Predicted Enthalpies of Formation for Silaethylene, Disilene, and Their Silylene Isomers

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Enthalpies of formation of silaethylene (SiH₂=CH₂), methylsilylene (HSiCH₃), disilene (SiH₂=SiH₂), and silylsilylene (HSiSiH₃) are predicted by using the recently developed GAUSSIAN-1 method for computing accurate molecular energies. The predicted enthalpies of formation of the silylenes are compared with enthalpies of formation determined from isodesmic reactions. Very good agreement is found between these two methods and improved values for the enthalpies of formation of silaethylene and disilene are suggested.

Introduction

Accurate enthalpies of formation are essential in understanding the thermodynamics of any given class of reactions. Furthermore, a knowledge of enthalpies of formation for a reaction or a group of related reactions is a necessary first step in the deduction of the mechanisms for these reactions. Unfortunately, the thermodynamic properties of many silicon compounds are not well-known experimentally. In particular, the enthalpies of formation of the prototypical unsaturated silicon compounds silaethylene (SiH₂=CH₂) and disilene (SiH₂=SiH₂) and their silylene isomers (HSiCH₃ and HSiSiH₃, respectively) are not well-known experimentally and continue to be debated.¹-⁴ Fortunately, for molecules with just 1-2 heavy atoms, theory is now able to provide quantitative guidance regarding thermodynamic quantities. Theoretical methods are used here to help unravel the thermodynamics of the four unsaturated silicon-containing compounds mentioned above.

Several techniques for the theoretical prediction of enthalpies of formation of molecules have recently been developed.⁵-¹⁰ Among these is the GAUSSIAN-1 methodology⁴ of Pople and coworkers (hereafter referred to as G1), which uses large basis sets and quadratically convergent configuration interaction (QCI)¹¹ to predict enthalpies of formation and other properties of small

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molecules to within 1–2 kcal/mol of the experimental values. Binkley and Melius\textsuperscript{10} apply empirical correction factors to fourth-order perturbation theory correlation energies to obtain enthalpies of formation for small compounds. For larger systems, the semiempirical methods of Dewar and Thiel and Stewart\textsuperscript{1} can be used to predict enthalpies of formation.

When enthalpies of formation are known for a subset of reference compounds, homodesmic reactions\textsuperscript{12} may be used to predict enthalpies of formation of moderately sized compounds to within 2–3 kcal/mol, using split-valence plus polarization basis sets and a modest level of theory (i.e., second-order perturbation theory) to determine correlation corrections.\textsuperscript{8} Such reactions have been utilized in calculating enthalpies of formation of several highly strained organic molecules and their silicon analogs\textsuperscript{13} as well as several alkylsilenes.\textsuperscript{14,15} Furthermore, recent studies have employed isodesmic reactions\textsuperscript{16} to predict the enthalpy of formation of (di)methylsilylene\textsuperscript{4} and methyl-substituted silenes and silienes.\textsuperscript{12} Thus, once the enthalpies of formation for selected reference compounds have been established from experiment or with a reliable level of theory (e.g., G\textsubscript{1}), the analogous properties for larger related compounds may be predicted with the aid of isodesmic or homodesmic reactions. This combination of G\textsubscript{1} theory and isodesmic/homodesmic reactions is thus a powerful tool for determining thermodynamic properties.

In the present work, G\textsubscript{1} total molecular energies are used to compute enthalpy differences for reactions which relate the compound of interest to its constituent elements. By combining these computed reaction enthalpies with the known enthalpies of formation for the elements, one then obtains predicted enthalpies of formation for the compound of interest. For comparison, an isodesmic reaction (analogous to one from an earlier paper\textsuperscript{17} used to predict the enthalpy of formation of methylsilylene) is used to calculate the enthalpy of formation of silylsilylene.

### Computational Methodology

The geometries for all compounds were initially optimized at the self-consistent field (SCF) level, using the 6-31G(d) basis set\textsuperscript{18} and the analytical gradient routines in Gaussian\textsuperscript{19}. All structures thus obtained were verified as local minima by demonstrating that their matrices of energy second derivatives are positive definite. The structures were then refined\textsuperscript{20} by using second-order many-body perturbation theory\textsuperscript{11} (denoted as MP2) and co-workers\textsuperscript{21}. The G\textsubscript{1} method of Pople et al.\textsuperscript{5} was then used to obtain accurate molecular energies for the prediction of reaction enthalpies: the G\textsubscript{1} energies are obtained by assuming that, beyond the MP4/6-31G(d) geometries, Pople and co-workers\textsuperscript{5} have done a refined 20 · 25 · 26 calculation, and the analytical gradient routines in Gaussian\textsuperscript{19} were used.

#### Results and Discussion

The G\textsubscript{1} total energies for all compounds considered in this paper are given in Table I. The experimental and predicted values for the enthalpies of formation are also listed here. (The MP2/6-31G(d) geometries have appeared elsewhere\textsuperscript{20,25,26} and so will not be given here.)

The predicted G\textsubscript{1} enthalpies of formation for silaethylene and its isomer methylsilylene are 46.5 and 50.6 kcal/mol, respectively. The predicted 4.1 kcal/mol difference between these two, with silaethylene more stable, is 3 kcal/mol smaller than Walsh's experimental estimate\textsuperscript{24} but is within the stated experimental error bars. Most earlier theoretical studies\textsuperscript{26,28} all of which use basis

| Table 1: G\textsubscript{1} Total Energies and Enthalpies of Formation\textsuperscript{4} |
|---------------------------------|-----------------|-----------------|-----------------|
| molecule\textsuperscript{b} | G\textsubscript{1} energy | \(\Delta H^\text{a}_{\text{f}}\text{p}^{\text{298}}\) | \(\Delta G^\text{a}_{\text{f}}\text{p}^{\text{298}}\) | \(\Delta S^\text{a}_{\text{f}}\text{p}^{\text{298}}\) |
| H\textsubscript{2} (\(\text{I}^\text{2}\)) | -1.165 00 | (0.0)\textsuperscript{c} | (0.0)\textsuperscript{c} | (31.2)\textsuperscript{c} |
| Si (\(\text{IP}\)) | -288.933 78 | (107.6)\textsuperscript{c} | (96.9)\textsuperscript{c} | (40.1)\textsuperscript{c} |
| C (\(\text{IP}\)) | -37.784 64 | (171.3)\textsuperscript{c} | (160.4)\textsuperscript{c} | (37.8)\textsuperscript{c} |
| SiH\textsubscript{2}CH\textsubscript{3} (\(\text{I}^\text{A}\)) | -329.411 52 | 46.5\textsuperscript{e} | 49.4 | -9.7 |
| HSICH\textsubscript{3} (\(\text{A}^\text{I}\)) | -329.405 39 | 50.6\textsuperscript{e} | 52.5 | -6.3 |
| Si\textsubscript{2}H\textsubscript{2} (\(\text{I}^\text{A}\)) | -580.430 65 | 64.9\textsuperscript{e} | 73.9 | 5.4 |
| HSISi\textsubscript{3} (\(\text{A}^\text{I}\)) | -580.418 10 | 72.8\textsuperscript{e} | 73.9 | 3.5 |

\textsuperscript{8} G\textsubscript{1} energies in hartrees, enthalpies and free energies of formation in kcal/mol, entropies in cal/(mol K). Experimental values in parentheses. \textsuperscript{9} The electronic state is given below the structure. \textsuperscript{10} (Gas phase): Chase, M. W. Jr.; Davies, C. A.; Downey, J. R.; Jr.; Furrip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed.; J. Phys. Chem. Ref. Data. 1985, Suppl. 1. \textsuperscript{11} From reaction 1a. \textsuperscript{12} From reaction 1b. \textsuperscript{13} Reference 3. \textsuperscript{14} Reference 29. \textsuperscript{15} From reaction 2a. \textsuperscript{16} From reaction 2b. \textsuperscript{17} Reference 34.
TABLE II: MP2/6-31G(d)/RHF/6-31G(d) Total Energies, Zero-Point Energies (ZPE), and Enthalpies of Formation for Reaction 3

<table>
<thead>
<tr>
<th>molecule</th>
<th>electronic state</th>
<th>total energy</th>
<th>ZPE</th>
<th>ΔH₂₉₈°</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₂</td>
<td>1A₁</td>
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<td>7.9</td>
<td>65.3b</td>
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<tr>
<td>SiH₃</td>
<td>1A₁</td>
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<td>8.2b</td>
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<tr>
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<td>1A₄</td>
<td>-581.46704</td>
<td>32.8</td>
<td>19.4b</td>
</tr>
<tr>
<td>H₂SiH₂</td>
<td>1A¹</td>
<td>-580.23039</td>
<td>20.6</td>
<td>75.8</td>
</tr>
</tbody>
</table>


sets of at least double-zeta plus polarization quality with correlation corrections, also predict silylene to be 2–4 kcal/mol more stable than methylsilylene (although a combined experimental–theoretical study predicts a somewhat larger energy difference of 10 kcal/mol). AM1 predicts silylene to be 23.4 kcal/mol more stable than its silylene isomer. Now let us compare the individual G1 enthalpies of formation with the experimental values. For silylene the theoretical value is nearly 10 kcal/mol higher than that proposed by Walsh, while for methylsilylene the G1 enthalpy of formation is 6 kcal/mol above Walsh’s result. For the latter isomer, there are other experimental estimates, in addition to the value of 44 kcal/mol obtained in this paper. These are 48 ± 2 and 53 ± 4 kcal/mol. If G1 theory is indeed accurate to 1–2 kcal/mol, these results suggest that the preferred experimental enthalpy of formation is that from Ring et al. In addition, it appears that the experimental enthalpy of formation of silylene needs to be reexamined. These assertions are reinforced by the fact that the G1 enthalpy of formation for methylsilylene agrees very well with an earlier theoretical study from this laboratory which used an isodesmic reaction analogous to reaction 3 and MP2/6-31G(d,p)/RHF/6-31G(d) energies to obtain an estimated enthalpy of formation of 49.2 kcal/mol.

The predicted G1 enthalpies of formation for disilene and silylsilylene are 64.9 and 72.8 kcal/mol, respectively. This 8 kcal/mol energy difference is twice as large as that found for silylene and is somewhat smaller than the (at least) 13 kcal/mol difference suggested by the experimental results of Walsh. The G1 difference is, however, in good agreement with several previous calculations which predict disilene to be more stable by 6–8 kcal/mol. A notable exception is the study by Ho et al which predicts disilene to be 23 kcal/mol more stable than silylsilylene (which is similar to the AM1 value of 25 kcal/mol); however, the empirical scaling techniques used in deriving that value have recently been questioned.

Of the two SiH₄ isomers, the G1 enthalpy of formation is in better agreement with experiment for silylene (75 ± 2 kcal/mol from Walsh; 75.3 kcal/mol from Ring et al.). The experimental estimate for disilene (262 kcal/mol) is in worse agreement and is the source of the disagreement in the isodetic reaction noted in the previous paragraph. An earlier theoretical study (at the MP4/6-31G(d,p)/RHF/6-31G(d) level) predicted the enthalpies of formation of disilene and silylsilylene to be 57 ± 10 and 80 ± 3 kcal/mol, respectively. From the isodesmic reaction 3, one obtains a predicted enthalpy of formation for silylsilylene of 75.8 kcal/mol (see Table II), in good agreement with the G1 result.

The above summary indicates a fairly wide range of possible enthalpies of formation for the four compounds of interest. However, we believe the present predictions to be accurate within 1–2 kcal/mol, based on the following:

1. The G1 method generally predicts thermodynamic properties (such as electron affinities, ionization potentials, and atomization energies) with an accuracy of 1–2 kcal/mol. Similar accuracy has been obtained for molecules containing two heavy atoms or a third-row element.

2. The G1 predicted enthalpies of formation of methylsilylene and silylsilylene are in very good agreement with the enthalpies of formation obtained from isodesmic reactions (which are generally accurate to within 3–5 kcal/mol).

3. The G1 relative enthalpies of formation are consistent with the results of several earlier high-level ab initio studies. Therefore, we are confident that the G1 computed enthalpies of formation of these four molecules represent improvements to the currently accepted values, particularly for silylene and disilene, and for the first time provide a consistent set of values for the four molecules of interest here.

To the extent that the G1 enthalpies are accurate to 1–2 kcal/mol, comparison of the experimental and G1 enthalpies of formation suggest that, experimentally, only the enthalpy of formation of silylsilylene is accurately known. The experimental enthalpy of formation of disilene appears to be somewhat low and thus the energy difference relative to silylene is overestimated. Although the enthalpy of formation of methylsilylene obtained by Ring et al. is consistent with the G1 result, the agreement among the three experimental determinations is rather poor. Furthermore, the large difference between the experimental and theoretical enthalpies of formation for silylene is disturbing. With the exception of silylene, the theoretical results presented here strongly suggest the need for further experimental measurements of the enthalpies of formation of these compounds.

Having established accurate enthalpies of formation of these four compounds, it is possible to design isodesmic and/or homodesmic reactions to predict the enthalpies of formation of several derivatives of the parent molecules. For example, the isodesmic reaction

\[
HRSi=SiH₂ + SiH₄ \rightarrow H₂Si=SiH₃ + SiH₂R
\]

can be used to compute the enthalpy of formation of HRSi=SiH₂ (where R denotes a general functional group), provided the enthalpy of formation of SiH₂R is known.

In a forthcoming paper, the enthalpies of formation of the methyl-substituted silaethylenes and disilenes, calculated by using isodesmic reactions and the enthalpies of formation of silylene and disilene computed in the present work, will be reported.

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