RMG Study Group

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Topics

- Silicon hydrides
- Solvation kinetics
- For each, will present theory, some results & its implementation in RMG-Py
Enable silicon hydride chemistry in RMG

• Simulate silicon hydride chemical vapor deposition, silicon nanoparticle formation

• Need to update and/or add reaction families, libraries, thermodynamics

• Need reasonable experimental comparisons
Two new reaction families and reaction libraries added to RMG

- Silylene Insertion (new)
- Silylene-to-Silene Isomerization (new)
- Hydrogen Abstraction (updated)
- Radical Recombination (updated)
- Reaction libraries, including ring opening reactions

Giunta et al., J. Appl. Phys. 67, 1990, 1062-1075
Adamczyk et al. Theor Chem Acc 128, 2011, 91-113
Thermodynamics data added to RMG

- Common species available in NIST database
- High level calculations for some ring species\(^1\)
- Group additivity values for stable species\(^2\)

- Newly developed hydrogen bond increment (HBI) values for radicals:
  * these were using G3//B3LYP

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Additions to Cantherm

• Spin orbit coupling value for Si
• Atomic energies for G3//B3LYP, CBS-QB3, and M062X/MG3S
• BAC for G3//B3LYP
Comparison to SiH$_4$ decomposition experiment

$T = 913$ K
$P = 39$ kPa
$y_0$(SiH$_4$) = $1.6 \times 10^{-4}$ in Argon

$\tau \approx 0.8$ s

$613$ K $\leq T \leq 963$ K
$P = 39$ kPa
$y_0$(SiH$_4$) = $1.6 \times 10^{-4}$ in Argon

With/without pressure dependence,
With/without radical reactions

Goodwin et al., Cantera, [http://www.cantera.org](http://www.cantera.org)
Model matches experiment within uncertainty

Experiment $= 913$ K

Model matches experiment within a 20 K temperature difference

Corresponds to 1-2 kcal/mol difference in activation energy
Model cannot capture effect of changing initial $y_{\text{SiH}_4}$

RMG-Py implementation

- On branch ‘bs lakman/RMG-Py/silicon-hydrides’ and ‘bs lakman/RMG-database/silicon-hydrides’
- Will get up to date with current master, and submit a pull request
- See http://pubs.acs.org/doi/abs/10.1021/acs.iecr.6b02402
Framework needed for liquid phase mechanism generation

Solvation thermo
- Linear solvation energy relationships (LSERs) and a molecular structure group additivity approach

Diffusion-limited kinetics
- Stokes-Einstein theory for bimolecular reaction rates

Solvation kinetics
- How can we generalize solvent effects in a quick, high-throughput way?
Reaction barrier is affected by solvation

 Barrier height changes depending on differing effect of solvent on reactant and transition state

$$\Delta E_A = E_{A}^{\text{liquid}} - E_{A}^{\text{gas}}$$

Adapted from Crim, F.F., Farad. Discuss., 2012
SMD energy calculation provides tradeoff between accuracy and speed

- SMD is a continuum solvation model with some corrections for the first solvent shell\(^1\)
- Full electron density used
- A single point energy calculation based on SMD is performed on gas-phase geometries and transition states to calculate \(\Delta E_A\)
- 8 solvents chosen to span a range of dielectric constant and 6 solvent categories\(^2\)

\[ \Delta E_A = E_A^{\text{liquid}} - E_A^{\text{gas}} \]

Results suggest $\Delta E_A$ can be predicted

- Method should modify gas phase $E_A$ based on
  - molecular structure of reactants
  - solvent
- Molecular structure tree for each solvent category, based on trends observed

\[
\begin{align*}
X-H & \quad 1.37 \\
R-O-H & \quad 1.28 \\
R-C-H & \quad -0.31 \\
C/H & \\
C/H & \quad C/H & \quad -1.26 & \quad O & \quad C & \quad C & \quad H & \quad 0.61 \\
C/H & \\
C/H & \quad C/H & \quad O & \quad C & \quad C & \quad H & \quad 1.17
\end{align*}
\]
Results: Trained group values from 47 $\Delta E_A$ values

Example: $\text{CH}_3\text{OH} + \cdot \text{OOH} \leftrightarrow \text{CH}_3\text{O} \cdot + \text{H}_2\text{O}_2$

<table>
<thead>
<tr>
<th>General</th>
<th>Specific</th>
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</table>
| X-H     | \begin{align*} 
\text{H} & \\
\text{H-C-O-} & \\
\text{H} & 
\end{align*} |
| 1.37    | +        | 0.51     | = 1.88 |

\begin{align*} 
\text{Y-} & \\
\cdot \text{O-O-} & \\
\text{-0.01} & + \quad 0.91 & = 0.90 
\end{align*}

$\Delta E_A = 2.78 \text{ kJ/mol}$
Will kinetic solvation corrections make a difference in existing models?

• Ben Amara et al. (2013) used RMG to build a detailed kinetic model for nC12/methyl oleate oxidation, and compared to experiments\(^1\)
  – Liquid-phase thermodynamic corrections were used
• 2924 of 3275 reactions (89%) were hydrogen abstraction
• We modified the H-abstraction rates using the group contribution method for \(\Delta E_A\) and simulated it with Cantera\(^2\)

Figure 3a from Ben Amara et al.; Comparison of induction times from detailed kinetic model with experiments.

Model simulation with Cantera

Updated model shows larger induction periods for 0% and 5% v/v methyl oleate content. Our Cantera simulation with Ben Amara et al. model is similar to their simulation.
Octane and methyl heptane mechanisms

- Recently, we modified updated mechanisms from IFP group, now with many more training reactions (> 1000), and for both hydrogen abstraction and intra-H migration reactions.
RMG-Py implementation

• Currently, a post processing script
  – ‘bslakman/my_scripts/modifyReactionBarriers.py’
    – Can add to script repository
  – Need to use with my updated solvation branches of RMG-Py and RMG-database
  – In process of making automated during mechanism generation
  – Benchmarking (Jason Cain)