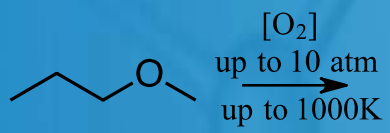
Co-Optimization of Fuels & Engines

Low Temperature Oxidation of Methylpropyl Ether

Mark R. Nimlos[1], Lintao Bu[1], Matthew S. Johnson[2], Dongil Kang[3], **Gina M. Fioroni**[1], Robert L. McCormick[1], Seonah Kim[1], Thomas D. Foust[1], S. Scott Goldsburough[3] and William H. Green[2]

[1]National Renewable Energy Laboratory, Golden, CO, USA,
[2]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA,
[3]Argonne National Laboratory, Lemont, IL, USA



Autoignition
Compression ignition
Knock

11th U.S. National Combustion Meeting
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Pasadena, California

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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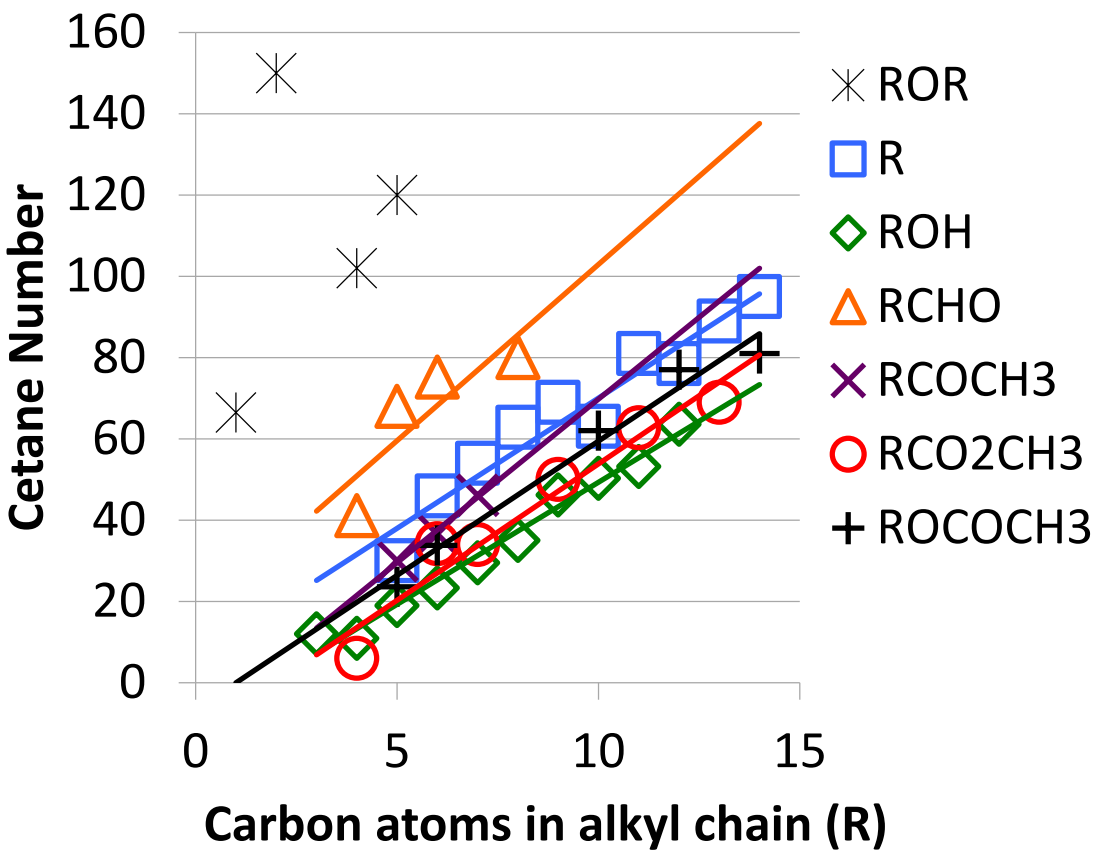
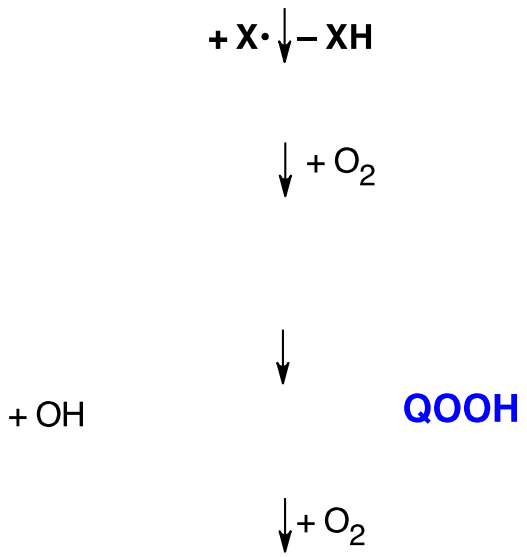
Ethers as a Performance Advantaged Biofuel

- Numerous pathways to ethers from biomass
- Ethers (ROR) can have high cetane number (CN)
- A better understanding of chemistry of autoignition can lead to greater predictability



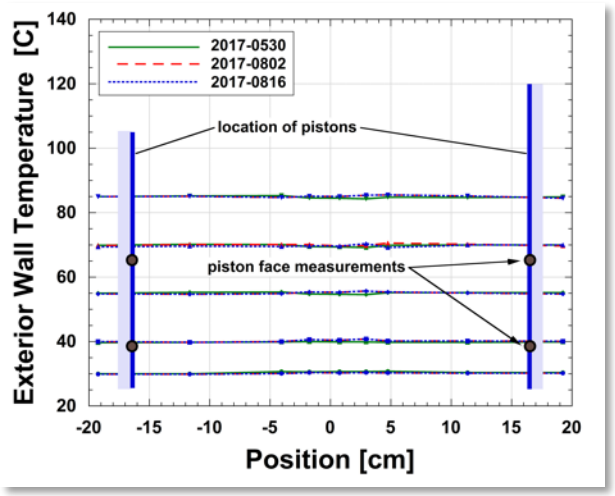
Autoignition Chemistry

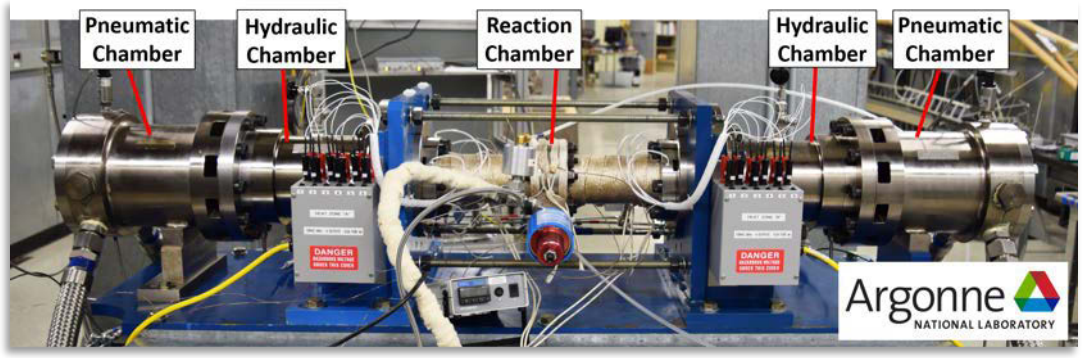


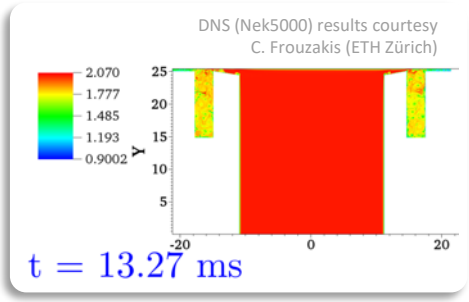
- Low temperatures and high pressures
- Alkyl radical formation
  RH -> R•
- Followed by oxygen addition
  R• + O_2 -> ROO
- Hydrogen transfer
  ROO -> QOOH
- Addition of second oxygen
- Competing side reactions

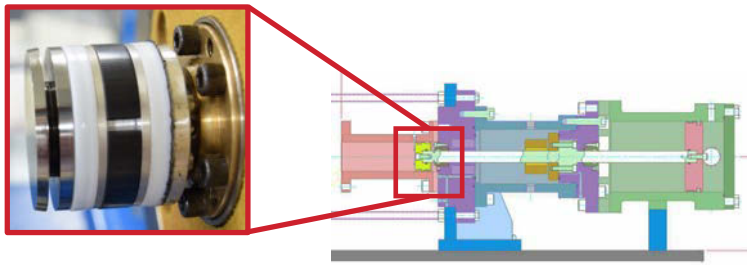
Twin-Piston Rapid Compression Machine

- Pneumatically-driven, hydraulically controlled
- Engine-relevant conditions to investigate homogeneous autoignition
  - Pc = 10–90+ bar, Tc = 600–1100 K, O_2 = 5–21%, ϕ = 0.2–2+; τ_1,τ = 1–150 ms
- Excellent control of reacting gas during/post compression
  - Thermal uniformity in reaction chamber via 5-zone heating system
  - Creviced piston used to suppress fluid motion







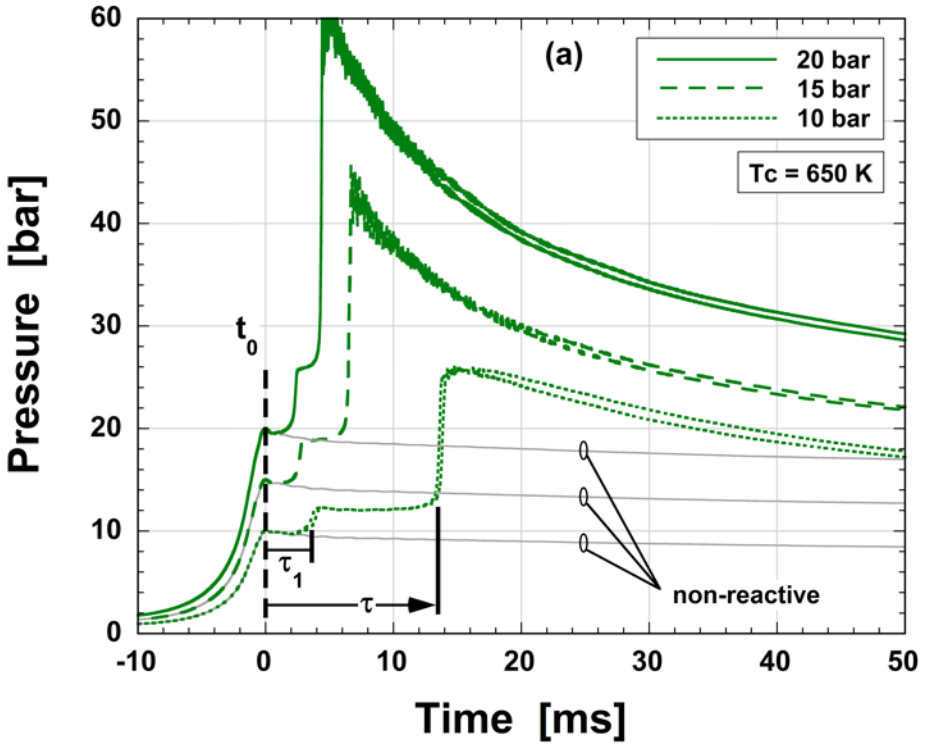


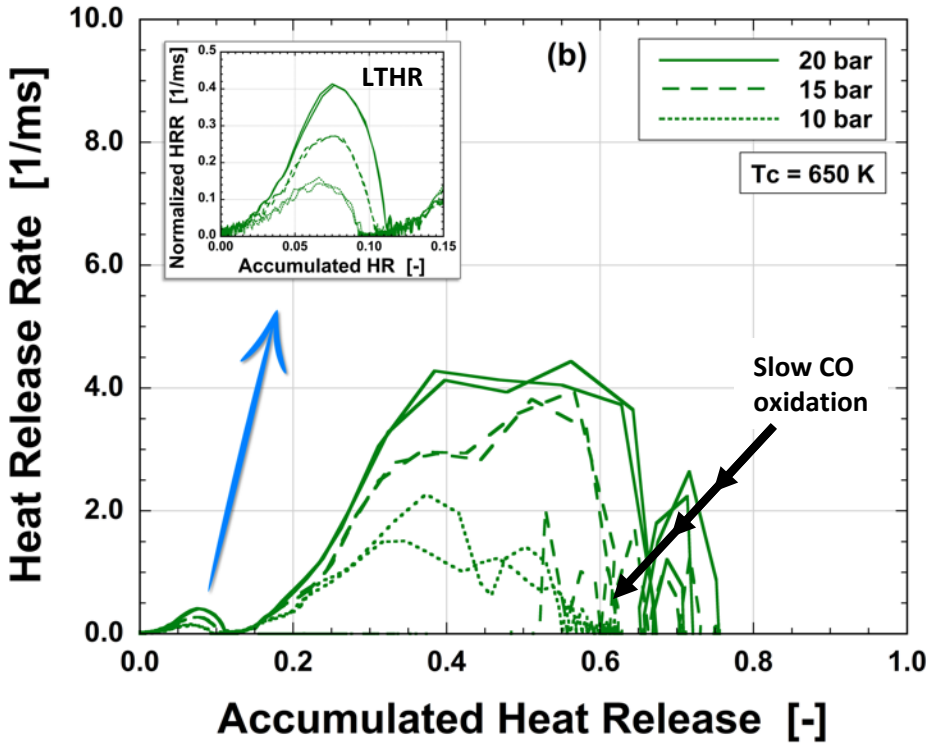
Fridlyand, et al. *Combustion and Flame*, **2019** 387.

Experimental methods

- Two tests conducted at each condition with excellent repeatability
- Non-reacting / reacting tests conducted to quantify first-stage / main ignition times, and evolution of exothermicity (heat release)
  - Normalized heat release rates highlight development of low temperature heat release (LTHR), transition through intermediate-temperature conditions, and evolution of high-temperature chemistry, including slow CO oxidation

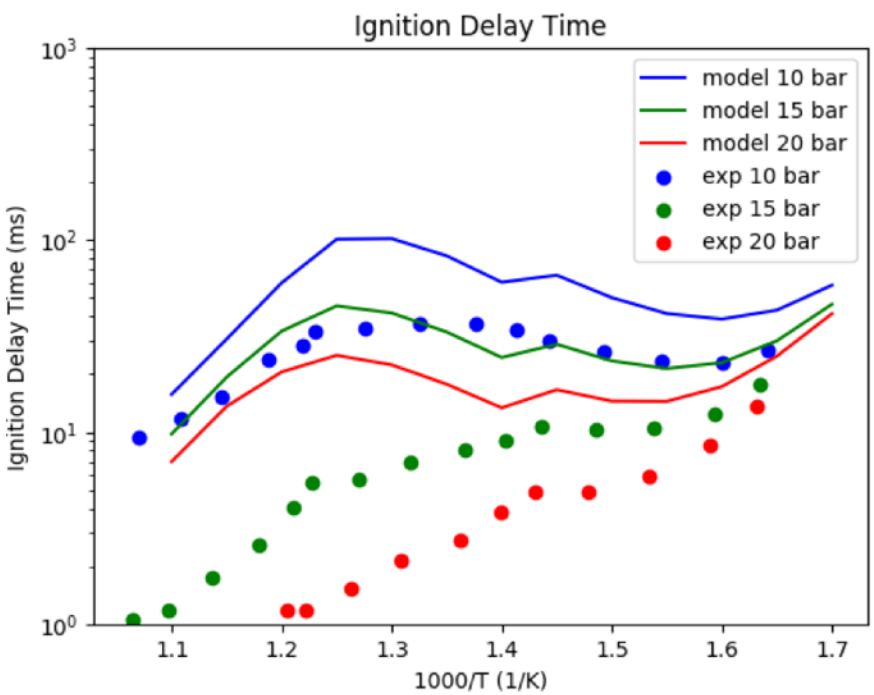
Goldsborough et al., *Proceedings of the Combustion Institute*, **2019**, 603.

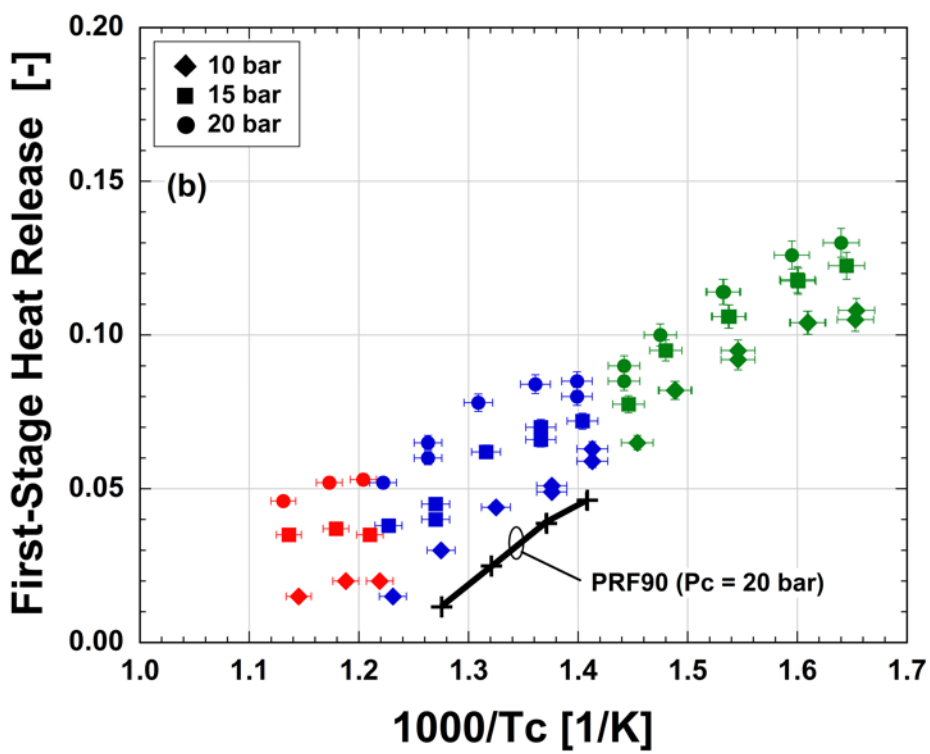




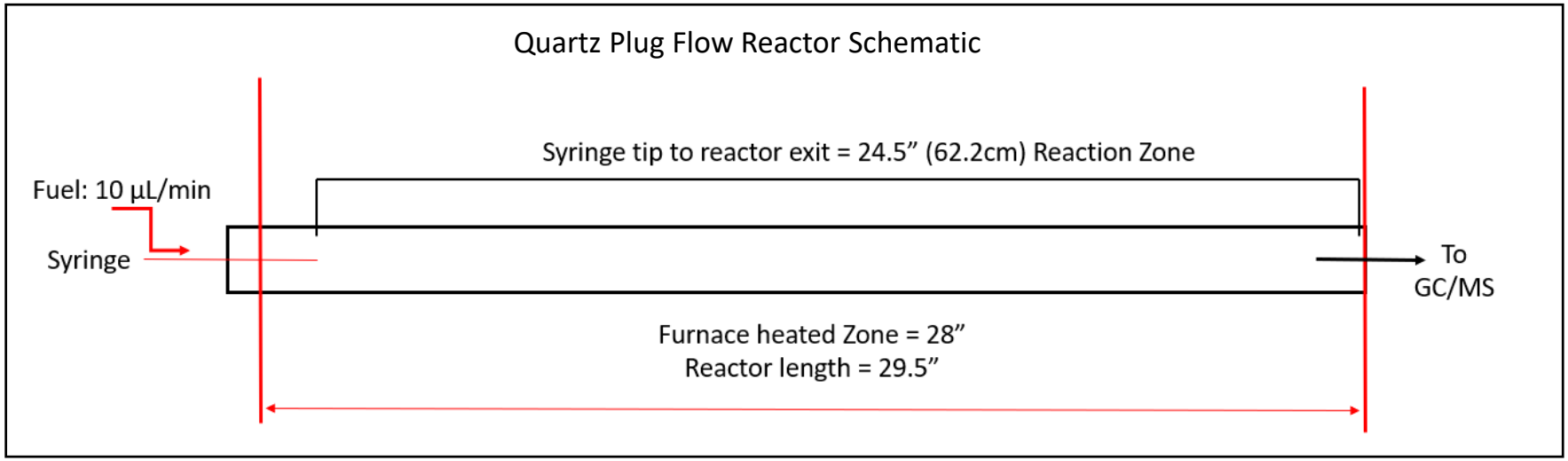
Experimental and Modeling Results

- RCM measurements identify NTC behavior for MPE
  - MPE is very reactive, with substantial influence of compressed pressure; general shapes of ignition delays captured by kinetic model. More work needed to capture pressure dependence – reactivity underestimated.
- First-stage / low-temperature heat release is significantly greater than that measured with a gasoline-relevant fuel (PRF 90)





Flow Reactor Schematic and Experimental Conditions



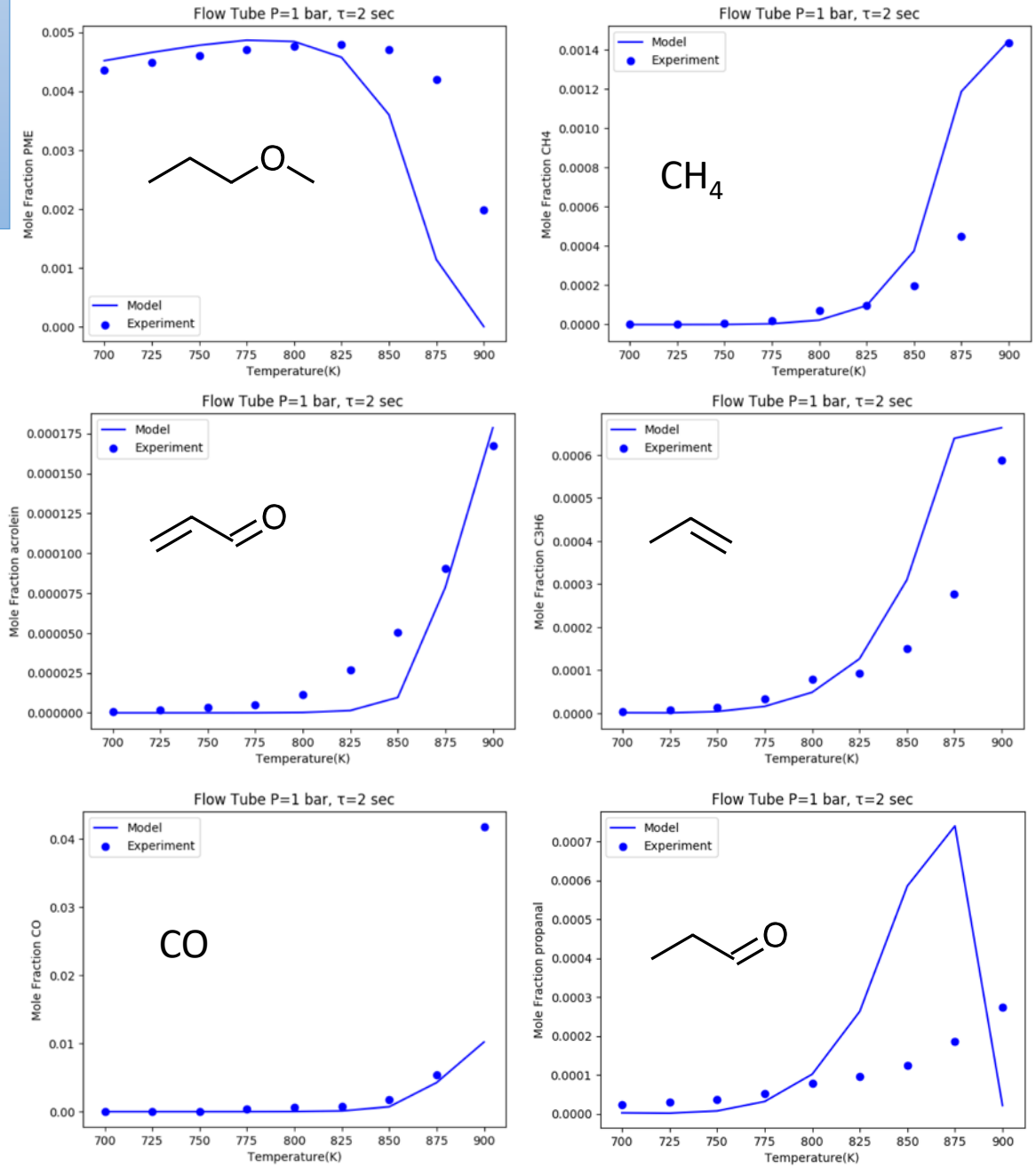
- Helium, oxygen, and fuel are fed at the front of the reactor
- The quartz tube is heated in a ceramic furnace
- MPE: 0.5 mol%, Oxygen: 9.5 mol%, Helium: 90 mol%- dilute conditions used to maintain plug flow conditions
- Helium flow was adjusted to keep a constant residence time of 2s at all temperatures investigated
- Temperature range was 700K to 900K
- Experiments were performed at 1 atmosphere

Species Analysis: Dual Gas Chromatographic System

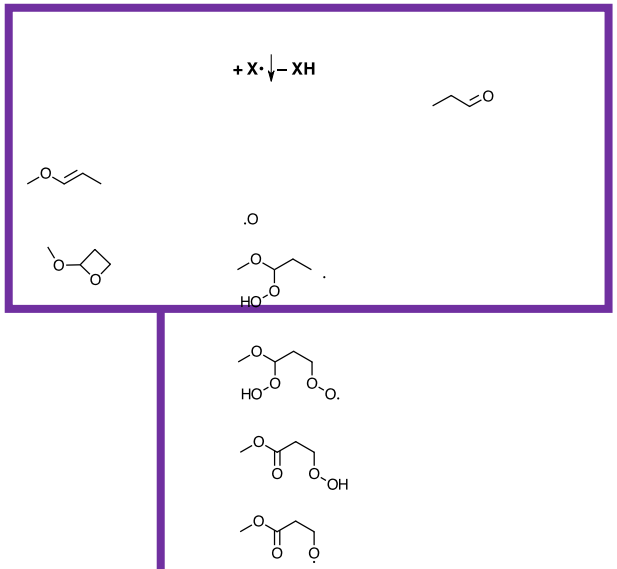
- Dual GC system is equipped with an inert gas sampling line (enclosed in copper for heat transfer), equipped with a vacuum pump for filling the GC sample loops, which is heated to 95°C to avoid condensation in the line
- Five detectors allow for analysis of the full range of hydrocarbons, most oxygenates, and low MW gases
- GC 1: Two 60m DB-1 columns for simultaneous analysis of C4+ hydrocarbons quantitation (FID) and positive ID by mass spec
- GC 2: Dean switch with 3 columns: Quantitation of low MW gases (e.g. methane and ethane), CO, and CO2 (FID + 2 TCDs)

Flow Reactor Results

- Kinetic model fits experimental results
- Exception is propanal – model over estimates yield
  - Removal could be underestimated

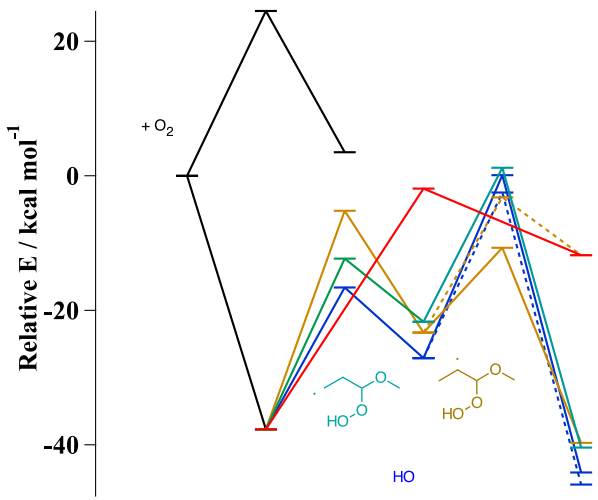


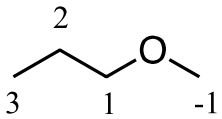
Quantum molecular modeling



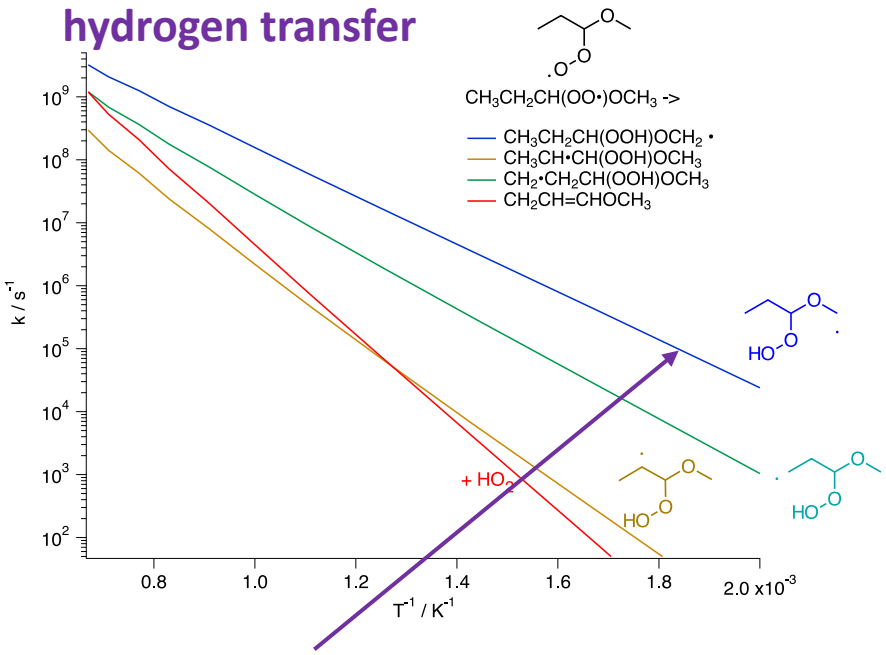
- **G4** level of theory – 0.83 kcal mol^{-1} accuracy (G3/5 set)
- **B3LYP/6-31G(2df,p):** Geometries, vibrational frequencies, IRC calculations, hindered rotor calculations
- **Potential energy surfaces (PES)**: barriers and reaction energies
- Transition states => **Intrinsic Reaction Coordinate (IRC)**
- Hindered rotors
- **Transition State Theory (TST)** for rate constants

PES for C1 radical



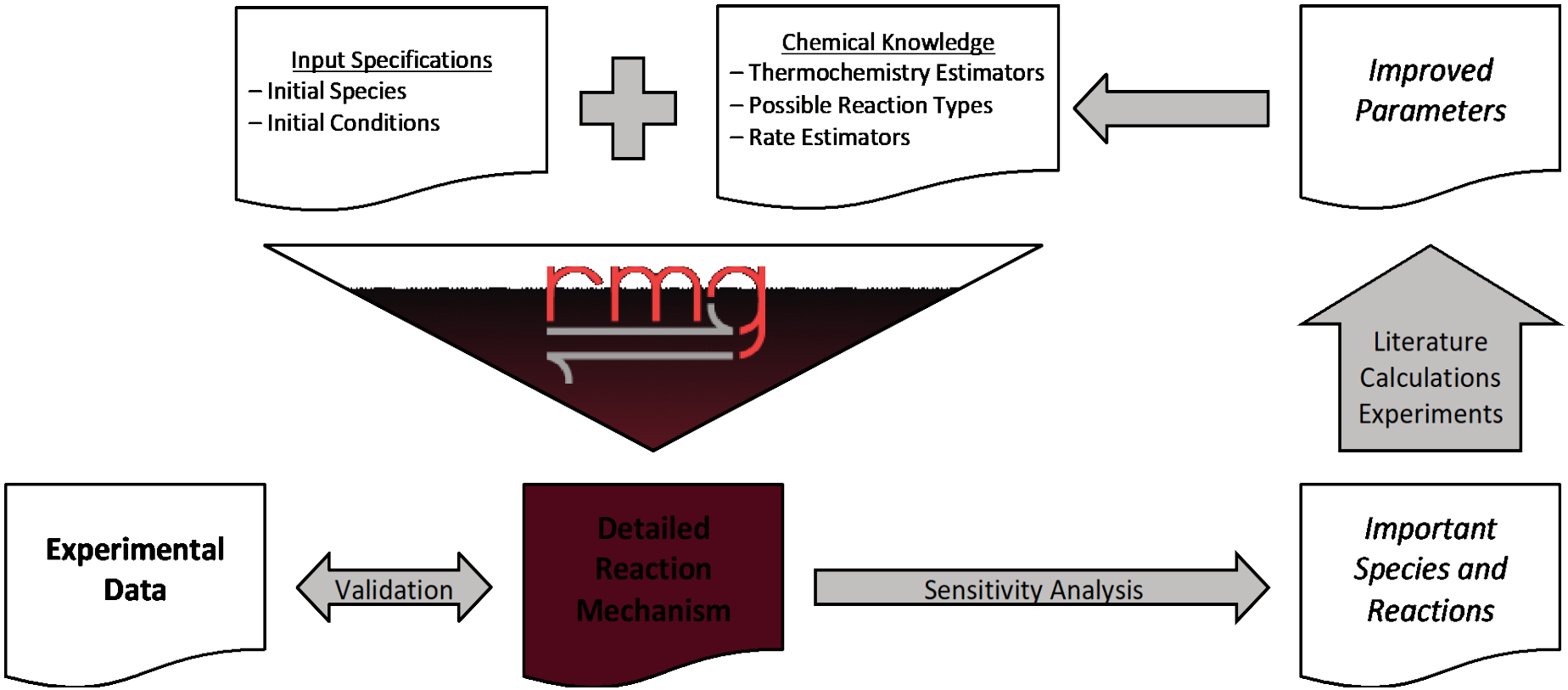


Rate constants for intramolecular hydrogen transfer



Transfer from C-1 carbon dominates

Reaction Mechanism Generator (RMG)



Gao et al. 2016

How RMG works

```
entry(
    index = 1,
    label = "H + O2 <=> O + OH",
    degeneracy = 1,
    kinetics = Arrhenius(
        A = (1.0504e+14, 'cm^3/(mol*s)'),
        n = 0,
        Ea = (15310, 'cal/mol'),
        T0 = (1, 'K'),
    ),
)

entry(
    index = 2,
    label = "OH + H2 <=> H + H2O",
    degeneracy = 1,
    kinetics = Arrhenius(
        A = (2.0671e+08, 'cm^3/(mol*s)'),
        n = 1.51,
        Ea = (3437, 'cal/mol'),
        T0 = (1, 'K'),
    ),
)
```

Inlet conditions and composition (T, P, X)

rmg

Kinetic model

CHEMKIN

Cantera

RMS

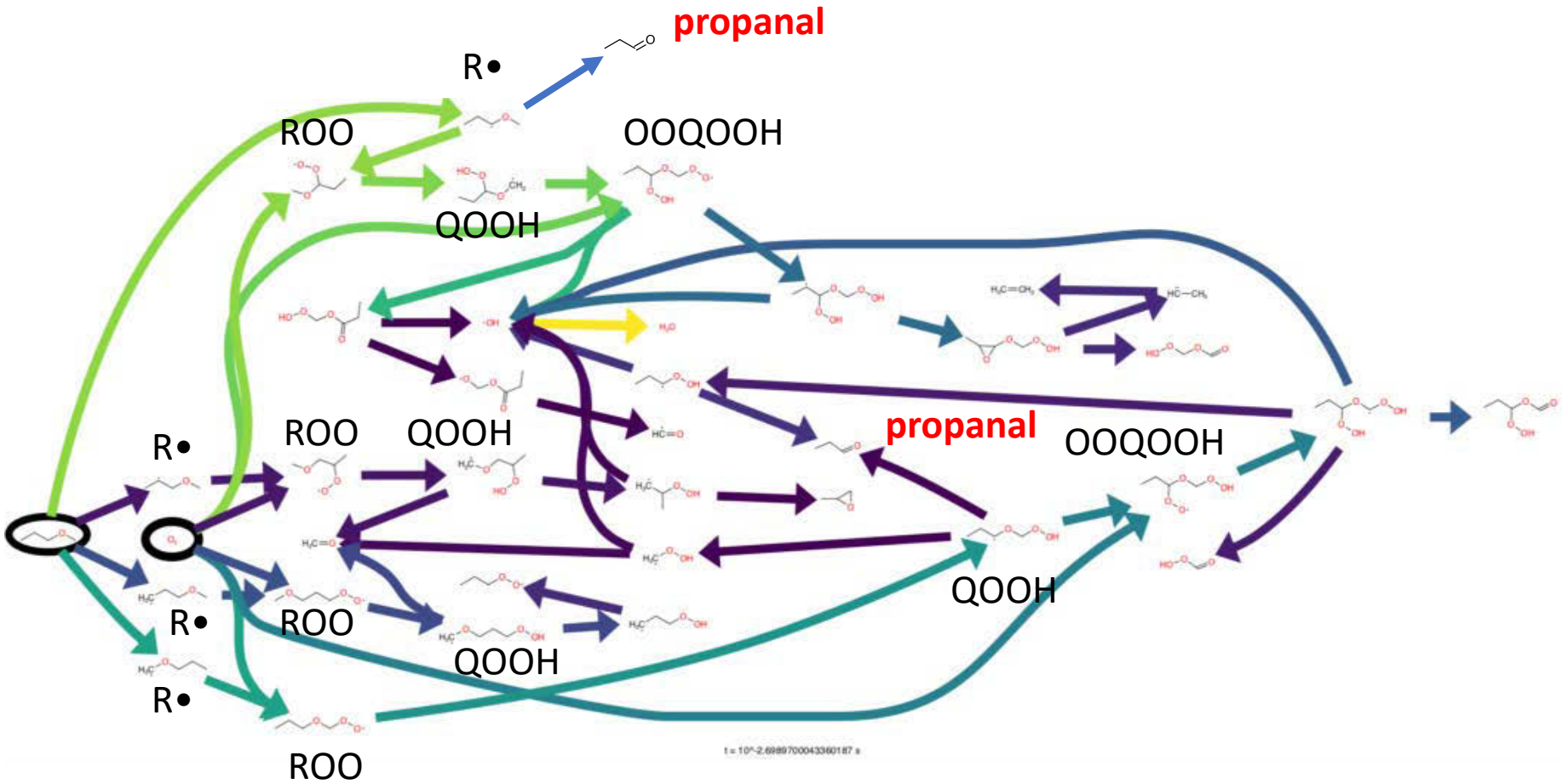
Tolerance

$$\frac{R'}{R_{char}} \overset{?}{>} \varepsilon$$

$$R_{char} = \sqrt{\sum_j R_j^2}$$

Termination criteria (time, conversion, or flux ratio)

Reaction Pathways from Kinetic Model

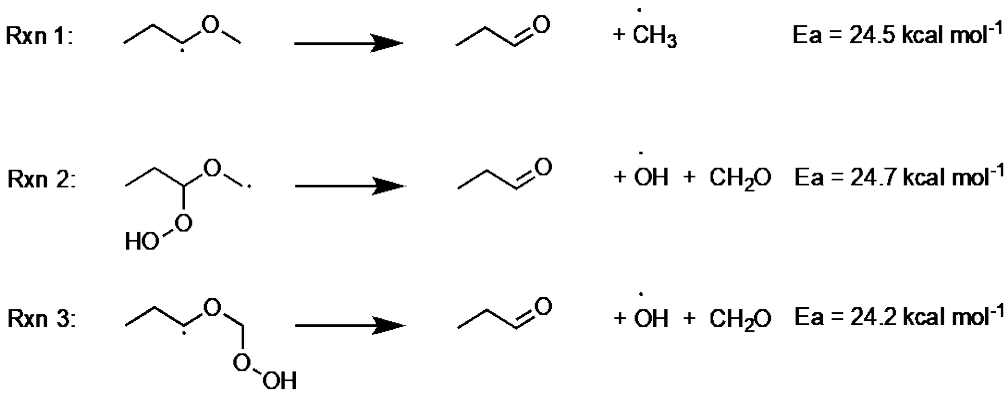


- Typical autoignition chemical pathway
- Propanal side reactions calculated

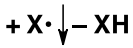
Reactions of Propanal

- Formation of propanal leads to radicals
- Weak C-H bonds in propanal (88 kcal mol^{-1})
- Subsequent autoignition reactions can lead to

Reactions forming propanal in model:

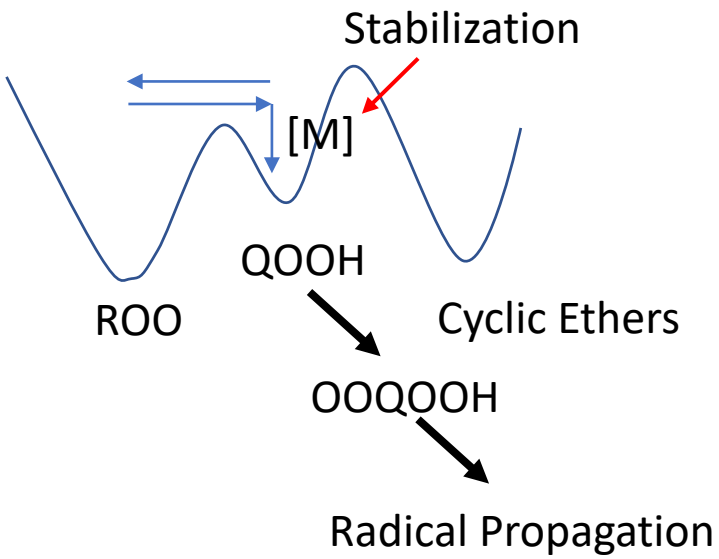


Potential reactions of propanal:



Future Work: Pressure Dependence

- High pressures stabilize QOOH, prevent returning to ROO
- Enables second O_2 addition to OOQOOH and further radical propagation
- We need to improve estimates of stabilization



Conclusions

- Autoignition chemical pathway can describe kinetics and products of methylpropyl ether oxidation
- Existing model needs improvements for pressure dependence
  - Pressure dependence of ROO -> QOOH -> OOQOOH
- Model overpredicts propanal formation
  - Need to improve reaction chemistry of propanal

Acknowledgements

Thank you!!!

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Gina M. Fioroni
National Renewable Energy Laboratory
Golden, CO
gina.fioroni@nrel.gov

www.nrel.gov

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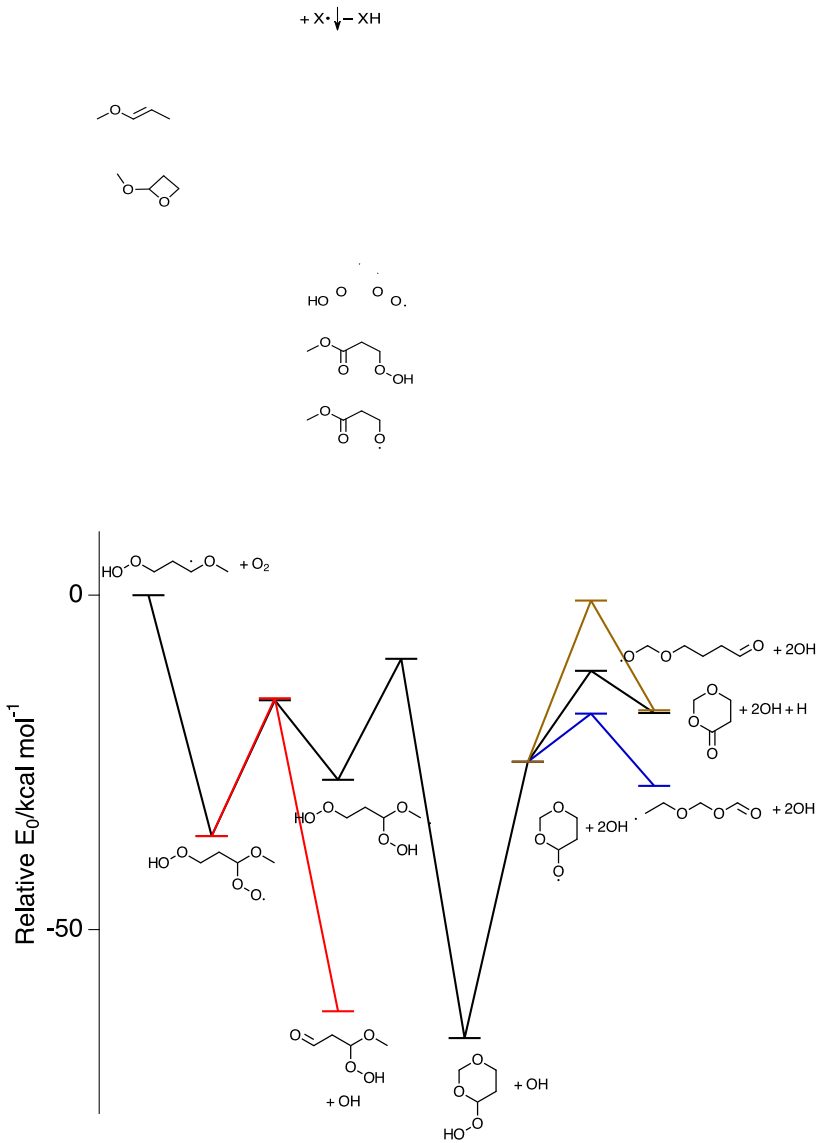
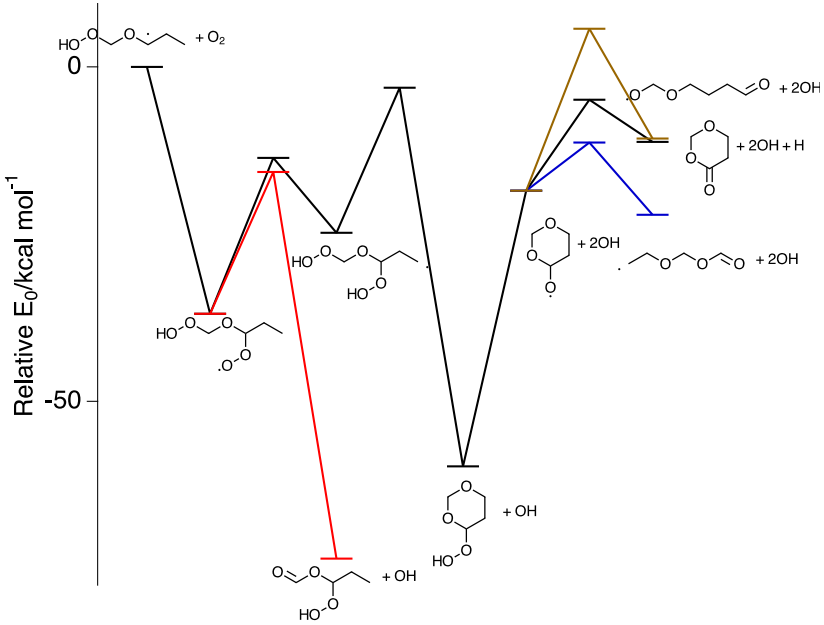
Extra Slides


+ X· ↓ – XH
Relative E0/kcal mol-1
0
-50
+ O2
+ 2OH
+ 2OH + H
+ OH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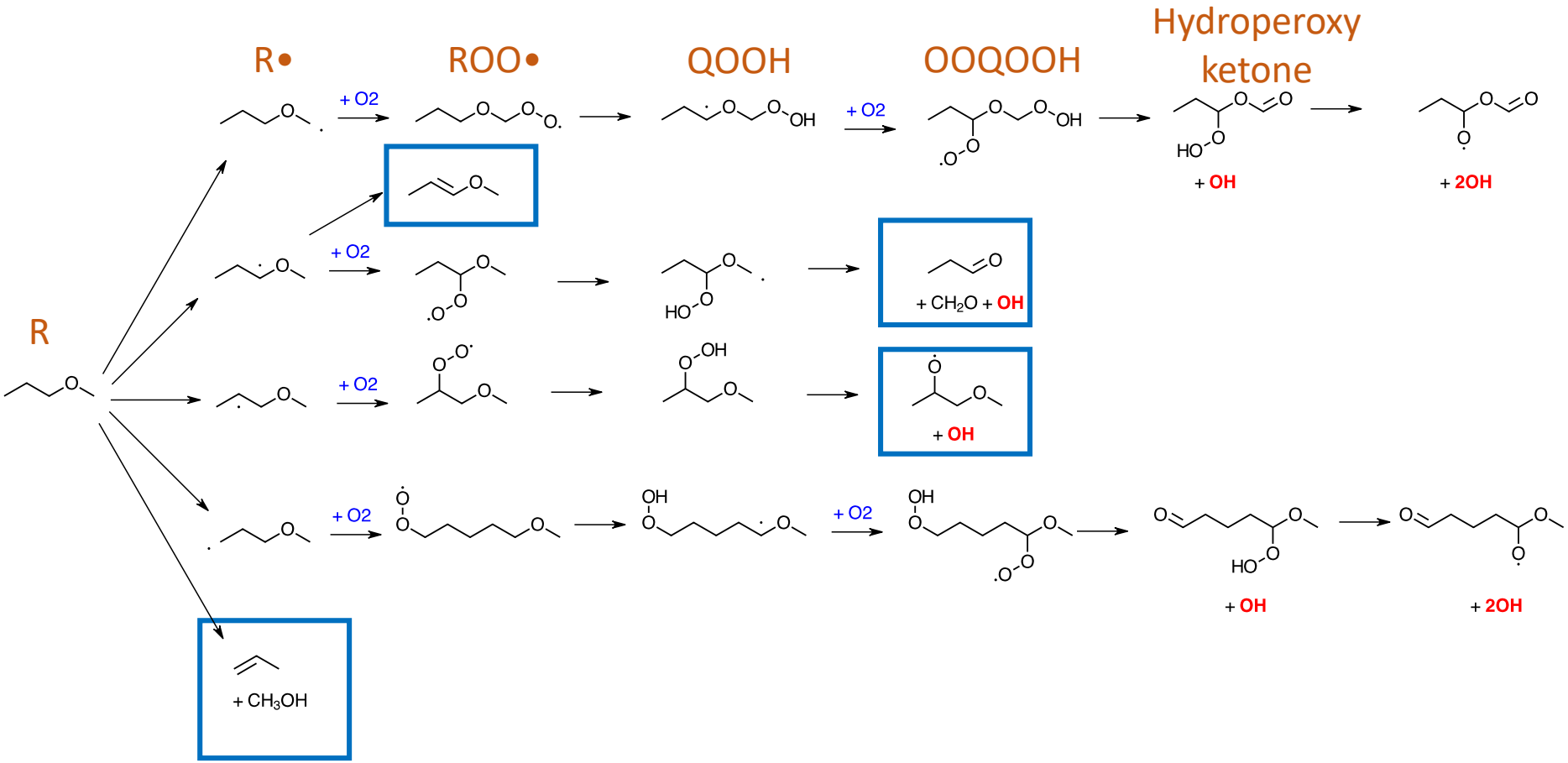
R
R•
ROO•
QOOH
OOQOOH
Hydroperoxy ketone
+ O2
+ OH
+ 2OH
+ CH2O + OH
+ CH3OH