RMG Study Group

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Topics

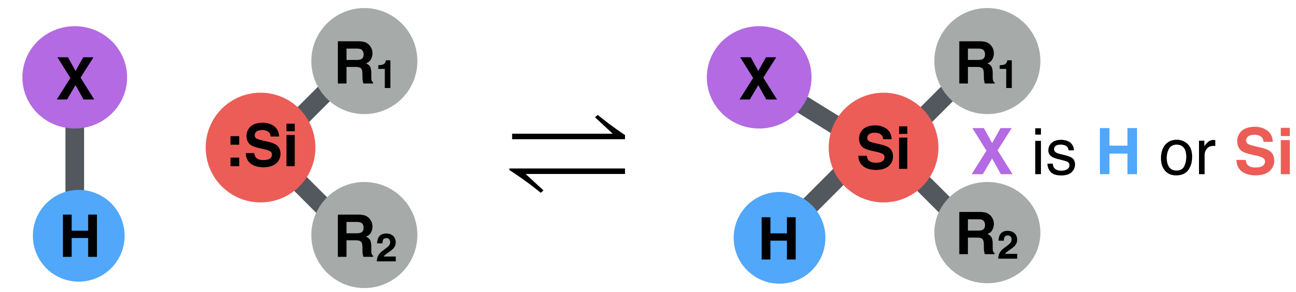
- Silicon hydrides
- Solvation kinetics
- For each, will present theory, some results & its implementation in RMG-Py

Enable silicon hydride chemistry in RMG

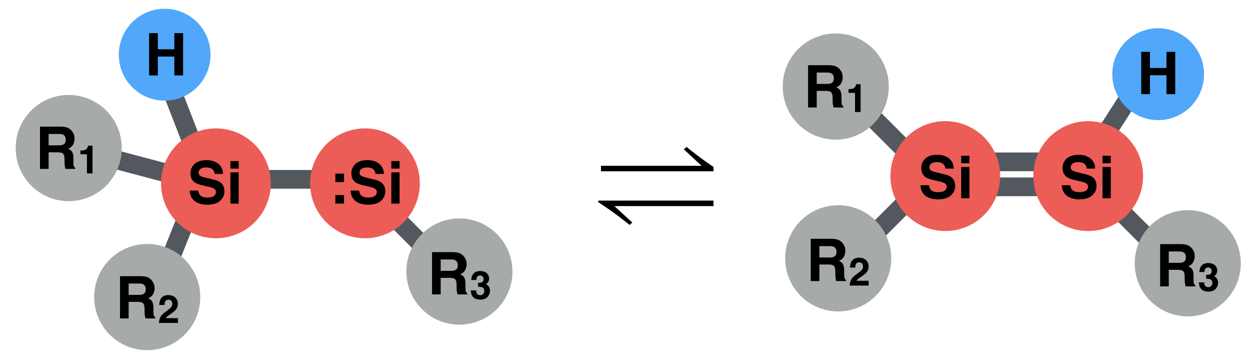
- Simulate silicon hydride chemical vapor deposition, silicon nanoparticle formation
- Need to update and/or add reaction families, libraries, thermodynamics
- Need reasonable experimental comparisons

Two new reaction families and reaction libraries added to RMG

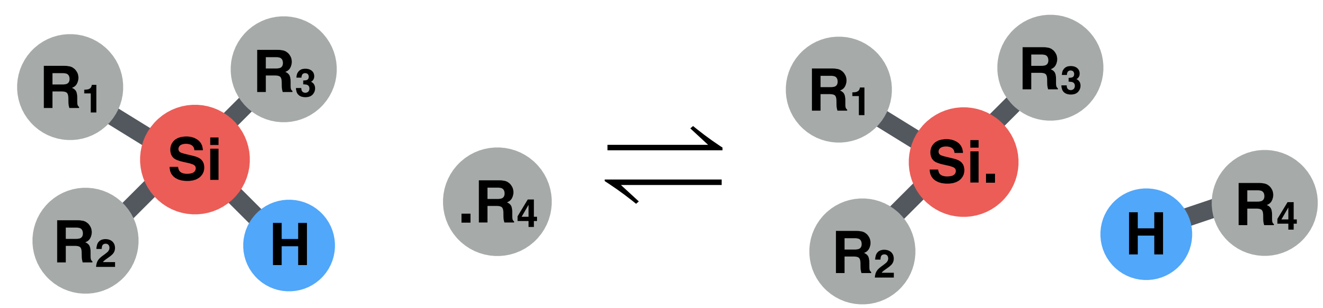
- Silylene Insertion (new)



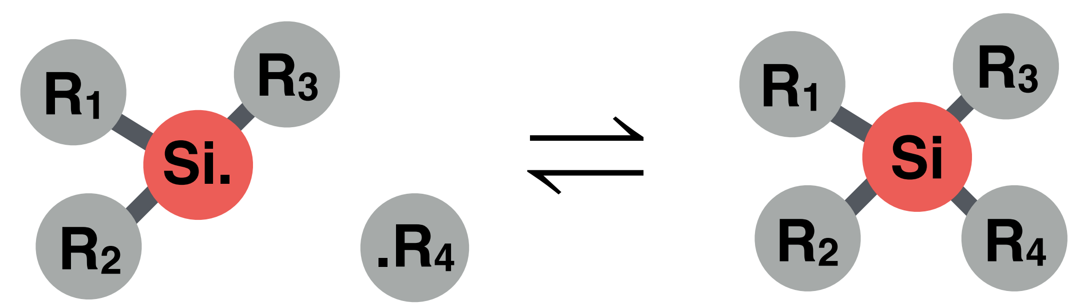
- Silylene-to-Silene Isomerization (new)



- Hydrogen Abstraction (updated)



- Radical Recombination (updated)

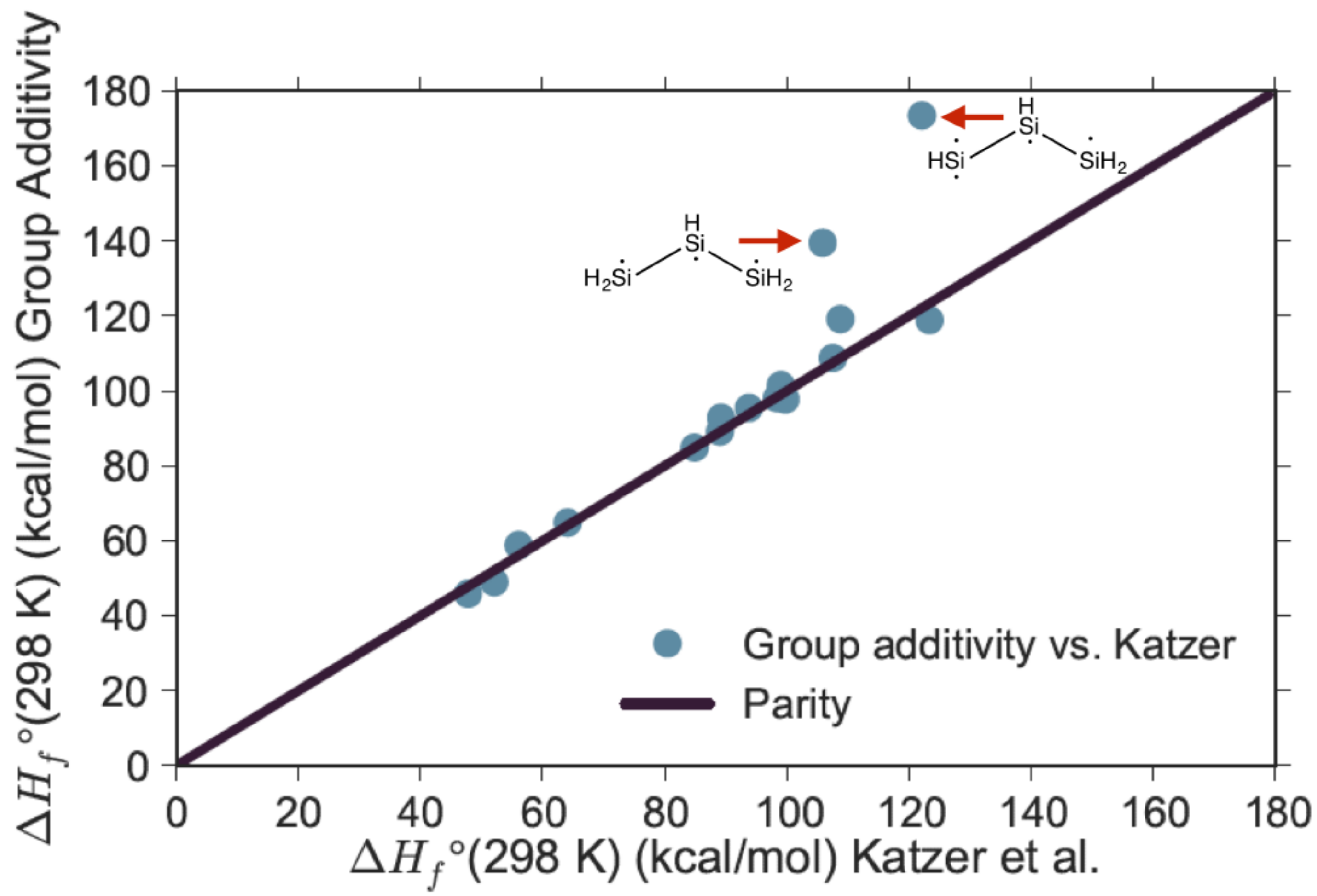


- Reaction libraries, including ring opening reactions

Giunta et al., *J. Appl. Phys.* **67**, 1990, 1062-1075
Dollet and de Persis, *J. Anal. Appl. Pyrolysis* **80**, 2007, 460-470
Adamczyk et al. *Phys. Chem. Chem. Phys.* **12,** 2010, 12676-12696
Adamczyk et al. *ChemPhysChem* **11,** 2010, 1978-1994
Adamczyk et al. *J. Phys. Chem. A* **113** 2009, 10933-10946
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



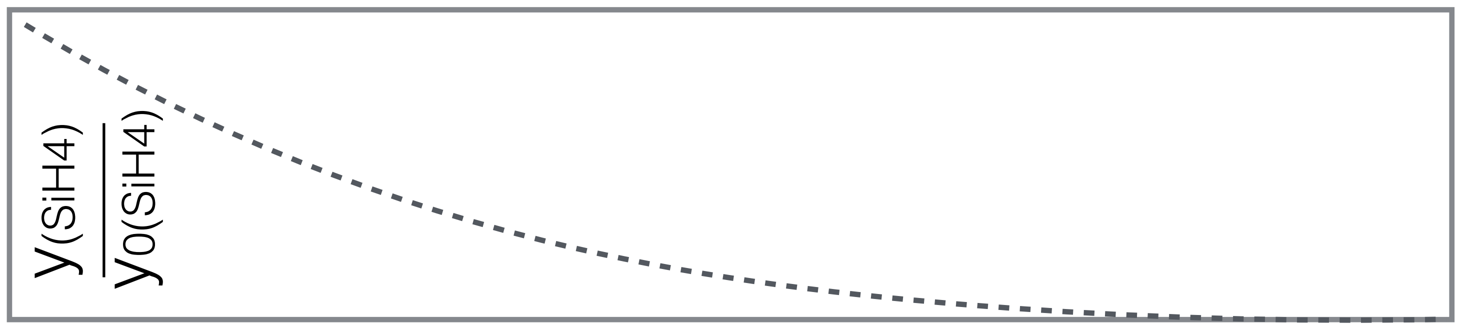
Slakman et al., *Ind. Eng. Chem. Res.*, 2016
1 Katzer et al., *J. Phys. Chem. A.* **101,** 1997, 3942-3958.
2 Wong et al., *J. Phys. Chem. A.* **108,** 2004, 874-897.

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
$y_{0(SiH4)} = 1.6 \times 10^{-4}$
in Argon



$\tau \approx 0.8$ s

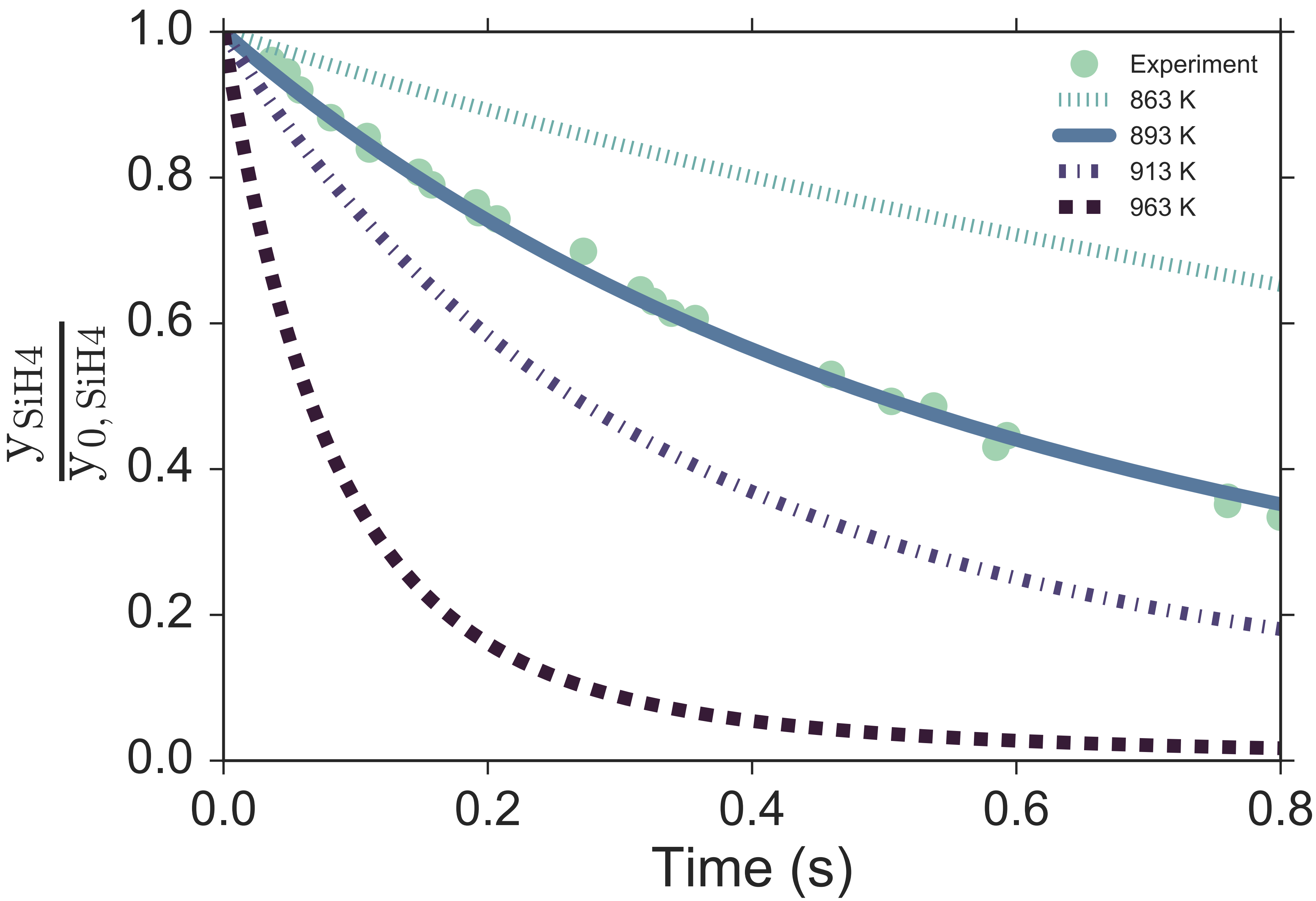
613 K ≤ T ≤ 963 K
P = 39 kPa
$y_{0(SiH4)} = 1.6 \times 10^{-4}$
in Argon

With/without pressure dependence,
With/without radical reactions

Cantera

Onischuk et al., *Int. J. Chem. Kinetics* **30(2)**, 1998, 99-110
Goodwin et al., *Cantera*, http://www.cantera.org

Model matches experiment within uncertainty



Experiment = 913 K

Model matches experiment within a 20 K temperature difference

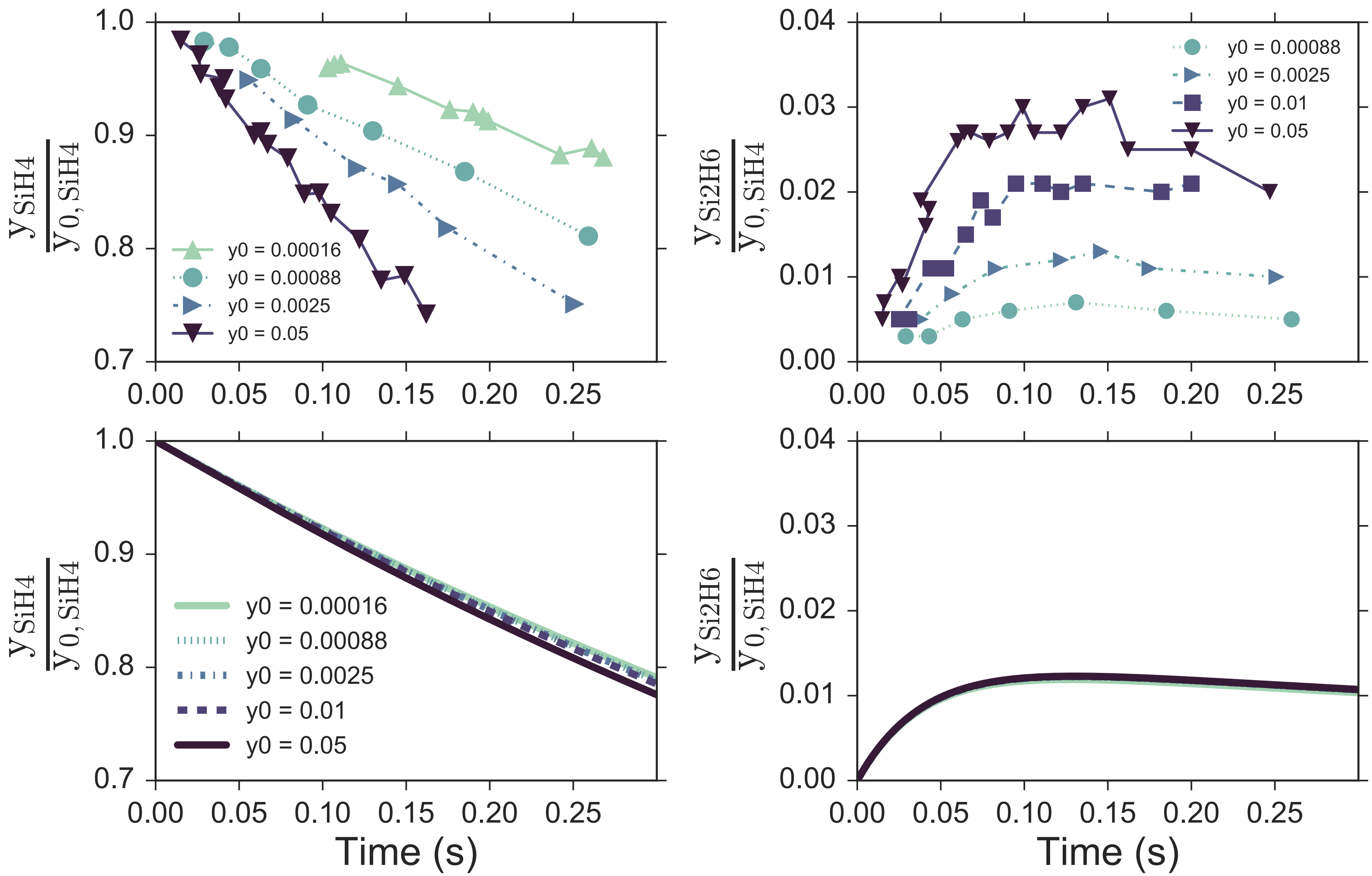
Corresponds to 1-2 kcal/mol difference in activation energy

Onischuk et al., *Int. J. Chem. Kinetics* **30(2)**, 1998, 99-110
Slakman et al., *Ind. Eng. Chem. Res.*, 2016.

Model cannot capture effect of changing initial y_{SiH4}

Experiment

Model



Onischuk et al., *Int. J. Chem. Kinetics* **30(2)**, 1998, 99-110
Slakman et al., *Ind. Eng. Chem. Res.*, 2016.

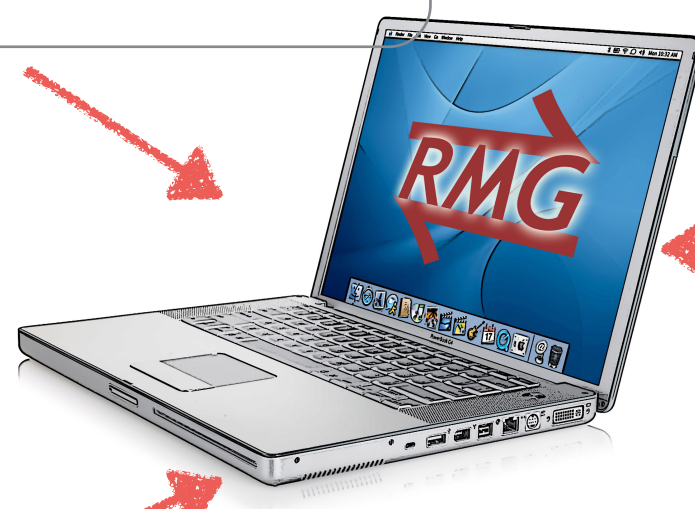
RMG-Py implementation

- On branch ‘bslakman/RMG-Py/silicon-hydrides’ and ‘bslakman/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



✘ **Solvation kinetics**

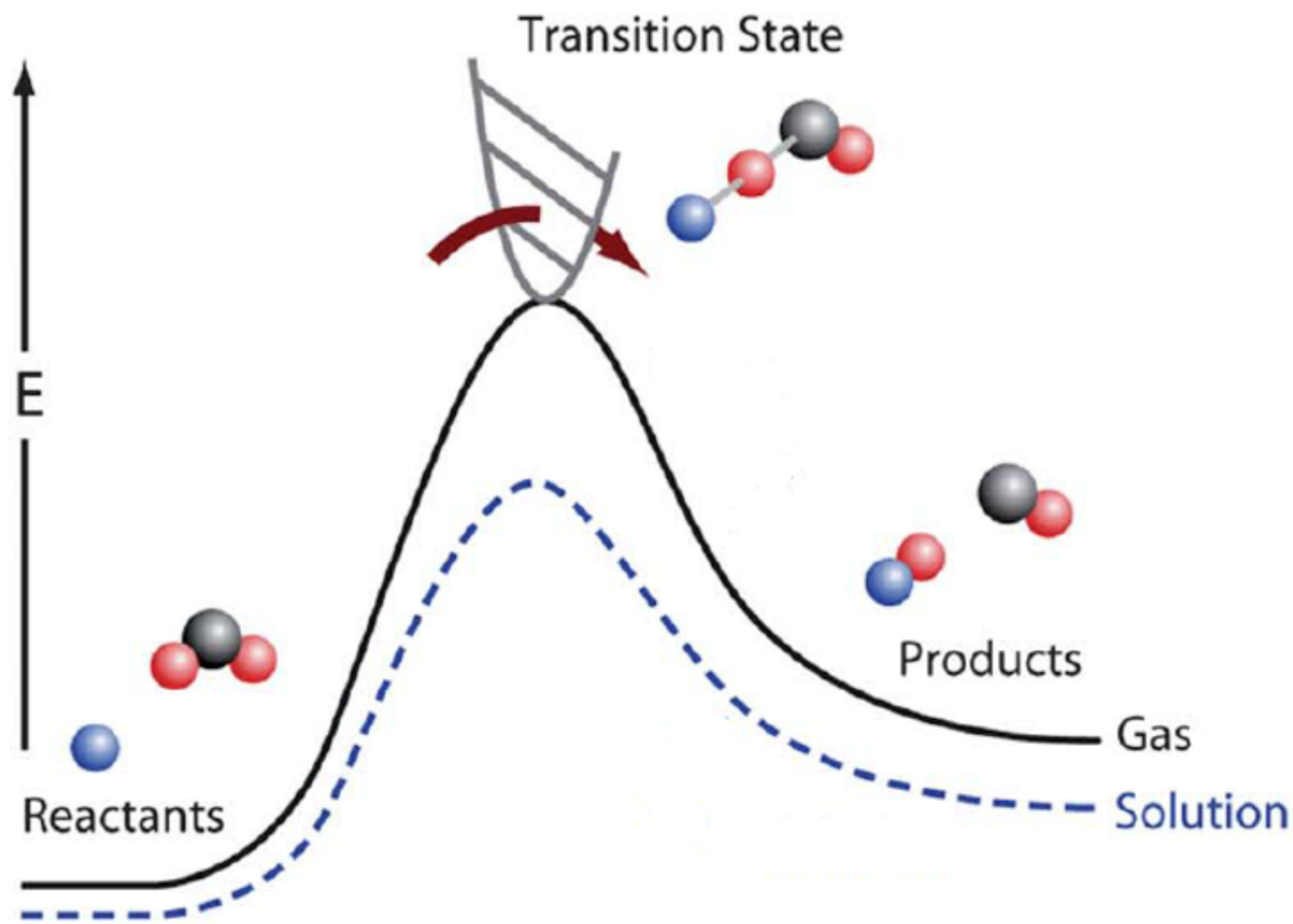
How can we generalize solvent effects in a quick, high-throughput way?

✔ **Diffusion-limited kinetics**

Stokes-Einstein theory for bimolecular reaction rates

A Jalan et al., *J. Phys. Chem. B*, 117(10), 2013

Reaction barrier is affected by solvation



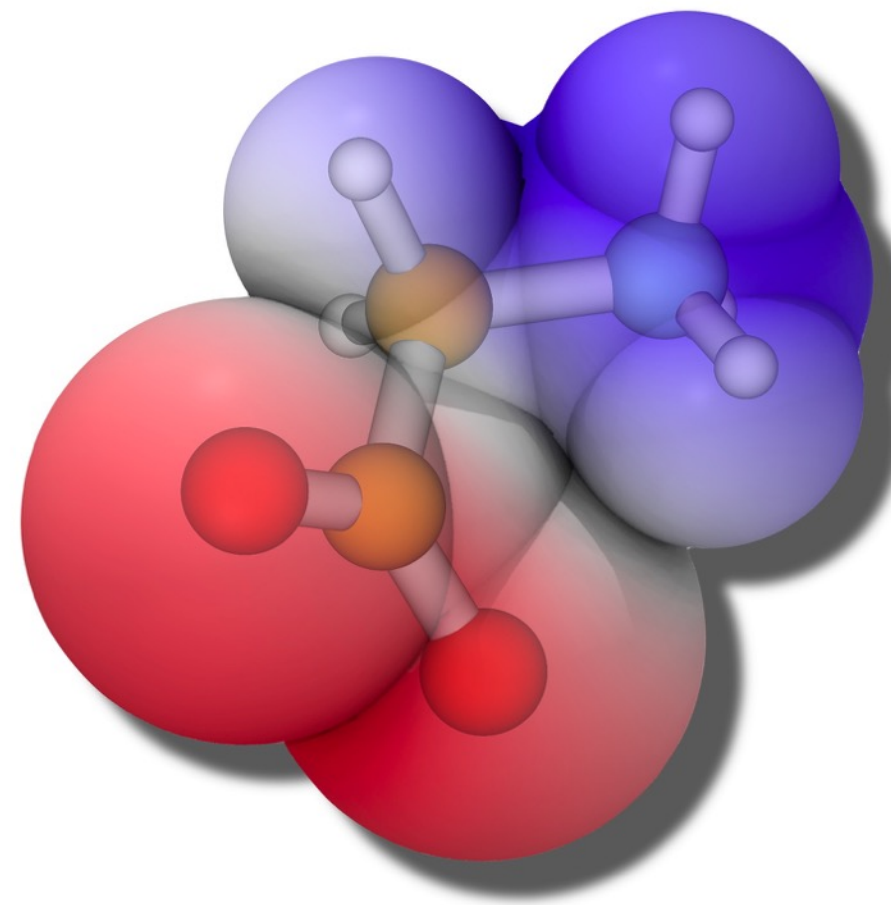
Adapted from Crim, F.F., *Farad. Discuss.*, 2012

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

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

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 ΔE_A
- 8 solvents chosen to span a range of dielectric constant and 6 solvent categories[2]

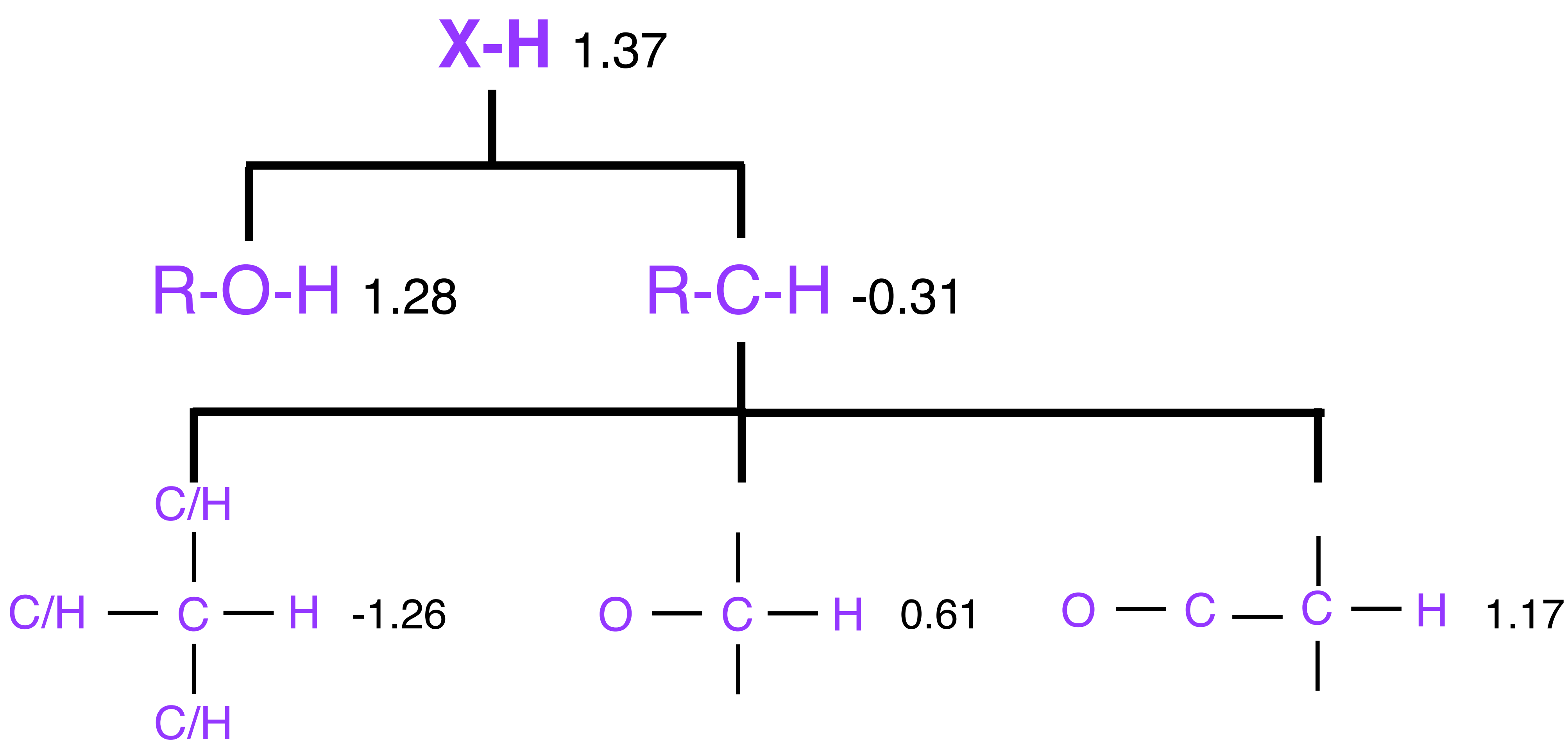


$$\Delta E_{\mathrm{A}} = E_{\mathrm{A}}^{\mathrm{liquid}} - E_{\mathrm{A}}^{\mathrm{gas}}$$

1. A.V. Marenich et al., *J. Phys. Chem. B.,* 113(18), 2009.
2. Schmid, *Handbook of Solvents*. George Wypych, ed., Ch. 13, 2001.

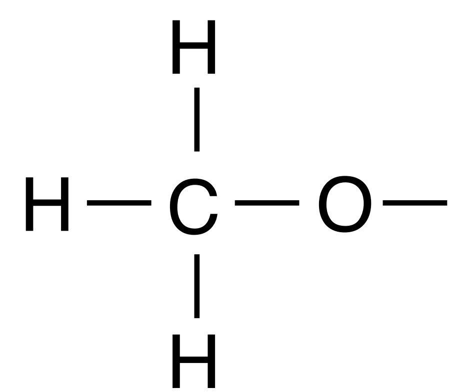
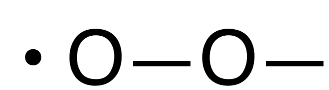
Results suggest ΔE_A can be predicted

- 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



Results: Trained group values from 47 ΔE_A values

Example: CH_3OH + •OOH ⇔ CH_3O• + H_2O_2

General		Specific		
X-H				
1.37	+	0.51	=	1.88
Y•				
-0.01	+	0.91	=	0.90

ΔE_A = 2.78 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 ΔE_A and simulated it with Cantera[2]

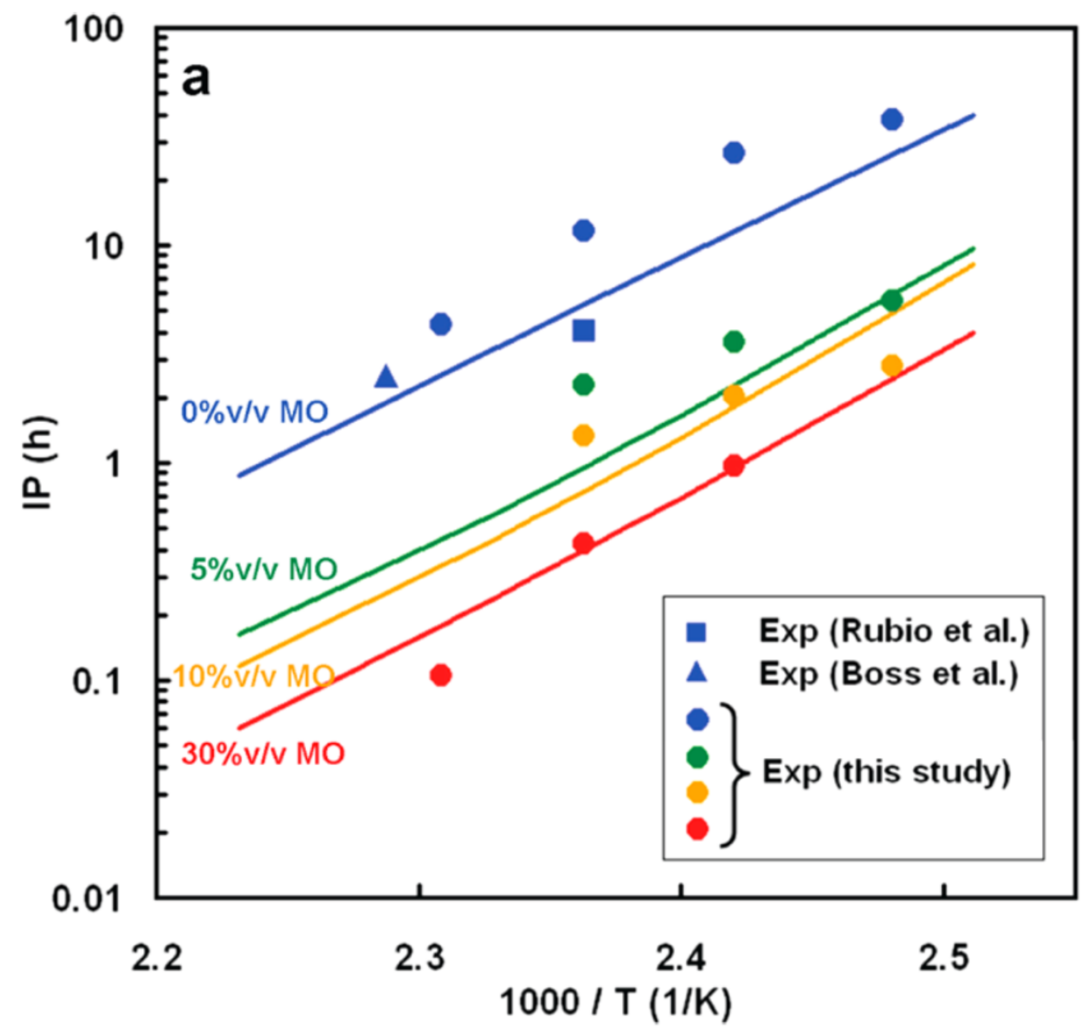
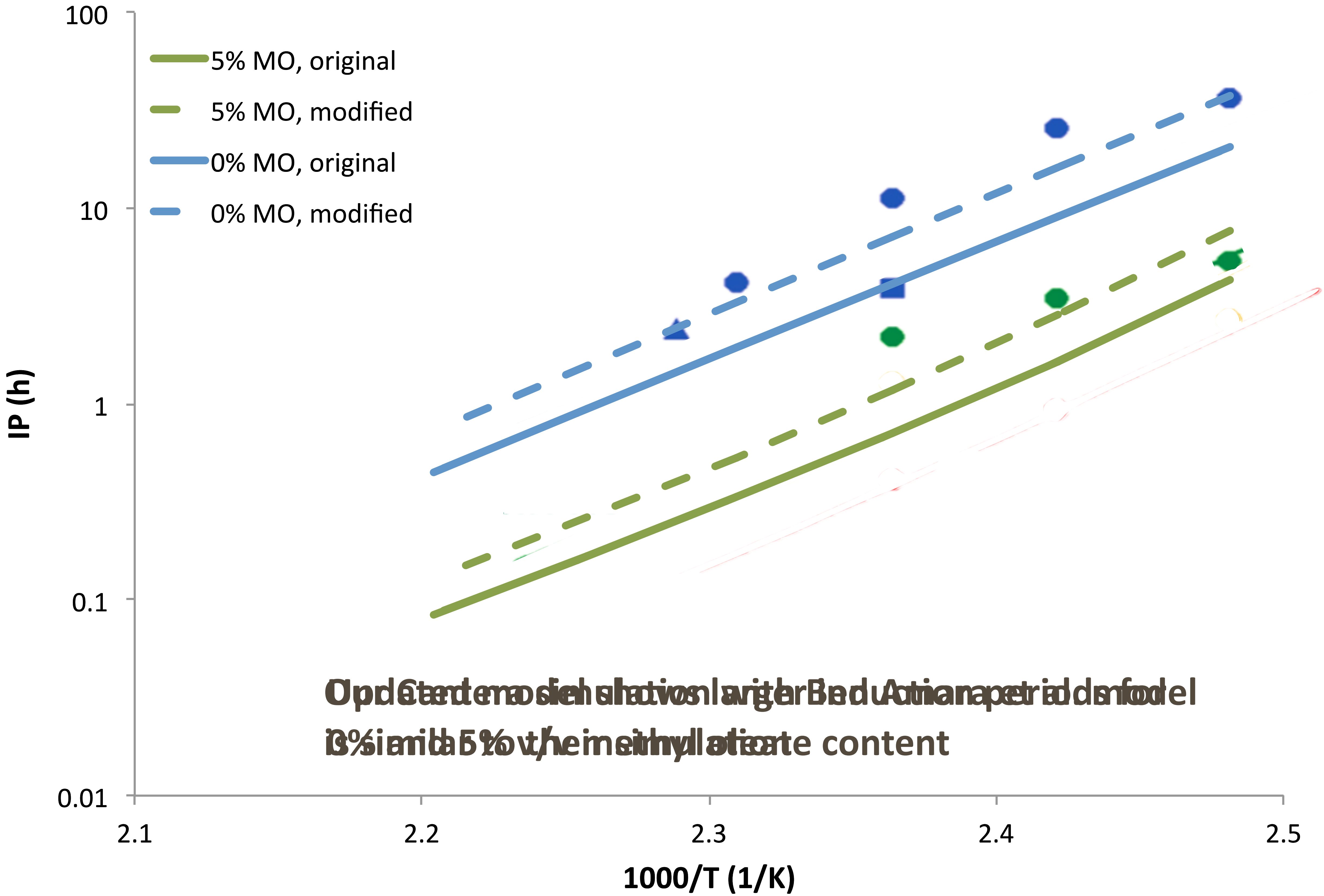


Figure 3a from Ben Amara et al.; Comparison of induction times from detailed kinetic model with experiments.

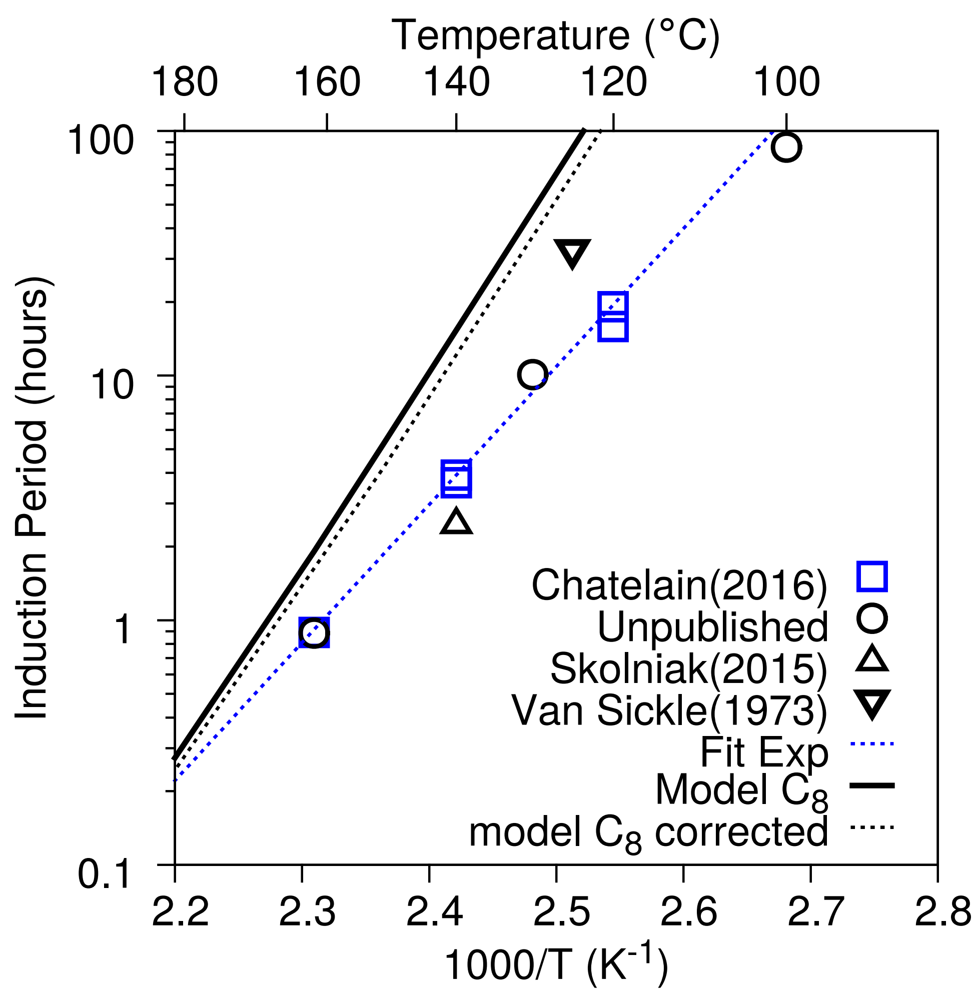
1. Ben Amara et al., *Energy & Fuels,* 27, 2013.
2. D.G. Goodwin et al. http://www.cantera.org, 2015. Version 2.2.0.

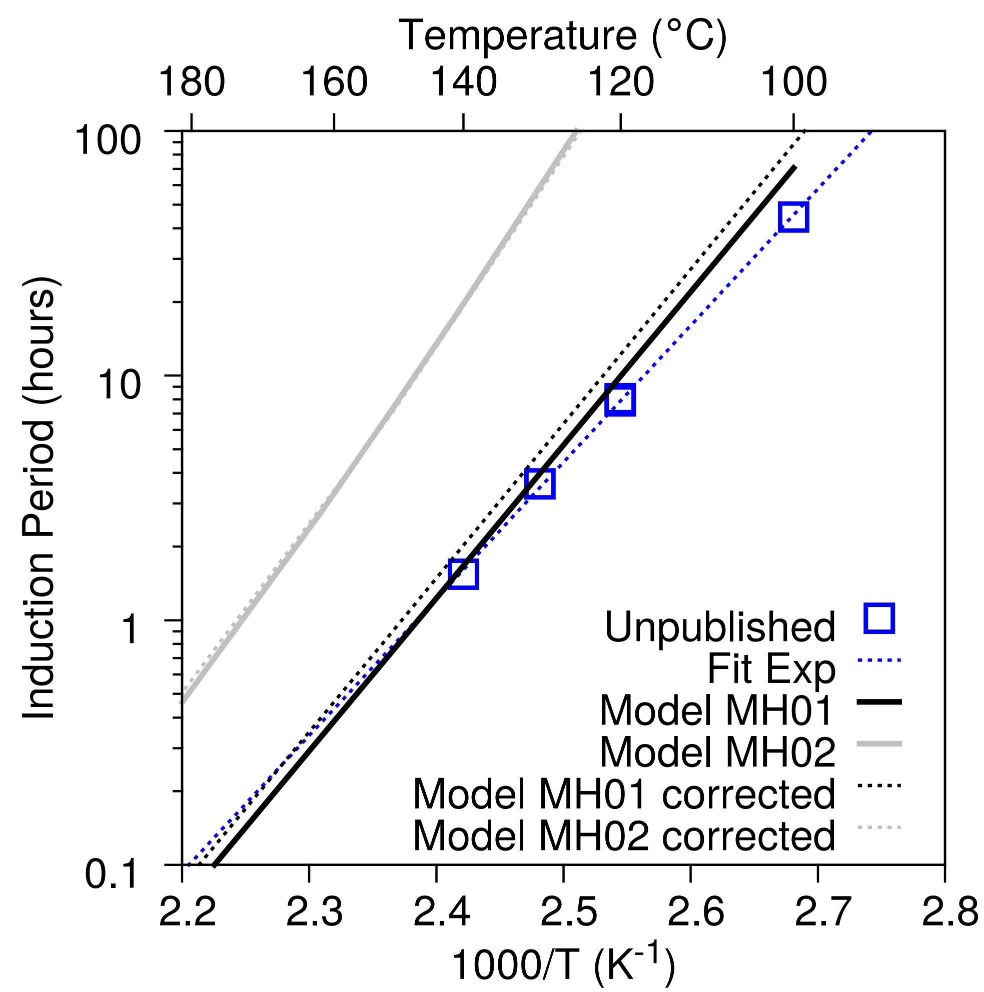
Model simulation with Cantera



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)