Lawrence Livermore National Laboratory

Reaction Rate Rules for High and Low Temperature Oxidation of Lightly Methylated Alkanes

July 2011

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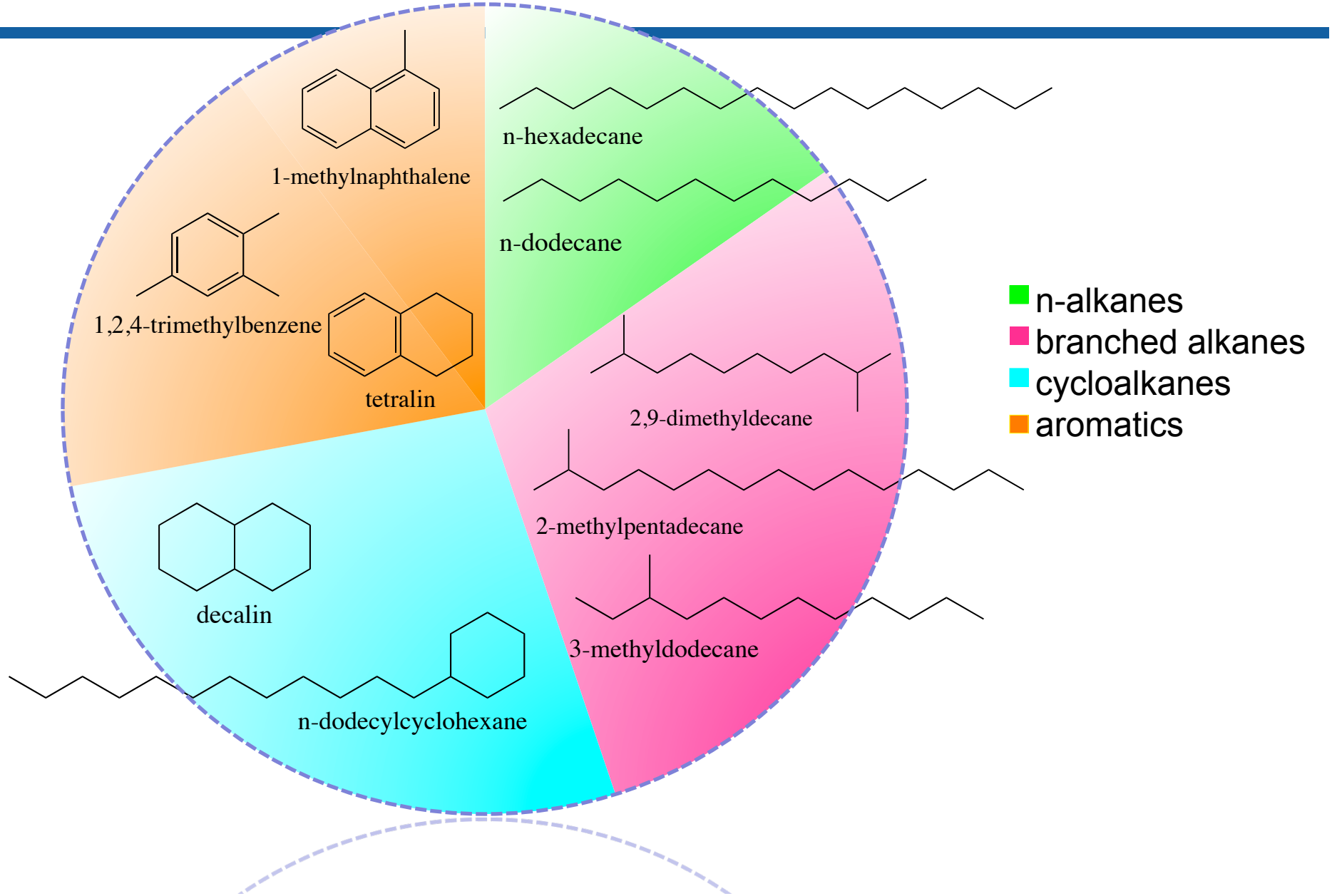
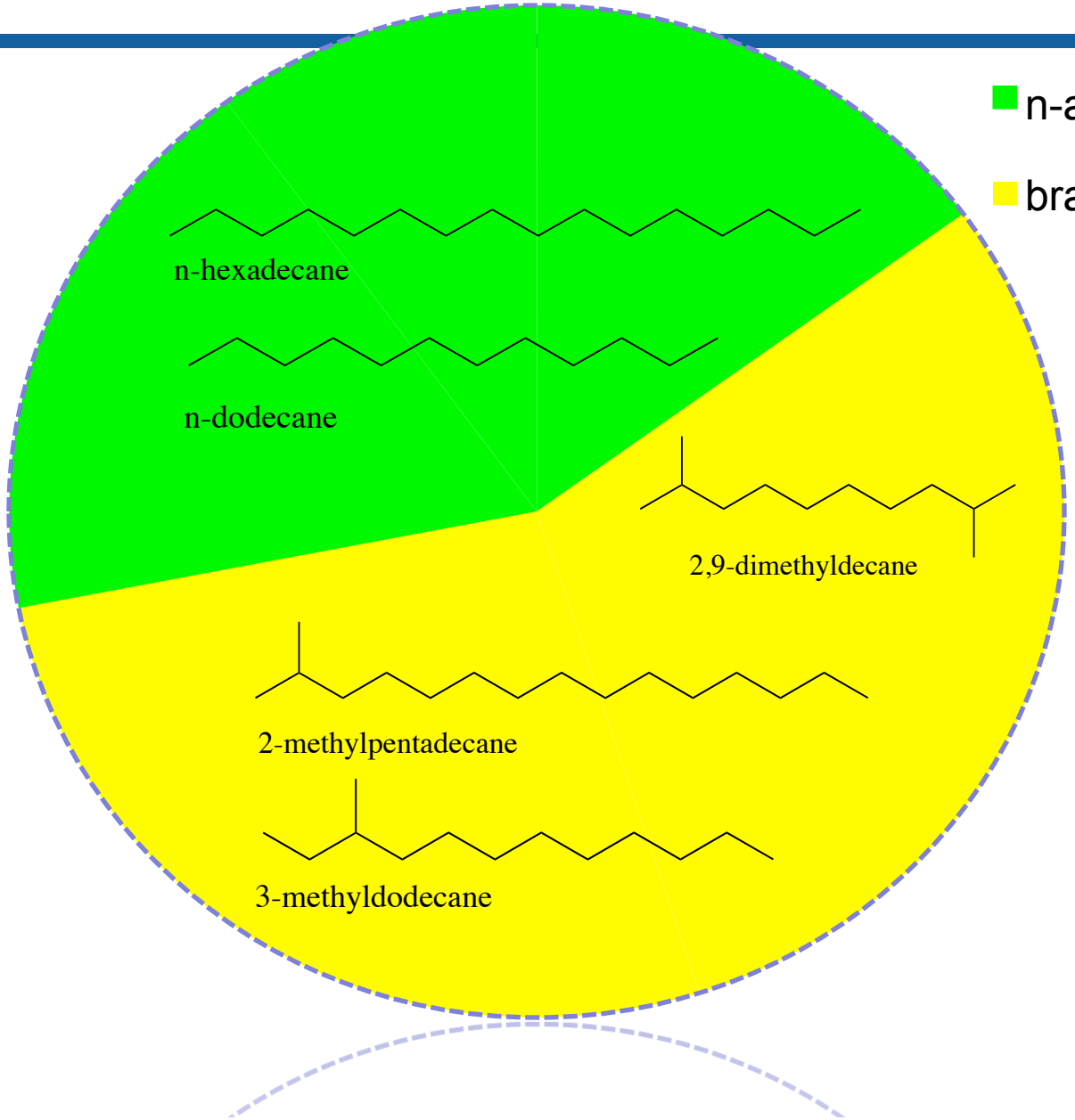
LLNL-PRES-502049

1. Pitz and Mueller, Prog. Energy Comb. Sci. (2010)

Petroleum diesel fuel surrogate palette



Renewable and Fischer-Tropsch diesel fuel palette



HVO

Oils and Fats

Deoxygenation

BTL

Biomass

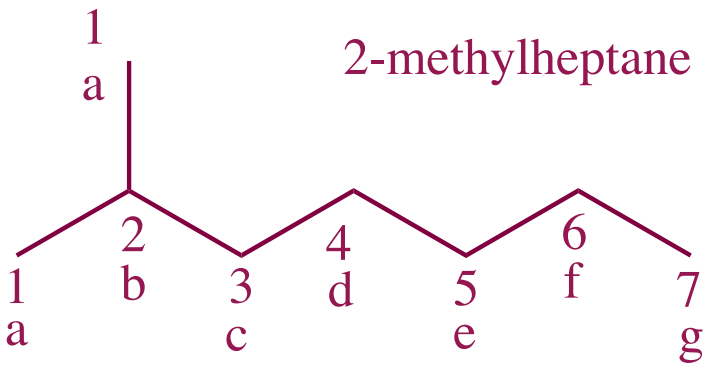
Gasification-FT

Selective Cracking/ Isomerization

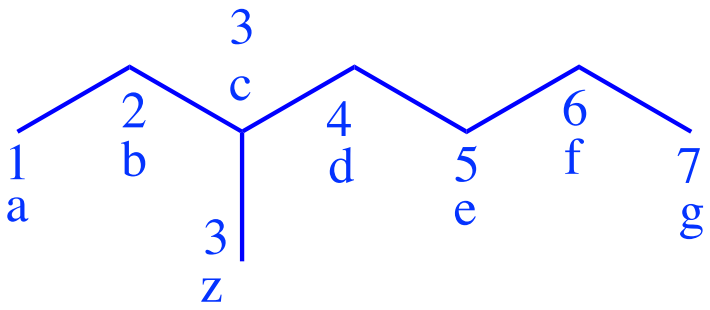
Synthetic Renewable Diesel

Surrogate molecules for larger alkanes

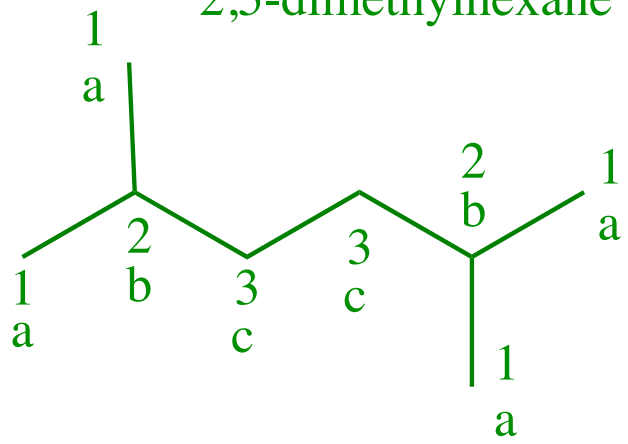
2-methylheptane



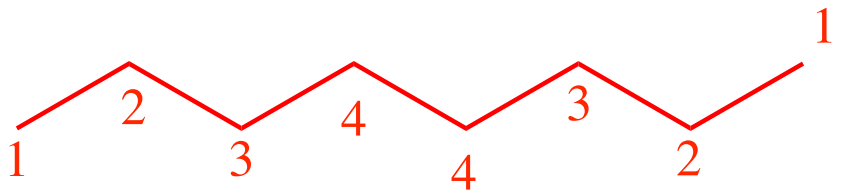
3-methylheptane



2,5-dimethylhexane



n-octane



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Motivation for current work

LLNL mechanisms have been developed for a wide variety of fuels and been successfully applied to practical simulations.

BUT

- Continuous improvement is needed to be consistent with fundamental and theoretical kinetic studies.
- Incorporate new reaction classes and develop new rate rules.
- Our models generally tend to be “RIGHT”, but we want to be “RIGHT” for the “RIGHT” reasons!

LLNL reaction classes for oxidation chemistry

High temperature mechanism

1: Unimolecular fuel decomposition

2: H atom abstractions from fuel

3: Alkyl radical decomposition

4: Alkyl radical isomerization

5: H atom abstraction from alkenes

6: Addition of radical species to alkenes

7: Alkenyl radical decomposition

8: Alkene decomposition

9: Retroene decomposition reactions

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LLNL reaction classes for oxidation chemistry

Low temperature mechanism

10: Alkyl radical addition to O_2 (R + O_2 = RO_2)

12,13, and 14: R + R'O_2 = RO + R'O

15: Alkylperoxy radical isomerization (RO_2=QOOH)

16: Concerted eliminations (RO_2 = alkene + HO_2)

17: RO_2 + HO_2 = ROOH + O_2

18: RO_2 + H_2O_2 = ROOH + HO_2

19: RO_2 + CH_3O_2 = RO + CH_3O +O_2

20: RO_2 + R'O_2 = RO + R'O + O_2

21: ROOH = RO + OH

22: RO decomposition

23: QOOH = cyclic ether + OH (cyclic ether formation)

24: QOOH = alkene+ HO_2 (radical beta to OOH)

25: QOOH = alkene + carbonyl + OH (radical gamma to OOH)

26: Addition of QOOH to molecular oxygen O_2 (QOOH+O_2=O_2QOOH)

27: O_2QOOH isomerization to carbonylhydroperoxide + OH

28: Carbonylhydroperoxide decomposition

29: Reactions of cyclic ethers with OH and HO_2

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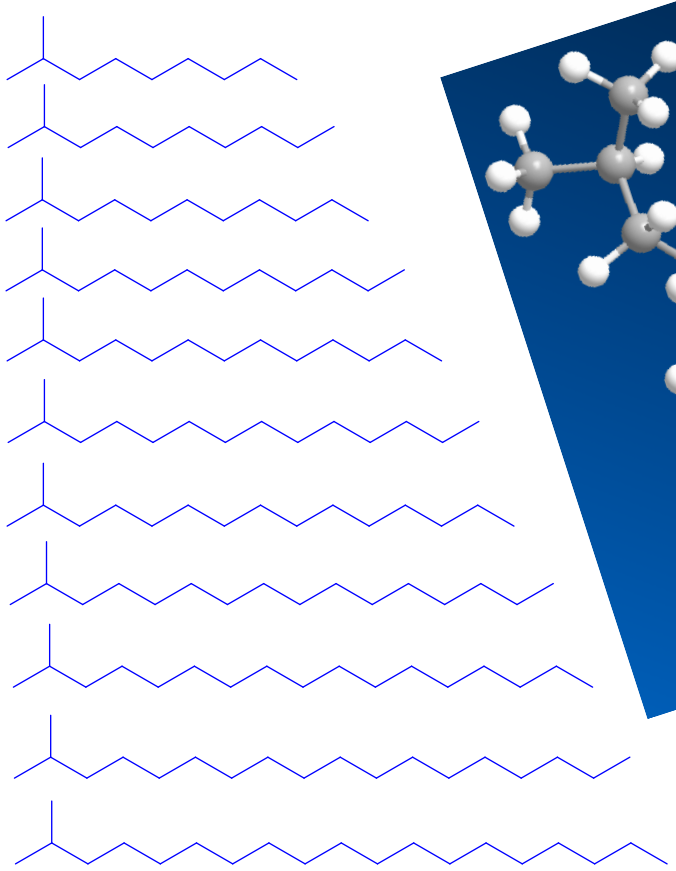
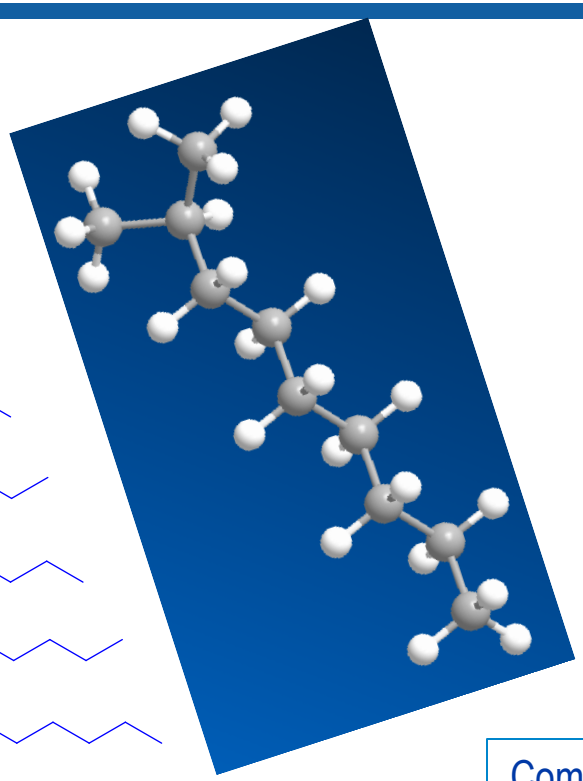
Chemical kinetic mechanism for n-alkanes and 2-methylakanes

Sarathy et al., Combust. Flame (2011)





Includes all n-alkanes upto C_{16} and 2-methylalkanes up to C_{20}, which covers the entire distillation range for gasoline and diesel fuels

Built with a consistent set of reaction classes and reaction rate rules

Complete Mechanism	C_8 High T Mechanism
7,200 species	714 species
31,400 reactions	3397 reactions

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Experimental data used to validate the chemical kinetic mechanism

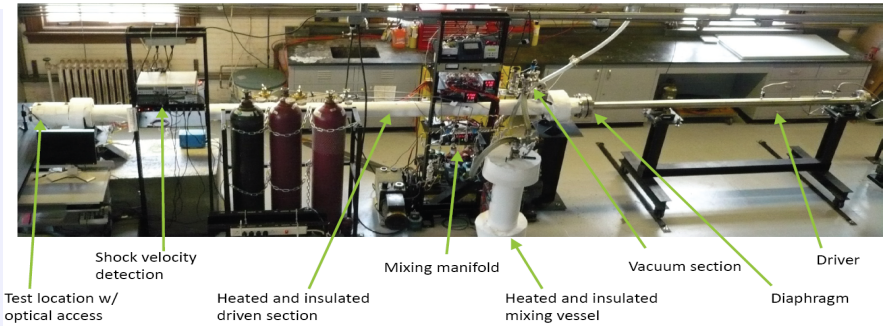
- Idealized chemically reacting flow systems with/without simplified transport phenomenon

Jet Stirred Reactors

Premixed Laminar Flames

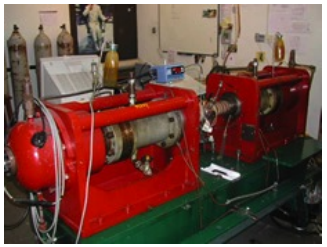
Twin premixed flames

Shock tube

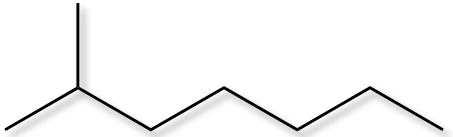


Non Premixed Flames

Rapid Compression Machines



Fuel used for model validation



2-methylheptane

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Some important reaction classes and rate rules

High temperature mechanism

2: H atom abstractions from fuel (specifically by HO_2)

4: Alkyl radical isomerization

Low temperature mechanism

15: Alkylperoxy radical isomerization (RO_2=QOOH)

16: Concerted eliminations (RO_2 = alkene + HO_2)

23: QOOH = cyclic ether + OH (cyclic ether formation)

27: O_2QOOH isomerization to carbonylhydroperoxide + OH

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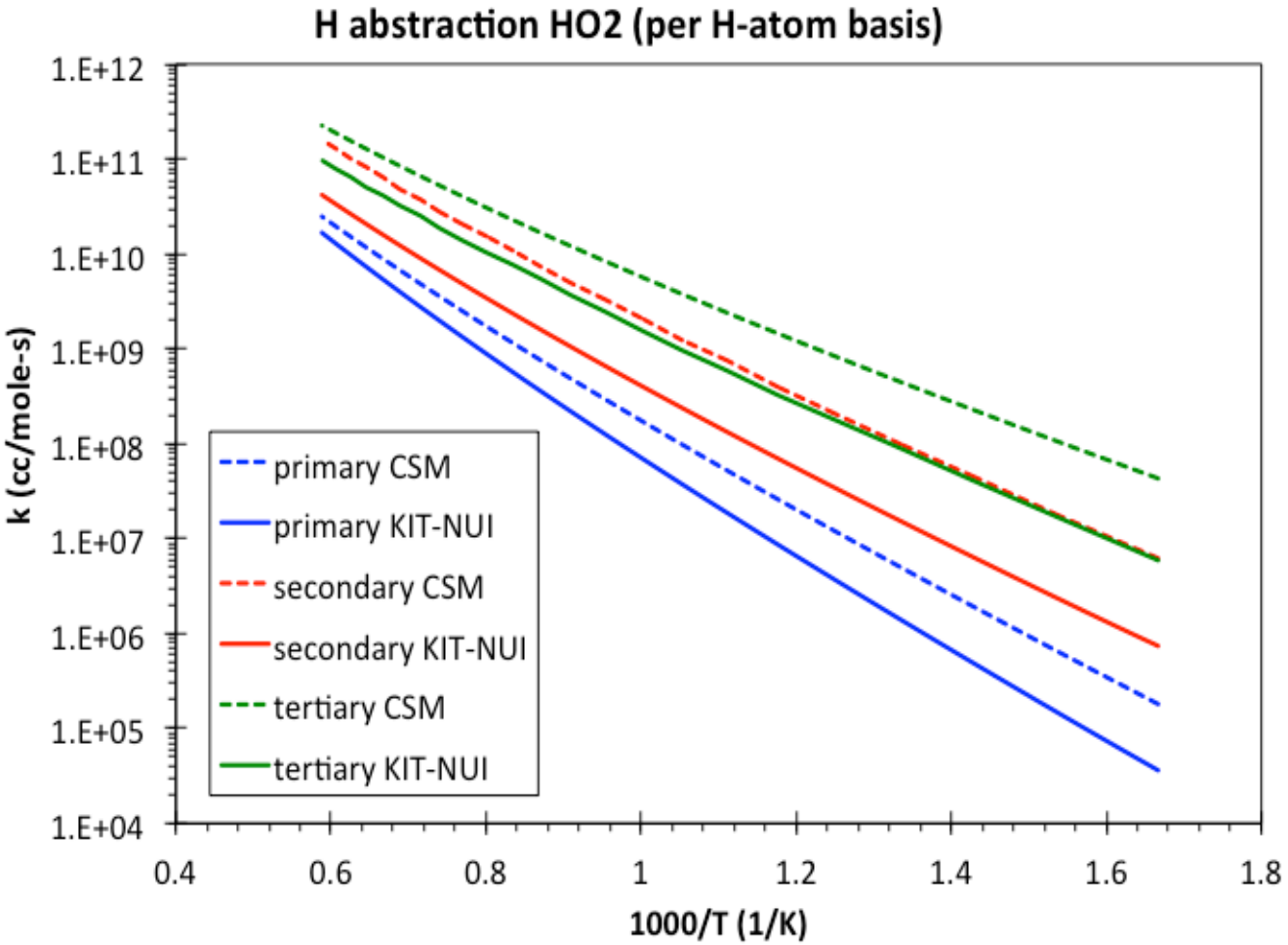
H-atom abstraction from fuel: Uncertainty in HO_2+fuel rate

Aguilera-Iparraguirre et al., J. Phys. Chem. A (2008)

Carstensen et al., Proc. Combust. Inst. (2007)

Class 2

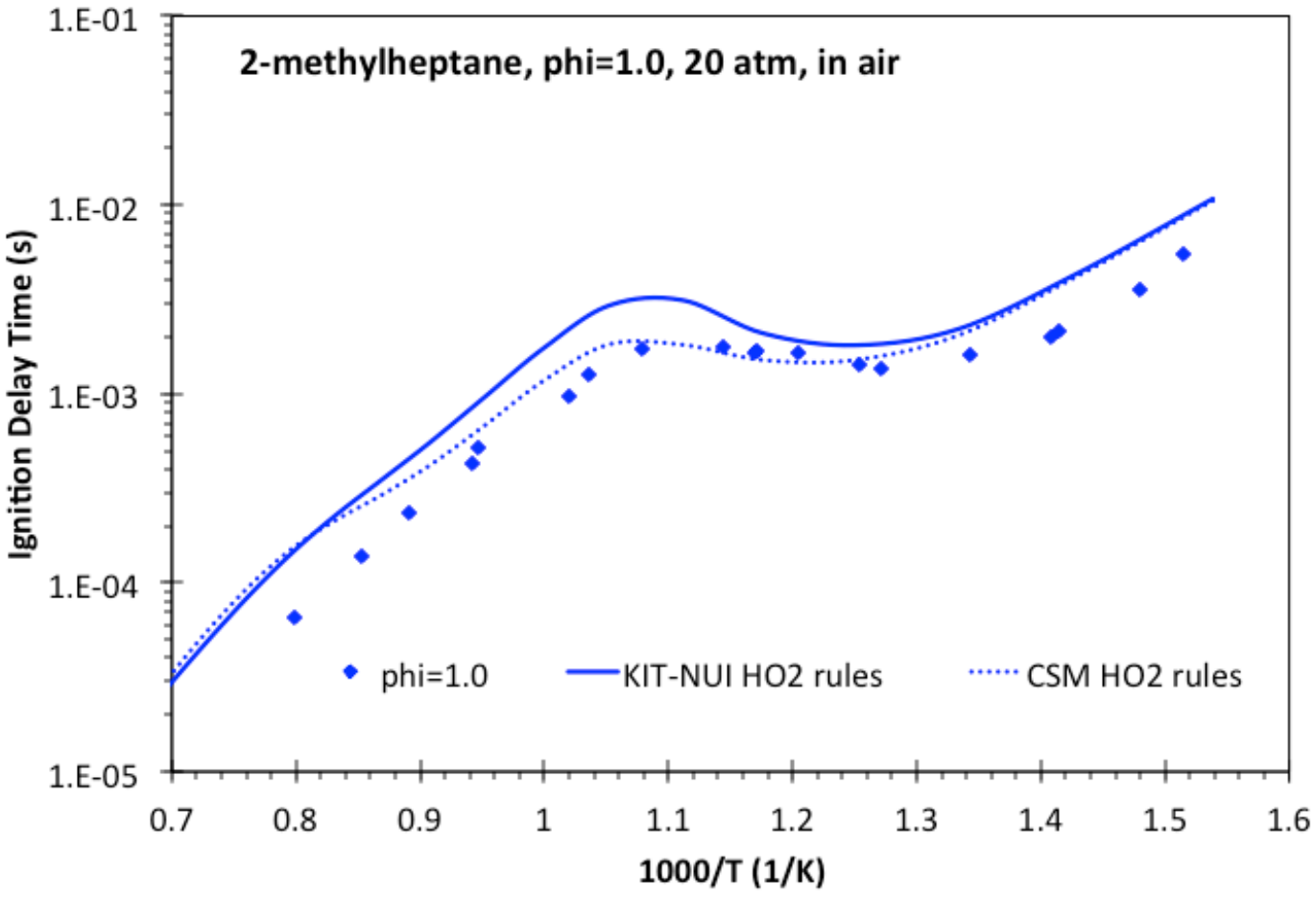


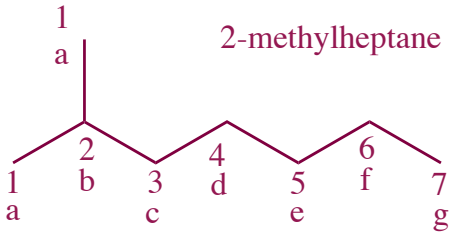
CSM rates are a 2-4x faster than KIT-NUI rate calculations for n-butane/ iso-butane systems.

KIT-NUI rate calculations appear to be in better agreement with experimental work.

Uncertainty in HO_2+fuel rate: Effect on shock tube ignition delay time

Class 2





LLNL uses KIT-NUI rate calculations as a rule for large branched alkanes.

Applying CSM estimates would improve intermediate temperature predictions.

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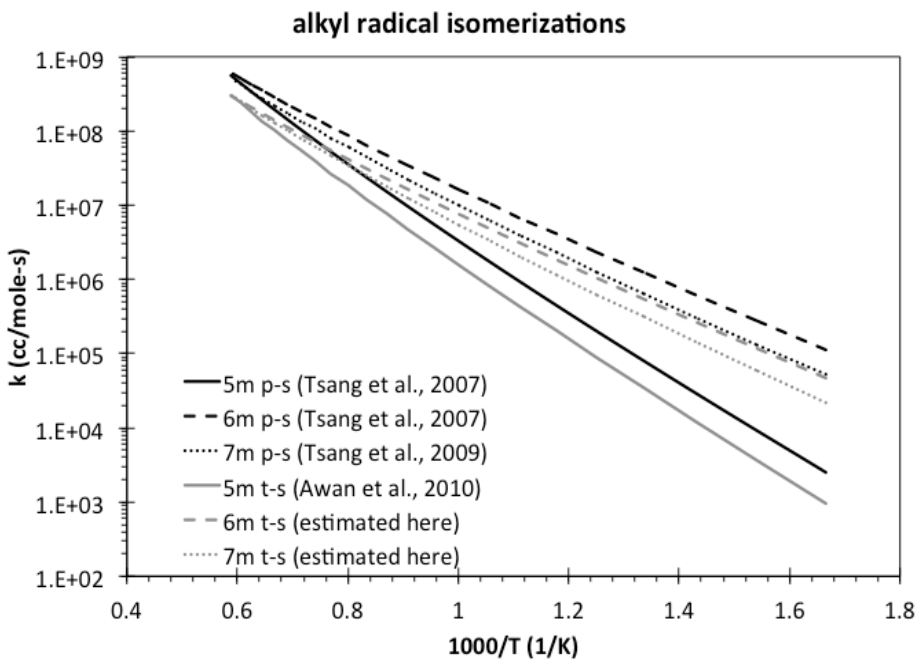
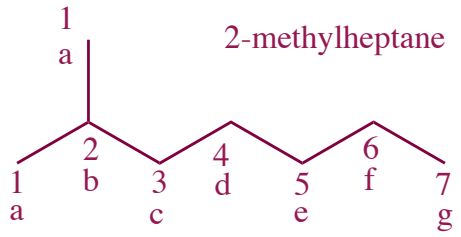
Alkyl radical isomerization: New rules and estimates

Awan et al., J. Phys. Chem. A (2010)

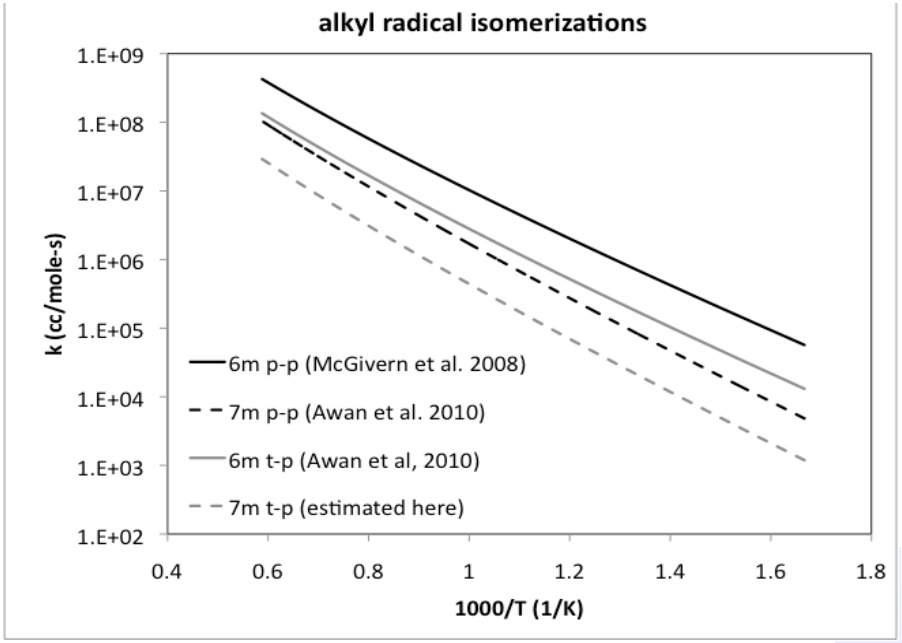
McGivern et al., J. Phys. Chem. A (2010)

Class 4





LLNL rate constants are based on recent experimental/theoretical work from NIST.

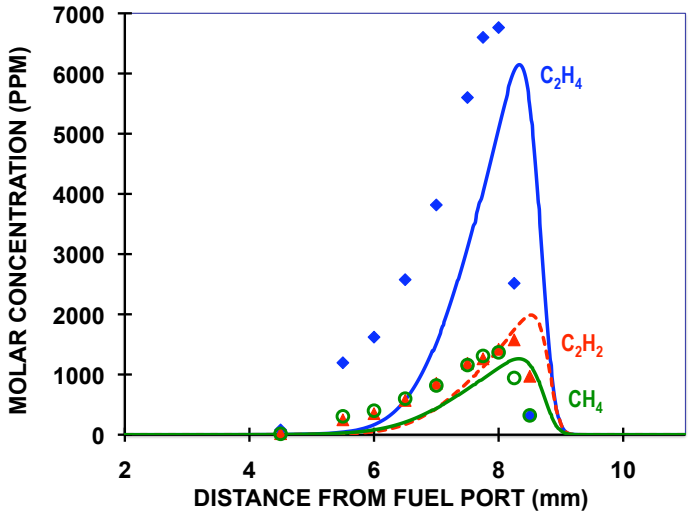


Analogies were made to estimate rate of isomerizations involving 6- and 7-membered transition states.

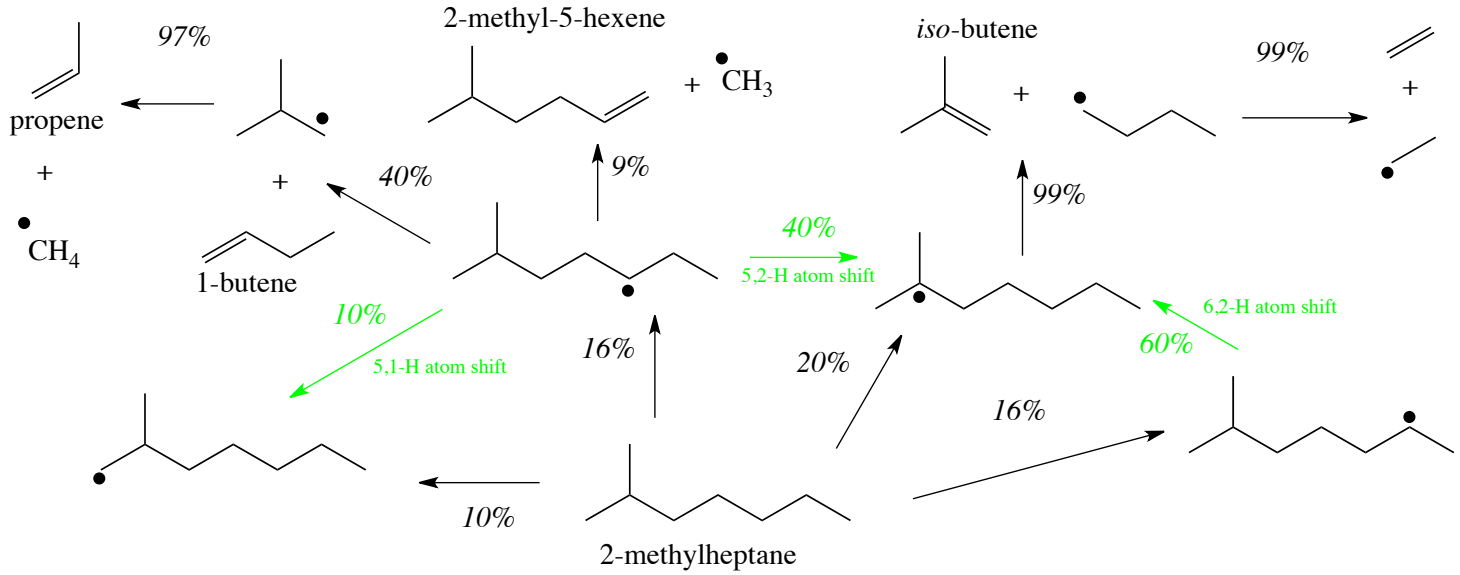
Alkyl radical isomerization: Chemistry in diffusion flames

Sarathy et al., Combust. Flame (2011)

Class 4



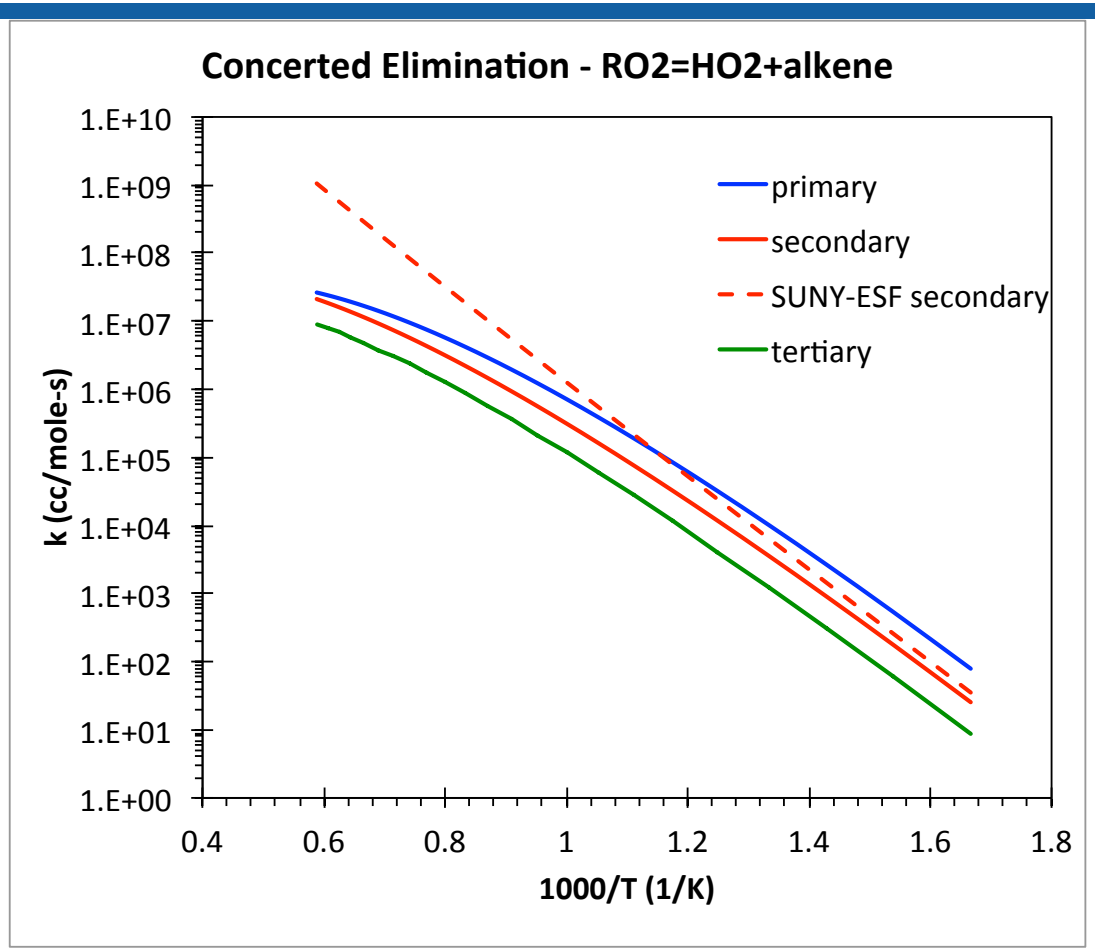
Correct prediction of straight and branched alkenes requires accurate isomerization rate constants.



Concerted elimination (RO_2 = alkene + HO_2)

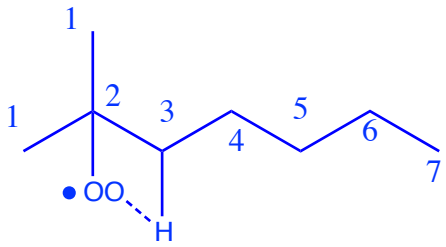
Class 16

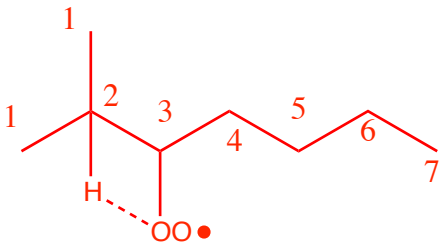
DeSain et al., J. Phys. Chem. A (2003)
Zhang et al., J. Phys. Chem. A (2011)
Healy et al., Combust. Flame. (2010)

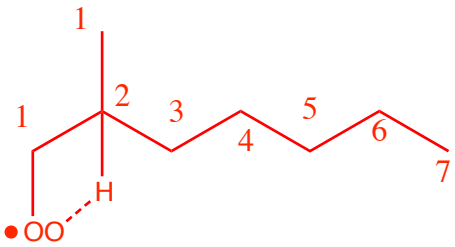


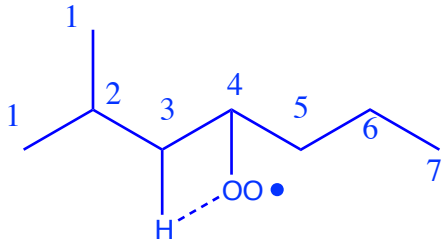
LLNL rules based on n-propylperoxy+O_2 and iso-propylperoxy+O_2 experimental and theoretical studies. Tertiary rate is a crude estimate.

Current rules only consider the nature of the C-H bond broken and not the nature of the C-OO bond.





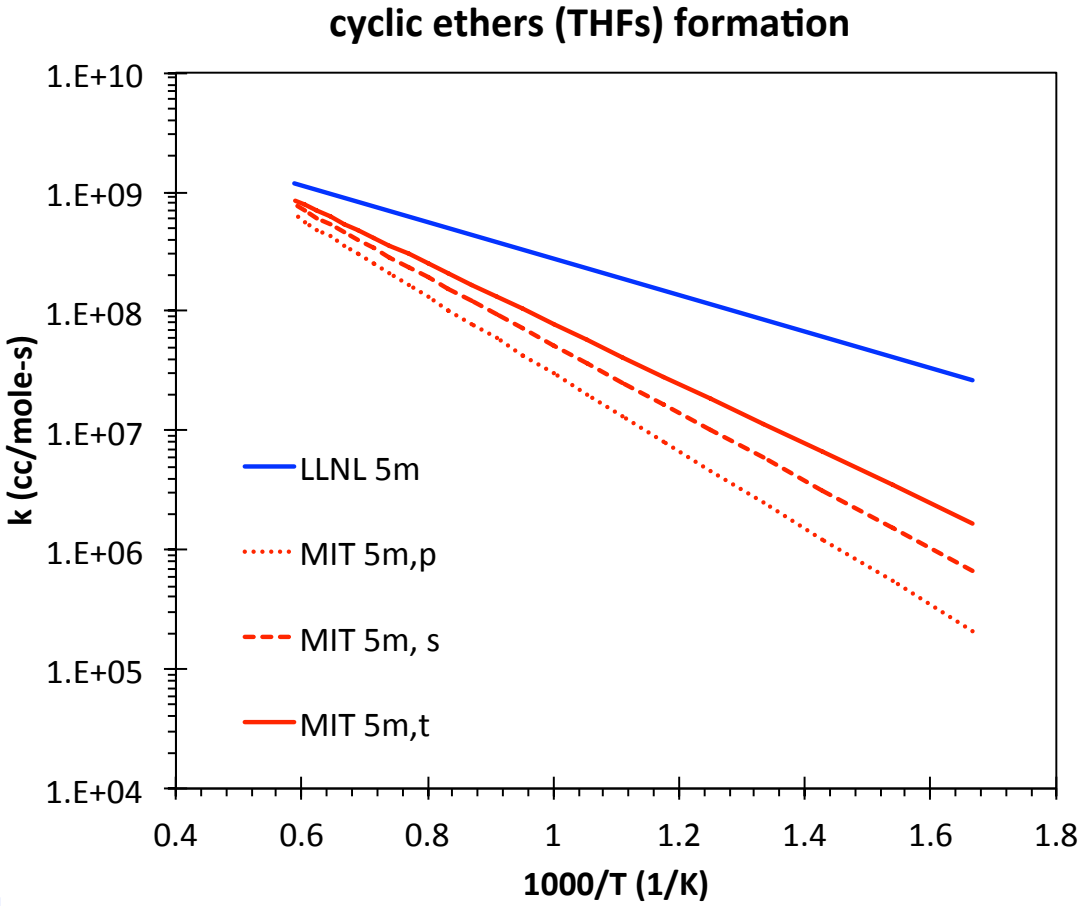




QOOH = cyclic ether + OH
Uncertainty in cyclic ether formation

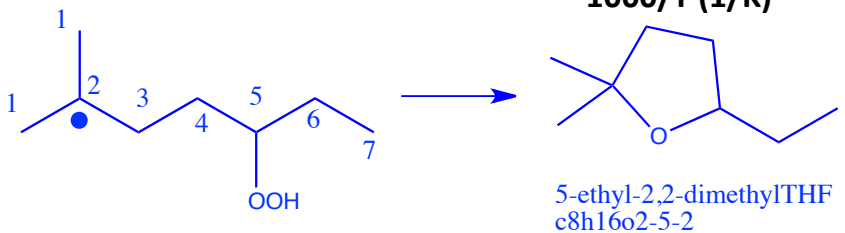
Wijaya et al., J. Phys. Chem. A (2003)

Class 23



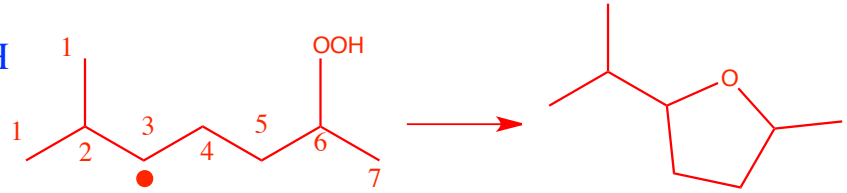
MIT prescribes rates according to the nature of the radical carbon site (i.e., primary, secondary, or tertiary).

LLNL rates for tetrahydrofuran formation are above 10x faster at low-to-intermediate temperatures.



5-ethyl-2,2-dimethylTHF
c8h16o2-5-2

+ OH

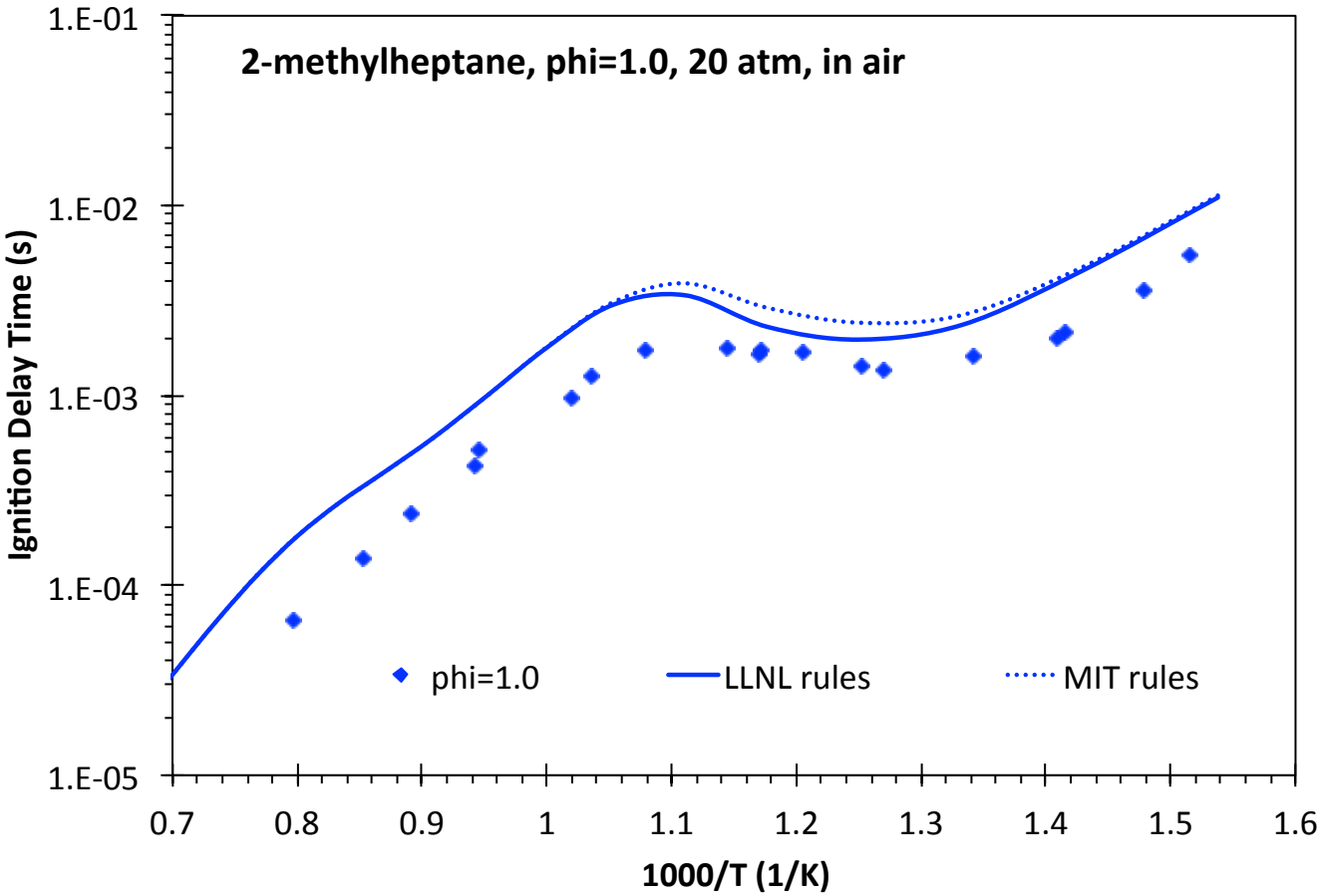


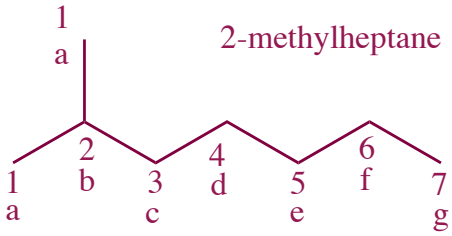
2-methyl-5-isopropylTHF
c8h16o3-6-2

+ OH

Cyclic ether formation rate: Effect on shock tube ignition delay time

Class 23





LLNL uses rules that are considerably different than MIT, but changing the rate rules does not alter ignition delay times significantly.

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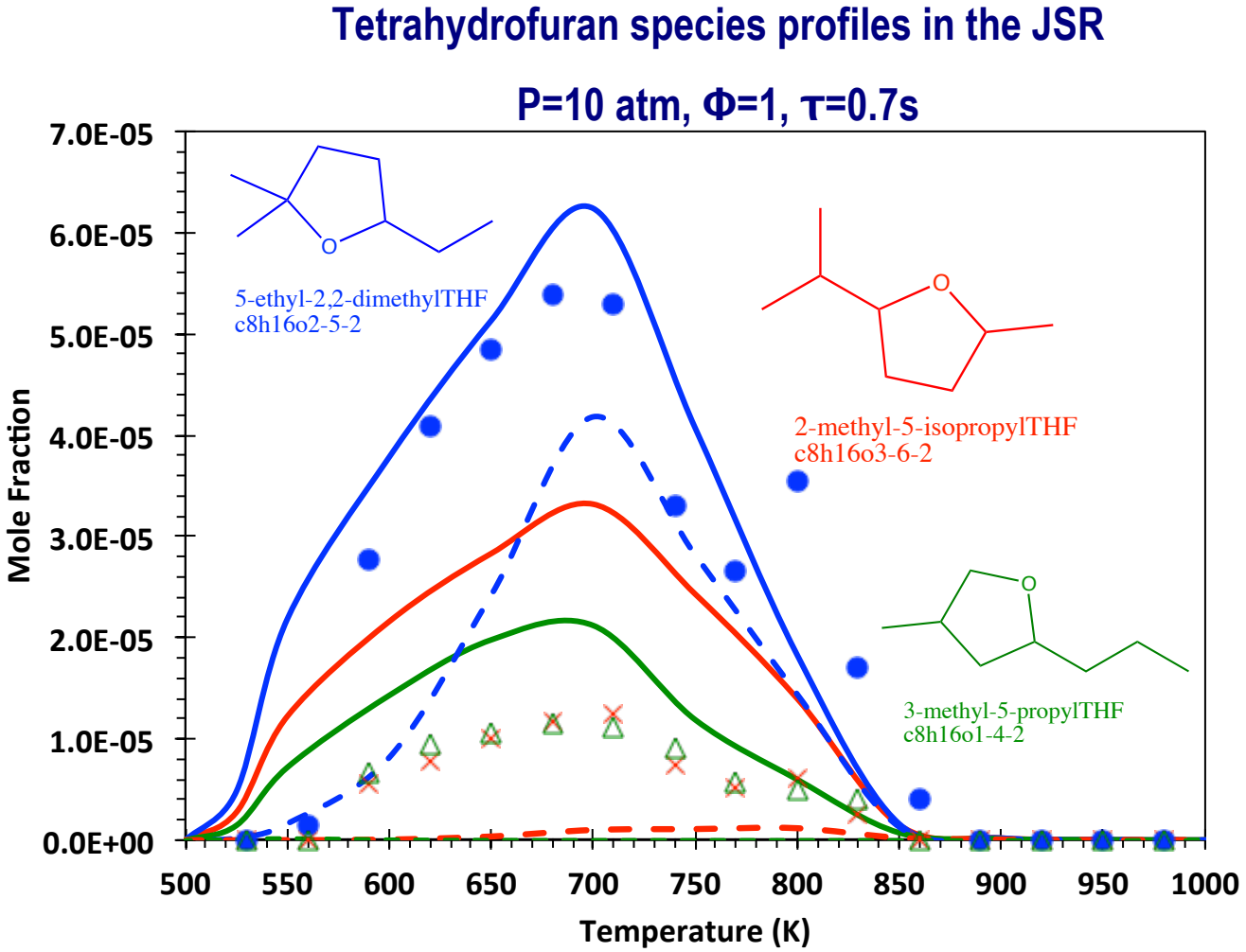
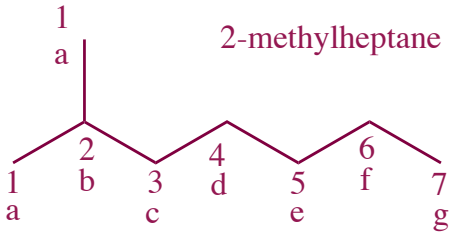
Cyclic ether formation rate: Effect on jet stirred reactor species profiles

Class 23





LLNL rules provide better agreement with JSR speciation data for THF, but room for significant improvement exists.

Adjusting LLNL rules to consider nature of the radical carbon site could improve predictions.

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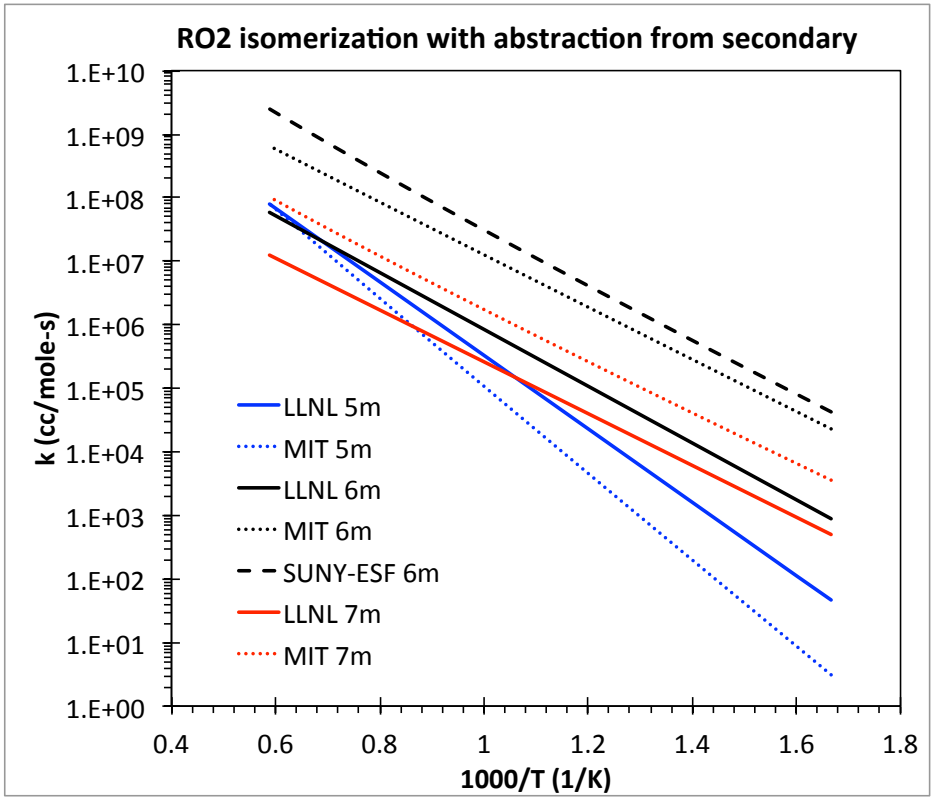
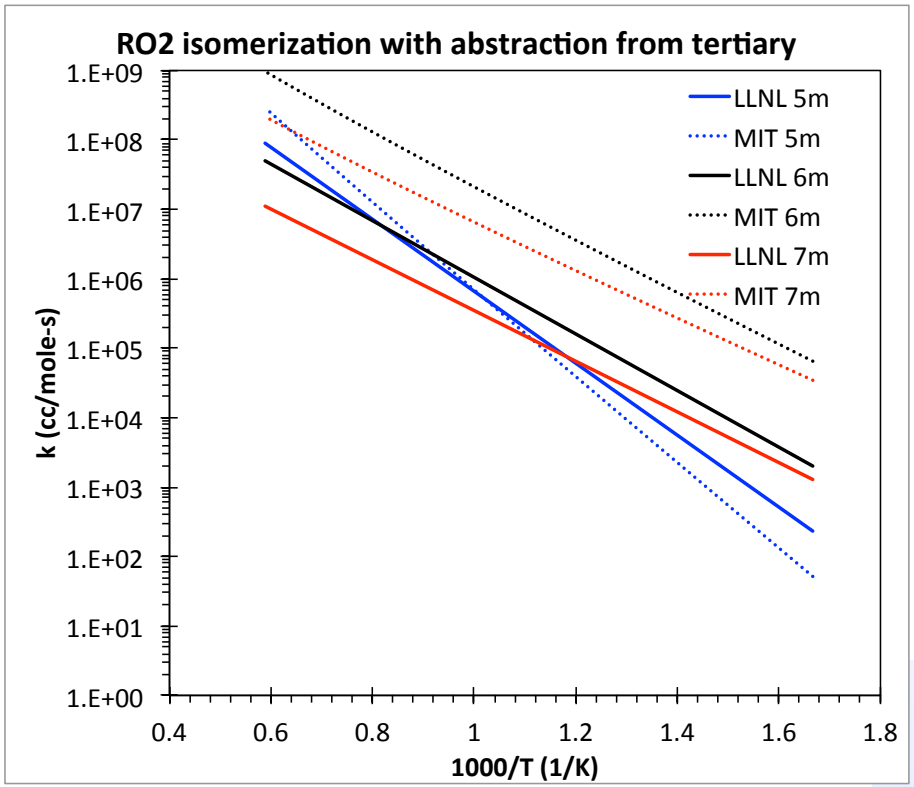
Alkylperoxy isomerization (RO_2=QOOH)
O_2QOOH isomerization

Sharma et al., J. Phys. Chem. A (2010)
Zhang et al., J. Phys. Chem. A (2011)

Class 15 and Class 27



LLNL uses estimates based on successful reproduction of ignition delay times for a wide variety of hydrocarbons.

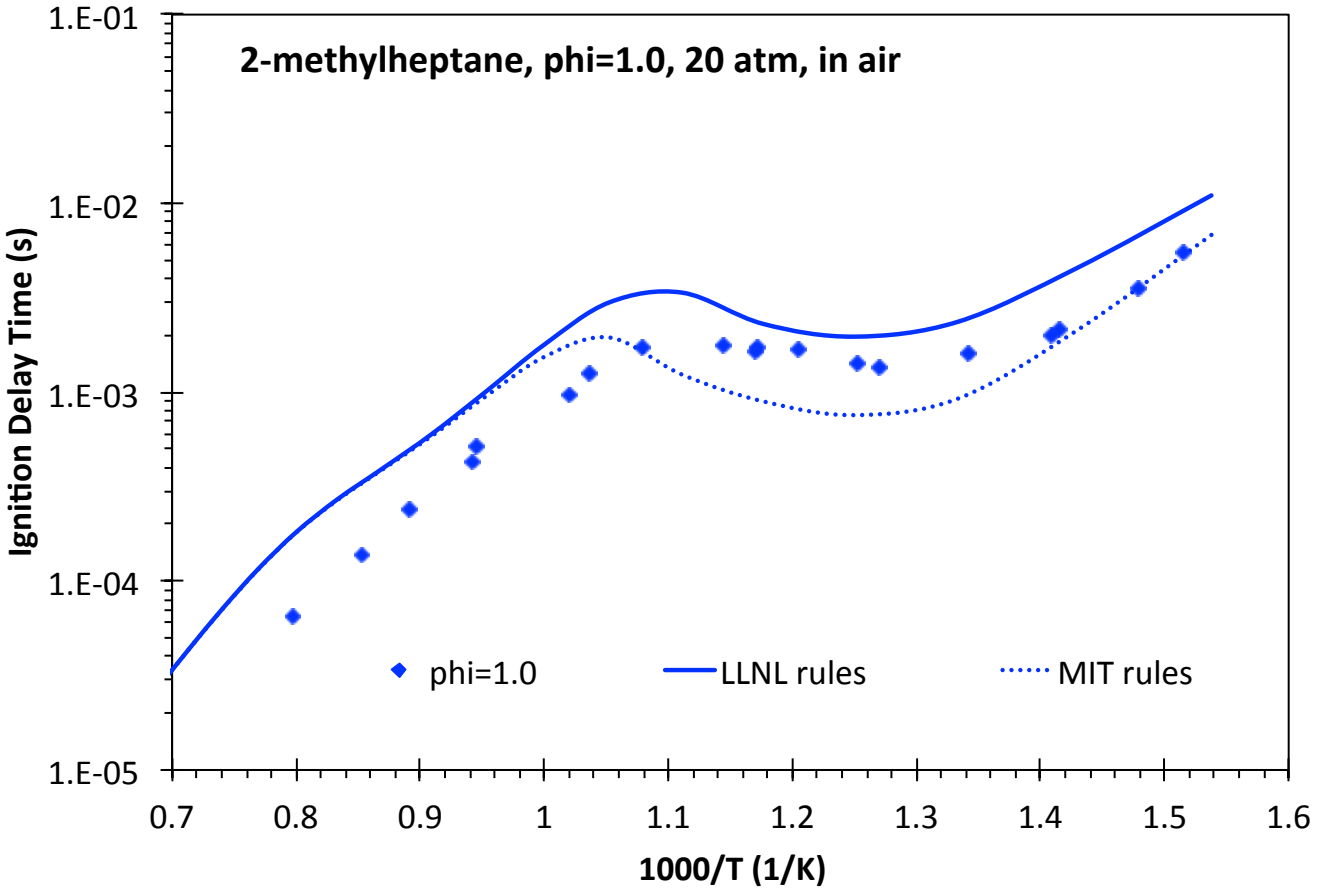


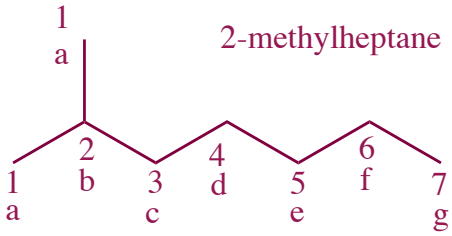
Theoretical calculations are 10-20x faster for 6-membered ring 7-membered ring iomserizations

RO_2=QOOH, O_2QOOH=ketohydroperoxide+OH: Effect on shock tube ignition delay time

Class 15

Class 27





LLNL uses rules that are considerably different than MIT, and changing the rate rules does appear to decrease ignition delay times.

Conclusions from Present Analysis

A novel chemical kinetic mechanism for 2-methylalkanes was effectively used to test specific reaction rate rules for lightly branched alkanes

- Discrepancies in radical abstraction reaction rate calculations can significantly alter ignition delay predictions.
- Studies that combine both experimental and theoretical work appear to provide the best platform for developing rate rules.
- Kinetic rate calculations appear to vary amongst theoreticians. Mechanism developers need to critically assess the data to develop a rate rule.

Future Work

LLNL and CSM working to implement rate rules from *ab initio* calculations using a consistent set of methods for all reaction classes.

Verification of thermochemistry also needs to be critically assessed in LLNL models.

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Publication: Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C7 to C20

S.M. Sarathy, C.K. Westbrook, M. Mehl, W.J. Pitz, C. Togbe, P. Dagaut, H. Wang, M.A. Oehlschlaeger, U. Niemann, K. Seshadri, P.S. Veloo, C. Ji, F.N. Egolfopoulos, T. Lu

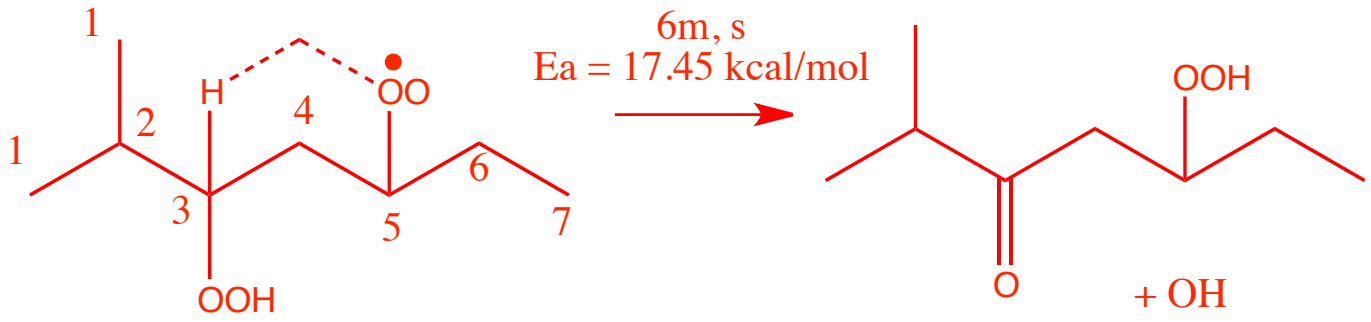
Combust. Flame (2011), doi:10.1016/j.combustflame.2011.05.007

Questions and Constructive Comments

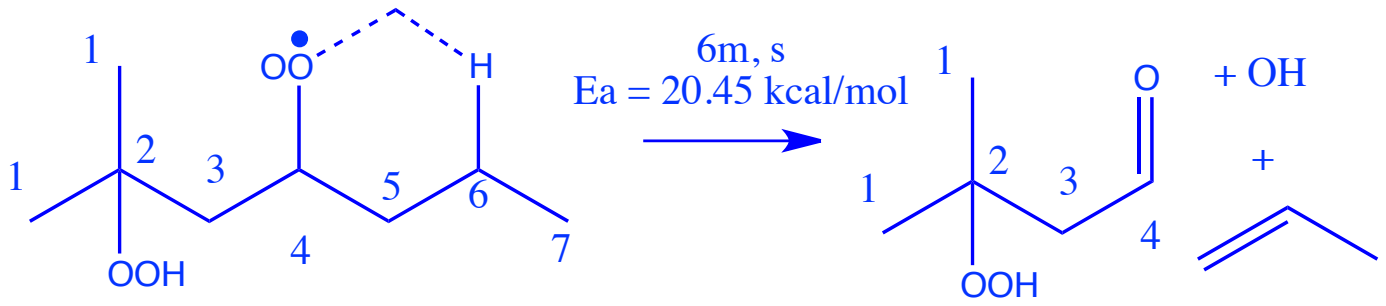
CAUTION: Harsh criticisms, insults, obscenities, and rotten tomatoes are welcome, but may be responded to with brute force. Proceed with caution.

O_2QOOH=ketohydroperoxide+OH: Alternate routes for tertiary C-H sites

Class 27



LLNL mechanisms assume O_2QOOH abstracts H atom for carbon bonded to OOH group.



This assumption cannot be applied to tertiary carbons, so alternate pathways must be included to avoid "dead-end" pathways.

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