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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 *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.[1-5]

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 nonempirical, or *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 accountings, the reader is referred to several excellent works.[6,7]

The two essential ingredients in an *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 l quantum number one higher than required in the isolated atoms. Commonly used basis sets at this level are those due to Dunning and Hay[8] and the well-known 6–31G(d) and 6–31G(d,p) basis sets developed by Pople and co-workers[9]. 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).[10] 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 electonic 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 Moller-Plesset (MP) formalism.[7] 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[11,12] 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.[13,14] 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* *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^4 to n^7 or worse, where n is the number of basis functions).[15] 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(2df,p)). 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:

$$\frac{n}{4}\,SiX_4 + \frac{4-n}{4}\,Si \rightarrow SiX_n \tag{1}$$

$$\frac{n}{4}\,SiX_4 + SiH_n \rightarrow \frac{n}{4}\,SiH_4 + SiX_n \tag{2}$$

$$\frac{n}{m}\,SiX_m + \frac{m-n}{m}\,SiH_m \rightarrow SiH_{m-n}X_n \tag{3}$$

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:

$$SiH_3CH_3 + CH_3CH_2CH_3 \rightarrow SiH_3CH_2CH_3 + CH_3CH_3 \tag{4}$$

Errors in homodesmic reactions can be ± 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 ± 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 isogyric reaction is one that conserves spin and eliminates a substantial fraction of the spin contamination error, provided the contamination is small:

$$SiH_n + a\,H \rightarrow Si + a\,H_2 + (n\text{-}a)\,H \qquad (5)$$

When perturbative methods are used for systems with substantial spin contamination, spin projection can be used to remove most of the error.[16] Iterative methods that include single excitations, such as UCISD, UQCISD and UCCSD are less susceptible to spin contamination.[16] 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[17,18,19] (BAC) assumes that a certain level of theory underestimates the dissociation energy of a given bond (e.g., Si-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):

$$\mathrm{BAC(Si\text{-}H)} = 1/4\,(\Delta H_r^\circ(\mathrm{exp}) - \Delta H_r^\circ(\mathrm{theor}))\ \text{for}\ SiH_4 \rightarrow Si + 4\,H \qquad (6)$$

This bond additivity correction is assumed to be constant (or have a simple bond length dependence[19]) 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.

Pople, Curtiss, Radom, and co-workers[20–22] have used theoretical atomization energies to calculate heats of formation without resorting to specific corrections for individual bonds. The atomization energies are computed using isogyric reactions, such as eq. (5), by adding sufficient hydrogen atoms so that the total spin on both sides is the same. The computed heat of reaction is combined with the experimental dissociation energy for H_2 to obtain a theoretical estimate of $\Delta H^{o}_{f\,298}$. This eliminates the need for a set of reference compounds (other than H_2) for which the heat of formation is well known. To control the computational expense, various assumptions are made concerning the additivity of basis set effects. The systematization and extension of this approach leads to the G-1 and G-2 levels of theory[23,24]. The G-1 approach[23] uses MP2/6–31G* optimized geometries, QCISD(T)/6–311G** energies with the effects of diffuse functions (6–311+G**) and extra polarization functions (6–311G(2df,p)) calculated at the MP4 level and assumed additive, with small empirical corrections for the number of paired and unpaired electrons:

$$E_{G1} = E_{QCISD(T)/6\text{-}311G^{**}} + (E_{MP4/6\text{-}311+G^{**}} - E_{MP4/6\text{-}311G^{**}}) \tag{7}$$

$$+ (E_{MP4/6\text{-}311G(2df,p)} - E_{MP4/6\text{-}311G^{**}}) - 0.00614 n_{pair} - 0.00019 n_{unpaired}$$

where the last two terms are in atomic units (au). The G-2 level of theory[24] improves on G-1 by removing most of the additivity assumptions:

$$\begin{aligned} E_{G2} = E_{G1} &+ (E_{MP2/6\text{-}311+G(3df,2p)} - E_{MP2/6\text{-}311G(2df,p)}) \\ &- (E_{MP2/6\text{-}311+G(d,p)} - E_{MP4/6\text{-}311G^{**}}) + 0.00114 n_{pair} \end{aligned} \tag{8}$$

The G-1 level of theory is accurate to ± 2 kcal/mol for first and second row hydrides, and for singly bonded two heavy atom systems.[23] 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.[24]

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.[25–28] The values recommended by these reviews are generally more reliable than some of the values in earlier collections.[29–31] A number of experimental determinations of $\Delta H^{o}_{f\,298}$ 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;[32] 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. *SiH$_n$*

The calculated and experimental heats of formation for SiH_n neutrals and cations are compared in Table 1. The experimental heat of formation of SiH_4 is well established[29] at $\Delta H^{o}_{f\,298} = 8.2 \pm 0.5$ kcal/mol obtained from the decomposition of SiH_4 into Si and H_2. A number of groups have reported values for SiH_3.[33–37] The most recent determination[37] is based on a careful analysis of the forward and reverse rates for $SiH_3 + HX \rightarrow SiH_4 + X$ (X = Br, I) and recommends $\Delta H^{o}_{f\,298} = 47.9 \pm 0.6$ kcal/mol. Only 10 years ago, the accepted value for the heat of formation of SiH_2 was about 58 kcal/mol.[25] However, theoretical studies[17,20] 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 SiH_2. A recent re-analysis[38] of the rate data for $SiH_4 \rightarrow SiH_2 + H_2$ from a number of different authors[39–45] recommends 65.5 ± 1.0 kcal/mol. This agrees very well with values from mass spectrometry, proton affinity measurements and photoexcitation studies (65.6 ± 0.7[36], 65.5 ± 1.5[34], 65.4 ± 1.6[46], 66 ± 3[47], 63.6 ± 2.8[48]). For SiH, spectroscopic studies[49] give $\Delta H^{o}_{f\,298} = 90 \pm 2$ kcal/mol and photoionization experiments[35] yield 89.6 ± 1.2 kcal/mol.

Ho, Melius and co-workers have calculated the heats of formation of SiH_n using the bond additivity correction (BAC) approach based on the MP4/6–31G**//HF/6–31G* level with[18,19] and without[17] a bond length dependence, with[19] and without[17,18] a correction for spin contamination. Horowitz and Goddard[50] applied a 1.5 kcal/mol correction to the Si-H, SiH-H and SiH_2-H bond dissociation energies obtained from GVB-CI calculations. Sax and Kalcher[51] used the BAC approach with CISD

Table 1. Theoretical and Experimental ΔH^{o}_{f298} for SiH_n and SiH_n+ (n = 1-4) (kcal/mol)

Level	*Ref.*	*SiH*	*SiH_2*	*SiH_3*	*SiH_4*
Neutral					
BAC-MP4	[17]	91.7	68.1	47.8	8.2^{a}
BAC-MP4	[18]	92.0	68.7	47.8	8.2^{a}
BAC-MP4	[19]	91.0	64.8	47.4	8.2^{a}
BAC-CISD	[51]	90.0	66.2	47.8	8.2^{a}
BAC-GVB	[50]	90.1	66.6	47.7	8.2^{a}
atomization	[20]	88.3	63.4	47.3	6.3
atomization	[21]	88.8	63.5	47.4	6.3
atomization	[22]	87.7	62.4	46.7	5.2
G1	[23]	88.0	62.6	47.1	6.4
G2	[24]	87.8	62.4	46.7	6.0
G2	[58]	88.2	63.3	48.1	8.0
isodesmic	[52]	89.9	65.7	47.7	8.2^{a}
Experiment		89.6 ± 1.2^{b}	65.5 ± 1.0^{c}	47.9 ± 0.6^{d}	8.2 ± 0.5^{e}
Cations					
atomization	[21,53,54]	271.5	276.6	234.1	264.9
BAC-MP4	[55]	273.0	274.1	232.4^{a}	265.6
isodesmic	[55]	273.6	276.7	235.2	266.1
G1	[23]	268.8	274.1	232.8	261.1
G2	[24]	268.6	273.9	232.3	260.5
Experiment		272.0^{b}	276.6^{b}	232.4^{b}	264.2^{b}
			276.1^{f}	236.9^{f}	
Anions					
isodesmic	[58]	65.0	47.4	24.2	
G-1	[23]	61.5	40.5	15.0	
G-2	[24]	60.6	39.6	14.0	
G-2	[58]	60.9	40.5	15.4	
Experiment		60.2^{g}	39.6^{g}	15.5^{h}	

[a] reference value [b] ref. [35] [c] ref. [38] [d] ref. [37] [e] ref. [29] [f] ref. [34] [g] ref. [56] [h] ref. [57]

calculations plus Davidson's correction (single reference and, where necessary, MCSCF reference) and a TZ + d + p basis set to obtain their estimates of the heats of formation of SiH_n. All of the BAC approaches give very good results for SiH_3, but tend to be 1–2 kcal/mol too high for SiH_2 and SiH. Pople, Curtiss, Radom and co-workers[20–22] have computed atomization energies using isogyric reactions. Similar results are found with[18] and without[20,21] basis set additivity assumptions and with 6–31G[21] or 6–311G[22] basis sets. The calculated heats of 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.[23,24] Isodesmic reactions such as eq. (3) have also been used to estimate $\Delta H^o_{f\,298}$ of SiH_n, based on the experimental heat of formation of SiH_4. At the MP4/6–311 + + G(3df,3p) level, these calculations[52] give heats of formation that are within 0.5 kcal/mol of experiment.

2.2.2. SiH_n^+

Berkowitz et al.[35] have used photoionization mass-spectroscopy studies to examine the thermochemistry of the SiH_n and SiH_n^+ systems. The heats of formation of SiH_n^+ were obtained from the adiabatic ionization threshold for SiH_4 and SiH_3, the appearance potential of SiH_2^+ from SiH_4 and the Rydberg spectrum of SiH. Shin and Beauchamp[47] have determined the proton affinity of SiH_2. Boo and Armentrout[34] have measured thresholds for $Si^+ + SiH_4 \rightarrow SiH^+ + SiH_3$, $SiH_2^+ + SiH_2$, $SiH_3^+ + SiH$ and have derived heats of formation for SiH_n^+.

The total atomization energies for the neutrals[20] have been combined with isogyric ionization reactions to yield calculated heats of formation of the cations[21,53,54]. Theoretical heats of formation of SiH_n^+ have been obtained[55] by combining the results from the BAC calculations (based on the observed $\Delta H^o_{f\,298}$ for SiH_3^+), computed proton affinities and isogyric ionization potential calculations at the MP4/6–31G** level. The $\Delta H^o_{f\,298}$ 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_3^+, whereas lower level calculations tend to be somewhat higher. For SiH^+ 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_n^-

Lineberger et al.[56] have determined the electron affinities of SiH and SiH_2 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_3^- and SiD_3^- by Ellison and Nimlos[57] 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[58] differ from the experimental values by 5–10 kcal/mol, but calculations by G-1 and G-2 theory[23,24,58] 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.[59,60] At the MP4(SDTQ)/6–311++G(3df,2pd)//HF/6–31G(d) level of theory, these authors predict the 0°K enthalpy for the reaction $XSiH_3 \rightarrow XSiH_2^- + H^+$ to be 16.15 eV, compared with the experimental value of 16.23eV, 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. Si_2H_n

The experimental thermochemistry of di-, tri- and tetrasilanes has been discussed by Becerra and Walsh[61] and by Ring and co-workers.[62] The energetics of the Si_2H_n neutrals and cations have recently been studied by Berkowitz and Ruscic[63] using photoionization/mass spectroscopy methods. A comprehensive theoretical study of the heats of formation and adiabatic ionization potentials of Si_2H_n has also been completed recently by Curtiss et al. using the G-2 level of theory.[64] Boatz and Gordon[65] had previously predicted the heats of formation for the two isomers of Si_2H_4 using G-1 theory. The energetics of some of the $Si_mH_n^+$ ions have also been studied theoretically by Raghavachari,[66,67] Kohler and Lischka,[68,69] and Colegrove and Schaefer.[70] Ho and Melius[19] employed the BAC-MP4 approach to calculate the $\Delta H^o_{f\,298}$ for the neutral Si_2H_n. Sax and Kalcher[51] have used CISD computations with a bond additivity approach to obtain $\Delta H^o_{f\,298}$ of Si_mH_n ($m = 1–5$). Goddard et al.[50] have calculated bond dissociation energies for a number of Si_2H_n with GVB-CI methods. Pathways for the thermal decomposition of disilane have been studied by Gordon et al.,[71]. Handy et al.[72], Pople et al.,[73] and Krogh-Jespersen[74] have also computed the geometries and relative energies of the Si_2H_4 isomers. Colegrove and Schaefer[75] have studied the isomers of Si_2H_2 and have reviewed previous work on this system. Other calculations have looked at the heats of formation of methyl-substituted disilanes,[76] the energetics of substituted disilenes and silylsilylenes[74] and π bond energies of Si compounds[77]. The G-2 calculations by Curtiss et al.[64] 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[65] using homodesmic reactions for the series of methylated disilanes. The G-2 results agree well with those of Ho and Melius[19] and Sax and Kalcher[51] and with recent experimental data from Berkowitz.[63] The approximate 10 kcal/mol discrepancies seen between the G-2 calculations and the values obtained by Horowitz and Goddard[50] can probably be traced to the lower level of calculation used in the latter.

2.2.5. *SiF_n*

The theoretical and experimental heats of formation for SiX_n and SiX_n^+ (X = F, Cl) are collected in Table 2. The experimental thermochemistry of silicon halogen compounds has been reviewed by Walsh.[26] The heat of formation of SiF_4 has recently been reconfirmed as $\Delta H^o_{f\,298}$ = 386.18 ± 0.1 kcal/mol by fluorine bomb calorimetry.[78] Doncaster and Walsh[79] obtained $D_0(F_3Si\text{-}H)$ = 100.1 kcal/mol from $SiF_3H + I \rightarrow SiF_3 + HI$, yielding $\Delta H^o_{f\,298}$ (SiF_3) = 239 ± 5 kcal.mol. Farber and Srivastava[80] find $\Delta H^o_{f\,298}$ = 259 ± 5 kcal/mol for SiF_3 using mass spectroscopy-effusion methods; Weber and Armentrout[81] obtained $\Delta H^o_{f\,298}(SiF_3)$ = -257 ± 3 kcal/mol by guided ion beam/mass spectroscopy. The heat of formation of SiF_2 seemed to be well established at -140.5 ± 2 kcal/mol.[26,80–82] From the wide range of values for SiF, Walsh[26] recommends that $\Delta H^o_{f\,298}(SiF)$ = -5 ± 6 be used with caution. Armentrout and co-workers[218] have recently determined the heats of formation of SiF_n by collision-induced dissociation and charge transfer reactions.

Theoretical heats of formation for SiF_n have been determined using atomization energies[83] (GVB + CI with a DZP basis set), the bond additivity approach[19] (at the MP4/G–31G** level with bond length and spin corrections), isodesmic reactions[52] (up to MP4/6–311 + + G(2df,2p)) and G1 theory.[58] The BAC, isodesmic and G-1 approaches are in good agreement with each other: all three clearly favor -239 kcal/mol for $\Delta H^o_{f\,298}(SiF_3)$ and indicate that $\Delta H^o_{f\,298}$ (SiF_2) should be about 10 kcal/mol more negative than the older values. The calculations are in very good agreement with the most recent experiments.[218]

2.2.6. *SiF_n^+*

The experimental heat of formation of SiF_3^+ has been obtained from the appearance potentials of SiF_3^+ from SiF_4 and SiF_3CH_3.[34,84,85] The

Table 2. Theoretical and Experimental ΔH^{o}_{f298} for SiX_n and SiX_n^+ ($n = 1-4$, X = F, Cl, CH_3), (kcal/mol)

Level	*Ref.*	*SiX*	*SiX_2*	*SiX_3*	*SiX_4*
SiF_n					
BAC-MP4	[19]	-12.4	-149.9	-237.4	-386.0^{a}
G-1	[58]	-14.0	-150.2	-234.9	-382.7
G-2	[58]	-13.5	-149.3	-233.3	-379.8
isodesmic	[52]	-14.2	-153.0	-240.7	-386.18^{a}
Experiment		-5 ± 6^{b}	-140.5 ± 2^{c}	-239 ± 5^{d}	-386.18 ± 0.1^{f}
		-11.2 ± 2.1^{e}	-152.4 ± 1.5^{e}	-238.4 ± 1.1^{e}	
SiF_n^+					
BAC-MP4	[55]	154.8	96.2	-31.4^{a}	-31.7
isodesmic	[55]	153.4	100.4	-29.5	-30.9
Experiment		$170 - 2.2^{l}$	$109 - 2^{l}$	$-31.4 - 2^{m}$	-35.9^{n}
		$153.3 - 1.1^{e}$	$98.0 - 1.2^{e}$	$-28.7 - 0.6^{e}$	31.0 ± 1.4^{e}
SiF_n^-					
isodesmic	[58]	-0.1	-143.8	-292.5	
G-1	[58]	-34.1	-157.7	-294.2	
G-2	[58]	-32.4	-154.7	-291.9	
Experiment				$\geq -307^{q}$	
$SiCl_n$					
BAC-MP4	[17]	37.9	-37.6	-76.5	-158.4^{a}
isodesmic	[96]	36.6	-38.9	-76.4	-158.4^{a}
Experiment		47.4 ± 1.6^{h}	-40.3 ± 0.8^{h}	-80.1 ± 2.2^{i}	-158.4 ± 1.3^{h}
		44 ± 6^{j}	-39.4 ± 3.4^{p}		
$SiCl_n^+$					
isodesmic	[96]	205.9	187.1	106.2	
Experiment		217 ± 7^{j}	188 ± 3^{j}	102 ± 3^{j}	115 ± 3^{j}
		203 ± 5^{k}	190 ± 6^{j}	99.8 ± 1.6^{p}	
		203.9 ± 2.5^{p}	187.3 ± 2.2^{p}		
$Si(CH_3)_n$					
BAC-MP4	[108]	74.5	32.2	3.1	
G-1	[65]		32–33		
Experiment			26 ± 2^{o}	-1 ± 2^{s}	55.7^{t}
			32 ± 2^{u}		

[a] reference value [b] ref. [26] [c] ref. [26,80,81] [d] ref. [27] [e] ref. [218] [f] ref. [78] [g] ref. [91] [h] ref. [29] [i] ref. [26] [j] ref. [92] [k] ref. [94,95] [l] ref. [81] [m] ref. [84] [n] ref. [85] [o] ref. [88] [p] ref. [89] [q] ref. [90] [r] ref. [114] [s] ref. [28] [t] ref. [111] [u] ref. [106]

experimental ionization potentials of SiF and SiF_2 are 7.26 eV[86] and 10.78 eV[87], respectively; the ΔH^{o}_{f298} (SiF_n^+) can then be obtained by combining the IP with the heats of formation of the neutrals. Armentrout and co-workers have used thresholds for $Si^+ + SiF_4 \rightarrow SiF^+ + SiF_3$, $SiF_2^+ + SiF_2$, $SiF_3^+ + SiF$[81] and for $Xe^+ + SiF_4$[88,218]

to determine ΔH^{o}_{f298} (SiF_n^+). The theoretical values[55] were obtained by the bond additivity method based on the experimental value for SiF_3^+ and from isodesmic and isogyric reactions $SiF_n + Si^+ \rightarrow SiF_n^+ + Si$ or $SiF_n + Si^+ + 2\ H \rightarrow SiF_n^+ + Si + H_2$ computed at the MP4/6–31G** level. Good agreement is found with the most recent experimental values.[218] The calculations[55,96] also agree well with the measured threshold for $Si^+ + SiF_4 \rightarrow SiF^+ + SiF_3$[81], but suggest that the channels leading to $SiF + SiF_3^+$ and $SiF_2^+ + SiF_2$ involve activation barriers.

2.2.7. SiF_n^-

The only experimental electron affinity data available in this series is for SiF_3[90], and this is only an upper bound. Michels, et al.[58] 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 SiH_n^-, 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 ΔH^{o}_{f} for $SiCl_4$ is -158.4 kcal/mol, determined from the heat of chlorination of silicon.[29] Walsh et al.[26] obtained $\Delta H^{o}_{f298}(SiCl_3) = 80.1 \pm 2.2$ kcal/mol from $SiHCl_3 + I$. Farber and Srivastava[91] find -93.3 ± 4 kcal/mol for $SiCl_3$ in their effusion/mass spectrometric study. There is good agreement among the experimental studies that the heat of formation of $SiCl_2$ is -40.3 ± 0.8 kcal/mol. Effusion/mass spectrometry studies[91] yield 47.1 ± 0.6 kcal/mol for $\Delta H^{o}_{f298}(SiCl)$, but spectroscopic studies give values that are 5–15 kcal/mol lower (with large uncertainties). Weber and Armentrout[92] obtained 44 ± 6 kcal/mol from studies on $Si^+ + SiCl_4$.

For $SiCl_n$, BAC calculations have been carried out at the MP4/6–316** level (with[19] and without[17] 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 ΔH^{o}_{f298} ($SiCl_3$). Good agreement with experiment is also found for $SiCl_2$, but SiCl is calculated to be 6–10 kcal/mol more stable than suggested by experiment.[29,92]

2.2.9. $SiCl_n^+$

The experimental heat of formation of $SiCl_3^+$ has been obtained from the appearance potentials of $SiCl_3^+$ from $SiCl_4$[93,94] and $SiHCl_3$.[93] Weber and Armentrout[92] have used thresholds for $Si^+ + SiCl_4 \rightarrow SiCl_2^+ + SiCl_2$, $SiCl_2^+ + SiCl + Cl$ to determine $\Delta H^o_{f\,298}$ ($SiCl_2^+$). Fisher and Armentrout[89] have used dissociative charge transfer reactions with $SiCl_4$ to obtain $\Delta H^o_{f\,298}(SiCl_n^+)$. The heat of formation of $SiCl^+$ has been obtained by extrapolating Rydberg series in SiCl[95], from appearance potentials from $SiCl_2$ and $SiCl_4$[94] and from thresholds for $Si^+ + SiCl_4 \rightarrow SiCl^+ + SiCl_2 + Cl$[92]. The theoretical $\Delta H^o_{f\,298}$ were obtained[96] as the average from isodesmic reactions $^n/_4\ SiCl_4 + SiH_n^+ \rightarrow {}^n/_4\ SiH_4 + SiCl_n^+$ and $SiCl_n + Si^+ \rightarrow SiCl_n^+ + Si$ computed at the MP4/6–31G** level. The agreement with experiment is quite good for $SiCl_2^+$, and the calculations favor the lower experimental value for $SiCl^+$ listed in Table 2.

2.2.10. SiH_mF_n and SiH_mCl_n

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 tables[29] have been obtained by linear interpolation. Farber and Srivastava[97–99] have used mass spectroscopy/effusion to determine $\Delta H^o_{f\,298}$ for SiH_nX_{4-n} (X = F, Cl, Br); however the validity of the SiH_nF_{4-n} results have been questioned.[19,26,52]

Given heats of formation for the perhydro and perhalo compounds, reliable estimates of the $\Delta H^o_{f\,298}$ for the partially halogenated compounds can be obtained using isodesmic reaction (3). For the fluoro derivatives, the $\Delta H^o_{f\,298}$ have been computed at the MP2/DZ+polarization,[100] MP4/6–31G*[215] and MP4/6–31++G(2d,2p)[52] 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, however, the calculations[17,19] are in good agreement with experiment (as well as the linearly interpolated values, not shown).

The heats of formation of the fluorinated silyl cations, $SiH_mF_n^+$, have been calculated at the MP4/6–31G** level[55] by using the BAC method, proton affinities and ionization energies. No calculations have

Table 3. Theoretical and Experimental ΔH^{o}_{f298} for SiH_mF_n and SiH_mCl_n

Level	*Ref.*	*$SiHX$*	*SiH_2X*	*$SiHX_2$*	*SiH_3X*	*SiH_2X^2*	*$SiHX_3$*
SiH_mF_n							
BAC-MP4	[19]	−35.7	−42.2	−139.6	−85.5	−186.4	−288.6
isodesmic	[100]				−85.6	−185.7	−287.7
isodesmic	[215]	−31.1	−42.5	−140.1	−84.9	−184.5	−287.1
isodesmic	[52]	−37.8	−44.9	−142.6	−85.8	−186.3	−288.2
Experiment		-41 ± 5^a	-49 ± 5^a	-144 ± 5^a	-90 ± 5^a	-189 ± 5^a	-287 ± 5^a
					-94 ± 2^b	-192 ± 2^b	-293 ± 2^b
$SiH_mF_n^+$							
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_mCl_n							
BAC-MP4	[17]	17.0	7.8	−34.3	−32.2	−74.5	−117.0
BAC-MP4	[19]	15.9	7.9	−34.0	−32.0	−74.4	−117.1
Experiment					-33.9 ± 2^c	-76.6 ± 3^c	-118.6 ± 1.5^c
					-32.4 ± 2.5^d	-75.3 ± 2^d	-119.3 ± 1.5^d
$SiH_m(CH_3)_n$							
isodesmic	[113]				−6.8	−22.6	−39.1
BAC-MP4	[108]	48.8	33.1	18.3	−7.3	−23.2	−39.4
G-1	[65]	50.6					
Experiment		44 ± 2^c	31 ± 2^f	15 ± 2^f	-6.9^f	-22.6^f	-39.0^f
		48 ± 2^g					

[a] ref. [29] (linear interpolation), [b] ref. [97], [c] ref. [29] (no interpolation), [d] ref. [98] [e] ref. [105] [f] ref. [27, 28, 111] [g] ref. [106]

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[101] 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[29] in parentheses): SiH_2FCl, −129.3; $SiHF_2Cl$, −230.3; $SiHFCl_2$, −171.6; SiF_3Cl, −329.5 (−315.0); SiF_2Cl_2, −272.9; $SiFCl_3$, −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 Methylsilylene*

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, methylsilylene. Early experimental estimates[25] suggested $\Delta H^{\circ}_{f298}(CH_2SiH_2) = 39 \pm 5$ kcal/mol and $\Delta H^{\circ}_{f298}(CH_3SiH) = 42 \pm 5$ kcal/mol; recent ion cyclotron resonance measurements[104] give 43 ± 3 and 53 ± 3 kcal/mol, respectively. Other experimental estimates for CH_3SiH include 44 ± 3 kcal/mol[105] and 48 ± 2 kcal/mol[106]. In agreement with a number of earlier theoretical studies, Pople et al.[73] 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_3SiH by 2.2 kcal/mol at the MP4/6–31G* level[73], by 3.2 kcal/mol at the MP4/6–311G** level[107] and by 7.9 kcal/mol at the BAC-MP4 level[108]. Calculations with the GVB-CI approach using a DZP basis[104] place silaethylene 11.6 kcal/mol lower than methylsilylene, but much higher level calculations by Grev et al.[109] 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 d functions, a set of f functions and diffuse orbitals. The G-1 level of theory gives $\Delta H^{\circ}_{f298}(CH_2SiH_2) = 46.5$ and $\Delta H^{\circ}_{f298}(CH_3SiH) = 50.6$ kcal/mol.[65] Isodesmic reactions support the latter, giving $\Delta H^{\circ}_{f298}(CH_3SiH) = 49.2$ kcal/mol. The heat of formation of silaethylene suggests a rather weak π bond; however, when the difference in electronegativity of carbon and silicon are taken into account, π bonds to carbon and silicon are similar.[77,110] The heats of formation of compounds with silicon-silicon multiple bonds were discussed above in the Si_2H_n section.

2.2.12. *Alkyl Silanes*

The experimental heats of formation have been reviewed by Walsh et al.[28,111] The measured $\Delta H^o_{f\,298}$ for SiH_3CH_3, $SiH_2(CH_3)_2$, $SiH(CH_3)_3$ and $Si(CH_3)_4$ are $-6.9 \pm 1.$, -22.6 ± 1, $-39.0 \pm 1.$ and -55.7 ± 0.8 kcal/mol, respectively.[27,111,112] Isodesmic reactions at the MP2/6–31G*// HF/3–21G level[113] and BAC-MP4 calculations[108] yield ΔH^o_f 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[108] also include theoretical heats of formation for H_mSiCH_n, H_2CCSiH_n, $HCCSiH_n$ and methyl silenes, and discuss available experimental data for these compounds. The experimental heats of formation of methyl-substituted silylenes have been obtained by O'Neal et al.[106] and by Walsh.[28,114] Isodesmic reactions by Gordon et al.[65,115] and BAC-MP4 calculations by Melius et al.[108] provide theoretical $\Delta H^o_{f\,298}$ that support the values of O'Neal.[106]

Gordon, Boatz and Walsh[111] report that the experimental heats of formation of the mono-, di- tri- and tetraethylsilanes are -34.2, -43.6 ± 1.4, (-48.0 ± 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 $\Delta H^o_{f\,298}$ and with *ab initio* calculations. *Ab initio* calculations on isodesmic reactions give -9.0 and -28.0 kcal/mol for $SiH_3CH_2CH_3$ and $SiH_2(CH_2CH_3)_2$ at the MP2/6–31G*//HF/3–21G level.[111,113] 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, silacyclopropane = 30.2, silacyclobutane = -9.3, silacyclopentane = -15.3, silacyclohexane = -22.0 kcal/mol. Strain energies have also been calculated for silacyclobutenes, silabicyclobutanes and silapropellane.[117,118] 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.[28] There have been no systematic *ab initio* studies of the heats of formation of alkylsilyl radicals; however, theoretical estimates of $\Delta H^\circ_{f\,298}$ for SiH_2CH_3 and $SiH_2CH_2CH_3$ 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[119] 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[76], at the MP2/6–31G(d,p)//HF/3–21G* level of theory. The theoretical heats of formation are systematically within about 1.0 kcal/mol of the experimental values of O'Neal, Ring and co-workers.[106] A similar systematic survey has been performed for methyl-substituted silaethylene and disilene, using isodesmic reactions.[65] 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[120] have used isodesmic reactions with MP4/6–31G(d)//HF/6–31G(d) energies to predict the heats of formation for fluorodisilane (−73.4 kcal/mol), 1,1- and 1,2-difluorodisilane (−174.0 and −166.2 kcal/mol, respectively), and several fluoro-substituted silylsilylenes, using the G-2 heat of formation of disilane as a reference value.

2.2.14. *Si_n Compounds*

Raghavachari[121,122] has performed the most extensive series of calculations on silicon clusters and predicted their binding energies relative to n Si (see also[123]), using both MP4 and CCSDT(4) with extended basis sets and the G-2 level of theory. The good agreement (within 0.2 eV) with experiment for Si_2 and Si_3 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 $Si_4 + Si_6$, in excellent agreement with the observed fragmentation patterns for the corresponding cations.[124]

3. REACTIONS AT SILICON CENTERS

Kinetics studies of the reactions of silicon centers have been of great interest for a considerable time.[125–131] A long-standing interest has been in the development of an understanding of how the reactions of silicon compounds compare with analogous reactions of carbon compounds. Experimentally, particular focus has been directed toward understanding kinetics and mechanisms of hydrogen-abstraction reactions[128], molecular isomerization processes[129], unimolecular decomposition processes, 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)[132,133] technologies, for which silicon containing compounds are principal precursors, has heightened the interest in developing a fundamental understanding of the mechanisms and rates of reaction processes 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.[1,3,102] 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 great 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 potential energy surfaces for the decompositions of silanes, halosilanes, and alkylsilanes. Related reactions, such as insertions, abstractions, and isomerizations will also be considered, insofar as they impact the thermal decomposition mechanisms.

A general alkylsilane $RSiH_2XH_n$ can decompose in several ways:

$$RSiH_2XH_n \dashrightarrow RXH_n + SiH_2 \qquad (1)$$

$$RSiH_2XH_n \longrightarrow RSiH + XH_{n+1} \quad (2)$$

$$RSiH_2XH_n \longrightarrow RSiXH_n + H_2 \quad (3)$$

$$RSiH_2XH_n \longrightarrow RSiH{=}XH_{n-1} + H_2 \quad (4)$$

$$RSiH_2XH_n \longrightarrow RSiH_2XH_{n-2} + H_2 \quad (5)$$

$$RSiH_2XH_n \longrightarrow RSiH_2 + XH_n \quad (6)$$

$$RSiH_2XH_n \longrightarrow R + SiH_2XH_n \quad (7)$$

$$RSiH_2XH_n \longrightarrow RSiH_2XH_{n-1} + H \quad (8)$$

$$RSiH_2XH_n \longrightarrow RSiHXH_n + H \quad (9)$$

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 H_2 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-HX Elimination Processes (X = H, F)

SiH_4, SiH_3X, SiH_2X_2. One of the prototypical reactions involving decompositions of compounds containing silicon centers is the 1,1-H_2 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, $SiH_4 \rightarrow SiH_2 + H_2$. The reverse of the 1,1-H_2 elimination process is SiH_2 insertion into H_2. The barrier we report here is for the reverse process of the 1,1-H_2 elimination process. Early calculations predicted this barrier to be in the range of 5–9 kcal/mol.

Gordon[134] calculated the barrier to be 8.6 kcal/mol, using the MP3/6–31G* level of theory, and calculations by Grev and Schaefer[135] predicted a barrier of 6.7 kcal/mol using MCSCF methods with large basis sets, augmented by CISD plus size consistent corrections. Sosa and Schlegel[136] obtained a barrier of 6.0 kcal/mol, at the MP4(SDQ)/6–31G*//HF/6–31G* level. Sax and Olbrich[137] 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.[138] 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[139], a barrier of 5.5 ± 1.0 kcal/mol had been the long standing reported value for the insertion reaction, $SiH_2 + H_2 \rightarrow SiH_4$, but more recent determinations estimate this barrier to be 0.5 kcal/mol.[38,140–142]

The work of Sosa and Schlegel[136] and Gordon et al.[138] 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[138] 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_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[143] used the 4–31G basis set, augmented by Rydberg functions on the central silicon, to demonstrate that silane undergoes Jahn-Teller distortion to either C_{2v} or C_{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[144] and several low-lying singlet[145] states of silane. The triplet state was predicted to dissociate to SiH_3 + H, while a barrierless channel was found to SiH + H + H_2 on the lowest singlet surface.

In an early series of papers, Sosa and Schlegel[136,146] 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 H_2 (at the MP4(SDQ)/6–31G*//HF/6–31G* level of theory) to 25.8 kcal/mol for SiHF and 61.4 kcal/mol for SiF_2. More recently, Ignacio and Schlegel[101] have examined the thermal decomposition pathways for the entire series SiH_mF_{4-m}, 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 H_2 insertion barriers from SiH_2 (2 kcal/mol) to SiHF (24 kcal/mol) to SiF_2 (55 kcalmol). Since the 1,1-H_2 elimination is the lowest energy process for each of these molecules, the predicted threshold decomposition barrier increases accordingly, from 57 to 70 to 86 kcal/mol. In 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 F_2 are all predicted to be essentially zero.

Despite the large insertion barriers upon fluorine substitution, molecular elimination processes are predicted to dominate the thermal decompositions of fluorinated silanes.[101] Elimination of molecular hydrogen is the preferred decomposition mode both thermodynamically and kinetically for SiH_4, SiH_3F, and SiH_2F_2, while HF elimination is found to be the preferred process for $SiHF_3$, with a barrier of 89 kcal/mol. Only for SiF_4, 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 SiF_2 insertion into H_2.

Related Ions. Kalcher[147] has used the CEPA-1 method, with a TZ2P basis set and effective core potential for Si to compare the stabilities of SiH_4^- and CH_4^-. Whereas the carbon species has two stable complexes, $CH_3—H^-$ and $H_2—CH_2^-$, 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_2^+ has been examined by Hirst and Guest[148] and Gonzalez and co-workers[149]. Since the former calculations were performed with a much higher level of theory, MRD-CI with a TZP basis set, we will only summarize that work. The $^2B_1$ state is predicted to be at least 0.35 ev above the dissociation products $Si^+ + H_2$, but there is a 3.5 ev barrier separating the two. The $^2A_1$ state is 0.6 kcal/mol below $Si^+ + H_2$ 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_4^+.[55,150–155] While all of these *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_s structure. The two most extensive sets of calculations on this system are those by Kudo and Nagase[155] and Padden-Row and Wong.[154] 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_s structure corresponds to a complex between SiH_2^+ and H_2. Dissociation to the latter products requires less than 10 kcal/mol and occurs with no additional barrier. A C_{3v} minimum that lies about 15 kcal/mol higher in energy than the C_s 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_3^+ + H are considerably higher in energy, the most likely decomposition channel appears to be $SiH_2^+ + H_2$.

The situation seems to be somewhat different for $SiMe_4^+$. 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_{3v}, with the C_s structure lying 16 kcal/mol higher in energy.[155] The C_{3v} structure is predicted to be 16 kcal/mol below the products $SiMe_3^+$ + Me, while the C_s isomer is only 6 kcal/mol below $SiMe_2^+ + C_2H_6$. 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.[156] examined the very complex $C_5H_{12}Si^+$

potential energy surface. While this study was performed at a modest level of theory, HF/6–31G(d)//HF/3–21G, 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-H_2 elimination, reaction (3):

$$RSiH_3 \rightarrow RSiH + H_2 \qquad (3)$$

Experimental results from numerous shock-tube and photodissociation studies[157–167] 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[107], have shown that the activation energy for 1,1-H_2 elimination to yield methylsilylene (CH_3SiH) and molecular hydrogen is 63.2 kcal/mol (MP4(SDTQ)/MC-311G**// MP2/6–31G*). This prediction is in good agreement with the reported experimental activation energy of 64.8–63.2 kcal/mol.[159,167] The competing 1,2-H_2 elimination to form silaethene ($CH_2=SiH_2$) is predicted to have a much higher barrier. The elimination of silylene to form methane is found to be competitive with the 1,1-H_2 elimination. Similar predictions have been made for the thermal decomposition mechanism of disilane[71], using MP4/6–31G(d,p) energies at the MP2/6–31G(d) geometries. Here too, the 1,1-H_2 and silylene eliminations are found to be much lower energy processes than the 1,2-H_2 elimination or homolytic bond cleavage. Indeed, the two-step formation of disilene ($SiH_2=SiH_2$) via the 1,1-H_2 elimination followed by a hydrogen shift is much more feasible energetically than the direct 1,2-H_2 elimination path.

Ethylsilane is the next simplest alkylsilane. Experiments show conclusively that the 1,1-H_2 elimination process dominates the dissociation process for ethylsilane.[157,158,168] Experimental groups report an activation energy for the process of 65.0[157] and 64.8[158] kcal/mol. The reaction has been predicted[169] to proceed with an activation energy

$$CH_3CH_2SiH_3 \rightarrow CH_3CH_2SiH + H_2 \qquad (10)$$

barrier of 66.0 kcal/mol (MP4(SDQ)/6–31G*//HF/6–31G*), in quite good agreement with the experimental results.

Organosilanes: Other Examples. The 1,1-H_2 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-H_2 elimination process predict activation energies of 64.4 kcal/mol for vinylsilane[170] (MP4(SDQ)/6–31G*//HF/6–31G*) and 64.6 kcal/mol for ethynylsilane[171] (MP4(SDTQ)/6–31G*//HF/6–31G*).

Table 4 summarizes theoretical and experimental results for 1, 1-H_2 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-SiH_3 unit has little influence on the activation energy for the 1,1-H_2 elimination. The series of fluorinated disilanes studied by Ignacio and Schlegel[120], using MP4/6–31G(d)//HF/6–31G(d) energies, also have a nearly constant barrier for 1,1-H_2 elimination, although the barrier height for these molecules is about 10 kcal/mol smaller than that for the alkylsilanes, 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-H_2 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-H_2 elimination is either the energetically favored decomposition path or one of

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

System	*Theory*	*Experiments*
$CH_3SiH_3 \rightarrow CH_3SiH + H_2$	63.2[a]	64.8[b], 63.2[c]
$CH_3CH_2SiH_3 \rightarrow CH_3CH_2SiH + H_2$	66.0[d]	65.0[e], 64.8[f]
$CH_2{=}CHSiH_3 \rightarrow CH_2{=}CHSiH + H_2$	64.4[g]	63.3[h], 63.96[i]
$CH{\equiv}CSiH_3 \rightarrow CH{\equiv}CSiH + H_2$	64.6[j]	61.2 ± 5.2[k]
$SiH_4 \rightarrow SiH_2 + H_2$	57[l]	
$SiH_3F \rightarrow SiHF + H_2$	70[l]	
$SiH_2F_2 \rightarrow SiF_2 + H_2$	86[l]	
$H_3SiSiH_3 \rightarrow H_3SiSiH + H_2$	55[m]	
$H_3SiSiFH_2 \rightarrow H_3SiSiF + H_2$	56[m]	
$H_3SiSiFH_2 \rightarrow H_2FSiSiH + H_2$	54[m]	
$H_3SiSiHF_2 \rightarrow F_2HSiSiH + H_2$	56[m]	
$H_2SiSiFH_2 \rightarrow H_2FSiSiF + H_2$	54[m]	

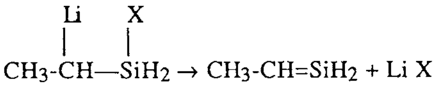
[a] ref. [107] [b] ref. [159] [c] ref. [167] [d] ref. [169] [e] ref. [157] [f] ref. [158] [g] ref. [170]
[h] ref. [157] [i] ref. [165] [j] ref. [171] [l] ref. [116] [m] ref. [120] [k] ref. [217]

2-3 energetically likely pathways (see below) for the fluorinated disilanes.

Theoretical examination of the unimolecular decomposition pathways of ethynylsilane reveals an alternative pathway which is energetically favored relative to 1,1-H_2 elimination processes.[171] 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-H_2 elimination. Consequently, the alkynylsilanes may be a class of organosilanes where the general rule of 1,1-H_2 elimination processes dominating the reaction process breaks down.

3.1.2. 1,2-H_2 Elimination Processes: Production of Silenes

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, $SiH_2 = CH_2$ has been extensively studied theoretically and extensively reviewed.[1,2,3] Although there has been great interest in the generation of silenes, most studies have focused on their generation via 1,2- hydrogen shift processes from alkylsilylenes.[2] 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



$$CH_3\text{-}\overset{\overset{\text{Li}}{|}}{CH}\text{—}\overset{\overset{X}{|}}{SiH_2} \rightarrow CH_3\text{-}CH{=}SiH_2 + \text{Li X} \tag{11}$$

A route that has not been explored as a means for generating silenes is from 1,2- H_2 elimination processes, reaction (4). The first calculation for the 1,2- H_2 elimination from methylsilane to produce silene and molecular hydrogen, namely:

$$CH_3SiH_3 \rightarrow CH_2{=}SiH_2 + H_2$$

was performed by Gordon and Truong.[107] 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-H_2 elimination from ethylsilane and vinylsilane at the HF/3–21G and HF/6–31G* levels are shown in Figure 1. Note that these transition

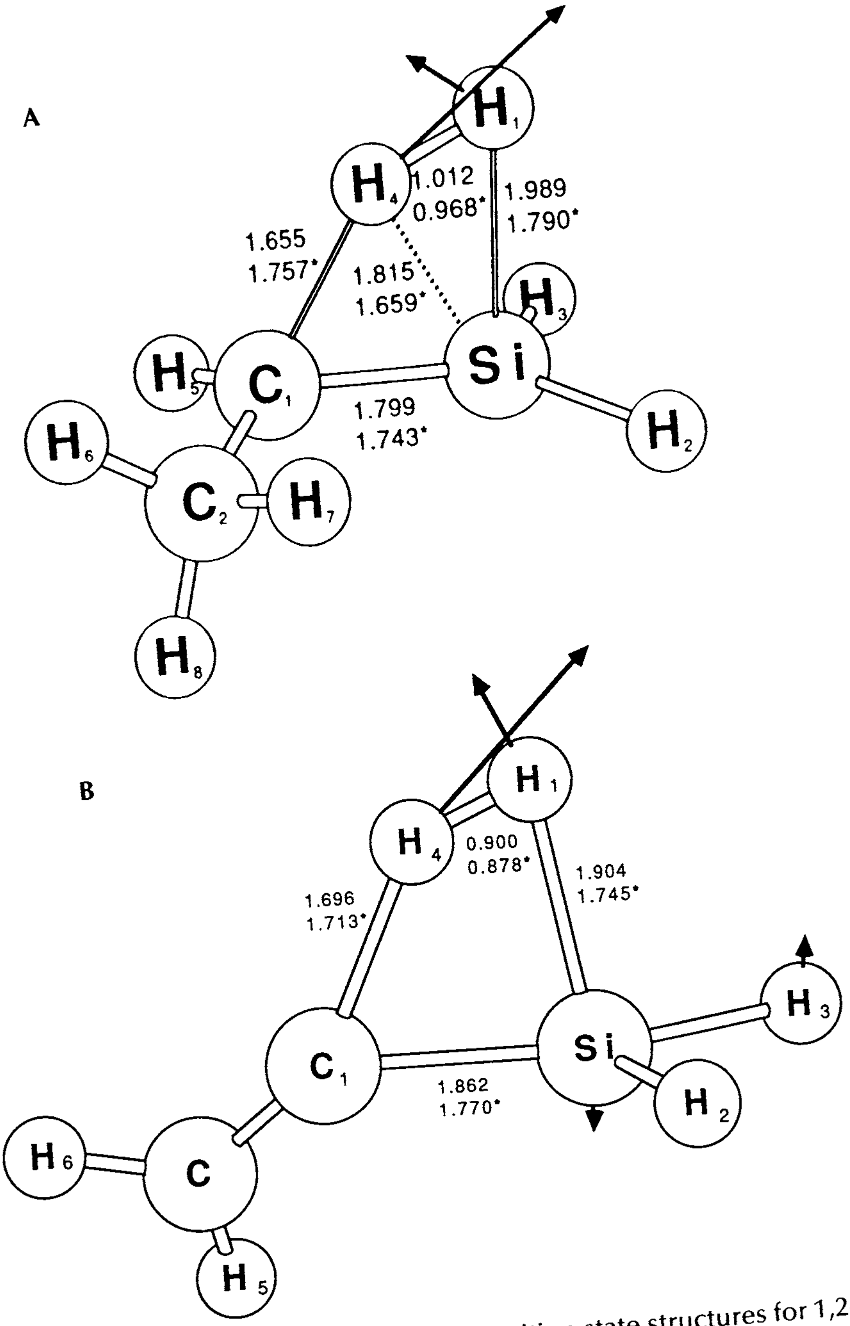


Figure 1. HF/3-21G and HF/6-31G* transition state structures for 1,2-H_2 elimination processes for ethylsilane and vinylsilane. Bond distances in Å, bond angles in deg.

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 apears to be typical for 1,2-H_2 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)/6–311G**//MP2/6–31G** level of theory, an activation energy of 89.0 kcal mol^{-1} is calculated by Gordon and co-workers.[71] Nagase and Kudo[172] found an 85 kcal/mol barrier for the elimination of HCl from methylchlorosilane at the HF/3-21G level of theory. Because of the rather high calculated barriers for 1,2-H_2 eliminations in disilane and the alkysilanes, 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.[173]

The activation energies for the 1,2-H_2 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-H_2 elimination processes.

Ohta et al.[174] 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 5. Calculated Activation Energy Barriers for 1,2-Hydrogen Elimination Processes

Reaction	*Barriers*	*Reference*
$SiH_3SiH_3 \rightarrow SiH_2{=}SiH_2 + H_2$	89.0	71
$CH_3SiH_3 \rightarrow CH_2{=}SiH_2 + H_2$	96.4	107
$CH_3CH_2SiH_3 \rightarrow CH_3CH{=}SiH_2 + H_2$	107.9	169
$CH_2{=}CHSiH_3 \rightarrow CH_2{=}C{=}SiH_2 + H_2$	113.9	171

disappears when the symmetry restriction is lifted. The silene fragments have different ground state spins and symmetries ($^3B_1$ for CH_2 and $^1A_1$ for SiH_2). 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[175] have investigated the addition of atomic hydrogen to silene to form either SiH_3CH_2 or CH_3SiH_2. The energetics for both reactions were predicted with both CASSCF/3–21G//CASSCF/3–21G and UMP4/6–31G(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_3CH_2 and CH_3SiH_2, respectively. Barton and co-workers[176] examined the 1,2-hydrogen shift connecting these two isomers with MP4/6–31G(d,p)//HF/6–31G(d) energies. They predict the reaction $SiH_3CH_2 \rightarrow CH_3SiH_2$ 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 Carbene Eliminations*

In this section we will review computational studies on SiH_2 and CH_2 elimination reactions, as well as the eliminations of substituted silylenes and carbenes. SiH_2 eliminations from silicon compounds usually form 3-center transition states. Examples of these processes are from *ab inito* studies of decomposition pathways of methylsilane[107], ethylsilane,[169,177] vinylsilane,[170] ethynylsilane,[170] disilane,[71] trisilane,[177] disilylmethane,[177] dimethylsilane,[177] silacyclopropane,[177,178] and silacyclobutane,[177] as well as the fluorinated disilanes.[120] Carbene eliminations have been investigated for the foregoing alkyl compounds, as well as propane.[177] Moreover, the reverse of these reactions can be considered as SiH_2 or CH_2 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_2

Table 6. Calculated Activation Energy Barriers for SiH_2 Elimination Processes

	Activation Energy
$CH_3SiH_3 \rightarrow CH_4 + SiH_2$	71.9[a]
$SiH_3SiH_3 \rightarrow SiH_4 + SiH_2$	56[a]
$CH_3CH_2SiH_3 \rightarrow C_2H_6 + SiH_2$	72.2, 76.5
$SiH_3SiH_2SiH_3 \rightarrow Si_2H_6 + SiH_2$	53.2[b]
$CH_2{=}CHSiH_3 \rightarrow C_2H_4 + SiH_2$	70.5
$CH{\equiv}CSiH_3 \rightarrow C_2H_2 + SiH_2$	76.5
$CH_3SiH_2CH_3 \rightarrow C_2H_6 + SiH_2$	115.1
$CH_3SiH_2SiH_3 \rightarrow CH_3SiH_3 + SiH_2$	71.6[c]
$SiH_3SiH_2SiH_3 \rightarrow Si_2H_6 + SiH_2$	58.4[c]
$c\text{-}CH_2CH_2CH_2SiH_2 \rightarrow c\text{-}C_3H_6 + SiH_2$	75.6
$SiH_3SiH_2F \rightarrow SiH_3F + SiH_2$	55
$SiH_3SiF_2H \rightarrow SiH_2F_2 + SiH_2$	55
$SiH_2FSiH_2F \rightarrow SiH_2F_2 + SiH_2$	48
$SiH_3SiH_2F \rightarrow SiH_4 + SiHF$	55
$SiH_3SiF_2H \rightarrow SiH_3F + SiHF$	58
$SiH_2FSiH_2F \rightarrow SiH_3F + SiHF$	50
$SiH_3SiF_2H \rightarrow SiH_4 + SiF_2$	71

[a] Results determined at the MP4SDTQ/MC/6-311G**//MP2/6-311G* level of theory; all other processes are determined with MP4/6-31G* energies and either HF/6-31G* or HF/3-21G geometries; see text for references.

[b] Elimination from X—H bond. [c] 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 processes seems to be rather minor. The barriers for silylene eliminations from SiH bonds are also quite constant, but they are a much lower 53–56 kcal/mol. Silylene eliminations 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.[177] Similar trends apply, of course, to the reverse insertion reactions. Insertions of silylene into SiH 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 Si. 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 insertion into ethane.[177] The other exception is an insertion into an unsaturated bond, as the insertion of silylene into the $C{=}C$ bond of ethylene[179] and the $C{\equiv}C$ bond of acetylene[180] 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 SiF_2 into acetylene is predicted to be 18 kcal/mol, at the MP4/6–31G(d,p)//3–21G(d) level of theory.[180] Similarly, the barrier to insertion into the ethylene $C{=}C$ bond increases in the order SiH_2 $(=0) < SiF_2 < SiCl_2$.[181] 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 SiH_2 elimination processes comes from the study of ethylsilane.[169] 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[182] 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

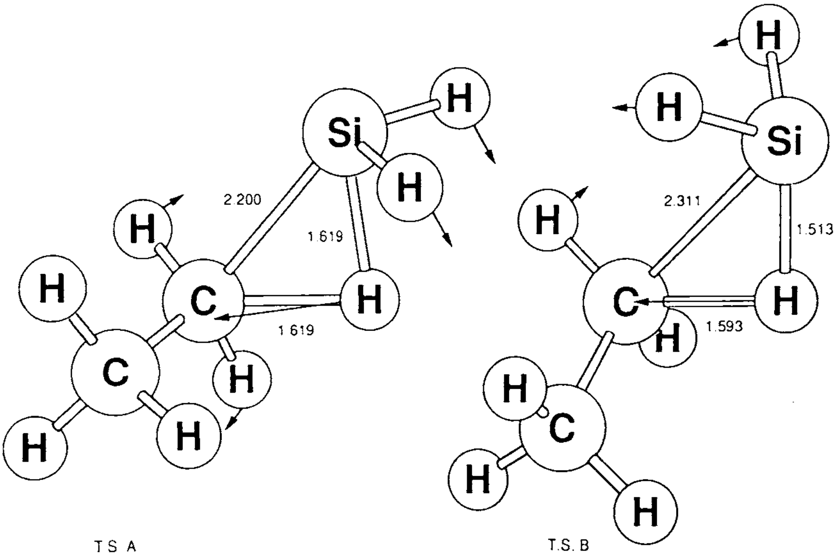


Figure 2. Transition structures and transition vectors for the primary photodissociation of ethylsilane (geometries optimized at the HF/3-21G level of theory).

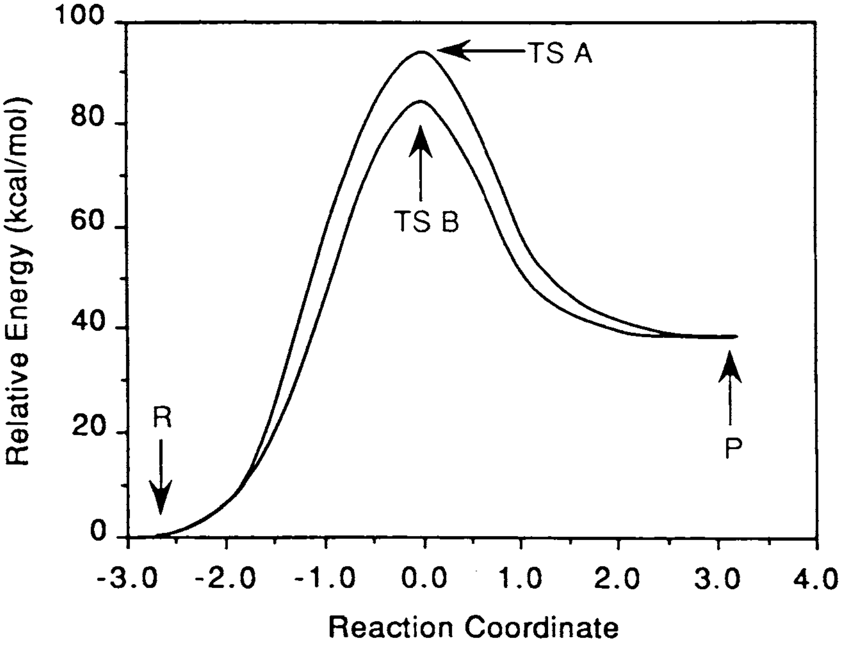


Figure 3. Reaction profiles for the paths connecting transition state **A** and **B** with reactants and products.

with their corresponding products, showed that the only difference in the two pathways is the orientation of the species SiH_2. For path A, the fragment SiH_2 rotates clockwise with respect to the SiH bond coming out of the plane of Figure 4, while in path B, the SiH_2 rotates counterclockwise with respect to the SiH bond pointing toward the plane. This suggests the possibility of two different SiH_2 rotational distributions.

As shown in Table 6, SiHF and SiF_2 elimination barriers are similar in magnitude to silylene eliminations. Indeed, the former are competitive with the silylene and 1,1-H_2 eliminations in fluorinated disilanes.[120] In contrast to silylene eliminations, carbene eliminations have much higher barriers, reflecting the much greater stability of SiH_2 than CH_2. For example, in methylsilane[107], 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 carbenes, respectively. The reverse of these eliminations, which have been studied by Sakai,

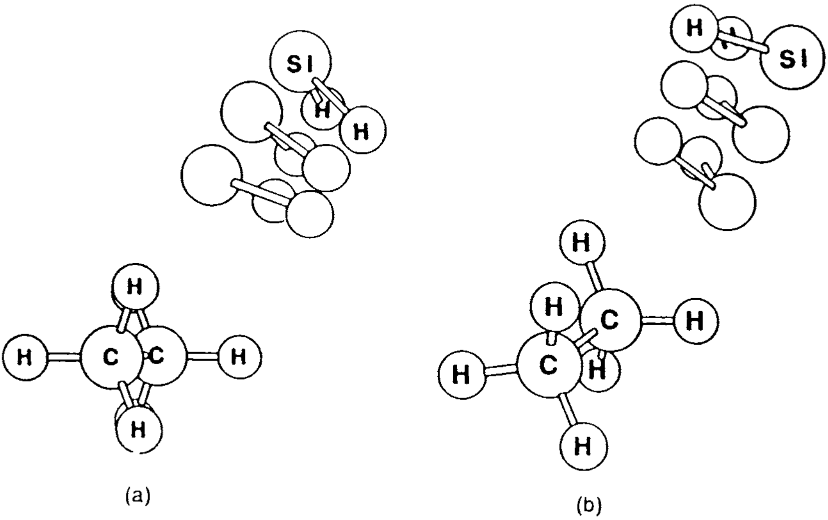


Figure 4. Change of the geometries along the reaction path from the transition state to the final products. (a) Reaction path for transition state **A**, (b) Reaction path for transition state **B**.

Deisz and Gordon[183] 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 (^1D) 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 (14.0 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 (^3P) 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 carbenes or silylenes are produced in their triplet states (the ground state for carbene), their prototypical secondary reactions are hydrogen abstractions. Gordon[184] investigated hydrogen abstractions by triplet CH_2 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[185] (from H_2 with POL-CI/6–31G(d) energies) and by Gordon, Nguyen, and Truhlar[186] (from silane with MP-SAC2/6–311G(d,p) energies).

Tachibana and co-workers[187] have examined a radical polymerization mechanism for silicon carbide 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, rather than the SiC phase, is preferred in the CVD process.

Davis et al.[188] 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_N2 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 hydrosilation reaction. The two SiH_4 eliminations which have been studied theoretically are the decompositions of ethylsilane[169] and vinylsilane.[170] 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_N2 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

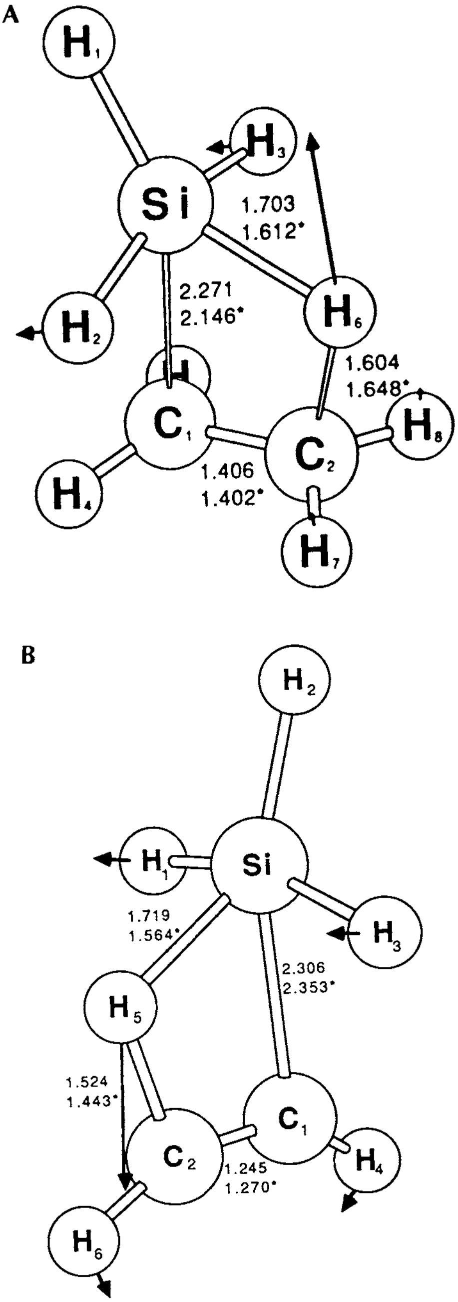


Figure 5. HF/3-21G and HF/6-31G* transition state structures for 1,2-eliminations of SiH_4 ethylsilane and vinylsilane.

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

Silylene ↔ Silene Systems. One of the most well studied isomerization reactions is that of methylsilylene (CH_3SiH) to silaethylene ($CH_2 = SiH_2$). 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 silaethylene of 41.4 kcal/mol.[189,190] Kohler and Lischka[191] 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 $CH_3\text{-}Si\text{-}CH_3 \rightarrow CH_3SiH{=}CH_2$ isomerization barrier, using CISD/6–31G*//HF/6–31G*.[192] As noted earlier, more recent, higher level calculations show that silaethylene 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[107] and disilane[71], the lowest energy route to the silene product (silaethylene 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.[193,194] Their theoretical calculations using STO-4G basis sets predict that methysilylene is more stable than silaethylene, but the most stable structure is silylmethylene (SiH_3CH). More accurate calculations by Goddard et al.[189] 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 methysilylene isomerization is to ethylsilylene. Isomerization of ethylsilylene (CH_3CH_2SiH) to methylsilaethylene ($CH_3CH_2{=}SiH_2$) was studied by Francisco[195] with the 6–31G* basis set. At the HF/6–31G* level of theory, ethylsilylene was found to be only 3.3 kcal/mol more stable than methylsilaethylene. However, using MP4(SDQ)/6–31G*//HF/6–31G* calculations the methylsilaethylene 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 ethylsilylene isomerization to methylsilaethylene was predicted. The prediction of a lower activation energy for the ethylsilylene 1,2 hydrogen shift isomerization suggests that substituent group effects do play a role in stabilizing the transition state structure in the isomerization process. The isomerization of triplet ethylsilylene was also studied. Triplet ethylsilylene was found to be 61.2 kcal/mol (MP4(SDQ)/6–31G*//HF/6–31G*) more stable than triplet methylsilaethylene, and no barrier for the isomerization was found.

Silaacetylenes. One of the simplest systems in which the 1,2-hydrogen shift isomerization process has been examined theoretically in some detail is $SiCH_2$.[196,197] Gordon and Pople[196] reported a barrier of 8.5 kcal/mol (MP3/6–31G**//HF/3–21G) for the exothermic hydrogen migration from *trans* bent silaacetylene HSiCH to silylidene $Si{=}CH_2$. Hoffman and co-workers[197] showed that the *trans* bent silaacetylene is a true minimum at the CI/DZ+d(C,Si) level and determined that the barrier to silylidene is 4.2 kcal mol^{-1}. They have also suggested that the vinylidene isomer $C{=}SiH_2$ is not a minimum on the singlet potential energy hypersurface of $SiCH_2$.

The analogous disilicon compound Si_2H_2 has been extensively studied and reviewed,[3,4] 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.[198] Koseki and Gordon[199,200] and Colegrove and Schafer[75] have clearly demonstrated that this system is one in which the role of electron correlation is crucial, even in the determination of the structure and nature of stationary points on the potential energy surfaces. For the singlet surface, the most extensive and recent series of calculations is that presented by Colegrove and Schaefer[75], using CISD/TZ2P and SCF/TZ2P energies. At this level of theory, the global minimum noted above is lower than planar silasilene, SiH_2Si by 11 kcal/mol, and the linear structure lies 43 kcal/mol above the global minimum and has two imaginary frequencies. The most interesting results, however, are that two new minima appear only when correlation is included in the geometry optimization step. These are a singly bridged species and a planar dibridged structure which are calculated to be 11.4 and 22.6 kcal/mol, 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 Si_2H_2 potential energy surface is that by Koseki and Gordon[199], who used MP4/6–31++G(d,p) energies and 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, H_2SiSi, is a minimum, rather than the previously predicted bent structure. Similarly, the global minimum on the triplet surface is predicted to be *trans* planar, 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[201,202] on the isomerization of silylsilanediyl 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.[203,204] However, it was the work of Nagase and Kudo[205] that presented a detailed theoretical examination of such shifts. They showed that the 1,2-silyl shift in $SiH_3SiH{=}CH_2$ has a barrier which is lower in energy than the 1,2-methyl shift in $CH_3SiH{=}CH_2$. 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 of a 1,2-shift is the isomerization of $SiH_3SiH{=}SiH_2$ to $HSi\text{-}SiH_2SiH_3$.[206] 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 Si—Si bonds are much more facile than across Si—C bonds.

Examples of 1,2-silyl shifts across carbon-carbon double and triple bonds come from theoretical studies of Francisco[170] and McDouall and co-workers[171]. A barrier[171] of 38.2 kcal/mol (MP4SDTQ/6–31G*//HF/6–31G*) for the 1,2-silyl shift across the $C{\equiv}C$ triple bond in ethynylsilane ($HC{\equiv}CSiH_3$) to form the silylvinylidene ($C{=}CHSiH_3$) intermediate was reported. The migrations of the SiH_3 group across $C{\equiv}C$ double bonds are found to be more difficult. In the case of the 1,2-silyl shift in vinylsilane, the reported barrier[170] for the process 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[66] and methylsilane[207,208]. The calculations on $Si^+ + SiH_4$ 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 $Si_2D_2{}^+$, $Si_3D_4{}^+$, $Si_4D_6{}^+$, and $Si_5D_{10}{}^+$ are observed upon the reaction of Si^+ with SiD_4.[209] No details regarding the nature of the products is available from the experiments, and an explanation for the termination of the clustering reactions at $Si_5D_{10}{}^+$ 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 $H_3Si\text{-}H{—}Si^+$, with the release of 24 kcal/mol. The complex is able to rearrange to $H_3Si\text{-}SiH^+$ (A3) and then to $H_2Si\text{-}SiH_2{}^+$ (A5) without moving higher in energy than the initial reactants. The barriers leading from A3 to dibridged $Si_2H_2{}^+$ and H_2SiSi^+ 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, H_2SiSi^+, 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 $H_3Si\text{-}SiH\text{-}Si^+$. Since the isomer $H_3Si\text{-}Si\text{-}SiH^+$ is not energetically accessible (the barrier is higher than reactants), the former isomer is identified with the observed Si_3D_4+ product. In a similar manner, $(H_3Si)_2SiSi^+$ is identified with the observed product

$Si_4D_6{}^+$, and termination is predicted to occur upon the formation of $(H_3Si)_3SiSiH^+$ 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.[209] 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.[210] The only observed products are $Si_2CH_4{}^+$ 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.[66] In agreement with experiment, 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 $H_3C\text{-}SiH\text{-}Si^+$ and $H_3C\text{-}Si^+$. Subsequent experiments by Armentrout and Fisher[211] have used a wider range of experimental conditions and were therefore able to observe several additional endothermic 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.[208]

In a continuation of the collaboration between theory and experiment, Raghavachari has most recently examined the clustering reactions of SiH^+ with silane, using MP4/6–31G(d,p)//MP2/6–31G(d,p) energies and scaled HF/6–31G(d) frequencies.[212] As in the preceeding paragraphs, the theoretical results are in excellent agreement with experiment[213], both qualitatively and quantitatively. The reaction termination is predicted to occur upon the formation of a stable cyclic $Si_4H_7{}^+$ 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 homodesmic 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 calculations 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 treating 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.

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