Impact of Fuel Structure on Ignition Kinetics

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The Impact of Alternative Fuels on Combustion Kinetics
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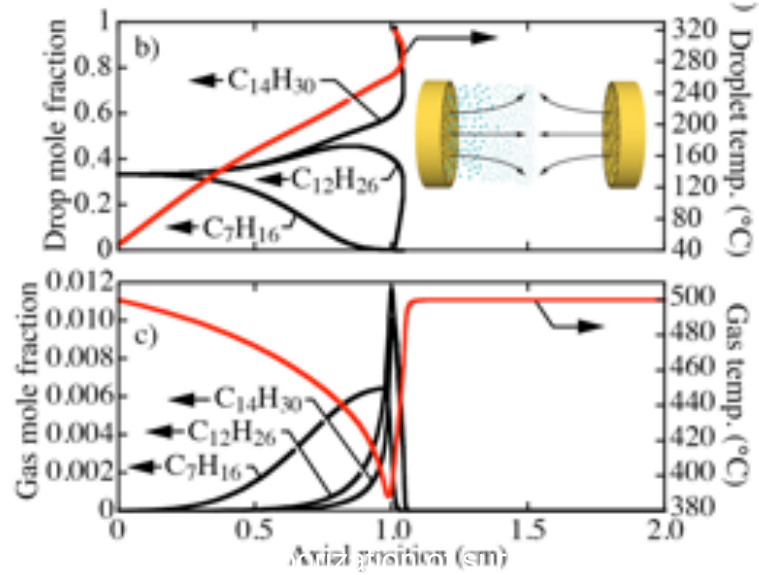
Objective:

- Develop improved models to assess impact of alternative fuels on Navy combustors
- Develop theoretically based rate estimation rules for incorporation into LLNL fuel oxidation mechanisms
- Predict impact of volatility differences of fuels on combustion events
- Deliver mechanisms and mixing models to UTRC for predictions in real combustors



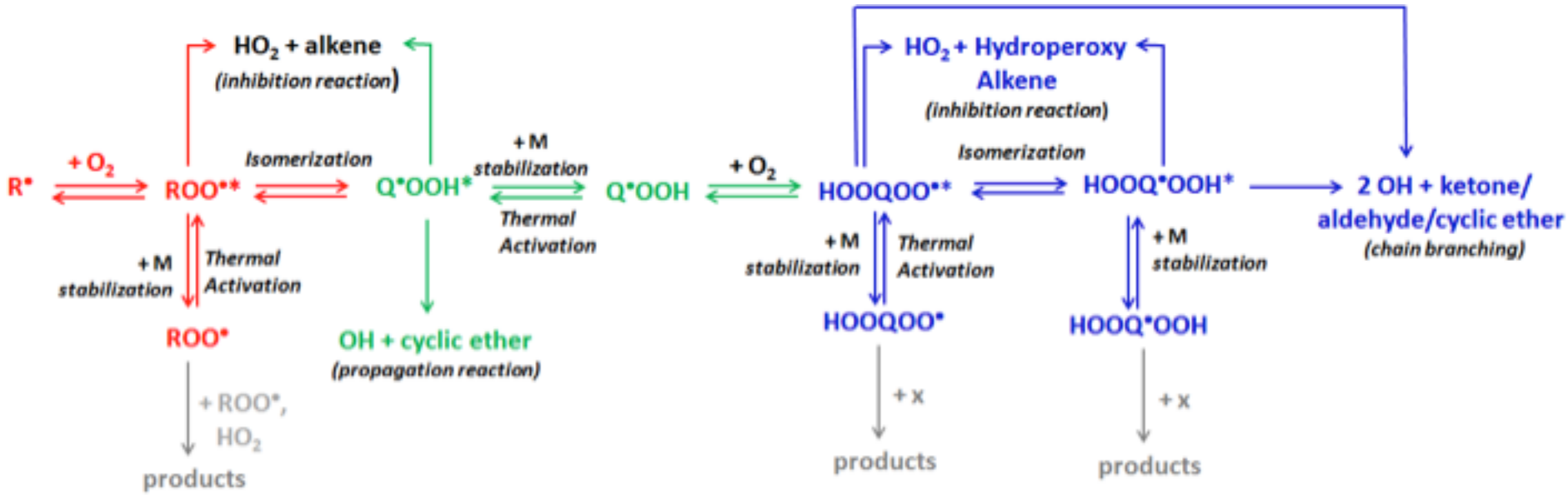
Approach:

- Use high-level electronic structure calculations on small alkane systems to obtain detailed understanding of low-T oxidation chemistry
- Generalize validated individual rate expressions to create rate estimation rules applicable for larger hydrocarbons
- Collaborate with LLNL to incorporate rate rules into their mechanisms
- Develop two-phase flow models to account for impact of vaporization rate on combustion
- Validate models with USNA data

Scientific or Naval Impact/ Results:

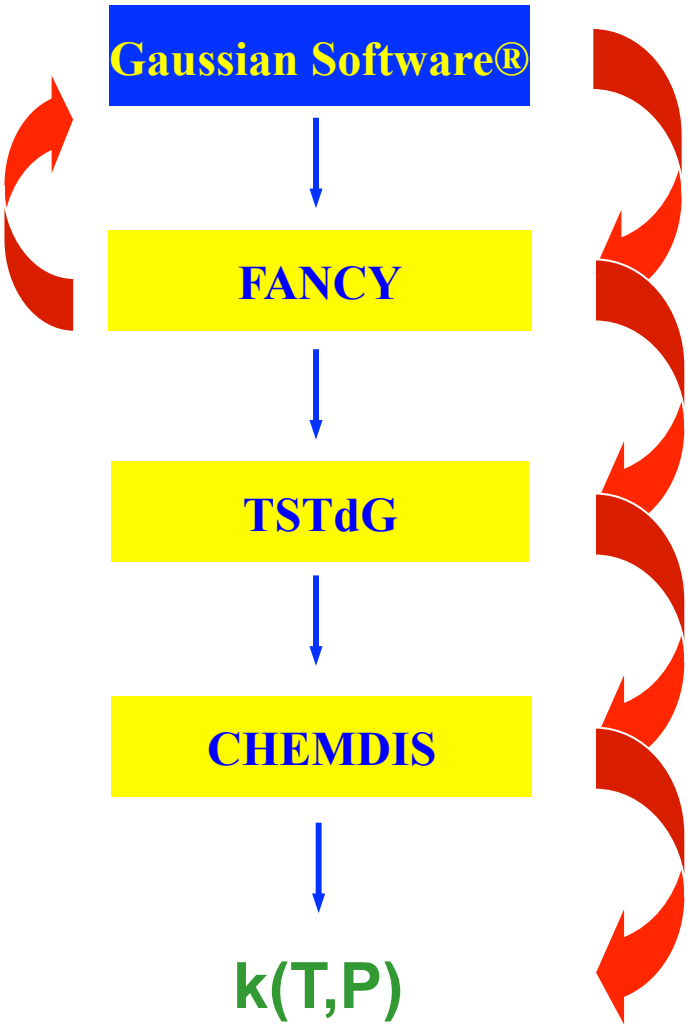
- Developed rate rules for RO_2 reactions and delivered to LLNL
- Demonstrated that high-pressure rate rules suitable for ignition calculations
- Developing rate rules for QOOH reactions
- Developed multicomponent vaporization model and calculated impact of drop size, temperature, pressure, fluid-mechanical strain, droplet composition, droplet size, and droplet loading density

Goal: Develop Rate Rules for Diesel Ignition



Rules needed for RO_2, $Q^{\bullet}OOH$, and $HOOQOO^{\bullet}$ reactions
Both rate constants and thermo important

Path from Electronic Structure Calculations to Pressure-Dependent Rate Constants



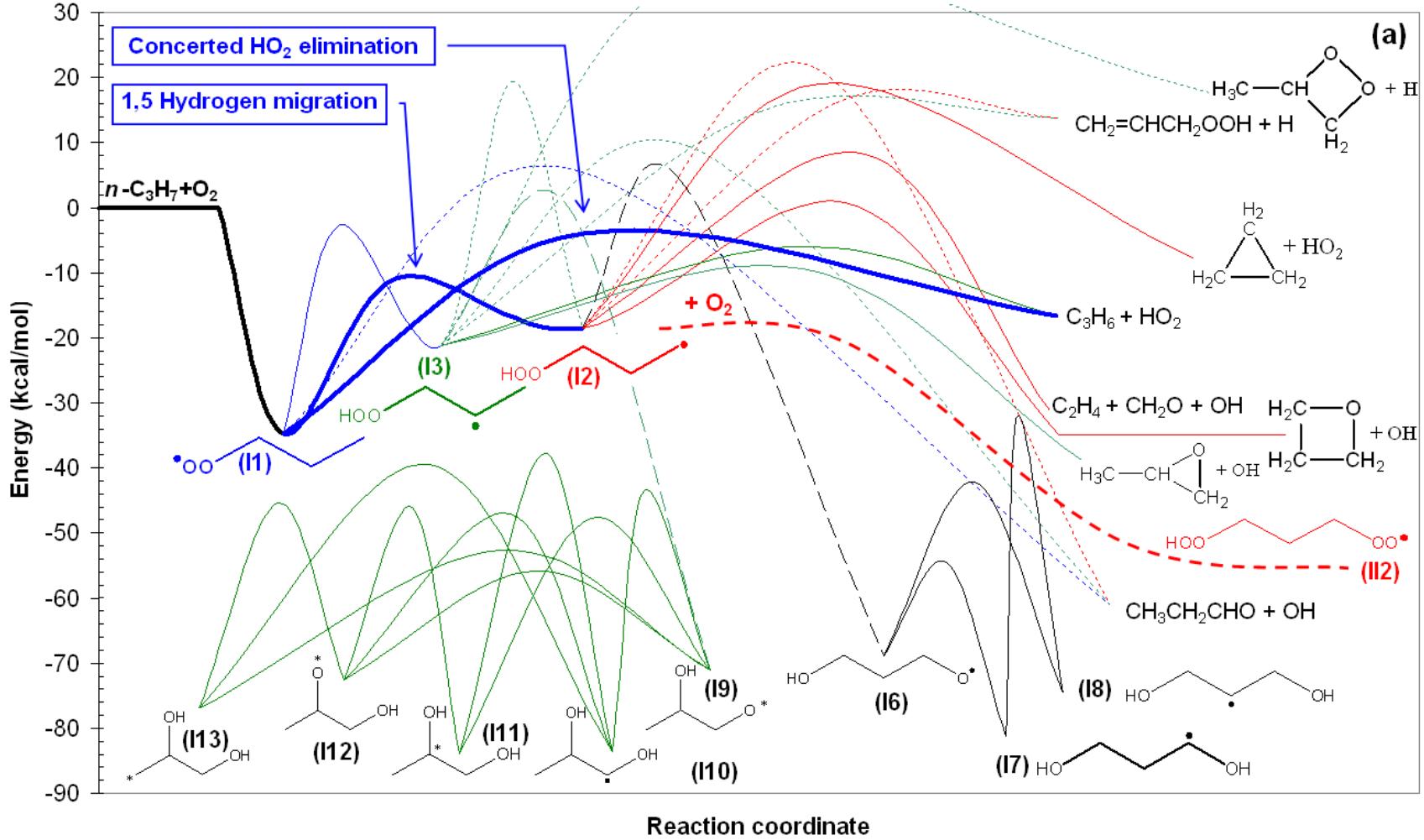
Geometry, Frequencies, Electronic Energy, Dipole Moment, Polarizability, …

Heat of Formation, Entropy, Heat Capacity 3-Freq Representation, NASA Polynomials

High-pressure Rate Constants $k_\infty(T)$ for Elementary Reactions

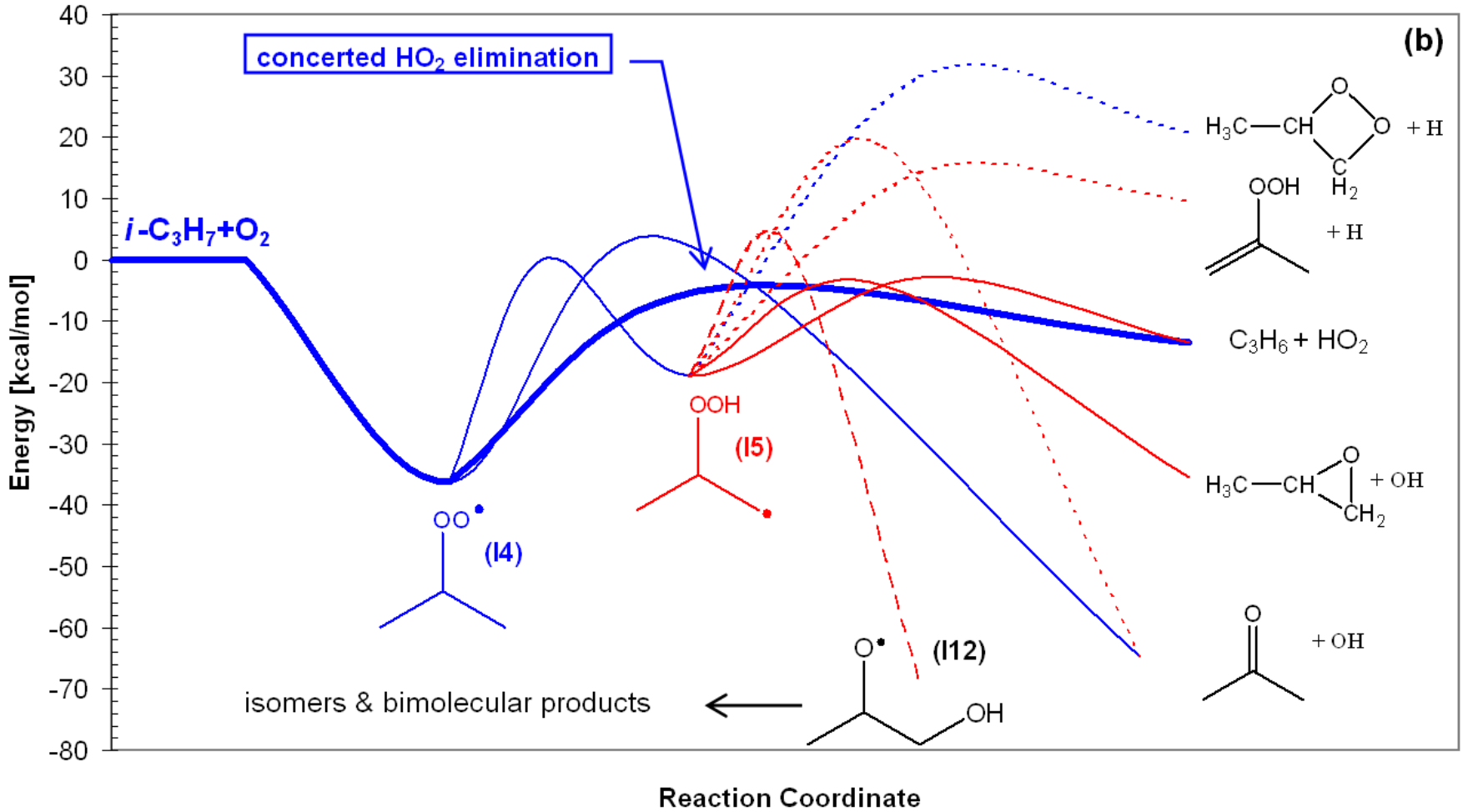
Pressure-dependent Rate Constants k(T,P) for Chemically-activated Reactions

Fast Isomerization of CCCOO• Adduct Leads to Chain Branching



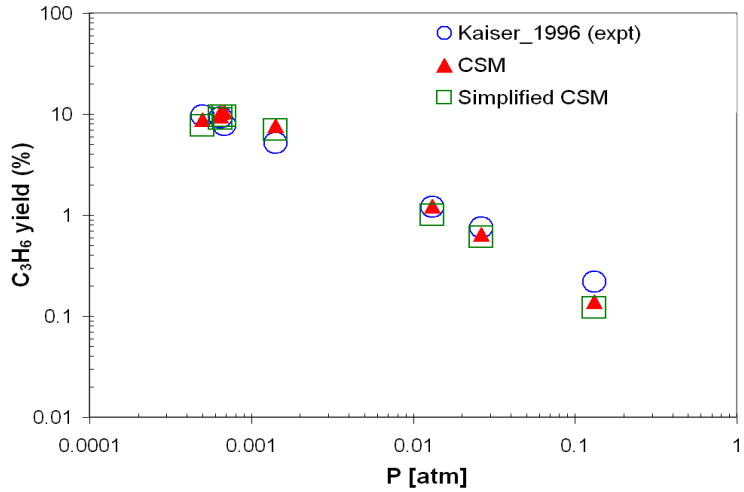
- **Only important pathways for n-propyl + O_2 are *isomerization, concerted elimination and redissociation***

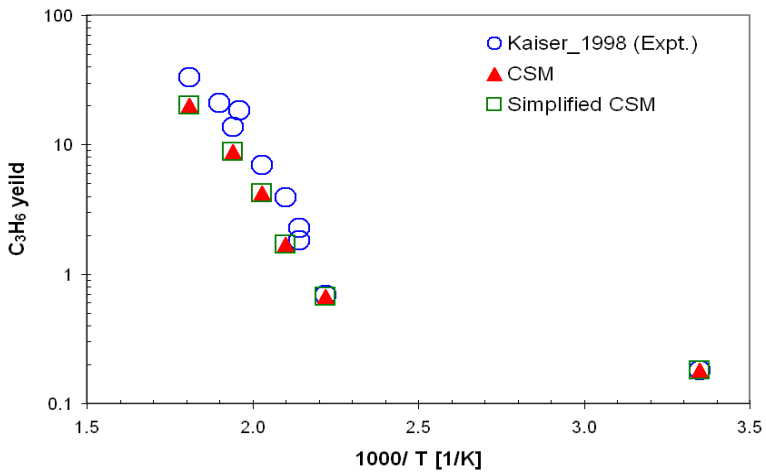
Slower Isomerization of CC(OO•)C Adduct Leads to Chain Inhibition



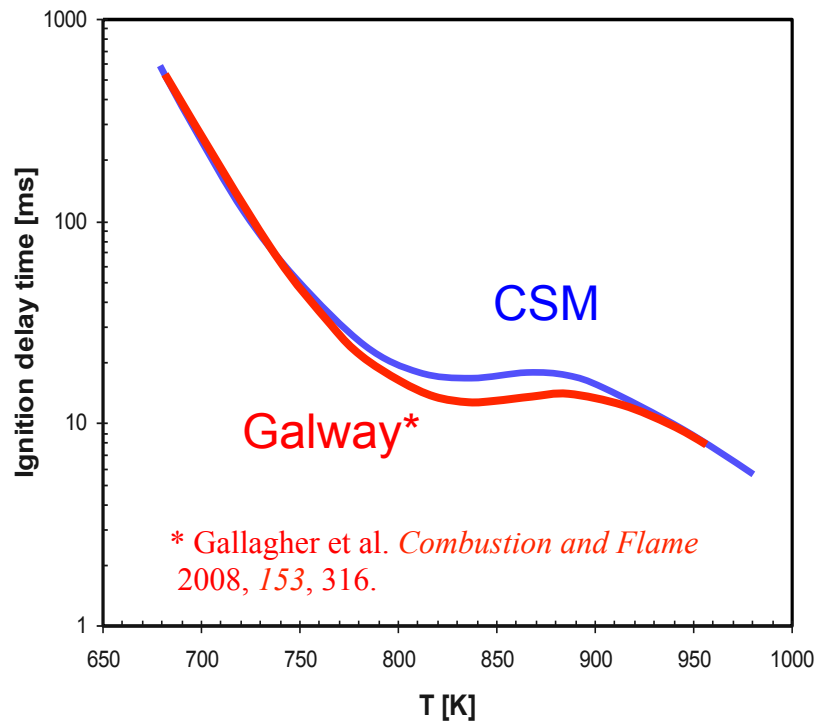
- ***Concerted elimination dominant*** **for isopropyl + O_2**
  – branching pathway inhibited
- **Detailed calculations show other pathways can be neglected**

Unadjusted Ab-initio Predictions Quantitatively Describe Propane Oxidation





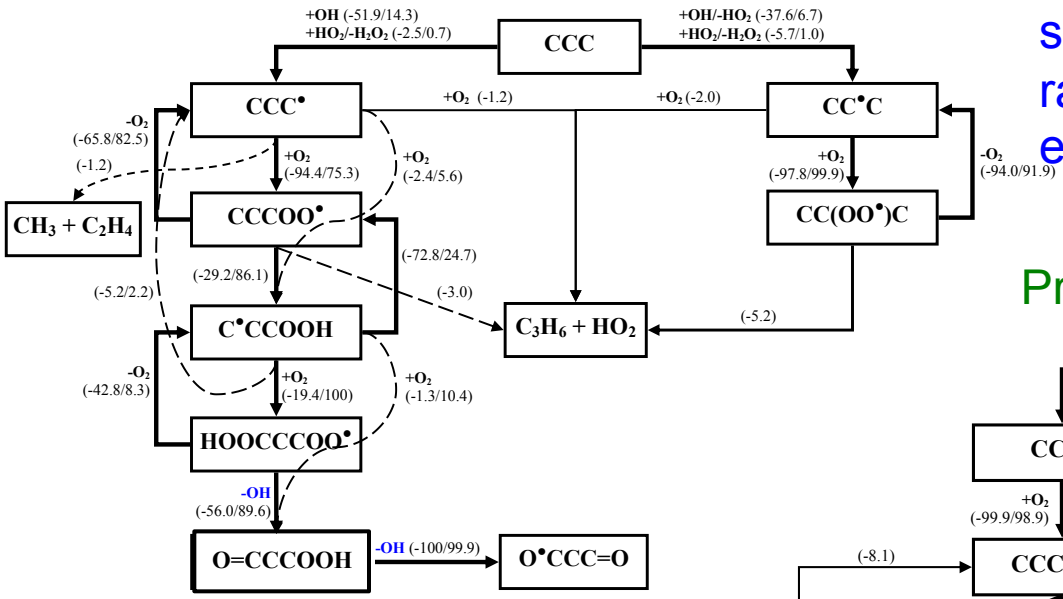
Huynh, L.K., H.-H. Carstensen, and A.M. Dean, J. Phys. Chem. A, 2010. **114**: p. 6594–6607.



- **However, reaction pathways in CSM model much different from Galway mechanism (that uses LNLL rate rules)**

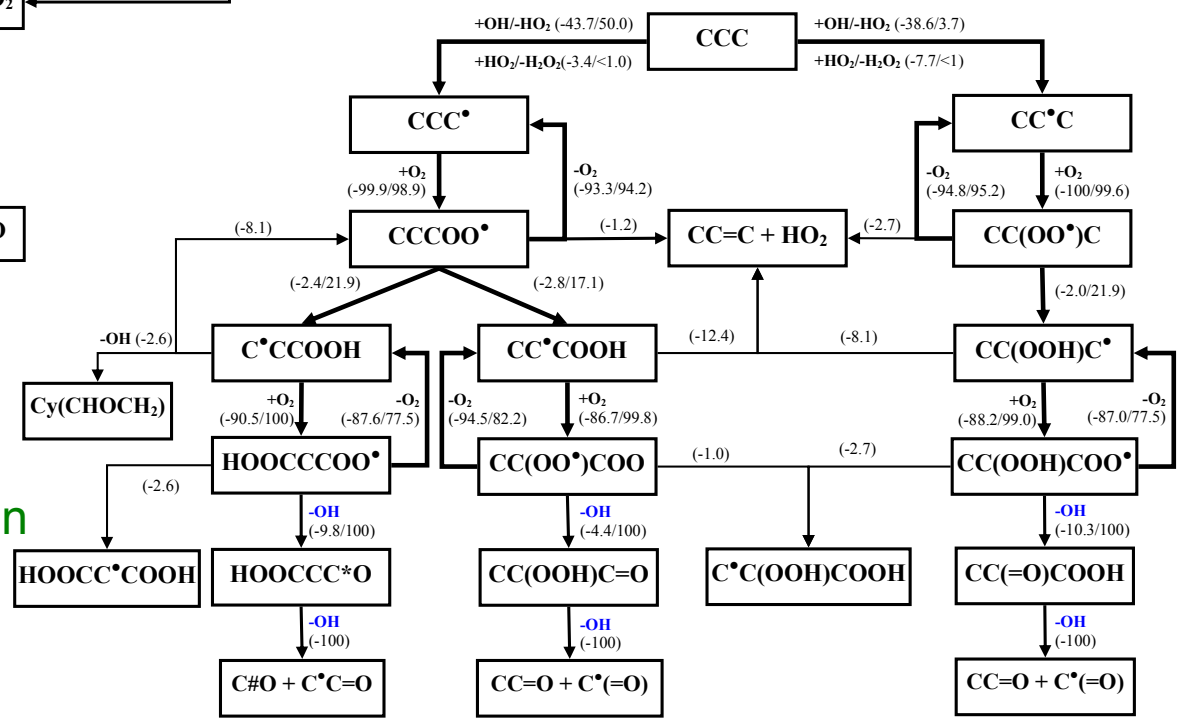
Significantly Different Pathways in CSM vs. Galway Models

Primary Pathways in CSM Model



CCC• dominates ignition kinetics since CC(OO•)C isomerization rate slow relative to concerted elimination of HO_2

Primary Pathways in Galway Model

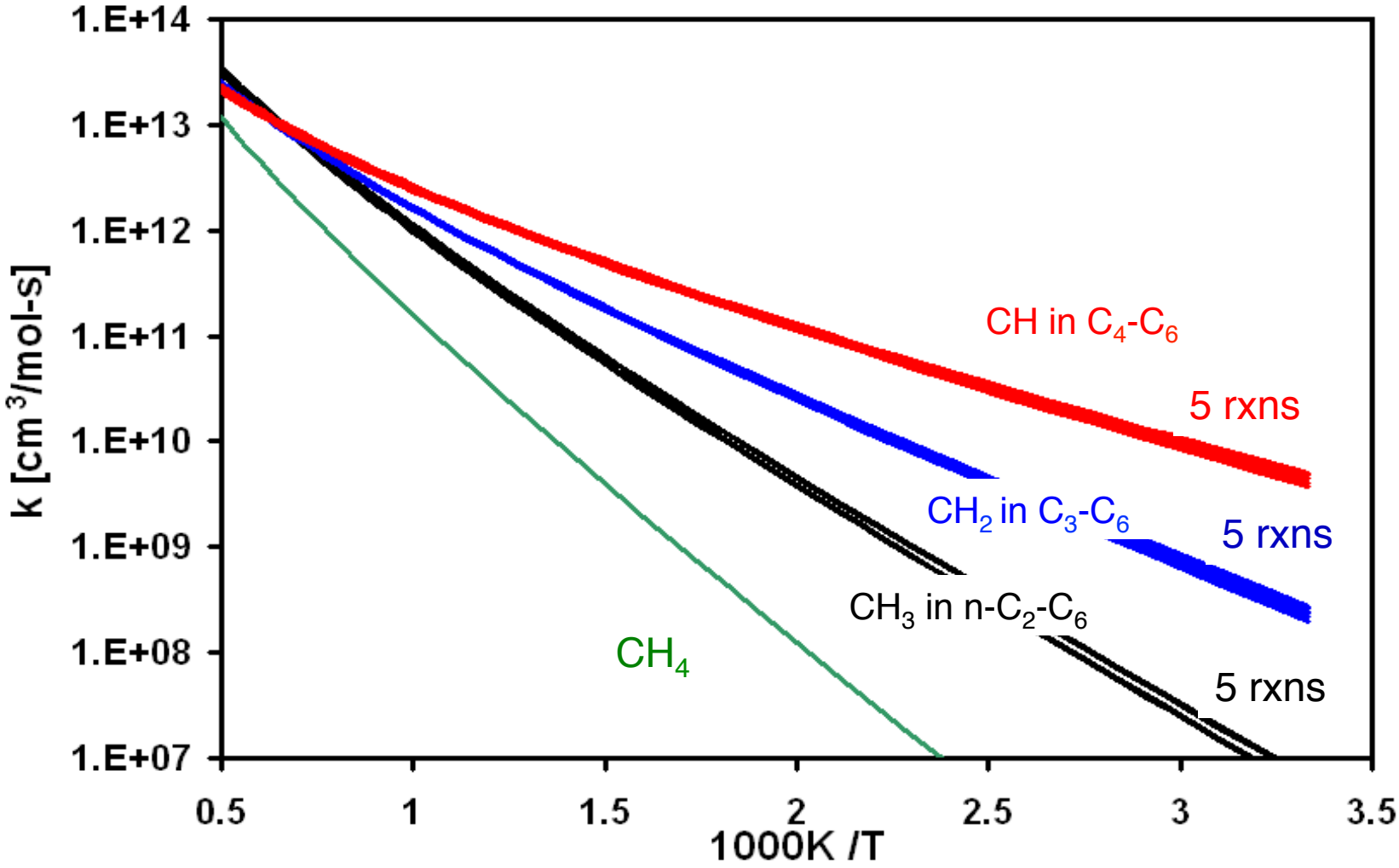


- Both CCC• and CC•C important since CC(OO•)C isomerization much faster in this mechanism

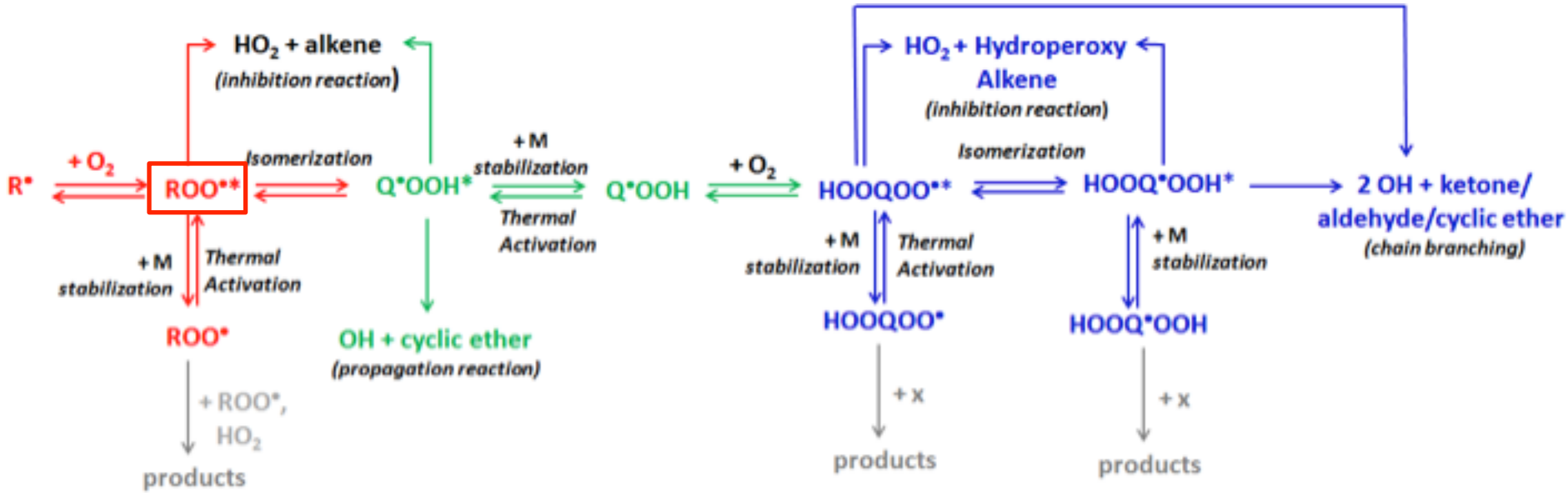
Extension to Larger Hydrocarbons

- Despite complexity of underlying potential energy surfaces, only a few reaction pathways are important.
- Approach to develop rate rules applicable to larger systems:
  - Use high-level theory for C_2-C_6 hydrocarbons
  - Generalize results on a per-site basis and use these for larger species
  - Use rule based rate constants as input for pressure-dependence analysis for recombination and addition reactions
- Transfer rate rules to LLNL for incorporation into their mechanisms

Calculated Rate Constants for a Given C-H Type Are Constant for H Abstraction From Alkanes By H Atoms

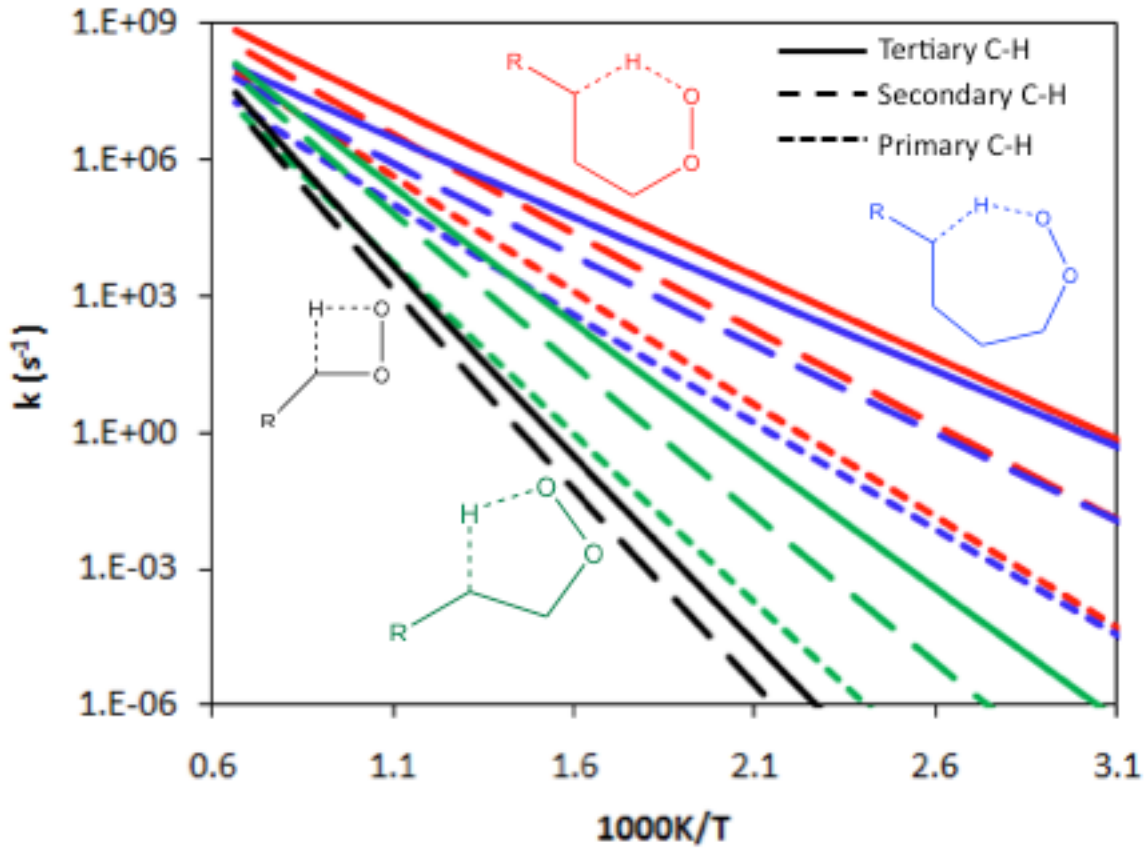


Important R + O_2 Reaction Channels



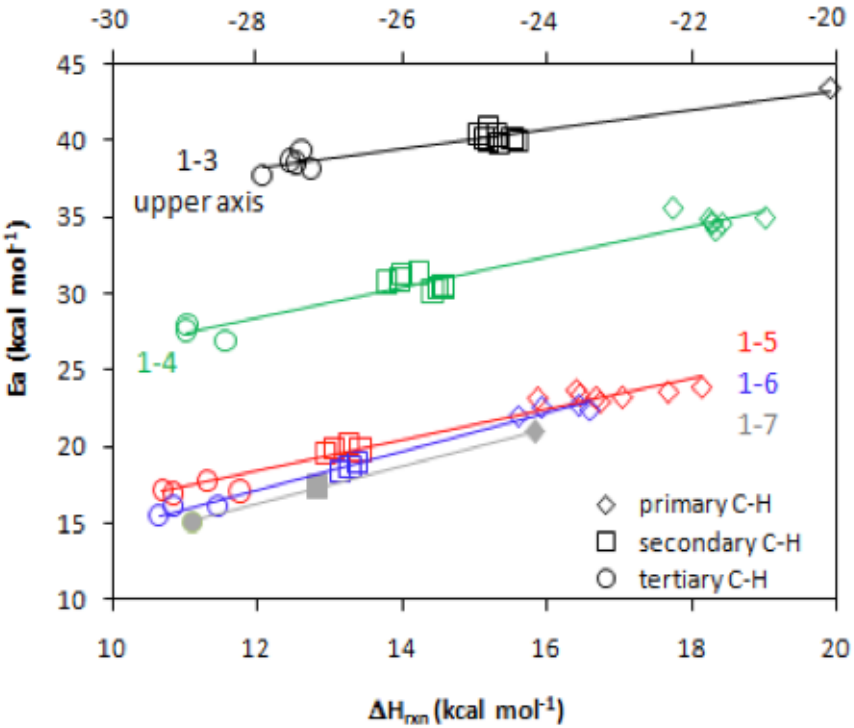
- RO_2 dissociation
- RO_2 isomerization
- RO_2 concerted elimination

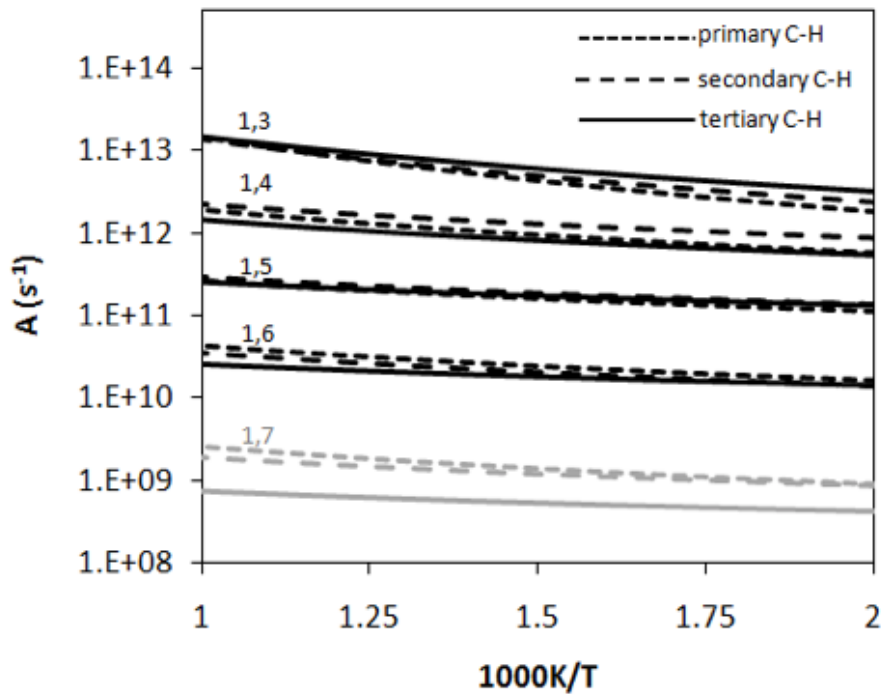
RO_2 Isomerization Rate Sensitive to Fuel Structure



- **Depends on ring size *and* overall thermochemistry.**
- **Significantly different from hydrocarbon analogs**
- **Results consistent with Sharma et al. *J. Phys. Chem. A*, 2010, *114,* 5689.**

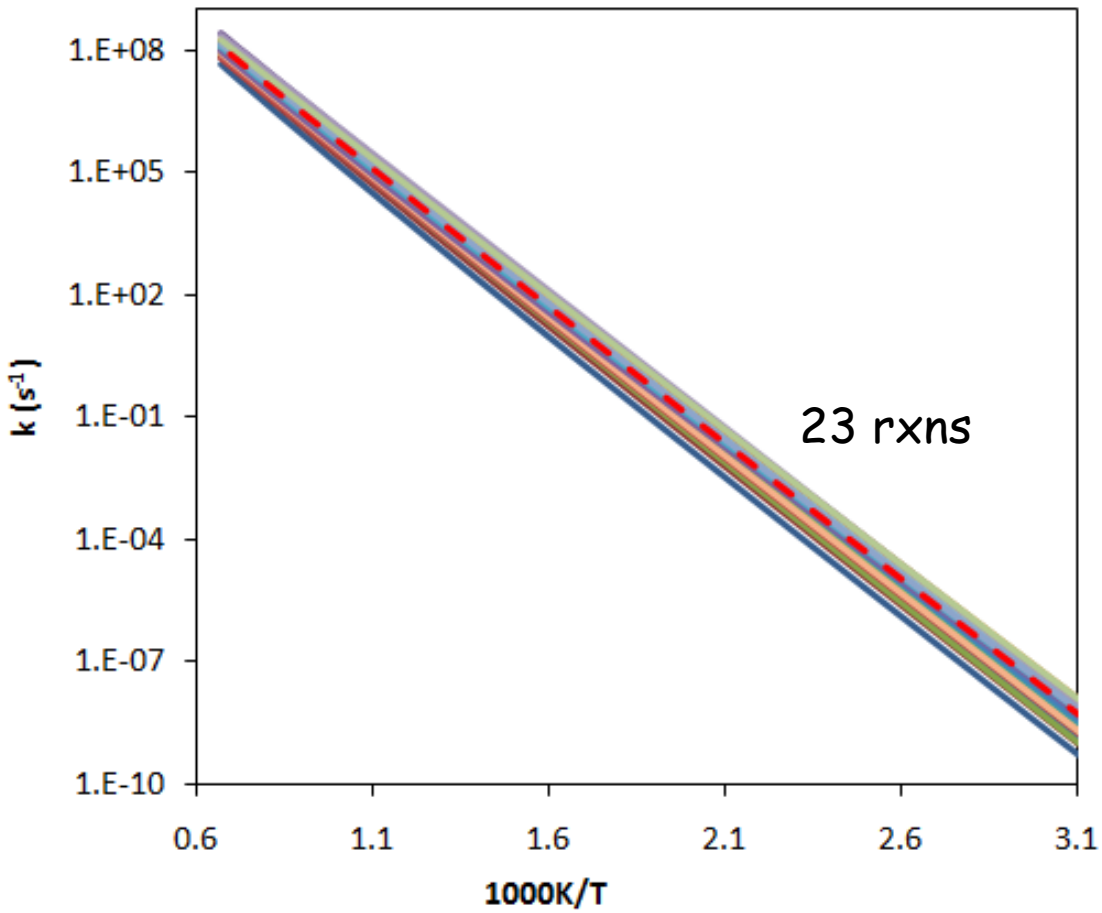
Isomerization Reaction Subsets Group Nicely





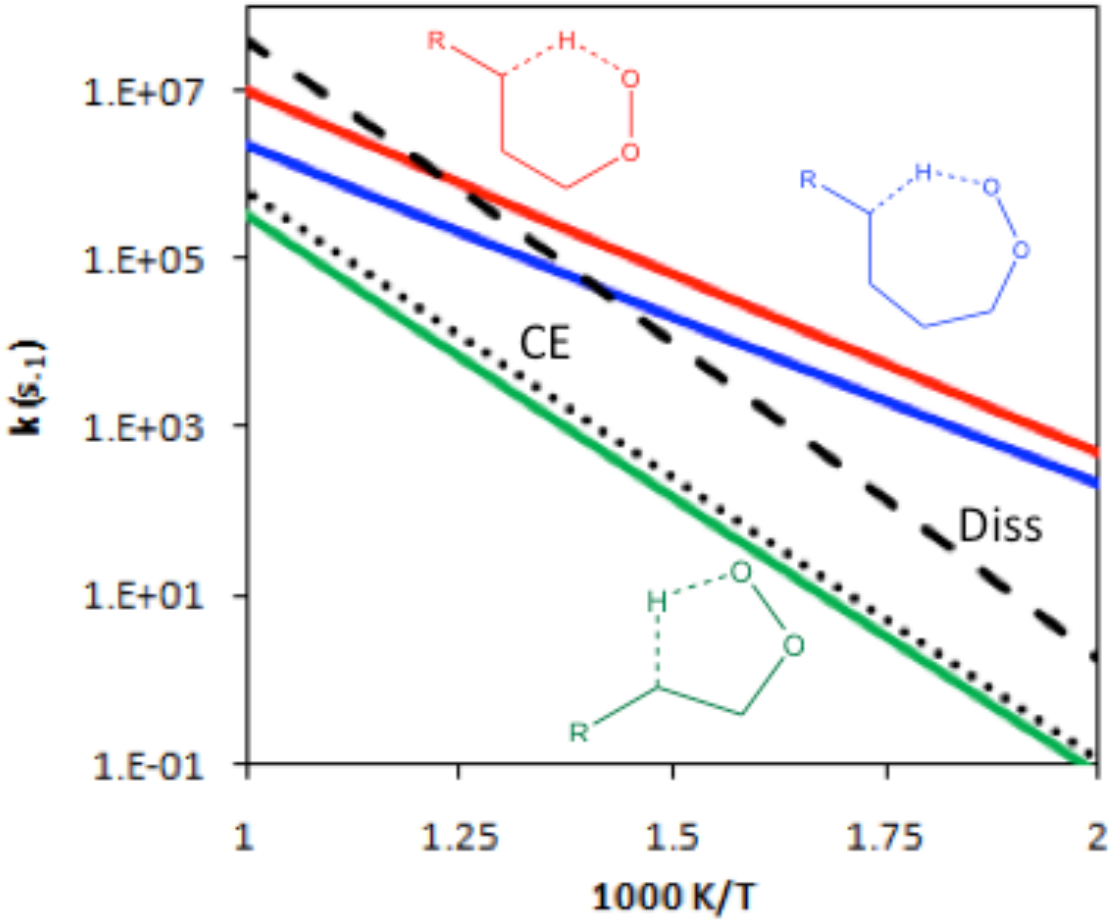
- Calculations allow quantification of Benson's ideas
  - Barrier depends on ring strain and enthaply change
  - A-factor strongly affected by loss of rotors in TS

HO_2 Concerted Eliminations Rate Constants Similar



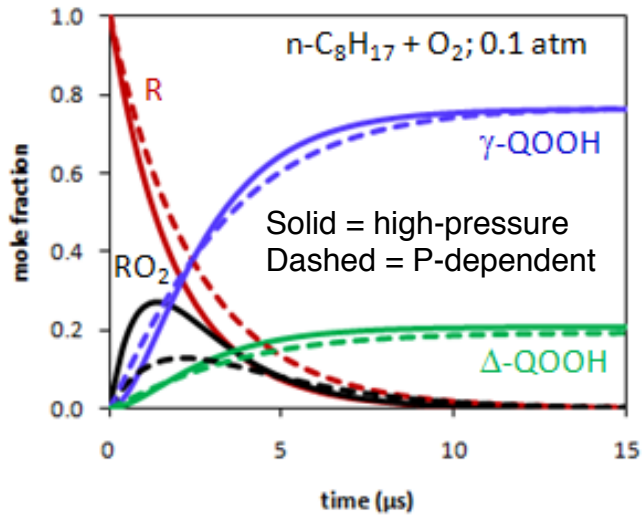
- **Unlike other reactions, very little effect of structure**
- **One rate constant seems sufficient for linear and branched alkyl peroxy radicals**

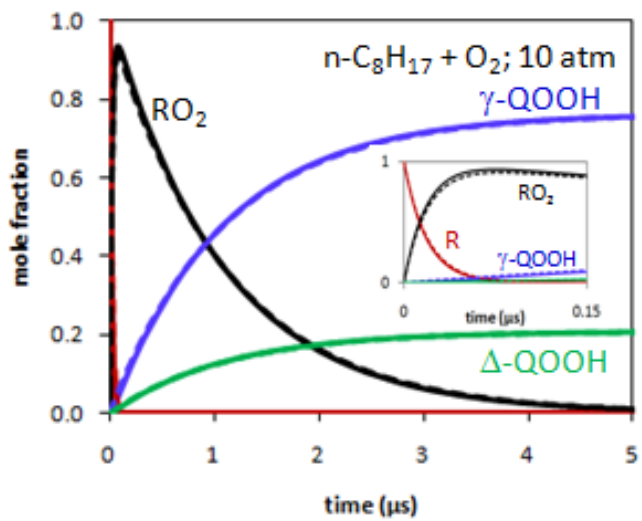
Competition between dissociation and isomerization for RO_2



- 6-and 7-member transition state isomerizations much faster than 5-member

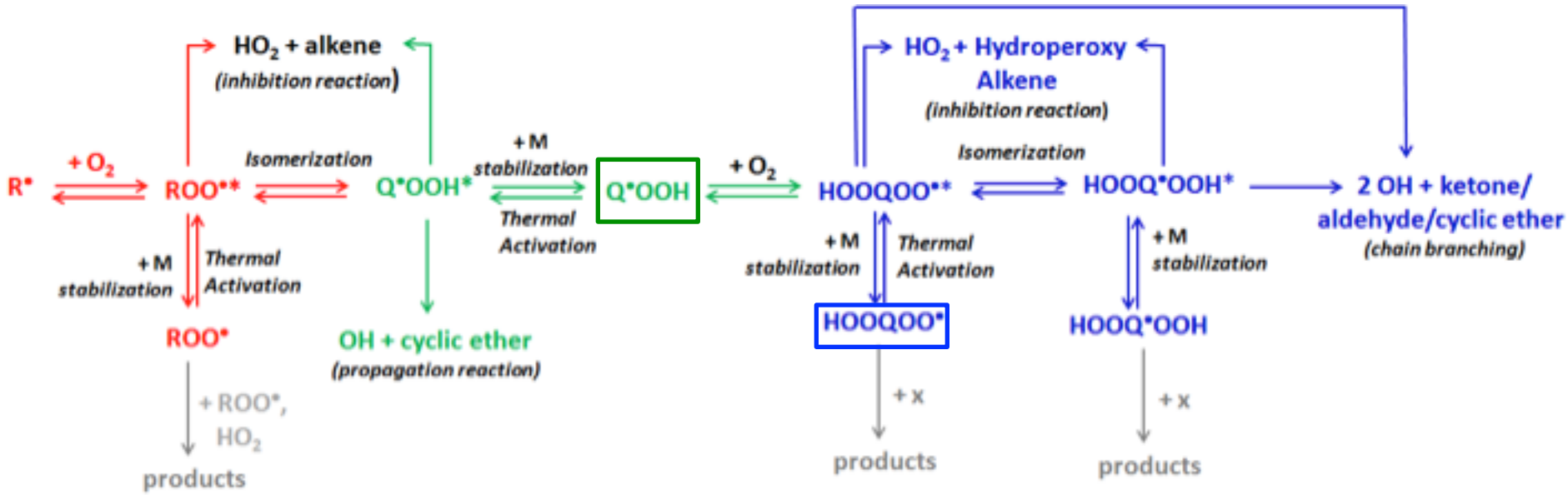
Isomerization Dominates RO_2 Reactions





- **Numerical integration results at 750K with n-C_8 as reactant**
- **Results verify that high-pressure values are adequate**
- **γ-QOOH product reflects faster rate for 6-member TS**
- **7-member TS product next most important**

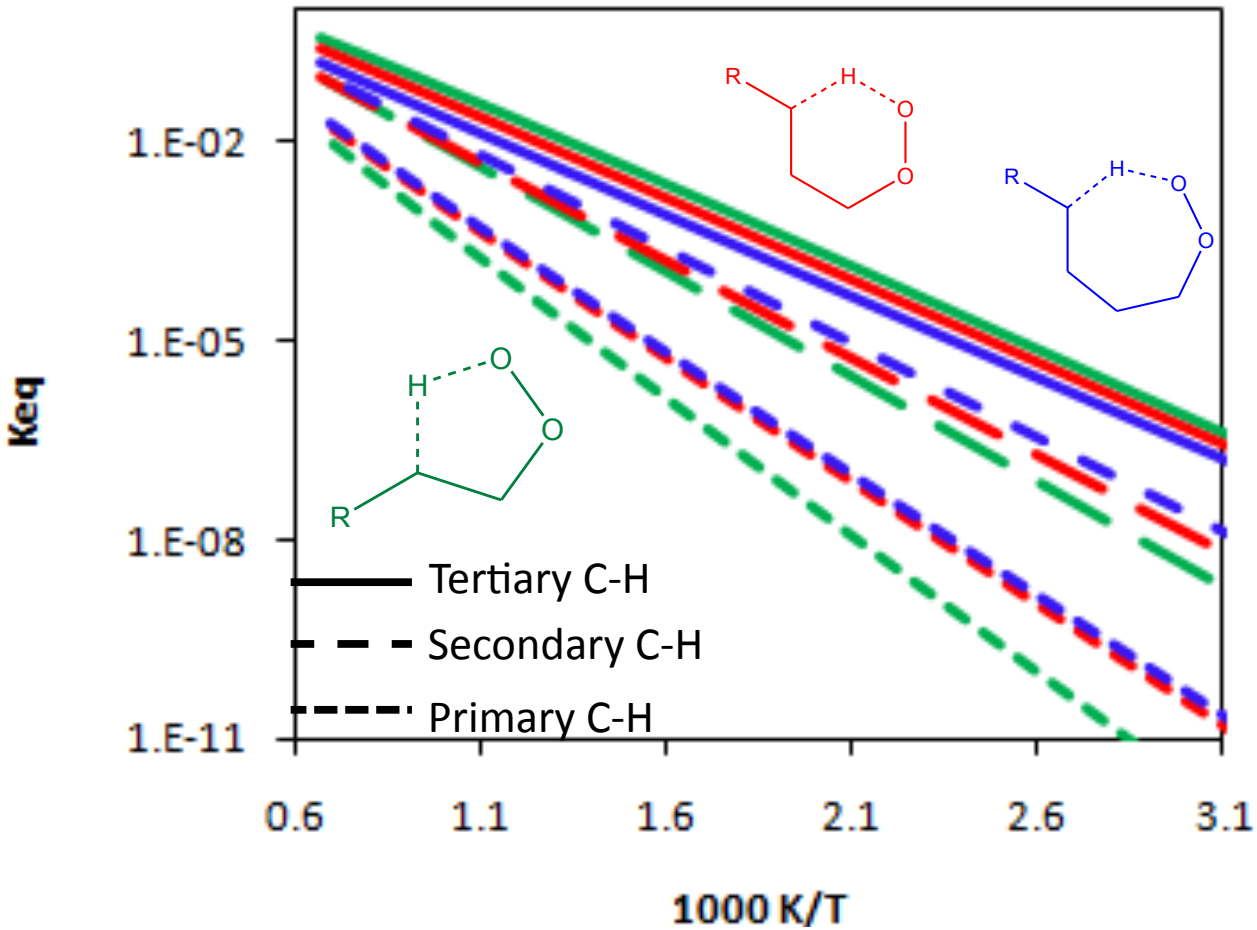
Important Q˙OOH and HOOQOO˙ Reactions



- Q˙OOH cyclic ether formation
- Q˙OOH isomerizations
- 2nd O_2 addition

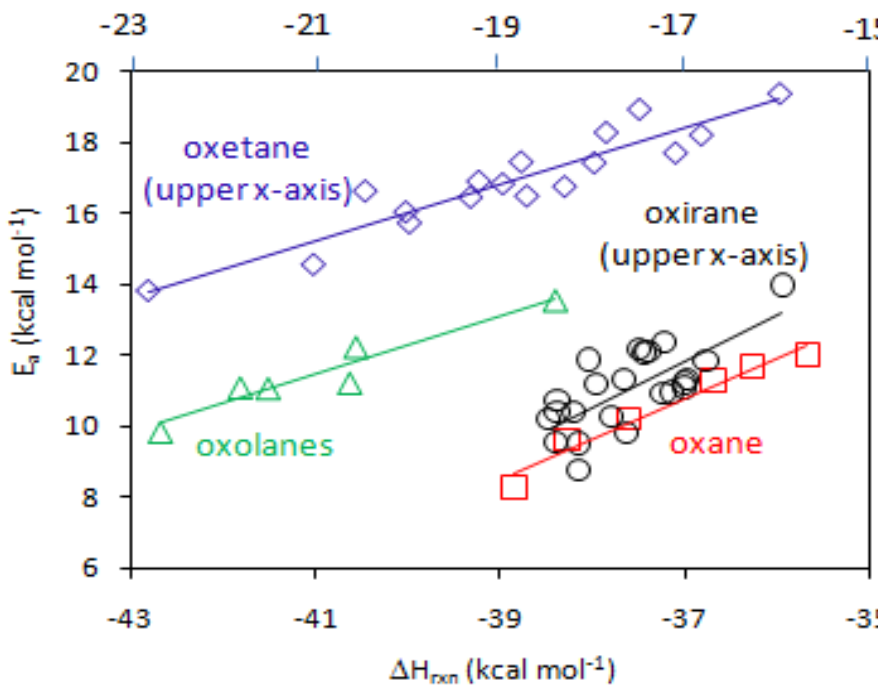
- HOOQOO˙ isomerizations
- HOOQOO˙ cyclic ether formation
- HOOQOO˙ dissociation (in progress)

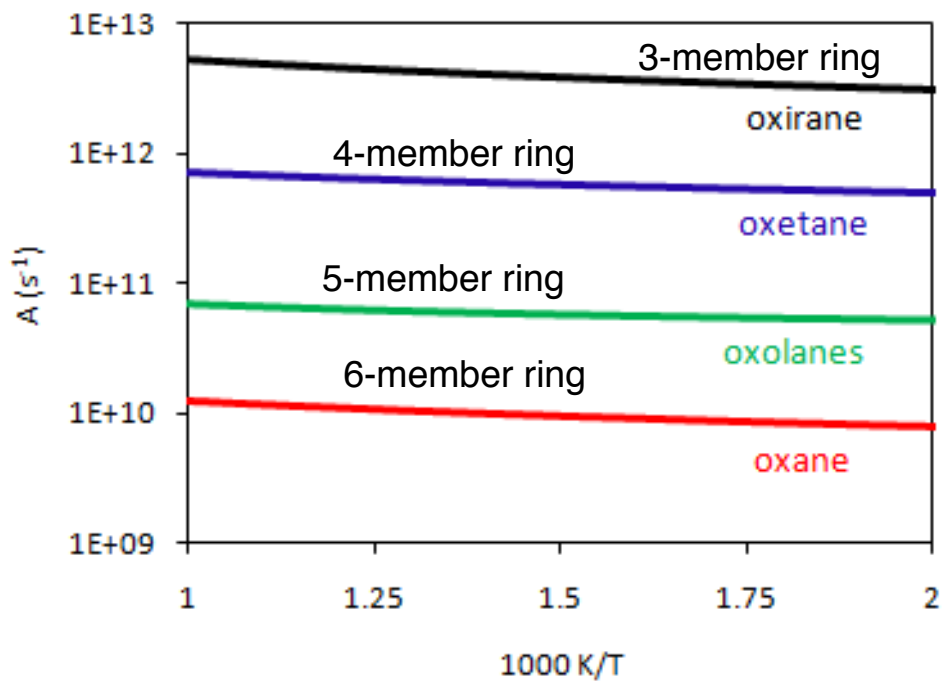
RO_2 = Q˙OOH Equilibrium Sensitive to Structure



- **Equilibrium shifted strongly toward more stable reactants**
- **Expect much higher concentration of tertiary QOOH**

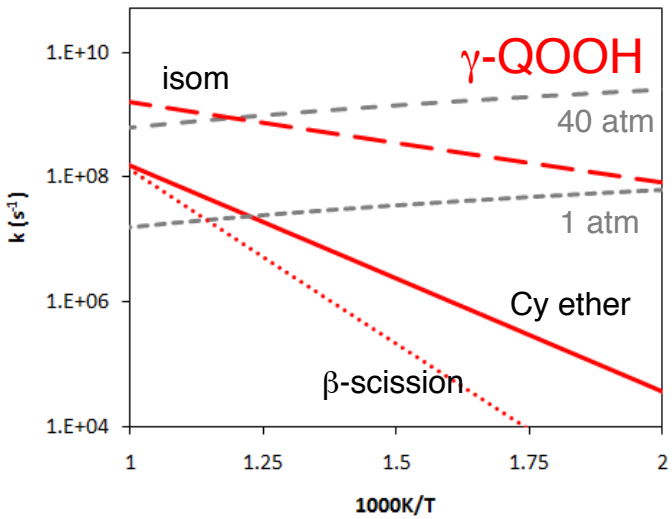
Oxirane Formation Surprisingly Fast

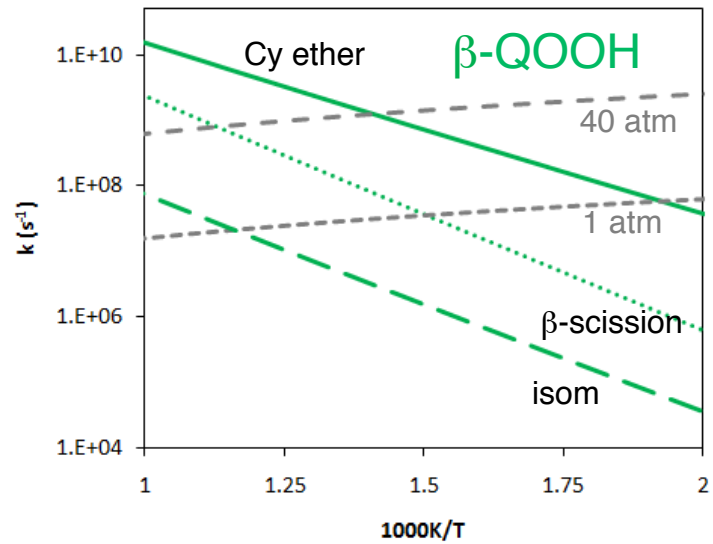


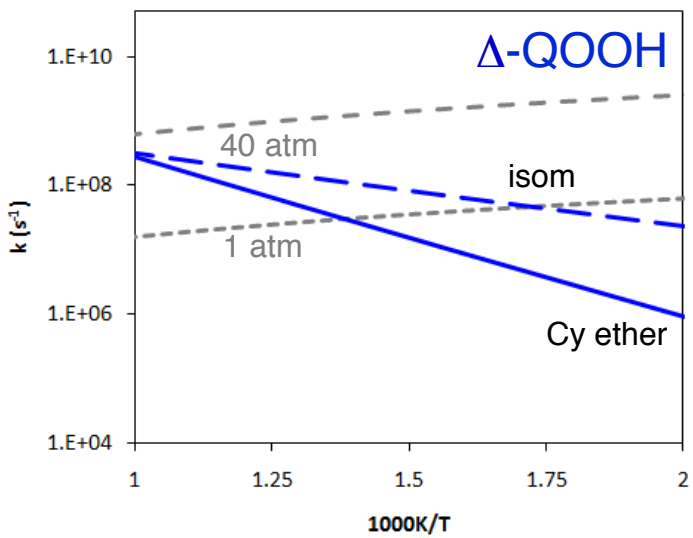


A-factors behave as expected in terms of restricted rotors, but very low barrier for 3-member ring

QOOH Competitive Reactions Sensitive to Structure





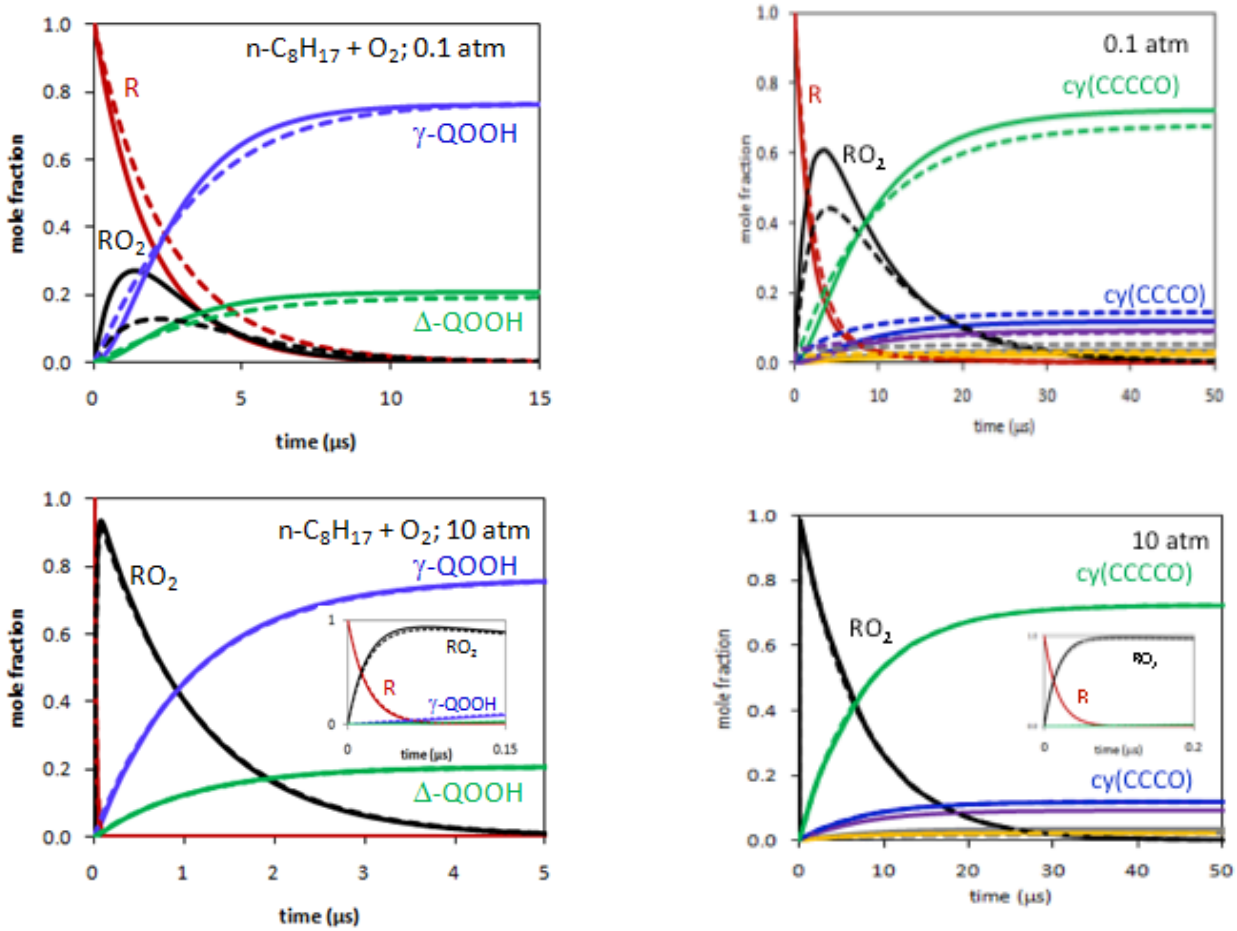


- **Very complex interplay among various channels**
- **Second O_2 addition scales linearly with pressure**
- **Difficult to generalize without extensive kinetic calculations**

Inclusion Of QOOH Reactions Dramatically Shifts Product Slate

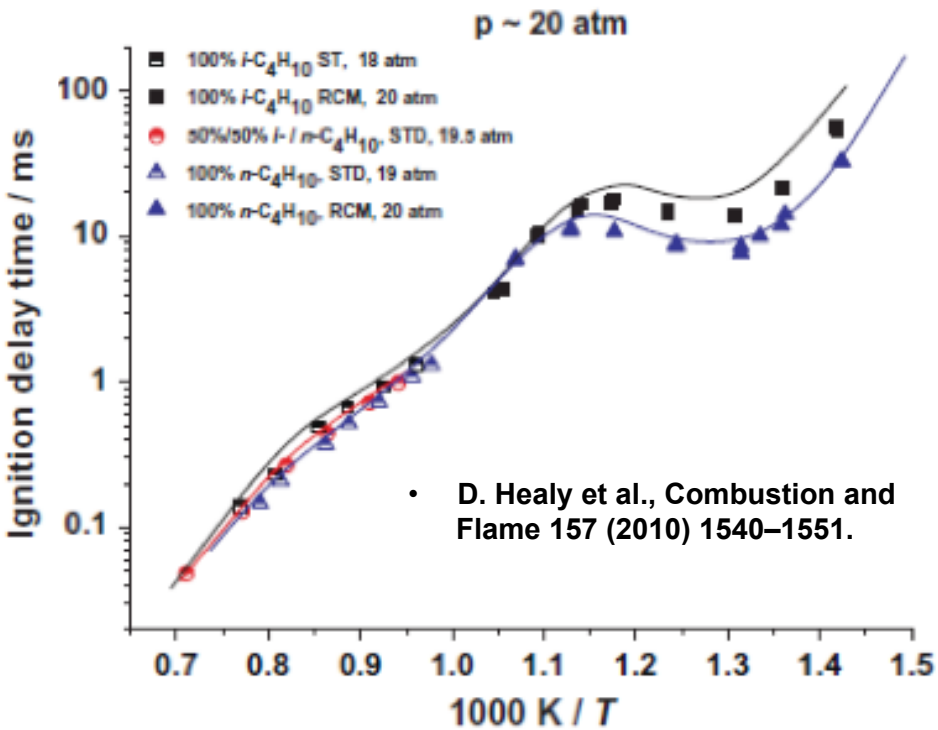
Only RO_2

RO_2 + QOOH

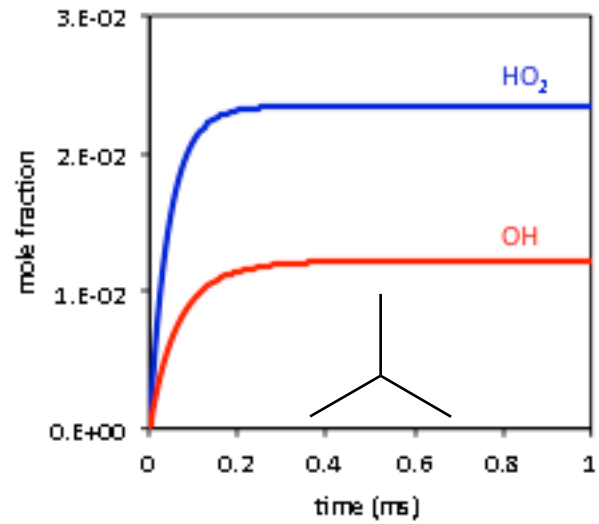


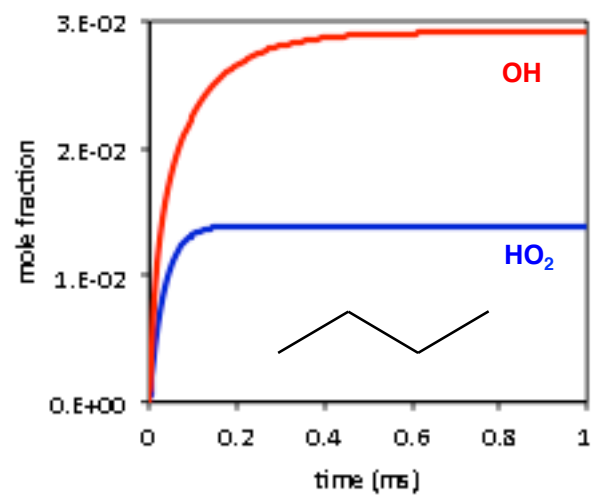
- **Reverse reaction of QOOH to RO_2 critical to product evolution**

Methyl Branch Inhibits Ignition



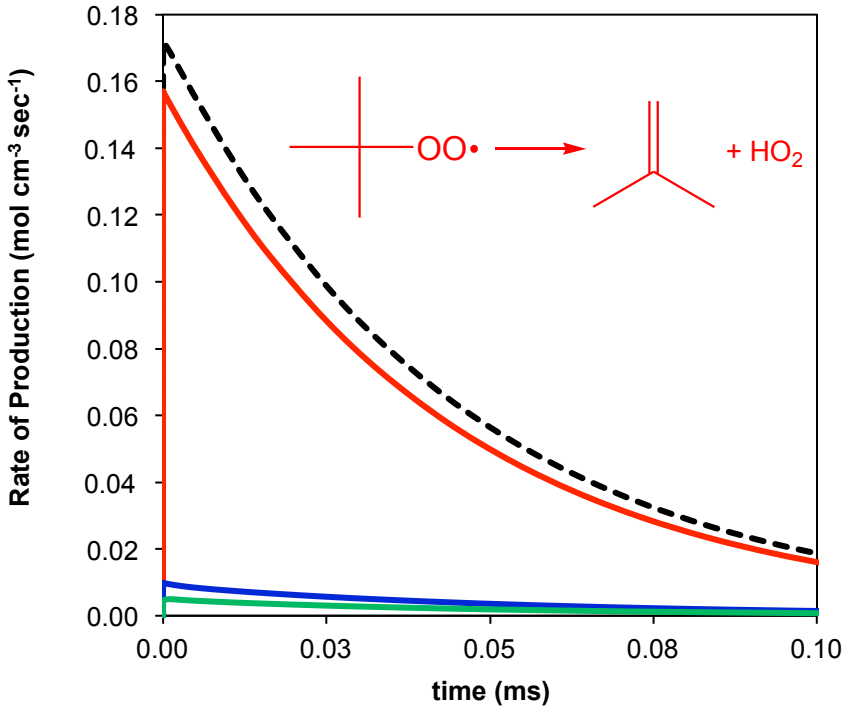
- D. Healy et al., Combustion and Flame 157 (2010) 1540–1551.



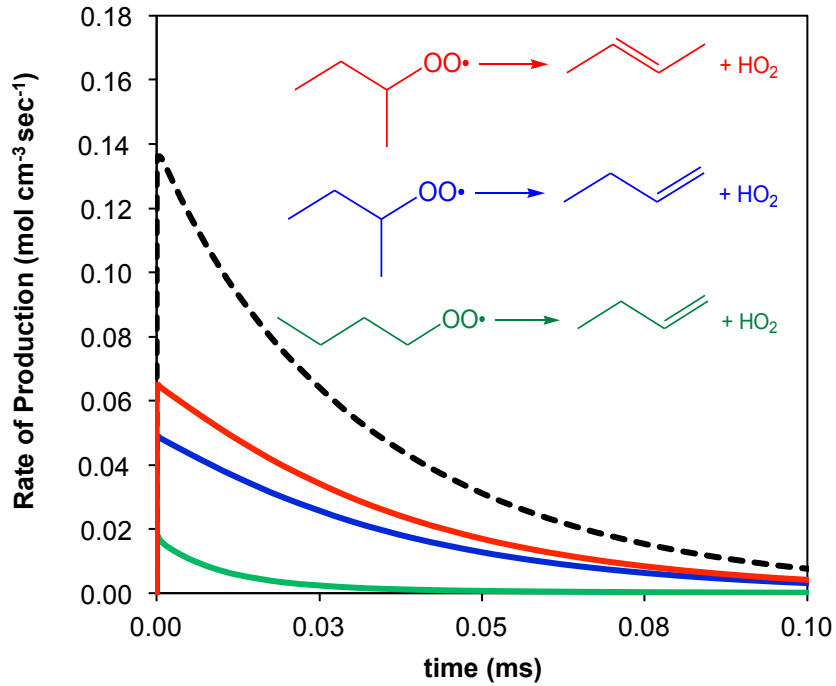


- **OH/HO_2 much greater for n-butane**
- **Consistent with faster ignition**

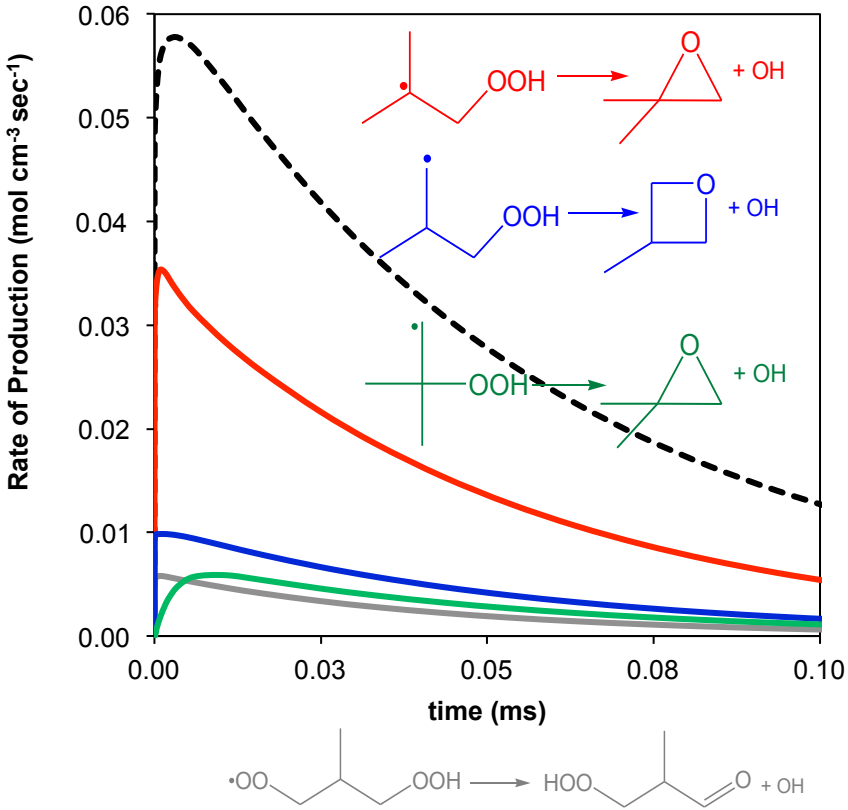
HO_2 Production Rate Similar for Both Structures



- **Formed from the concerted elimination of the alkyl peroxy radical**

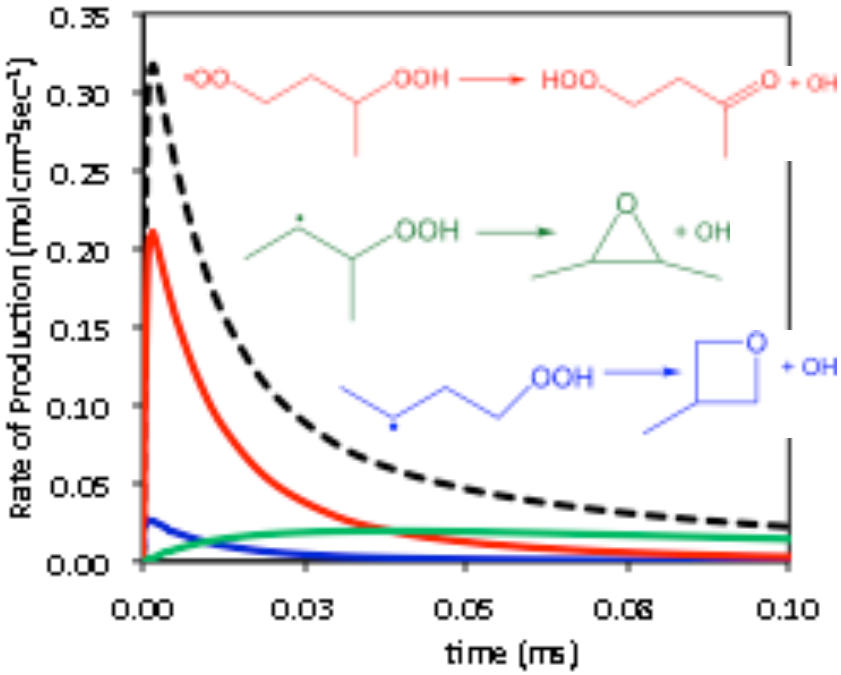


More Impact of Structure for OH Production



For iso-butane, OH is primarily produced though QOOH cyclic ether pathway

For n-butane, OH is primarily produced though O_2QOOH 1-5 isomerization.



Summary/Plans

- CBS-QB3 results successfully predict propane ignition
  - Suggest significantly different reaction pathways
- Subsequent calculations confirm similarity of reaction rate constants
  - Possible to generalize results to extract rate rules
- Rules generated for R+O_2 and Q$^{\bullet}$OOH reactions
  - Include both rate constants and thermo
  - Results suggest substantial impact of structure
  - High-pressure values should be adequate for most systems of interest

- Now working on $^{\bullet}$OOQOOH reactions

- Multicomponent vaporization analysis being extended to consider (reduced) detailed gas-phase reactions for counterflow diffusion flames

Acknowledgments

Program Manager:
Dr. Sharon Beermann-Curtin