An ab initio RRKM/Master Equation investigation of SiH4 and GeH4 decomposition kinetics using a Kinetic Monte Carlo approach

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Though the unimolecular decompositions of SiH4 and GeH4 are important reaction steps for the CVD of Si and Ge, only few studies are available in the literature on their kinetics. In this work we investigated the decomposition of SiH4 and GeH4, as well as the reactions between SiH3 and GeH3 and H adopting a combined ab initio-RRKM-master equation approach. Structures of reactants and transition states were determined at the B3LYP/aug-cc-pVTZ level, while energies were calculated using coupled cluster theory with single and double excitations and perturbational estimate of triple excitations and extrapolated to infinite basis set using cc-pVTZ and cc-pVQZ basis sets.1 The first reaction investigated was Silane decomposition, which can take place through two different reaction channels:

1) SiH4 $\rightarrow$ SiH3 + H
2) SiH4 $\rightarrow$ SiH2 + H2

The potential energy surface of reaction (1) is characterized by a progressive increase of the energy with the H-SiH3 bond length, as is the case for methane decomposition to methyl, while reaction (2) has a maximum and thus a distinct transition state. The fastest is reaction (2), since SiH2, differently from methylidene, is a relatively stable molecule. High pressure rate constants for reaction 1) and 2) were determined adopting microvariational J-resolved transition state theory and classic transition state theory, respectively, and are reported in Table 1, while the calculated energy dependent microvariational rate constants are sketched in Fig. 1.

Table 1. High-pressure kinetic constants for SiH4 decomposition reactions interpolated between 300 and 2200 K to the modified Arrhenius expression (k = AT^n exp(-Ea/RT[K]). Activation energies are reported in kcal/mol. The bimolecular kinetic constant has dimensions of cm^3/mol/s.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>Ea</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH4 $\rightarrow$ SiH3 + H</td>
<td>1.2x10^{11}</td>
<td>0.477</td>
<td>57.6</td>
</tr>
<tr>
<td>SiH4 $\rightarrow$ SiH2 + H</td>
<td>1.0x10^{18}</td>
<td>-0.503</td>
<td>92.9</td>
</tr>
<tr>
<td>SiH3 + H $\rightarrow$ SiH4</td>
<td>4.2x10^{11}</td>
<td>0.802</td>
<td>-0.33</td>
</tr>
</tbody>
</table>

Pressure dependent unimolecular kinetic constants were computed solving the 1 dimensional master equation using the Gillespie’s exact stochastic method. Rotational effects were considered by expressing the master equation as a function of the rotational and vibrational energy and calculating the RRKM rate constants k(E) averaging k(E,J) rate coefficients on pseudo-steady state J-resolved populations. After solving the RRKM/ME system using the KMC approach it is necessary to post process the simulation results to extract the desired information. The kinetic constant was determined using a new protocol performing a linear regression on the total number of reacted molecules over simulation time. A stable solution is usually reached when about two hundred molecules have reacted.

Finally, our calculations of the reactions between SiH3 (GeH3) and H predicted that the main reaction products are SiH2 (GeH2) and H2 and suggest that kinetic constants reported in the literature for reactions between SiH3 (GeH3) and H may be significantly underestimated (up to a factor of 5).

References.

Fig. 1. Calculated RRKM SiH4 decomposition kinetic constants as a function of the energy of the excited complex.

The simulation results agree well with experimental data for the decomposition of SiH4 and GeH4. A comparison between calculated and experimental data for SiH4 decomposition is sketched in Fig. 2.

Fig. 2. Comparison between calculated and experimental (Koshi et al.,2 Petersen et al.,3 Votintsev et al.,4 and Mick et al.5) SiH4 unimolecular decomposition kinetic constant at two different pressures: a) 0.6 bar, b) 1.0 bar.