COMBUSTION
RESEARCH
FACILITY

SAND2013-5104P

Chemical Kinetics and Combustion of Novel Biofuels

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Sandia National Laboratories

Combustion is a Complicated Mix of Chemistry and Fluid Dynamics

Comprehensive Kinetic Mechanism

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c7h15o2-1=c7h14ooh1-2 2.000e+11 0.000 26850.0 !12-l 5s c7h15o2-1=c7h14ooh1-3 2.500e+10 0.000
c7h14ooh1-4 3.125e+09 0.000 19050.0 !12-l 7s c7h15o2-1=c7h14ooh1-5
2-l 8s c7h15o2-2=c7h14ooh2-1 3.000e+11 0.000 29400.0 !12-l 5p c7h15o2-
.000 26850.0 !12-l 5s c7h15o2-2=c7h14ooh2-4 2.500e+10 0.000 20850.0
h2-5 3.125e+09 0.000 19050.0 !12-l 7s c7h15o2-2=c7h14ooh2-6 3.912e+08
5o2-3=c7h14ooh3-1 3.750e+10 0.000 24400.0 !12-l 6p c7h15o2-
.000 26850.0 !12-l 5s c7h15o2-3=c7h14ooh3-4 2.000e+11 0.000 26850.0
h3-5 2.500e+10 0.000 20850.0 !12-l 6s c7h15o2-3=c7h14ooh3-6 3.125e+09
5o2-3=c7h14ooh3-7 5.860e+08 0.000 25550.0 !12-l 8p c7h15o2-4=c7h14ooh4-
1 9.376e+09 0.000 22350.0 !12-l 7p c7h15o2-4=c7h14ooh4-2 5.000e+10 0.000 20850.0 !12-l 6s c7h15o2-
4=c7h14ooh4-3 4.000e+11 0.000 26850.0 !12-l 5s ! c6h13o2-1=c6h12ooh1-2 2.000e+11 0.000 26850.0
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0.000 19050.0 !12-l 7s c6h13o2-2=c6h12ooh2-6 5.860e+08 0.000 25550.0 !12-l 8p c6h13o2-
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!12-l 5s c6h13o2-3=c6h12ooh3-4 2.000e+11 0.000 26850.0 !12-l 5  c6h13o2-3=c6h12ooh3-5 2.500e+10
0.000 20850.0 !12-l 6s c6h13o2-3=c6h12ooh3-6 4.688e+09 0.000 2  50.0 !12-l 7p ! c5h11o2-
1=c5h10ooh1-2 2.000e+11 0.000 26850.0 !12-l 5s c5h11o2-1=c5h10   1-3 2.500e+10 0.000 20850.0
!12-l 6s c5h11o2-1=c5h10ooh1-4 3.125e+09 0.000 19050.0 !12-l 7s c    2-1=c5h10ooh1-5 5.860e+08
0.000 25550.0 !12-l 8p c5h11o2-2=c5h10ooh2-1 3.000e+11 0.000 294        l 5p c5h11o2-
2=c5h10ooh2-3 2.000e+11 0.000 26850.0 !12-l 5s c5h11o2-2=c5h10oo        e+10 0.000 20850.0
!12-l 6s c5h11o2-2=c5h10ooh2-5 4.688e+09 0.000 22350.0 !12-l 7p c5h1           0ooh3-1 7.500e+10
0.000 24400.0 !12-l 6p c5h11o2-3=c5h10ooh3-2 4.000e+11 0.000 26850.         4h9o2=c4h8ooh1-
2 2.000e+11 0.000 26850.0 !12-l 5s !pc4h9o2=c4h8ooh1-3 2.500e+10 0.00              6s
!pc4h9o2=c4h8ooh1-4 4.688e+09 0.000 22350.0 !12-l 7p !sc4h9o2=c4h8oo             000 29400.0
!12-l 5p !sc4h9o2=c4h8ooh2-3 2.000e+11 0.000 26850.0 !12-l 5s !sc4h9o2=c             10 0.000
24400.0 !12-l 6p !
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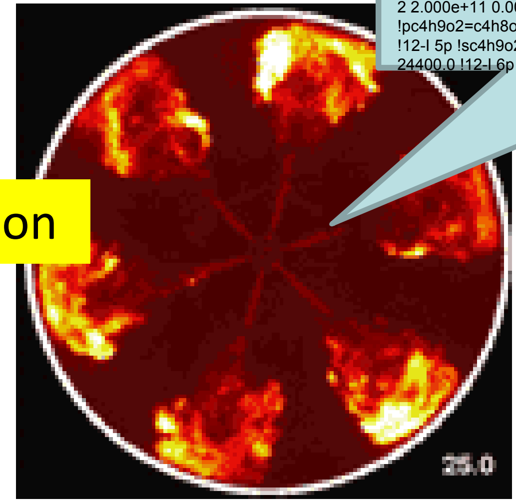
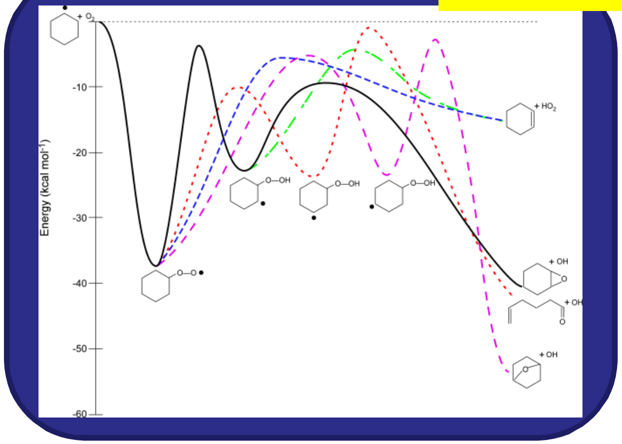
Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Turbulent, multiphase flows interact with the chemistry

Autoignition



R + O_2 reactions

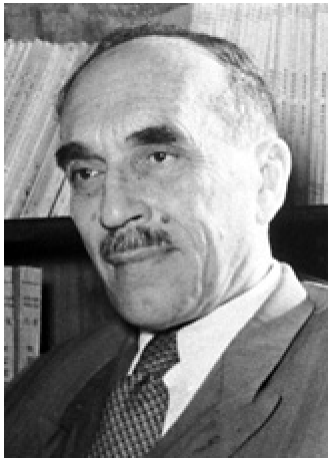


Charles Mueller, CRF

You Don’t Need to Know Much Chemistry to Make an Engine!

Nikolaus August Otto (1832-1891)

Rudolf Christian Karl Diesel (1858 –1913)



Nikolai Nikolaevic Semenov (Chemistry Nobel, 1956) “Some problems relating to chain reactions and to the theory of combustion”

In Some Key Areas the Details of the Chemistry Make a Big Difference

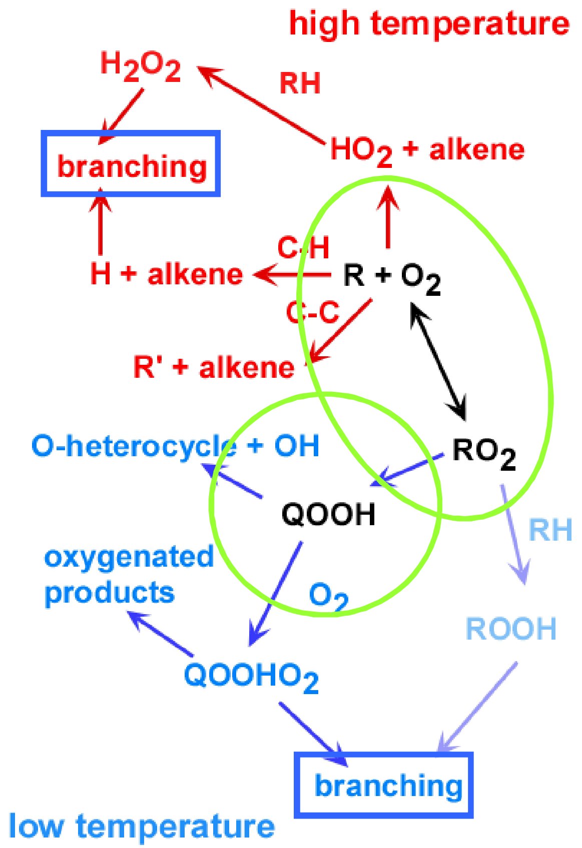
Pollutant Formation:

- Detailed combustion chemistry determines nature and amount of pollutants
- Soot is initiated by reactions of small unsaturated hydrocarbon radicals

Ignition Chemistry:

- Chain-branching pathways are a “nonlinear feedback” for autoignition
- Alkyl + O_2 and “QOOH” reactions are central to low-temperature chain branching

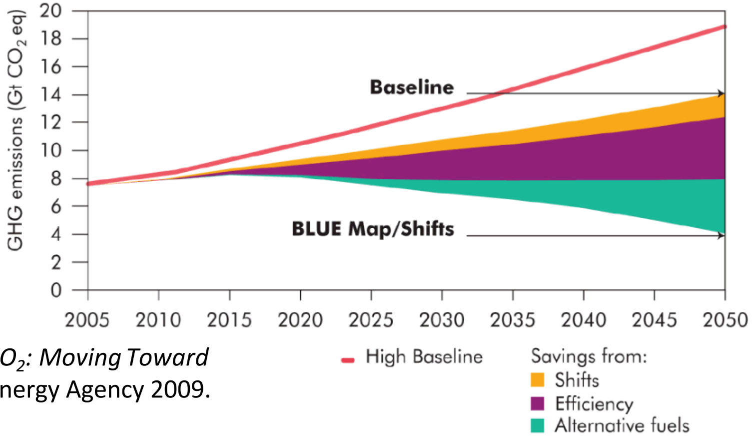
General Alkyl Radical Oxidation Scheme



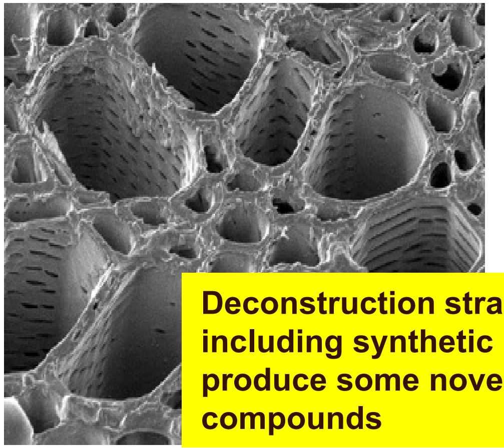
Adapted from Walker and Morley, "Basic Chemistry of Combustion," in *Low Temperature Combustion and Autoignition*, Ed. M. J. Pilling, (Comprehensive Chemical Kinetics Vol. 35) Elsevier, 1997

In Response to Climate and Energy Security Challenges the Fuel Stream Is Changing

- **Reducing “foreign oil” dependence requires new energy sources**
- **Mitigation of climate change demands multifaceted urgent action**
- **Advanced biofuels and combustion efficiency are important parts of the path forward**



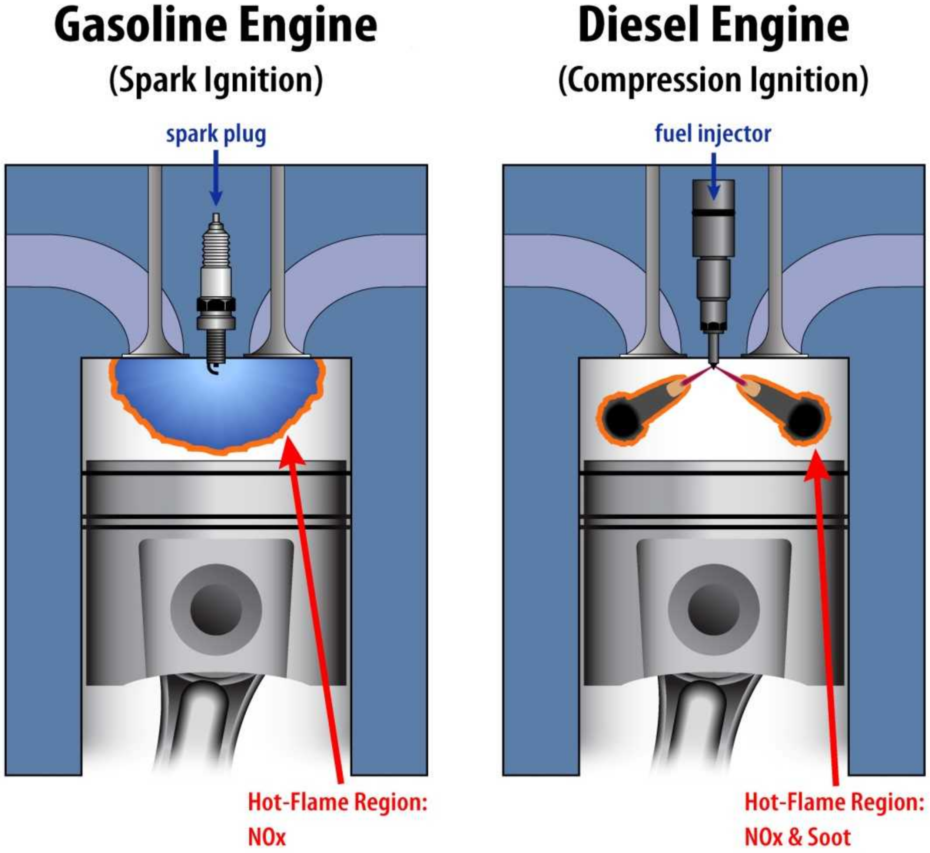
from *Transport, Energy and CO_2: Moving Toward Sustainability*, International Energy Agency 2009.



Deconstruction strategies – including synthetic biology – produce some novel fuel compounds

- Biomass-derived fuels
  - Current biofuels – ethanol & biodiesel – give relatively small reduction of GHG relative to petroleum
  - Cellulosic biofuels could give much greater GHG reduction, not compete with food production
    - Lignocellulosic biomass is challenging to deconstruct
    - Many new platforms are under development

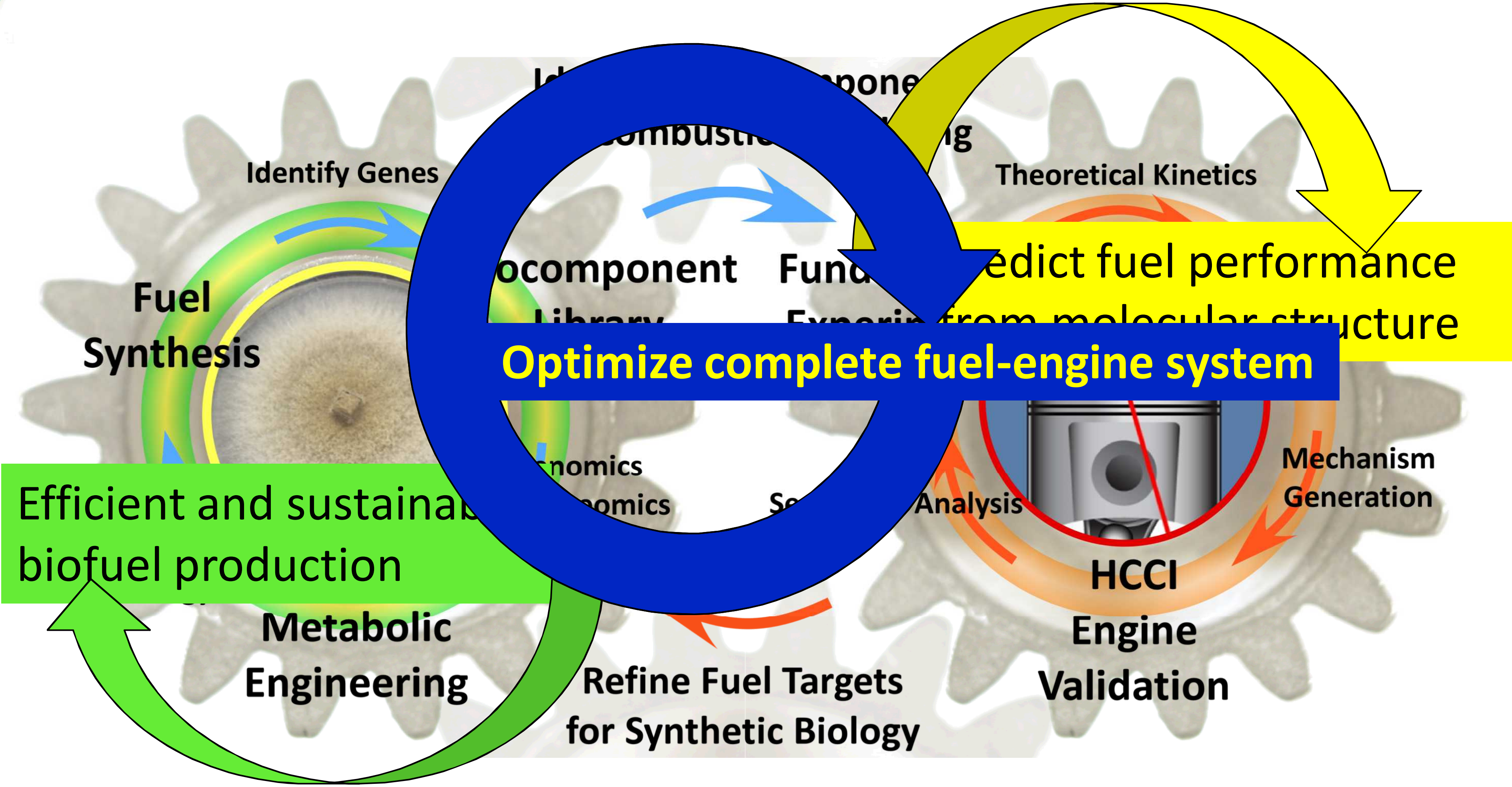
Advanced Engines Rely on Autoignition Chemistry to an Unprecedented Degree



Fuel chemistry is important – but fuel stream is already changing!

- New fuels can be disruptive, but they can also be enabling
- How can combustion studies mesh with new fuel development?

Tailoring Next-Generation Biofuels and their Combustion in Next-Generation Engines

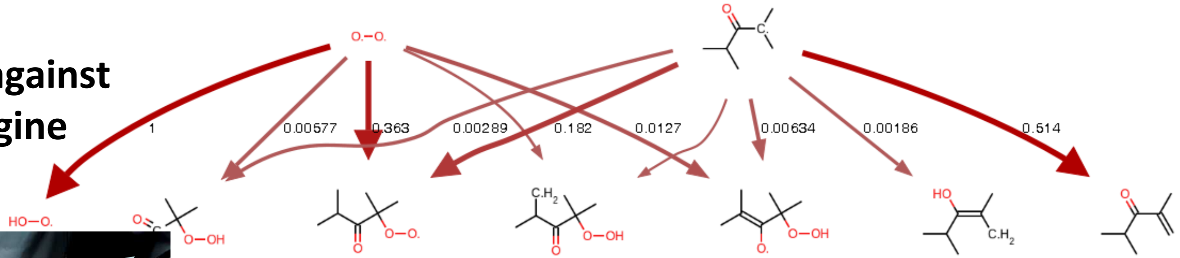


Optimize complete fuel-engine system

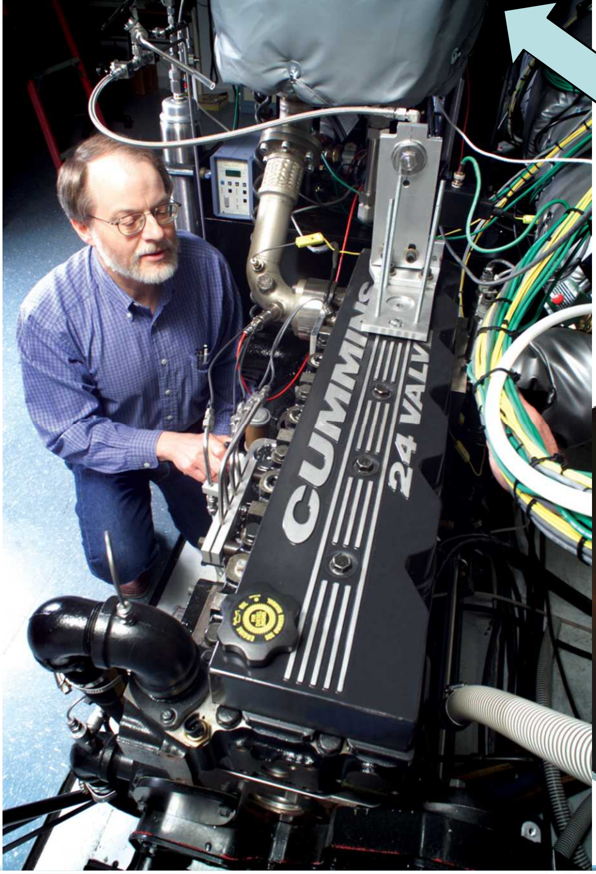
edict fuel performance
from molecular structure

Efficient and sustainab
biofuel production

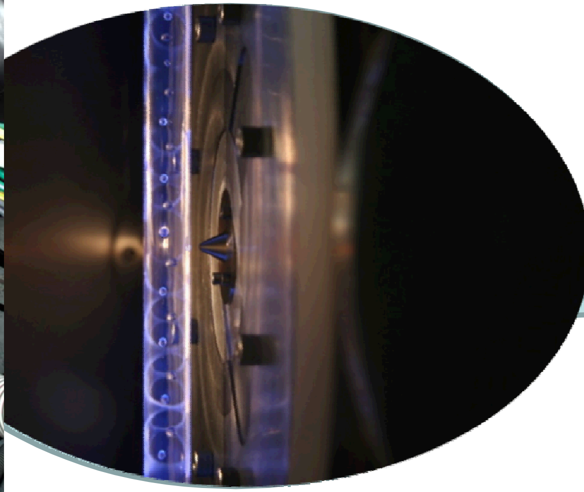
Combustion Chemistry Studies Build From Elementary Reactions to Engine Models



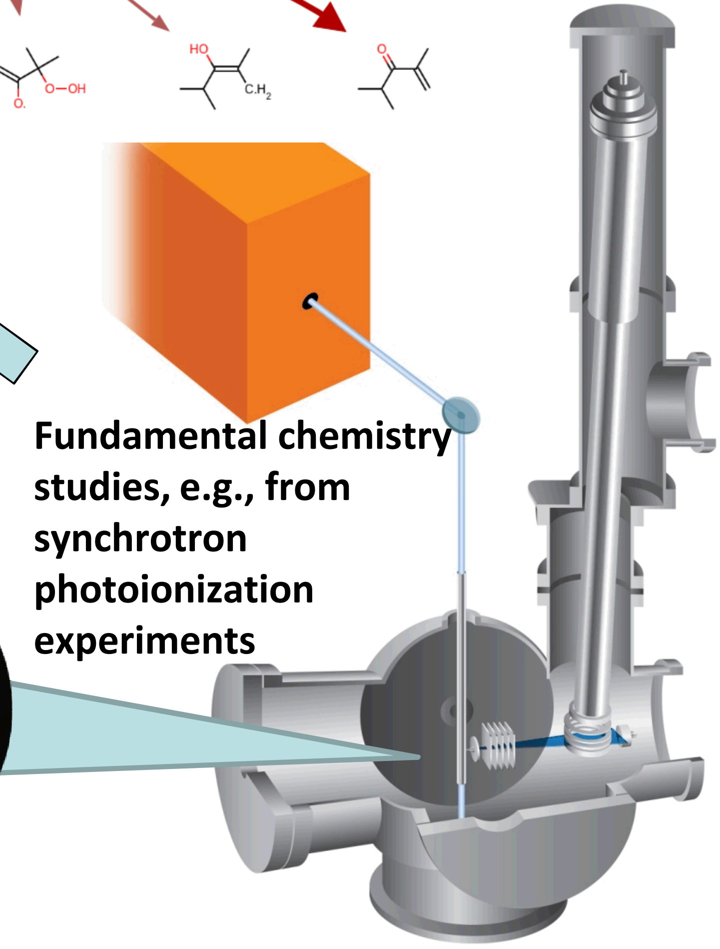
Which are validated against ignition delay and engine measurements



Inform new chemistry models, such as produced by MIT's Reaction Mechanism Generation framework

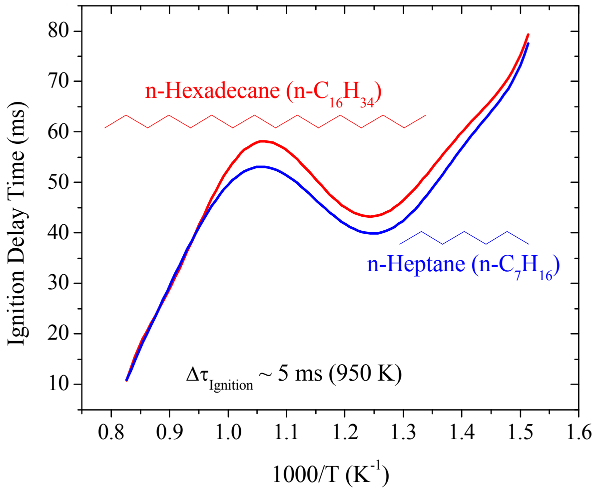


Fundamental chemistry studies, e.g., from synchrotron photoionization experiments

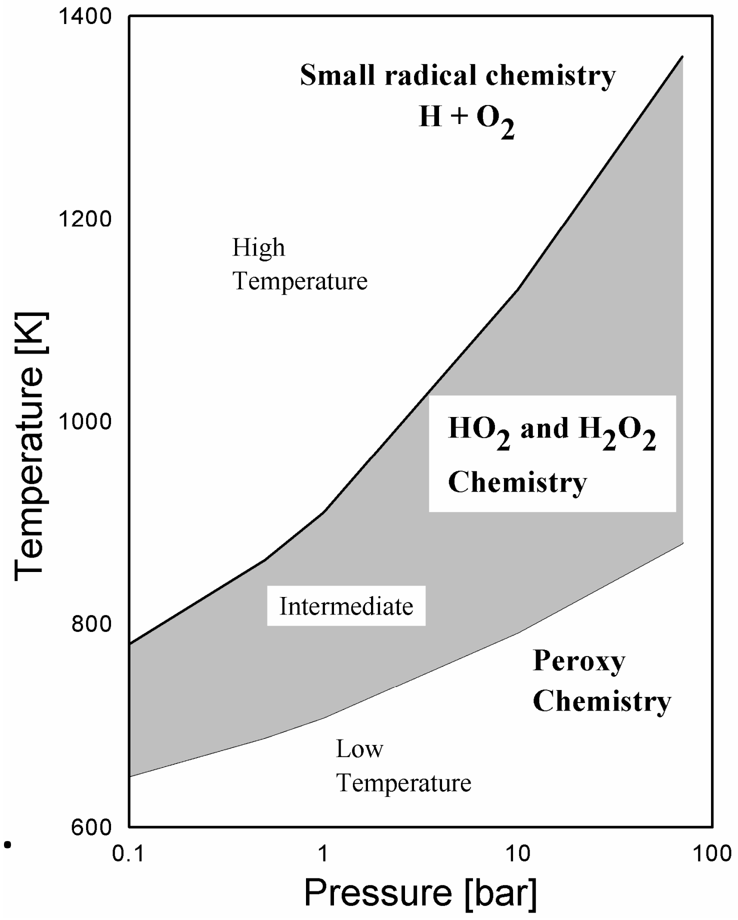


Fuel Effects on Ignition are Dominated by Low-Temperature Oxidation Chemistry

Ignition behavior of different fuels tend to coincide at high temperature



Westbrook et al., *Combust. Flame, 156 (2009)*

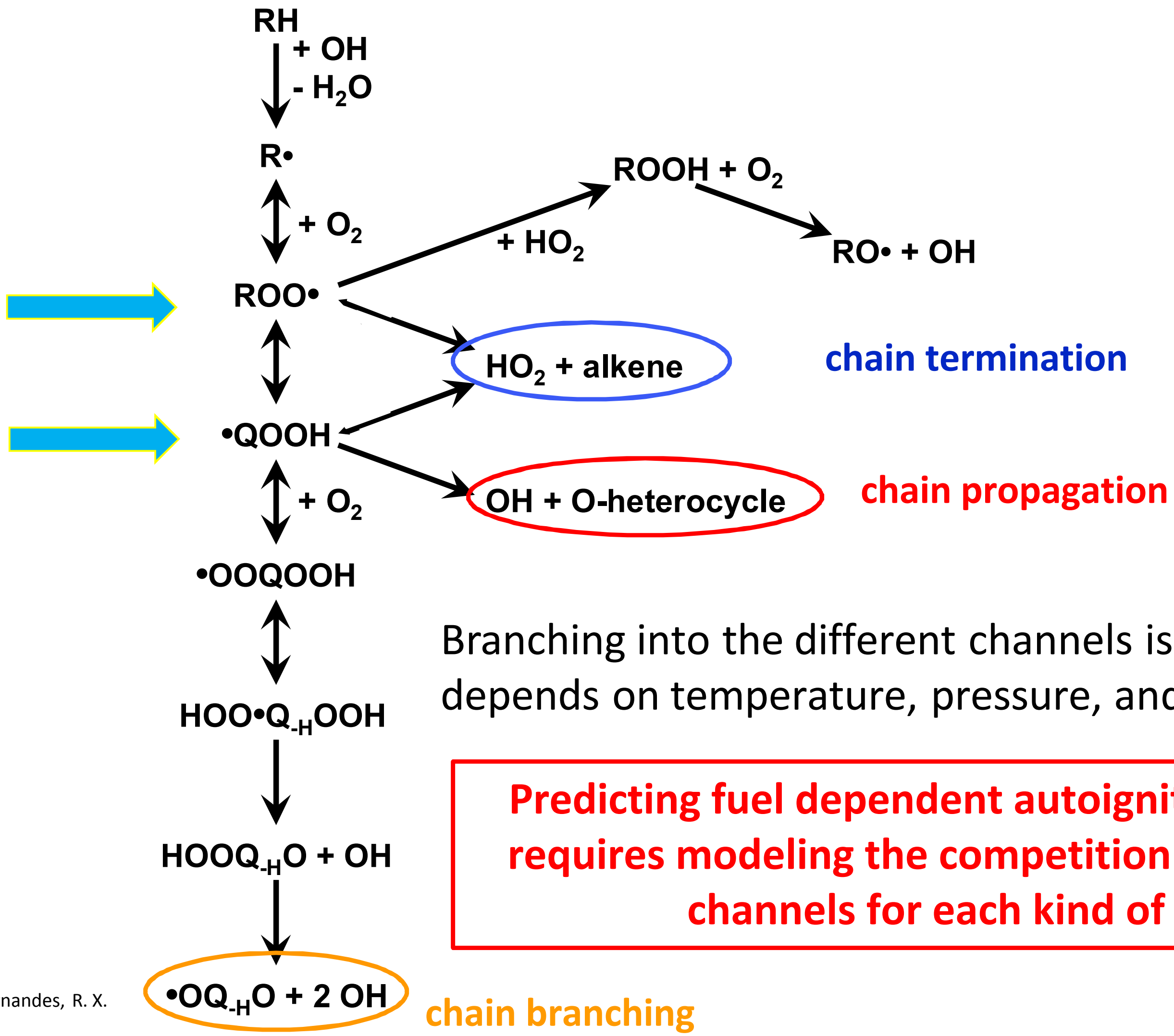


Vranckx et al, *Combust Flame* **2011**, 148, 1444 (1-butanol)

Fuel-chemistry effects on autoignition behavior appear in negative temperature coefficient region.

→ Fundamental kinetic studies in the low-temperature regime are critical

Predicting Low-Temperature Oxidation Requires Understanding Chemistry of Intermediates



RH

+ OH

- H_2O

R•

+ O_2

ROO•

+ HO_2

ROOH + O_2

RO• + OH

•QOOH

HO_2 + alkene

chain termination

+ O_2

OH + O-heterocycle

chain propagation

•OOQOOH

HOO•Q$_{-H}$OOH

HOOQ$_{-H}$O + OH

•OQ$_{-H}$O + 2 OH

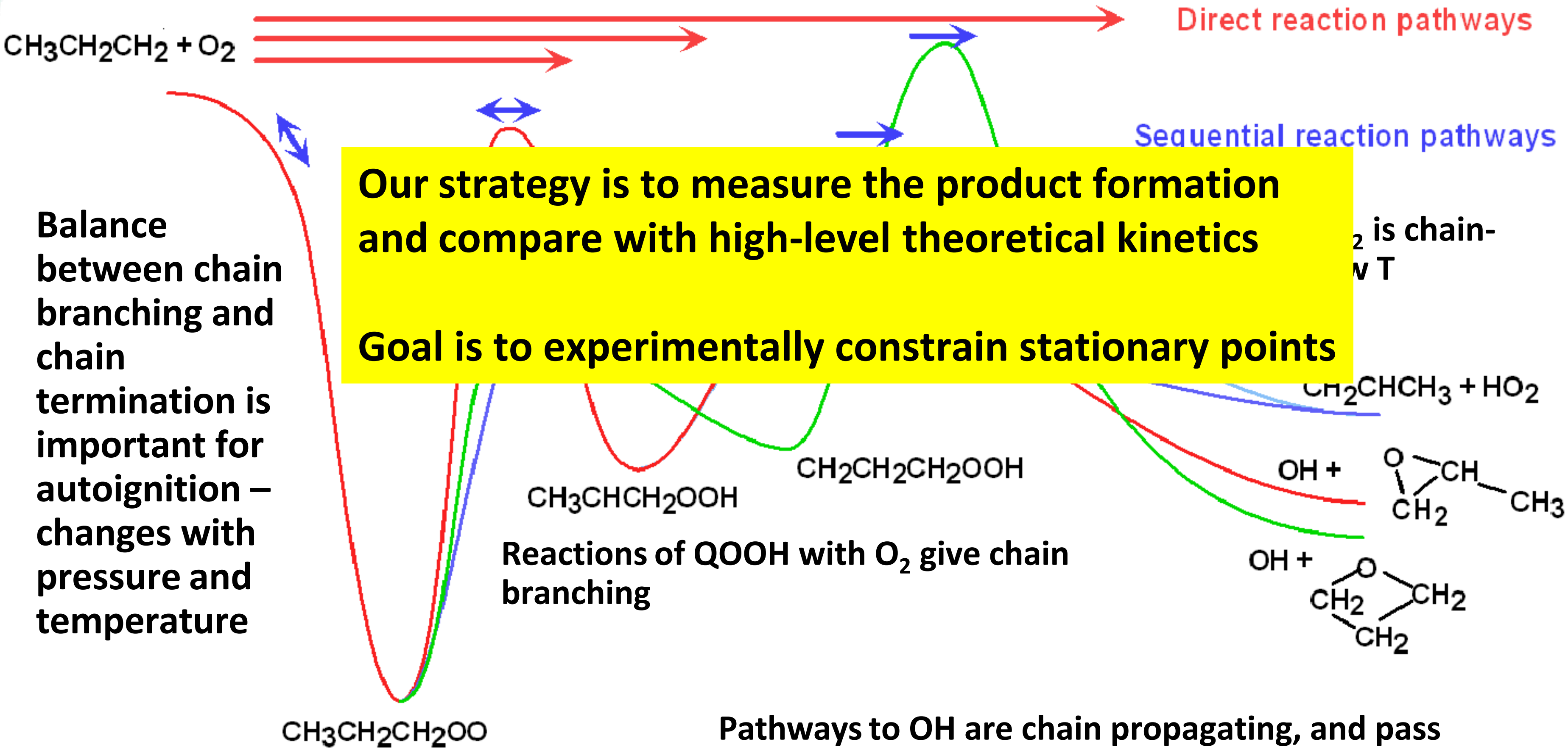
chain branching

Branching into the different channels is fuel-specific and depends on temperature, pressure, and O_2 concentration

Predicting fuel dependent autoignition behavior requires modeling the competition among these channels for each kind of fuel

Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *PECS* **2011**, *37*, 341.

The R + O_2 Reactions Are Critical in Low- and Intermediate Temperature Oxidation



Our strategy is to measure the product formation and compare with high-level theoretical kinetics

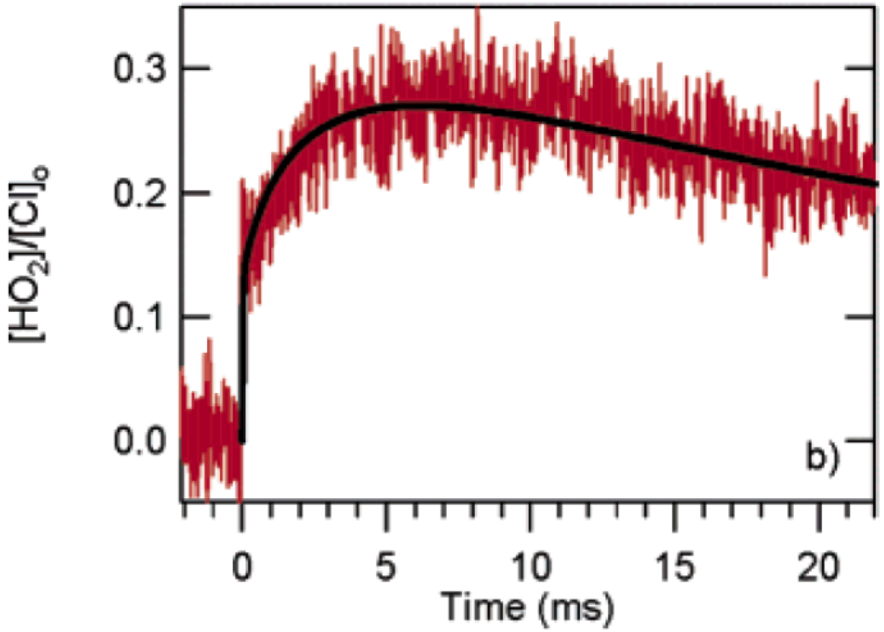
Goal is to experimentally constrain stationary points

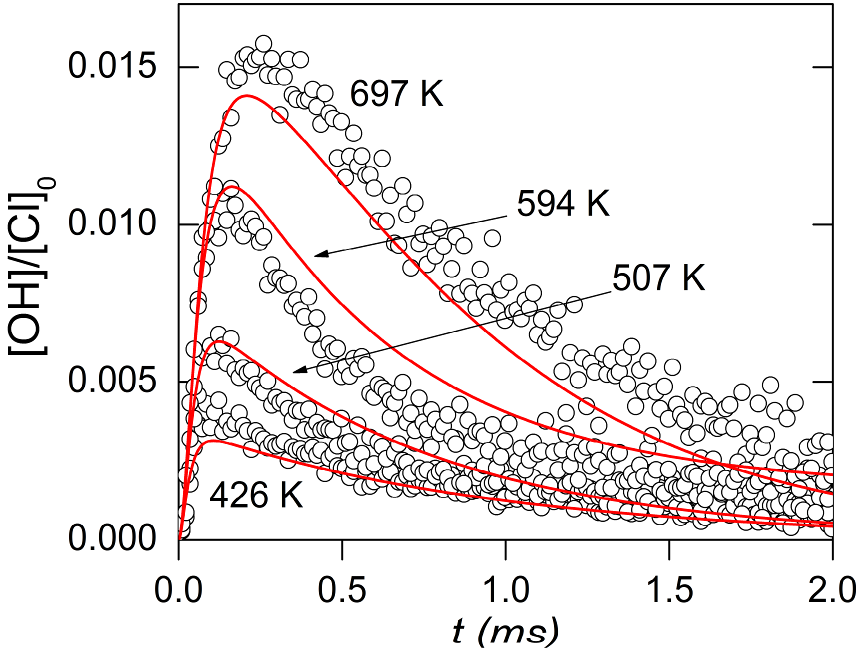
Balance between chain branching and chain termination is important for autoignition – changes with pressure and temperature

Reactions of QOOH with O_2 give chain branching

Pathways to OH are chain propagating, and pass through “QOOH” intermediate

Measurements of the important radical products HO_2 and OH constrain calculations





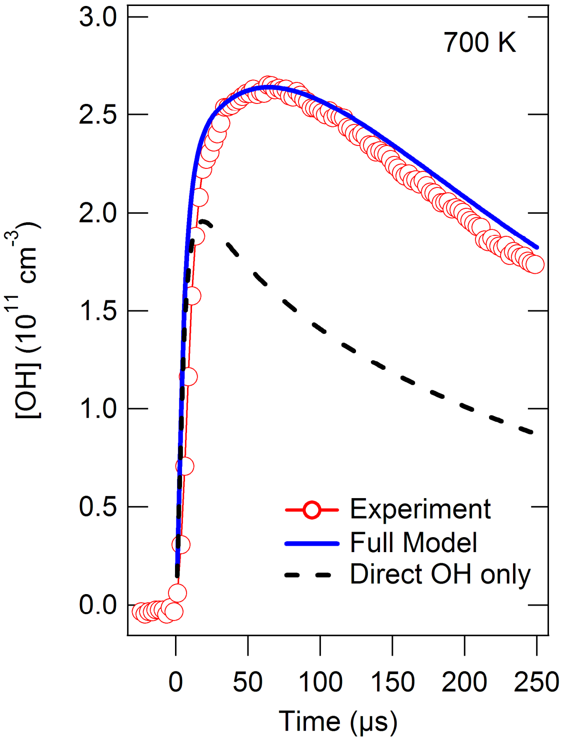
Pulsed photolytic Cl-initiated oxidation, with absorption detection of radicals

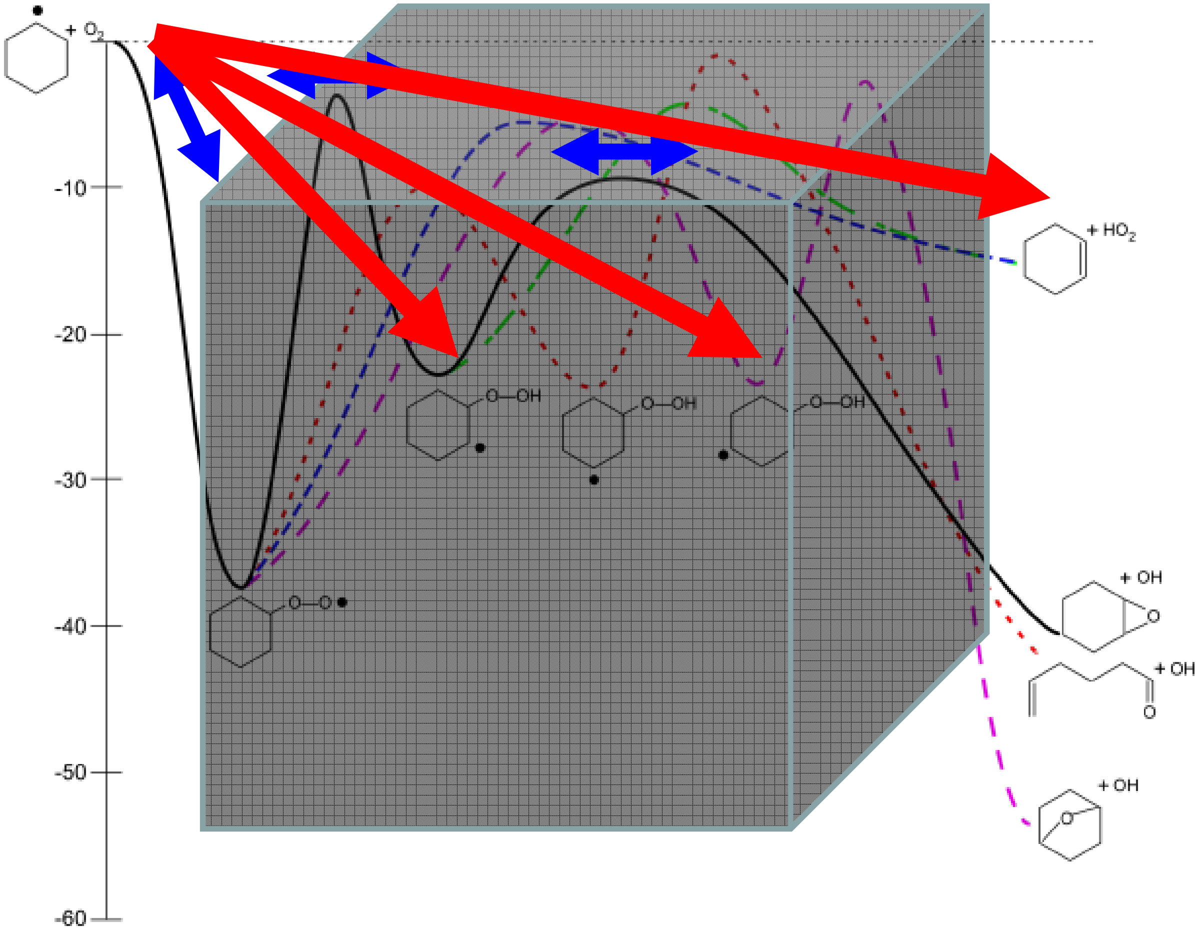
Direct and sequential product formation are kinetically separated

Stationary point *energies* are adjusted to match all data.

How Does This Tell Us Anything about the Intermediates? Deal with the **Black Box!**

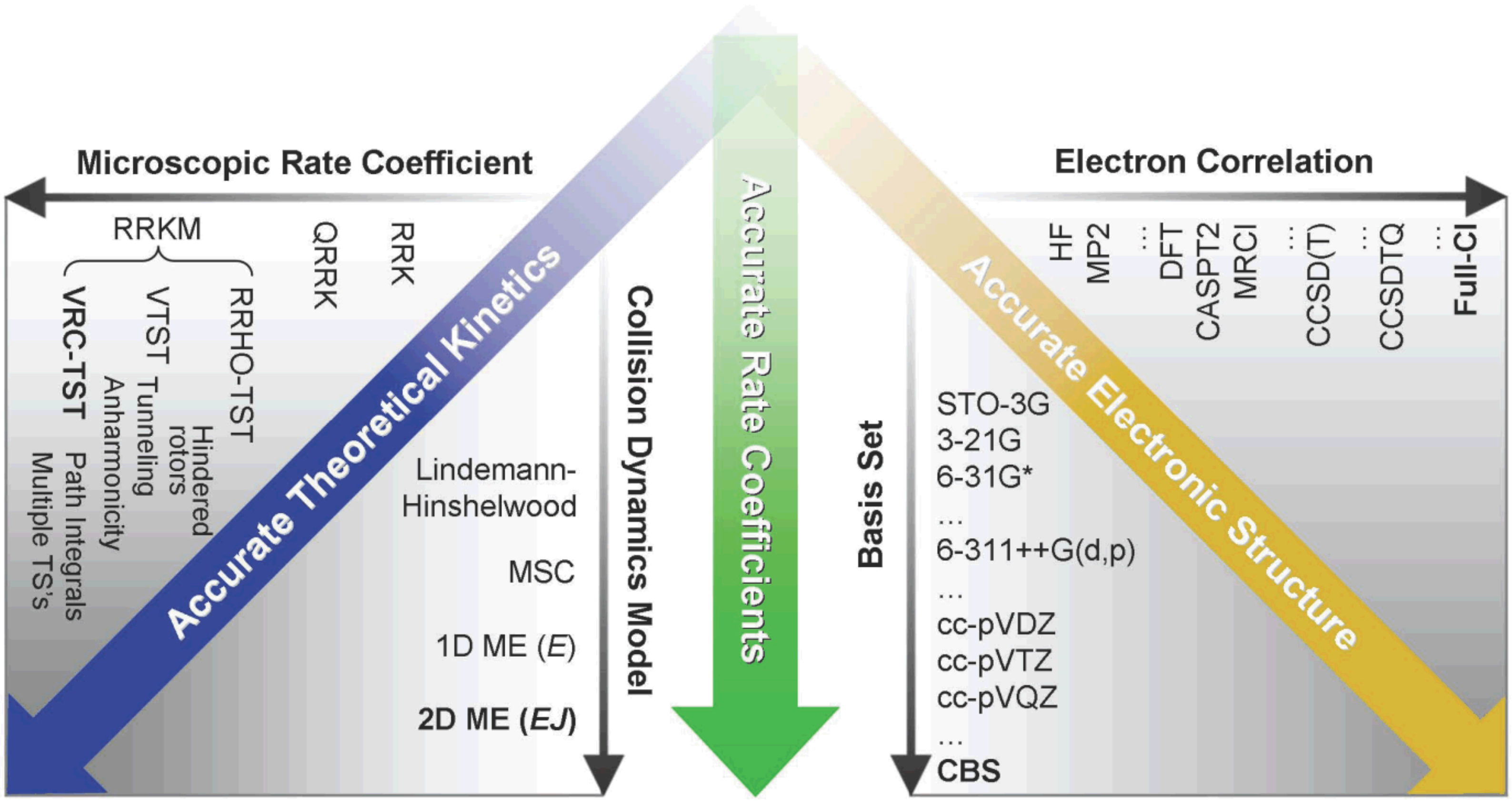
Measured products from pulsed photolytically initiated R + O_2 reactions compared to theory





Experimental ambiguity: e.g., OH measurements don't tell *which* QOOH contributes

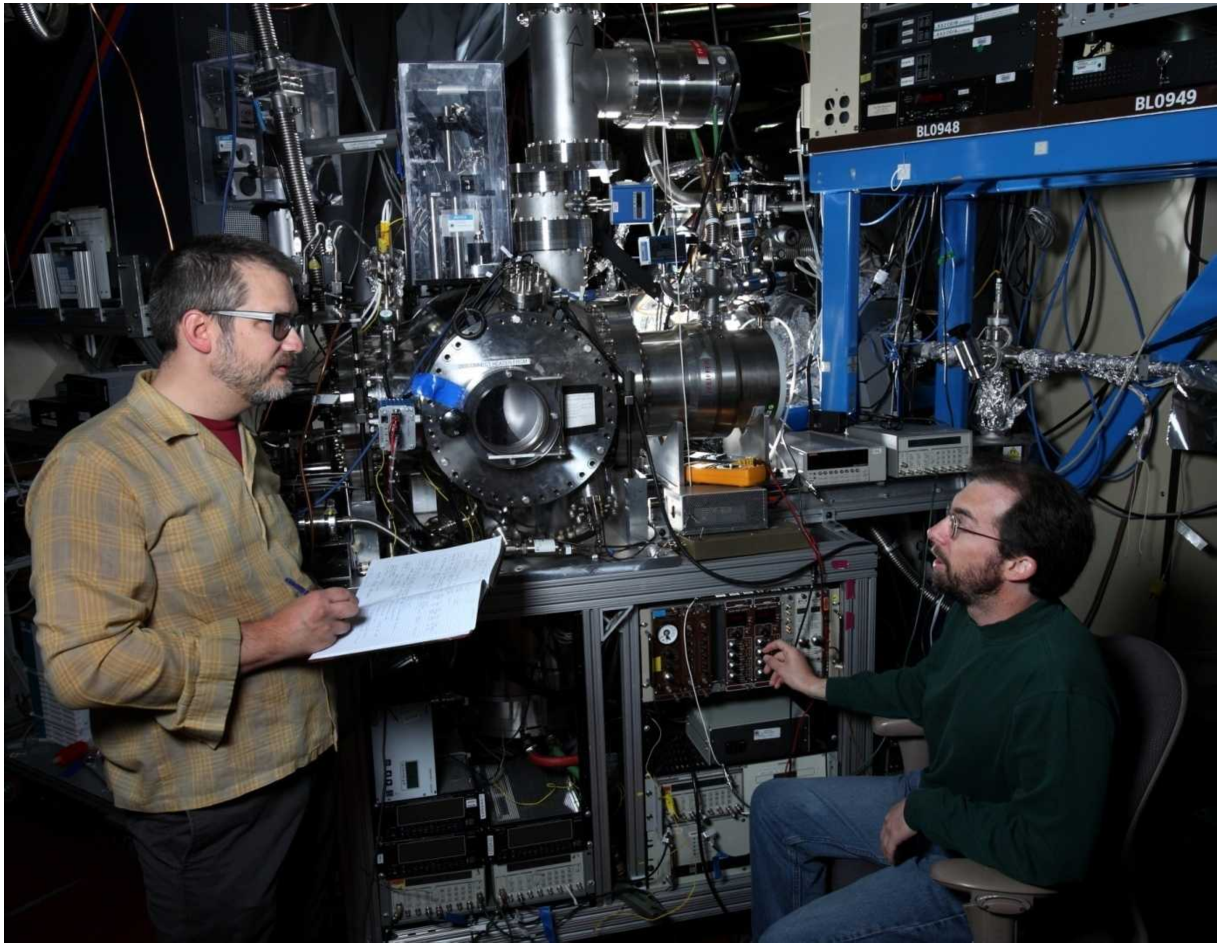
Experimental kinetics *indirectly* relates to physical characteristics of the potential energy surface



Experimental constraints on the stationary point characteristics rely on the accuracy of the theoretical kinetics method

More accurate quantum chemistry may highlight inadequacies in the kinetics!

Molecular structure effects on autoignition: two products (OH and HO_2) aren't always enough



Tunable synchrotron photoionization mass spectrometry

Collaboration between Sandia CRF (**David Osborn,** C.A.T.) and LBNL (Musa Ahmed, Kevin Wilson, Steve Leone)

Osborn et al., *Rev. Sci. Instrum.* **79**, 104103 (2008)

Laser photolysis reactor is coupled to time-of-flight mass spectrometer with synchrotron photoionization

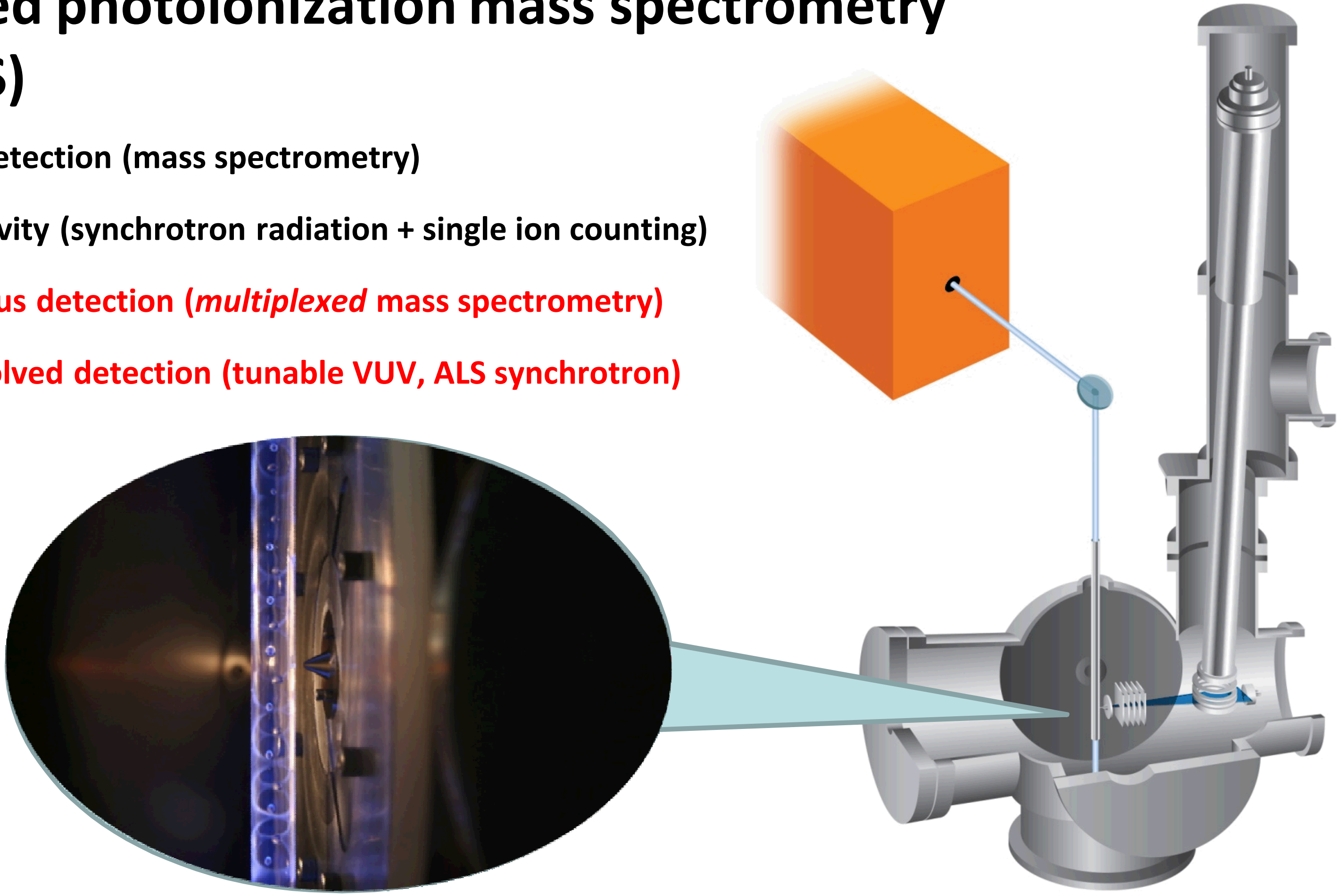
Multiplexed photoionization mass spectrometry (MPIMS)

Universal detection (mass spectrometry)

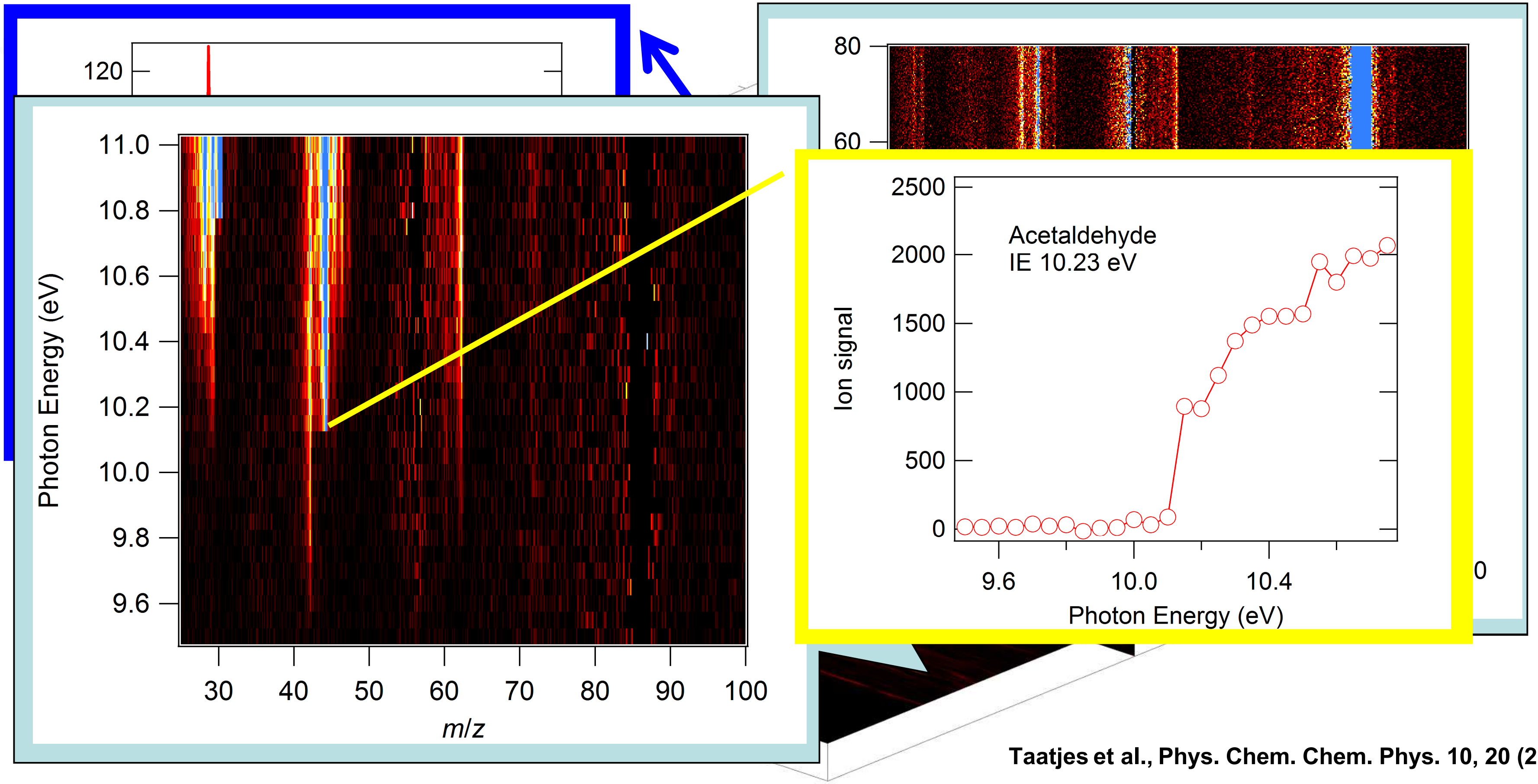
High sensitivity (synchrotron radiation + single ion counting)

Simultaneous detection (*multiplexed* mass spectrometry)

Isomer-resolved detection (tunable VUV, ALS synchrotron)



Kinetic Data is Acquired as a Function of Time, Mass, and Photoionization Energy



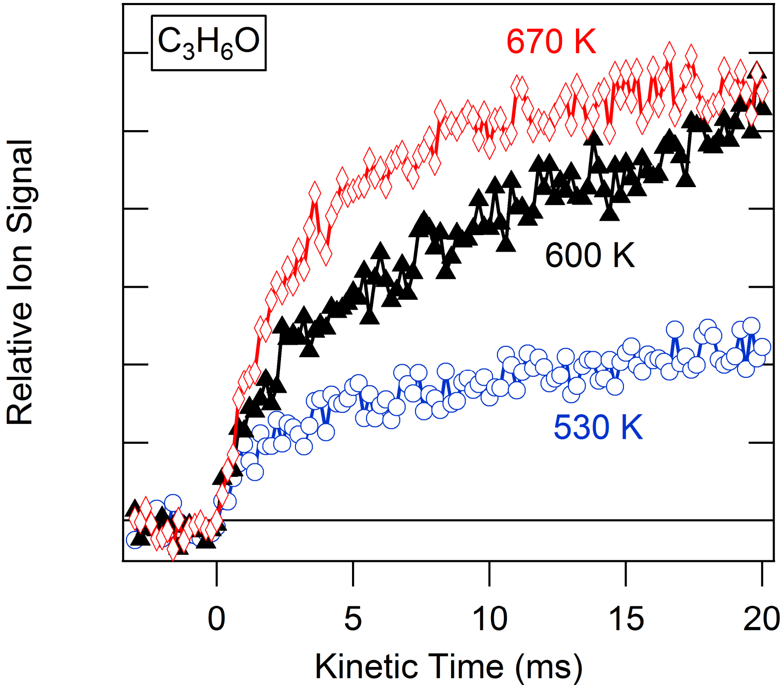
Taatjes et al., Phys. Chem. Chem. Phys. 10, 20 (2008).

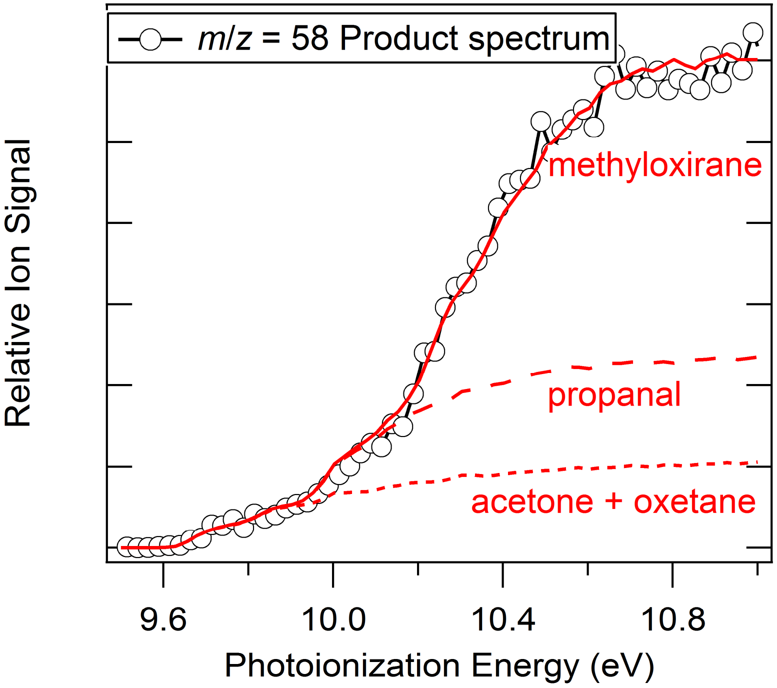
3-D dataset can be "sliced" along different axes to probe different aspects of the reaction

Mass spectroscopic measurements can identify isomeric pathways

Time profiles of stable products reflect same bimodal behavior as radicals

Multiple C_3H_6O isomers are formed in unimolecular reactions of ROO



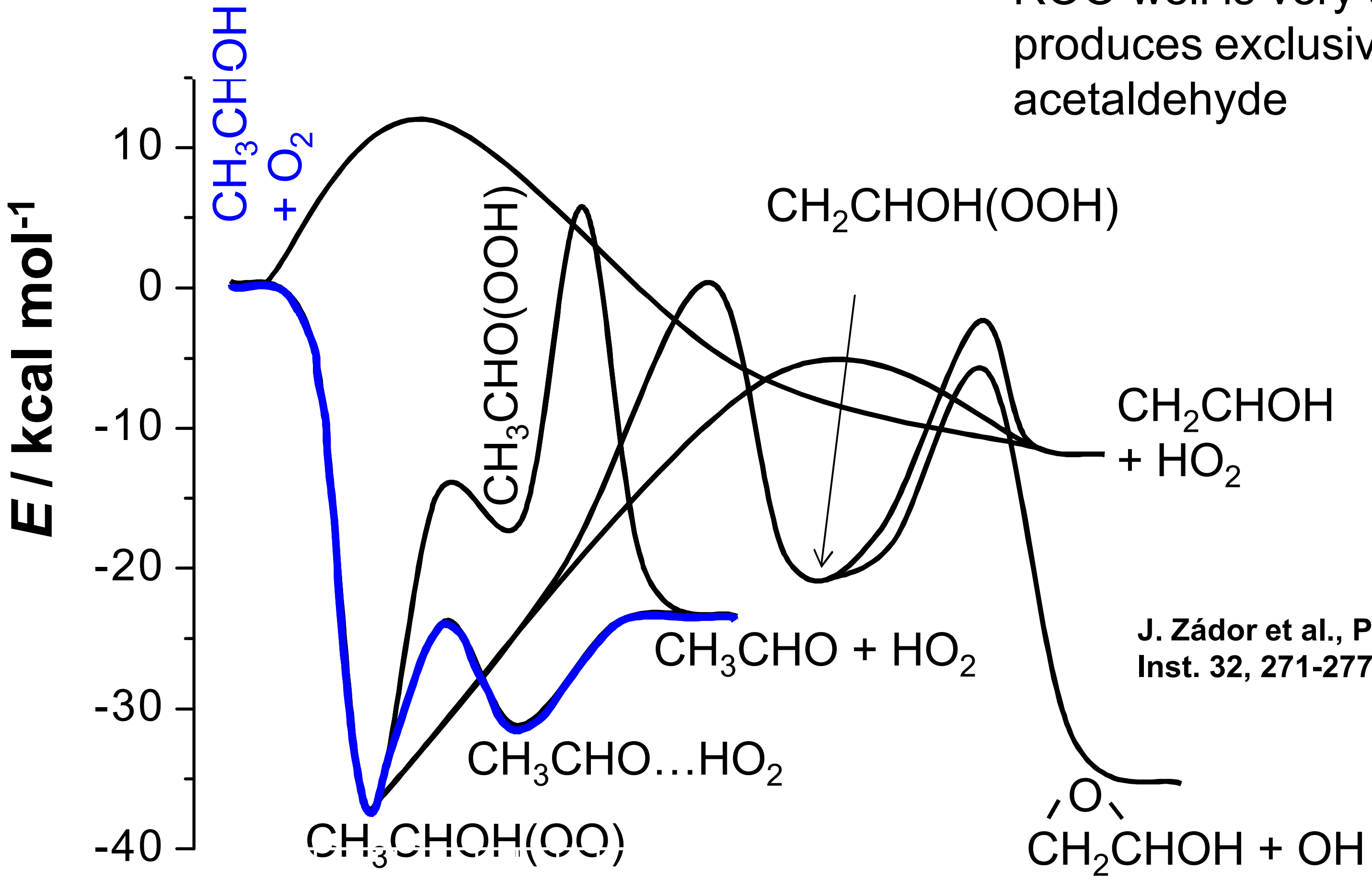


Combine with high-pressure MPIMS (Lenny Sheps), radical product measurements and literature experiments: multi-scale informatics (Mike Burke et al., Argonne)

How Might Functionalization Affect Ignition Chemistry? Alcohols Give One Example

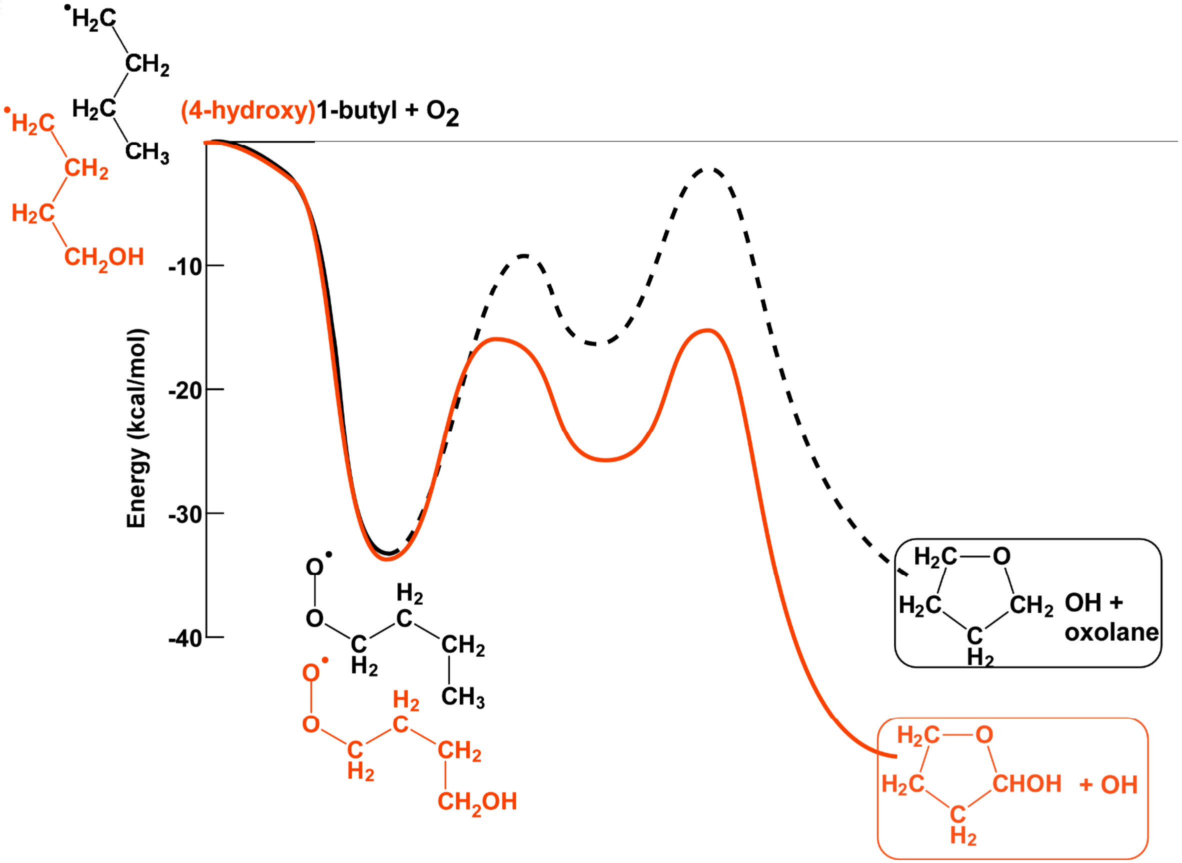
OH group changes the thermochemistry

1-hydroxyethyl + O_2
ROO well is very shallow – produces exclusively HO_2 + acetaldehyde



J. Zádor et al., Proc. Combust. Inst. 32, 271-277 (2009)

In n-butanol oxidation, all hydroxybutyl + O_2 reactions are affected by OH group



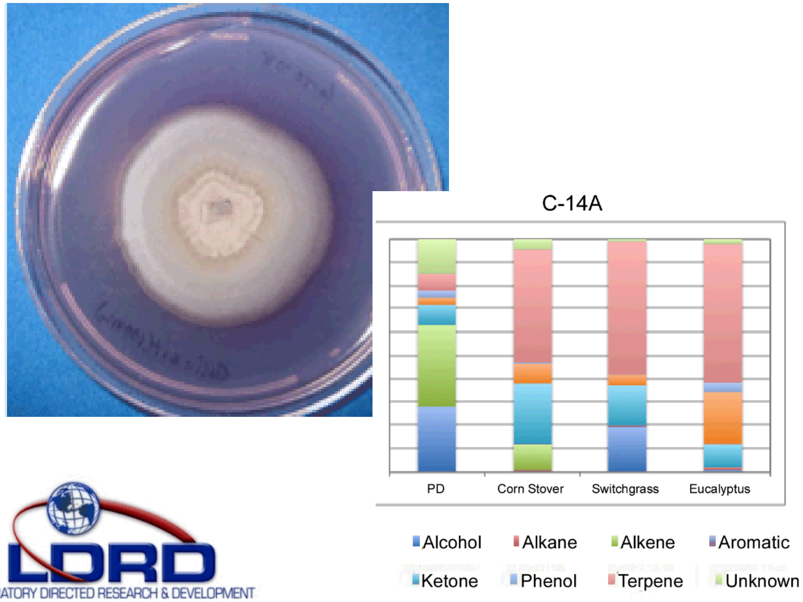
α-hydroxyalkyl reaction forms HO_2

β-hydroxyalkyl reaction Waddington mechanism

Weaker α-C—H bond favors OH formation

Oliver Welz, July 16

What might other "next-generation" biofuel production platforms offer?



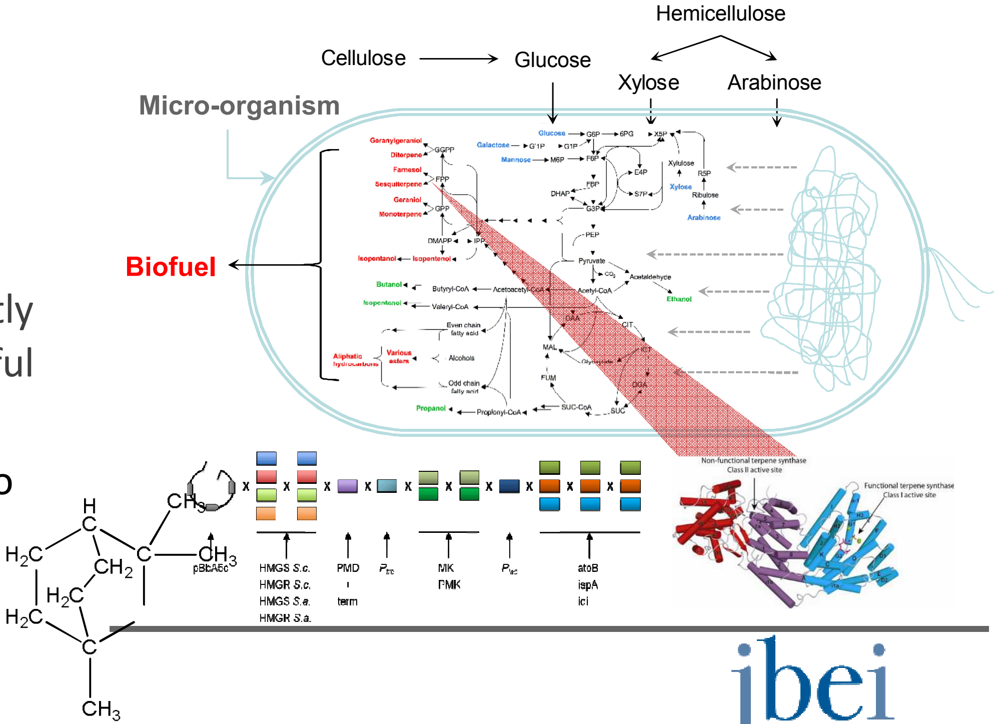
Bioengineered organisms may be able to efficiently convert sugars to useful fuels

Terpenes, **sesquiterpenes** and their derivatives are prominent targets

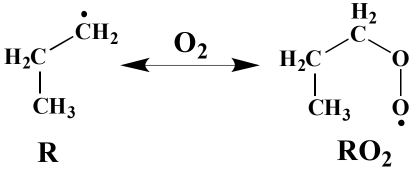
Endophytic fungi can degrade cellulose directly and produce a spectrum of potentially useful organic compounds

Synthetic biology tools are being employed to exploit metabolic pathways of fungi

Ketones and cyclic ethers (e.g., cineole) are among the natural fungal products



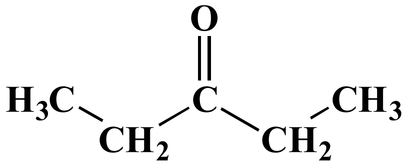
Recall the oxidation mechanism of *n*-propyl radicals



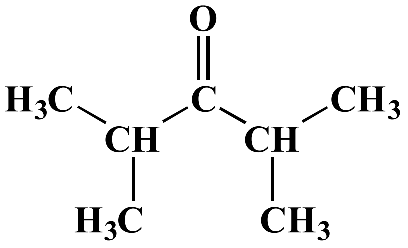
J. D. DeSain et al. *J. Phys. Chem. A* **2003**, *107*, (4415).

- Coproducts of HO_2 elimination appear at fuel mass – 2 (unsaturated hydrocarbon) and coproduct of OH at fuel + 14 (e.g., cyclic ether)

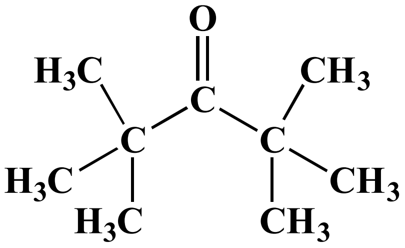
Fundamental ignition chemistry of potential fungal biofuels: ketones



Diethyl Ketone

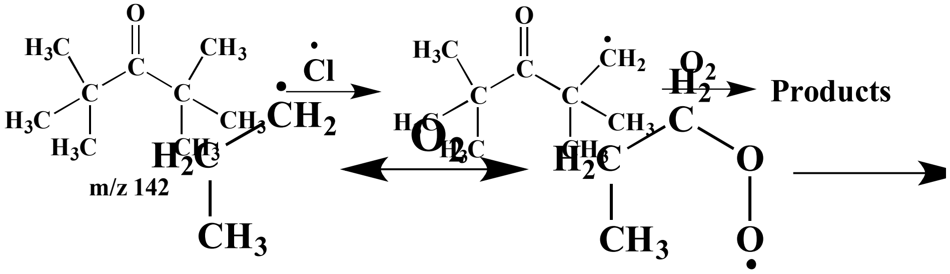


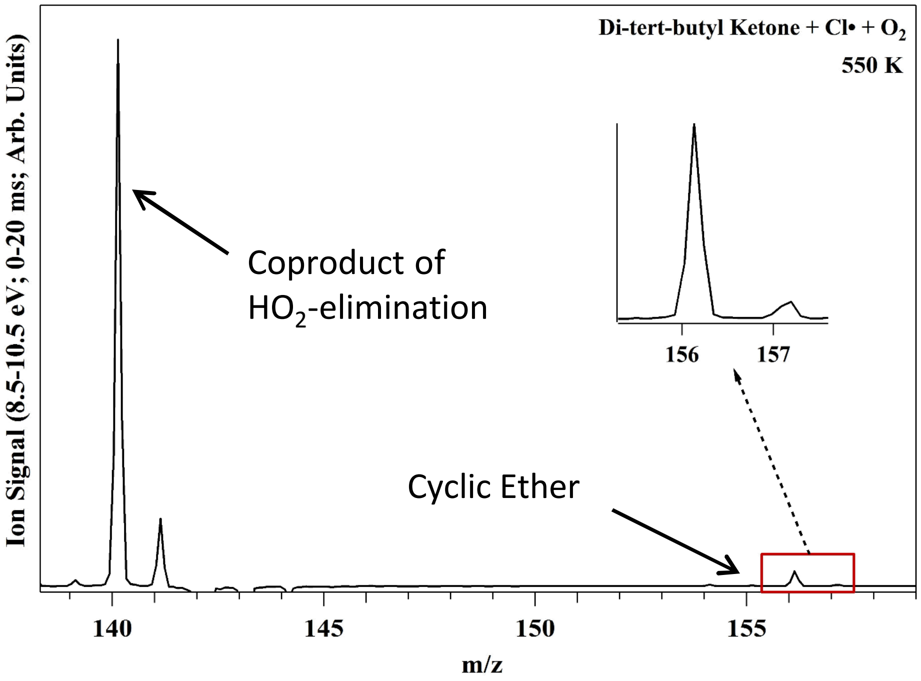
Diisopropyl Ketone



Di-tert-butyl Ketone

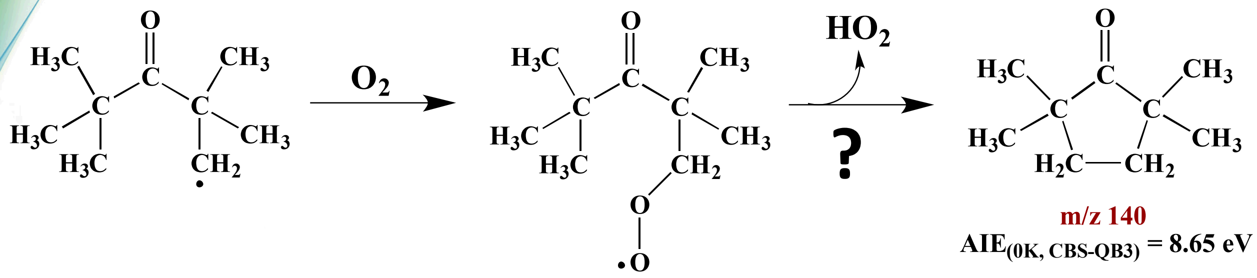
Di-tert-butyl ketone is the largest and m
possible initial radical; no expected HO_2-



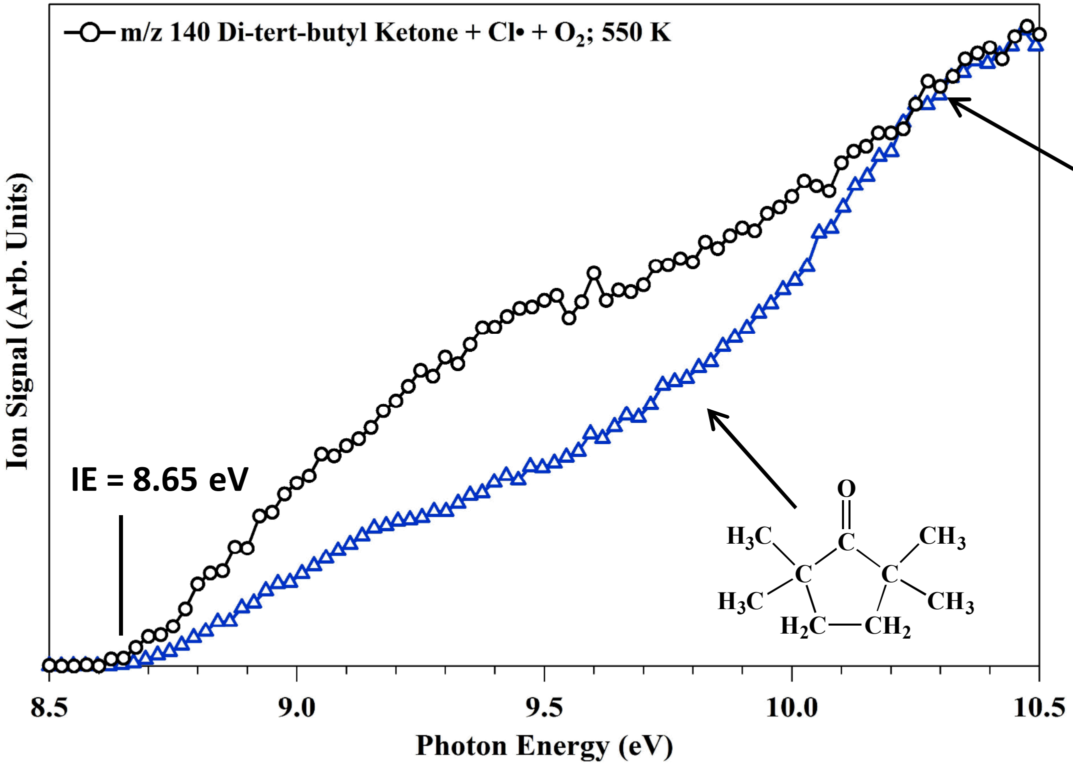


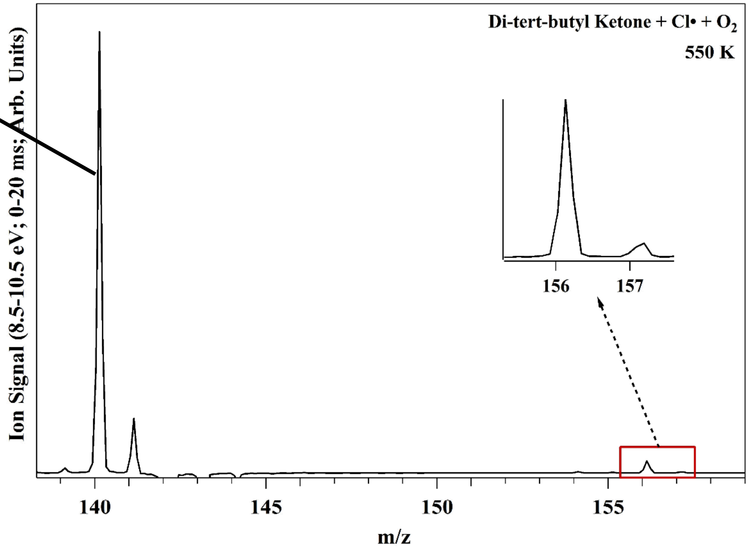
Structure requirement for HO_2-eliminatio
each also bound to at least one H atom

Could this be Ring Closure Yielding HO_2-Elimination?

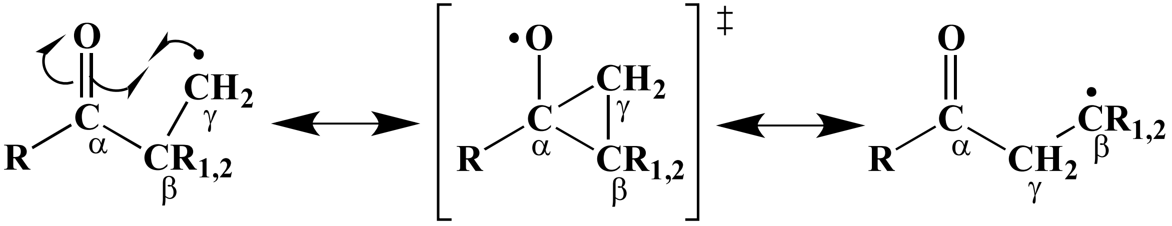


Calculated ionization energy matches experimental onset.



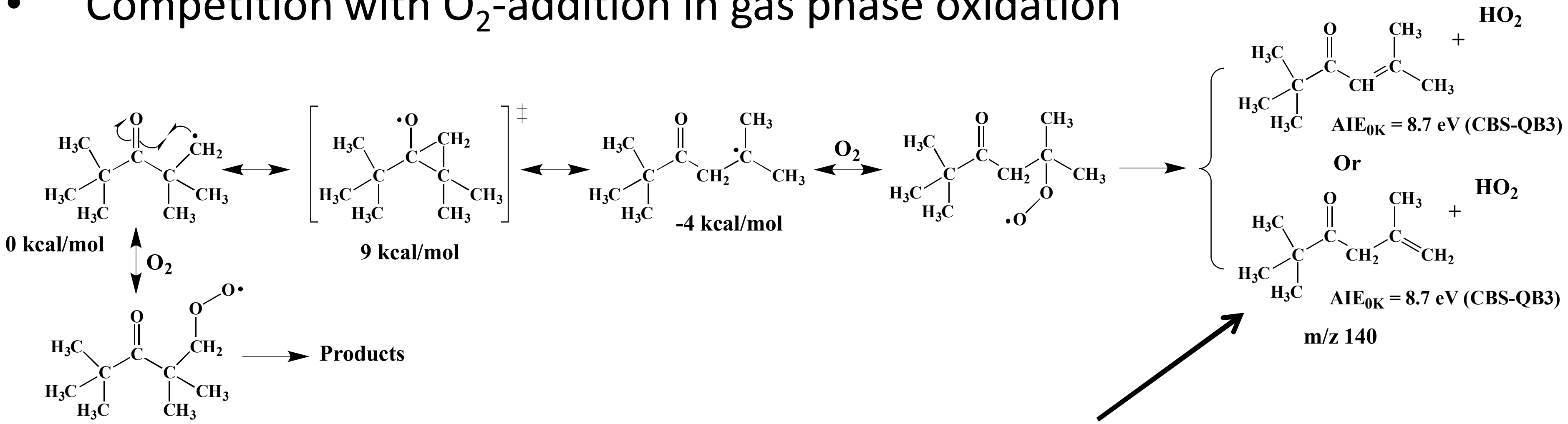


Maybe the initial radical isomerizes rapidly?



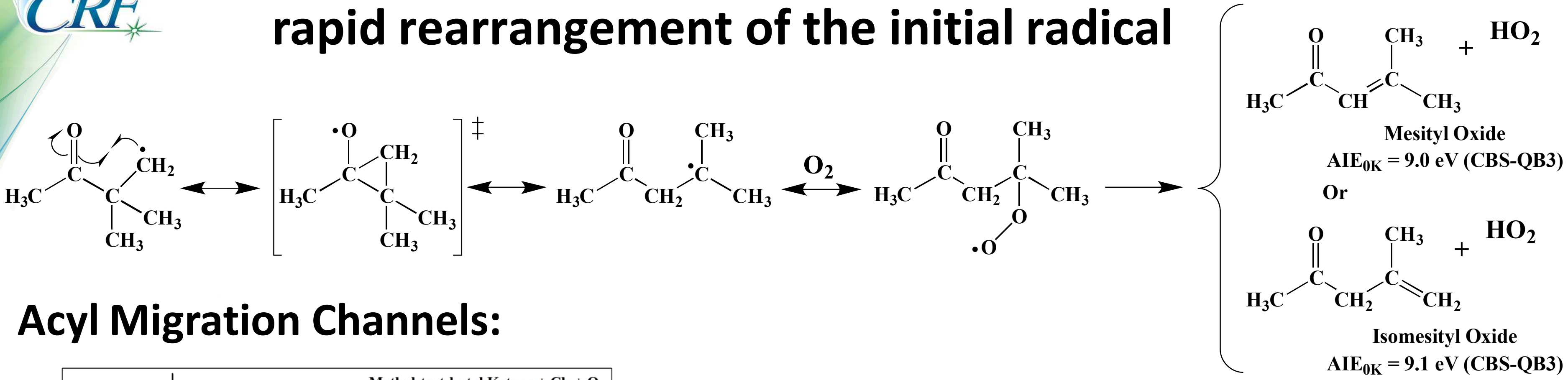
Karl et al. *J. Org. Chem.* **37**, 2834 (1972)

- Thermodynamic driving force depending on substituents
- Competition with O_2-addition in gas phase oxidation



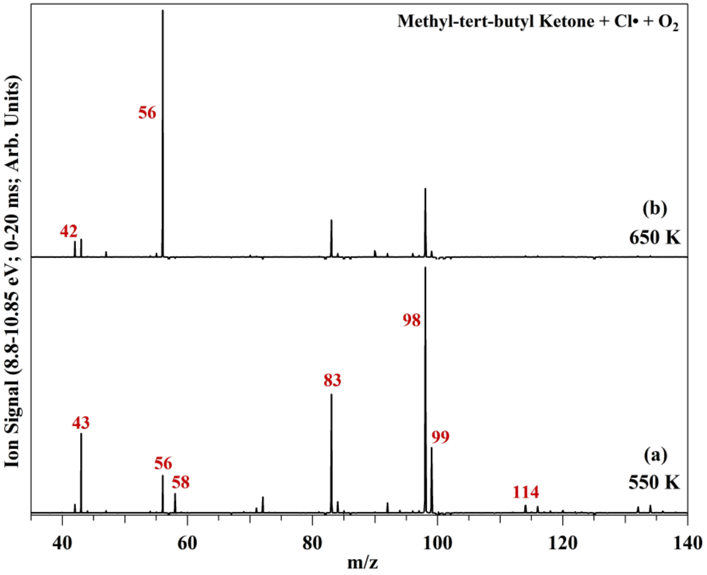
- Neither product commercially available

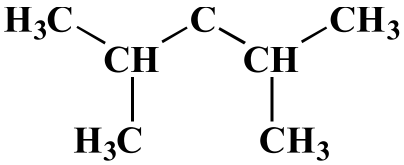
Methyl-tert-butyl ketone oxidation demonstrates the rapid rearrangement of the initial radical



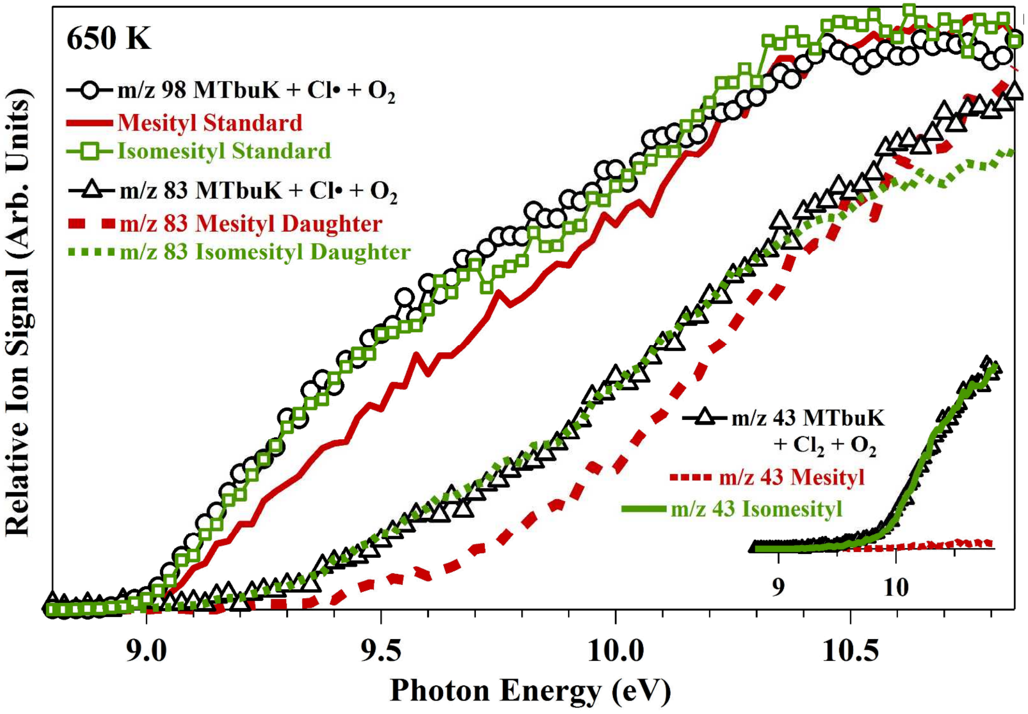
m/z 98

Acyl Migration Channels:

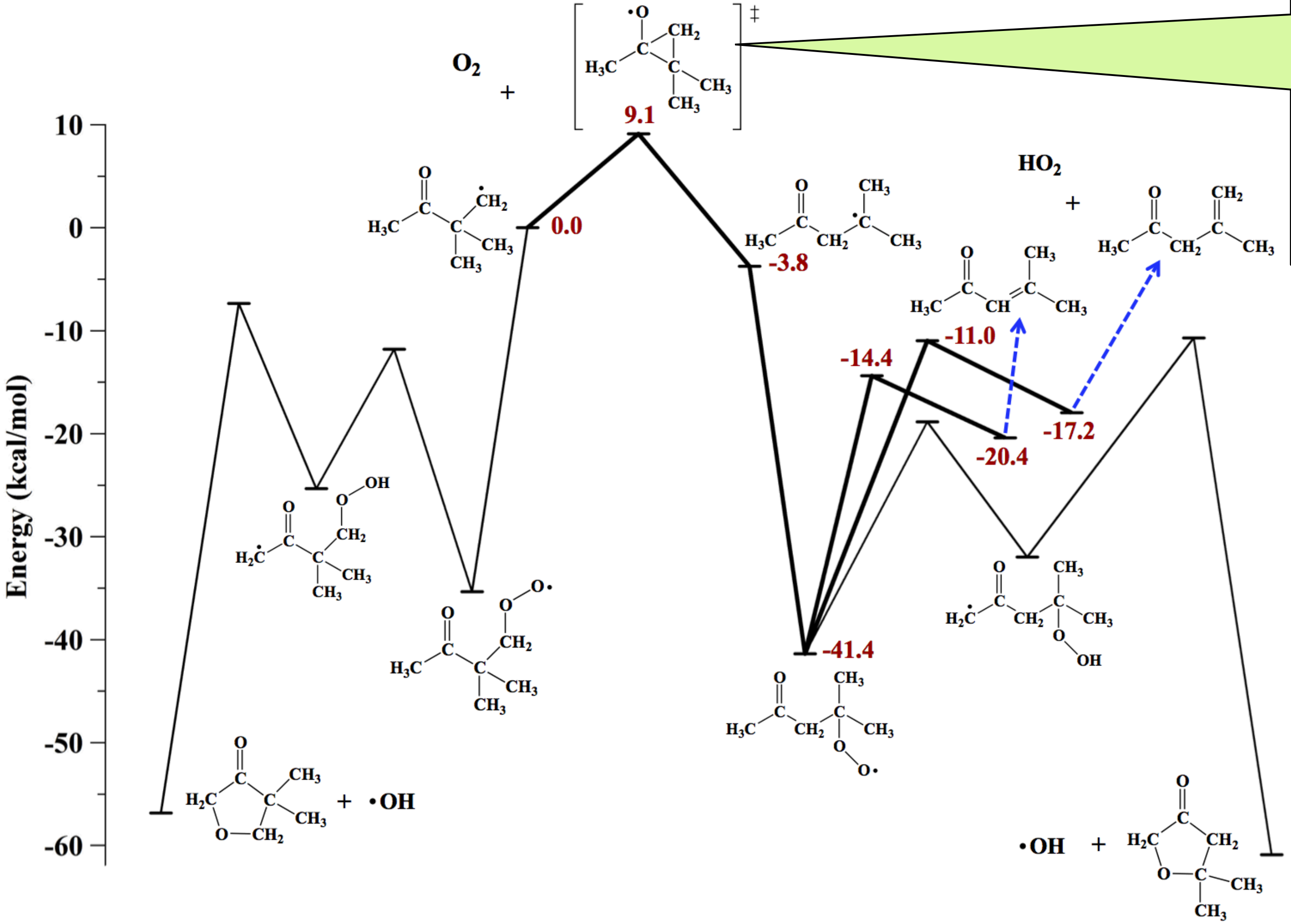


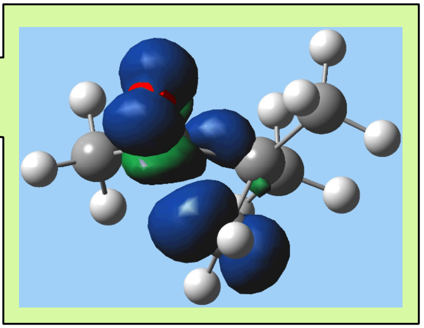


Diisopropyl Ketone



Rearrangement over a small barrier is rapid enough to compete with O_2 addition



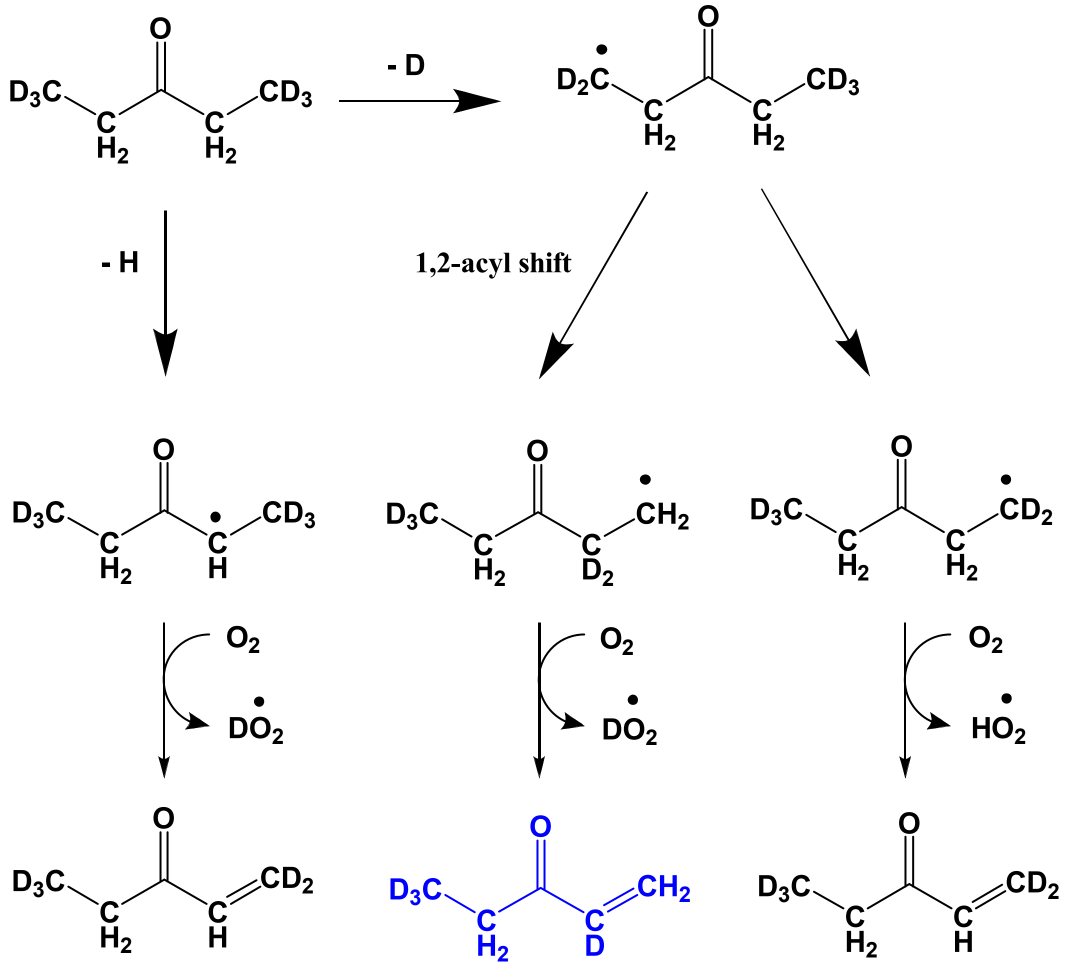


Transition state is not simple cyclopropoxy

Thermodynamics favors the rearranged product for MtBK

Isomerization changes amount of chain propagation and termination

Even without any Enthalpic Driver, the isomerization is observed

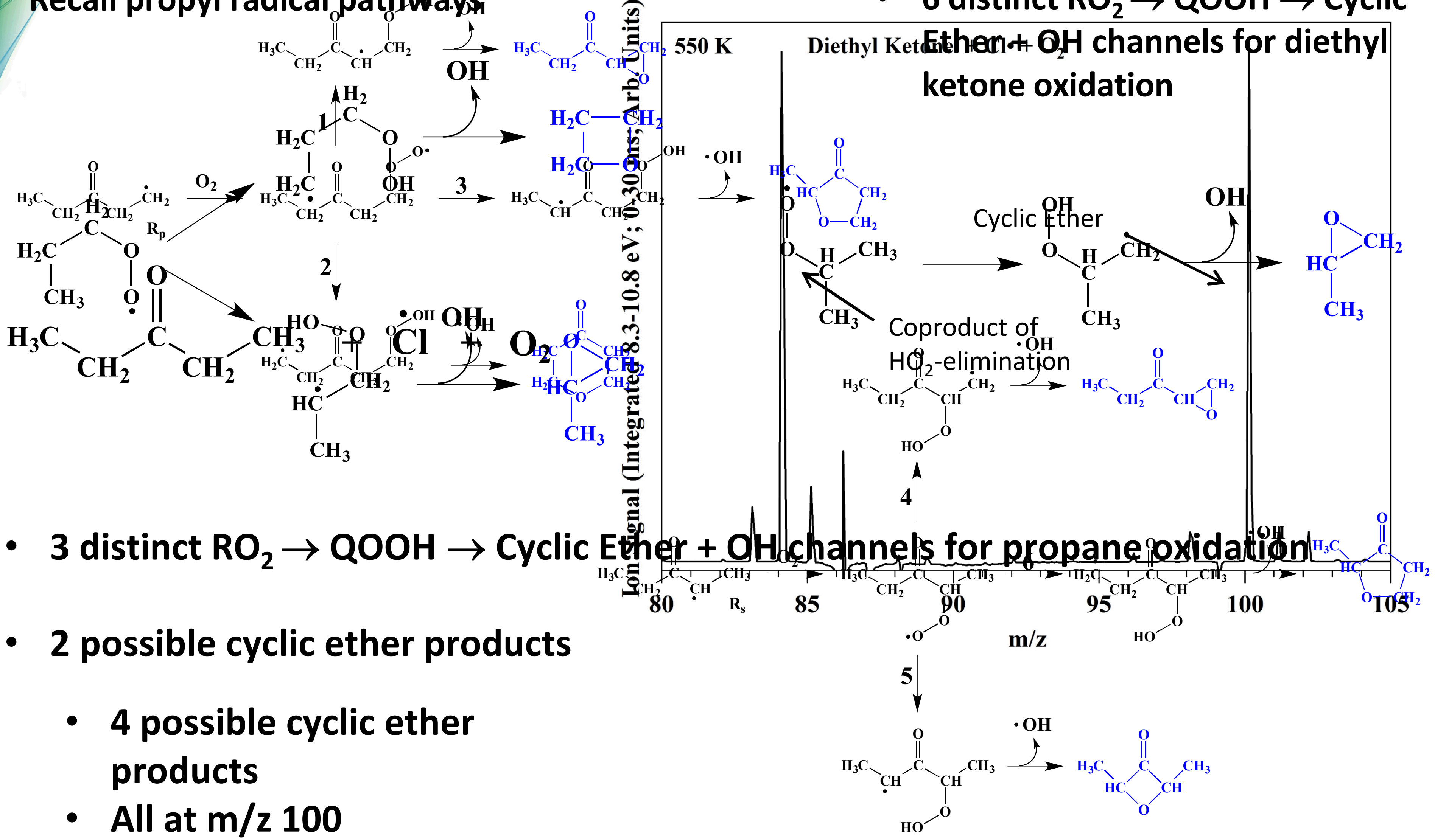


MVK-d_5 $m/z = 89$ MVK-d_4 $m/z = 88$ MVK-d_5 $m/z = 89$

Now Consider Cyclic Ether Formation Possibilities in Ketone Oxidation

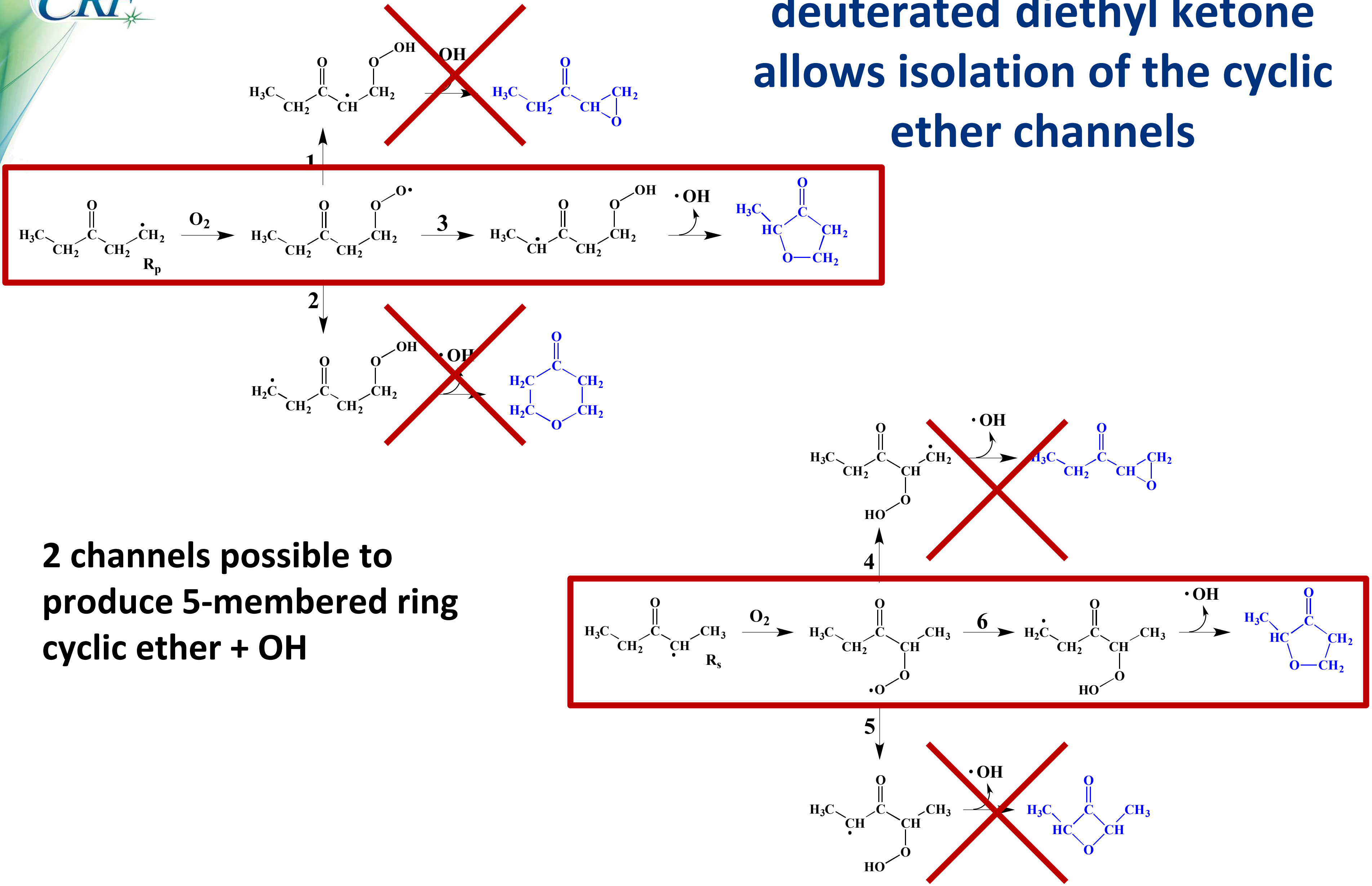
Recall propyl radical pathways

- 6 distinct $RO_2 \rightarrow QOOH \rightarrow$ Cyclic Ether + OH channels for diethyl ketone oxidation



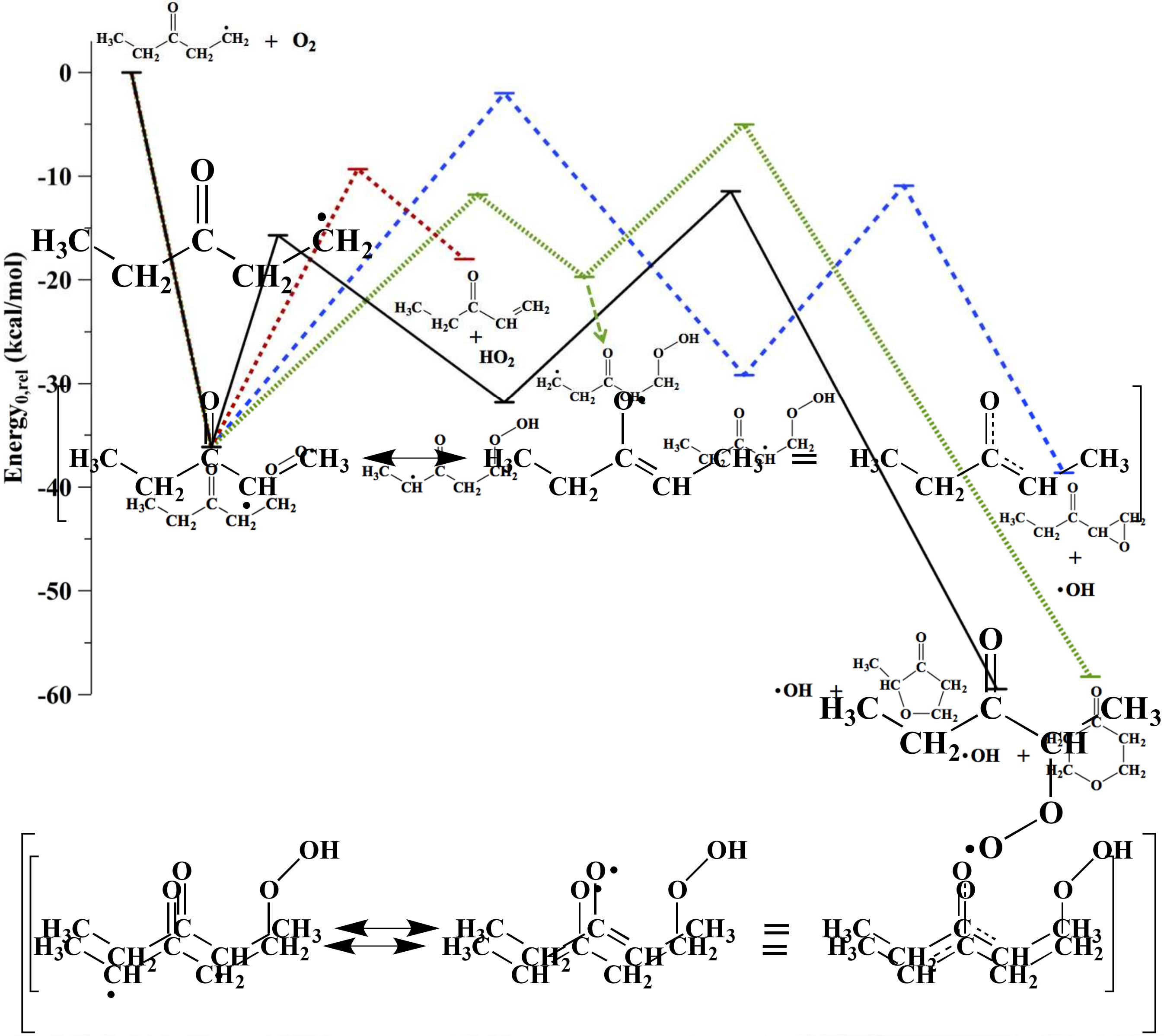
- 3 distinct $RO_2 \rightarrow QOOH \rightarrow$ Cyclic Ether + OH channels for propane oxidation
- 2 possible cyclic ether products
  - 4 possible cyclic ether products
  - All at m/z 100

Oxidation of partially deuterated diethyl ketone allows isolation of the cyclic ether channels



2 channels possible to produce 5-membered ring cyclic ether + OH

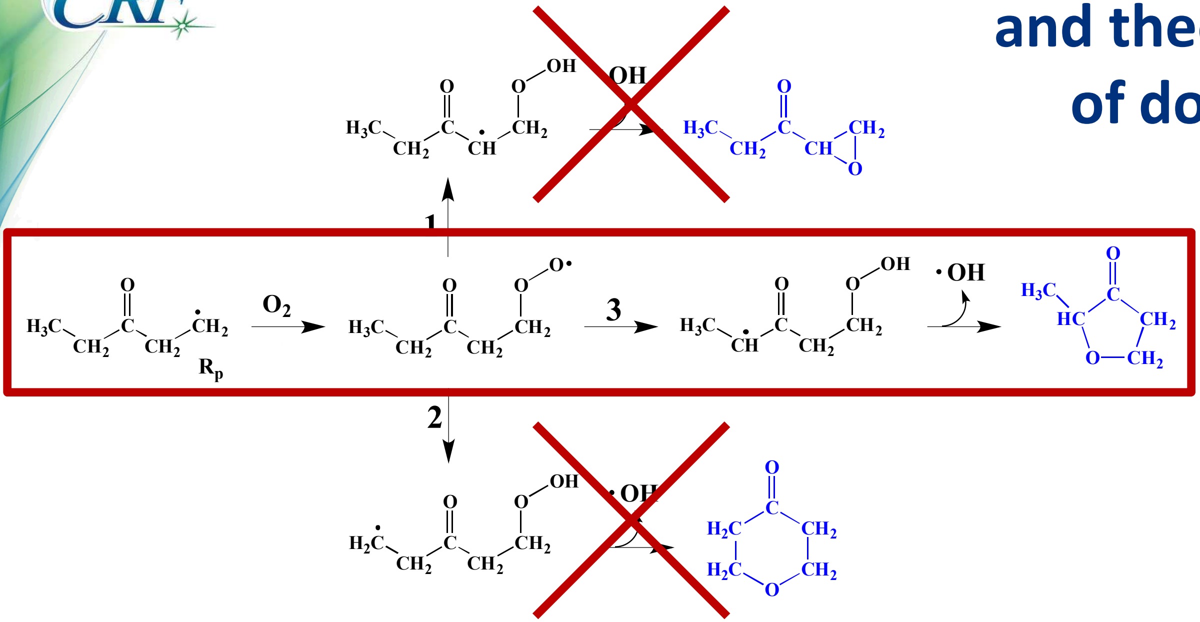
Thermodynamics Drives Cyclic Ether Selectivity in Diethyl Ketone Oxidation

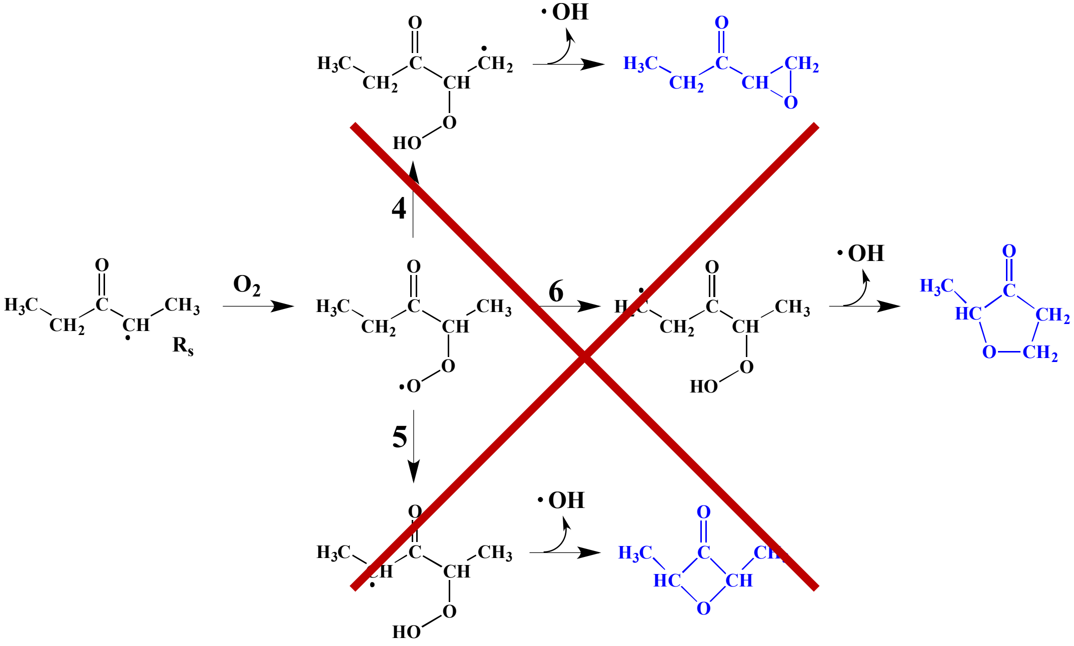


- Resonance stabilization of secondary radical
- RO_2-well ~ 24 kcal/mol – shallow!
- R + O_2 ⇌ RO_2 shifted to reactants
- All cyclic ether, HO_2-elimination and bond breaking pathways above entrance channel

- No resonance stabilization of primary radical
- RO_2-well ~ 36 kcal/mol
- R + O_2 ⇌ RO_2 shifted to products
- 5-membered ring pathway lowest energy and benefits from resonantly stabilized QOOH

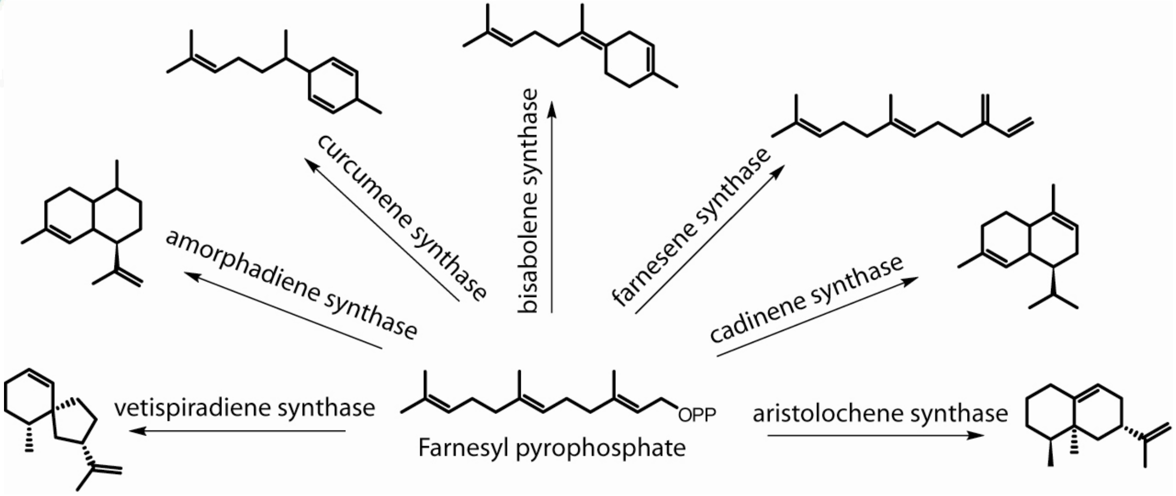
Combination of experiment and theory allows assignment of dominant cyclic ether channel

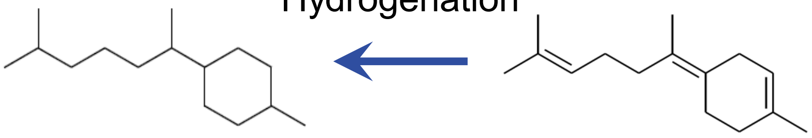




Reaction proceeds through the resonance stabilized QOOH

Other Resonance Stabilized Radicals: Allylic Stabilization in Hydrocarbon Fuels





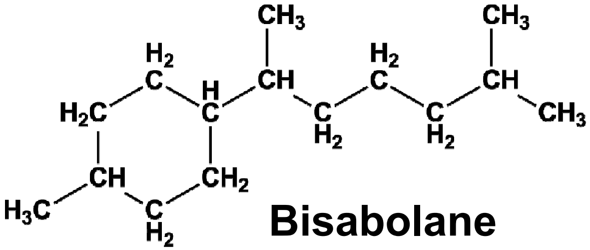
Chemical Hydrogenation

Bisabolane

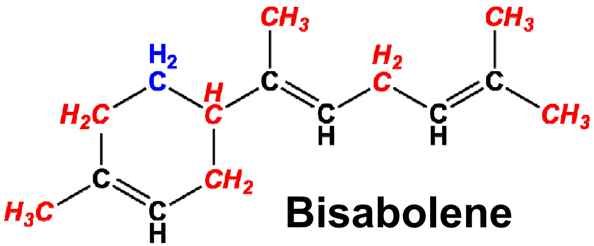
Biofuel Precursor

Bisabolane is a promising target

Peralta-Yahya et al.
Nature Communications, 2011



Bisabolane



Bisabolene

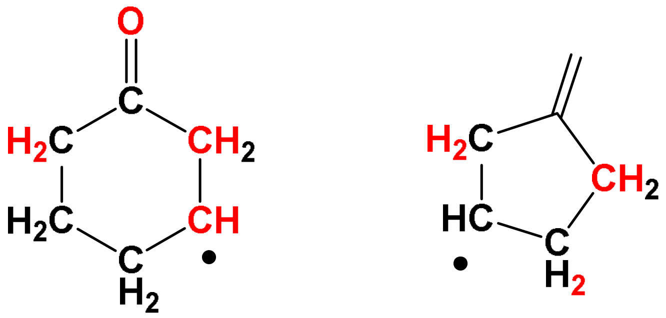
Involves hydrogenation of bisabolene product

Efficiency of production could favor retaining some bisabolene

Oxidation of unsaturated products of HO_2 elimination

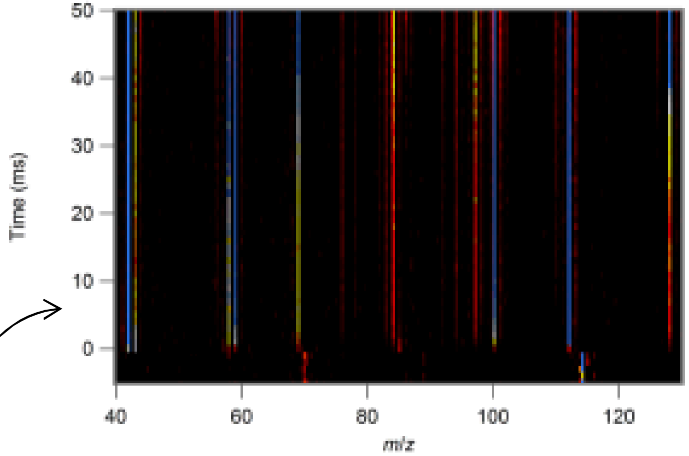
Vinoxylic Stabilization is an Important Determinant for Ketone Oxidation

Formation of OH and cyclic ethers occurs when a less stable ROO can form a resonance-stabilized QOOH: what about cyclic ketones where this isomerization is hindered?



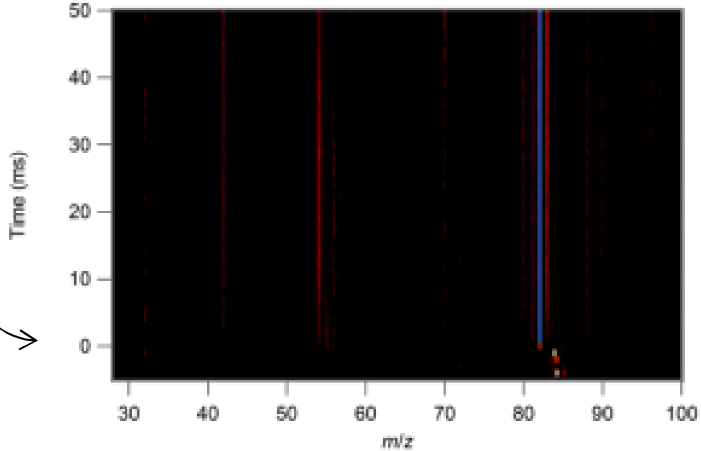
Di-isopropyl ketone: shows species associated with <u>chain-propagating OH formation</u>.

Expect some intermediate temperature heat release (ITHR) in engine



Cyclopentanone: almost exclusively cyclopentenone formation, associated with <u>chain-terminating HO_2 formation</u>.

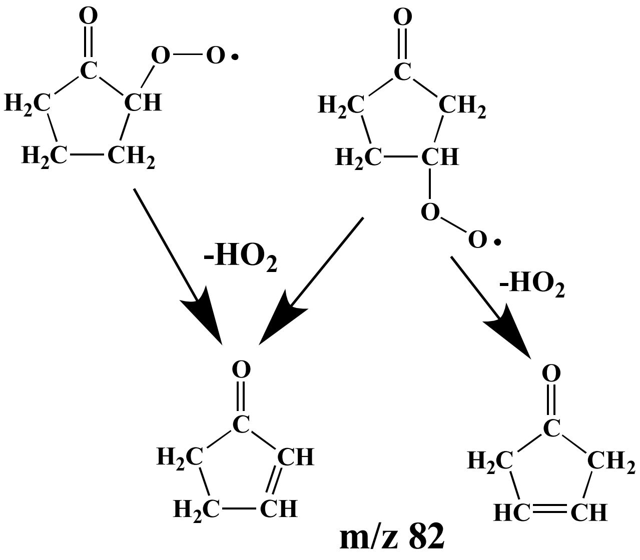
Expect very little ITHR in engine.

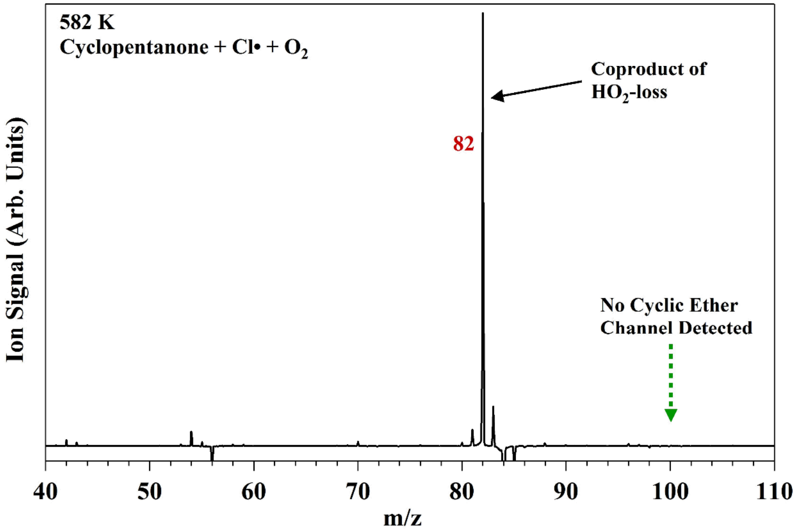


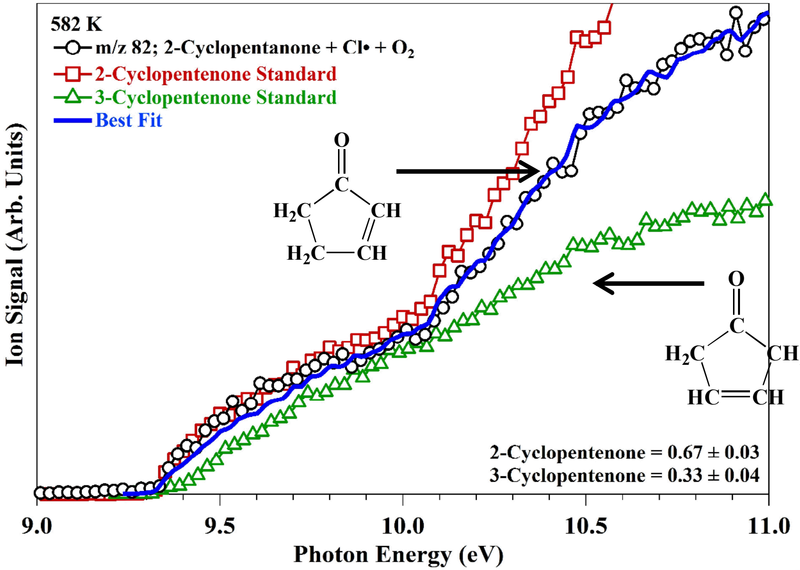
Investigating fundamental ignition chemistry of promising biofuels: Cyclic ketones

Radicals from **cyclic ketones** almost exclusively undergo HO_2-elimination after reaction with O_2

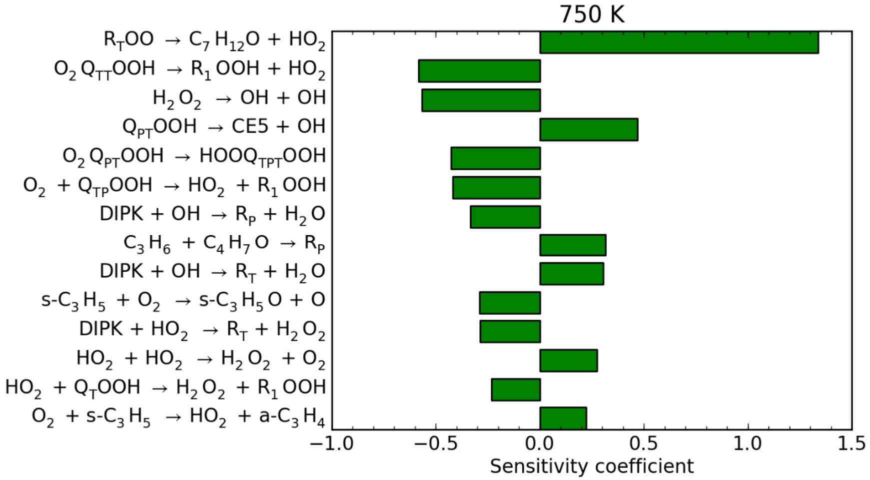
No cyclic ether product observed.







Cl-initiated oxidation of representative ketones guides mechanism development

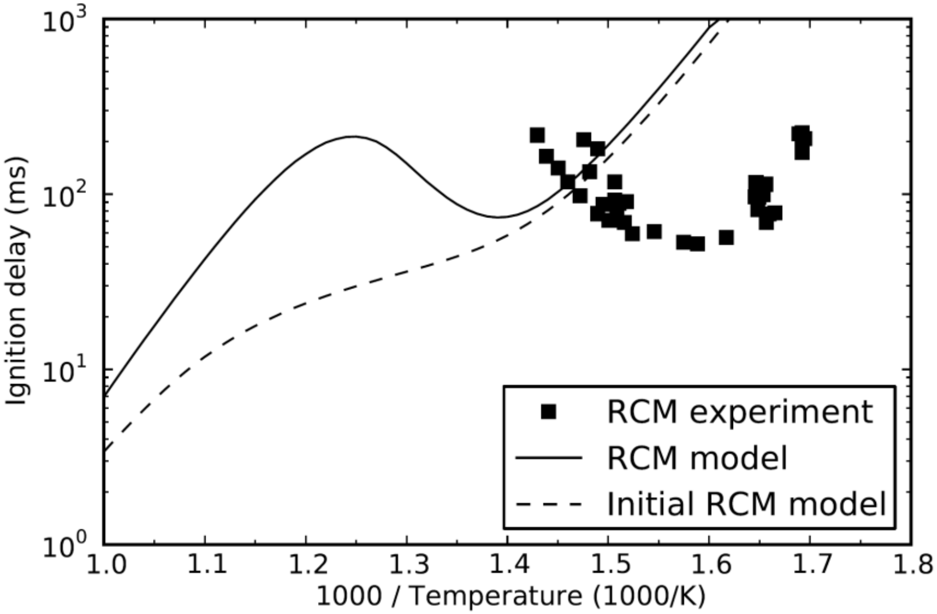


Rate rules are used in RMG (Bill Green, MIT) to model ignition (Ravi Fernandes, Aachen) and pyrolysis (Fei Qi, Hefei)

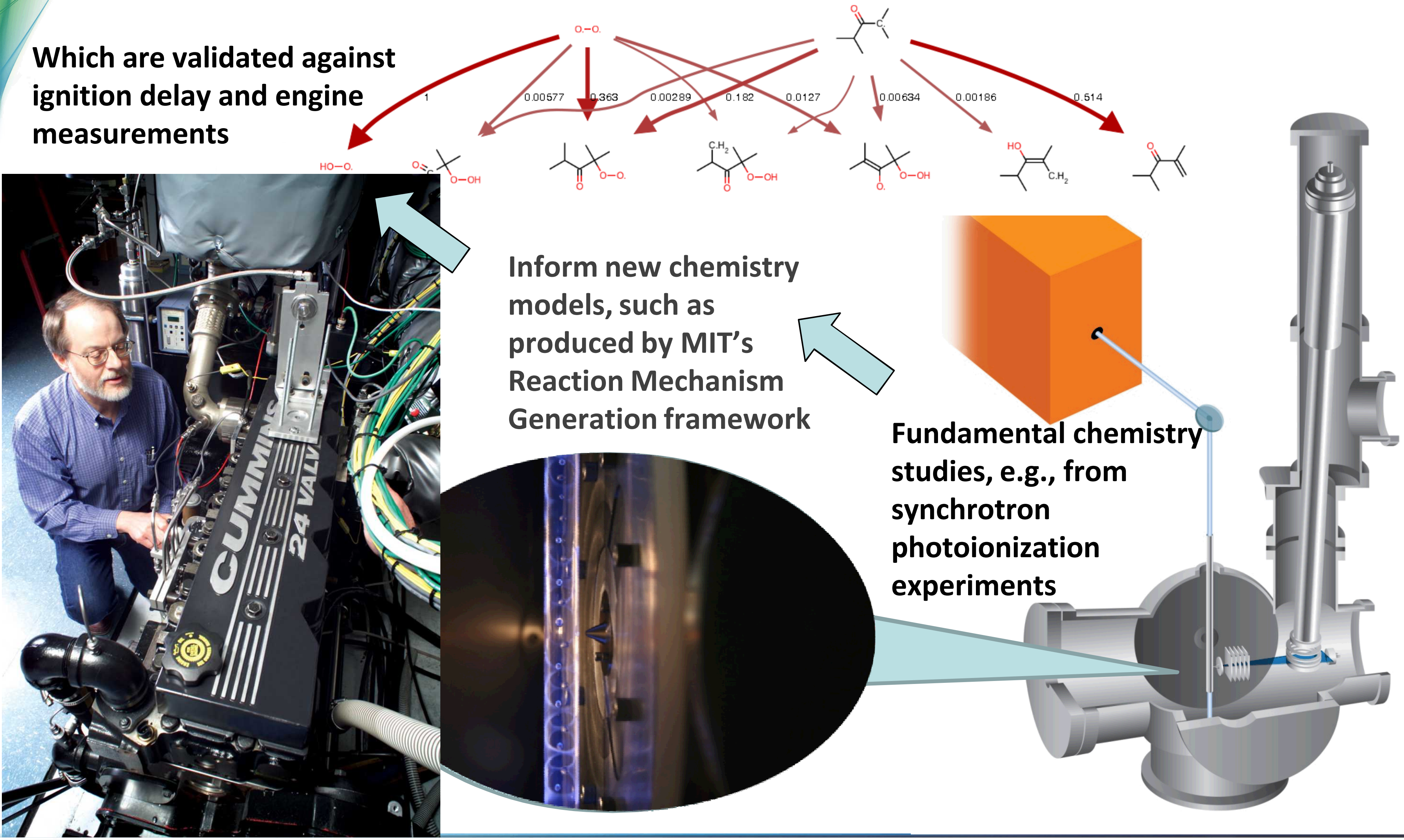
"Validated" rules can be applied to predict engine performance

2,4-dimethylpentan-3-one (DIPK) is one prototype for ketone ignition chemistry

Rate rules are devised based on the new ALS experiments – discrepancies are addressed by rigorous theoretical kinetics, *not fitting*



Combustion Chemistry Studies Build From Elementary Reactions to Engine Models



Which are validated against ignition delay and engine measurements

Inform new chemistry models, such as produced by MIT's Reaction Mechanism Generation framework

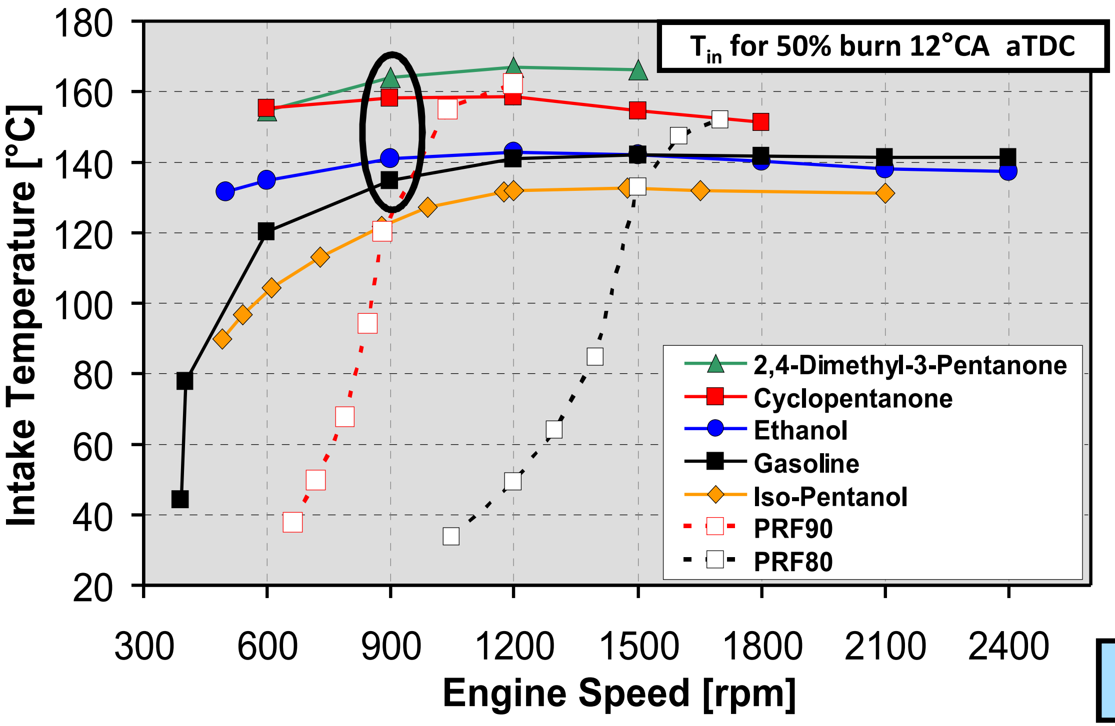
Fundamental chemistry studies, e.g., from synchrotron photoionization experiments

= 0.38

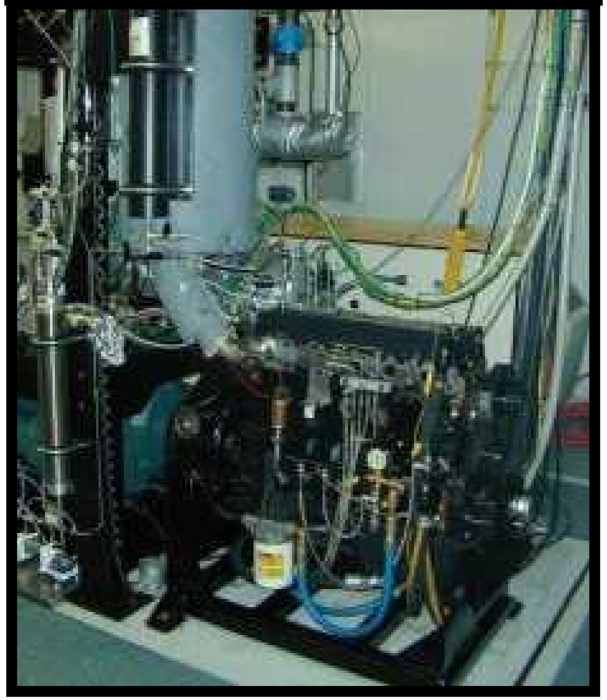
Engine Tests on Ketone Fuels (John Dec)

Auto-ignition characteristics of selected ketone fuels examined in a Homogeneous Charge Compression Ignition (HCCI) engine.

Intake temperature (T_{in}) vs. Speed sweep characterizes relative overall reactivity.



HCCI Research Engine



Ketone behavior is overall similar to gasoline and ethanol, but . . .

Significantly higher T_{in} is required.

Low-T chemistry (LTC) not significant on engine timescales.

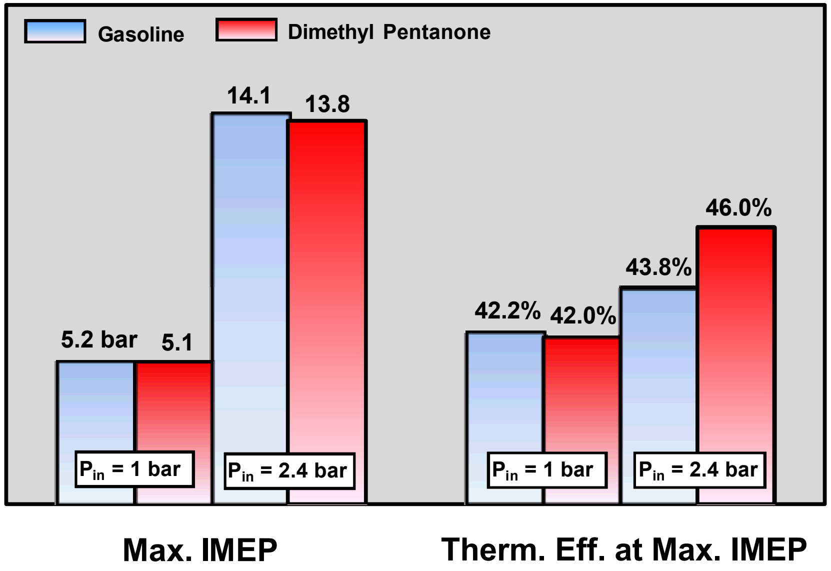
PRF fuels demonstrate behavior of fuels with more LTC.

Ketones could raise octane no. of gasoline.

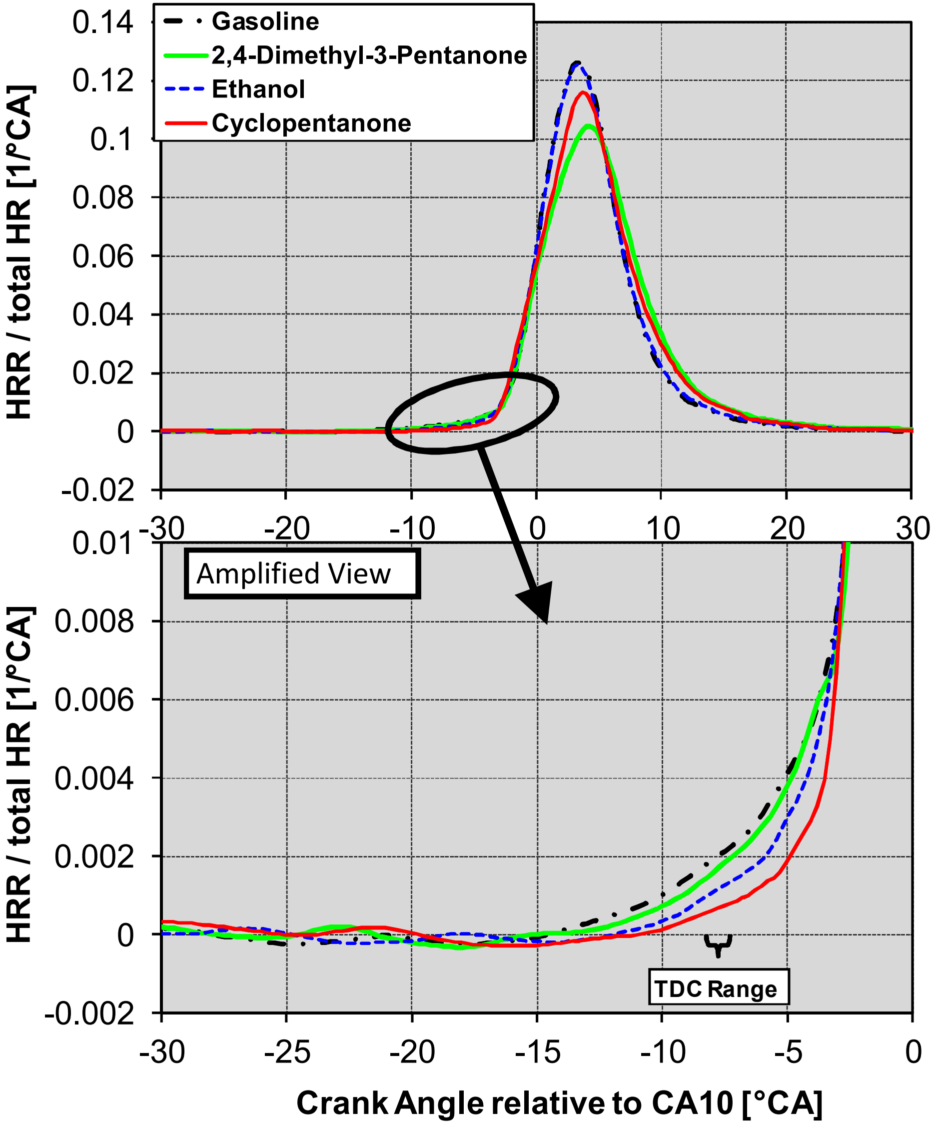
Pre-Ignition Activity of Ketone Fuels in Engines Qualitatively Follows Kinetics Prediction

Pre-Ignition reactions are key to performance differences in fuels.

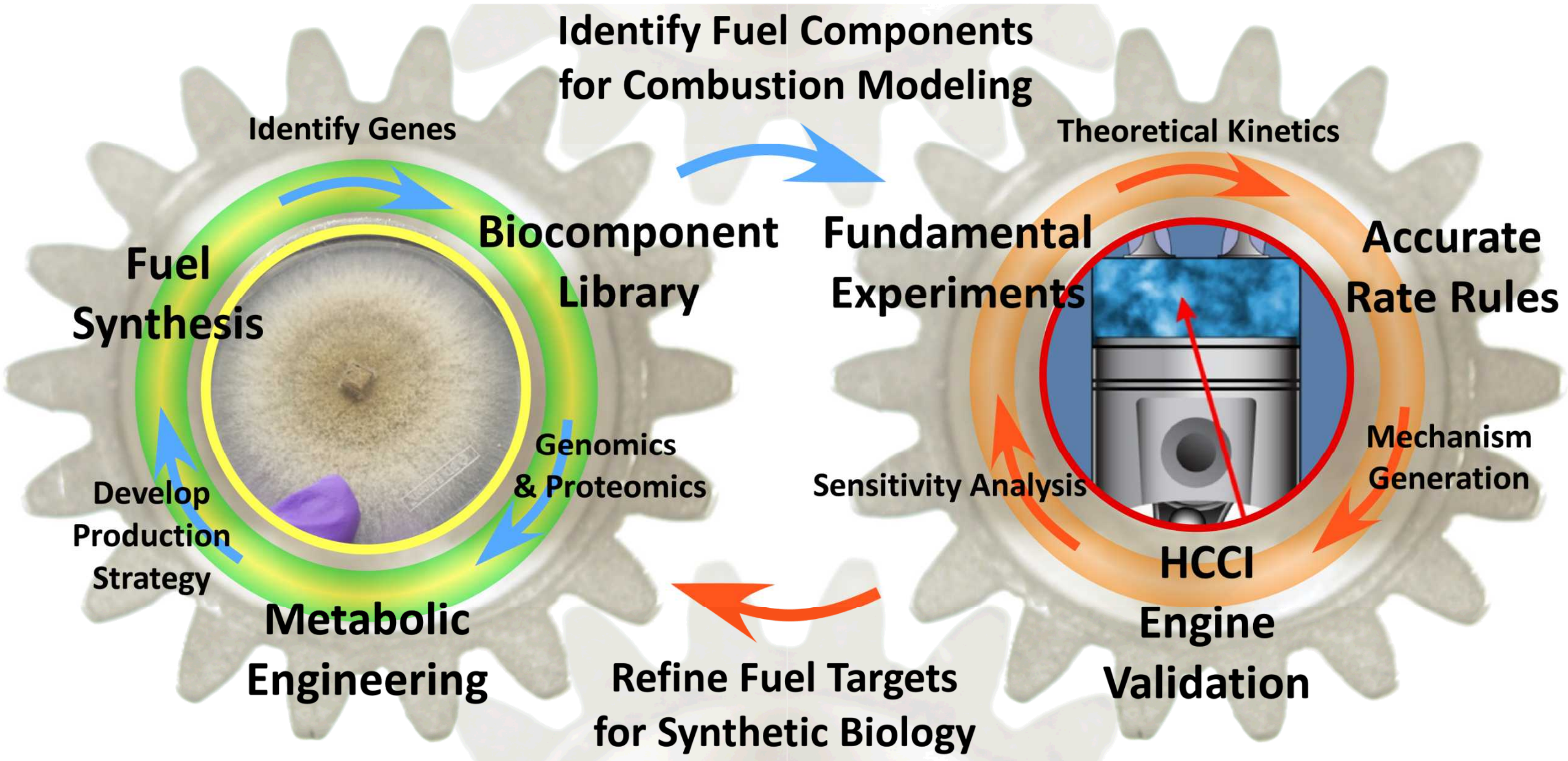
- Low-temp. heat release (LTHR), 760 K – 880 K.
- Intermediate-temp. heat release (ITHR), 950 K – 1050 K.



In fact, DIPK shows higher efficiency than gasoline at high load



What is next?



Identify Fuel Components for Combustion Modeling

Identify Genes

Biocomponent Library

Genomics & Proteomics

Metabolic Engineering

Develop Production Strategy

Fuel Synthesis

Theoretical Kinetics

Accurate Rate Rules

Mechanism Generation

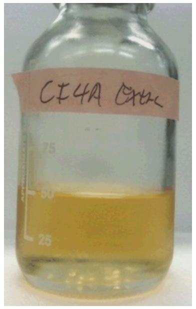
HCCI Engine Validation

Sensitivity Analysis

Fundamental Experiments

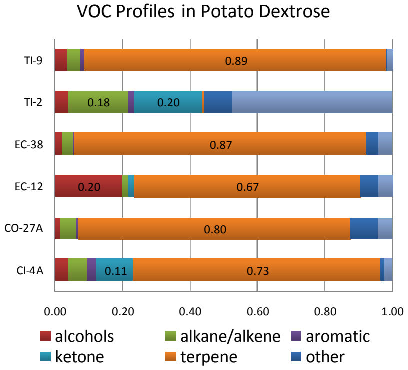
Refine Fuel Targets for Synthetic Biology

Framework for Codevelopment of Advanced Biofuels and Advanced Engines

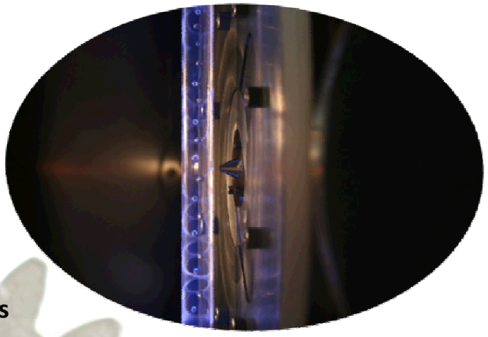


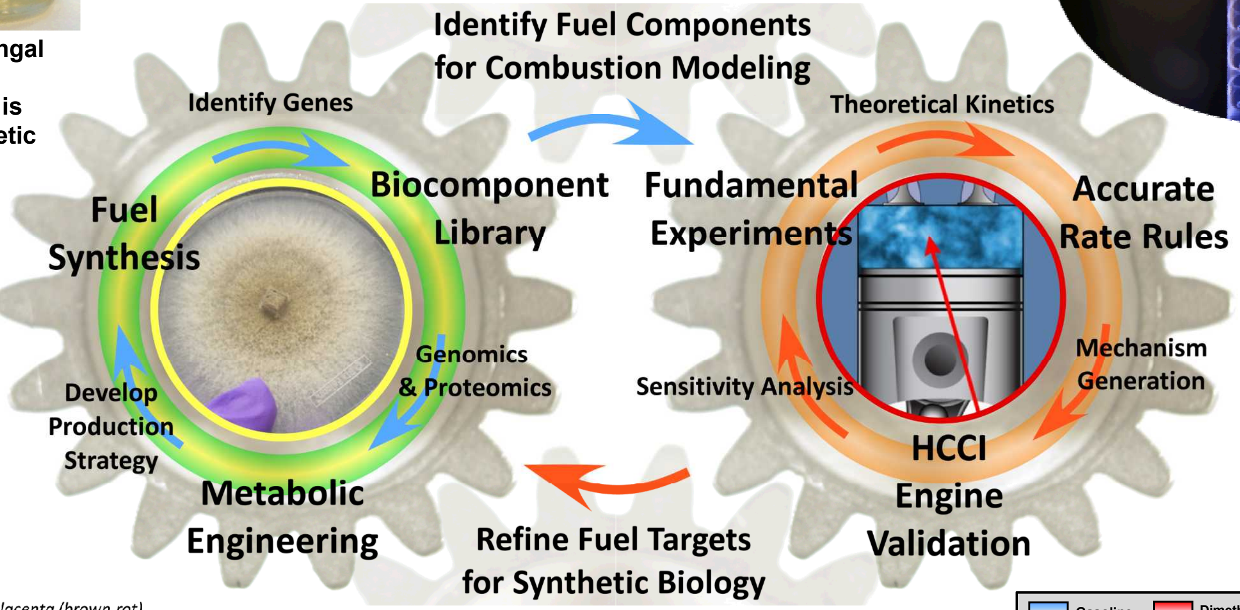
Direct VOC production from fungal action on biomass (i.e., consolidated bioprocessing) is pursued in parallel with synthetic biology methods.

Natural products of the endophytes include ketones, whose ignition chemistry is poorly known.



Laser-initiated experiments probe the chemical kinetics of key elementary ketone combustion reactions, helping to develop chemical mechanisms .





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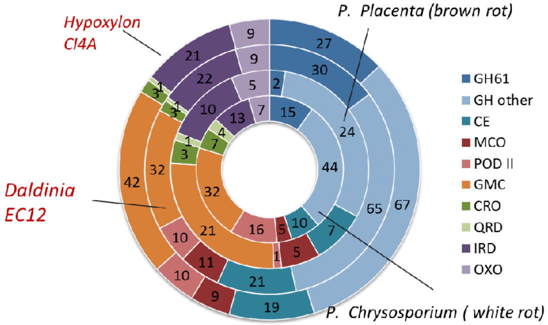
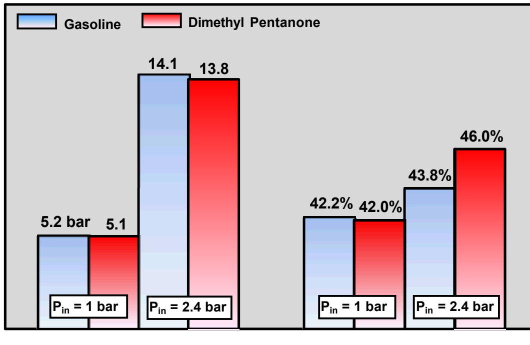
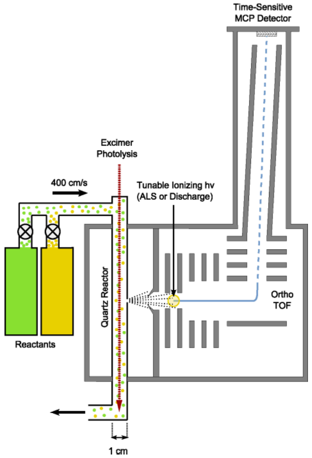


Distribution of Oxidative Lignin Genes in Endophyte Genomes. Endophytes have machinery for enzymatic and non-enzymatic lignocellulose degradation.

Some ketones show improved efficiency in HCCI engines over gasoline at similar load (IMEP). New mechanisms successfully predict autoignition.

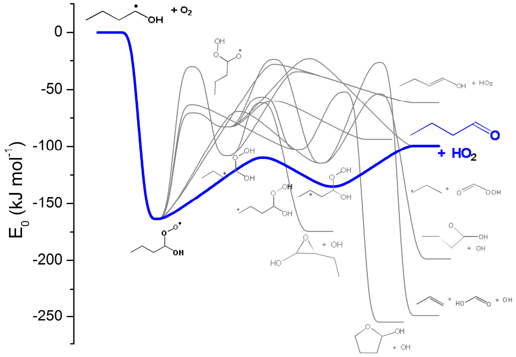


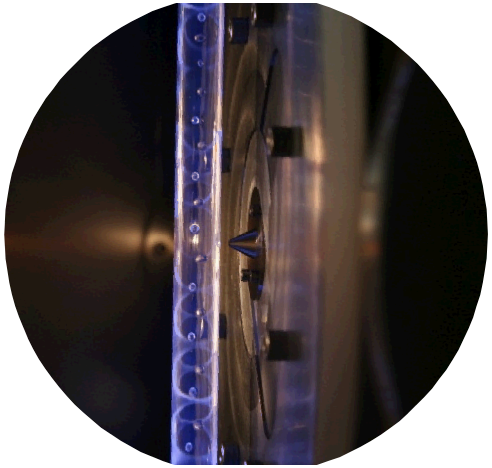
Summary



Combination of QM/ME and MPIMS studies on the low-temperature oxidation is a powerful means for understanding mechanisms

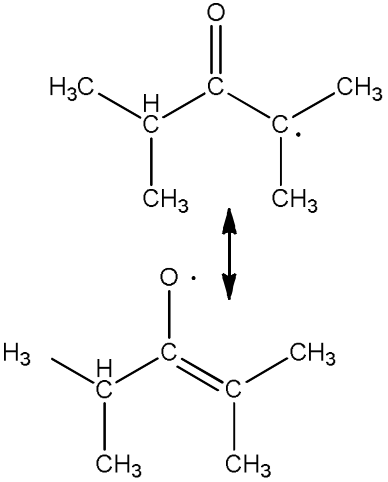
O





Unsaturation and formation of resonance stabilized radicals can alter R + O_2 reactions

Early involvement of combustion models is an important guide for biofuel development



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Similar Load Achieved with Higher Efficiency

Although the ITHR of DIPK is less than gasoline, it is greater than that of the other biofuels.

Combined with the lower HRR, this allows loads similar to gasoline with acceptable ringing index

Thermal efficiency is higher for DIPK than for gasoline at a given load (gross IMEP).

- **Due to more advanced combustion timing, enabled by higher T-sensitivity.**
- **Also due to much less EGR required to control combustion timing.**

DIPK reaches similar max. loads to gasoline at both P_{in} = 1 bar & 2.4 bar.

DIPK achieves *significantly* higher thermal efficiency at the max load for P_{in} = 2.4 bar.