Theoretical Studies of Reactions of Silanes

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Abstract

Computational investigations of abstraction reactions of the form \( X + \text{SiR}_3H \rightarrow XH + \text{SiR}_3 \) are reviewed, where \( X = \text{H, O, F and Cl} \) and \( \text{SiR}_3H \) represents \( \text{SiH}_4, \text{Si}_2\text{H}_6 \) and \( (\text{CH}_3)_n\text{SiH}_{4-n} \) (\( n = 1-3 \)). Si-H bond dissociation enthalpies and energy barriers for the formation of transition states can be calculated to within 5 kJ mol\(^{-1}\) using e.g. Gaussian 2 theory. Analysis of isodesmic reactions provides a route to reliable thermochemistry for systems too large for Gaussian 2 theory. Expressions for rate constants calculated \textit{ab initio} using transition state theory are given; they are in generally good agreement with experimental measurements.
1. INTRODUCTION

The gas-phase kinetics of silanes, especially SiH₄, are important in chemical vapor deposition of silicon and silicon compounds such as the oxide and nitride, and in silane combustion. In this paper computational investigations of H-atom abstraction from Si-H bonds in silanes will be summarized. The overall goal is reliable prediction of the thermochemistry and reactivity of silanes so as to be able to model their gas-phase chemistry. To test these predictions we have carried out laboratory measurements of individual elementary reactions; quantitative comparisons with theory will be presented. Silanes are valence-isoelectronic with alkanes, which have been extensively studied in the context of hydrocarbon combustion and whose properties can be rationalized according to simple semi-empirical principles including e.g. the Polanyi-Semenov [1][2] and Bond-Order Bond-Energy (BEBO) [3] relationships. Important differences between Si-H and C-H bonds include the greater charge separation in the former, because Si is more electropositive than C, and the possibility of formation of pentacoordinated Si species by participation of low-lying d-orbitals on Si. Here it will be demonstrated that, although semi-empirical methods break down for silanes, usefully accurate results may be obtained via ab initio methods.

The focus is on SiH₄ and substituted silanes where H atoms are replaced by CH₃ or SiH₃. Computational investigations of Si-H bond dissociation enthalpies and reactivity towards atomic H, O and halogens in reactions of the type

\[ X + SiR₃H \rightarrow SiR₃ + HX \]  \hspace{1cm} (1)

carried out by our group and others will be discussed.
2. COMPUTATIONAL APPROACH

Quantitative molecular orbital theory is applied using methods detailed elsewhere [4][5], implemented with the GAUSSIAN series of programs [6]. Briefly, the atomic orbitals are represented mathematically by a selected basis set. Molecular orbitals are constructed from linear combinations of the atomic orbitals, optimized variationally to give the lowest energy at a selected geometry. The geometry is then varied, using analytical gradients, to obtain the stationary points on the potential energy surface (PES). Harmonic vibrational frequencies are calculated at each stationary point to verify it as a true minimum, with all real frequencies, or a transition state with a single imaginary frequency that corresponds to motion along the reaction coordinate. Typically these geometry and frequency calculations are carried out with the split-valence 3-21G(*) and/or 6-31G* atomic basis sets, using self-consistent field Hartree-Fock theory. For closed-shell singlet species spin-restricted RHF theory is applied, and unrestricted UHF theory for open-shell species. For some species a partial correction for electron correlation effects is obtained using Møller-Plesset perturbation theory to second-order (MP2). HF frequencies are scaled by a factor of 0.89 and MP2 frequencies by a factor of 0.95.

Next, single-point energies at these geometries are obtained using larger basis sets and better corrections for correlation such as MP4 and QCISD(T) theory. The highest level of theory applied here is the Gaussian-2 (G2) methodology of Pople et al. [7][8][9], which approximates a complete QCISD(T)/6-311+G(3df,2p) calculation with a series of additive corrections to the MP4/6-311G** energy. In some cases an extra term has been added to correct for spin-contamination (this is larger for transition states than most bound molecules), defined as the energy change upon projecting-out spin contamination [10] at the PMP4/6-311G**
level, and the results are denoted as P-G2 [11]. When zero-point vibrational energies are included, the energy difference between the reactants and products corresponds to the reaction enthalpy at 0 K, \( \Delta H_0 \). The enthalpy difference between reactants and the transition state (TS) at 0 K, \( E^d_0 \), represents the barrier to reaction and controls the kinetics, and is usually similar but not identical to the empirical activation energy, \( E_a \). The second-order rate constants for the bimolecular abstraction reactions considered here (reaction 1) are obtained via conventional transition state theory (TST) [12]:

\[
k_{TST} = \Gamma \cdot \frac{\hbar}{k_B T} \frac{Q^+_{TS}}{Q_x Q_{silane}} \exp\left(-\frac{E^d_0}{RT}\right)
\]  

(2)

The partition functions \( Q \) are calculated from the \textit{ab initio} geometries and frequencies [13]. Rotational symmetry factors are ignored and symmetry is taken into account by the reaction path degeneracy \( \ell^+ \). \( \Gamma \) represents a correction factor for quantum mechanical tunneling which is \( \geq 1 \), although for most of the reactions considered here \( E^d_0 \) is small enough to neglect any enhancement of reactivity by tunneling i.e. \( \Gamma \approx 1 \). An exception is \( H + SiH_4 \) for which the Wigner approximation [14] is employed,

\[
\Gamma = 1 + \frac{1}{24} \left( \frac{\hbar \nu^*}{k_B T} \right)^2
\]  

(3)

where \( \nu^* \) is the conjugate of the complex frequency of the TS.

3. RESULTS AND DISCUSSION

3.1 Si-H Bond Dissociation Enthalpies

There have been numerous theoretical investigations of the Si-H bond strength in silanes.
Several have been summarized by Apeloig [15] while halogenated species were recently reviewed by Gordon et al. [16]; some recent studies of D₆(SiH₃-H) include those by Ho et al. (377.0 kJ mol⁻¹) [17], Curtiss and Pople (383.8 kJ mol⁻¹) [18], Curtiss et al. (382.0 kJ mol⁻¹) [9], Grev and Schaefer (376.6 kJ mol⁻¹) [19] and Maître and Ohanessian (377.4 kJ mol⁻¹ once zero-point vibrational energies are included) [20]. These values compare well to the best experimental estimate derived from the ratio of the forward and reverse rate constants for [21]

\[ \text{Br} + \text{SiH}_4 \leftrightarrow \text{SiH}_3 + \text{HBr} \]  

(4)

that imply [19] \( D_0 = 377.8 \pm 2 \) kJ mol⁻¹.

The effect of methyl substitution in SiH₄ has been studied computationally. Trimethylsilane is too large for high-level calculations such as G2, but the bond strength can be related to that in SiH₄ by analysis of the isodesmic reaction

\[ \text{SiH}_3 + \text{HSi(CH}_3)_3 \rightarrow \text{SiH}_4 + \text{Si(CH}_3)_3 \]  

(5)

which conserves the number and type of each bond [22]. \( \Delta H \) can be reliably calculated even at modest levels of theory because errors arising from deficient basis sets and incomplete corrections for electron correlation largely cancel. This \( \Delta H \) equals the difference between D((CH₃)₃Si-H) and D(SiH₃-H). MP3/6-31G* results indicate that trimethyl substitution increases the Si-H bond dissociation enthalpy by 13.5 kJ mol⁻¹ [23], in excellent accord with experimental data that show an increase of 14 ± 3 kJ mol⁻¹ [24]. For monomethylsilane and dimethylsilane experiments suggest smaller increases of 4 ± 5 and 7 ± 5 kJ mol⁻¹, respectively, over \( D_0(\text{SiH}_3-H) \) [25]. Isodesmic reactions at up to MP4/6-31G* theory show no significant increase in D(Si-H) for these two molecules [25], but the discrepancies are close to the
experimental uncertainty. BAC-MP4 results do show a steady rise of D(Si-H) with the degree of methyl substitution, of about 4 kJ mol\(^{-1}\) per methyl group [17][26].

Analysis of D(Si-H) in disilane via

\[ \text{SiH}_3 + \text{Si}_2\text{H}_6 \rightarrow \text{SiH}_4 + \text{Si}_2\text{H}_5 \]  \( (6) \)

at the MP4/6-31G* level indicates that silyl substitution in SiH\(_4\) weakens the Si-H bonds by 12 kJ mol\(^{-1}\) [27]. This change is in excellent accord with an experimental reduction of 12 ± 5 kJ mol\(^{-1}\) [27] and earlier computational values [28][29][30].

Coolidge and Borden [31] drew attention to the application of Bent’s Rule [32] to rationalize the influence of substituents on the Si-H bond strengths. Because CH\(_3\) is more electronegative than H, which is more electronegative than Si, bonding in trimethylsilane from Si to C would be expected to involve hybrid orbitals with greater p character than in the sp\(^3\) Si-H bonds of SiH\(_4\), and thus the remaining Si-H bond would have greater s character, better overlap and stronger bonding. In disilane, the Si-Si bond would have more s character and thus the remaining Si-H bonds less, relative to sp\(^3\) in SiH\(_4\), and therefore the Si-H bonds are weakened. However, the CSiC angle of 110.4° in trimethylsilane (HF/6-31G* calculation) contradicts this explanation, and apparently the steric repulsion between the CH\(_3\) groups leads to less p character in the C-Si bonds than sp\(^3\). An alternative explanation is based on the inductive effect. The electron-withdrawing methyl groups will destabilize (CH\(_3\))\(_3\)Si· over SiH\(_3\)·, thus raising the bond dissociation enthalpy, whereas the electron-donating SiH\(_3\) group stabilizes Si\(_2\)H\(_5\)· and reduces the Si-H bond dissociation enthalpy in Si\(_2\)H\(_6\), similar to the lowering of D(C-H) in C\(_2\)H\(_6\) as compared to CH\(_4\).

In summary, computational chemistry yields Si-H bond strengths in silanes with an
accuracy comparable to experiment.

3.2 The Reaction of H Atoms with Silanes

Two initial computational investigations of the transition state for H-atom abstraction yielded barriers of 32 and 45 kJ mol\(^{-1}\) [33][34], higher than is consistent with laboratory measurements [35]. Recently, it was shown that G2 theory predicts \(E_0^a = 20.7\) kJ mol\(^{-1}\), and 15.1 kJ mol\(^{-1}\) at the P-G2 level, results that are close to the experimental value of 17.1 ± 3 kJ mol\(^{-1}\) [36]. Table 1 summarizes values of \(\Delta H_0\) and \(E_0^a\) for

\[
H + SiH_4 \rightarrow H_2 + SiH_3
\]  \hspace{1cm} (7)

at selected levels of theory. It may be seen that \(\Delta H_0\) is calculated accurately more easily, i.e. at lower levels of theory, than \(E_0^a\). We observe similar patterns of decreasing barrier height with increasing sophistication of the calculations for other silane abstraction reactions discussed below. The P-G2 barrier height was combined with MP2/6-31G* information about the geometry and frequencies of the TS to calculate rate constants using TST (equation 2) with a Wigner tunneling correction. The results may be described by

\[
k_\gamma = 2.44 \times 10^{16} \text{ (T/K)}^{1.90} \exp(-860 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}
\]

and are plotted in Arrhenius form on Figure 1. Also shown there are measurements from our laboratory [36]: agreement is seen to be satisfactory, with the difference arising almost entirely from a 2 kJ mol\(^{-1}\) discrepancy between theory and experiment for \(E_0^a\). No computational evidence for a neutral bound SiH\(_3\) intermediate has been obtained, and it appears plausible that direct abstraction dominates the reactivity of SiH\(_4\).

The reaction of H with Si\(_2\)H\(_6\) has been studied at the G2 level by Dobbs and Doren [37]. They predict that \(E_0^a\) for abstraction is about 14 kJ mol\(^{-1}\), which would be similar to
that found in SiH₄. The weak Si-Si bond opens the possibility of a substitution reaction

\[ \text{H} + \text{Si}_2\text{H}_6 \rightarrow \text{SiH}_4 + \text{SiH}_3 \]  \hspace{1cm} (8)

where the most energetically favorable substitution pathway had about the same barrier as abstraction. Thus for disilane abstraction and substitution are predicted to be competitive [37], which is consistent with experiments indicating that substitution accounts for around 20% of the total reactivity at room temperature [38].

### 3.3 The Reactions of O Atoms with Silanes

Horie et al. have noted that the BEBO method "fails completely" for the reactions of ground-state O(^3P) atoms with SiH₄ and methylsilanes [39]. The reactivity trend is for the rate constant at room temperature to increase with the number of CH₃ groups [39], even as the Si-H bond energy goes up (see Section 3.1) and thus in contradiction to the Polanyi-Semenov rule. The calculated P-G2 barrier for

\[ \text{O} + \text{SiH}_4 \rightarrow \text{OH} + \text{SiH}_3 \]  \hspace{1cm} (9)

of \( E^\ddagger = 11.3 \text{ kJ mol}^{-1} \) is in excellent accord with our experimental value of \( 11.8 \pm 3 \text{ kJ mol}^{-1} \) [11]; the agreement between TST rate constants (\( k_9 = 5.17 \times 10^{-17} (\text{T/K})^{2.15} \exp(-1000 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1} \)) and measurements [11] may be seen in Figure 2. As in the case of reaction 7, no evidence was found for a bound pentacoordinate intermediate on the triplet PES.

CH₃ is more electronegative than H, so that the central Si atom is expected to be more positive in trimethylsilane than in SiH₄. This is consistent with the Mulliken charges calculated from the HF/6-31G* wavefunction: the charges on Si and H in SiH₄ are +0.41 and -0.10, respectively, and change to +1.16 and -0.15 in (CH₃)₃SiH. The effect of increased polarization
on the reactivity of the Si-H bond has been investigated through consideration of the TS for

$$\text{O} + (\text{CH}_3)_3\text{SiH} \rightarrow \text{OH} + (\text{CH}_3)_3\text{Si}$$

(10)

at the MP2/6-31G*//HF/3-21G* level [40]. At this level of theory $E_0^\ddagger$ is very inaccurate (for reaction 9 the error was 39 kJ mol$^{-1}$, which corresponds to a factor of more than $10^6$ in $k_9$ at 298 K [11]), but trimethylsilane is too large for e.g. a G2 analysis. Instead, $E_0^\ddagger$ for reaction 10 can be derived from the isodesmic reaction

$$(\text{CH}_3)_3\text{SiH} + \text{SiH}_4\text{O}^\ddagger \text{(TS9)} \rightarrow (\text{CH}_3)_3\text{SiHO}^\ddagger \text{(TS10)} + \text{SiH}_4$$

(11)

for which $\Delta H_0 = E_{0,10}^\ddagger - E_{0,9}^\ddagger = -13.0$ kJ mol$^{-1}$ at the MP2/6-31G*//HF/3-21G* level. This is in qualitative agreement with the lower barrier measured for reaction 10 [40], although the reduction in $E_0^\ddagger$ is slightly overestimated: fitting to experimental $k_9$ and $k_{10}$ data indicates that methylation reduces the barrier by 10.5 kJ mol$^{-1}$ rather than 13.0 kJ mol$^{-1}$ [40]. Using the latter purely theoretical value together with $E_{0,9}^\ddagger = 11.3$ kJ mol$^{-1}$ discussed above implies an unphysically negative value for $E_{0,10}^\ddagger$ of -1.7 kJ mol$^{-1}$; the corresponding TST rate constant of $k_{10} = 1.87 \times 10^{-17} (T/K)^{2.13} \exp(+360 K/T)$ cm$^3$ s$^{-1}$ agrees with experimental measurements to within an order of magnitude [40] as shown on Fig. 2. The difference corresponds to an underestimation of only 4.5 kJ mol$^{-1}$ in the theoretical $E_{0,10}^\ddagger$, and presumably indicates an incomplete accounting for basis set size and changes in electron correlation in the calculation of $\Delta H_0$ for reaction 11.

The reduction in barrier to O-atom abstraction with alkylation of the silane is interesting because it violates the Polanyi-Semenov rule. A qualitative rationalization is that the bonding $\sigma$ orbital between Si and H is distorted towards the H atom, because of the latter’s greater electronegativity, and thus the corresponding $\sigma^*$ orbital is distorted towards the Si atom. This
antibonding MO accepts an electron from the attacking O atom in the TS, and is stabilized by other electron-withdrawing groups on Si such as CH₃. Thus the energy of the TS is lowered by alkylation of the central Si atom.

3.4 The Reactions of Halogen Atoms with Silanes

Sato et al. have studied the reaction

\[ \text{F} + \text{SiH}_4 \rightarrow \text{HF} + \text{SiH}_3 \]  \hspace{1cm} (12)

and obtained a significant barrier of about 15 kJ mol⁻¹ at the MP4/6-21G**//HF/6-21G** level of theory [41]. However, available experimental evidence suggests an effectively zero barrier for reaction 12 because \( k_{12} = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) at room temperature [42][43] which implies that F and SiH₄ react at every collision. Results from our own laboratory are summarized in Table 2 [44], and it may be seen as the calculations are improved the predicted \( E_\delta^s \) and \( \Delta H_0 \) decrease, similar to the pattern noted above for reaction 7. HF theory gives a very poor estimate of the overall \( \Delta H_0 \) for reaction 12, while the G2 result is in excellent accord with experiment. The MP2/6-31G* potential energy surface has a saddle point (see Table 2), but at this geometry the G2 energy lies between that of the reactants and products i.e. \( E_\delta^s \) is negative. This is suggestive of a purely attractive interaction between F and SiH₄ with no barrier to reaction.

The TS for the reaction

\[ \text{Cl} + \text{SiH}_4 \rightarrow \text{HCl} + \text{SiH}_3 \]  \hspace{1cm} (13)

shows similar behavior (Table 2). At the G2 level of theory the energy at the MP2/6-31G* TS geometry is again below that of the reactants, so there is apparently no barrier to reaction [44].
This is in accord with experiments that show a high rate constant, around \(3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\), and a slightly negative activation energy of \(E_a \approx -2 \text{ kJ mol}^{-1}\) [45]. One interpretation is that the mechanism involves formation of an adduct between Cl and SiH₄, which preferentially dissociates back to reactants [46]. However, searches of the HF and MP2 PES revealed no bound species, except for a very loose van der Waals-like complex between SiH₃ + HCl which is bound by about RT or less [44] and is therefore unlikely to affect the kinetics significantly. An alternative explanation of the negative \(E_a\) is based on TST [46], where if \(E_{0,13}^\dagger \approx 0\) and the temperature dependences of \(Q_{\text{vib}}^\dagger\) and \(Q_{\text{vib, SiH₄}}\) cancel, then \(E_a\) is expected to approach -RT/2 i.e. about -1.6 kJ mol⁻¹ for the experiments, close to that observed [45].

4. CONCLUSIONS

Transition states for the reactions of atoms with SiH₄ are well-characterized at the G2 level of theory, to within 5 kJ mol⁻¹, and rate constants derived via TST are in accord with experimental results. The properties of more complicated silanes, that are too large for the application of G2 theory, may be related to those of SiH₄ through isodesmic reactions. This analysis at the MP2/6-31G* and/or MP4/6-31G* levels of theory yields good results for the variation of the Si-H bond dissociation enthalpy with methyl and silyl substitution. Isodesmic reactions also seem promising for analysis of transition states, and give a reasonable estimate of the relative reactivities of SiH₄ and (CH₃)₃SiH towards O atoms. All these reactions have been interpreted in terms of direct H-atom abstraction, and so far no theoretical evidence for participation by bound pentacoordinate intermediates has been found.
5. ACKNOWLEDGMENTS

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REFERENCES


44. A. Goumri, L. Ding and P. Marshall, unpublished work.


TABLE 1: Enthalpies of the transition state and products relative to reactants at 0 K, $E_t^d$, and $\Delta H_0$, for $H + SiH_4 \rightarrow SiH_3^+ \rightarrow H_2 + SiH_3$. Data taken from ref. 36.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>$E_t^d$, kJ mol$^{-1}$</th>
<th>$\Delta H_0$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G*</td>
<td>66.6</td>
<td>-25.2</td>
</tr>
<tr>
<td>MP2/6-31G*</td>
<td>54.8</td>
<td>-34.4</td>
</tr>
<tr>
<td>MP4/6-31G*</td>
<td>46.0</td>
<td>-44.8</td>
</tr>
<tr>
<td>MP4/6-311G**</td>
<td>29.1</td>
<td>-50.7</td>
</tr>
<tr>
<td>G2</td>
<td>20.7</td>
<td>-54.7</td>
</tr>
<tr>
<td>P-G2</td>
<td>15.1</td>
<td>-55.5</td>
</tr>
<tr>
<td>Expt.</td>
<td>17.1 ± 3.0</td>
<td>-54.0 ± 2.5</td>
</tr>
</tbody>
</table>
TABLE 2: *Ab initio* TS energies and enthalpies of the TS ($E_\text{TS}$) and products ($\Delta H_0$) relative to reactants at 0 K for $X + \text{SiH}_4 \rightarrow \text{SiH}_4X^+ \rightarrow \text{HX} + \text{SiH}_3$ ($X = \text{F}$ and Cl).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>HF/6-31G**</th>
<th>MP2/6-31G**b</th>
<th>G2**</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiH}_4\text{F}^+$ TS energy (hartrees)</td>
<td>-390.56304</td>
<td>-390.80398</td>
<td>-391.05676</td>
<td></td>
</tr>
<tr>
<td>$E_\text{TS}^+$ for F + $\text{SiH}_4$ (kJ mol$^{-1}$)</td>
<td>61.3</td>
<td>4.6</td>
<td>-12.9</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_0$ for HF + $\text{SiH}_3$ (kJ mol$^{-1}$)</td>
<td>-51.4</td>
<td>-166.4</td>
<td>-188.1</td>
<td>-187.8</td>
</tr>
<tr>
<td>$\text{SiH}_4\text{Cl}^+$ TS energy (hartrees)</td>
<td>-750.64849</td>
<td>-750.87300</td>
<td>-751.10390</td>
<td></td>
</tr>
<tr>
<td>$E_\text{TS}^+$ for Cl + $\text{SiH}_4$ (kJ mol$^{-1}$)</td>
<td>54.4</td>
<td>5.3</td>
<td>-21.6</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_0$ for HCl + $\text{SiH}_3$ (kJ mol$^{-1}$)</td>
<td>10.4</td>
<td>-27.6</td>
<td>-47.3</td>
<td>-49.7</td>
</tr>
</tbody>
</table>

*At the HF/6-31G* geometry. The TS for F + $\text{SiH}_4$ has r(F-H) = 1.26 Å and r(Si-H) = 1.61 Å. The TS for Cl + $\text{SiH}_4$ has r(Cl-H) = 1.49 Å and r(Si-H) = 1.79 Å. $E_\text{TS}^+$ and $\Delta H_0$ include corrections for zero-point vibrational energy.

*At the MP2/6-31G* geometry. The TS for F + $\text{SiH}_4$ has r(F-H) = 1.66 Å and r(Si-H) = 1.51 Å. The TS for Cl + $\text{SiH}_4$ has r(Cl-H) = 1.58 Å and r(Si-H) = 1.66 Å. $E_\text{TS}^+$ and $\Delta H_0$ include corrections for zero-point vibrational energy.
FIGURE CAPTIONS

Fig. 1  Comparison of rate constants from *ab initio* theory (dashed line) and experiment (solid line) for H + SiH₄.

Fig. 2  Comparison of rate constants from *ab initio* theory (dashed lines) and experiment (solid lines) for O + SiH₄ and O + (CH₃)₃SiH.
Fig. 1  Comparison of rate constants from *ab initio* theory (dashed line) and experiment (solid line) for H + SiH₄.
Fig. 2 Comparison of rate constants from *ab initio* theory (dashed lines) and experiment (solid lines) for $O + \text{SiH}_4$ and $O + \text{(CH}_3\text{)}_3\text{SiH}$. 