

# Phenolic polymer pyrolysis via reactive molecular dynamics simulation

## PRESENTED BY

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## Rationale

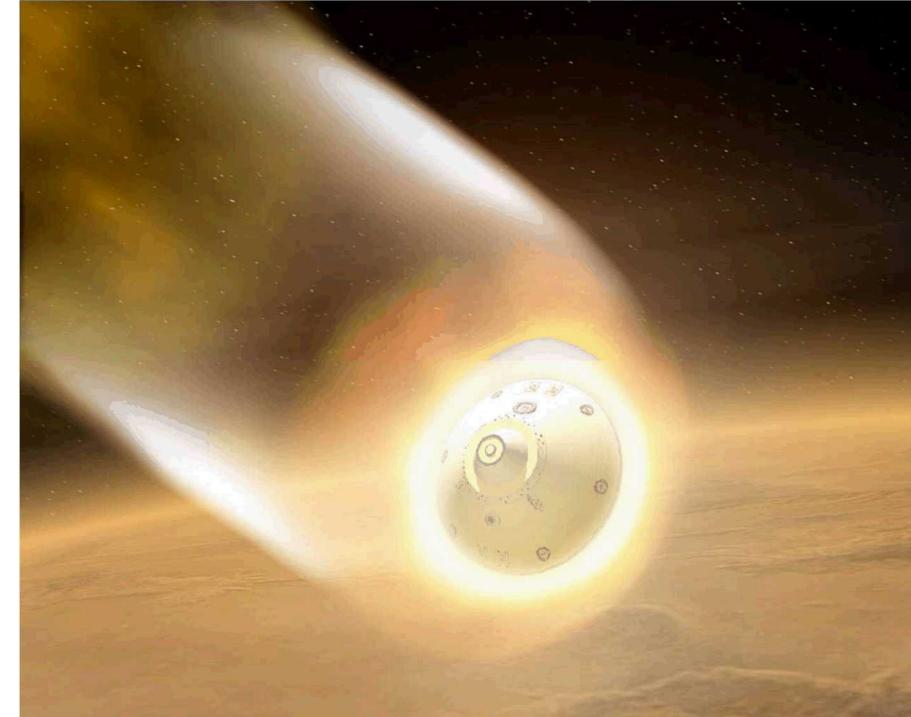
Phenolic polymer is an ablative material commonly used in thermal protection systems (TPS).

Many TPS models are empirically based, limiting their scope of accuracy.

Chemical degradation of phenolic is a key precursor to TPS ablation.

Atomistic simulations have the potential to improve ablation models.

We seek to develop a thermokinetic model for phenolic pyrolysis informed by molecular dynamics simulations.



<https://mars.nasa.gov/resources/2071/mars-exploration-rovers-entering-the-mars-atmosphere/?site=insight>

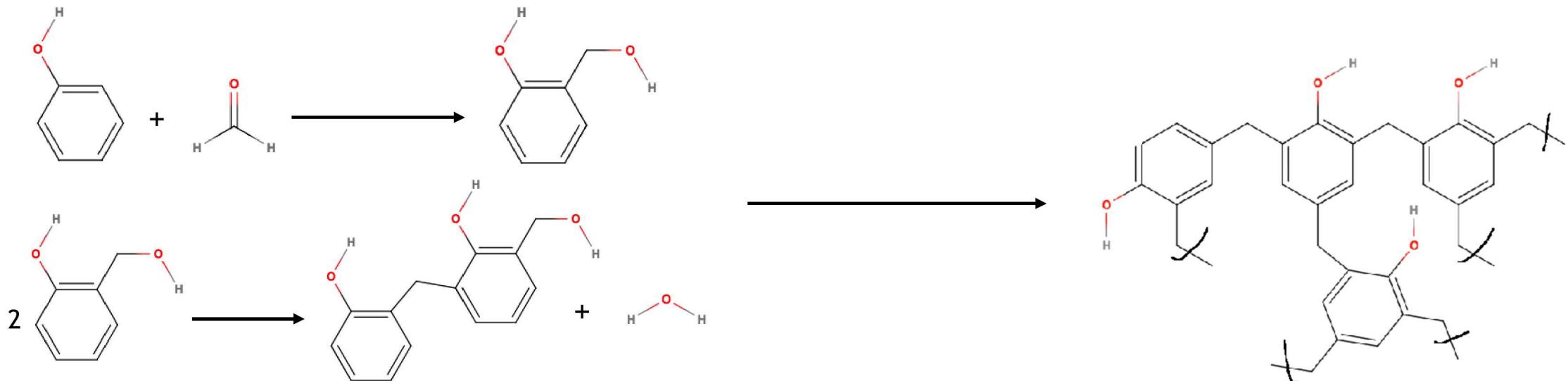
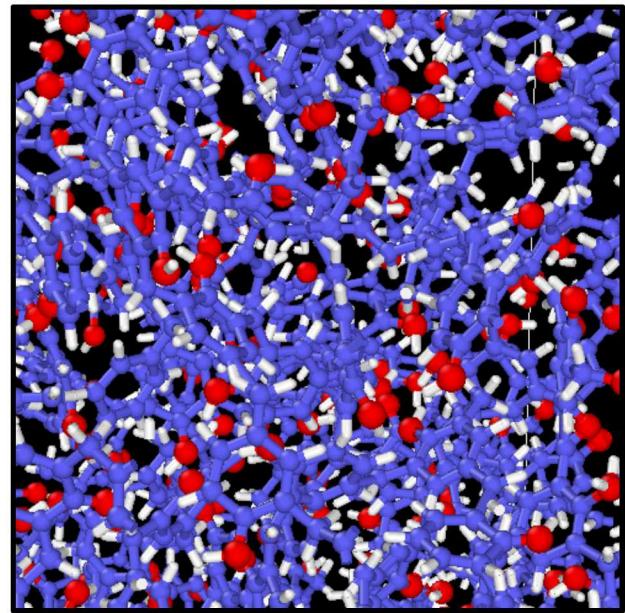
# Introduction

## Phenolic polymers

- Key components in carbon composites in heat shields in extreme environments.
- Can vary greatly, depending on curing conditions, in crosslink extent, initial density, stoichiometry, molecular structure.

Reactive molecular dynamics (MD) can provide insight into

- Processes that occur during pyrolysis.
- The relationship between molecular structure, density, and pyrolytic breakdown.



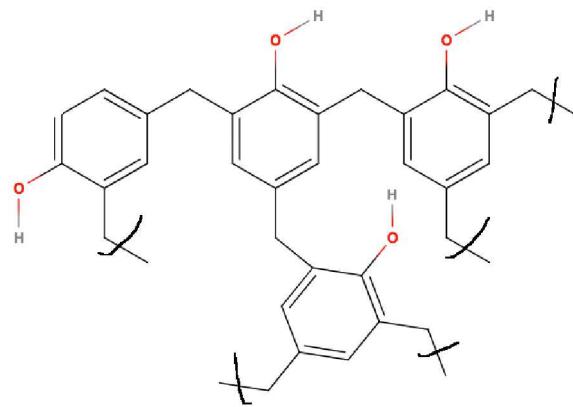
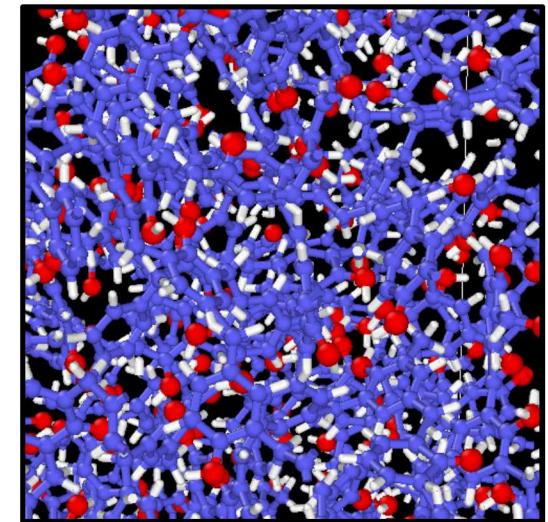
## 4 Reax parametrizations

ReaxFF – Bond order MD potential that handles chemistry.

Various parametrizations for different combinations of atoms under different conditions.

We studied phenolic pyrolysis with 3 different ReaxFF parametrizations using the LAMMPS MD package:

- 1.) CHO – commonly used for hydrocarbon reactivity.
- 2.) Mattsson – Past success simulating polymers under chemistry-inducing shock (up to 60 GPa). Well tested for systems containing H and C.
- 3.) Hybrid parametrization – Mattsson parametrization utilizing the O-H---O hydrogen bonding parameters from CHO introduced to capitalize on the strengths of the other two.



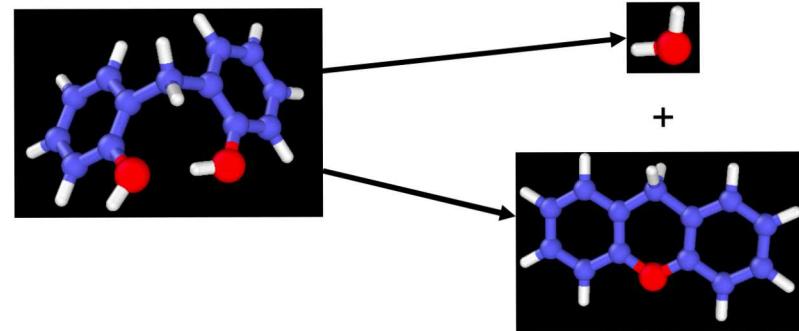
S. Plimpton *J. Comp. Phys.* **117**, 1-19 (1995).  
A. C. T. van Duin et al. *J. Phys. Chem.* **105**, 9396-9409 (2001).  
K. Chenoweth et al. *J. Phys. Chem. A* **112**, 1040-1053 (2008).  
A. Harpale et al. *Carbon* **130**, 315-324 (2018).  
T. R. Mattsson et al. *Phys. Rev. B* **81**, 054103 (2010).  
J. Matthew D. Lane and N. W. Moore *J. Phys. Chem. A* **122**, 3962-3970 (2018).

# Chemical pathways to water formation



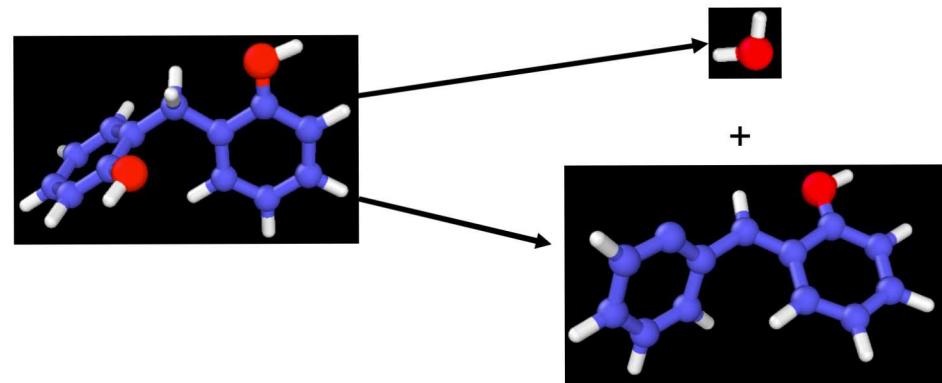
2 primary mechanisms with 2 submechanisms

OH – OH transfer

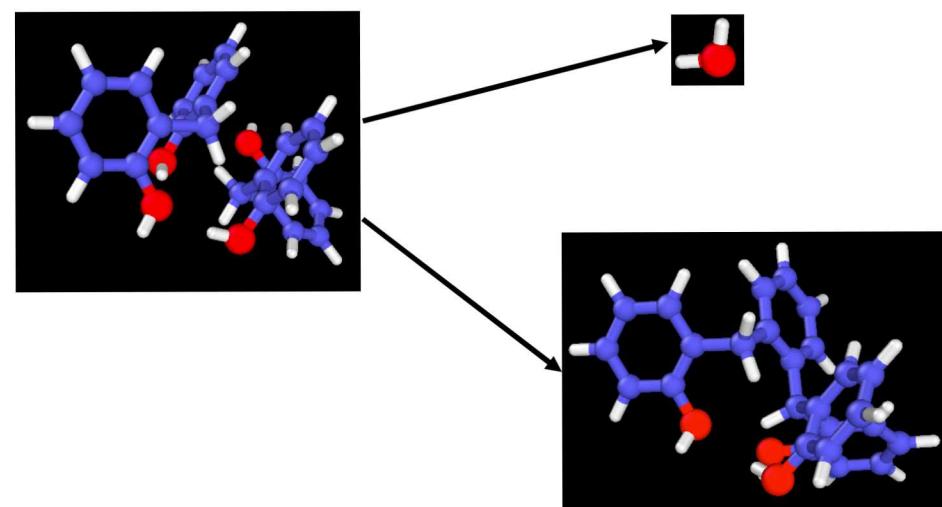
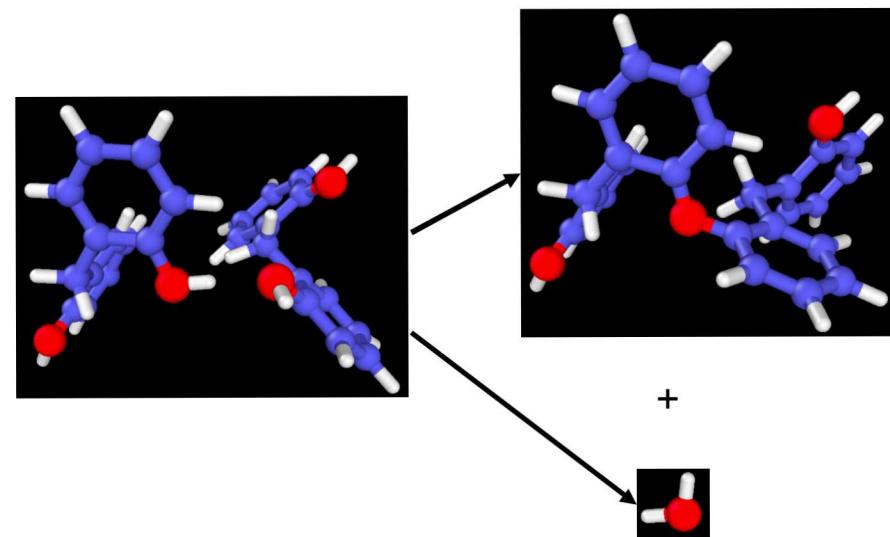


**Intramolecular**

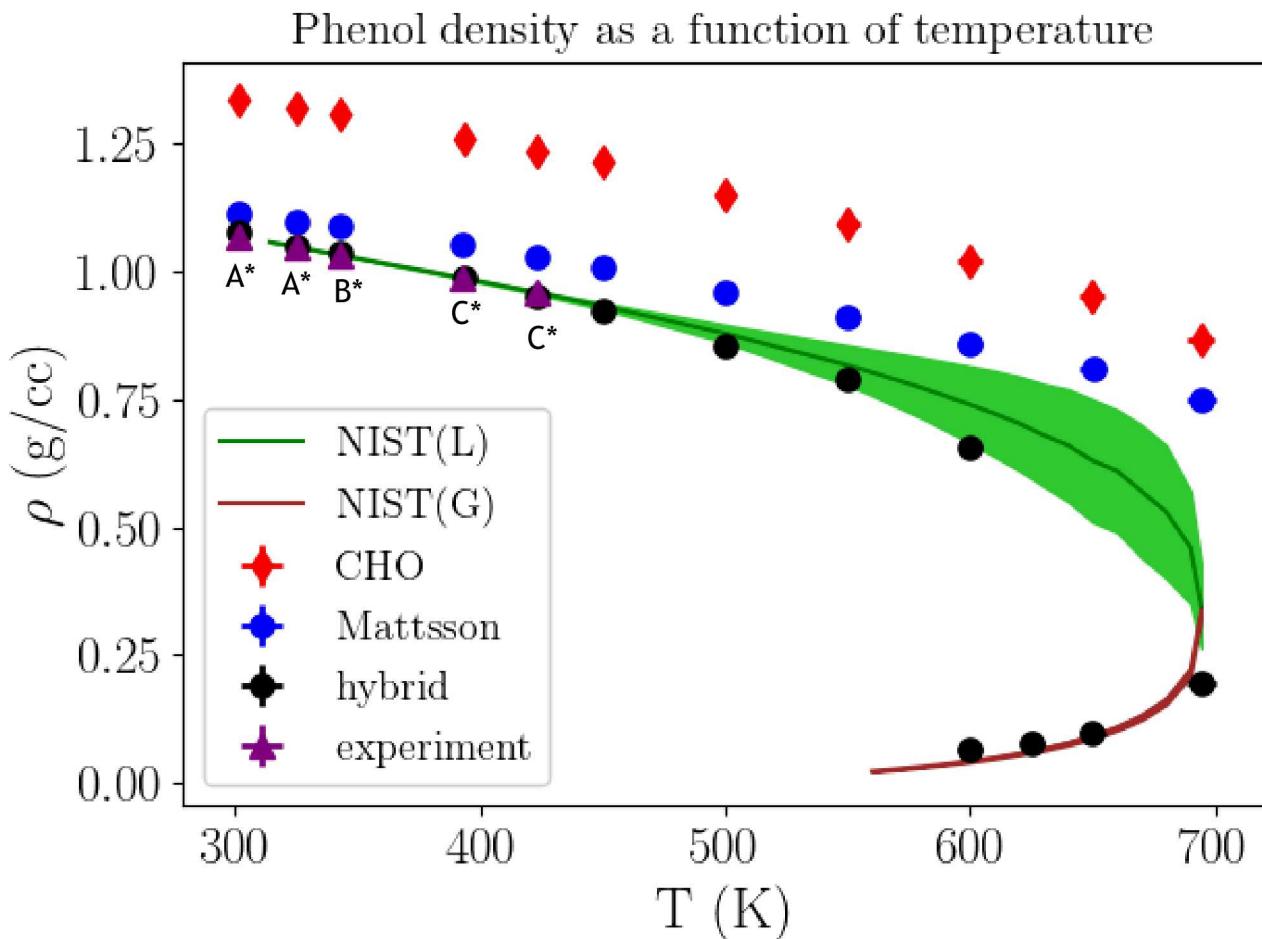
**-CH2- hydrogen extraction**



**Intermolecular**



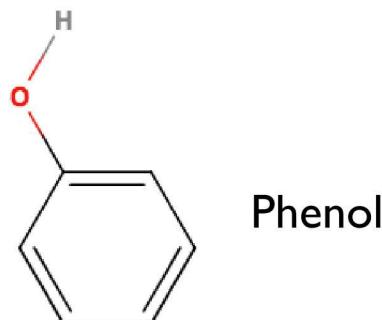
# Phenol density at various temperatures



Hybrid agrees with experiment and the NIST model to a greater degree than the parametrizations from which it was derived.

Phenol equilibration - various points in P,T space along L/G coexistence curve.

Phenol data extracted from NIST web thermo data tables – derived from ThermoData Engine.



A\* R. B. Badachhape et al. *J. Chem. And Eng. Data* **10**, 143 (1965).

B\* D. L. Cunha et al. *J. Chem. Eng. Data* **58**, 2925-2931 (2013).

C\* C.A. Buehler et al. *J. Am. Chem. Soc.* **54**(6), 2398-2405 (1932).

E.W. Lemmon et al. 2018 <https://dx.doi.org/10.18434/T4JS3C>

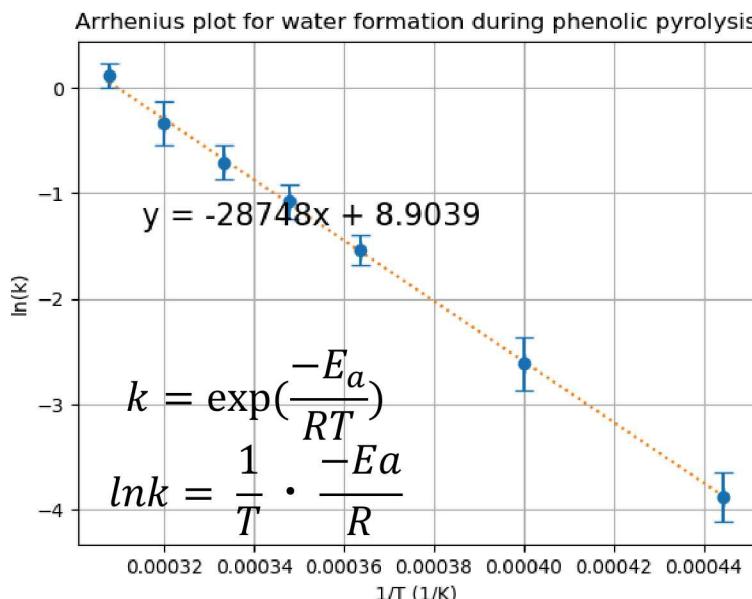
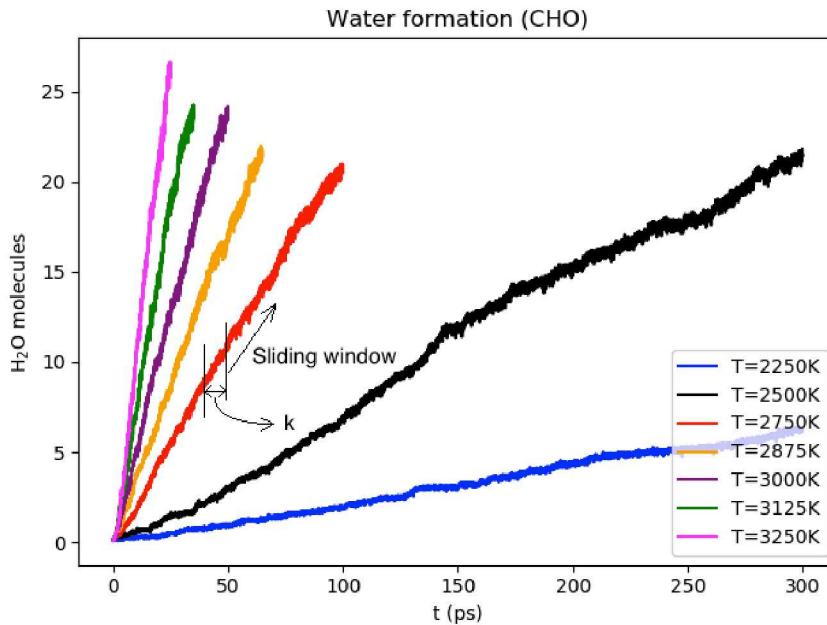
*J. Chem. Inf. Model.* **45**, 816-838 (2005).

*J. Chem. Inf. Model.* **47**, 1713-1754 (2007).

*J. Chem. Inf. Model.* **49**, 503-517 (2009).

*J. Chem. Inf. Model.* **49**, 2883-2896 (2009).

# Phenolic pyrolysis activation energies



## Methodology

- 1.) 16 linear chains – 15 instances.
- 2.) Product formation rates determined at various temperatures.

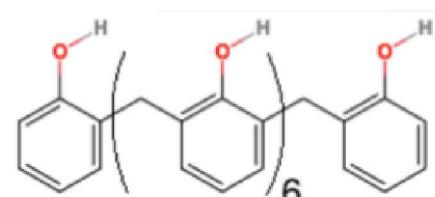
## Water

- Abundant phenolic pyrolysis byproduct
- Formation kinetics studied with MD in the past.

## ”Global”

- Mass of all volatilizable species as a function of time
- Closer proxy to experimentally determined activation energies based on thermogravimetric analysis (TGA).
- Mass cutoff(s) based on heaviest gaseous products observed experimentally.

- 3.) Activation energies (E<sub>a</sub>) extracted using the Arrhenius equation



D. Jiang et al. *J. Phys. Chem. A* **113**, 6891-6894 (2009).  
 T. G. Desai et al. *Polymer* **52**, 577-585 (2011).  
 K.A. Trick et al. *Carbon* **33**(11), 1509-1515 (1995).  
 K.A. Lincoln *AIAA Journal* **21**(8), 1204 (1983).

# Phenolic pyrolysis activation energies

NVT ensemble

1776 atoms – 16 linear phenolic chains

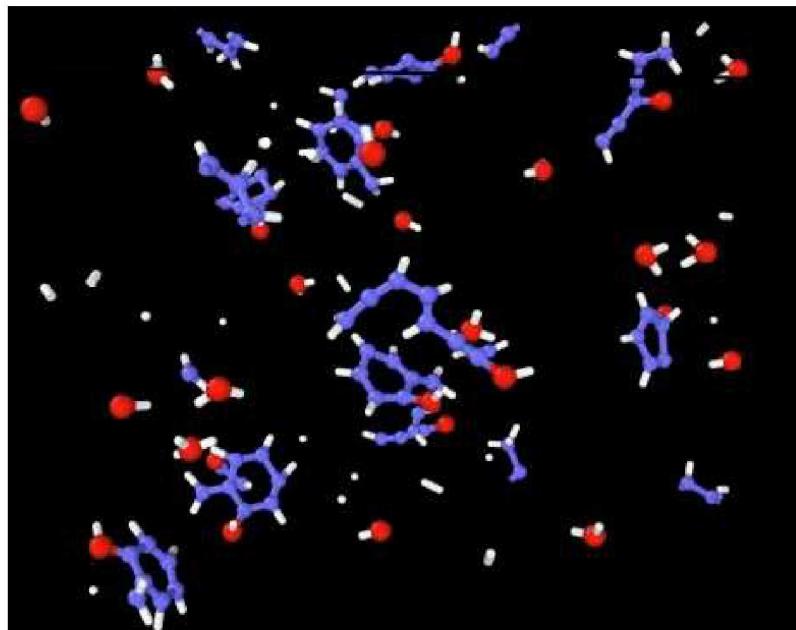
Periodic boundary conditions

15 instances

7-10 temperatures ranging from 2000 – 3250 K.

10s to 100s of ps per simulation

0.25 fs timestep



CHO 3250 K volatiles  
snapshot

$\rho = 1.25 \text{ g/cc}$	$E_a (\text{H}_2\text{O})$ (kj/mol)	$E_a$ (Global) (kj/mol)	Source of variation
Exp, Jiang	-----	223-305	Temperature region and heating rates
Exp, Trick	-----	74-198	Temperature region and heating rates
Exp, Friedman	-----	192 - 293	Heating rate, method of determination
MD, Jiang	332 +/- 64	-----	
MD, Desai	286 +/- 46	-----	
This work, CHO	246 +/- 23	301 +/- 32	
This work, hybrid	172 +/- 22	206 +/- 23	
This work, Mattsson	130 +/- 6	191 +/- 13	

All reax parametrizations agree with experiment - variation too great to constrain MD results, which vary.

H. Jiang et al. *Carbon* **48**, 352-358 (2010).

K.A.Trick et al. *Carbon* **35**(3), 393-401 (1997).

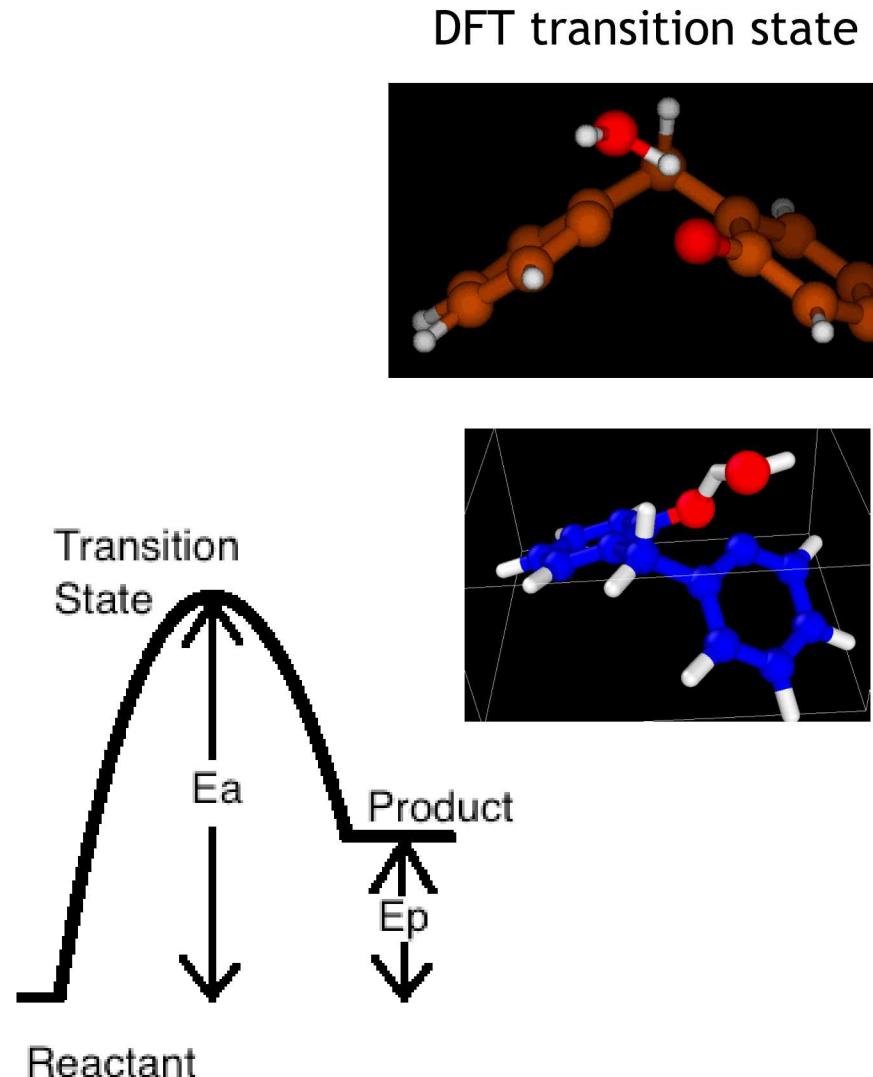
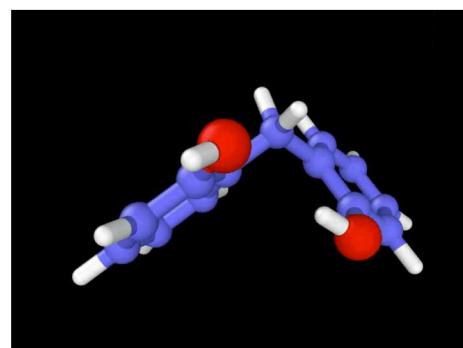
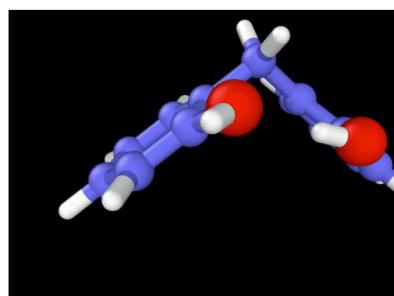
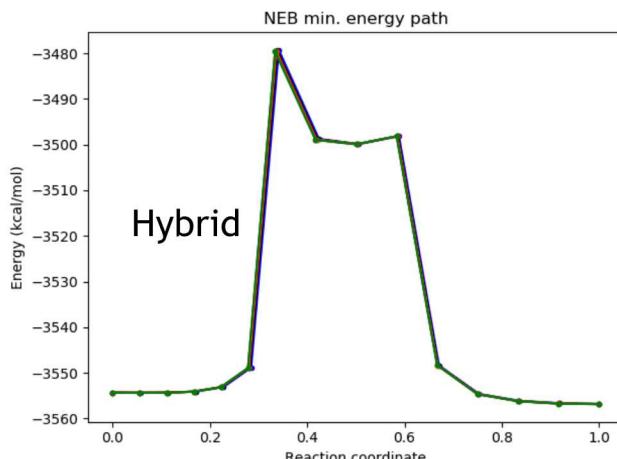
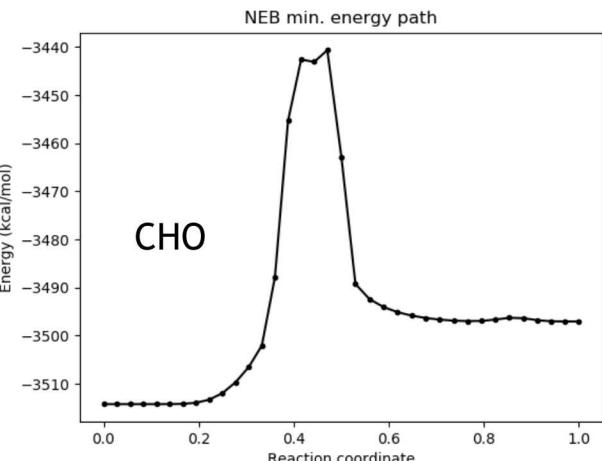
H. L. Friedman *J. Polym. Sci. C* **6**(1), 183-195 (1964).

G. P. Shulman et al. *J. Appl. Polym. Sci.* **10**, 619-635 (1966).

## 9 Water formation pathways and energy barriers

The “Nudged Elastic Band” procedure, available in LAMMPS, was used to evaluate the activation energies for water formation with the hybrid and CHO ReaxFF parametrizations.

This procedure interpolates a set of structures between reactants and products and converges to the minimum energy path between them.



# Intramolecular OH-OH water formation pathway – dimer

Water formation energies

Formulation	$E_a$ (kcal/mol)	$E_p$ (kcal/mol)
ReaxFF - hybrid	73.6	0.8
ReaxFF - CHO	73.6	-----
ReaxFF - CHO	85.8	25.1
DFT - B3LYP	67.9	5.8
CCSD(T)/6-31G**	70.9	6.1

Energy barrier with ReaxFF - CHO improves relative to DFT in comparison with previous work when using nudged elastic band, ReaxFF-optimized structures.

Previously calculated ReaxFF activation energies used DFT-optimized transition states.

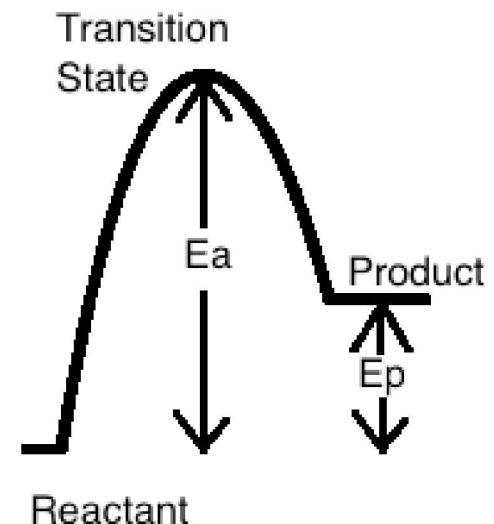
- ReaxFF energy barriers agree with quantum chemical calculations within 3-6 kcal/mol.
- ReaxFF-hybrid product energy agrees within 5 kcal/mol with DFT.

Identical energy barriers with different force fields?

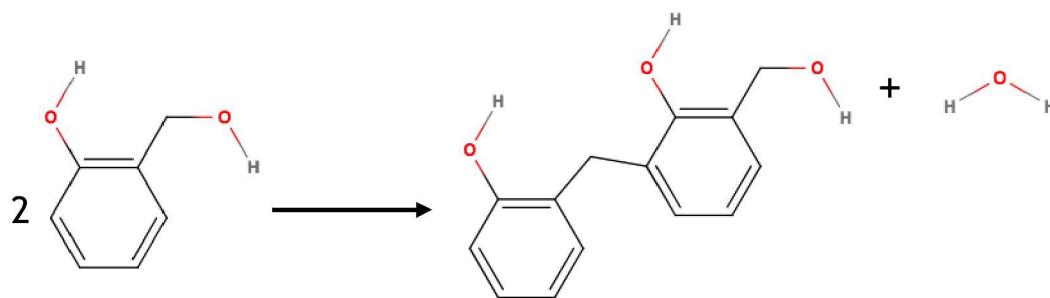
Yes, different paths, however.

Does not contradict initial pyrolysis results, as many water formation mechanisms are accessed, and a different model for phenolic polymer is utilized.

How to proceed?



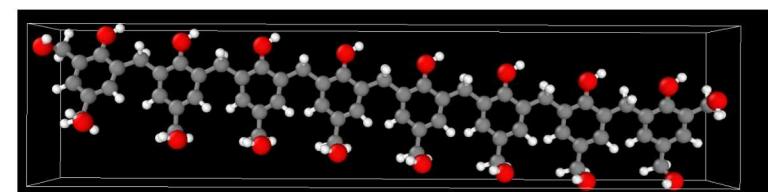
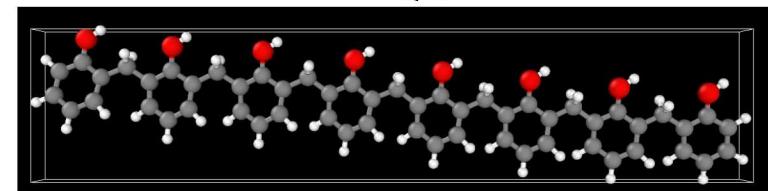
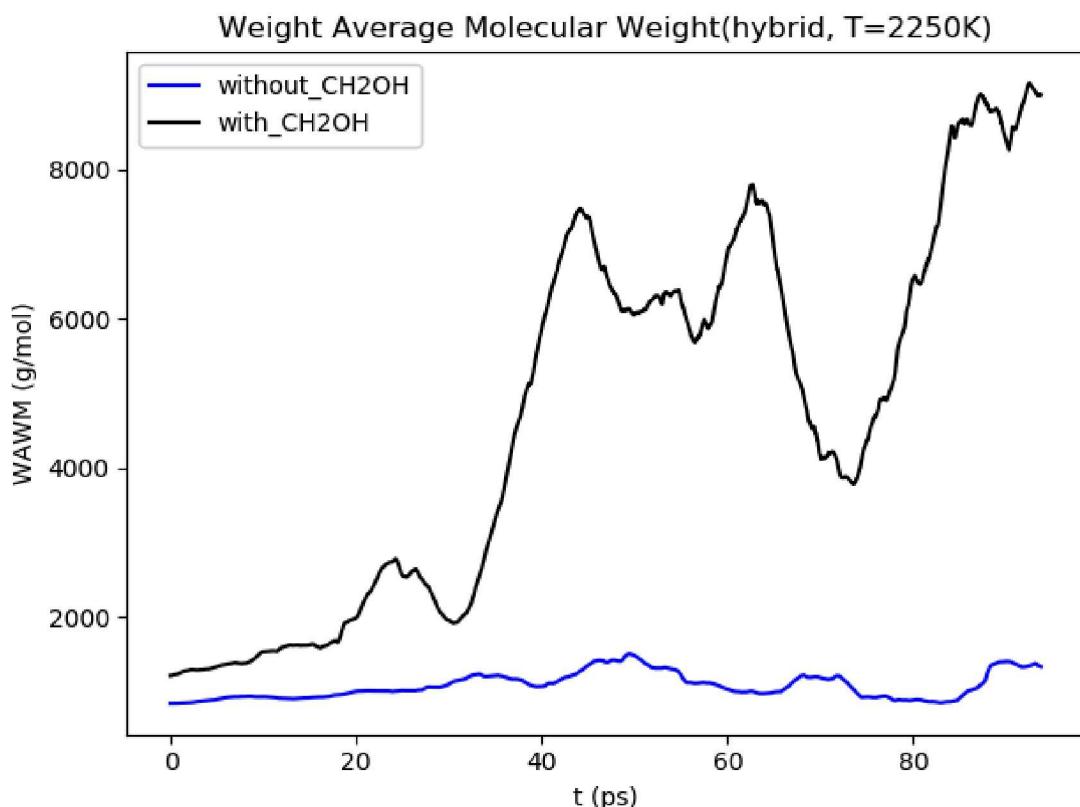
# Methylol (-CH<sub>2</sub>OH) groups enhance crosslinking and lower E<sub>a</sub>



ReaxFF-CHO activation energies  
with and without methylol groups

-CH <sub>2</sub> OH	Water formation	Global
Without	246 +/- 23	301 +/- 32
With	222 +/- 11	259 +/- 31

Methylol groups cause residual crosslinking upon heating, and lowered activation energies, as observed in experiments.



# Conclusions and future work

- 1.) New hybrid ReaxFF parametrization most accurately represents intermolecular interactions relevant for phenolic polymers across a range of temperatures.
- 2.) ReaxFF accurately models pyrolysis, based on a comparison with experimental pyrolysis results and a single DFT water formation mechanism.
- 3.) ReaxFF shows that methylol groups promote crosslinking and lowered pyrolysis activation energies, consistent with experimental results.

## Future work

Thermokinetic property determination at variable heating rates.

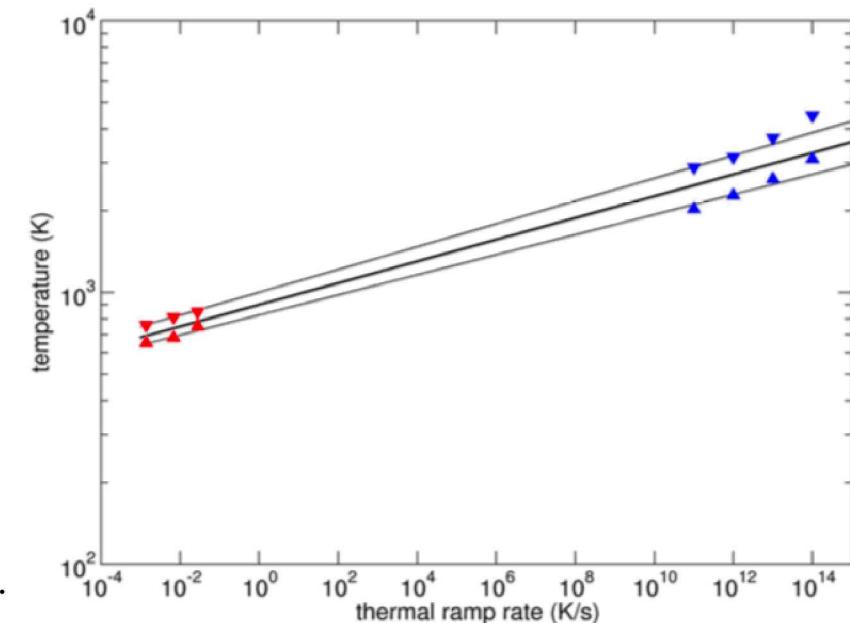
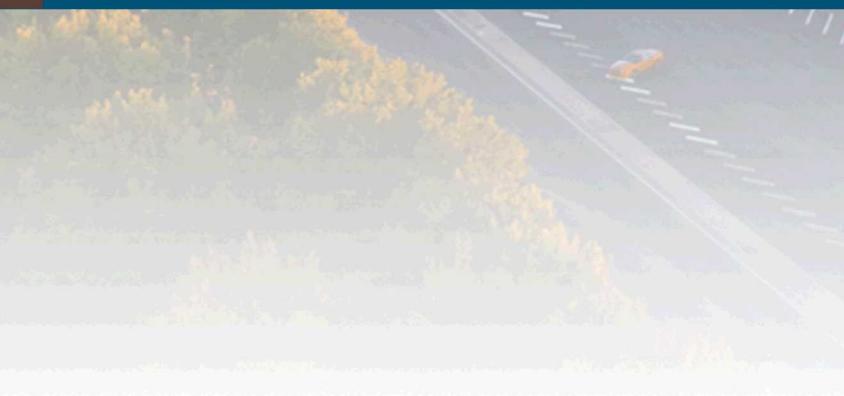


Image taken with permission:  
J. M. D. Lane and N. W. Moore *J. Phys. Chem. A* **122**, 3962 (2018).



# Acknowledgements



Sandia National Laboratories  
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NIST

Dr. Kenneth Kronlein

# Bonus slide – DFT transition states

$\frac{\partial^2 E}{\partial x_1^2}$	$\frac{\partial^2 E}{\partial y_1 \partial x_1}$	...	$\frac{\partial^2 E}{\partial z_n \partial x_1}$
$\frac{\partial^2 E}{\partial x_1 \partial y_1}$	$\frac{\partial^2 E}{\partial y_1^2}$	...	$\frac{\partial^2 E}{\partial z_n \partial y_1}$
...	...	...	...
$\frac{\partial^2 E}{\partial x_1 \partial z_n}$	$\frac{\partial^2 E}{\partial y_1 \partial z_n}$	...	$\frac{\partial^2 E}{\partial z_n^2}$

3n x 3n Hessian (n = # of atoms) -

Diagonalization -> 3n pairs of eigenvalues and eigenvectors.

Eigenvectors - Vector of atomic displacements from converged geometry.

Correspond to vibrational normal modes.

Eigenvalues - Proportional to square of vibrational frequency of corresponding mode.

-All positive: System has converged to local minimum.

-One negative: System has converged to first order saddle point.

May correspond to reasonable representation of transition state.

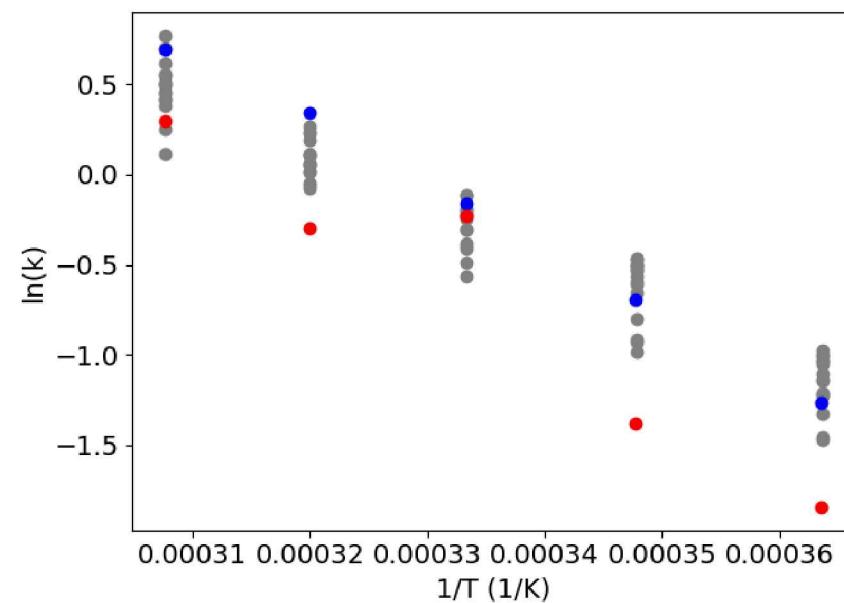
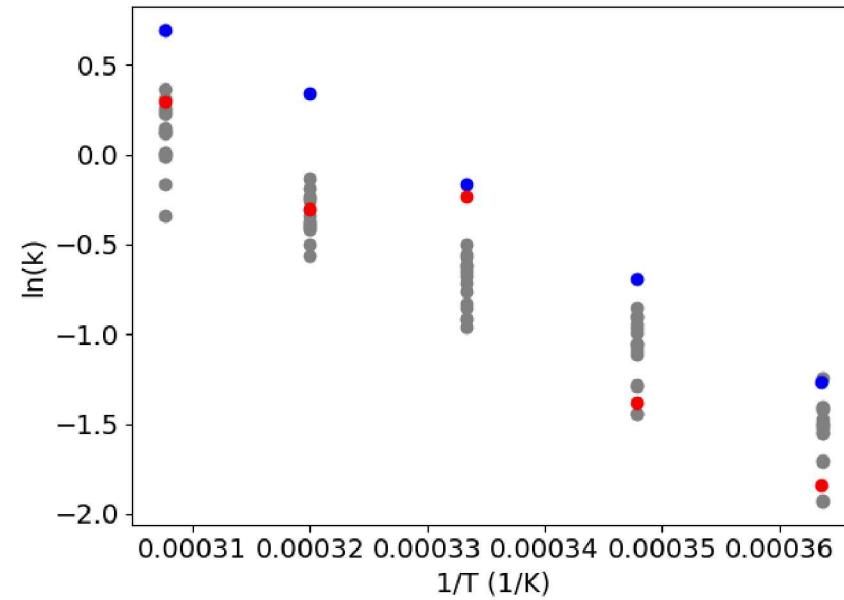
Can be verified by visualization. Skill lies in pulling specific atoms out of equilibrium positions, such that optimizer converges to desired transition state.

Optimizations are time consuming. Trial and error is necessary.

E = system energy

# Bonus slide

Water Formation Arrhenius Plot



- Red circle: D. Jiang et al. *J. Phys. Chem. A* **113**, 6891-6894 (2009).
- Blue circle: T. G. Desai et al. *Polymer* **52**, 577-585 (2011).