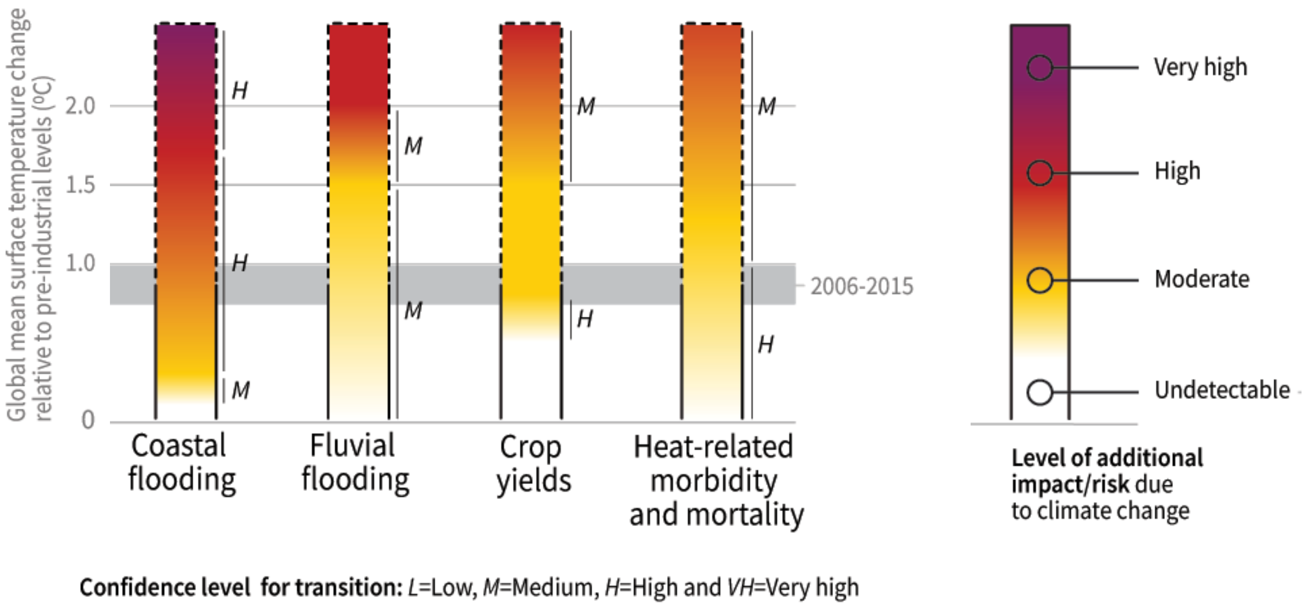
Illuminating reaction pathways in low-temperature combustion, pyrolysis & atmospheric oxidation

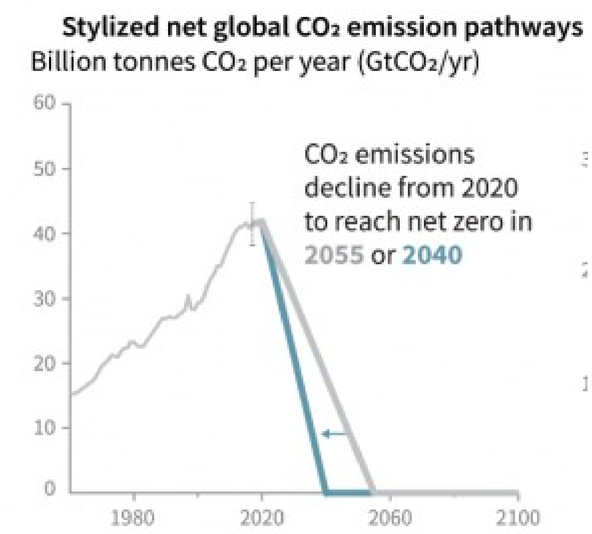
Mark Jacob Goldman

Nov 25, 2019

Thesis Defense

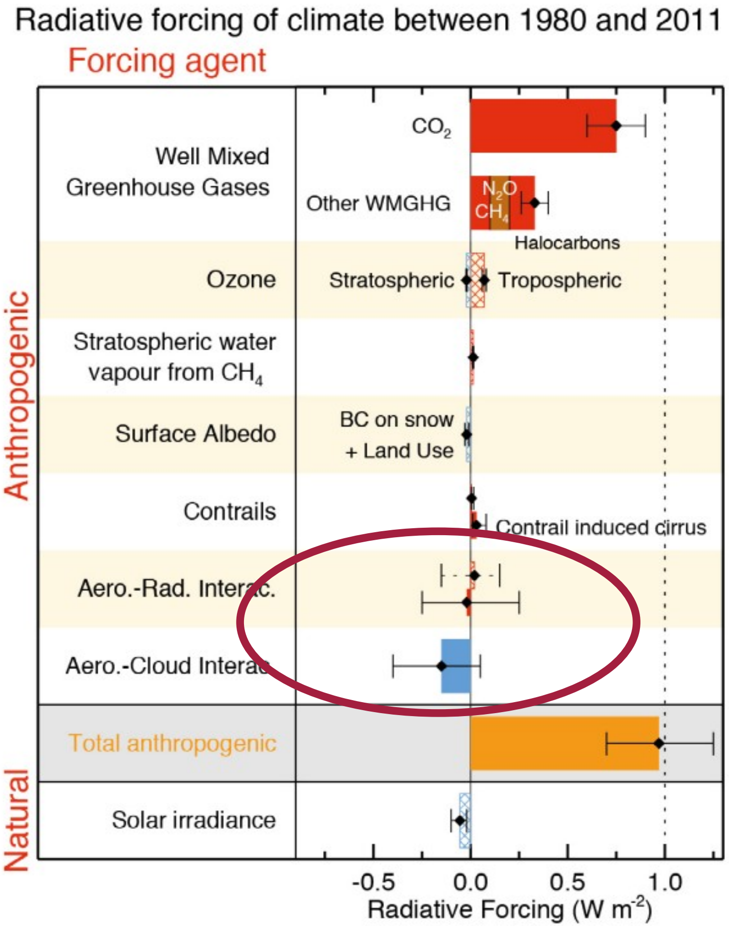
Lower CO_2 emissions can save lives





Intergovernmental Panel on Climate Change. Global Warming of 1.5C; Special Report 15; 2018.

Aerosols effect on climate uncertain



Intergovernmental Panel on Climate Change. Climate Change 2013; AR5; 2013.


3 floods in 2014-2019 worse
than anytime 1993-2010

Thesis focuses on two goals

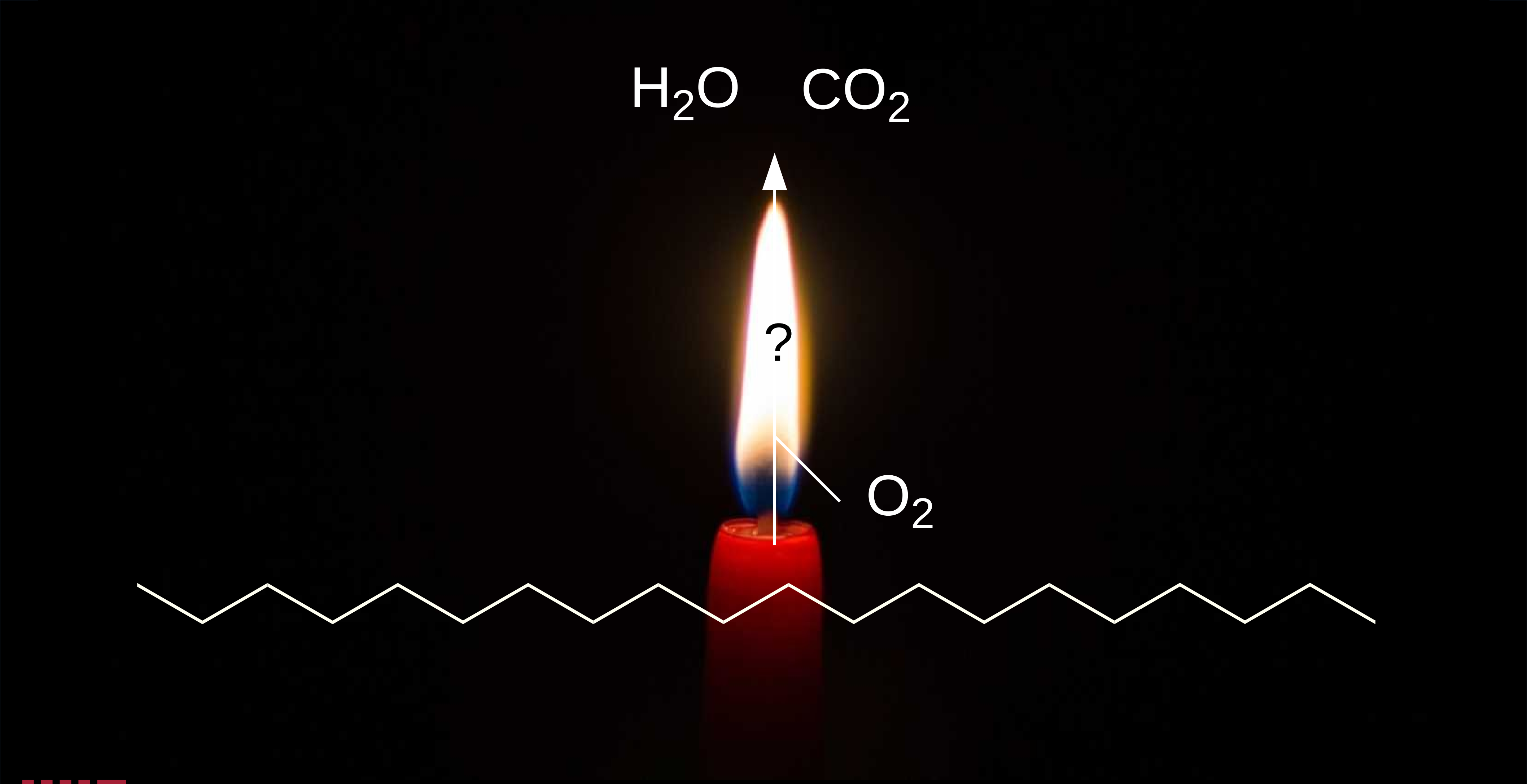
1. develop zero-carbon transportation technology

→ biofuels → isobutanol → combustion chemistry

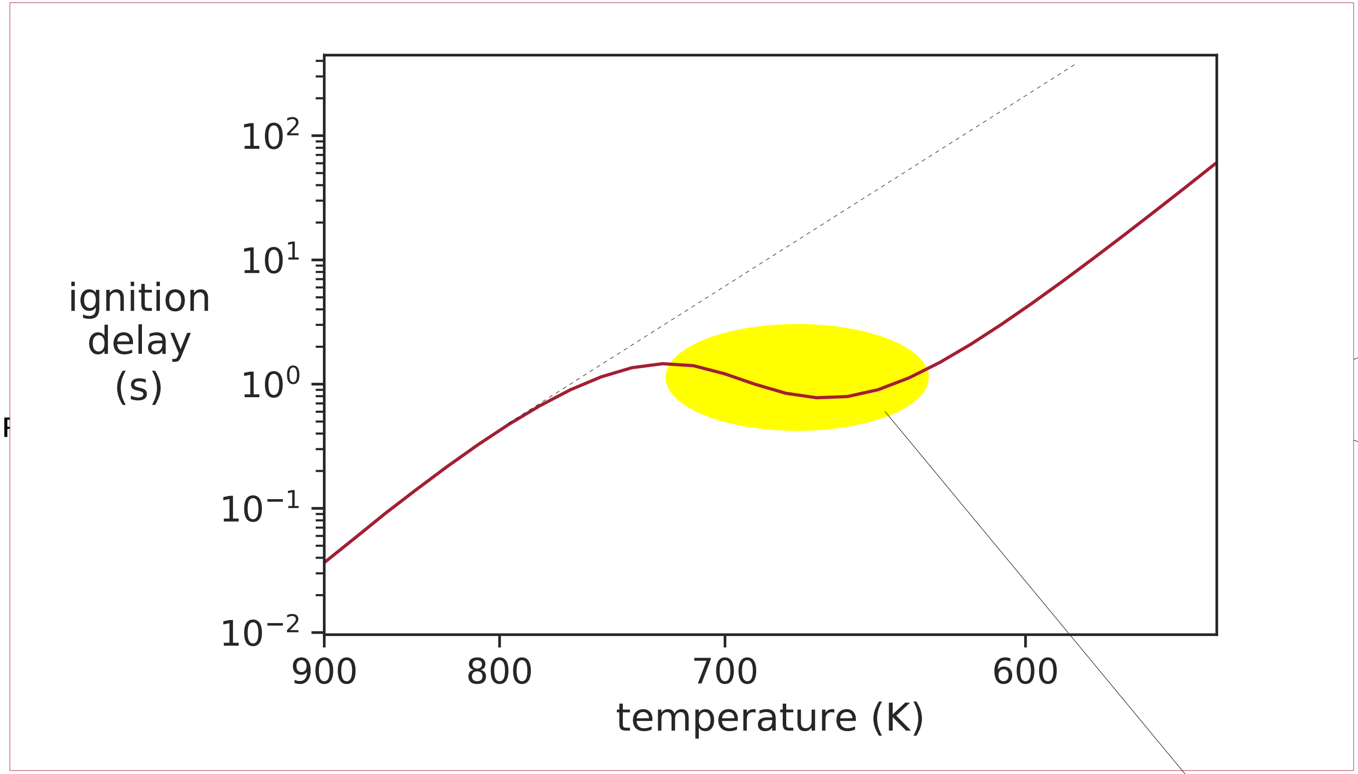
2. improve predictability of climate models

→ atmosphere → chemistry → particulate matter

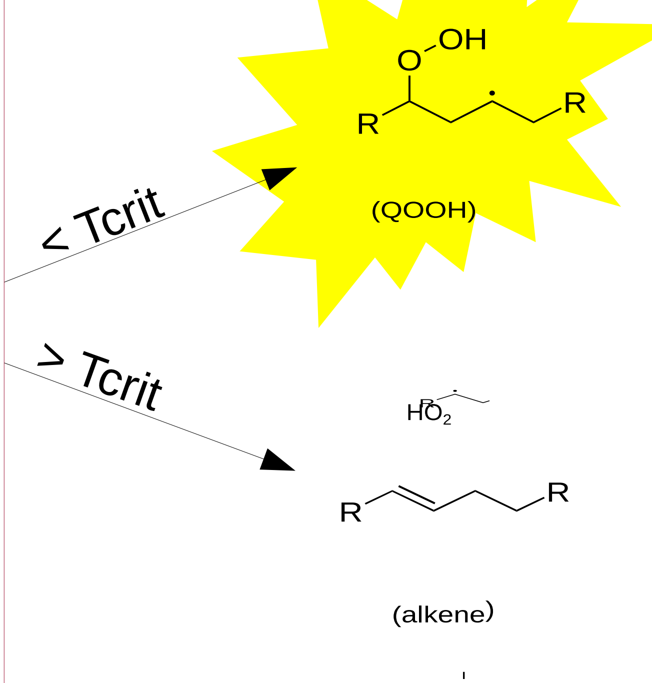
unified by chemistry of peroxy radical (RO_2)


H_2O CO_2
?
O_2

Peroxy combustion chemistry

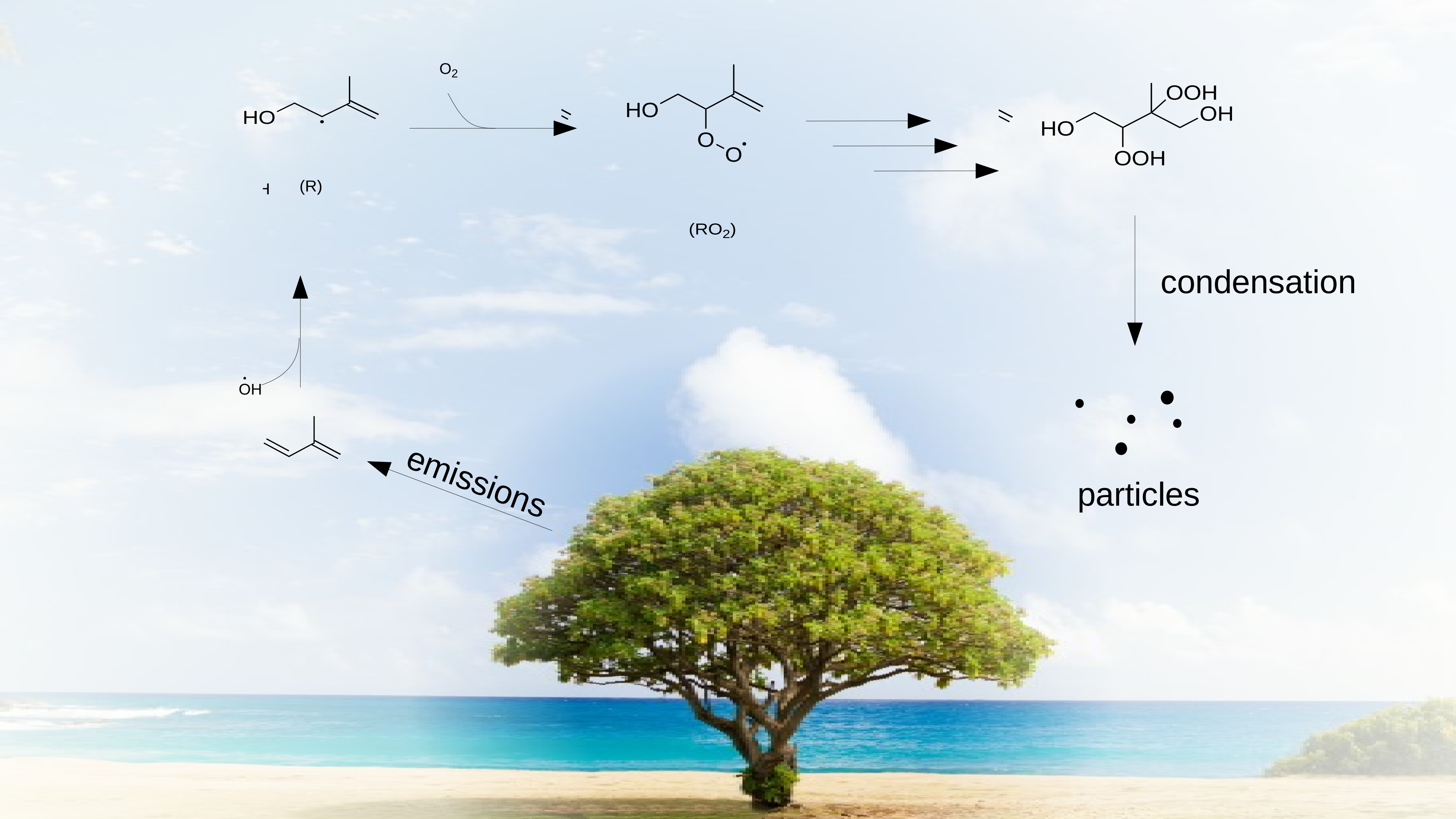


produces 3 OH radicals

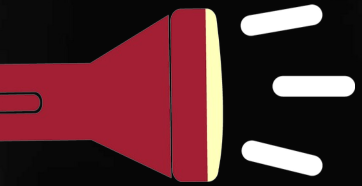


produces 1 HO_2 radical

Negative temperature coefficient (NTC) region

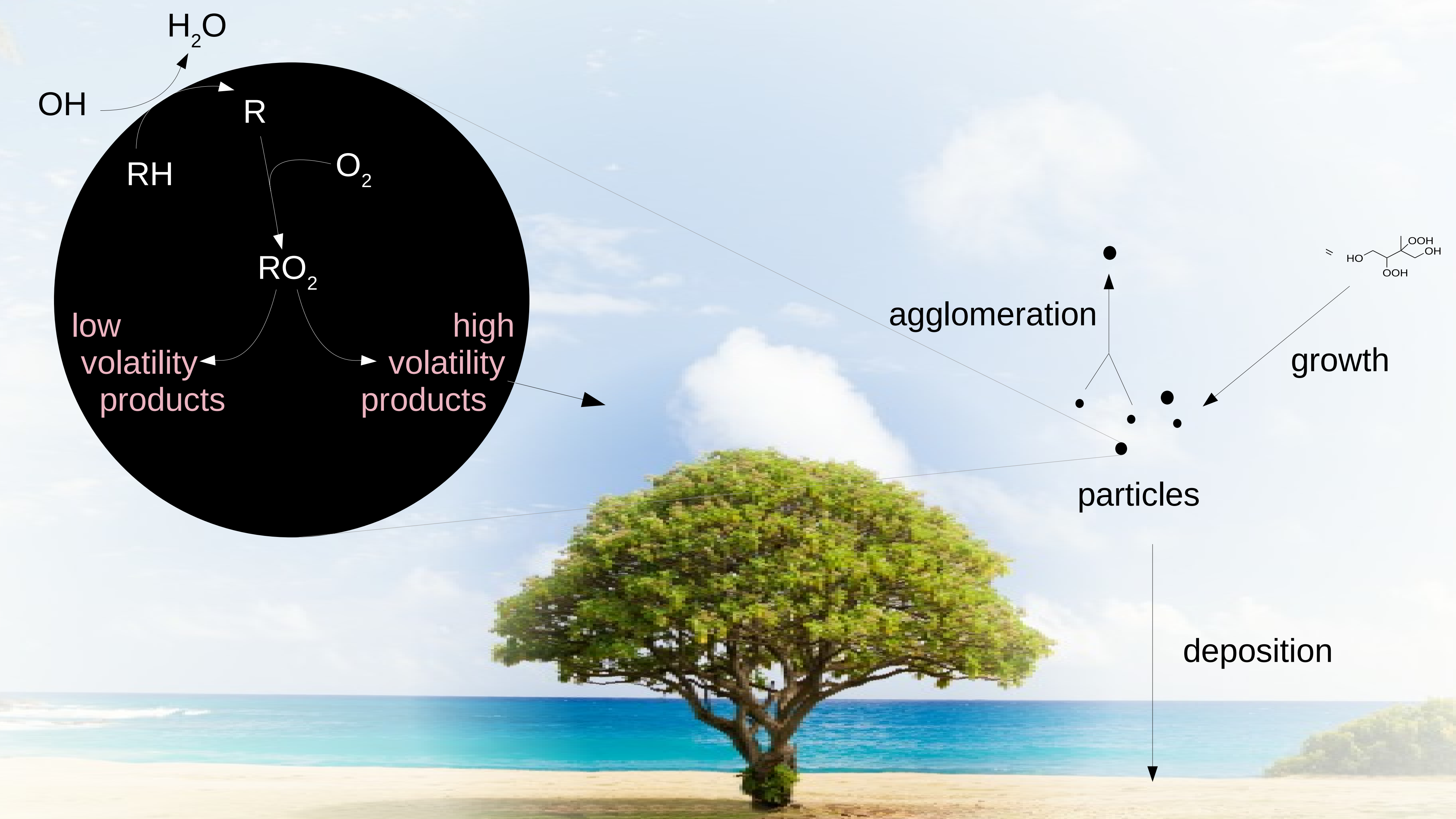


HO
(R)
O2
HO
O
O
(RO2)
HO
OOH
OH
OOH
condensation
particles
OH
emissions



Aerosol’s impacts

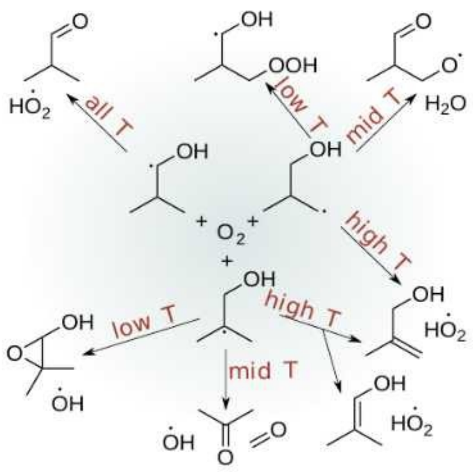
1. modifies earth’s heat balance
2. harms human health



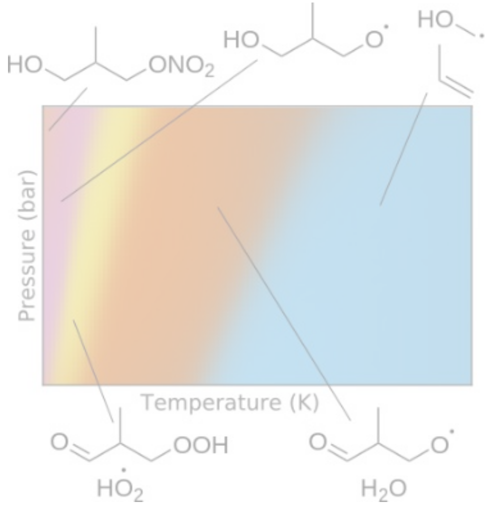
H_2O
OH
R
RH
O_2
RO_2
low volatility products
high volatility products
agglomeration
growth
particles
deposition

Three peroxy projects

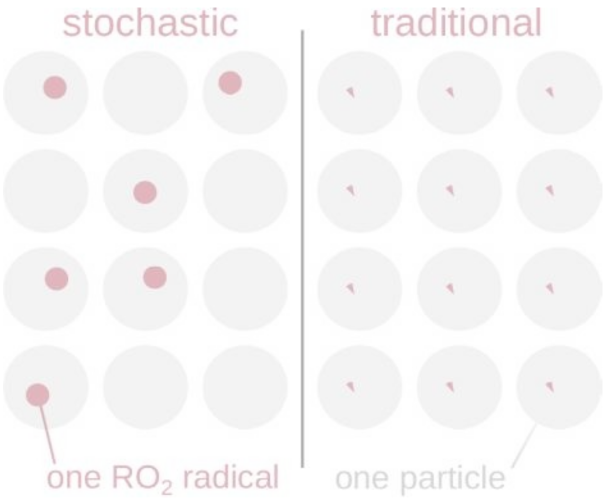
calculate biofuel rate coefficients



predict peroxy fate



model particle oxidation rate



Isobutanol: better than ethanol

less volatile

less hydroscopic

higher energy density

13

higher octane

EPA approved isobutanol in gasoline

E. Scott Pruitt
Administrator

June 12, 2018

Mr. James J. Baustian
Fuel Product Manager
Butamax Advanced Biofuels, LLC
Experimental Station / 356
P.O. Box 8352
Wilmington, Delaware 19803

Dear Mr. Baustian:

Pursuant to your June 7, 2011, notification, the following fuel additive has been registered per 40 CFR 79.23 (our internal identification number precedes the name):

[redacted] Isobutanol

Note that per 40 CFR 79.21(f) you would be required to notify us in writing if certain information in your notification were to change. In addition, note that, with your notification, you have provided assurances that you will not represent, directly or indirectly, in any notice, circular, letter or other written communication, or any written, oral or pictorial notice or other announcement in any publication or by radio or television, that registration constitutes endorsement, certification or approval by any agency of the United States.

If you have any questions, please contact Byron J. Bunker, Director of the Compliance Division within the Office of Air and Radiation at (202) 343-9648.

Respectfully yours,

E. Scott Pruitt

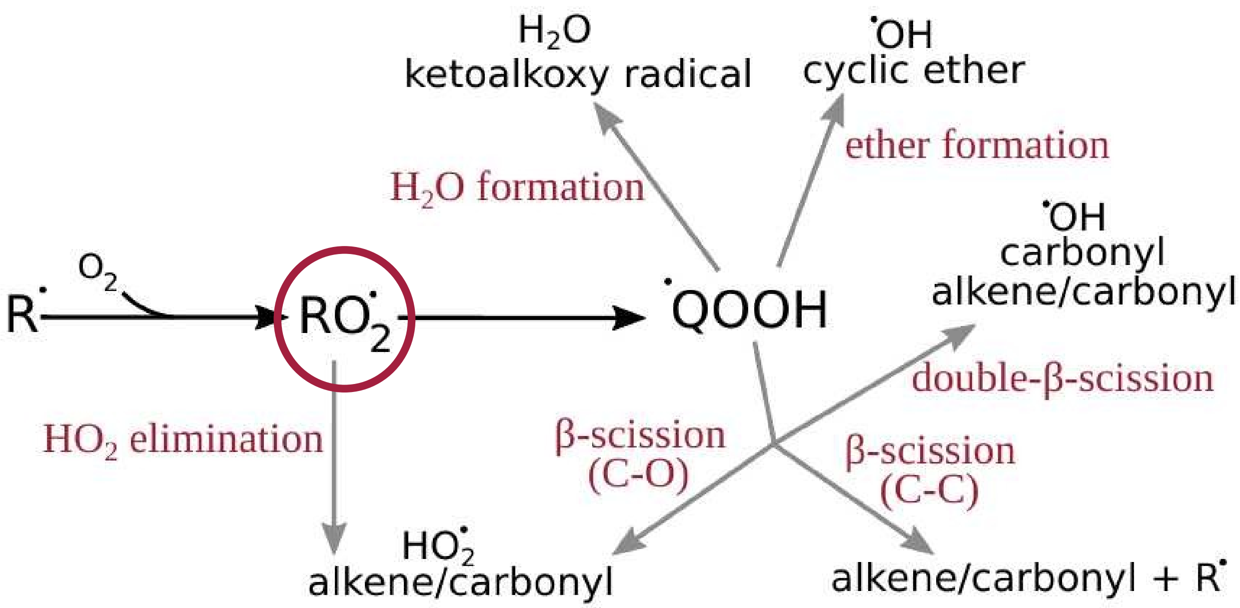
- Butamax approved to blend isobutanol into gasoline.
- Can blend up to 16 wt%

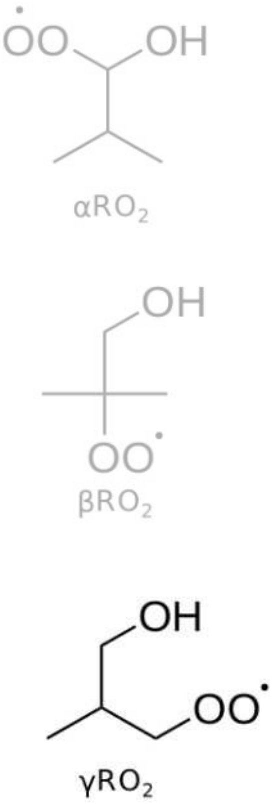
Inaccuracies in isobutanol chemistry

- wider variation among models than other butanol isomers[1,2]
- unable to predict pressure effect at fuel-lean conditions[3]
- more inaccurate at low-temperature (500-800 K) conditions[4]

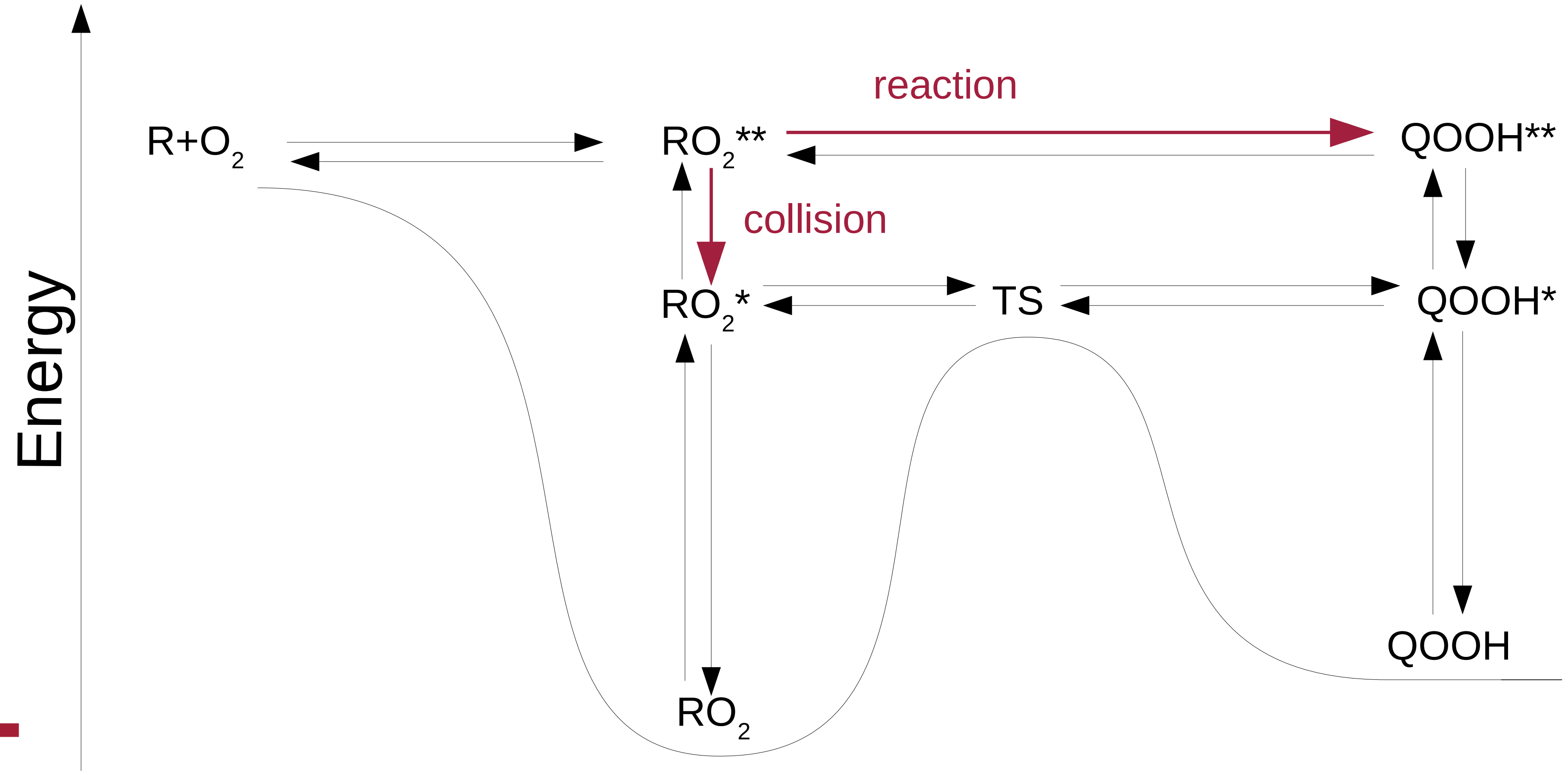
(1) Shahsavan, M.; Mack, J. H. Energ. Convers. Manage. 2018, 157, 28–40.
(2) Pan, L.; Zhang, Y.; Tian, Z.; Yang, F.; Huang, Z. Energy Fuels 2014, 28 (3), 2160–2169.
(3) Weber, B. W.; Sung, C.-J. Energy Fuels 2013, 27 (3), 1688–1698.
(4) Hui, X.; Niemeyer, K. E.; Brady, K. B.; Sung, C.-J. Energy Fuels 2017, 31 (1), 867–881.

Goal: more accurate RO_2 rates

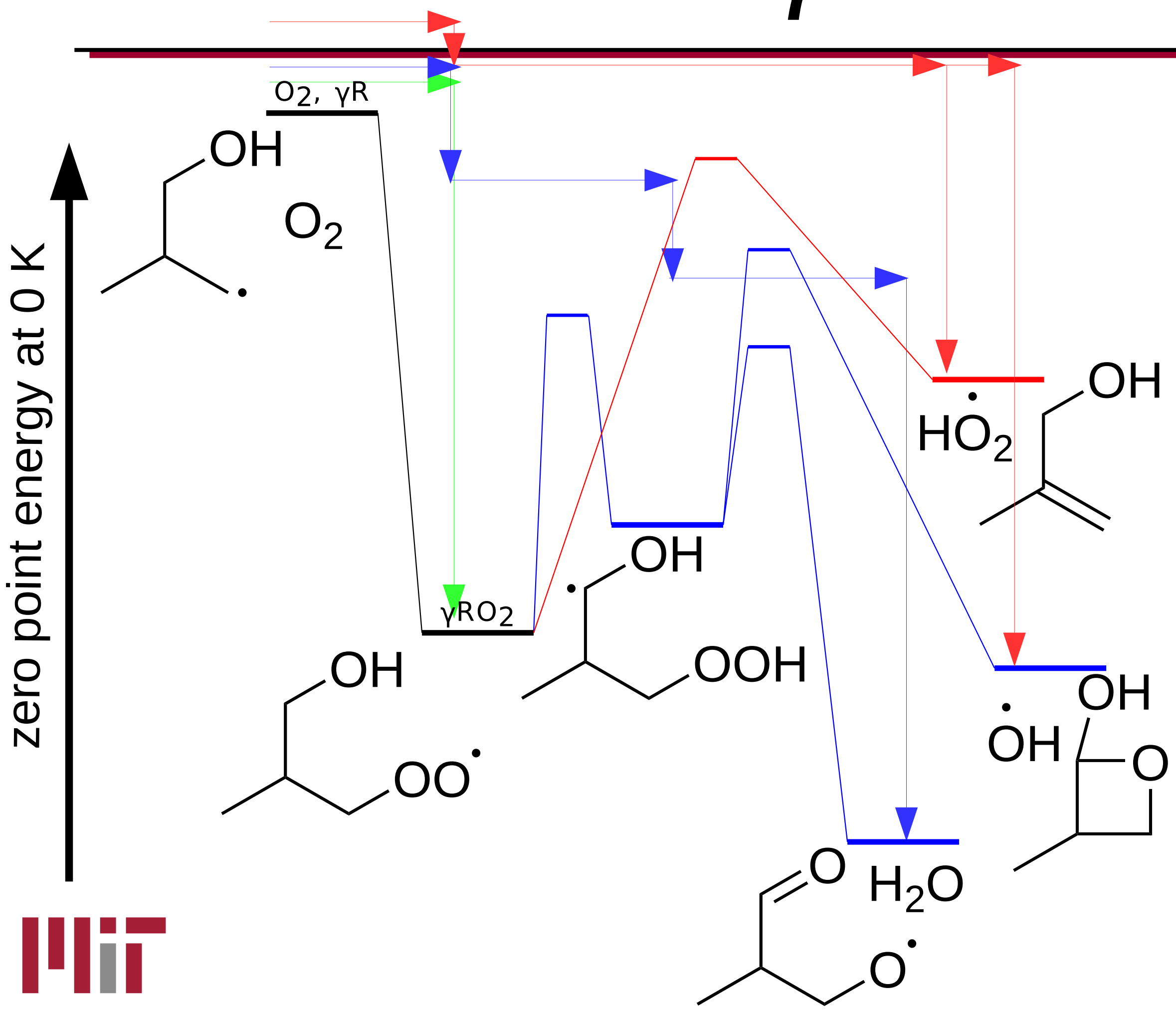




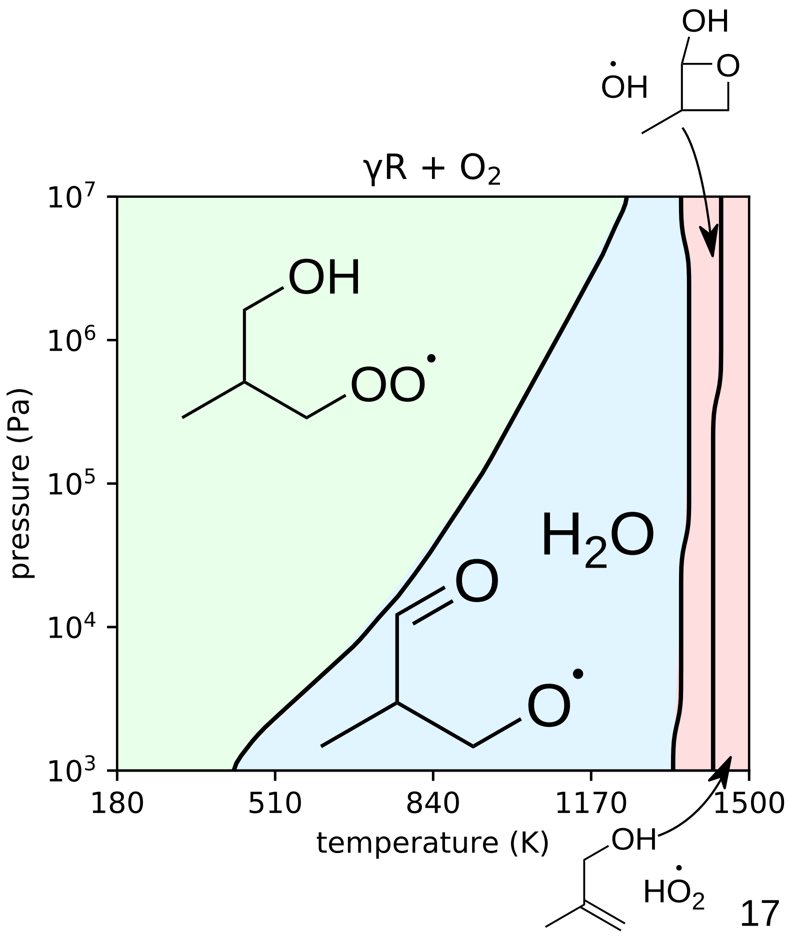
Pressure-dependent reactions



γ-network

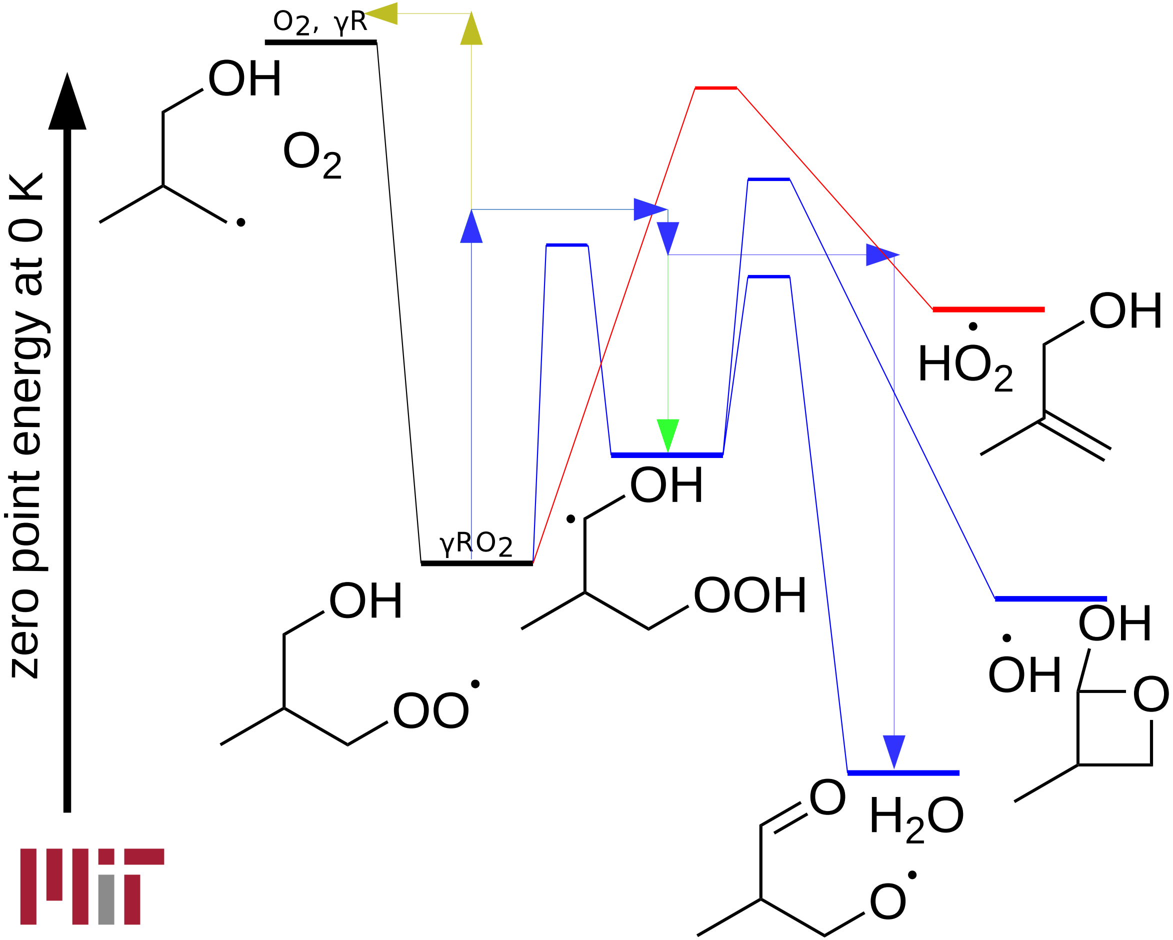


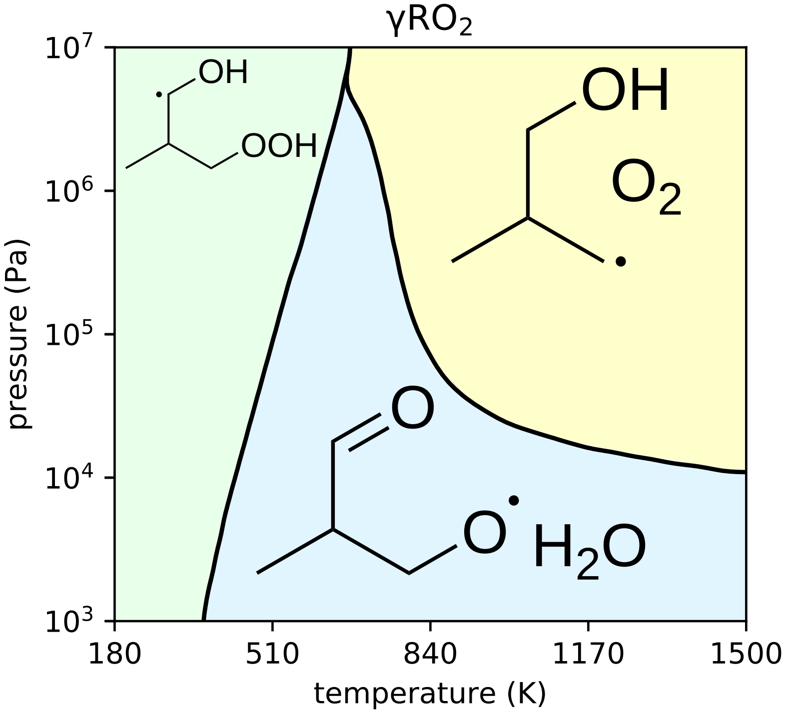
O2, γR
OH
O2
zero point energy at 0 K
γRO2
OH
OO•
OH
OOH
HO2
OH
OH
O
H2O
O•
OH
O
OH



OH
•OH
O
γR + O2
10^7
10^6
10^5
10^4
10^3
pressure (Pa)
OH
OO•
H2O
O
O•
180
510
840
1170
1500
temperature (K)
OH
HO2

γ-network

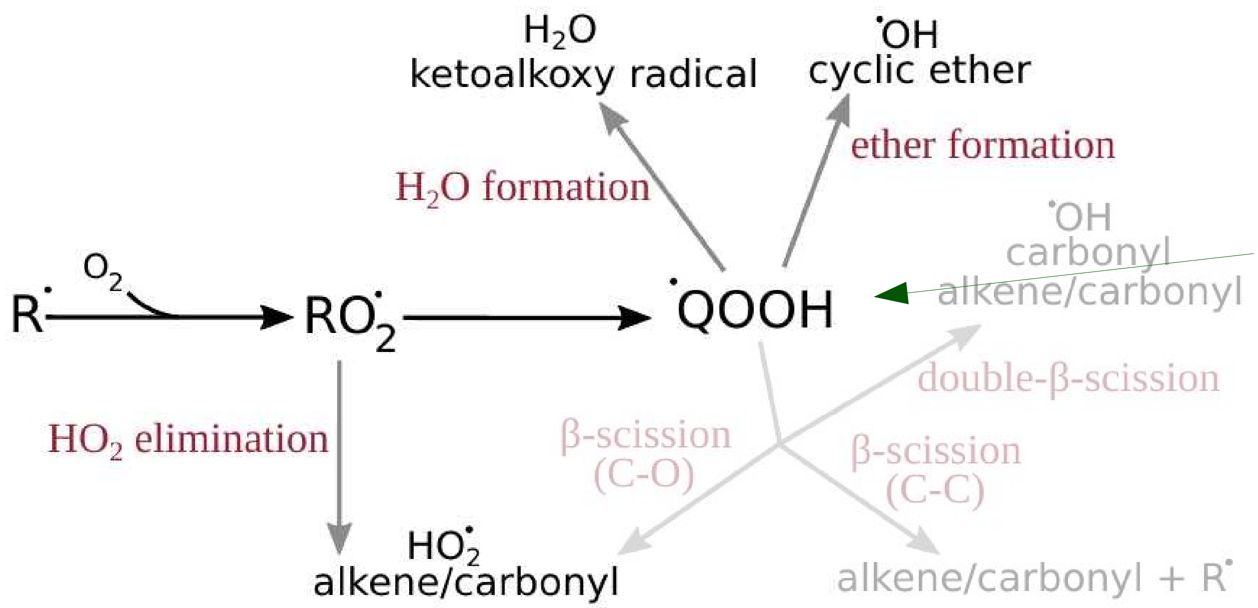

zero point energy at 0 K
O2, γR
OH
O2
γRO2
OH
OO
OH
OOH
HO2
OH
OH
O
OH
O
H2O
O


γRO2
10^7
10^6
10^5
10^4
10^3
pressure (Pa)
180
510
840
1170
1500
temperature (K)
OH
OOH
OH
O2
O
O
H2O

γ-pathway

produces one OH

produces one OH



produces one HO_2 followed by two OH

limited to T < 550 K

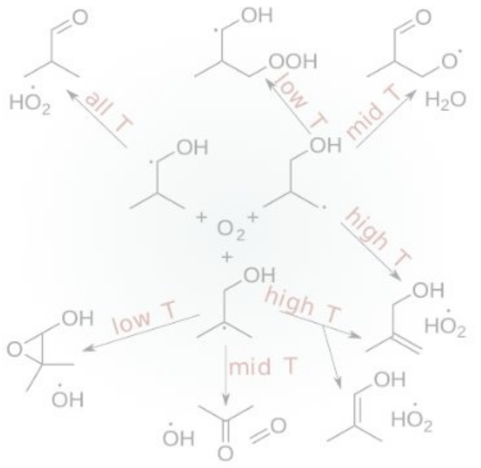
produces one HO_2

Outcomes

- quantified RO_2 pathways for isobutanol
- no negative temperature coefficient branching in low-T ignition
- results can be applied to other alcohol-based biofuels

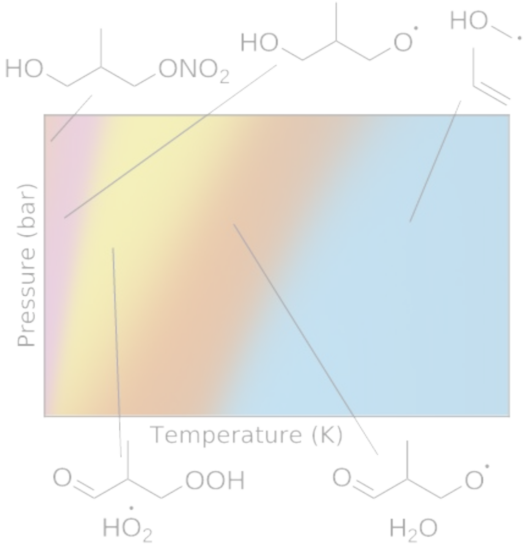
Three peroxy projects

calculate biofuel rate coefficients



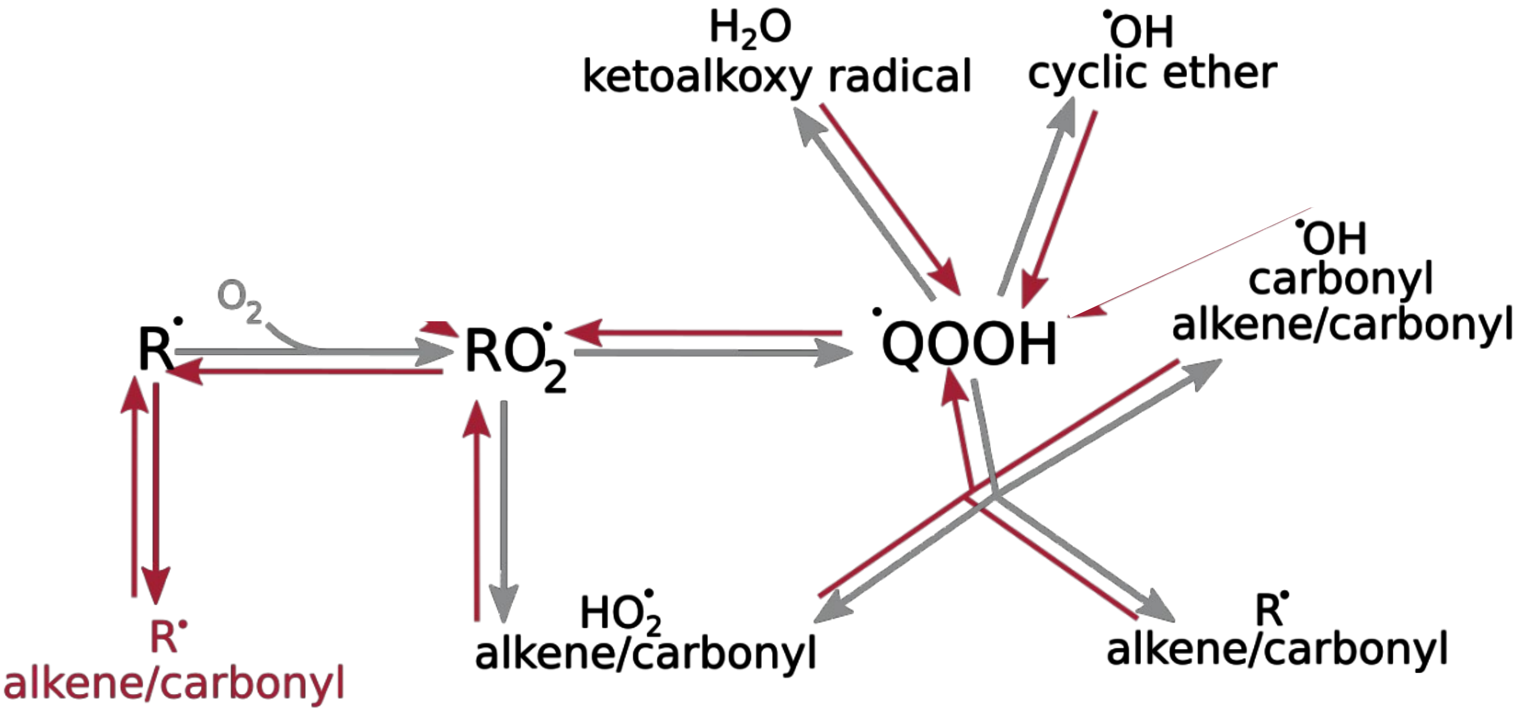
improve biofuel ignition predictions

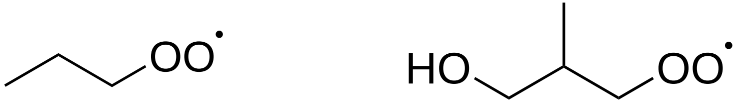
predict peroxy fate



model particle oxidation rate

Adding reaction complexity

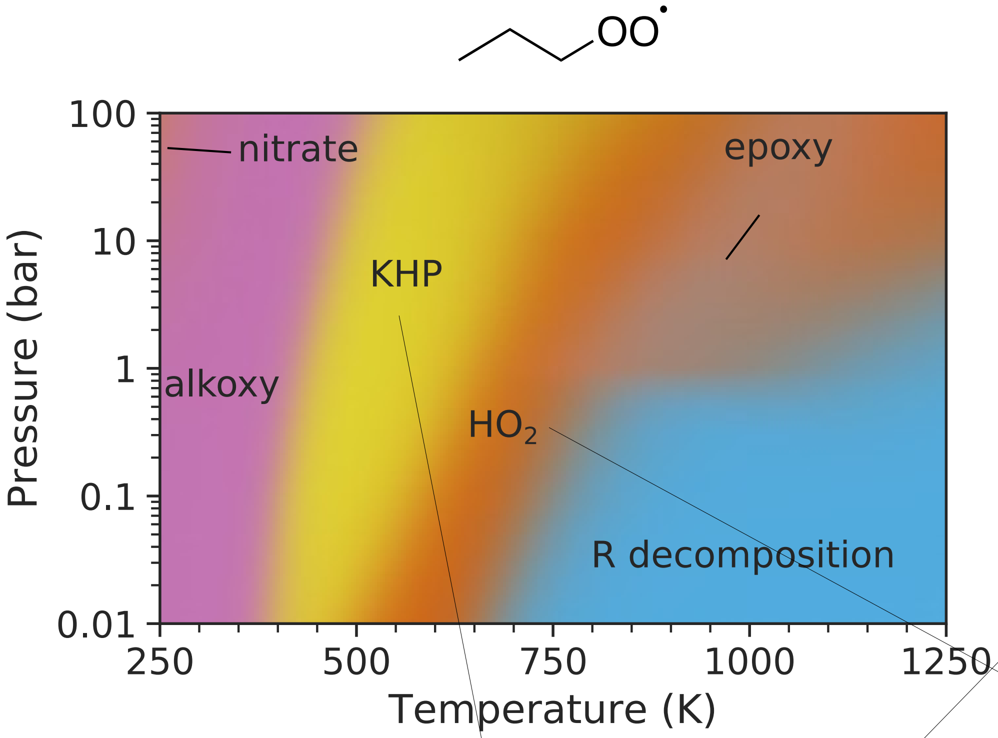




Project goals

- Connect observations in combustion with those of the atmosphere (and vise versa)
- Observe effect of functionalization on peroxy chemistry.

final product paths at various T & P

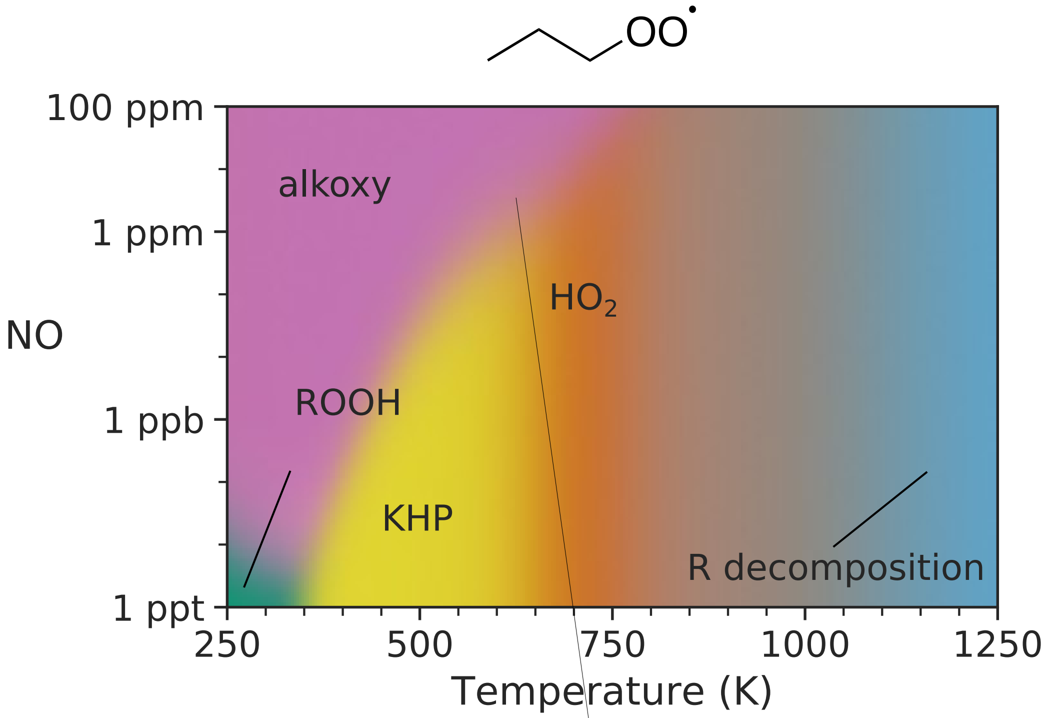


temperature shifted ~ 200 K

different dominant reactions

[NO] = 1 ppb

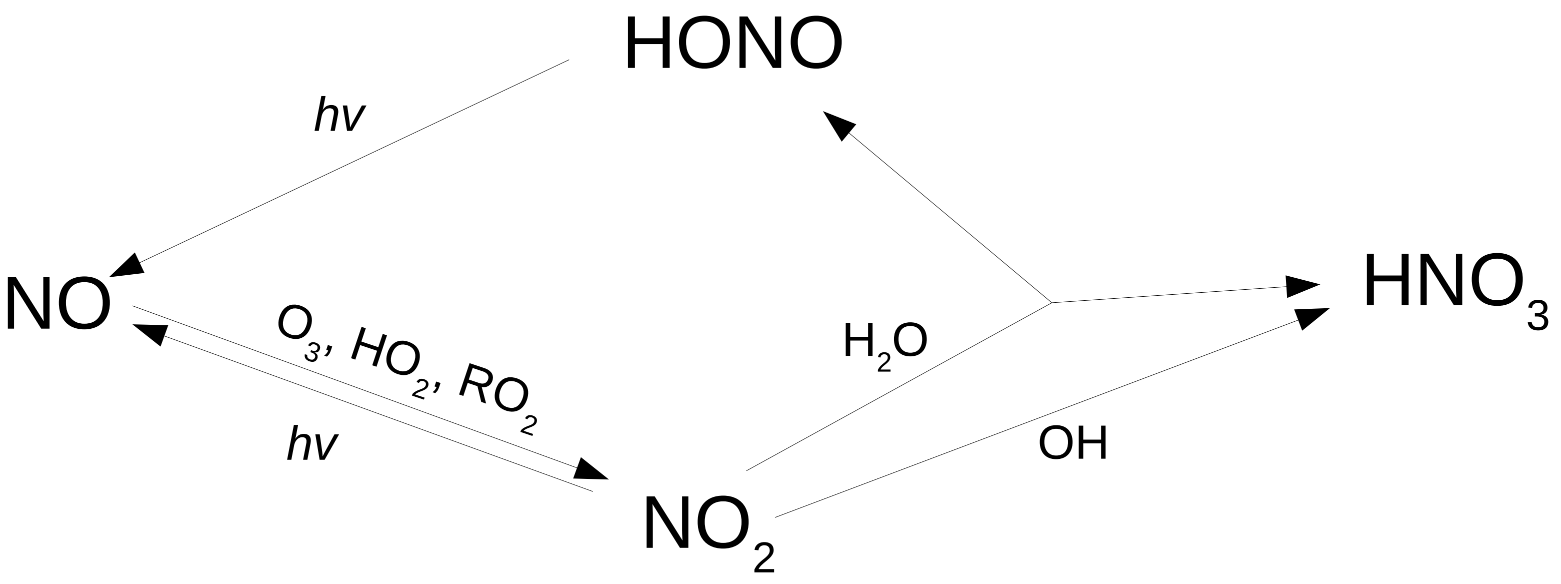
final product paths at various T & NO



at high NO, KHP production stops

pressure = 1 bar

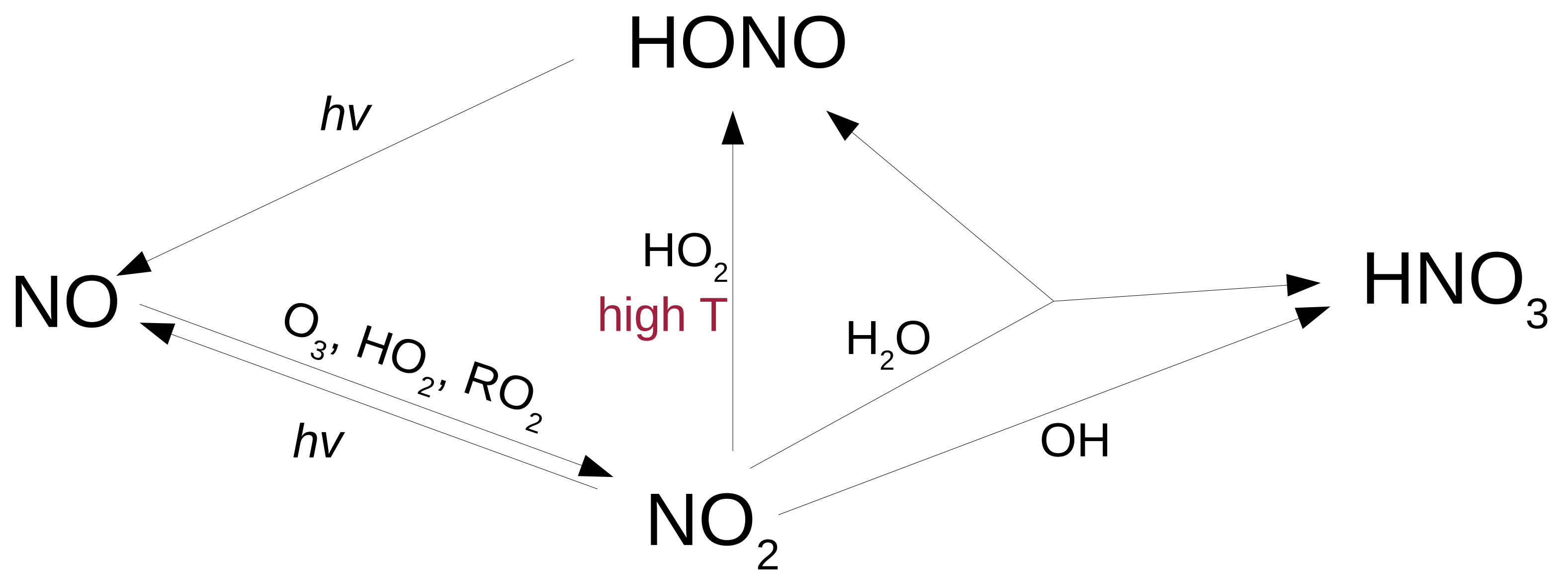
NO chemistry in the atmosphere



$$NO_y = NO + NO_2 + HONO + HNO_3$$

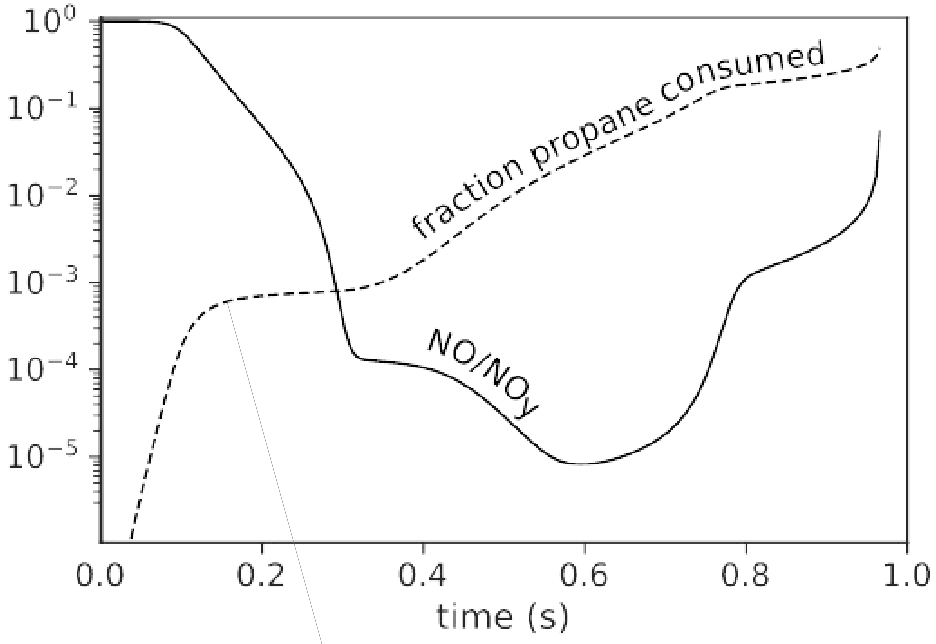
$$NO/NO_y \approx 10\%$$

NO chemistry in combustion

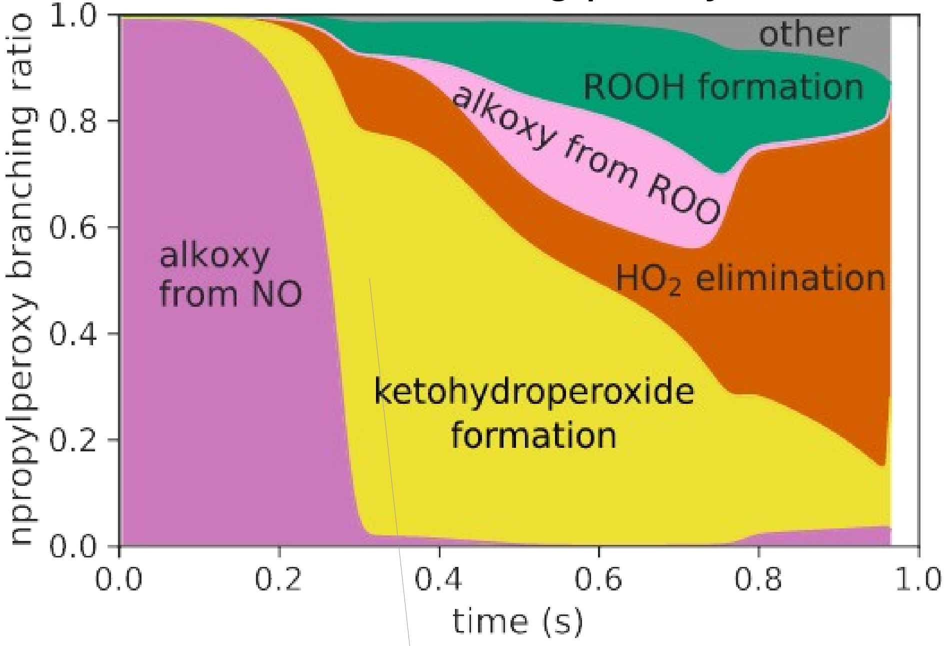


$$NO_y = NO + NO_2 + HONO + HNO_3$$

Simulation with 100 ppm NO



reactions consuming peroxy radicals



reactivity slows as NO consumed

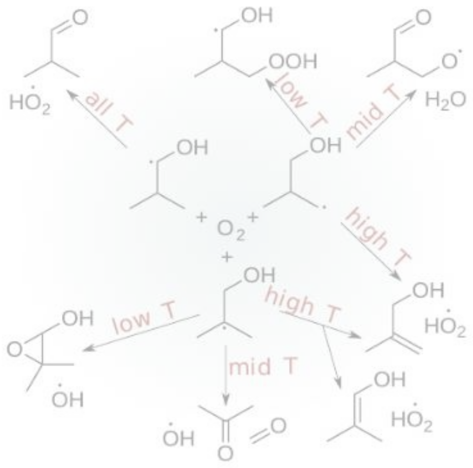
normal ignition after NO reacted

Outcomes

- Loss of NTC in combustion conditions connected with ketohydroperoxide formation in atmosphere
- Lack of photolysis in combustion limits NO's ignition effect.

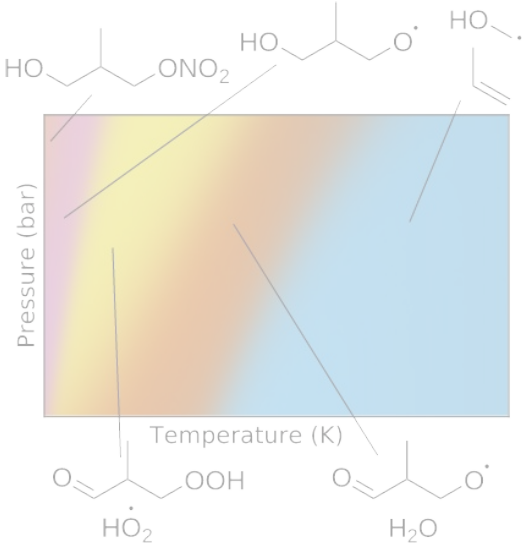
Three peroxy projects

calculate biofuel rate coefficients



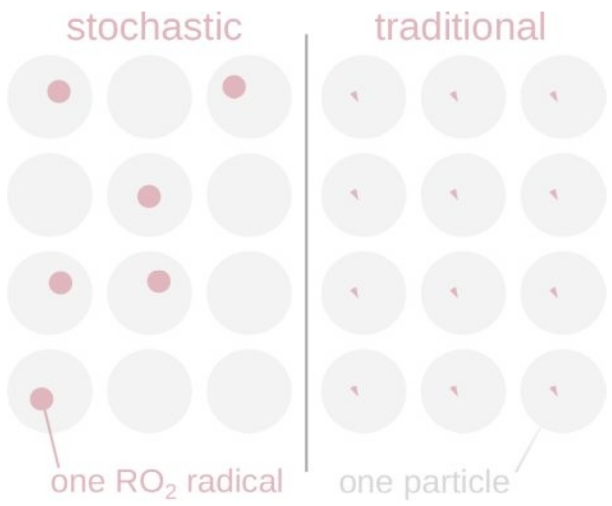
improve biofuel ignition predictions

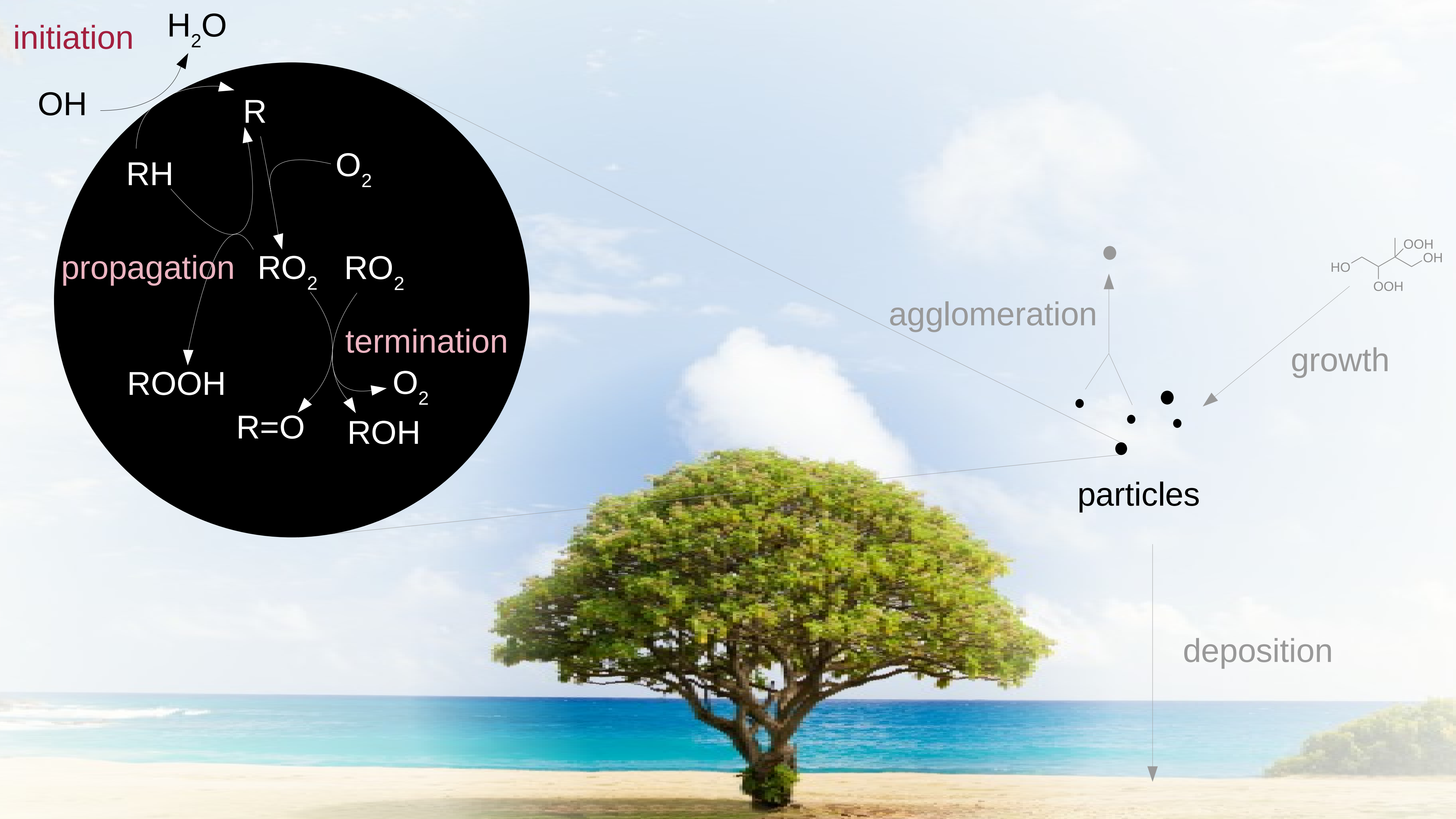
predict peroxy fate



uncover differences from NO cycling & functional groups

model particle oxidation rate




initiation
H_2O
OH
R
RH
O_2
propagation
RO_2
RO_2
termination
ROOH
O_2
R=O
ROH
HO
OOH
OH
OOH
agglomeration
growth
particles
deposition

Two types of kinetics

$$RO_2 + RO_2 \longrightarrow ROH + R{=}O + O_2$$

traditional kinetics

$$\text{reaction rate} = k_t[\mathrm{RO_2}]^2$$

$$\text{reaction rate} > 0$$

RO_2

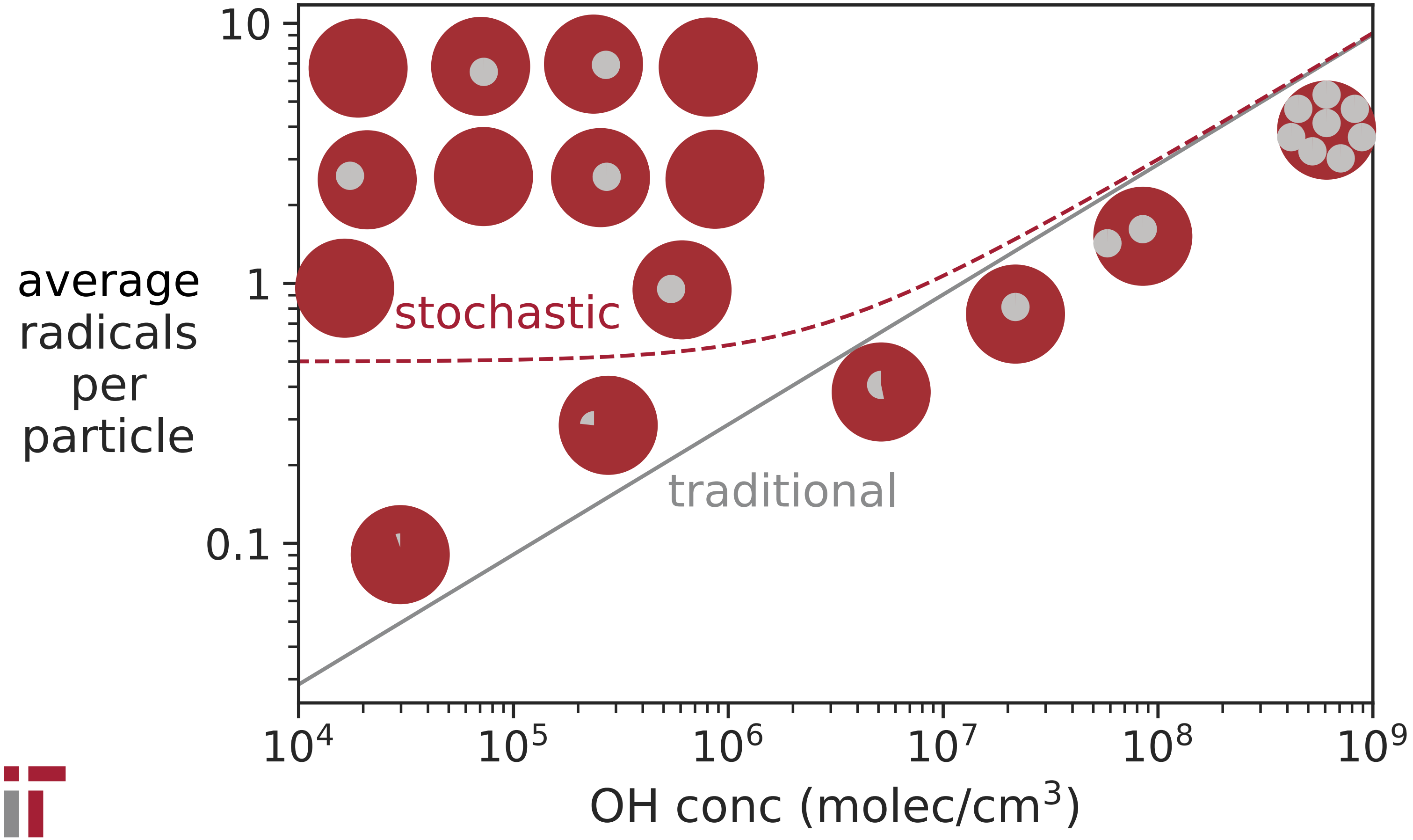
stochastic kinetics

$$\text{reaction rate} = k_t N_{\mathrm{RO_2}}(N_{\mathrm{RO_2}} - 1)$$

$$\text{reaction rate} = 0$$

$$\text{reaction rate} = k_t \sum_{N_{\mathrm{RO_2}}=2}^{\infty} p_{N_{\mathrm{RO_2}}} N_{\mathrm{RO_2}}(N_{\mathrm{RO_2}} - 1)$$

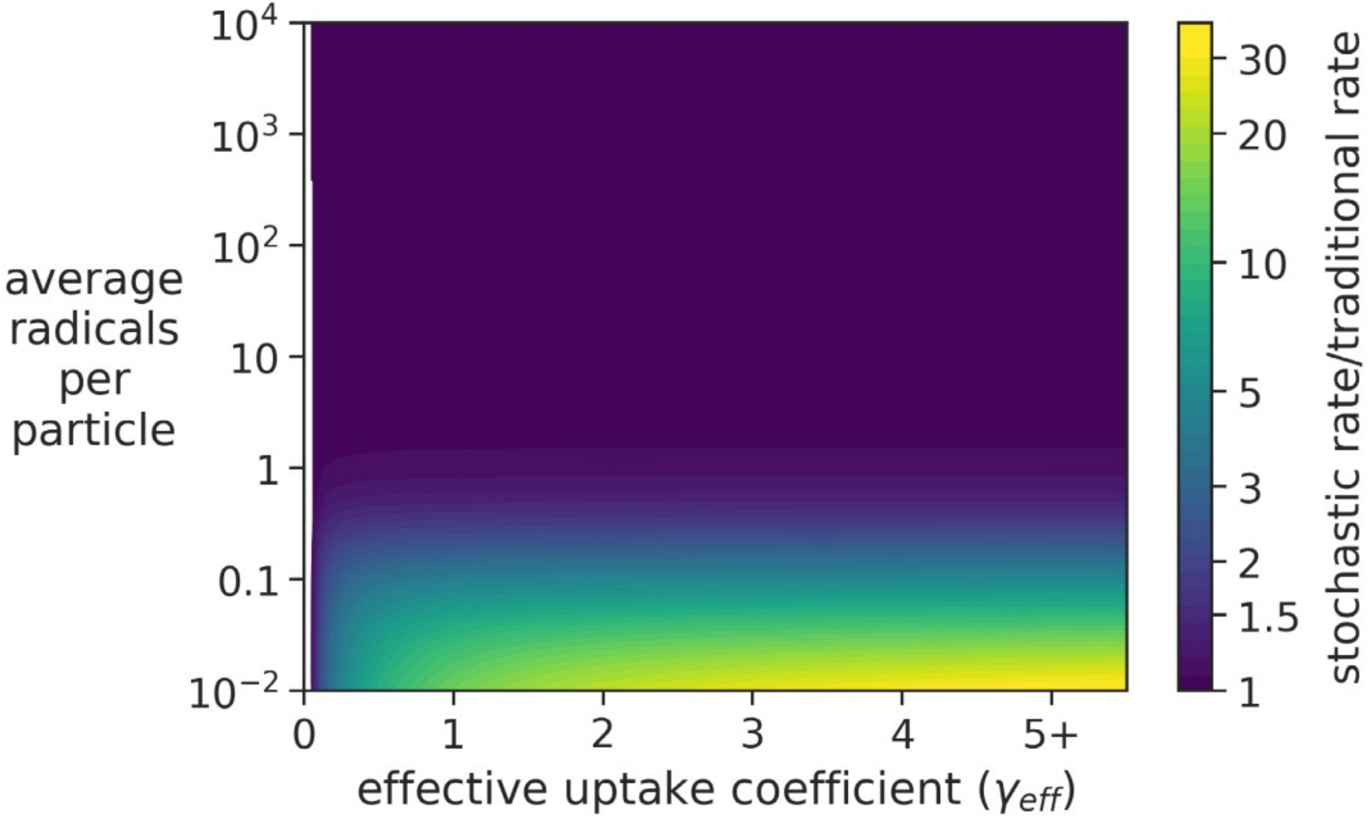
Rates at various OH concentrations



Causes of stochastic effects

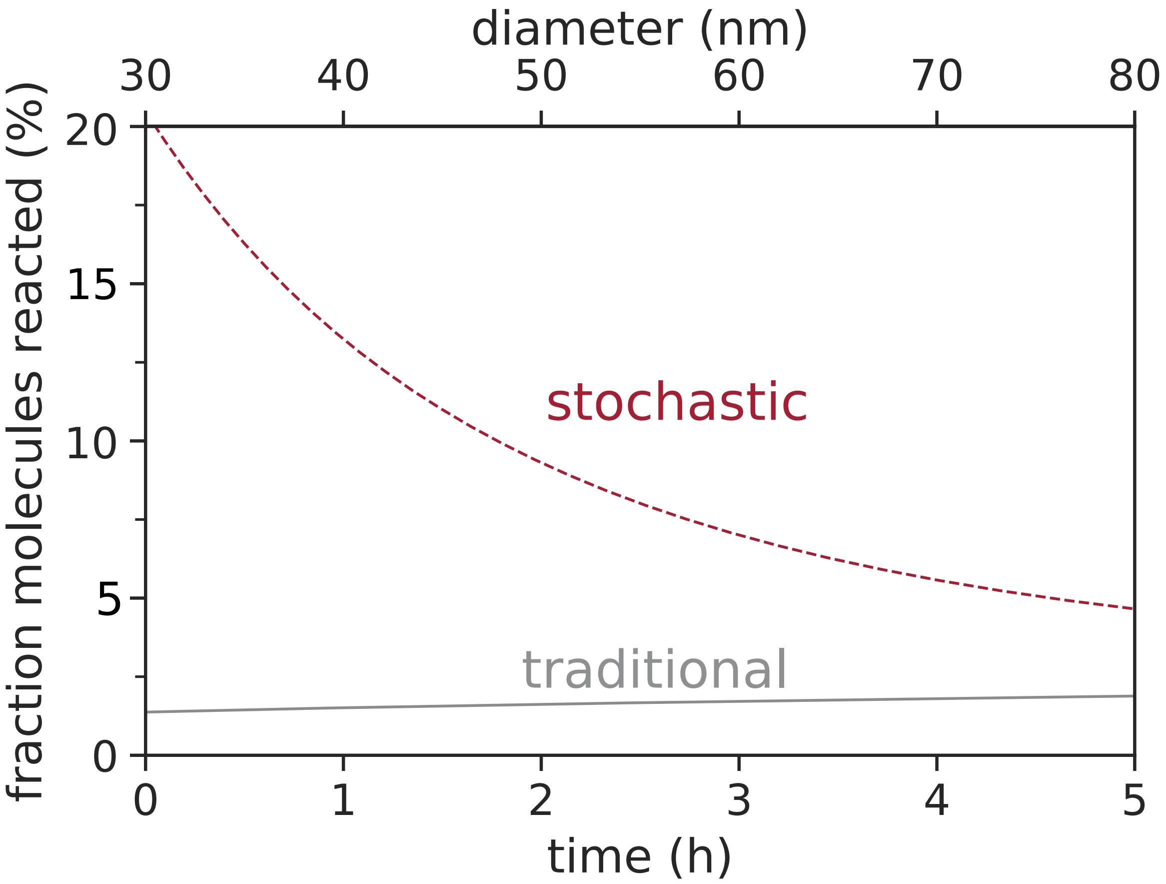
parameters	reaction rates	effect
diameter		
[OH]	$r_{initiation}$	
relative humidity	$k_{termination}$	oxidation $rate_{relative}$
molecular composition	$k_{propagation}$	

Previous experiments not stochastic



A Ruehl et al., 2013
B Cheng et al., 2016
C Kwong et al., 2018
D Jacobs et al., 2019
E Kolesar et al, 2014
F Lim et al., 2017
G Lam et al., 2019
H George et al., 2007
I Smith et al., 2009
J Hearn et al., 2006
K McNeill et al., 2008
L Nah et al., 2014
M Che et al., 2009
N Chim et al., 2018
O Heine et al., 2016
P Lambe et al., 2007
Q Nah et al., 2013
R Arangio et al., 2015
S Richards-Henderson et al., 2016
T Chim et al., 2017

Nighttime particle growth simulation



over 10x reacted at 30 nm

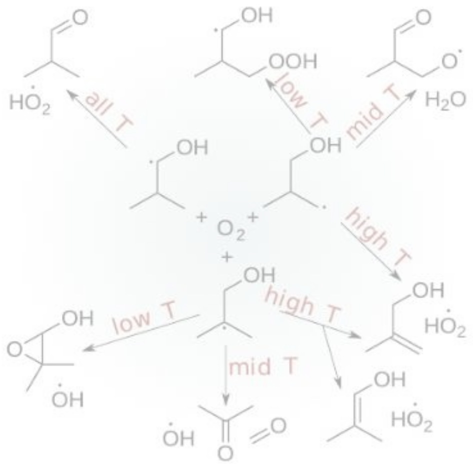
over 2x reacted at 80 nm

Outcomes

- Stochastic kinetics might matter with:
  - small particles
  - low oxidant concentrations
  - fast propagation chemistry
  - less viscous particles
- Previous literature hasn’t measured in this region
- Could impact nighttime nucleation events

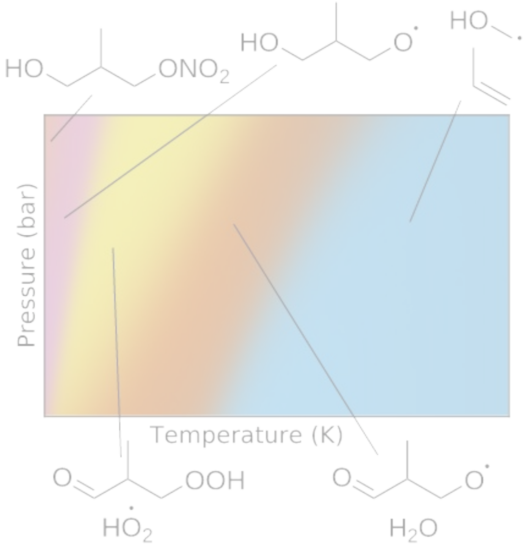
Three peroxy projects

calculate biofuel
rate coefficients



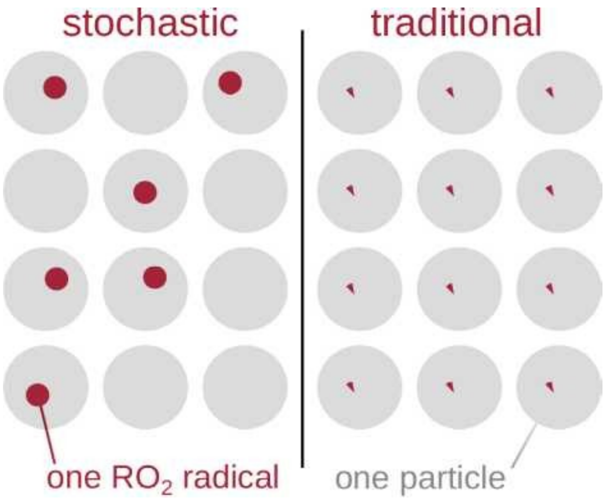
improve biofuel
ignition predictions

predict peroxy
fate



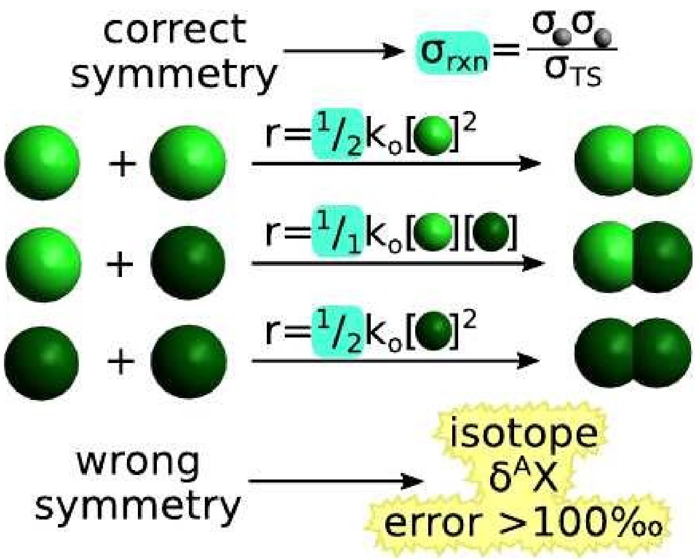
uncover differences
from NO cycling &
functional groups

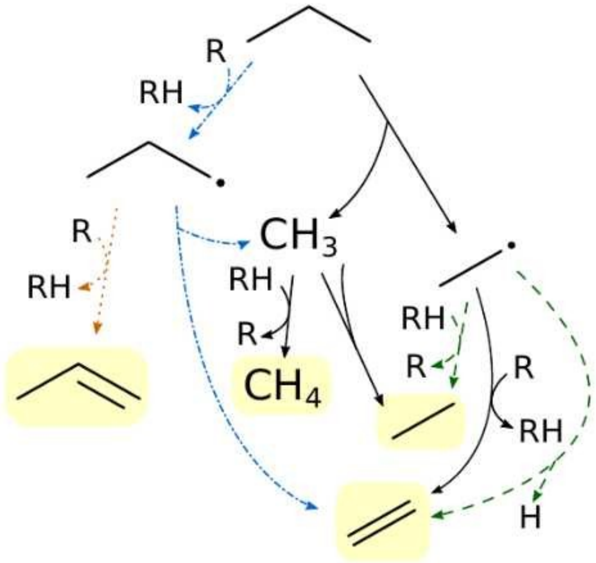
model particle
oxidation rate



show stochastic chemistry
can impact particle growth

Other projects in thesis



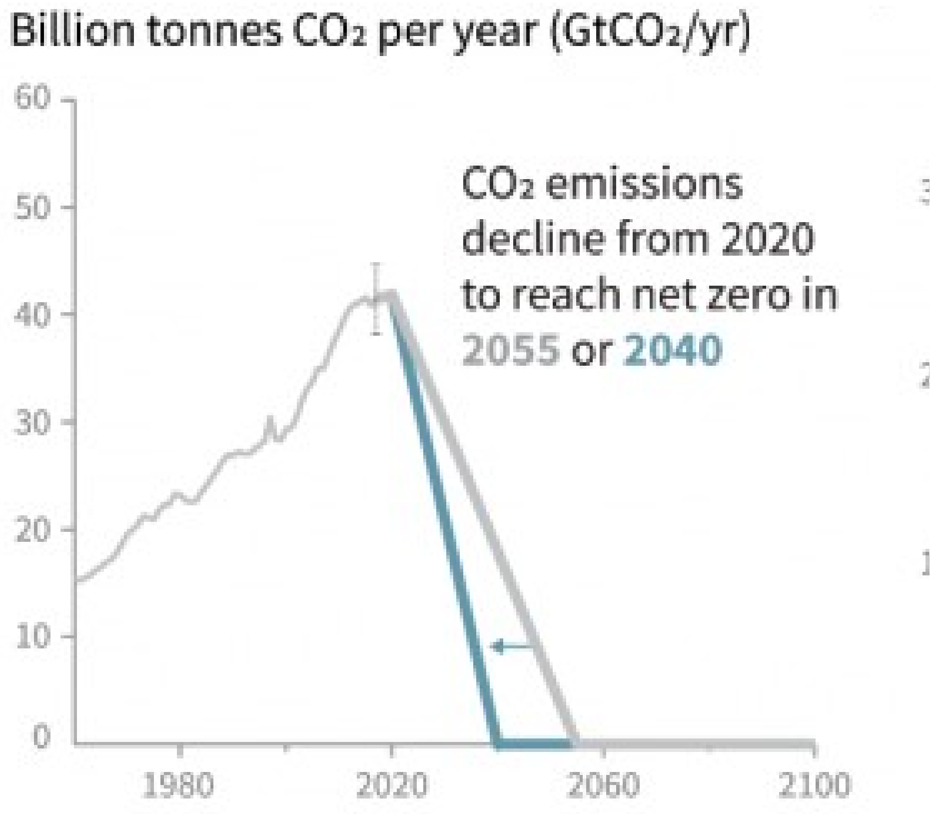


Proper way to calculate reaction rates from identical reactants[1]

Develop algorithm to aid identification of molecular origins[2]

(1) Goldman, M. J.; Ono, S.; Green, W. H. J. Phys. Chem. A 2019, 123 (12), 2320–2324.
(2) Goldman, M. J.; Vandewiele, N. M.; Ono, S.; Green, W. H. Chemical Geology 2019, 514, 1–9.

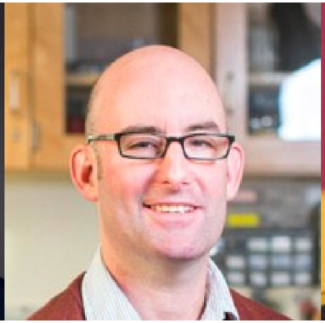
Remaining challenges



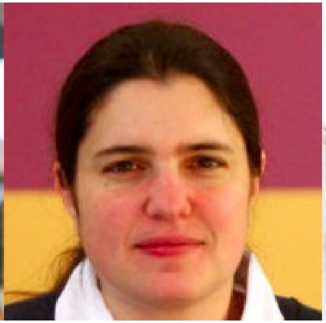
Intergovernmental Panel on Climate Change. Global Warming of 1.5C; Special Report 15; Incheon, Republic of Korea, 2018.

Acknowledgements

Bill Green



Jesse Kroll

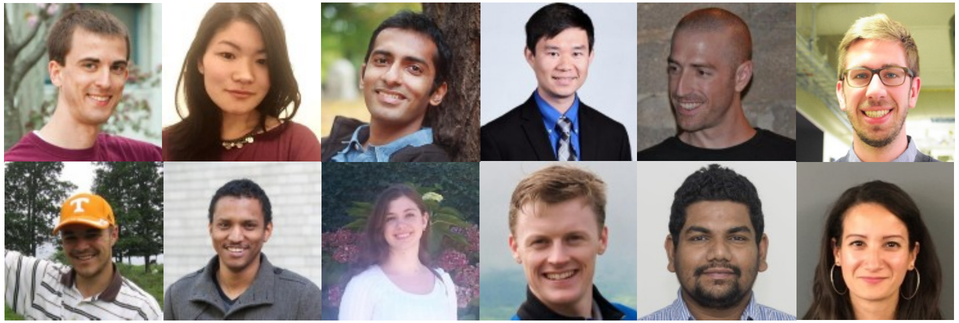


Heather Kulik

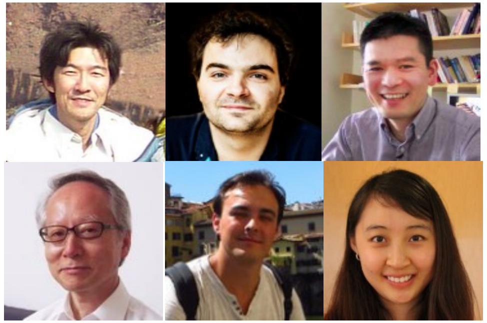
Linda Broadbelt

Nathan Yee

Nick Vandewiele



Software Collaborators



Experimental Collaborators

Acknowledgements

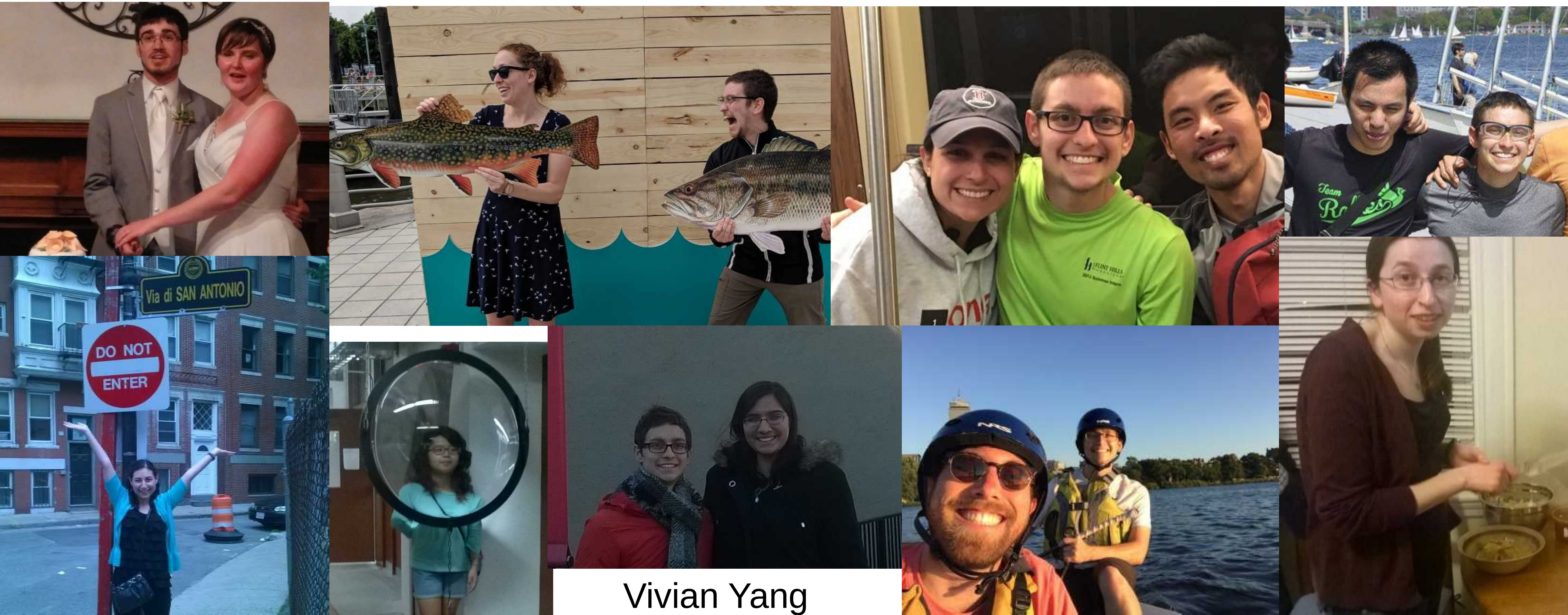
green group

kroll group

parsons lab

Acknowledgements

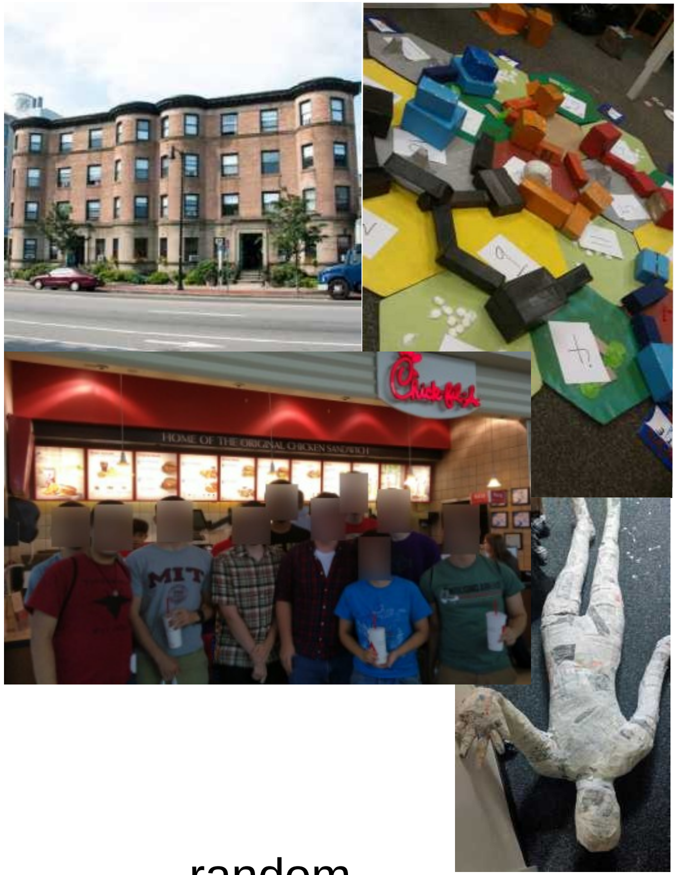
Acknowledgements



Vivian Yang

Acknowledgements

pika



random

Acknowledgements

Acknowledgements

MIT Presidential Fellowship

MIT TA Funding

National Science Foundation

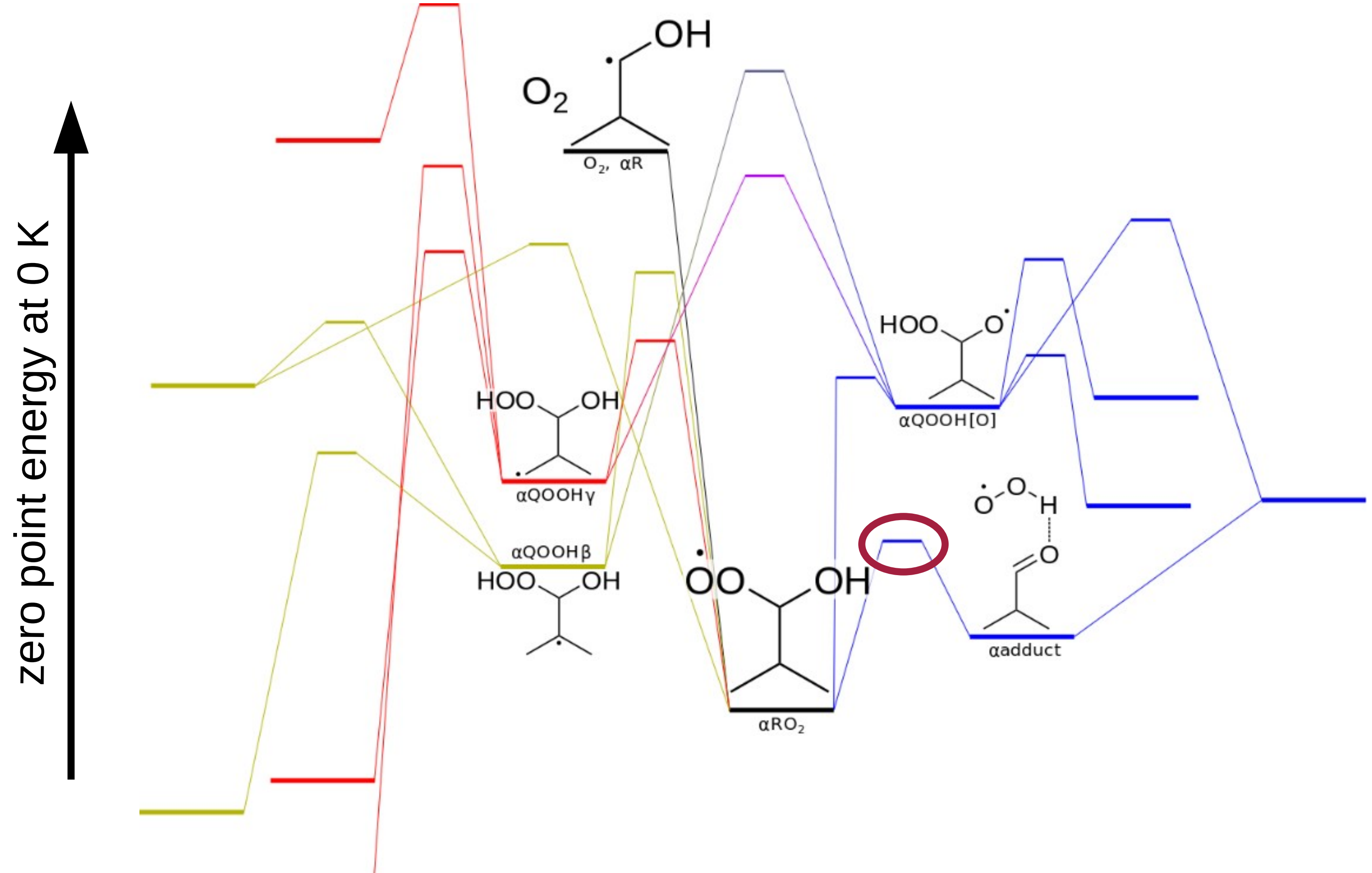
Department of Energy

by contributions
to the U.S. government
by taxpayers like you

Thank you

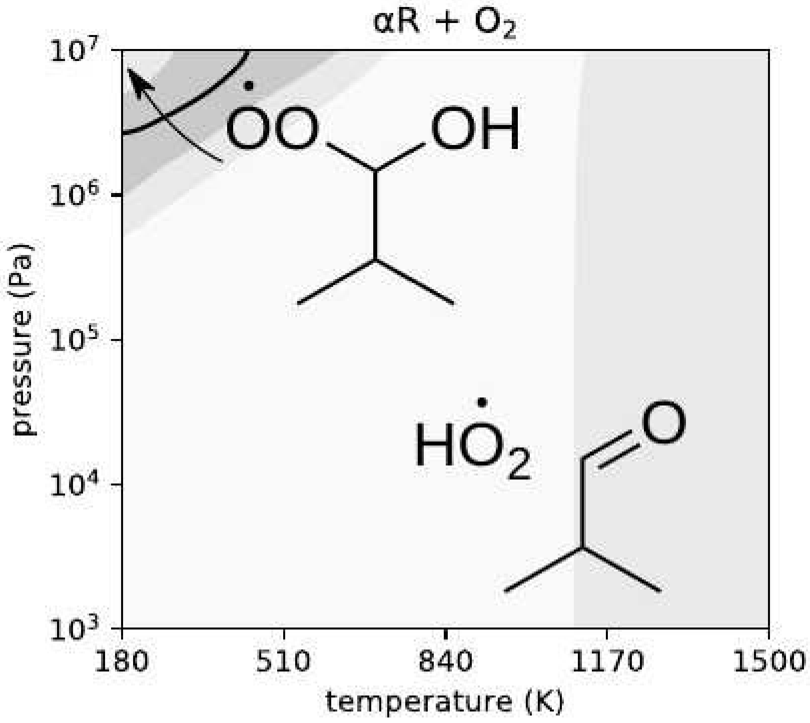
Supporting Slides

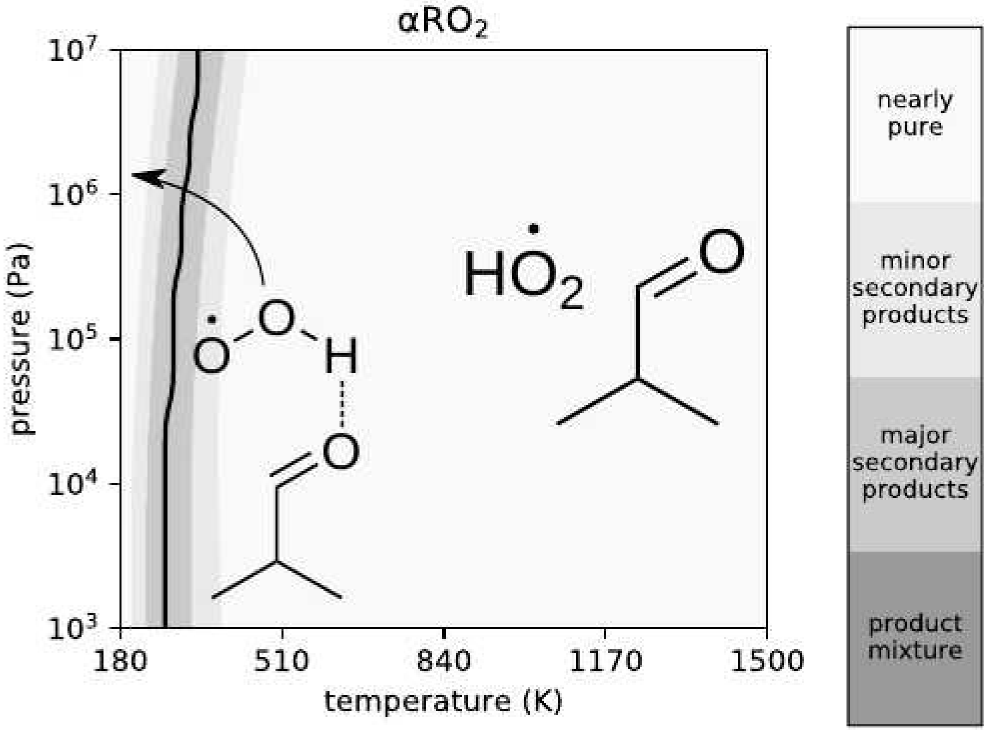
α-network



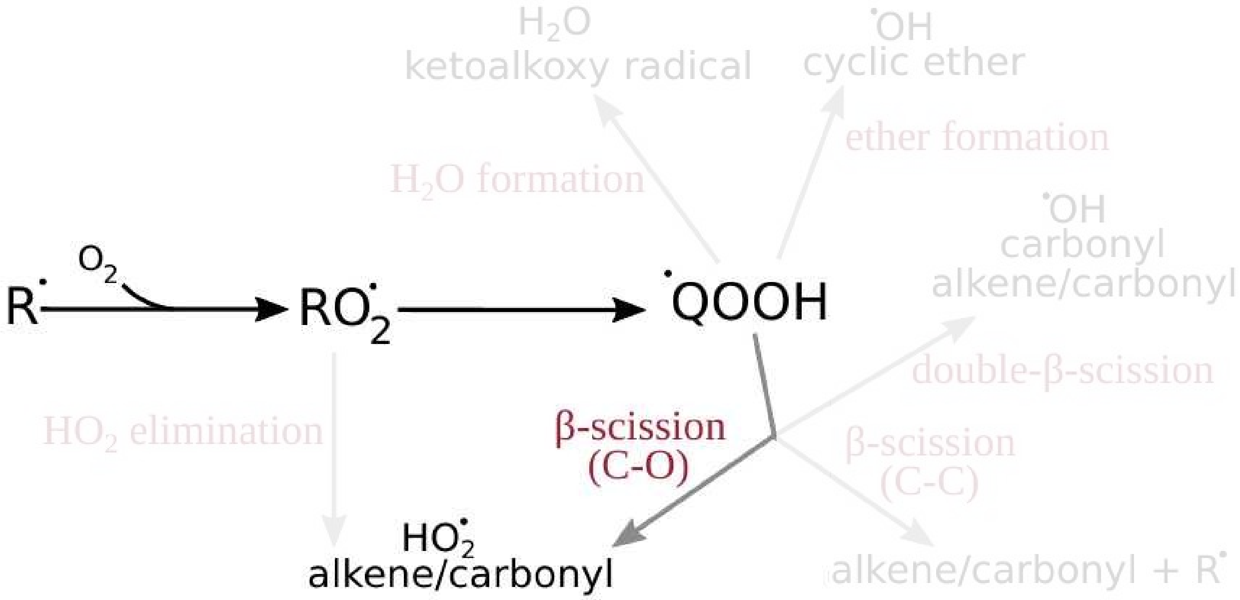
zero point energy at 0 K
O2
OH
O2, αR
HOO OH
αQOOHγ
αQOOHβ
HOO OH
OO OH
αRO2
HOO O
αQOOH[O]
O O H
O
αadduct

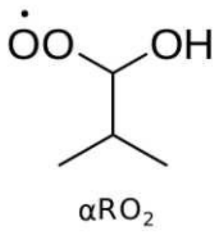
products in α-peroxy network





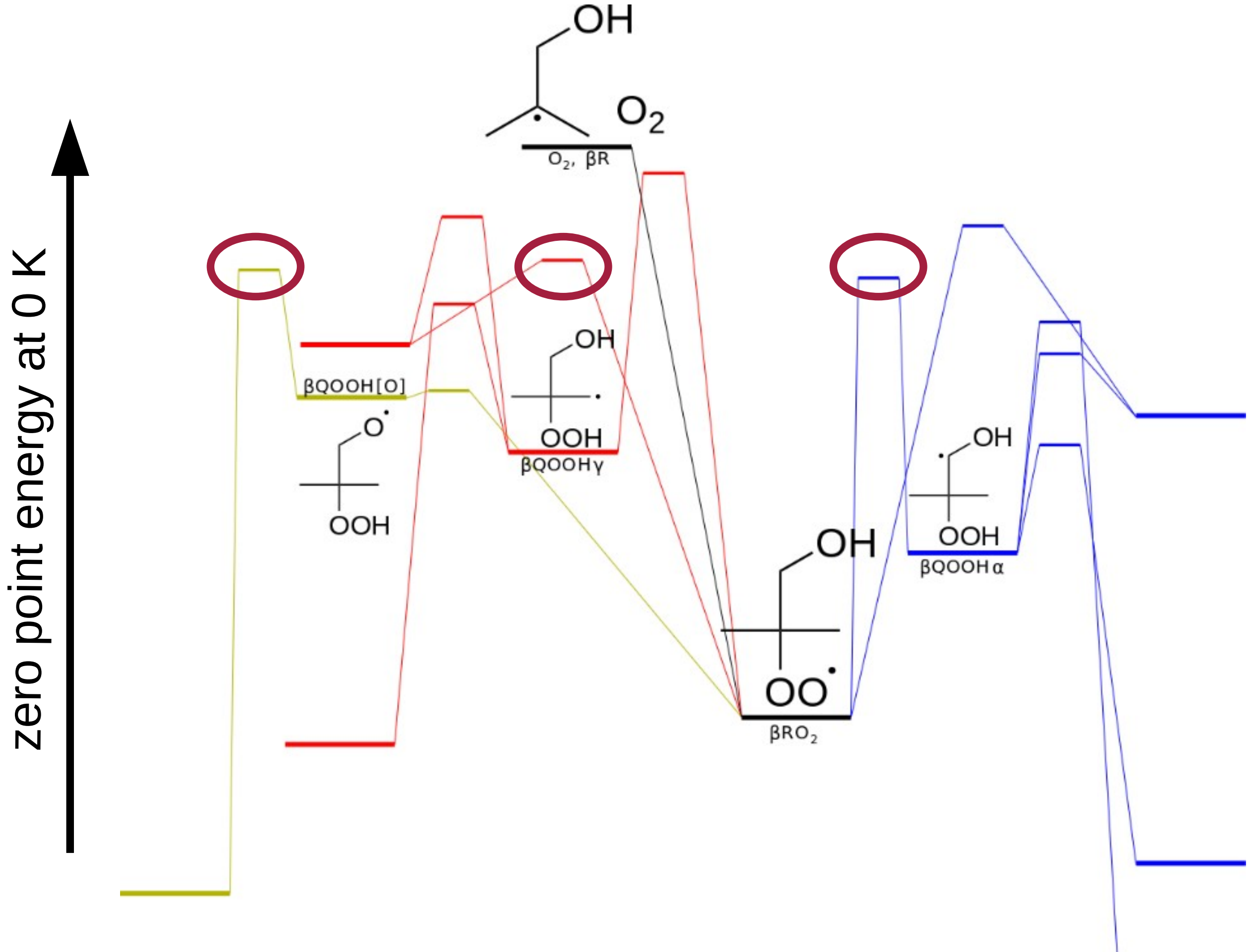
α-pathway





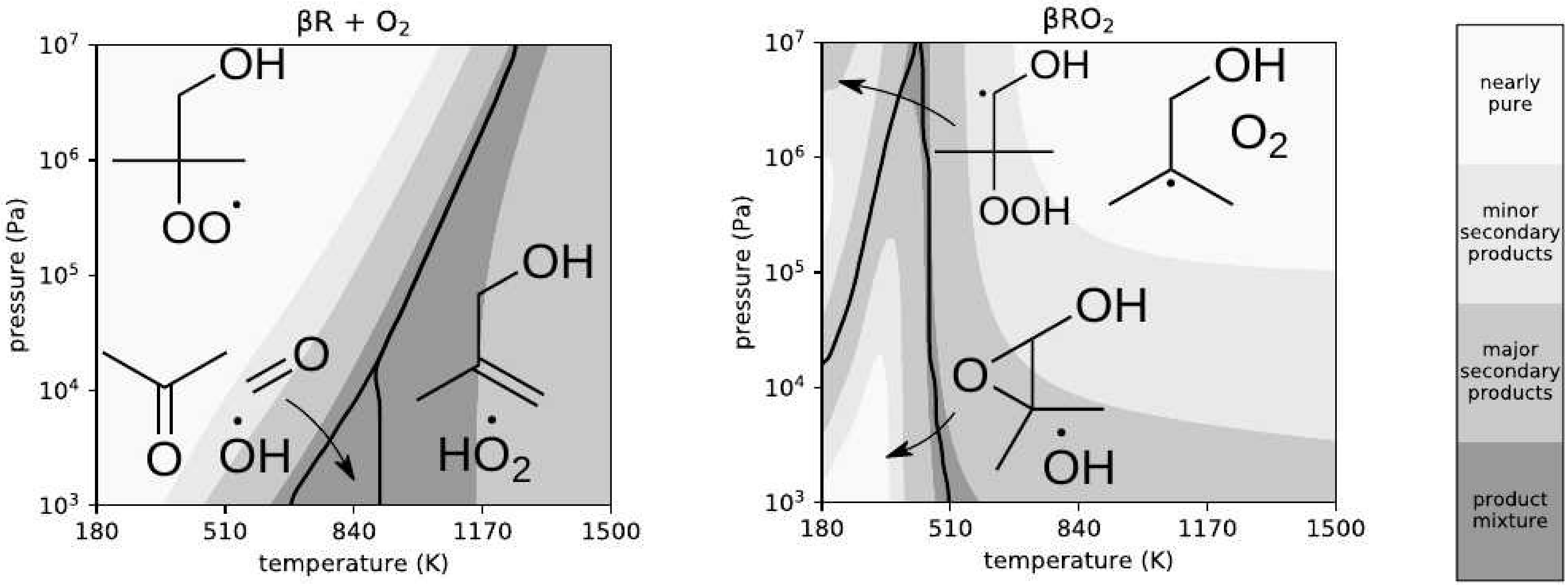
no OH production. Low reactivity

β-network

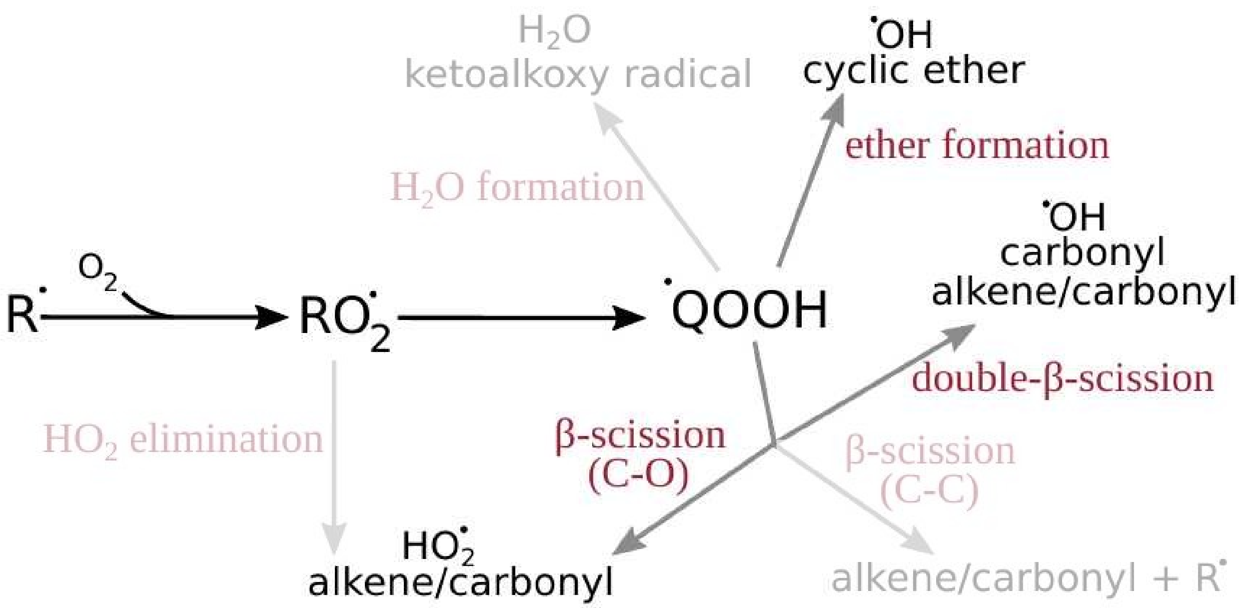


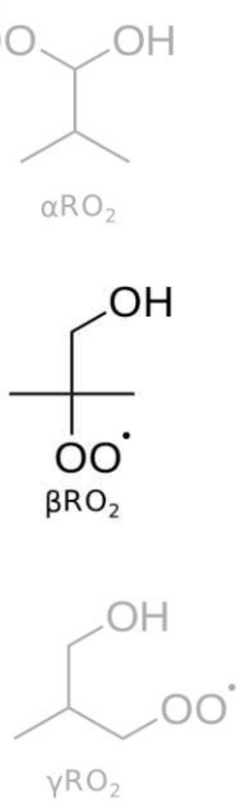
zero point energy at 0 K
OH
O_2
O_2, βR
βQOOH[O]
O
OOH
OH
OOH
βQOOHγ
OH
OO
$βRO_2$
OH
OOH
βQOOHα

products in β-peroxy network



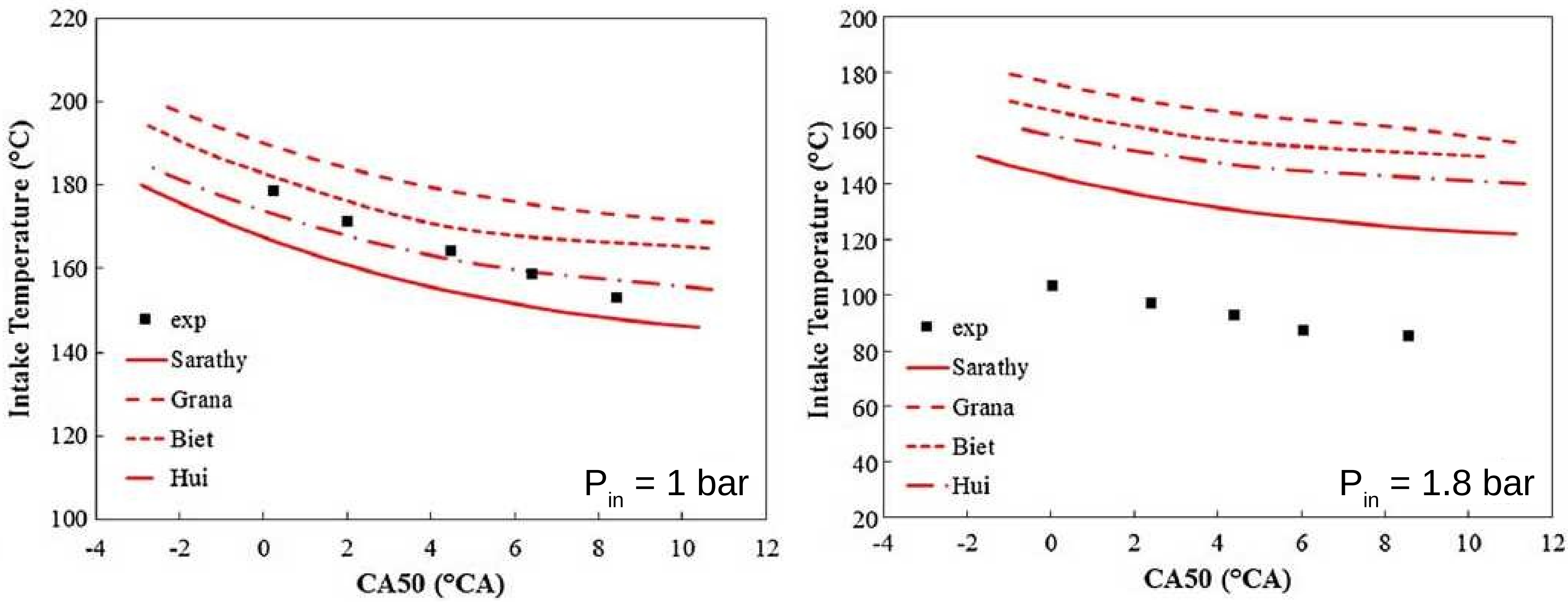
β-pathway





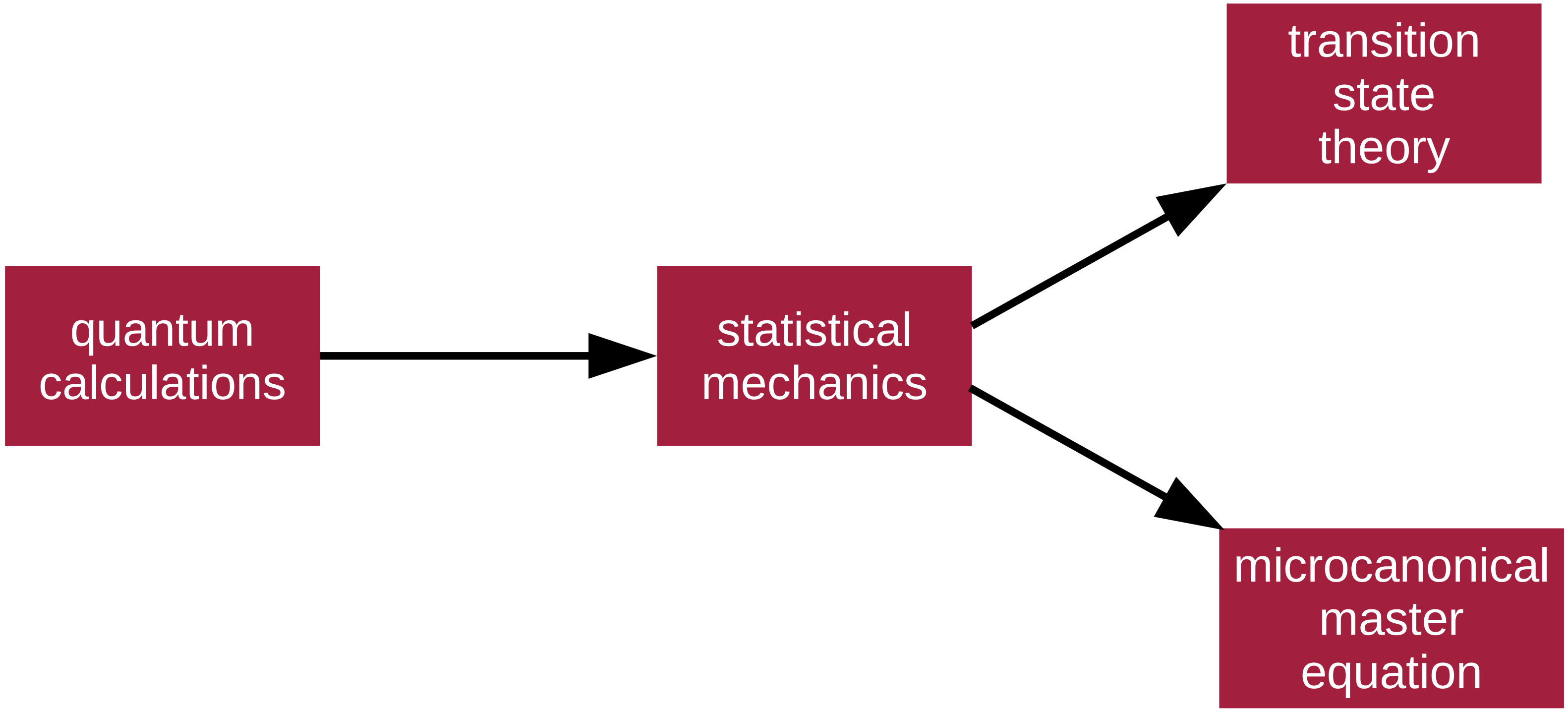
one OH produced at low to mid temperatures

Pressure dependence missed in model



Weber, B. W.; Sung, C.-J. Energy Fuels 2013, 27 (3), 1688–1698.

Rates from quantum calculations



Aerosol sizes