had previously predicted the heats of formation for the two isomers of Si\(_2\)H\(_4\) using G-1 theory. The energetics of some of the Si\(_2\)H\(_n^+\) ions have also been studied theoretically by Rahavachari,\(^{28}\) Kohler and Lisichka,\(^{29}\) and Colegrove and Schaefer.\(^{31}\) Ho and Melius\(^{32}\) employed the BAC-MP4 approach to calculate the \(\Delta H_{298}^\circ\) for the neutral Si\(_2\)H\(_4\), Sax and Kalcher\(^{26}\) have used CSD computations with a bond additivity approach to obtain \(\Delta H_{298}^\circ\) of Si\(_2\)H\(_4\) (m = 1–5). Goddard et al.\(^{15}\) have calculated bond dissociation energies for a number of Si\(_2\)H\(_4\) with GVB-CI methods. Pathways for the thermal decomposition of disilane have been studied by Gordon et al.\(^{31}\), Handy et al.\(^{71}\), Pople et al.\(^{72}\) and Krogh-Jespersen\(^{26}\) have also computed the geometries and relative energies of the Si\(_2\)H\(_4\) isomers. Colegrove and Schaefer\(^{27}\) have studied the isomers of Si\(_2\)H\(_4\) and have reviewed previous work on this system. Other calculations have looked at the heats of formation of methyl-substituted disilanes,\(^{34}\) the energetics of substituted disilenes and silylsilylenes\(^{35}\) and \(\pi\) bond energies of Si compounds.\(^{36}\) The G-2 calculations by Curtiss et al.\(^{27}\) are the most comprehensive and reliable set of theoretical heats of formation for the disilane-derived species. The same may be said about the
heats of formation predicted by Boatz and Gordon\textsuperscript{7} using homodesmic reactions for the series of methylsubstituted disilanes. The G-2 results agree well with those of Ho and Mielius\textsuperscript{2} and Sax and Kofler\textsuperscript{14} and with recent experimental data from Berkovits.\textsuperscript{15} The approximate 10 kcal/mol discrepancies seen between the G-2 calculations and the values obtained by Horowitz and Goddard\textsuperscript{16} can probably be traced to the lower level of calculation used in the latter.

2.2.5. $\text{SiF}_n$\textsuperscript{14}

The theoretical and experimental heats of formation for $\text{SiX}_n$ and $\text{SiX}_n$\textsuperscript{14} ($X = F, C\text{I}$) are collected in Table 2. The experimental thermochemistry of silicon halogen compounds has been reviewed by Walsh.\textsuperscript{16} The heat of formation of $\text{SiF}_4$ has recently been reconfirmed as $\Delta H_{298} = 386.18 \pm 0.1$ kcal/mol by fluorine bomb calorimetry.\textsuperscript{13} Doncaster and Walsh\textsuperscript{17} obtained $D_{2}(\text{Si-F}) = 100.1$ kcal/mol from $\text{SiF}_2 + \text{H} \rightarrow \text{SiF}_3 + \text{HF}$, yielding $\Delta H_{298} (\text{SiF}_3) = 239 \pm 5$ kcal/mol. Farber and Srivastava\textsuperscript{18} find $\Delta H_{298} = 259 \pm 5$ kcal/mol for $\text{SiF}_4$ using mass spectrometry-efusion methods; Weber and Armentrout\textsuperscript{19} obtained $\Delta H_{298} (\text{SiF}_3) = -257 \pm 3$ kcal/mol by guided ion beam/mass spectroscopy. The heat of formation of $\text{SiF}_2$ had been well established at $-140.2 \pm 2$ kcal/mol.\textsuperscript{14,20} From the wide range of values for $\text{SiF}$, Walsh\textsuperscript{16} recommends that $\Delta H_{298} (\text{SiF}) = -5 \pm 6$ be used with caution. Armentrout and co-workers\textsuperscript{20} have recently determined the heats of formation of $\text{SiF}_4$ by collision-induced dissociation and charge transfer reactions.

Theoretical heats of formation for $\text{SiF}_4$ have been determined using atomization energies\textsuperscript{21} (GVBJ-4 with a DZP basis set), the bond additivity approach\textsuperscript{22} (at the MP4/S-31 + + G(2df,2p) and G1 theory).\textsuperscript{14} BAC, isodesmic and G-1 approaches are in good agreement with each other: all three clearly favor $-239$ kcal/mol for $\Delta H_{298}$ (SiF$_4$) and indicate that $\Delta H_{298}$ (SiF$_3$) should be about 10 kcal/mol more negative than the older values. The calculations are in very good agreement with the most recent experiments.\textsuperscript{21}

2.2.6. $\text{SiF}_n$\textsuperscript{14}

The experimental heat of formation of $\text{SiF}_4$\textsuperscript{14} has been obtained from the appearance potentials of $\text{SiF}_4$ from $\text{SiF}_4$ and $\text{SiF}_3\text{Cl}_2$.\textsuperscript{18,20} The
Table 2. Theoretical and Experimental ΔH°₂₉₈ for Si₆X₄ and SiX₆⁺ (n = 1−4; X = F, Cl, CH₃) (kcal/mol)

<table>
<thead>
<tr>
<th>Level</th>
<th>Ref</th>
<th>SiX₄</th>
<th>SiX₆⁺</th>
<th>SiX₆⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(n = 1−4; X = F, Cl, CH₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIF₆₂⁺</td>
<td>BAC-MP4 [19]</td>
<td>−12.4</td>
<td>−49.9</td>
<td>−257.4</td>
</tr>
<tr>
<td></td>
<td>G-1  [58]</td>
<td>−14.0</td>
<td>−150.2</td>
<td>−234.9</td>
</tr>
<tr>
<td></td>
<td>G-2  [58]</td>
<td>−13.5</td>
<td>−149.3</td>
<td>−233.3</td>
</tr>
<tr>
<td></td>
<td>isotropic [52]</td>
<td>−14.2</td>
<td>−153.0</td>
<td>−240.7</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>−5 ± 60</td>
<td>140.5 ± 20</td>
<td>−239 ± 50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−11.2 ± 2.1'</td>
<td>−152.4 ± 1.5'</td>
<td>−238.4 ± 1.1'</td>
</tr>
<tr>
<td>SIF₆⁺</td>
<td>BAC-MP4 [55]</td>
<td>154.8</td>
<td>96.2</td>
<td>−31.4</td>
</tr>
<tr>
<td></td>
<td>isotropic [55]</td>
<td>153.4</td>
<td>100.4</td>
<td>−29.5</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>170 ± 7.2'</td>
<td>109 ± 2'</td>
<td>−34.4 ± 2'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153.3 ± 1.1'</td>
<td>98.0 ± 1.2'</td>
<td>−26.7 ± 0.6'</td>
</tr>
<tr>
<td>SIF₅⁺</td>
<td>isotropic [58]</td>
<td>−0.1</td>
<td>−143.8</td>
<td>−202.5</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>170 ± 7.2'</td>
<td>109 ± 2'</td>
<td>−34.4 ± 2'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153.3 ± 1.1'</td>
<td>98.0 ± 1.2'</td>
<td>−26.7 ± 0.6'</td>
</tr>
<tr>
<td>SICl₄</td>
<td>BAC-MP4 [17]</td>
<td>37.9</td>
<td>−37.6</td>
<td>−76.5</td>
</tr>
<tr>
<td></td>
<td>isotropic [96]</td>
<td>36.6</td>
<td>−38.9</td>
<td>−76.4</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>47.4 ± 1.0'</td>
<td>40.3 ± 0.8'</td>
<td>−80.1 ± 2.2'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.4 ± 0.6'</td>
<td>−39 ± 3.4'</td>
<td></td>
</tr>
<tr>
<td>SICl₃</td>
<td>isotropic [96]</td>
<td>205.9</td>
<td>187.1</td>
<td>106.2</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>217 ± 7'</td>
<td>188 ± 9</td>
<td>102 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>203 ± 2.5'</td>
<td>190 ± 0.6</td>
<td>99.8 ± 1.6'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>187.3 ± 2.3'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SICl₂₂</td>
<td>BAC-MP4 [108]</td>
<td>74.5</td>
<td>32.2</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>G-1  [65]</td>
<td>74.5</td>
<td>32.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>26 ± 2'</td>
<td>26 ± 2'</td>
<td>−1 ± 2'</td>
</tr>
</tbody>
</table>

*Experimental ionization potentials of SIF and SIF₆ were 7.26 eV and 10.74 eV, respectively; the ΔH°₂₉₈ (SIF₆⁺) can then be obtained by combining the IP with the heats of formation of the neutrals. Arm-

neutral and co-workers have used thresholds for Si+ + SIF₆ → SIF₆+ + SIF₃, SIF₅⁺ + SIF₃, and for Xe+ + SIF₆.  

The see formation of SiX₆ and SiX₆⁺ has been obtained from SIF₆ and SIF₆CH₃. The
to determine $\Delta H_{298}^\circ (\text{SiF}_n^\circ)$. The theoretical values were obtained by the bond additivity method based on the experimental value for SiF$_3^\circ$ and from isodesmic and isoglyclic reactions SiF$_n^\circ$ + Si$^+$ + Si or SiF$_n^\circ$ + Si$^+$ + 2 H → SiF$_n^\circ$ + Si + H$_2$ computed at the MP4/6-31G** level. Good agreement is found with the most recent experimental values. The calculations also agree well with the measured threshold for SiF$_2^+ +$ SiF$_3$ → SiF$_4^+$ + SiF$_2^\circ$, but suggest that the channels leading to SiF$_2^+ +$ SiF$_3^\circ$ and SiF$_3^\circ +$ SiF$_2^\circ$ involve activation barriers.

2.2.7. SiF$_n^\circ$

The only experimental electron affinity data available in this series is for SiF$_n^\circ$, and this is only an upper bound. Michels, et al. have computed the electron affinities of SiF$_n$ by isodesmic reactions and by G-1 and G-2 theory. The accuracy of the latter two is probably similar to the corresponding calculations on SiF$_2^\circ$, where experimental values are available for comparison.

2.2.8. SiCl$_n$

The calculated and experimental heats of formation for SiCl$_n$ are summarized in Table 2. The $\Delta H_f$ for SiCl$_4$ is $-158.4$ kcal/mol, determined from the heat of chlorination of silicon. Waldb et al. obtained $\Delta H_{298}^\circ (\text{SiCl}_4) = 80.1 \pm 2.2$ kcal/mol from SiHCl$_3$ + H. Farber and Srivastava find $-93.3 \pm 4$ kcal/mol for SiCl$_4$ in their effusion/mass spectrometric study. There is good agreement among the experimental studies that the heat of formation of SiCl$_n$ is $-40.3 \pm 0.8$ kcal/mol. Effusion/mass spectrometry studies yield $47.1 \pm 0.6$ kcal/mol for $\Delta H_{298}^\circ (\text{SiCl}_n)$, but spectroscopic studies give values that are 5–15 kcal/mol lower (with large uncertainties). Weber and Armbrutova obtained $44 \pm 6$ kcal/mol from studies on Si$^+$ + SiCl$_4$.

For SiCl$_n$, BAC calculations have been carried out at the MP4/6–31G** level (with $n$ and without bond length or spin corrections). Heats of formation have also been computed using isodesmic reactions (1) and (2) at the MP4/6–31G** level. Both sets of calculations support the $-80$ kcal/mol for $\Delta H_{298}^\circ (\text{SiCl}_3)$. Good agreement with experiment is also found for SiCl$_3$, but SiCl$_3$ is calculated to be 6–10 kcal/mol more stable than suggested by experiment.\textsuperscript{10}
data available in this series. Michels, et al.14 have indosmec reactions and by other two is probably sinlar 15, where experimental val-

of formation for SiCl<sub>4</sub> are SiCl<sub>4</sub> is −158.4 kcal/mol, of silicon.15 Walsh et al.16 17/mol from SiCl<sub>4</sub> + I, kcal/mol for SiCl<sub>4</sub> in their is good agreement among of formation of SiCl<sub>4</sub> is pectometry studies17 yield : spectroscopic studies give large uncertainties). Weber of from studies on SI + 18 , carried out at the MP4(6- 21G or spin corrections), 19 using indosmec reactions 20 Both sets of calculations (Cl<sub>4</sub>). Good agreement with CI is calculated to be 6-10 experiment.21,22

2.2.9. SiCl<sub>4</sub><sup>+</sup>

The experimental heat of formation of SiCl<sub>4</sub><sup>+</sup> has been obtained from the appearance potentials of SiCl<sub>4</sub><sup>+</sup> from SiCl<sub>4</sub><sup>+</sup> and SiHCl<sub>3</sub>17,18 Weber and Armentrout19 have used thresholds for Si<sup>+</sup> + SiCl<sub>4</sub> → SiCl<sub>2</sub><sup>+</sup> + Si + H<sub>2</sub> com-

- agreement is found with the calculations15,18 also agree well SiP<sub>3</sub> also SiF<sub>3</sub><sup>+</sup> and SiF<sub>2</sub><sup>+</sup>, but + SiP<sub>3</sub><sup>+</sup> and SiF<sub>2</sub><sup>+</sup> + SiF<sub>2</sub>

2.2.10. SiH<sub>3</sub>F<sub>3</sub> and SiH<sub>4</sub>Cl<sub>2</sub>

The heats of formation for the partially halogenated silanes, silyl radicals and silylenes, Table 3, are less well known than their perhalo counterparts. Some of the values listed in standard tables22 have been obtained by linear interpolation. Farber and Srivastava23,24 have used mass spectroscopy/refusion to determine ΔH<sub>f</sub>(298) for SiH<sub>3</sub>X<sub>3</sub>(X = F, Cl, Br); however the validity of the SiH<sub>3</sub>X<sub>3</sub> results have been ques-

- tioned.25,26 Given heats of formation for the perhydro and perhalo compounds, reliable estimates of the ΔH<sub>f</sub>(298) for the partially halogenate compunds can be obtained using indosmec reaction (3). For the fluoro derivatives, the ΔH<sub>f</sub>(298) have been computed at the MP2/DZ + polarization,27 MP4/6-31G** and MP4/6-31G** + G(2d,2p) levels. Along with the BAC-MP4 calculations, these results indicate the values obtained by Farber and Srivastava are in error by 5–10 kcal/mol and that linear interpolation is not a good approximation for the partially fluorinated compounds. For the chlorine compounds, how-

- ever, the calculations21,22 are in good agreement with experiment (as well as the linearly interpolated values, not shown).

The heats of formation of the fluorinated silyl cations, SiH<sub>3</sub>F<sub>3</sub><sup>+</sup>, have been calculated at the MP4/6-31G** level28 by using the BAC method, proton affinities and ionization energies. No calculations have
| Table 3. Theoretical and Experimental $\Delta H_{298}$ for SiH$_4$, SiH$_2$X, SiH$_2$X$^*$, SiH$_4$, and SiH$_4$Cl$_4$ |
|---|---|---|---|---|---|---|---|---|
| SiH$_4$ |  |  |  |  |  |  |  |  |
| BAC-MP4 |  [19] |  35.7 |  -42.2 |  -139.6 |  -85.5 |  -586.4 |  -288.6 |  |
| isodesmic |  [200] |  |  |  |  |  |  |  |
| isodesmic |  [215] |  -31.7 |  -42.5 |  -140.1 |  -85.6 |  -185.7 |  -287.7 |  |
| isodesmic |  [52] |  -37.8 |  -44.9 |  -142.6 |  -85.8 |  -186.3 |  -289.2 |  |
| Experiment |  |  $-41 \pm 3^\circ$ |  $-49 \pm 5^\circ$ |  $-144 \pm 5^\circ$ |  $-90 \pm 5^\circ$ |  $-189 \pm 5^\circ$ |  $-287 \pm 5^\circ$ |  |
| $\text{SiH}_2X^*$ |  |  |  |  |  |  |  |  |
| BAC-MP4 |  [55] |  181.6 |  140.6 |  49.8 |  176.3 |  84.5 |  -4.7 |  |
| [55] |  183.0 |  141.5 |  50.5 |  177.3 |  85.3 |  -3.4 |  |
| SiH$_2$Cl$_4$ |  |  |  |  |  |  |  |  |
| BAC-MP4 |  [17] |  17.0 |  7.8 |  $-34.3$ |  $-32.2$ |  $-74.5$ |  $-117.0$ |  |
| [19] |  15.9 |  7.9 |  $-34.0$ |  $-32.0$ |  $-74.4$ |  $-117.1$ |  |
| Experiment |  |  $-33.9 \pm 2^\circ$ |  $-32.4 \pm 2.5^\circ$ |  $-76.6 \pm 3^\circ$ |  $-75.3 \pm 2^\circ$ |  $-118.6 \pm 1.5^\circ$ |  $-119.3 \pm 1.5^\circ$ |  |
| $\text{SiH}_4(\text{CH}_3)_2$ |  |  |  |  |  |  |  |  |
| isodesmic |  [113] |  |  |  |  |  |  |  |
| BAC-MP4 |  [108] |  48.8 |  33.1 |  18.3 |  $-7.3$ |  $-23.2$ |  $-39.4$ |  |
| C-1 |  [65] |  50.6 |  31.1 |  15.2 |  $-6.9^\circ$ |  $-22.6^\circ$ |  $-39.0^\circ$ |  |
| Experiment |  |  $44 \pm 2^\circ$ |  $31 \pm 2^\circ$ |  $15 \pm 2^\circ$ |  $-6.9^\circ$ |  $-22.6^\circ$ |  $-39.0^\circ$ |  |

$^*$ref. [29] (linear interpolation), $^*$ref. [97], $^*$ref. [29] (no interpolation), $^*$ref. [98], $^*$ref. [105]
been published for the chlorine series. Experimental vertical ionization potentials are available for some of the fluoro and chloro compounds, but adiabatic ionization potentials have not been reported.

Ignacio and Schlegel\(^1\) have used isodesmic reactions to predict the heats of formation for several mixed fluorochlorosilanes at 298K and 1 atm. In kcal/mol, these are (experimental values from the JANAF tables\(^2\) in parentheses): SiH\(_4\)FCl\(_3\) = \(-129.3\); SiH\(_4\)F\(_2\)Cl\(_2\) = \(-230.3\); SiHF\(_2\)Cl\(_3\) = \(-171.6\); SiF\(_2\)Cl\(_4\) = \(-329.5\) (\(-315.0\)); SiF\(_3\)Cl\(_2\) = \(-272.9\); SiF\(_4\)Cl\(_2\) = \(-215.8\) (\(-201.0\)). The deviations between theory and experiment are much larger than expected for this level of theory, suggesting that the experimental values may be in error.

### 2.2.11. Silaethylene and Methylisilylene

The archetype of the silicon-carbon bond, silaethylene, deserves a special place in any survey of silicon compounds (for reviews of earlier work see refs 102 and 103). In the last few years there has been considerable activity related to the stability of silaethylene and its isomer, methylisilylene. Early experimental estimates\(^3\) suggested \(\Delta H^\text{f}\text{mol}(\text{CH}_2\text{SiH}) = 39 \pm 5\) kcal/mol and \(\Delta H^\text{f}\text{mol}(\text{CH}_2\text{SiH}) = 42 \pm 5\) kcal/mol. Recent ion cyclotron resonance measurements\(^4\) gave 43 \pm 3 and 53 \pm 3 kcal/mol, respectively. Other experimental estimates for CH\(_2\)SiH include 44 \pm 3 kcal/mol\(^5\) and 48 \pm 2 kcal/mol\(^6\). In agreement with a number of earlier theoretical studies, Pople et al.\(^7\) find the lowest surface to be the singlet and silaethylene to be the most stable isomer. Silaethylene is calculated to be more stable than CH\(_2\)SiH by 2.2 kcal/mol at the MP4/6-31G\(^*\) level,\(^8\) by 3.2 kcal/mol at the MP4/6-311G\(^**\) level\(^9\) and by 7.9 kcal/mol at the BAC-MP4 level.\(^10\) Calculations with the GVB-Cl approach using a DZP basis set place silaethylene 11.6 kcal/mol lower than methylisilylene, but much higher level calculations by Gre et al.\(^11\) indicate that silaethylene is only 4 kcal/mol more stable by CCSDT-1 computations with a triple zeta basis set augmented by 2 sets of f functions, a set of f functions, and diffuse orbitals. The G-1 level of theory gives \(\Delta H^\text{f}\text{mol}(\text{CH}_2\text{SiH}) = 46.5\) and \(\Delta H^\text{f}\text{mol}(\text{CH}_2\text{SiH}) = 50.6\) kcal/mol. Isodesmic reactions support the latter, giving \(\Delta H^\text{f}\text{mol}(\text{CH}_2\text{SiH}) = 49.2\) kcal/mol.

The heat of formation of silaethylene suggests a rather weak bond; however, when the difference in electronegativity of carbon and silicon are taken into account, \(\pi\) bonds to carbon and silicon are similar.\(^12\) The heats

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experiment</th>
<th>Isomer 1</th>
<th>Isomer 2</th>
<th>GC (298)</th>
<th>GC (298)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH(_4)FCl(_3)</td>
<td>-129.3</td>
<td>-118.8</td>
<td>-118.8</td>
<td>-118.8</td>
<td>-118.8</td>
</tr>
<tr>
<td>SiH(_4)F(_2)Cl(_2)</td>
<td>-230.3</td>
<td>-226.5</td>
<td>-226.5</td>
<td>-226.5</td>
<td>-226.5</td>
</tr>
<tr>
<td>SiHF(_2)Cl(_3)</td>
<td>-171.6</td>
<td>-122.6</td>
<td>-122.6</td>
<td>-122.6</td>
<td>-122.6</td>
</tr>
<tr>
<td>SiF(_2)Cl(_4)</td>
<td>-329.5 (315.0)</td>
<td>-272.9</td>
<td>-272.9</td>
<td>-272.9</td>
<td>-272.9</td>
</tr>
<tr>
<td>SiF(_3)Cl(_2)</td>
<td>-215.8 (201.0)</td>
<td>-189.4</td>
<td>-189.4</td>
<td>-189.4</td>
<td>-189.4</td>
</tr>
</tbody>
</table>
of formation of compounds with silicon-silicon multiple bonds were discussed above in the Si₃H₅ section.

2.2.12. Alkyl Silanes

The experimental heats of formation have been reviewed by Walsh et al. ³⁹ The measured ΔH₂⁰ for SiH₃CH₂, SiH₃(CH₃)₂, SiH(CH₃)₃, and Si(CH₃)₄ are −6.9±1.1, −22.6±1.1, −39.0±1.1, and −55.7±0.8 kcal/mol, respectively. ⁴⁰ Isodesmic reactions in the MP2/6-31G*//HF/3–21G level⁴¹ and BAC-MP4 calculations⁴² yield ΔH° that are in good agreement with the revised experimental heats of formation, as can be seen from Tables 2 and 3. The BAC-MP4 calculations also include theoretical heats of formation for H₃SiCH₂, H₂CCSH₂, HCCSH₂, and methyl silenes, and discuss available experimental data for these compounds. The experimental heats of formation of methyl substituted silylene have been obtained by O’Neal et al. ⁴³ and by Walsh. ⁴⁴ Isodesmic reactions by Gordon et al. ⁴⁴ and BAC-MP4 calculations by Melius et al. ⁴⁵ provide theoretical ΔH₂⁰ that support the values of O’Neal. ⁴⁶

Gordon, Boatz and Walsh⁴⁷ report that the experimental heats of formation of the mono-, di- tri- and tetraethylsilanes are −34.2, −43.6±1.4, −48.9±3.6, −52.0±1.2) and (70.9±1.4, −63.4±3.7) kcal/mol, respectively and note that the values for mono- and diethylsilane are in substantial disagreement with additivity estimates of ΔH₂⁰ and with ab initio calculations. Ab initio calculations on isodesmic reactions give −9.0 and −28.0 kcal/mol for SiH₃CH₂, and SiH₃(CH₃)₂ at the MP2/6-31G*//HF/3–21G level.⁴⁸ In addition, these authors have used homodesmic reactions to calculate the following heats of formation: 1-silapentane = −14.7, 2-silapentane = −25.4, 1-silahexane = −24.5, 2-silahexane = −35.6, silacyclopentane = 30.2, silacyclobutane = −9.3, silacyclopentane = −15.3, silacyclohexane = −22.0 kcal/mol. Strain energies have also been calculated for silacyclobutenes, silabicyclobutanes and silapropellane.⁴⁹ Heats of formation for ethyl-, ethenyl- and ethynylsilane can also be estimated from their thermal decomposition reactions (discussed below), provided that appropriate isodesmic reactions are used.

Experimental heats of formation for a variety of alkyl substituted silyl radicals are known.⁵⁰ There have been no systematic ab initio studies of the heats of formation of alkylsilyl radicals; however,
Silanes, Halosilanes, and Alkylsilanes

Theoretical estimates of $\Delta H_{\text{f},0}^\circ$ for SiH$_2$CH$_3$ and SiH$_2$CH$_2$CH$_3$ radicals can be obtained from the thermal decomposition reactions (discussed below) with the aid of suitable isodesmic reactions. The effect of substituents on the stability of silyl radicals has also been studied and found to be much smaller than the effect on carbon-centered radicals.

2.2.13. Alkyldisilanes

As noted above, homodesmic reactions generally provide more reliable estimates of heats of formation than do isodesmic reactions. A systematic survey of the heats of formation of all possible methyl-substituted disilanes has recently been performed, using homodesmic reactions, at the MP2/6-31G(d,p)/HF/3-21G* level of theory. Theoretical heats of formation are systematically within about 1.0 kcal/mol of the experimental values of O'Neal, Ring and co-workers.$^{66}$ A similar systematic survey has been performed for methyl-substituted silaethylene and disilene, using isodesmic reactions.$^{67}$ The calculated heats of formation for methyl- and 1,1-dimethyl silaethylene (31 and 15 kcal/mol, respectively) are both 10 kcal/mol higher than the experimental values. Since one expects isodesmic reactions to predict heats of formation more accurately, and since the G-1 and G-2 heats of formation for the parent silaethylene are also 10 kcal/mol higher than the experimental estimate, it was suggested that the experimental value needs to be re-evaluated.

Ignacio and Schlegel$^{70}$ have used isodesmic reactions with MP4/6-31G(d)/HF/6-31G(d) energies to predict the heats of formation for fluoro disilane ($-73.4$ kcal/mol), 1,1- and 1,2-difluoro disilane ($-174.0$ and $-166.2$ kcal/mol, respectively), and several fluoro-substituted silaethylidienes, using the G-2 heat of formation of disilene as a reference value.

2.2.14. $Si_n$ Compounds

Raghavachari$^{113}$ has performed the most extensive series of calculations on silicon clusters and predicted their binding energies relative to $n$ Si (see also$^{116}$), using both MP4 and CCSD(T) with extended basis sets and the G-2 level of theory. The good agreement (within 0.2 eV) with experiment for $Si_3$ and $Si_4$ was used to produce a set of scaled binding energies for the clusters $Si_n$ ($n = 4-10$). The binding energies...
per atom are predicted to increase steadily with n. For all clusters up to 

$n = 10$, the lowest energy fragmentation process is predicted to be 

$Si_n \rightarrow Si_{n-1}$; however, $Si_{10}$ is predicted to fragment preferentially into 

$Si_6 + Si_4$, in excellent agreement with the observed fragmentation 

patterns for the corresponding cations.$^{138}$

3. REACTIONS AT SILICON CENTERS

Kinetic studies of the reactions of silicon centers have been of great 

interest for a considerable time.$^{129-131}$ A long-standing interest has been 
in the development of an understanding of the reactions of silicon 
compounds compare with analogous reactions of carbon compounds. 

Experimentally, particular focus has been directed toward understand- 
ings the kinetics and mechanisms of hydrogen-abstraction reactions$^{2-9}$, mo- 

cellular ionization processes$^{96}$, unimolecular decomposition pro- 
ces, and polymerization mechanisms. Theoretical calculation of the 

transition states, barrier heights and reaction rates of many of these 

processes can in principle lead to a more fundamental understanding of 
silicon center reactivity. The emergence of chemical vapor deposition 

(CVD)$^{12,13}$ technologies, for which silicon containing compounds are 

principal precursors, has heightened the interest in developing a funda- 

mental understanding of the mechanisms and rates of reaction pro- 
cesses involving silicon compounds.

Much of the theoretical emphasis in problems relating to silicon 

chemistry has focused on understanding the nature of silicon-carbon 
and silicon-silicon bonding.$^{11,10}$ The application of ab initio methods 
to the calculation of transition states, barrier heights and reaction rates 
to help elucidate mechanistic issues has been less extensive. Some 
simple systems have been studied in detail, because they are 

small enough to allow very high level calculations to be tested against 
reliable experimental results. The potential energy surfaces of more 

complex silicon compounds are now being actively studied.

The emphasis in this section will be on theoretical studies of poten-
tial energy surfaces for the decompositions of silanes, halosilanes, and 
alicysilanes. Related reactions, such as insertions, abstractions, and 
ionizations will also be considered, insofar as they impact the 
thermal decomposition mechanisms.

A general alkylysilane $RSiH_3XH_4$ can decompose in several ways:

$$RSiH_2XH_3 \rightarrow RXH_4 + SiH_2$$

(1)
CONS C EN TERS

n centers have been of great standing interest because of how the reactions of silicon derivatives of carbon compounds have been directed toward understanding the abstraction reactions of molecular decomposition processes. Theoretical calculation of the reaction rates of many of these fundamental understanding of chemical vapor deposition on containing compounds are interest is developing a framework and rate of reaction problems relating to silicon. The nature of silicon-carbon siliconation of ab initio methods are highly accurate and reaction rates are less extensive. Some cases described in this work are the reaction of silicon, halosilanes, and silicones, insertions, abstractions, and insertion as they impact the decomposition in several ways:

Reactions (1) and (2) correspond to silylene eliminations, while (3)–(5) are three alternative ways of eliminating molecular hydrogen. If X = C, the carbene eliminations analogous to (1) and (2) are also possible. Since carbenes are generally much less stable than silylenes, the carbene eliminations tend to be thermodynamically higher energy processes. The remaining reactions (6)–(9) are homolytic cleavages, so their energy requirements will reflect the corresponding bond energies. Of the alternative H₂ elimination processes, the 1,2-eliminations (4) are generally found to have higher barriers than the 1,1-eliminations.

3.1. Unimolecular Concerted Molecular Processes

3.1.1. 1,1-H₂ Elimination Processes (X = H, F)

SiH₄ + SiH₂X X = H, F. One of the prototypical reactions involving decompositions of compounds containing silicon centers is the 1,1-H₂ elimination process, reaction (3). In fact, it is frequently one of the dominant processes in unimolecular decompositions. The simplest and most well studied example is silane decomposition to silylene and molecular hydrogen, SiH₄ → SiH₂ + H₂. The reverse of the 1,1-H₂ elimination process is SiH₂ insertion into H₂. The barrier we report here is for the reverse process of the 1,1-H₂ elimination process. Early calculations predicted this barrier to be in the range of 5–9 kcal/mol.
Gordon\textsuperscript{14} calculated the barrier to be 8.6 kcal/mol, using the MP3/6-31G* level of theory, and calculations by Grev and Schafer\textsuperscript{15} predicted a barrier of 6.7 kcal/mol using MCSCF methods with large basis sets, augmented by CSD plus size consistent corrections. Sosa and Schlegel\textsuperscript{16} obtained a barrier of 6.0 kcal/mol, at the MP4(SDQ)/6-31G*/HF/6-31G* level. Sax and Olbrich\textsuperscript{17} examined the silane potential energy surface with multi-reference configuration interaction (MRD-CI) wavefunctions and the 6-311G(d,p) basis set. These authors found a classical barrier height of 4.9 kcal/mol and an activation energy (at 600K) of 6.3 kcal/mol. All of the foregoing calculations used what may be considered to be modest basis sets, with varying levels of correlation corrections. The extensive calculations of Gordon et al.\textsuperscript{18} suggest that the barrier is much smaller, on the order of 1-2 kcal/mol. These calculations used similar levels of correlation (MP4SDTQ), but much larger basis sets (6-311G(3df,3pd)) and correlated geometries (MP2/6-311G(2d,2p)). Experimentally\textsuperscript{19}, a barrier of 5.5 ± 1.0 kcal/mol had been the long standing reported value for the insertion reaction, SiH\textsubscript{4} + H\textsubscript{2} → SiH\textsubscript{3}H, but more recent determinations estimate this barrier to be 0.5 kcal/mol.\textsuperscript{20-22}

The work of Sosa and Schlegel\textsuperscript{16} and Gordon et al.\textsuperscript{18} demonstrate that the calculated barriers are much too high at Hartree-Fock levels and that both basis set and electron correlation corrections to these barriers are significant. When electron correlation is included and large enough basis sets are used, the agreement between theory and experiment is excellent. Indeed, the highest quality theoretical results\textsuperscript{16} led the experimental determination in the case of the ground state unimolecular decomposition of silane. As noted in Section II, this was also the case for the heat of formation of SiH\textsubscript{2}. An interesting feature that only appears at correlated levels of theory is a long-range minimum in the entrance channel, between reactants and the transition state.

Several authors have examined the photochemical dissociation of silane, in view of the importance of this process in chemical vapor deposition. Gordon\textsuperscript{18} used the 4-31G basis set, augmented by Rydberg functions on the central silic-on, to demonstrate that silane undergoes Jahn-Teller distortion to either C\textsubscript{2v} or C\textsubscript{3v} symmetry in its lowest singlet excited state and subsequently dissociates to silylene and molecular hydrogen, with no barrier. The transformation of the vertical excited Rydberg state into a valence state upon dissociation was noted.

Oikawa and co-workers examined both the lowest triplet\textsuperscript{23} and several
Silanes, Halosilanes, and Alkylsilanes

low-lying singlet states of silane. The triplet state was predicted to dissociate to SiH + H, while a barrierless channel was found to SiH + + H on the lowest singlet surface.

In an early series of papers, Sosa and Schlegel examined the effects of fluorine substitution on the barrier to silane decomposition. These authors found that successively replacing silylene hydrogens with fluorines significantly increases the insertion barrier into H₂ (at the MP4/SDQ/6-31G* level of theory) to 25.8 kcal/mol for SiHF and 61.4 kcal/mol for SiF₂. More recently, Ignacio and Schlegel have examined the thermal decomposition pathways for the entire series SiHₓF₄₋ₓ using a combination of MP4/SDTQ/6-31G(d,p) energies and a sequence of isodesmic reactions. As in the earlier work, these authors predict a substantial increase in the H₂ insertion barriers from SiH₂ (2 kcal/mol) to SiHF (24 kcal/mol) to SiF₂ (55 kcal/mol).

Contrast, the analogous barriers for insertion into HF increase at a much slower rate, from 7 to 11 to 21 kcal/mol, respectively, upon successively replacing H with F in silylene. In keeping with the very weak bond in molecular fluorine, the corresponding insertions into F₂ are all predicted to be essentially zero.

Despite the large insertion barriers upon fluorine substitution, molecular elimination processes are predicted to dominate the thermal decomposition of fluorinated silanes. Elimination of molecular hydrogen is the preferred decomposition mode both thermodynamically and kinetically for SiH₄, SiHF, and SiF₂, while HF elimination is found to be the preferred process for SiH₉F₅, with a barrier of 89 kcal/mol. Only for SiF₄, for which the only molecular elimination produces the weakly bound fluorine molecule, is the preferred process a homolytic cleavage to produce atomic fluorine. For nearly all of these potential energy surfaces, a long-range minimum or "cluster" is found in the insertion entrance channel, in analogy with the silane case discussed above. The only case for which such a cluster is not found is the SiF₂ insertion into H₂.

Related ions. Kalchenko used the CEPA-1 method, with a TZ2P basis set and effective core potential for Si to compare the stabilities of SiH₄⁻ and CH₄⁻. Whereas the carbon species has two stable complexes, CH₄⁻H" and H₂−CH₄⁻, for silicon the former
species leads directly to proton abstraction. In addition, the latter complex between silylene anion and molecular hydrogen is only marginally stable (0.1 kcal/mol) to dissociation.

The potential energy surface of SiH\textsubscript{2}⁺ has been examined by Hirst and Guest\textsuperscript{14} and Gonzalez and co-workers\textsuperscript{15}. Since the former calculations were performed with a much higher level of theory, MRD-Cl with a TZP basis set, we will only summarize that work. The \(^3\text{B}₁\) state is predicted to be at least 0.35 ev above the dissociation products Si⁺ + H\textsubscript{2}, but there is a 3.5 ev barrier separating the two. The \(^2\text{A}₂\) state is 0.6 kcal/mol below Si⁺ + H\textsubscript{2} and again separated from dissociation by a large (4.2 ev) barrier. In contrast, the collinear ground state \(^2\Sigma\) approach of Si⁺ + H-H to give SiH⁺ + H occurs with essentially no barrier.

Several groups have investigated the molecular and electronic structure of SiH\textsubscript{2}⁺.\textsuperscript{16-20} While all of these \textit{ab initio} calculations predict this cation to have a Jahn-Teller-distorted geometry, only the three most recent papers correctly predict the global minimum to be a \(C\text{₂}₀\) structure. The two most extensive sets of calculations on this system are those by Kudo and Nagase\textsuperscript{16} and Padden-Row and Wong.\textsuperscript{20} These calculations were performed at the MP4/6-31 + G(2df,2p)/MP2/6-31g(d,p) and MP4/6-31G(d,p)/MP2/6-31G(d,p) levels of theory, respectively, and are in essential agreement that the \(C\text{₂}₀\) structure corresponds to a complex between SiH\textsubscript{2}⁺ and H\textsubscript{2}. Dissociation to the latter products requires less than 10 kcal/mol and occurs with no additional barrier. A \(C\text{₂}₀\) minimum that lies about 15 kcal/mol higher in energy than the \(C\text{₂}₀\) structure is separated from the more stable isomer by a barrier of less than 1 kcal/mol and is therefore unlikely to be observed.

Since the products SiH\textsubscript{2}⁺ + H are considerably higher in energy, the most likely decomposition channel appears to be SiH\textsubscript{2}⁺ + H\textsubscript{2}.

The situation seems to be somewhat different for SiMe\textsubscript{2}⁺. The minimum energy structure for this species is predicted at the MP2/6-31G(d)/HF/6-31G(d) level of theory to be \(C\text{₂}₀\), with the \(C\text{₂}₀\) structure lying 16 kcal/mol higher in energy.\textsuperscript{17} The \(C\text{₂}₀\) structure is predicted to be 16 kcal/mol below the products SiMe\textsubscript{2}⁺ + Me, while the \(C\text{₂}₀\) isomer is only 6 kcal/mol below SiMe\textsubscript{2}⁺ + C\textsubscript{₂}H\textsubscript{₄}. While no search for transition states was performed for this system, the available evidence suggests that both sets of products are likely to be observed. Based on the large effect of basis set and correlation on the structure and stability of the smaller cation, however, these results may be modified at higher levels of theory. Apeloig et al.\textsuperscript{18} examined the very complex C\textsubscript{₅}H\textsubscript{₅}Si⁺.
In addition, the latter molecular hydrogen is only minor.

A has been examined by Hirst et al. Since the former calculation level of theory, MRD-CI correlates that work. The 18 state of the dissociation products Si + H occurs with essentially no potential energy surface. While this study was performed at a modest level of theory, HF(6-31G(d)/HF/6-31G), the predictions appear to be in essential agreement with the experimental evidence.

Organosilanes: Methylsilane and Ethylsilane. It has become generally accepted that one of the predominant dissociation processes in organosilanes such as the alkylsilanes is the formation of hydrogen via 1,1-H2 elimination, reaction (3):

\[ \text{SiH}_{3} \rightarrow \text{SiH}_{2} + \text{H}_{2} \]  \hspace{1cm} (3)

Experimental results from numerous shock-tube and photodissociation studies of a variety of organosilanes support the general claim that reaction (3) dominates the dissociation of alkylsilanes. Here we consider two examples for the simplest alkylsilane family which provide both experimental and theoretical support for this assertion.

Theoretical studies on methylsilane\(^{111-113}\), have shown that the activation energy for 1,1-H2 elimination to yield methylsilylene (CH\(_{3}\)SiH) and molecular hydrogen is 63.2 kcal/mol (MP4(SDQ)/6-31G(d,p) levels of theory, relevant that the C\(_{2}\) structure corre-

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Organosilanes: Other Examples. The 1,1-H₂ elimination process for other classes of organosilanes has also been examined. The simplest systems from the class of alkenylsilanes and alkynylsilanes are vinylsilane and ethynylsilane, respectively. Theoretical studies of the 1,1-H₂ elimination process predict activation energies of 64.4 kcal/mol for vinylsilane<sup>16</sup> (MP4/6-31G(d)/HF/6-31G*) and 64.6 kcal/mol for ethynylsilane<sup>16</sup> (MP4/6-31G(d)/HF/6-31G*).

Table 4 summarizes theoretical and experimental results for 1,1-H₂ elimination reactions for the simple cases of alkyl-, alkenyl-, and alkynyl-silanes. A common feature of these reactions is that the substitution of various R groups on the R-SiH₃ unit has little influence on the activation energy for the 1,1-H₂ elimination. The series of fluorinated disilanes studied by Ignacio and Schlegel<sup>17</sup>, using MP4/6-31G(d)/HF/6-31G(d) energies, also have a nearly constant barrier for 1,1-H₂ elimination, although the barrier height for these molecules is about 10 kcal/mol smaller than that for the alkyllanes, as shown in Table 4. On the other hand, as noted above and illustrated in Table 4, successive substitution of F for H in silane increases the barrier for the 1,1-H₂ elimination by more than 10 kcal/mol for each fluorine, so there can be a substantial substituent effect in a given homologous series. As for the other compounds discussed above, 1,1-H₂ elimination is either the energetically favored decomposition path or one of

### Table 4. Comparison of Activation Energies for 1, 1-H₂ Elimination Processes for Simple Classes of Organosilanes

<table>
<thead>
<tr>
<th>System</th>
<th>Theory</th>
<th>Experiments</th>
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<tbody>
<tr>
<td>CH₃SiH₃ → CH₂SiH₂ + H₂</td>
<td>63.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>64.8, 63.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH₃SiH₁ → CH₂SiH₂ + H₂</td>
<td>66.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>65.0&lt;sup&gt;b&lt;/sup&gt;, 64.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH≡C≡SiH₁ → CH≡C≡SiH₂ + H₂</td>
<td>64.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>63.3&lt;sup&gt;a&lt;/sup&gt;, 63.96&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH≡C≡SiH₁ → CH≡C≡SiH₂ + H₂</td>
<td>64.9&lt;sup&gt;b&lt;/sup&gt;</td>
<td>61.2±5.2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiH₃ → SiH₂ + H₂</td>
<td>53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiH₂F → SiHF + H₂</td>
<td>70&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiH₂F → SiHF + H₂</td>
<td>80&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>H₂SiH₁ → H₂SiH₂ + H₂</td>
<td>55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>H₂SiH₁ → H₂SiH₂ + H₂</td>
<td>55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>H₂SiH₁ → H₂SiH₂ + H₂</td>
<td>54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>H₂SiH₁ → H₂SiH₂ + H₂</td>
<td>54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup>ref. 107<sup>a</sup> ref. 159<sup>a</sup> ref. 167<sup>a</sup> ref. 169<sup>a</sup> ref. 157<sup>a</sup> ref. 158<sup>a</sup> ref. 170<sup>a</sup> ref. 157<sup>a</sup> ref. 165<sup>a</sup> ref. 171<sup>a</sup> ref. 116<sup>a</sup> * ref. 120<sup>a</sup> * ref. 217<sup>a</sup>
1,1-H₂ elimination process has been examined. The studies of alkyl- and alkenylsilanes are theoretical studies of the energies of 64.4 kcal/mol (31G*) and 64.6 kcal/mol (4F6-31G*).

Theoretical results for 1,1-H₂ elimination reactions is that the H₂ unit has little influence on the reactions. The series of Schlegel, using MP4/6-31G* nearly constant barrier for ght for these molecules is alkylsilanes, as shown in and illustrated in Table 4, increases the barrier for the nol for each fluorine, so in a given homologous of above, 1,1-H₂ elimination is a non-misposition path or one of the possible pathways.

### 2.3 energetically likely pathways (see below) for the flusilanes.

Theoretical examination of the urinoloc decomposition pathways of ethynylsilane reveals an alternative pathway which is energetically favored relative to the 1,1-H₂ elimination processes. This involves a 1,2-silyl shift across the carbon-carbon triple bond. The calculated activation energy of 38.2 kcal/mol is ca. 28 kcal/mol lower than the activation energy for 1,1-H₂ elimination. Consequently, the alkynylsilanes may be a class of organosilanes where the general rule of 1,1-H₂ elimination processes dominating the reaction process breaks down.

### 3.1.2. 1,2-H₂ Elimination Processes: Production of Silanen

Ab initio studies have played a major role in clarifying the present understanding of the SiC double bond. Theoretical and experimental studies have focused on characterizing the nature and fundamental properties of silicon compounds containing SiC double bonds. One of the most simple cases, silene, 

\[
\text{SiH}_2=\text{CH}_2
\]

has been extensively studied theoretically and extensively reviewed. Although there has been great interest in the generation of silenes, many studies have focused on their generation via 1,2-hydrogen shift processes from alkylsilanes. Other attempts to generate silenes by thermal reaction have utilized 1,2-eliminations from α-lithiated silanes carrying a leaving group (X) on the silicon, such as a halogen. namely

\[
\text{Li}_2 \xrightarrow{X} \text{CH}_3-\text{CH}=\text{SiH}_2 \rightarrow \text{CH}_3=\text{CH}=\text{SiH}_2 + \text{Li} X
\]

A route that has not been explored as a means for generating silenes is from 1,2-H₂ elimination processes, reaction (4). The first calculation for the 1,2-H₂ elimination from methylysilane to produce silene and molecular hydrogen, namely:

\[
\text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_2=\text{SiH}_2 + \text{H}_2
\]

was performed by Gordon and Truong. At the MP4(SDTQ)/6-311G**/MP2/6-31G** level of theory, the activation energy was predicted to be 96.4 kcal mol⁻¹. The transition state structures for 1,2-H₂ elimination from ethynylsilane and vinylsilane at the HF/3-21G and HF/6-31G* levels are shown in Figure 1. Note that these transition
Figure 1. HF/3-21G and HF/6-31G* transition state structures for 1,2-H₂ elimination processes for ethylsilane and vinylsilane. Bond distances in Å, bond angles in deg.
state structures are rather asymmetric, with both of the leaving hydrogens closer to the more electronegative carbon. Indeed, the methylsilane transition state resembles a methane-silylene complex. This arrangement appears to be typical for 1,2-H₂ eliminations from silanes. The activation energies of the latter two reactions at the MP4(SDQ)/6-31G**//HF-6-31G* level of theory are 107.9 and 113.9 kcal/mol, respectively. The most facile of the 1,2-hydrogen eliminations for alkylsilanes that have been studied by ab initio methods occurs for disilane dissociation into disilene and molecular hydrogen. At the MP4(SDQ)/6-31G***/MP2/6-31G** level of theory, an activation energy of 89.0 kcal mol⁻¹ is calculated by Gordon and co-workers. Nagase and Kudo found an 85 kcal/mol barrier for the elimination of HCl from methylchlorosilane at the HF3-21G level of theory. Because of the rather high calculated barriers for 1,2-H₂ eliminations in disilane and the alkylsilanes, the analogous reactions were not considered for the fluorinated disilanes. It is interesting to note, however, that the 1,2-elimination of molecular hydrogen from silanol to form silanone has been predicted to be one of the competitive pathways for silanol decomposition.

The activation energies for the 1,2-H₂ elimination processes are summarized in Table 5. It is difficult to draw valid conclusions from the trends in the data since each have been performed at different levels of theory. Nevertheless, the compilation does suggest that substituent effects may play an important role in determining the barrier heights of 1,2-H₂ elimination processes.

Ohta et al. have used CASSCF (4 orbitals, 4 electrons) plus second order configuration interaction (SOCI) with a DZP basis set to examine the dimerization of two silylenes to disilene and compare this process to both the ethylene analog, as well as the mixed dimerization to silene. For disilene, the least motion (LM) dimerization path is symmetry forbidden for two ground state silylene singlets. As a result, there is a nonzero energy barrier along this path, but this barrier

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Barrier</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃H₄ + H₂ = Si₃H₃ + H₂</td>
<td>89.0</td>
<td>71</td>
</tr>
<tr>
<td>CH₂SiH₂ + CH = CH₂SiH₂ + H₂</td>
<td>96.4</td>
<td>107</td>
</tr>
<tr>
<td>CH₂CH₂SiH₂ + CH₂CH₂SiH₂ + H₂</td>
<td>107.9</td>
<td>169</td>
</tr>
<tr>
<td>CH₂⁺CH₃SiH₂ + CH₂⁺CH₃SiH₂ + H₂</td>
<td>113.9</td>
<td>171</td>
</tr>
</tbody>
</table>
disappears when the symmetry restriction is lifted. The silene fragments have different ground state spins and symmetries (1\(^B\) for CH\(_3\) and 1\(^A\) for SiH\(_3\)). Along the LM path, the combination of two singlets to form singlet silene again encounters a barrier which disappears when the symmetry constraint is relaxed. The singlet coupling of two triplets to form the same product has no barrier along the LM path.

Sakai and Gordon have investigated the addition of atomic hydrogen to silene to form either SiH\(_3\)CH\(_3\) or CH\(_3\)SiH\(_3\). The energetics for both reactions were predicted with both CASSCF/3–21G/CASSCF/3–21G and MP4/6–31G(d,p)/CASSCF/3–21G. Although the two levels of theory agree quite well with regard to the thermodynamics, there is significant spin contamination and configurational mixing at the transition state structures, leading to rather different predicted barrier heights. The CASSCF barriers are both quite small: 0.4 and 2.1 kcal/mol for SiH\(_3\)CH\(_3\) and CH\(_3\)SiH\(_3\), respectively. Barton and co-workers examined the 1,2-hydrogen shift connecting these two isomers with MP4/6–31G(d,p)/6-31G(d) energies. They predict the reaction SiH\(_3\)CH\(_3\) → CH\(_3\)SiH\(_3\) to be 10.8 kcal/mol exothermic and to occur with a 42.6 kcal/mol activation barrier. These results are both in excellent agreement with the experimental values of 8.9 and 41.0 kcal/mol, respectively.

3.1.3. Silylene and Carbone Eliminations

In this section we will review computational studies on SiH\(_3\) and CH\(_3\) elimination reactions, as well as the eliminations of substituted silenes and carbenes. SiH\(_3\) eliminations from silicon compounds usually form 3-center transition states. Examples of these processes are from \(ab\) \(into\) studies of decomposition pathways of methylsilane, ethylsilane, vinylsilane, ethynylysilane, disilane, trisilane, disilylmethane, dimethylsilane, silacyclop propane, and silacyclobutane, as well as the fluorinated disilanes. Carbone eliminations have been investigated for the foregoing alkyl compounds, as well as propane. Moreover, the reverse of these reactions can be considered as SiH\(_3\) or CH\(_3\) insertion reactions into the CH or SiH bonds.

Activation barriers for silylene eliminations are frequently similar in magnitude to those for 1,1-eliminations of molecular hydrogen, especially for disilanes, as may be seen by comparing the values given in Tables 1 and 3. As shown in Table 6, the activation barriers for SiH\(_3\)
is lifted. The silene fragment with symmetries $B_1$, for CH$_2$ reactivation of two singlets barrier which disappears $\mathbb{S}$ the siglet coupling of two $\mathbb{S}$. Along the LM path, $\mathbb{S}$ addition of atomic hydride, $\mathbb{S}$. The energetics for $\mathbb{S}$SCF/3-21G/CASSCF/3- $\mathbb{S}$G. Although the two level $\mathbb{S}$ thermodynamics, there is $\mathbb{S}$ ignatorial mixing at the $\mathbb{S}$ different predicted barrier $\mathbb{S}$ small: 0.4 and 2.1 kcal/ $\mathbb{S}$. Barton and co-workers $\mathbb{S}$ g these two isomers with $\mathbb{S}$ They predict the reaction $\mathbb{S}$ exothermic and to occur $\mathbb{S}$ these results are both in $\mathbb{S}$ alues of 8.9 and 41.0 kcal/ $\mathbb{S}$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$SiH$_4$ → CH$_2$ + SiH$_4$</td>
<td>71.9 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$SiH$_4$ → SiH$_4$ + SiH$_4$</td>
<td>50.0 kcal/mol</td>
</tr>
<tr>
<td>CH$_2$SiH$_2$SiH$_2$ → C$_2$H$_2$ + SiH$_4$</td>
<td>72.2 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$SiH$_2$SiH$_2$ → SiH$_4$ + SiH$_4$</td>
<td>53.2 kcal/mol</td>
</tr>
<tr>
<td>CH$_2$SiH$_2$SiH$_2$ → C$_2$H$_2$ + SiH$_4$</td>
<td>70.5 kcal/mol</td>
</tr>
<tr>
<td>C$_2$H$_2$SiH$_2$SiH$_2$ → C$_2$H$_2$ + SiH$_4$</td>
<td>76.5 kcal/mol</td>
</tr>
<tr>
<td>CH$_2$SiH$_2$CH$_2$SiH$_2$ → C$_2$H$_4$ + SiH$_4$</td>
<td>115.1 kcal/mol</td>
</tr>
<tr>
<td>CH$_2$SiH$_2$SiH$_2$ → CH$_2$SiH$_4$ + SiH$_4$</td>
<td>71.6 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$SiH$_4$SiH$_4$ → SiH$_4$ + SiH$_4$</td>
<td>58.4 kcal/mol</td>
</tr>
<tr>
<td>c-CH$_2$,SiH$_2$:CH$_2$:SiH$_2$:c-CH$_2$,SiH$_4$ + SiH$_4$</td>
<td>75.6 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$:F + SiH$_4$</td>
<td>55 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$:SiH$_4$</td>
<td>55 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$ + SiF$_4$</td>
<td>48 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$ + SiF$_4$</td>
<td>55 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$ + SiF$_4$</td>
<td>58 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$ + SiF$_4$</td>
<td>50 kcal/mol</td>
</tr>
<tr>
<td>SiH$_4$:SiH$_4$F → SiH$_4$ + SiF$_4$</td>
<td>71 kcal/mol</td>
</tr>
</tbody>
</table>

*Results determined at the MP4(SDQ)/M06-2X/6-311G* level of theory; all other processes are determined with MP2/6-31G* energies on either HF/6-31G* or HF/3-21G geometries; see text for references.

* Elimination from X-H bond. * * Elimination from X-Y bond.

Eliminations from CH bonds tend to be in the range of 70 ± 7 kcal/mol. The influence of the perturbing nature of the moiety attached to the CH bond on the energetics of these reactions seems to be rather minor. The barriers for silylene eliminations from SiH$_4$ bonds are also quite constant, but they are a much lower range of 53–56 kcal/mol. Silylene formations from X-Y bonds reflect both the length and strength of these heavy atom-heavy bonds. As X-Y changes from C-C to C-Si to Si-Si (Table 6), the barrier decreases from 115 to 72 to 58 kcal/mol. Similar trends apply, of course, to the reverse insertion reactions. Insertions of silylene into SiH$_4$ bonds tend to occur with little or no barrier, while insertions into CH bonds can have barriers as large as 15–20 kcal/mol. Barriers for insertions into X-H bonds tend to be much lower than into X-Y bonds, where Y = C or S. There are, however, two important exceptions to this general rule. If the X-Y bond is highly strained, the silylene insertion barrier is greatly decreased. For example, insertion into the CC bond of cyclopropane is 17 kcal/mol, compared with 58 kcal/mol for the corresponding inser-
tion into ethane. The other exception is an insertion into an unsaturated bond, as the insertion of silylene into the C=C bond of ethylene and the C≡C bond of acetylene both occur with no barrier. Substitution of electronegative substituents for the hydrogens in silylene can increase the barrier, however, by stabilizing the silylene species. For example, the barrier for insertion of SiF₃ into acetylene is predicted to be 18 kcal/mol, at the MP4/6-31G(d,p)//3-21G(d) level of theory. Similarly, the barrier to insertion into the ethylene C=C bond increases in the order SiH₂ (≠0) < SiF₃ < SiCl₂. The latter again suggests that size as well as electronegativity plays a role in determining these trends.

One of the most intriguing findings of the SiH₂ elimination processes comes from the study of ethylsilylene. Two different transition state structures (See Figure 2) were found. Each was confirmed to be a true first order saddle point from a full vibrational analysis of the transition state (one imaginary frequency). Reaction pathway following studies showed that the two transition state structures do indeed connect the same reactants with the same products (See Figure 3). Mapping several points along the path connecting the transition states

Figure 2. Transition structures and transition vectors for the primary photodissociation of ethylsilylene (geometries optimized at the HF/3-21G level of theory).
Insertion into an unsaturated C=C bond of ethylene, with no barrier. Substitution in silylene can generate the silylene species. For a acetylene is predicted to 2H2 level of theory. The latter again plays a role in determining the transition states of SiH₂ elimination processes. Two different transition states were confirmed to be a rational analysis of the reaction pathway followed by the five-membered ring. The corresponding products, showed that the only difference in the two pathways is the orientation of the species SiH₂. For path A, the fragment SiH₂ rotates clockwise with respect to the SiH bond coming out of the plane of Figure 4, while in path B, the SiH₂ rotates counterclockwise with respect to the SiH bond pointing toward the plane. This suggests the possibility of two different SiH₂ rotational distributions.

As shown in Table 6, SiHF and SiH₂SiH₂ elimination barriers are similar in magnitude to silylene elimination. Indeed, the former are competitive with the silylene and 1,1-H₂ eliminations in fluorinated disilanes. In contrast to silylene eliminations, carbene eliminations have much higher barriers, reflecting the much greater stability of SiH₂ than CH₂. For example, in methylsilylammonium, the silylene and carbene elimination barriers are 72 and 114 kcal/mol, respectively. For this reason, carbene elimination paths are frequently not investigated computationally. Closely related to silylene and carbene eliminations are eliminations of atomic silicon or carbon from silylenes or carbonates, respectively. The reverse of these eliminations, which have been studied by Sakai,
Deiss and Gordon\textsuperscript{50} at the MP4/6-31G(d,p)//HF/6-31G(d) level of theory, are the insertions of singlet or triplet atoms into CH and SiH bonds. Elimination of singlet (\(^1\)D) carbon from either methylcarbene or methylsilylene is predicted to be endothermic by more than 80 kcal/mol, whereas elimination of singlet silicon requires about 30 kcal/mol less energy. Interestingly, the barriers for the Si elimination (14.6 and 2.4 kcal/mol above the products for methane and silane, respectively) bracket those for the C elimination (7.8 kcal/mol). Elimination of triplet (\(^3\)P) carbon is also predicted to be much more endothermic than that of triplet silicon. Even so, the barrier for elimination of triplet Si from silylsilylene to produce silane is predicted to be only 7 kcal/mol above the products.

If carbones or silylmes are produced in their triplet states (the ground state for carbene), their prototypical secondary reactions are hydrogen abstractions. Gordon\textsuperscript{51} investigated hydrogen abstractions by triplet CH, and SiH\(_2\) from methane and silane, using MP3/6-31G(d,p)//HF/3-21G energies. In each case it was predicted that the barrier for abstracting a hydrogen from silane is about half that for the corresponding abstraction from methane: 9.1 vs. 17.9 kcal/mol for carbene and 15.9 vs. 32.6 for silylene. This is a reflection of the
relative strengths of the C-H vs. Si-H bond. Abstractions by silyl radical have also been studied by Gordon, Gano and Boatz from $H_2$ with POL-CD6-31G(d) energies and by Gordon, Nguyen, and Truhlar from silane with MP-SCC2/6-31G(d,p) energies.

Tachibana and co-workers have examined a radical polymerization mechanism for silicon carbfde formation in chemical vapor deposition (CVD) processes, with the aid of MP3/6-31G(d,p)//HF/6-31G(d) and CISD/6-31G(d,p)//HF/6-31G(d) calculations. By examining a sequence of hydrogen abstractions from methane and silane by H, methyl and silyl, and comparing the predicted thermodynamics and barrier heights with SiH and CH bond strengths, they conclude that the order of ease of bond formation via radical chain reactions is Si-Si > Si-C > C-C. This suggests, in agreement with experimental findings, that the Si-C bond is preferred in the CVD process.

Davis et al. have studied the competing reactions of abstraction vs. substitution when F attacks silane, using MP3/6-31G(d,p)//HF/3-21G, and find that there is no activation energy for the abstraction, whereas the S$_2$H activation energy is 6.5 kcal/mol, even though it is the thermodynamically favored process.

### 3.1.4. 1,2 Elimination of SiH$_4$

To our knowledge, there have been just two computational studies of SiH$_4$ elimination reactions, other than the silylene eliminations from disilanes discussed above, despite the fact that silane elimination is the reverse of the important hydrosilylation reaction. The two SiH$_4$ eliminations which have been studied theoretically are the decompositions of ethylsilane and vinylsilane. The transition state for unimolecular decomposition of ethylsilane via the 1,2 elimination of SiH$_4$ to yield ethylene and silane is shown in Figure 5. Also shown in this figure is the transition state for the 1,2 elimination of SiH$_4$ from vinylsilane.

Both transition states involve tight four-centered structures including three heavy atoms and a hydrogen. The transition states are very similar to transition states for $S_2$ reactions, in that the silicon appears to be penta-coordinated and the SiH$_3$ group undergoes an inversion of configuration. The nature of the bonding across the carbon does seem to have an effect on the activation energy barriers which at MP4SDQ/6-31G*//HF/6-31G* levels are 90.0 and 105.5 kcal/mol for ethylsilane and vinylsilane, respectively. It is interesting to note that the barriers for these processes are well described at the Hartree-Fock
Figure 5. HF/3-21G and HF/6-31G* transition state structures for 1,2-eliminations of SiH₄ ethylysilane and vinylsilane.
level, provided medium to large basis sets are used. Electron correlation effects lower the activation energy only slightly for these processes.

3.2. Isomerization Processes: Some Important Examples

3.2.1. 1,2 Hydrogen Shifts

Silene ↔ Silene Systems. One of the most well studied isomerization reactions is that of methylsilylene (CH$_3$SiH) to silaethyne (CH=SiH). The thermodynamics of this process has been discussed above (Section 2), so the focus here will be on calculated barrier heights. Early theoretical investigations, which used modest basis sets and levels of theory predicted the most stable isomer to be methylsilylene. The closed shell singlet state of this isomer was found to be the ground state, with a barrier to isomerization of silaethyne of 41.4 kcal/mol. Kohler and Lischka have predicted this barrier to be in the range of 40 kcal/mol. Nagase and Kudo have reported similar results (41.4 kcal/mol) for the CH$_2$Si-CH$_3$ ↔ CH$_3$SiH = CH=SiH isomerization barrier, using C3D/6-31G*+HF/6-31G*+. As noted earlier, more recent, higher level calculations show that silaethyne is lower in energy than methylsilylene by a few kcal/mol.

The foregoing analysis is fairly typical of silylene ↔ silene isomerizations, in that lower levels of theory tend to favor the silylene, whereas larger basis sets and correlation corrections tend to favor the silene structure. This is important in the context of the current review. The thermodynamically favored isomer at the highest levels of theory is almost always the silene. However, as noted above, the direct route to such species, a 1,2-elimination, is generally kinetically disfavored relative to the 1,1-eliminations leading to silylenes. Indeed, in the case of both methylsilane and disilane, the lowest energy route to the silene product (silaethyne or disilene) is initial formation of the silylene via a 1,1-H$_2$ elimination, followed by isomerization to the lower energy silene isomer.

The isomerization of methylsilylene on the triplet surface has been studied by Strausz and co-workers. Their theoretical calculations using STO-3G basis sets predict that methylsilylene is most stable than silaethyne, but the most stable structure is silylmethylene (SiH$_2$CH). More accurate calculations by Goddard et al. using DZ-basis sets predict that triplet methylsilylene is lower than triple silylmethylene by 26 kcal/mol. The barriers for the isomerization have not been reported.
An obvious extension of the methylylene isomerization is to ethyl-
silylene. Isomerization of ethylsilene (CH₂CH₂SiH₂) to methylsila-
ethylene (CH₂CH₂SiH₂) was studied by Francisco and with the 6-
31G* basis set. At the HF/6-31G* level of theory, ethylsilene was
found to be only 3.3 kcal/mol more stable than methylsilathylene.
However, using MP4(SDQ)/6-31G*/HF/6-31G* calculations the
methylsilathylene isomer was predicted to be more stable by 3.5 kcal
mol. A barrier of 31.7 kcal/mol (MP4(SDQ)/6-31G*/HF/6-31G*) for
the ethylsilene isomerization to methylsilathylene was predicted.
The prediction of a lower activation energy for the ethylsilene 1.2
hydrogen shift isomerization suggests that substituent group effects do
play a role in stabilizing the transition state structure in the isomeri-
zation process. The isomerization of triplet ethylsilene was also
studied. Triplet ethylsilene was found to be 61.2 kcal/mol
(MP4(SDQ)/6-31G*/HF/6-31G*) more stable than triplet methyl-
silathylene, and no barrier for the isomerization was found.

Silacetylenes. One of the simplest systems in which the 1,2-
hydrogen shift isomerization process has been examined theoretically
in some detail is SiCH₂. Gordon and Pople reported a barrier of
8.5 kcal/mol (MP3/6-31G**/HF/3–21G) for the exothermic hydrogen
migration from trans bent silacetylene HSiCH to silylene Si=CH₂.
Hoffman and co-workers showed that the trans bent silacetylene is a
true minimum at the CVDZ + d(C, Si) level and determined that
the barrier to silylene is 4.2 kcal mol⁻¹. They have also suggested that
the vinylidene isomer C=SiH₂ is not a minimum on the singlet
potential energy hypersurface of SiCH₂.

The analogous disilicon compound Si₂H₂ has been extensively stud-
ied and reviewed, so only the most recent work is discussed here. All
calculations which include electron correlation agree that the global
minimum is a closed shell singlet dibridged form of disilyne and that
the linear acetylenic form is not a minimum on the potential energy
surface. Koseki and Gordon and Colegrove and Schaefer have
clearly demonstrated that this system is one in which the role
of electron correlation is crucial, even in the determination of the struc-
ture and nature of stationary points on the potential energy surfaces.
For the singlet surface, the most extensive and recent series of calcu-
lations is that presented by Colegrove and Schaefer, using CISD/TZ2P
and SCF/TZP energies. At this level of theory, the global minimum
noted above is lower than planar silasilene, Si₂Si by 11 kcal/mol, and
isomerization is to ethyl-
\(\text{C}_2\text{H}_5\text{SiH})\) to methylsila-
Francisco\(^{**}\) with the 6-
theory, ethylsilene was
more stable by 1.5 kcal
\(\text{Si}_2\text{H}_6\) for
ethylene was predicted,
for the ethylsilylene 1,2
\(\text{Si}_2\text{H}_6\) structure in the isomeri-
etylsilene was also
be 61.2 kcal/mol
than triple methyl-
lation was found.

stems in which the 1,2-
examined theoretically
\(\text{Si}_2\text{H}_6\) reported a barrier of the
exothermic hydrogen
\(\text{H} \rightarrow \text{SiH}_2\),
and bent silacycylene is a
and determined that the
have also suggested that
minimum on the single
as been extensively stud-
work is discussed here. All
ion agree that the global
form of disilyne and that
on the potential energy
grove and Schaefer\(^{**}\) have
role of the struc-
temporal energy surfaces.
recent series of calcula-
ctor, the global minimum
\(\text{Si}_2\text{H}_6\) by 11 kcal/mol, and

the linear structure lies 43 kcal/mol above the global minimum and has
\(\text{Si}_2\text{H}_6\) respectively, above the global minimum. The transition state
connecting the two lowest minima is predicted to have no symmetry
and to lie 13 kcal/mol above the global minimum.

The most recent examination of the triplet \(\text{Si}_2\text{H}_6\) potential energy
surface is that by Koseki and Gordon\(^{**}\), who used MP4/6-
\(\text{Si}_2\text{H}_6\) geometries with both HF/6-31G(d,p) and
MP2/6-31G(d,p). These authors find that when correlation and zero
point vibrational corrections are included, planar silasilene, \(\text{H}_2\text{SiSi}\), is a
minimum, rather than the previously predicted bent structure. Simi-
larly, the global minimum on the triplet surface is predicted to be
\(\text{Si}_2\text{H}_6\) rather than twisted.

3.2.2. 1, 2-Methyl and 1, 2-Silyl Shifts

The investigations of 1,2 methyl and 1,2-silyl shifts in silicon
compounds were largely motivated by the experimental studies\(^{**}\) on
the isomerization of silylsilanediyli which showed that the process
proceeds rapidly at room temperature. These results suggested that
1,2-silyl shifts in isomerization processes may play an important role.
Other experimental studies have documented examples of 1,2-silyl
shifts.\(^{**}\) However, it was the work of Nagase and Kudo\(^{**}\) that
presented a detailed theoretical examination of such shifts. They
showed that the 1,2-silyl shift in \(\text{Si}_2\text{H}_6\) has a barrier which is
lower in energy than the 1,2-methyl shift in \(\text{CH}_3\text{SiCH}_3\). At the
MP3/6-31G* level of theory, the activation energy barriers are 26.2
kcal/mol and 54.7 kcal/mol for the 1,2-silyl and 1,2-methyl shifts,
respectively. Another important example is the 1,2-shift is the isomeri-
ization of \(\text{Si}_2\text{H}_6\) to \(\text{SiH}_2\text{SiH}_4\).\(^{**}\) At the MP3/6-31G*
level of theory a barrier of 8.5 kcal/mol is predicted. This suggests that
1,2-silyl shifts across \(\text{Si} \rightarrow \text{Si}\) bonds are much more facile than across
\(\text{Si} \rightarrow \text{C}\) bonds.

Examples of 1,2-silyl shifts across carbon-carbon double and triple
bonds come from theoretical studies of Francisco\(^{**}\) and McDouall and
co-workers\(^{**}\). A barrier of 38.2 kcal/mol (MP4SDTQ/6-31G*/
HF/6-31G*) for the 1,2-silyl shift across the \(\text{C} \equiv \text{C}\) triple bond in
ethylsilsilane (HC≡CSiH₃) to form the silylvinyldene (C≡CHSiH₃) intermediate was reported. The migrations of the SiH₃ group across C≡C double bonds are found to be more difficult. In the case of the 1,2-silyl shift in vinylsilsilane, the reported barrier is 66.5 kcal/mol (MP4SDTQ/6-31G**/HF/6-31G*). In general, it appears that the barrier to 1,2-silyl shifts across A≡B bonds increases as the strength of the A≡B bond increases.

3.3. Reactions of Si⁺ and SiH⁺ with Silanes

Raghavachari and co-workers have investigated the detailed potential energy surfaces for the reactions of Si⁺ with silane and methylsilane. The calculations on Si⁺ + SiH₄ are an excellent illustration of the interplay between theory and experiment that is possible with current levels of computational capability. Experimentally, it is found that only the products Si₂D₄⁺, Si₂D₂⁺, Si₂D⁺, and Si₃D₀⁺ are observed upon the reaction of Si⁺ with SiD₄. No details regarding the nature of the products is available from the experiments, and an explanation for the termination of the clustering reactions at Si₃D₀⁺ and the observed kinetics was needed. These insights were provided by the computational results, obtained at the MP4/6-31G(d,p)/HF/6-31G(d) and MP2/6-31G(d,p)/HF/6-31G(d) levels of theory. In each step of the process, it is found that a complex is formed exothermally between a cation and silane. For example, in the initial reaction, Si⁺ reacts with silane to form the complex H₃Si-H-Si⁺, with the release of 24 kcal/mol. The complex is able to rearrange to H₂Si-SiH⁺ (A3) and then to H₂Si-SiH⁺ (A5) without moving higher in energy than the initial reactants. The barriers leading from A3 to dibridged Si₂H₄⁺ and H₂SiSi⁺ are 9.1 kcal/mol above and 1.0 kcal/mol below, respectively, the separated reactants. So, even though the dibridged structure is the lower energy isomer, theory predicts the higher energy isomer is the one that is seen experimentally. No other transition states were found that are below the reactants. The reactions of the predicted product, H₃SiSi⁺, with silane were investigated in the same manner. Again, the initial exothermic formation of a complex is followed by several energetically accessible rearrangements leading eventually to the product H₂Si-SiH⁺. Since the isomer H₂Si-SiH⁺ is not energetically accessible (the barrier is higher than reactants), the former isomer is identified with the observed Si₂D₄⁺ product. In a similar manner, (H₃Si)₂SiSi⁺ is identified with the observed product...
with Silanes

tigated the detailed poten-
with silane* and methyl-
are an excellent illustra-
tion that is possible.
Experimenterially, it is
Si$_2$D$_6^+$, and Si$_2$D$_4^-$. The
details regarding
the experiments, and
ring reactions at Si$_2$D$_n^+$
the insights were provided
the MP4/6-31G(d,p)/
1G(d) levels of theory. In
complex is formed exother-
ically, in the initial reaction,
(\text{H}_2\text{Si}-\text{H}-\text{Si}^+), with the
the range to \text{H}_2\text{Si-SiH}^+
moving higher in energy
from A3 to dibridged
1.0 kcal/mol below,
though the dibridged
reduces the higher energy.
No other transition states
reactions of the predicted
ated in the same manner.
\text{c} complex is followed by
higher energy eventually
H$_2$Si-Si-Si$^+$ is not
than reactants, the
for 3 Si$_2$D$_2$+ product. In a
the observed product

\text{Si}_2\text{D}_6^+ \text{, and termination is predicted to occur upon the formation of (H$_2$Si)$_2$SiH}^+ since it is difficult to eliminate H$_2$ from this compound.

In addition to these explanations based on the theoretical, potential energy surfaces, the experimental group used the predicted energies, structures and vibrational frequencies, combined with statistical phase space theory, to predict the observed kinetics of the clustering reaction. Agreement with experiment is excellent.

Like the foregoing reaction, when the experiments are carried out at low temperatures and pressures, only the exothermic products are observed in the reaction of Si$^+$ with methylsilane. The only observed products are Si$_2$CH$_4^+$ and SiCH$_3^+$. The potential energy surface for this reaction has been studied at the MP4/6-31G(d,p)/HF/6-31G(d) level of theory. In agreement with experimental, exothermic routes to the two observed products are found to occur via the initial formation of an addition complex. The two products are identified as H$_2$C-SiH-Si$^+$ and H$_2$C-Si$^+$. Subsequent experiments by Armont and Fisher have used a wider range of experimental conditions and were therefore able to observe several additional exothermic products. A more detailed examination of the potential energy surface, at the same level of theory and making use of minimum energy paths, is currently in progress.

In a continuation of the collaboration between theory and experiment, Raghavachari has most recently examined the clustering reactions of SiH$_4$ with silane, using MP4/6-31G(d,p)/MP4/6-31G(d,p) energies and scaled HF/6-31G(d) frequencies. As in the preceding paragraphs, the theoretical results are in excellent agreement with experiment, both qualitatively and quantitatively. The reaction termination is predicted to occur upon the formation of a stable cyclic Si$_2$H$_2^+$ species which only forms a complex with silane.

4. PROSPECTUS

What does the future hold? Already, theory, with the aid of models such as G-1, G-2, BAC, and homedismic reactions together with extended basis sets and high levels of correlation, is able to predict energetic properties with 2-5 kcal/mol accuracy for molecules of modest size. The implementation of direct methods, already becoming commonplace for SCF, MP2 and CI levels of theory, combined with the increasing feasibility of performing electronic structure calcula-
tions with massively parallel computers, will greatly increase the size and complexity of the species that can be treated at a level comparable to experimental accuracy. Already, the level of activity in creating condensed phase systems is encouraging, although this area of theoretical chemistry is clearly in its infancy.

The development of efficient and reliable procedures for following reaction paths is likewise a first step in the prediction of reaction kinetics and dynamics, by combining such calculations with dynamics techniques like variational transition state theory and semiclassical trajectory calculations. This interfacing of electronic structure theory and dynamics calculations will be a powerful tool with which to interact with experimental kinetics studies of silicon chemistry.

REFERENCES AND NOTES

Silanes, Halosilanes, and Alkylsilanes