SAND2014-0015C

Autoignition chemistry of oxygenated molecules: Linking biofuel development with combustion

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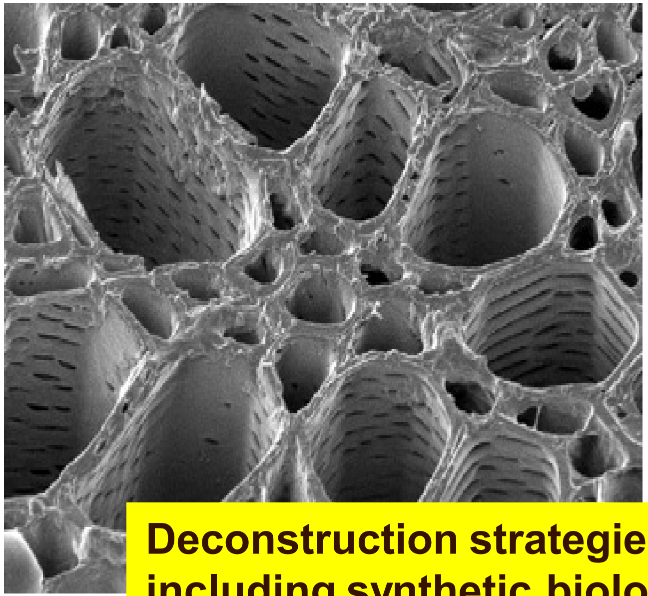
In Response to Climate and Energy Security Challenges the Fuel Stream Is Changing

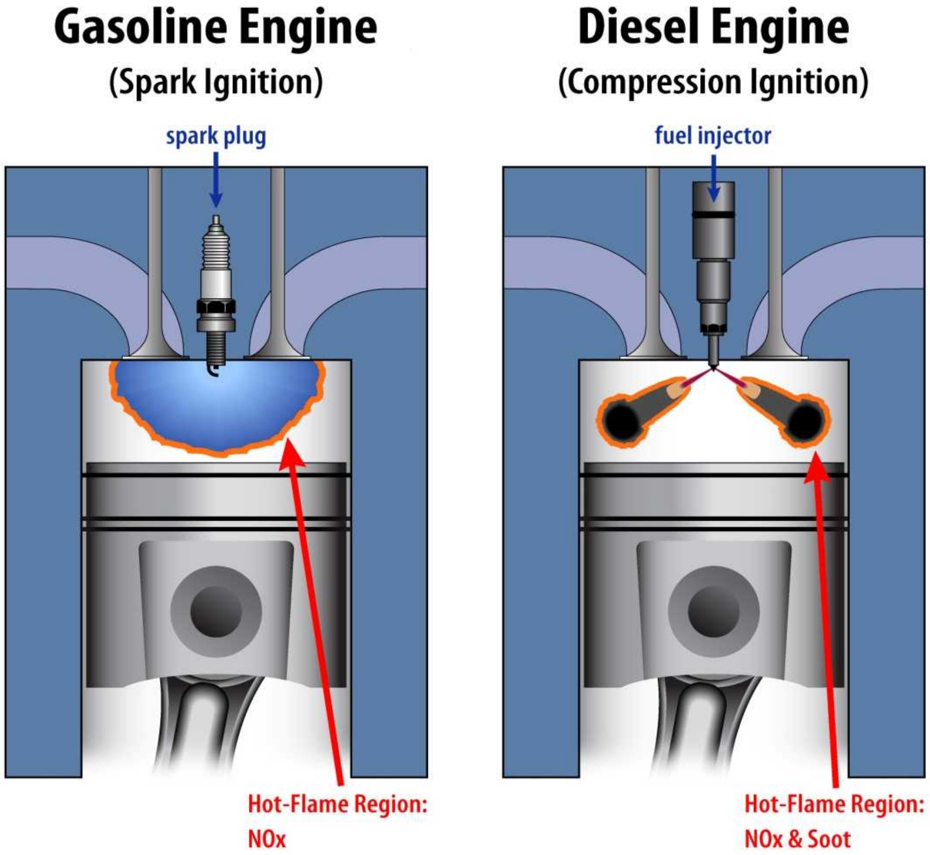
- *Advanced biofuels and combustion efficiency are important parts of the path forward for energy security and mitigation of climate change*



Deconstruction strategies – including synthetic biology – may 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

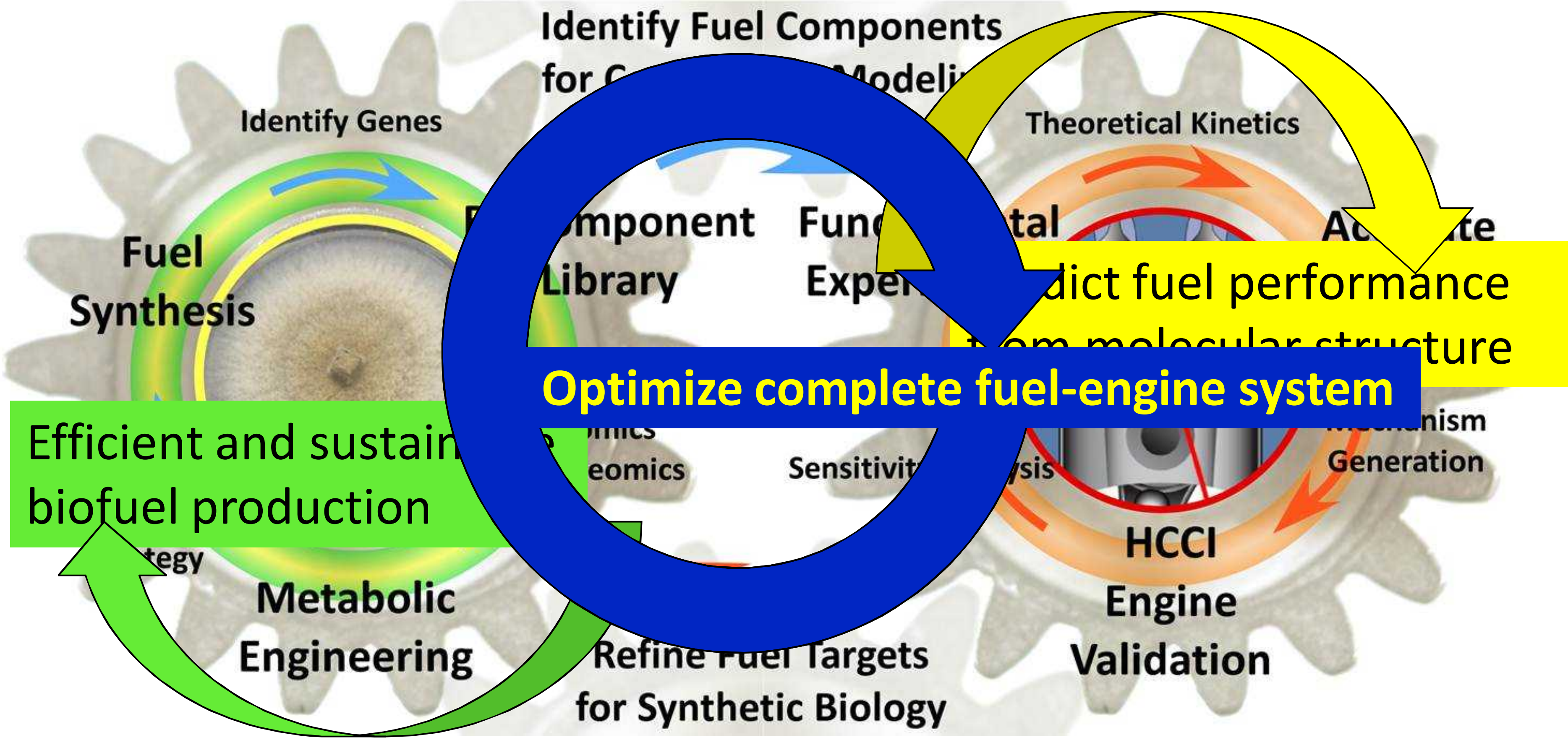


Fuel chemistry is important – but fuel stream is already changing!

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



dict fuel performance
from molecular structure

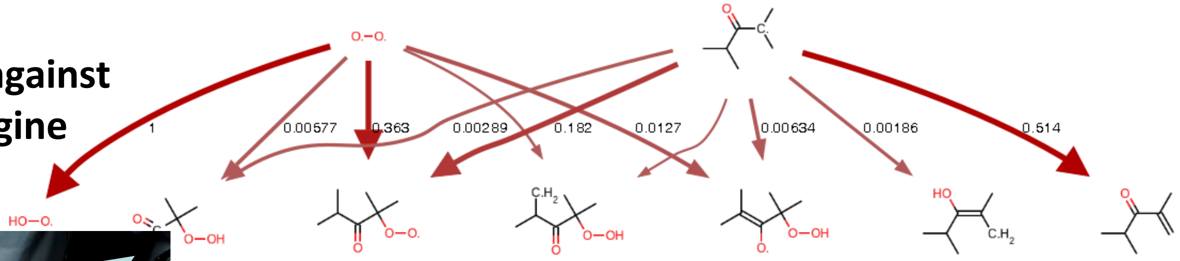
Optimize complete fuel-engine system

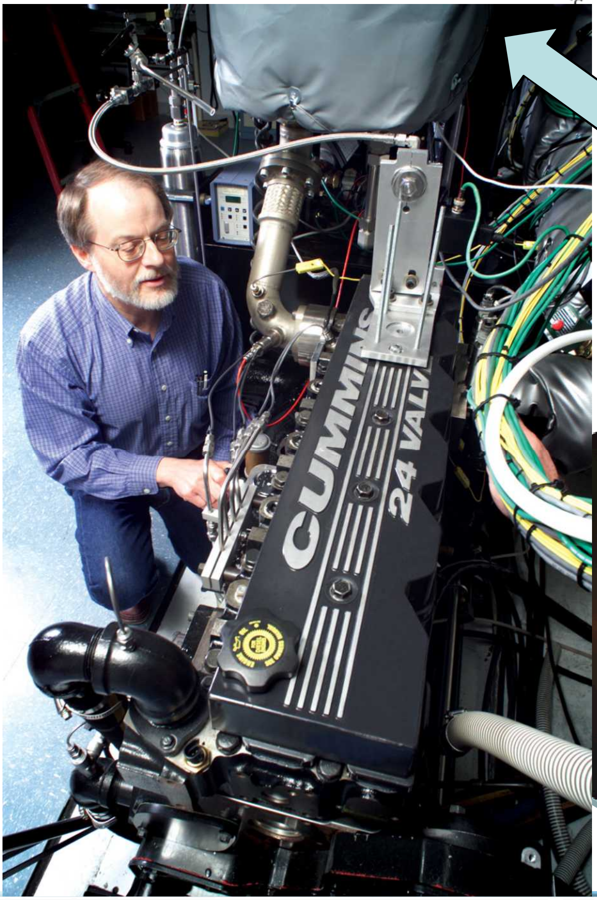
Efficient and sustain
biofuel production

Gladden, Taatjes *et al.*, Sandia report SAND2013-10094 (2013)

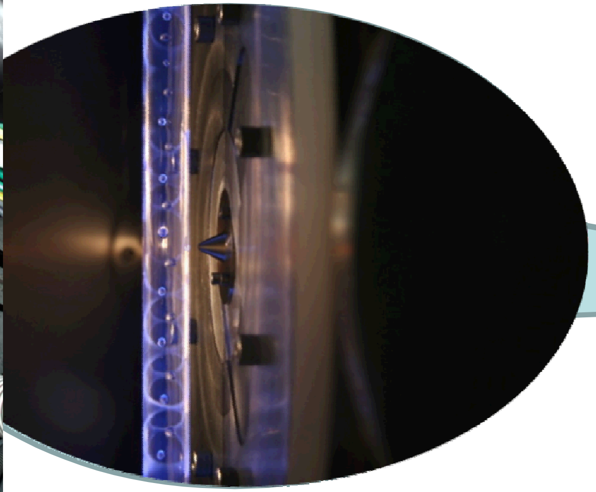
Combustion Chemistry Studies Build From Elementary Reactions to Engine Models

Which are validated against ignition delay and engine measurements

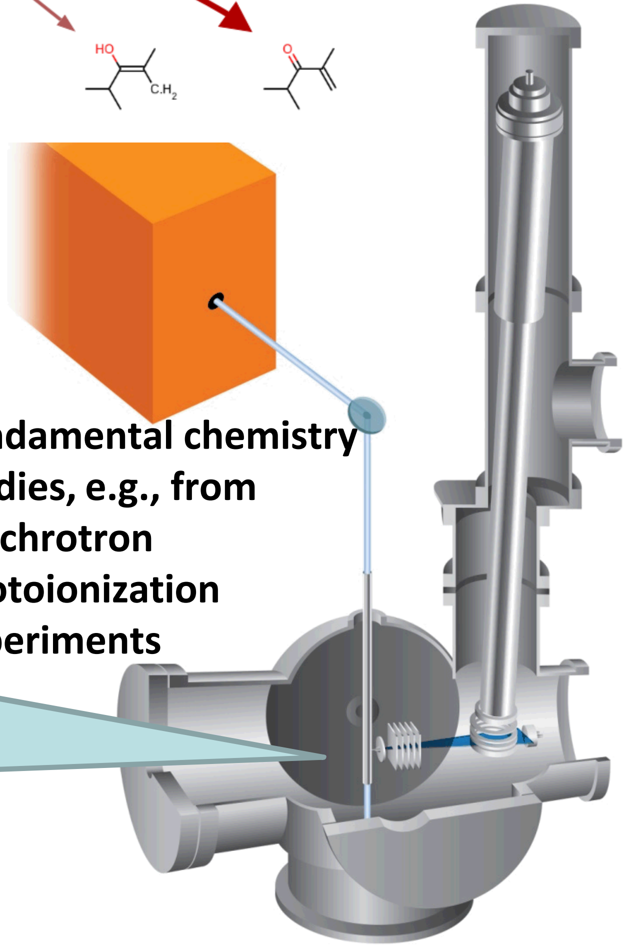




Inform new chemistry models, such as produced by MIT's Reaction Mechanism Generation framework



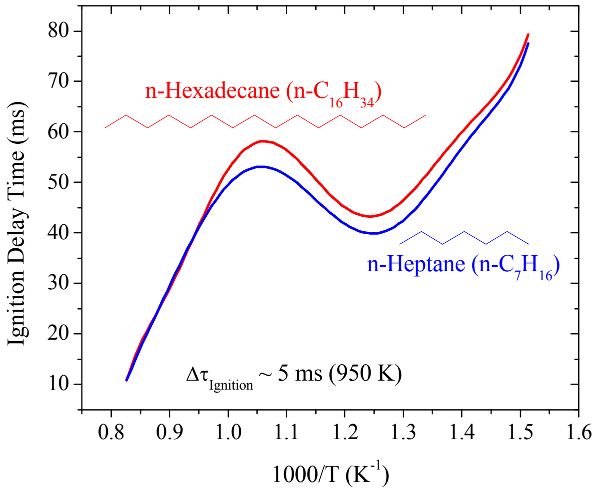
Fundamental chemistry studies, e.g., from synchrotron photoionization experiments



Gladden, Taatjes *et al.*, Sandia report SAND2013-10094 (2013)

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

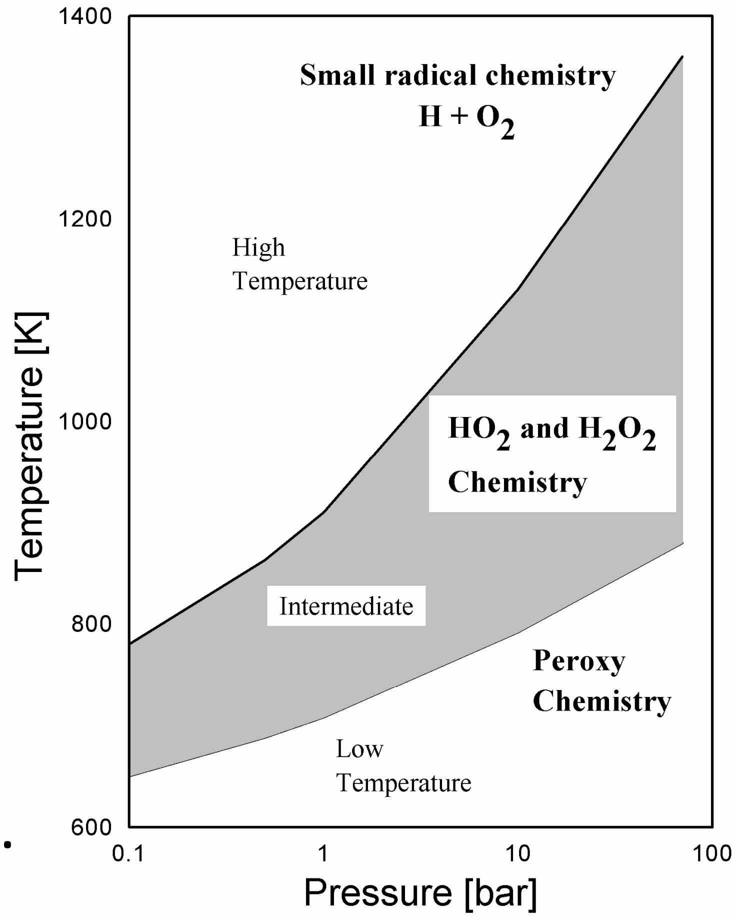
Ignition behavior of different fuels tend to coincide at high temperature



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

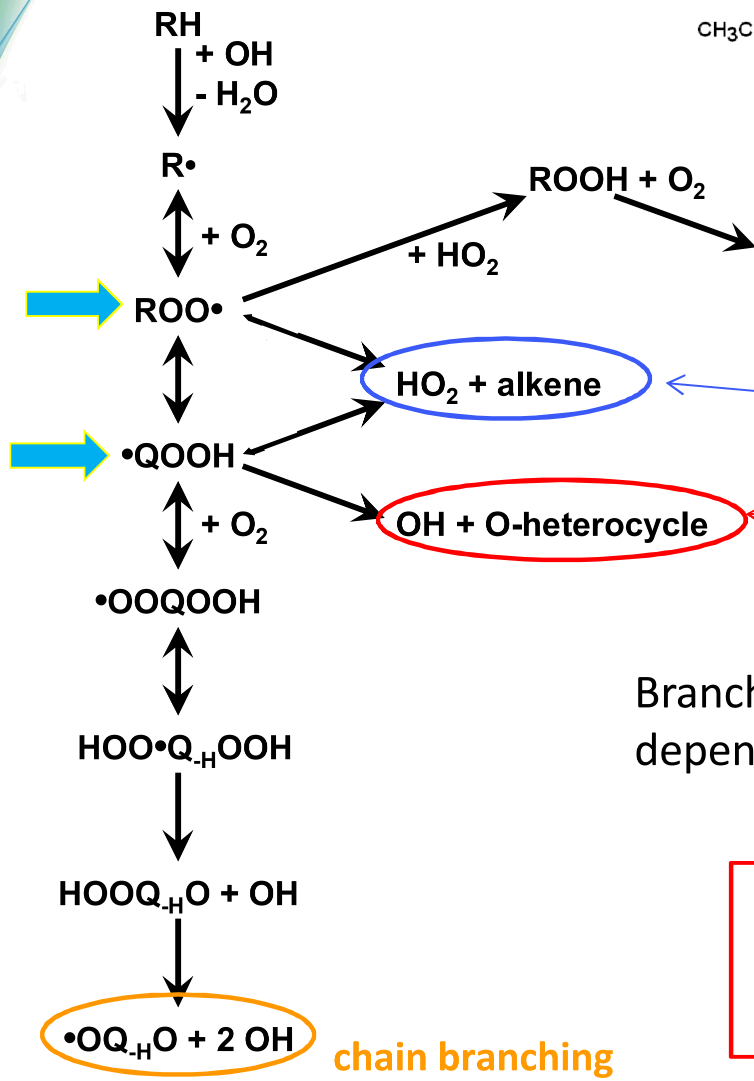
Fuel-chemistry effects on autoignition behavior appear in negative temperature coefficient region.

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



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

Predicting Low-Temperature Oxidation Requires Understanding Chemistry of Intermediates



RH

+ OH

- H_2O

R•

+ O_2

ROO•

+ HO_2

ROOH + O_2

RO• + OH

HO_2 + alkene

•QOOH

OH + O-heterocycle

+ O_2

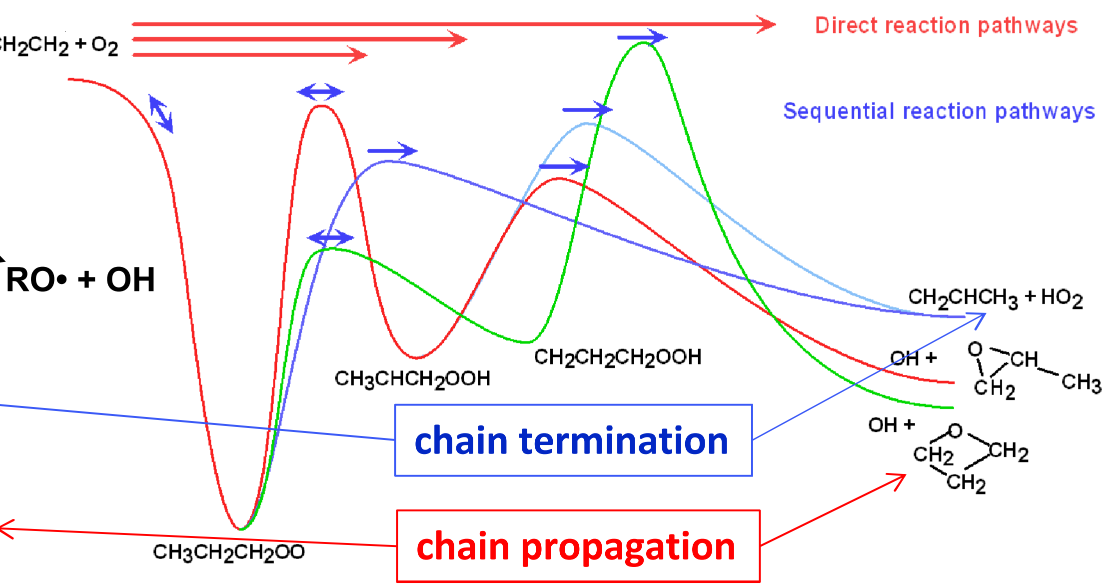
•OOQOOH

$HOO•Q_{-H}OOH$

$HOOQ_{-H}O$ + OH

$•OQ_{-H}O$ + 2 OH

chain branching



chain termination

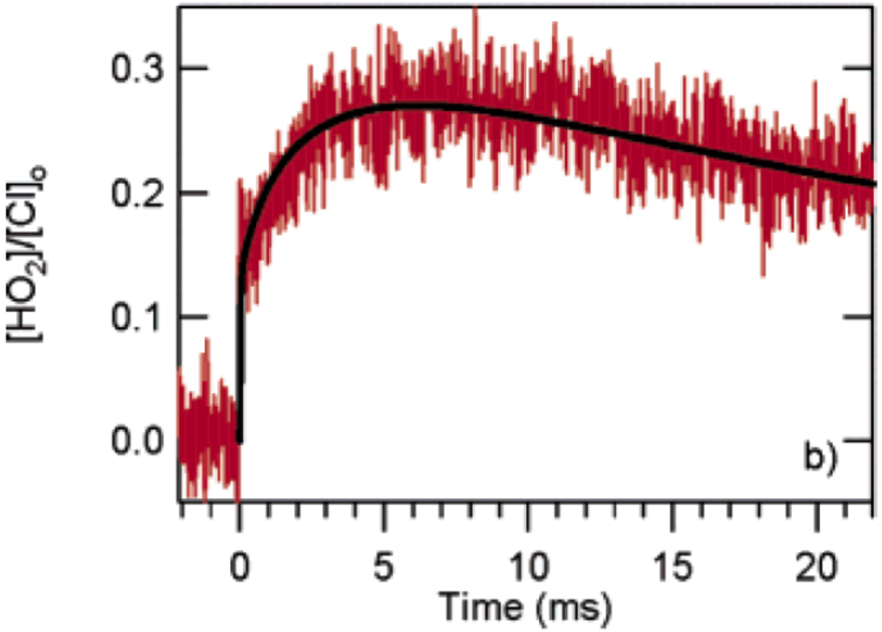
chain propagation

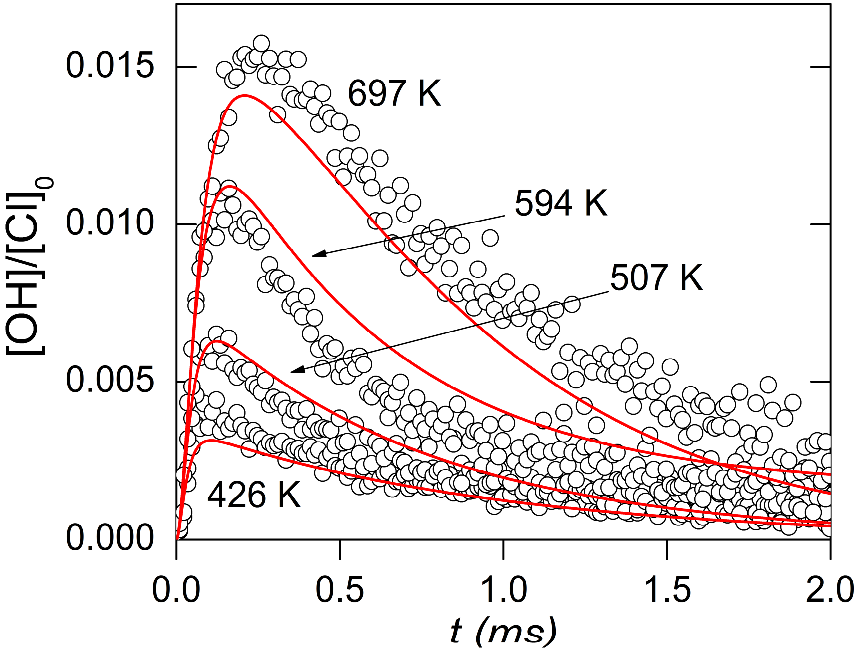
Branching into the different channels is fuel-specific and depends on temperature, pressure, and O_2 concentration

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*, **37**, 341 (2011)

Measurements of the important radical products HO_2 and OH constrain calculations



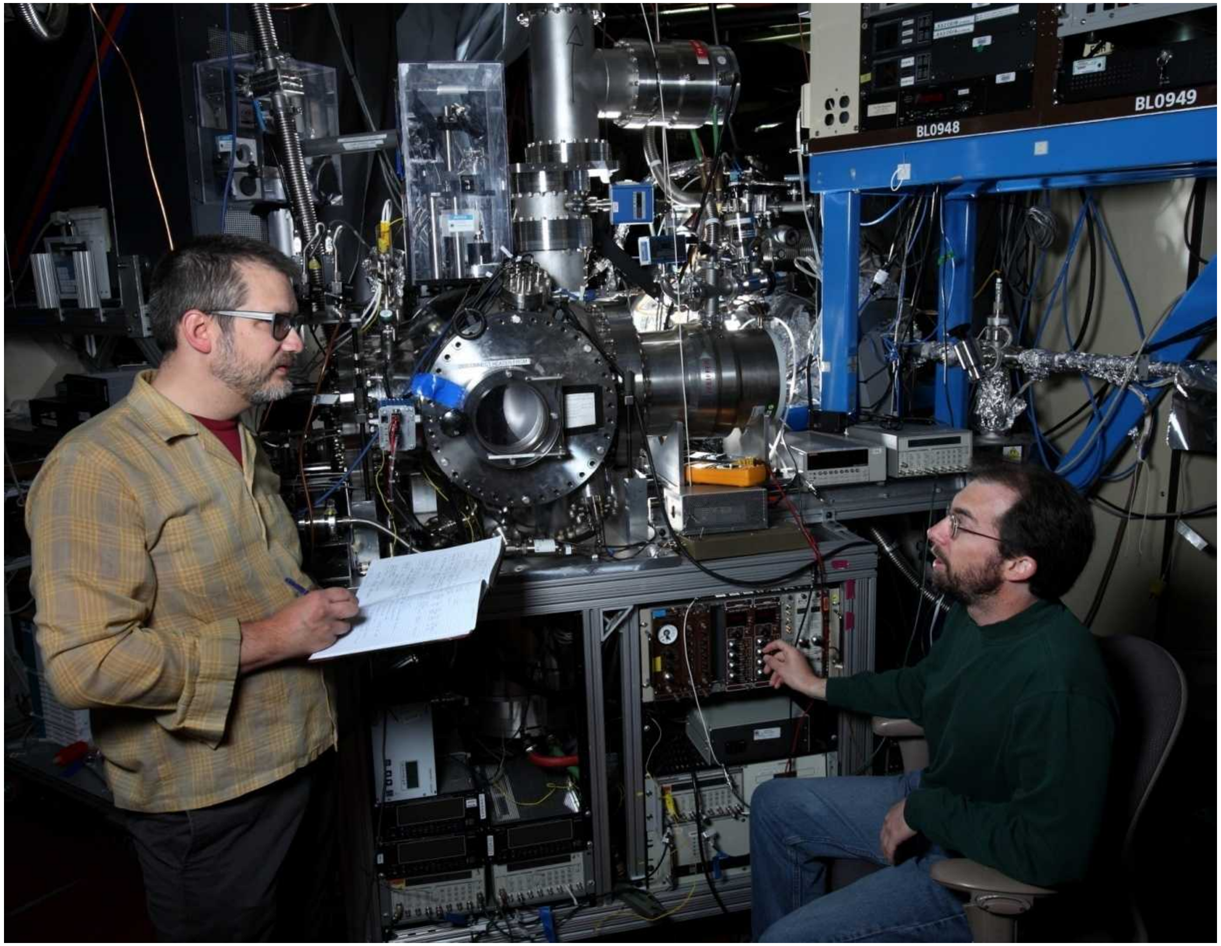


Pulsed photolytic Cl-initiated oxidation, with absorption detection of radicals

Can match data, but significant ambiguities remain

Which QOOH is making the OH? Is there any chain branching?

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

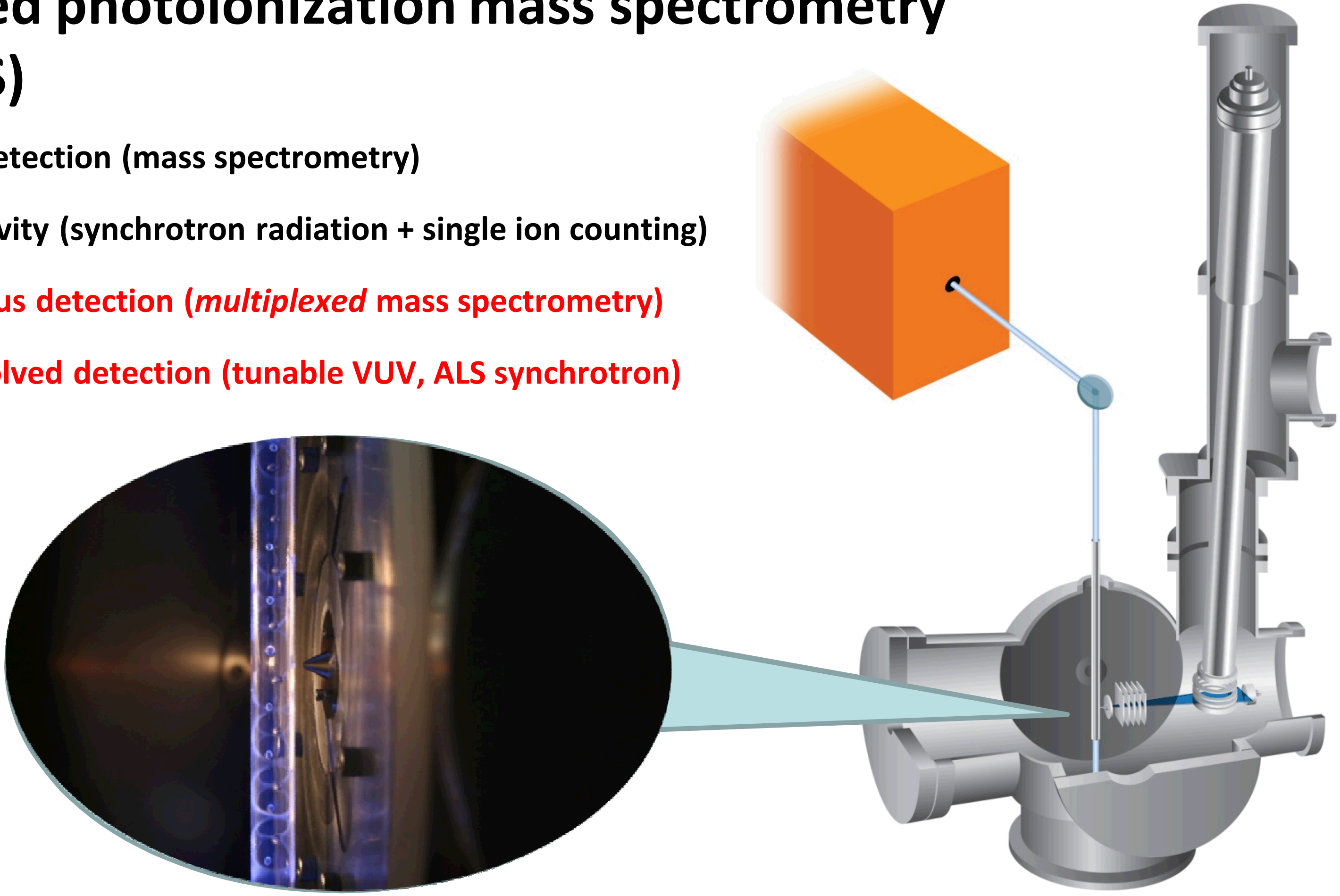
Multiplexed photoionization mass spectrometry (MPIMS)

Universal detection (mass spectrometry)

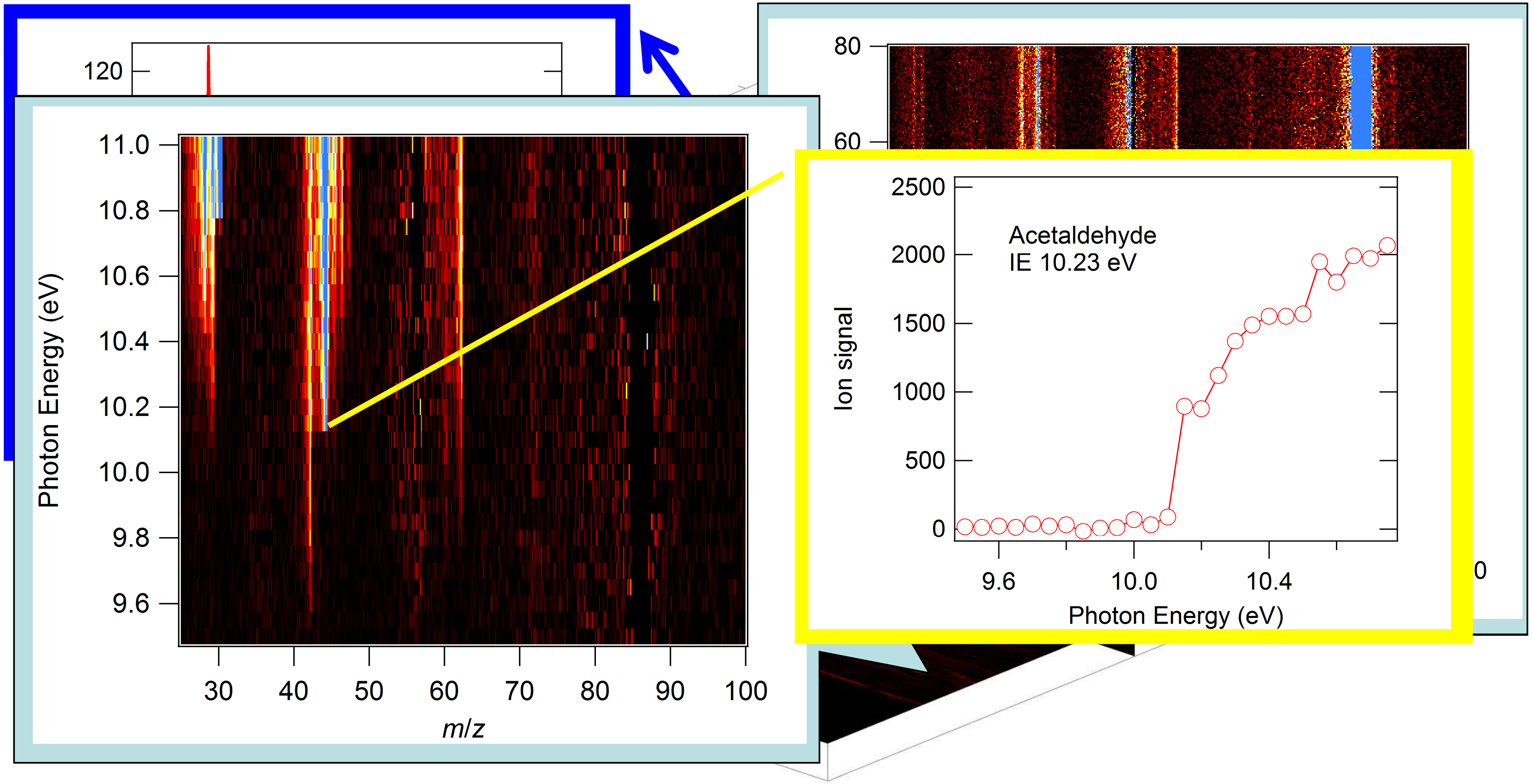
High sensitivity (synchrotron radiation + single ion counting)

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

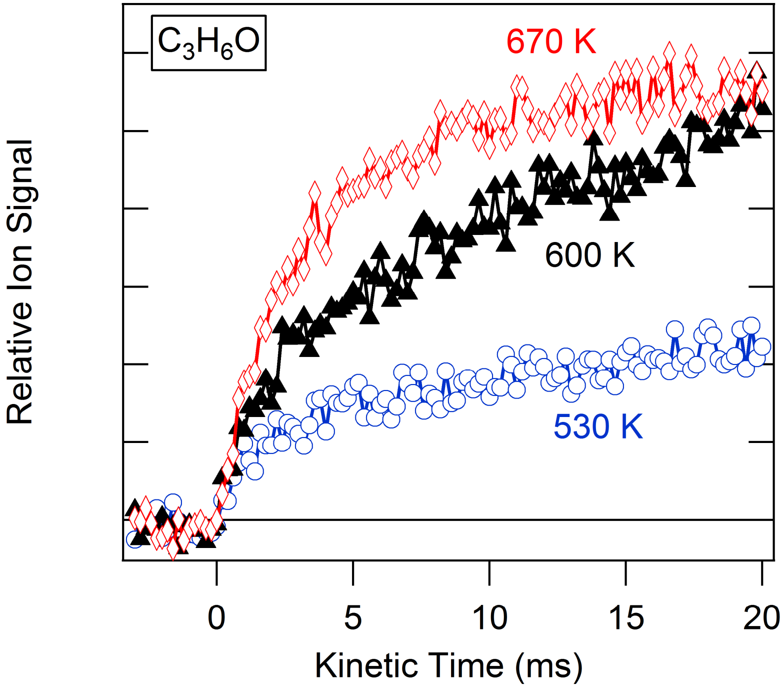


3-D dataset can be “sliced” along different axes to probe different aspects of the reaction

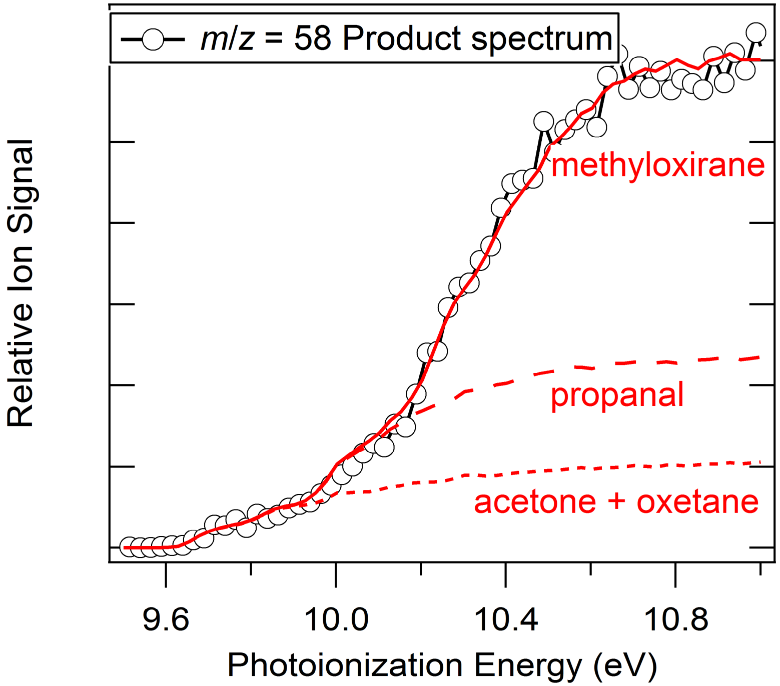
Taatjes et al., *Phys. Chem. Chem. Phys.* **10**, 20 (2008).

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



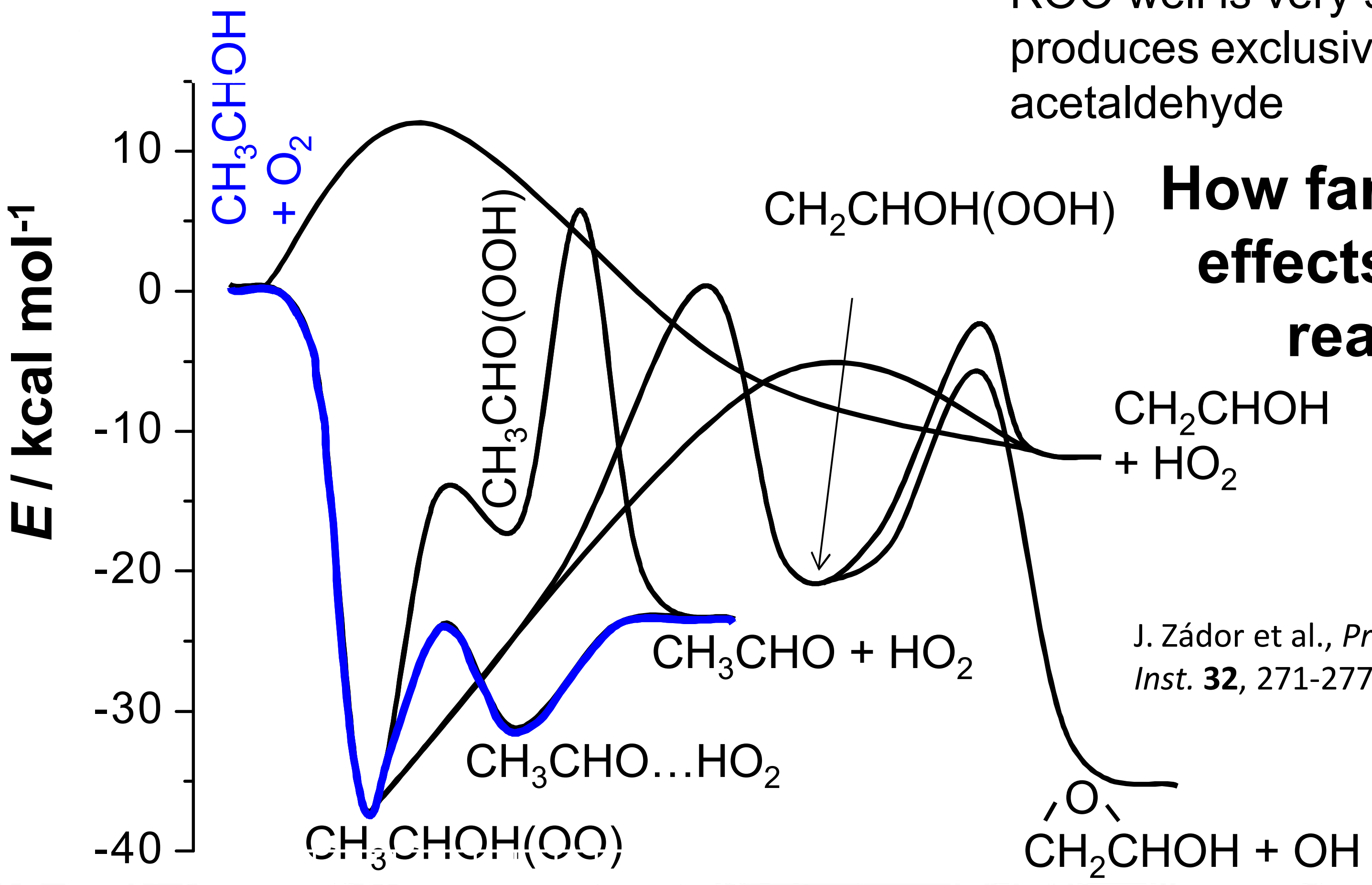
Combination of high-pressure MPIMS, radical product measurements and literature experiments with application of "multi-scale informatics" (Mike Burke et al., Argonne)

Much better constraints on primary reaction characteristics

How Might Functionalization Affect Ignition Chemistry? Alcohols Give One Example

OH group changes the **thermochemistry**

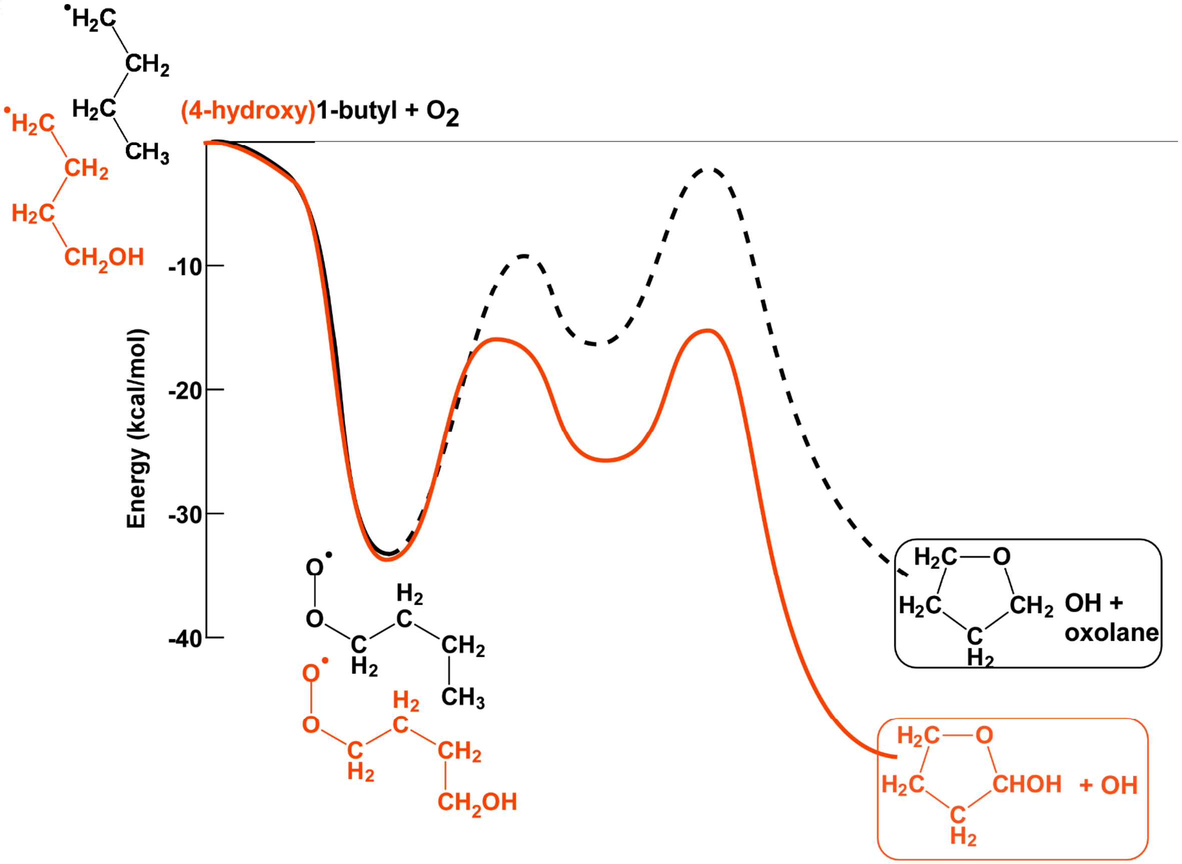
1-hydroxyethyl + O_2
ROO well is very shallow – produces exclusively HO_2 + acetaldehyde



How far can the effects of OH reach?

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



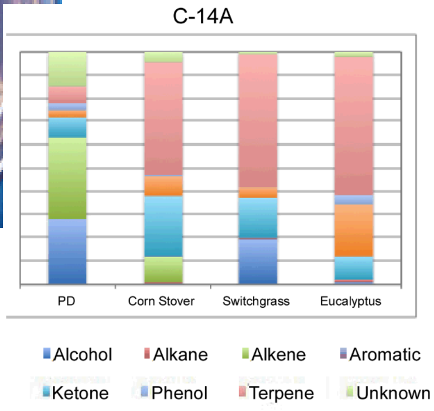
α-hydroxyalkyl reaction forms HO_2

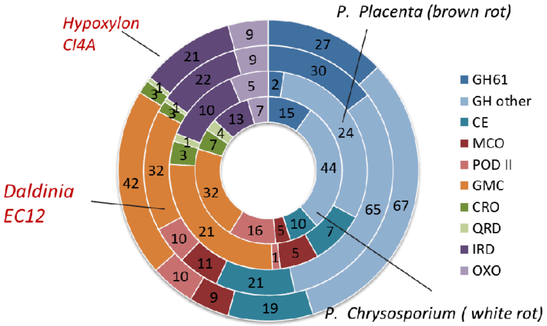
β-hydroxyalkyl reaction follows “Waddington” mechanism

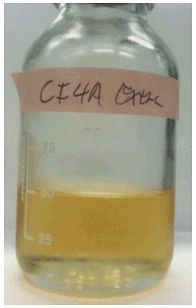
Weaker α-C—H bond favors OH formation

Oliver Welz et al., *J. Phys. Chem. A*, ASAP **DOI:** 10.1021/jp403792t

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



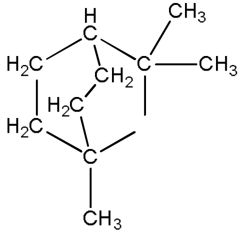




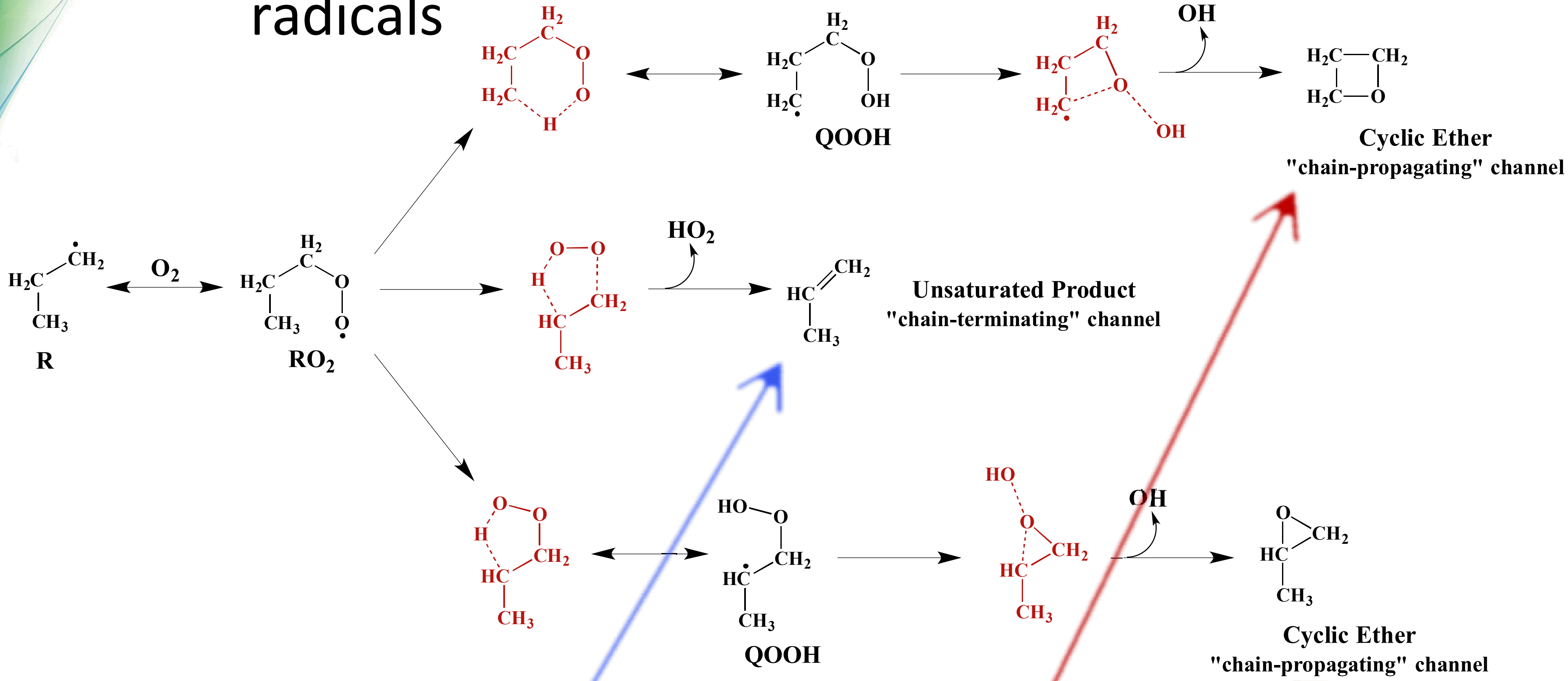
Endophytic fungi can degrade cellulose directly and produce a spectrum of potentially useful organic compounds

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



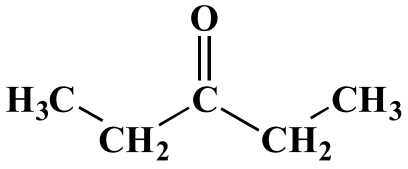
Compare the oxidation mechanism of *n*-propyl radicals



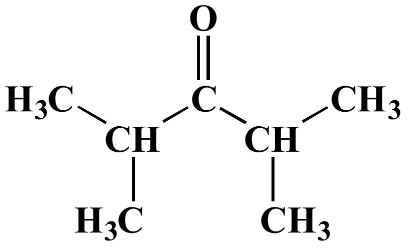
J. D. DeSain et al. *J. Phys. Chem. A* **2003**, *107*, (4415).

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

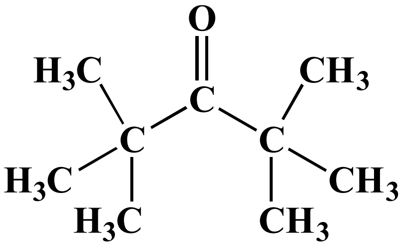
Fundamental ignition chemistry of potential fungal biofuels: ketones



Diethyl Ketone

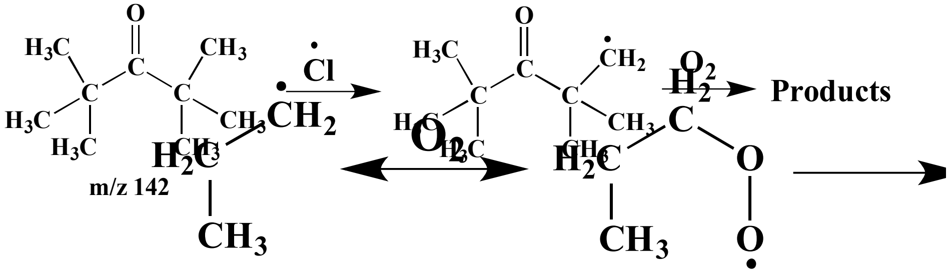


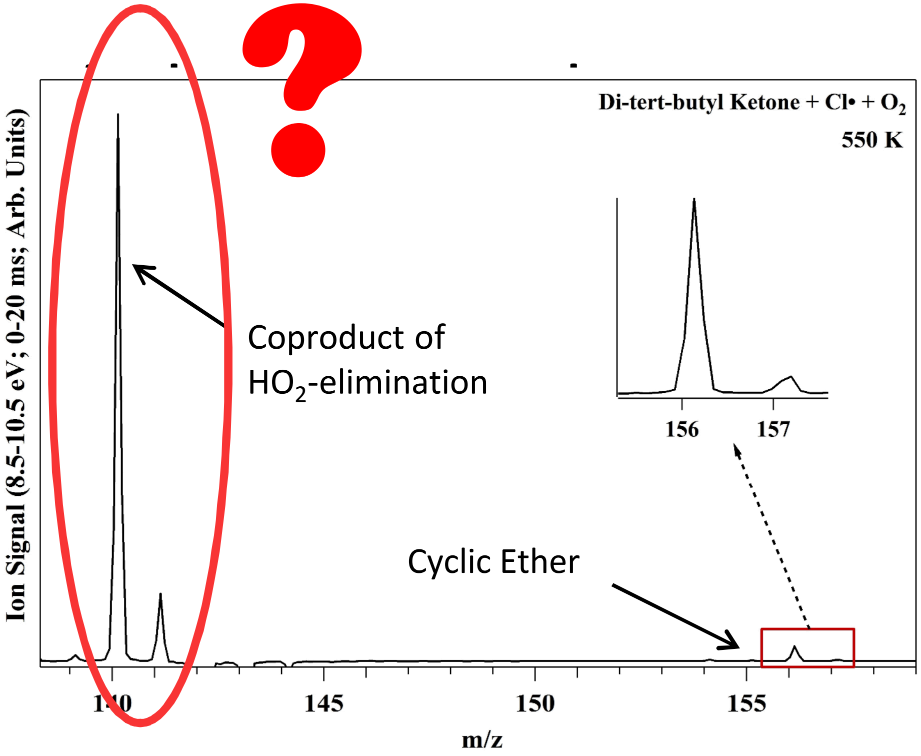
Diisopropyl Ketone



Di-tert-butyl Ketone

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



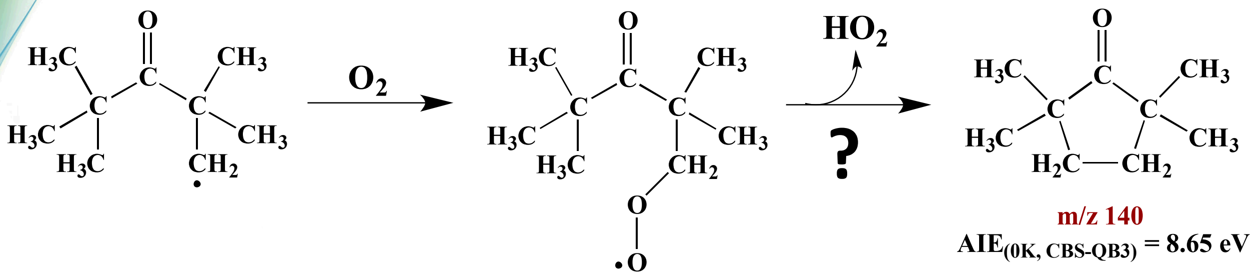


Coproduct of HO_2-elimination

Cyclic Ether

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

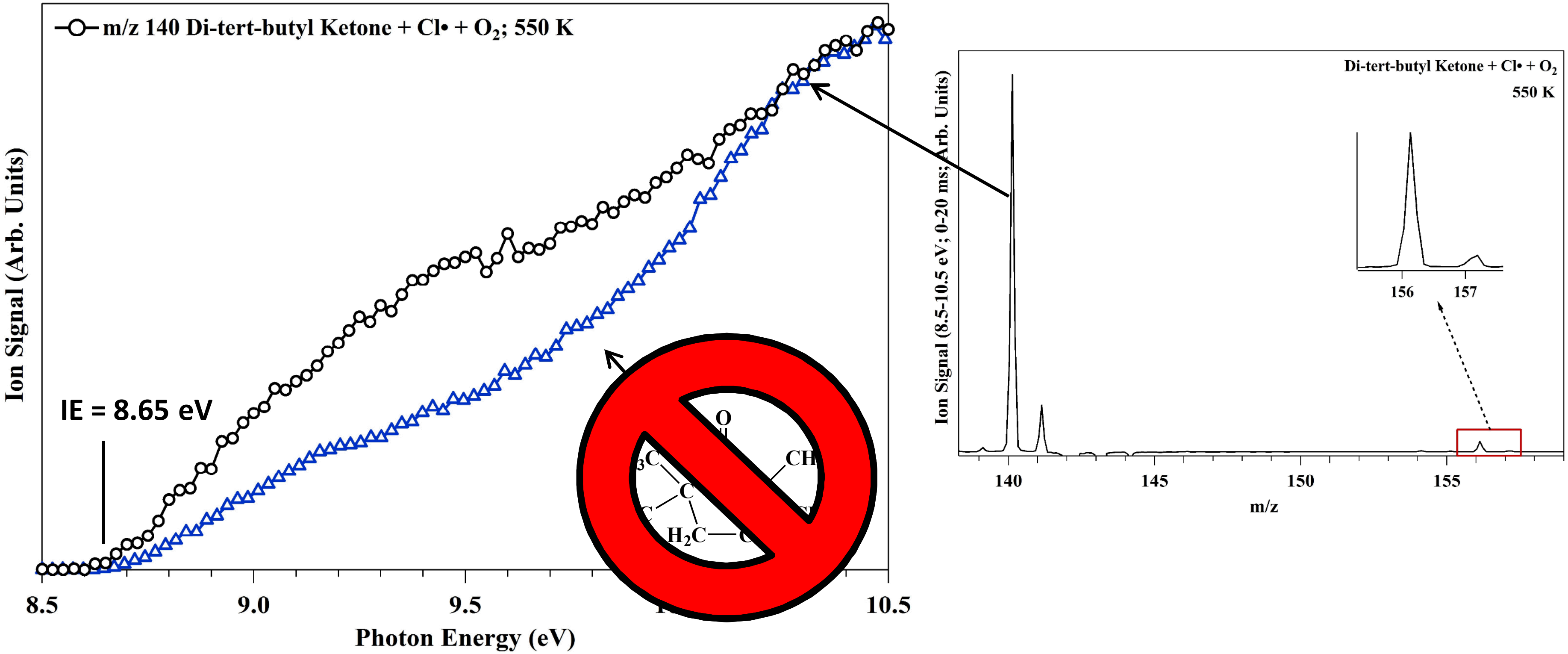
Could this be Ring Closure with HO_2 Elimination?



m/z 140

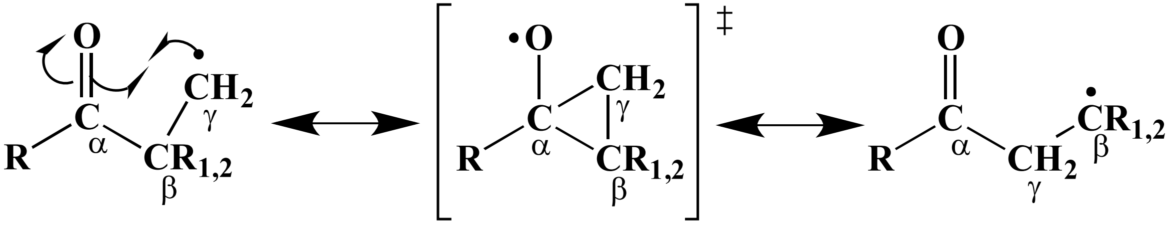
AIE$_{(0K,\ CBS\text{-}QB3)}$ = 8.65 eV

Calculated ionization energy matches experimental onset.



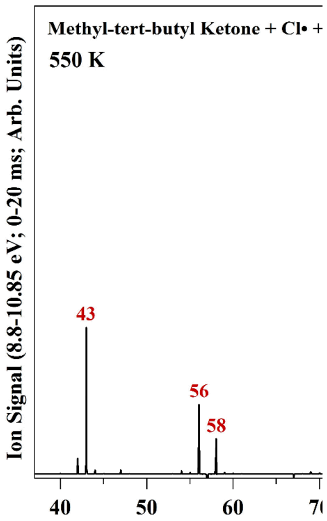
Instead, the initial radical isomerizes rapidly

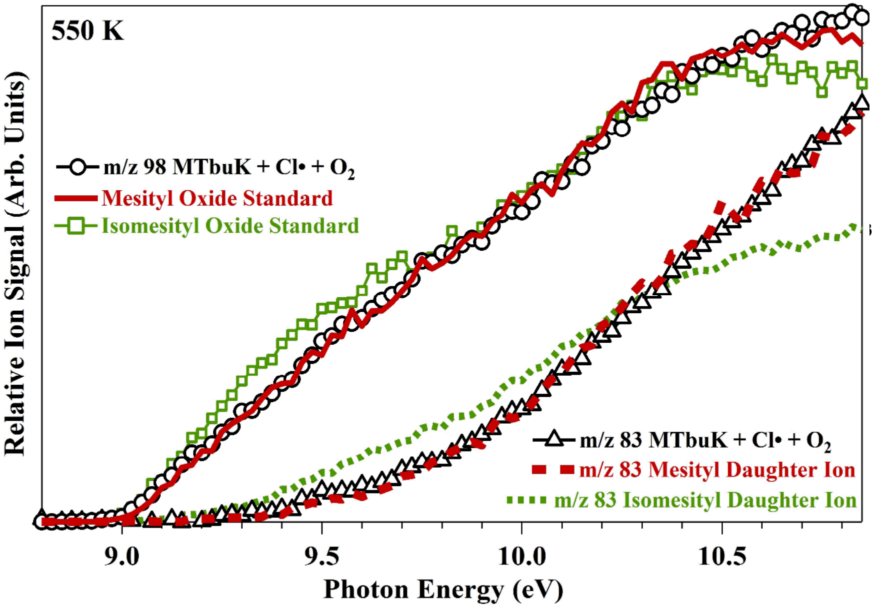
Known in solution-phase chemistry

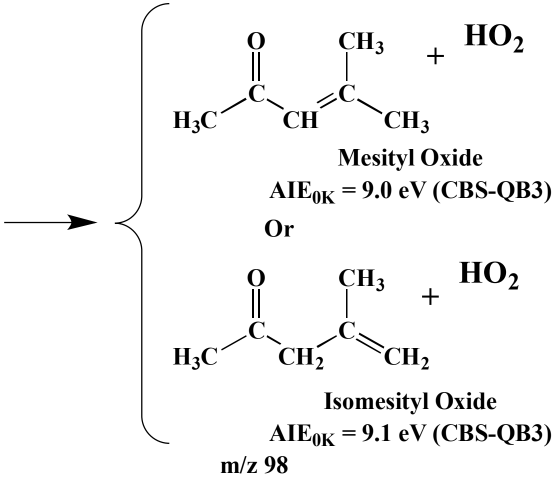


Karl et al. *J. Org. Chem.* **37**, 2834 (1972)

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







Mesityl Oxide

AIE_{0K} = 9.0 eV (CBS-QB3)

Or

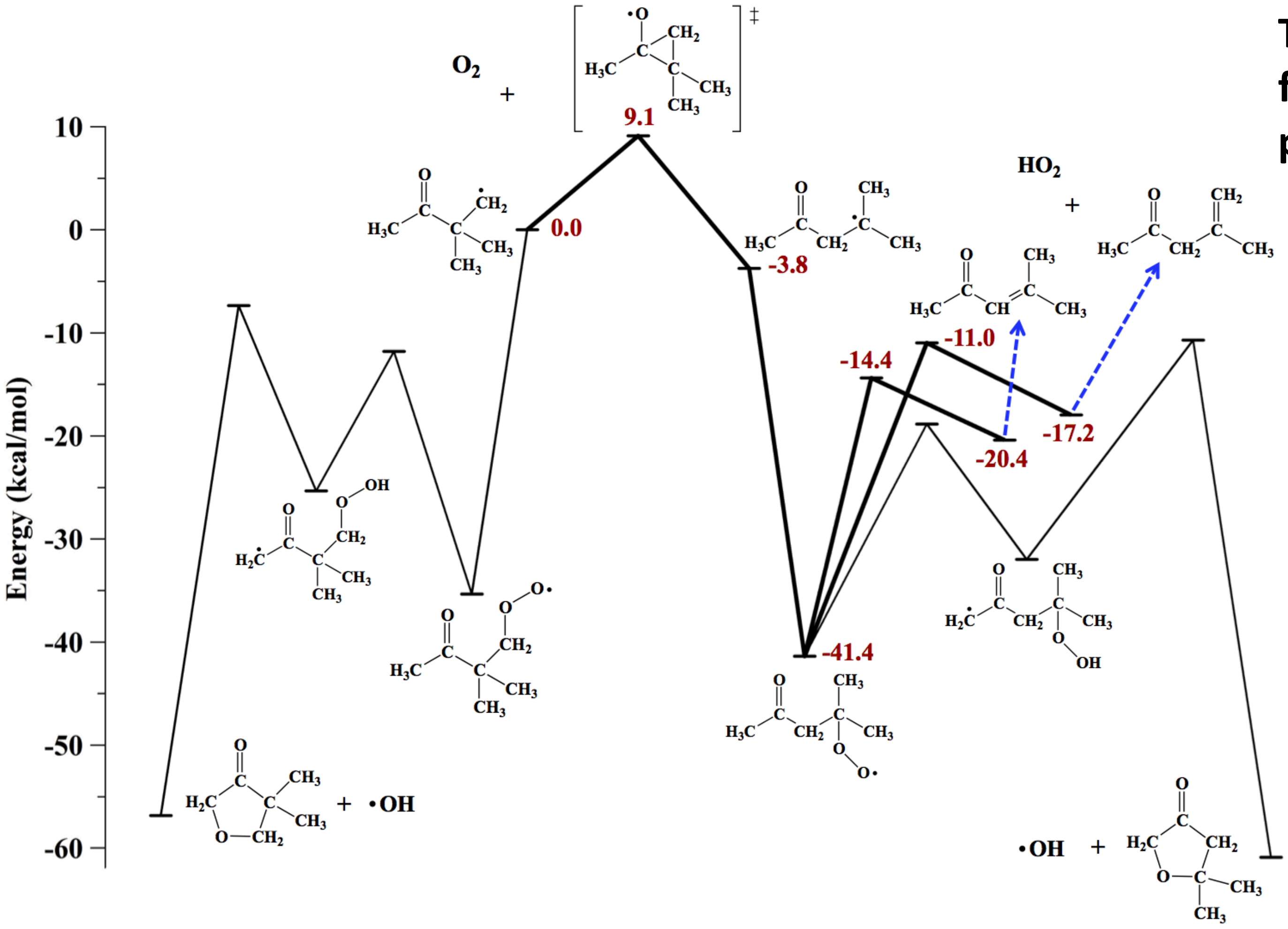
Isomesityl Oxide

AIE_{0K} = 9.1 eV (CBS-QB3)

m/z 98

A. M. Scheer et al., *J. Am. Chem. Soc.* **135**, 14256–14265 (2013)

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



Thermodynamics favors the rearranged product for MtBK

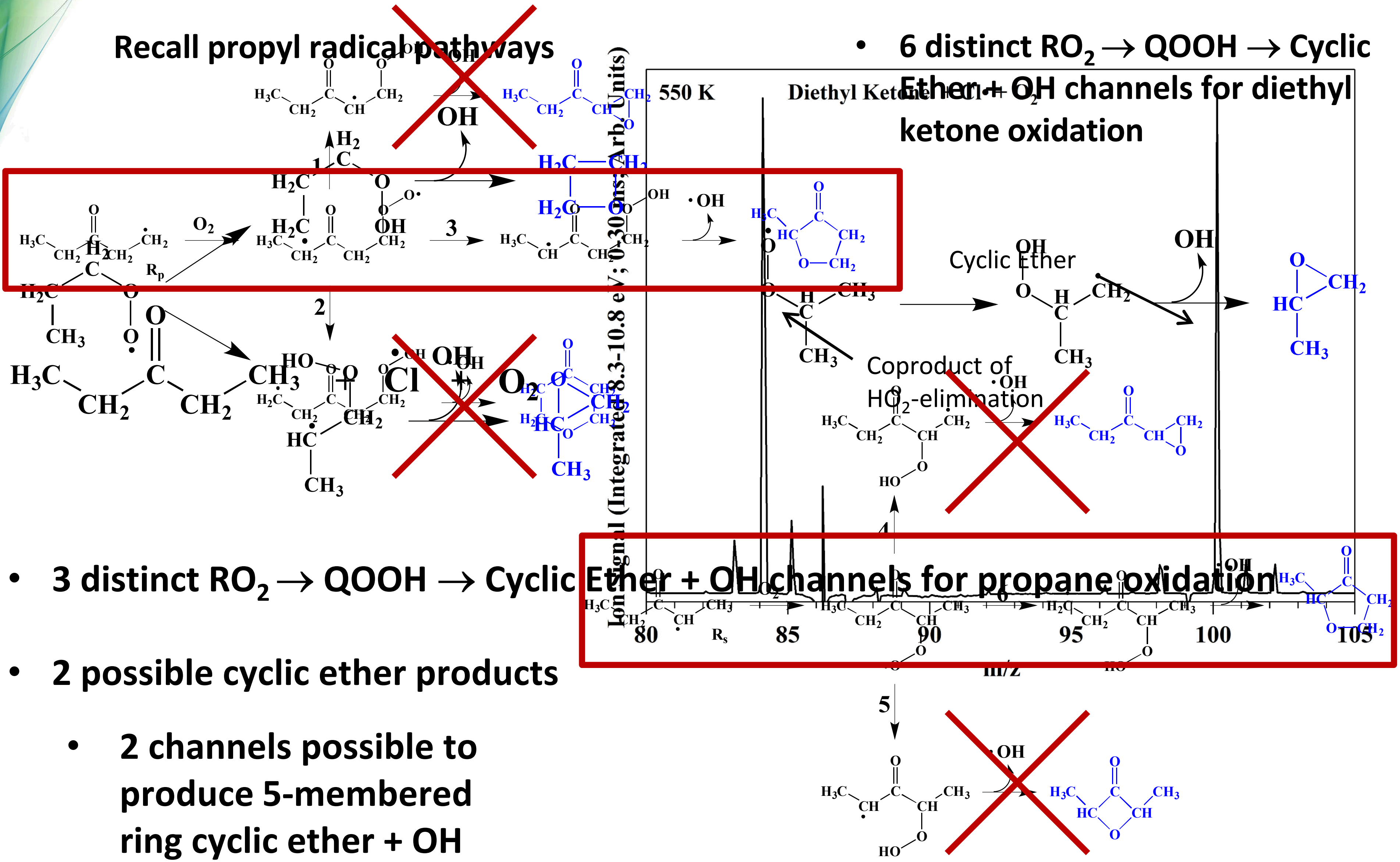
Isomerization changes amount of chain propagation and termination

A. M. Scheer et al., *J. Am. Chem. Soc.* **135**, 14256–14265 (2013)

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

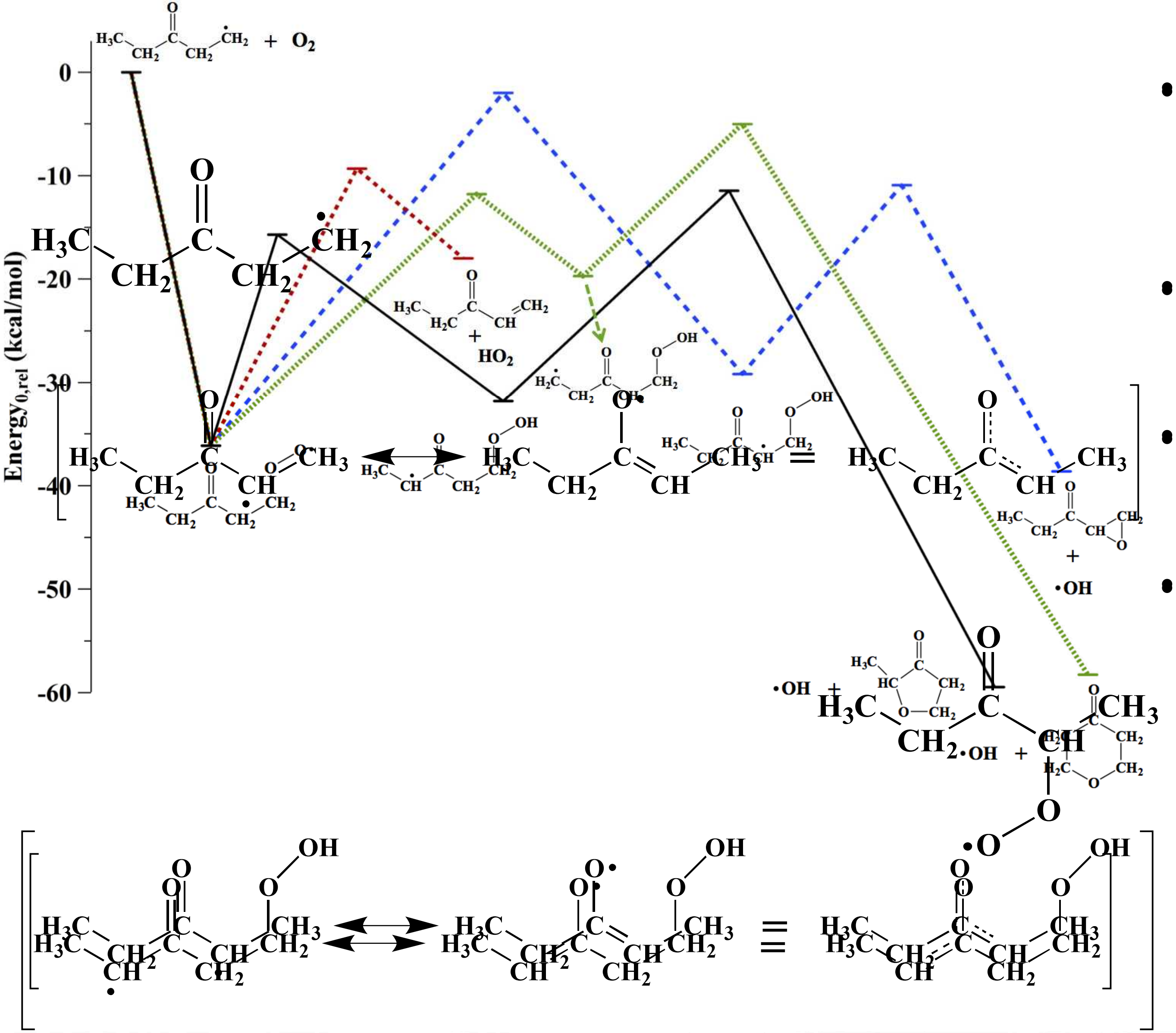


Cyclic Ether

Coproduct of HO_2-elimination

- 3 distinct $RO_2 \rightarrow QOOH \rightarrow$ Cyclic Ether + OH channels for propane oxidation
- 2 possible cyclic ether products
  - 2 channels possible to produce 5-membered ring cyclic ether + OH

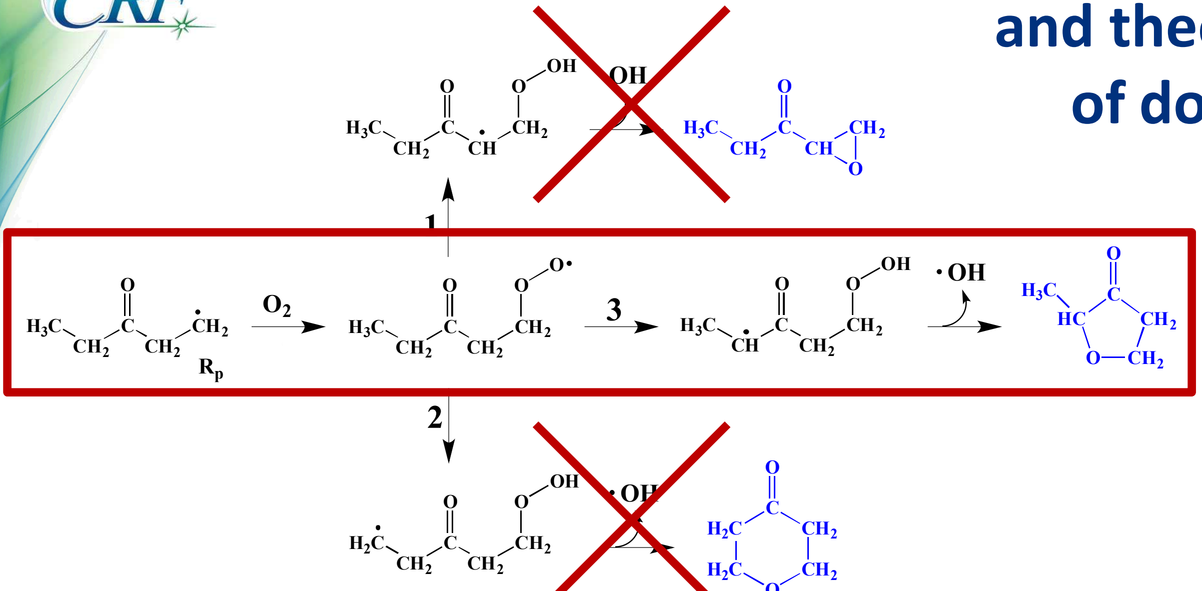
Thermodynamics Drives Cyclic Ether Selectivity in Diethyl Ketone Oxidation

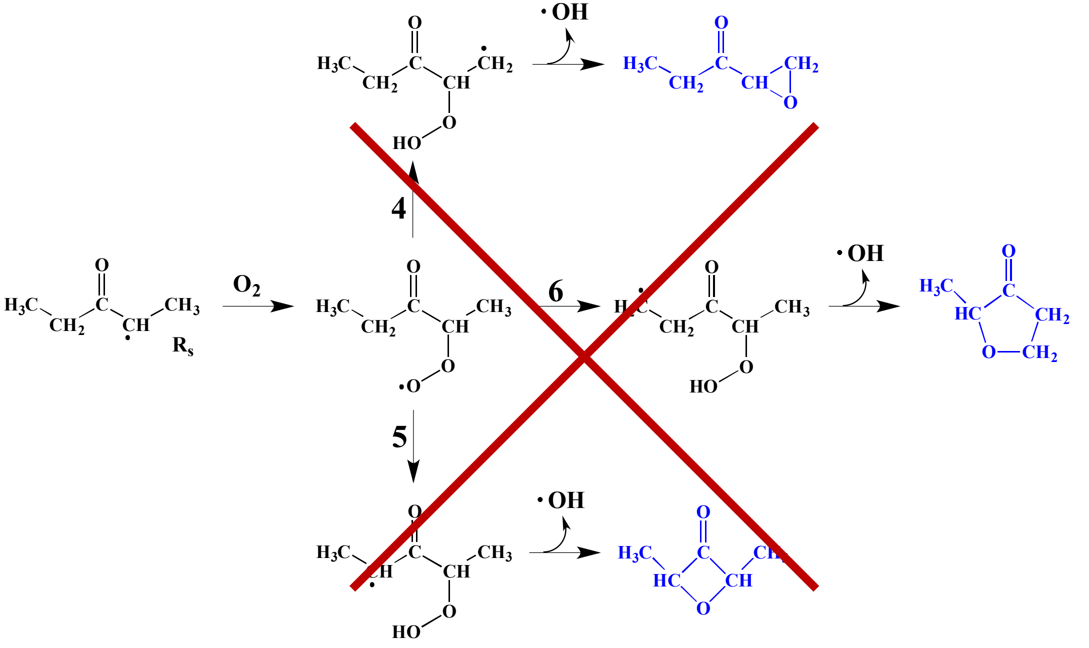


- No resonance stabilization of primary radical
- RO_2-well ~ 36 kcal/mol
- $R + O_2 \rightleftharpoons RO_2$ shifted to products
- 5-membered ring pathway lowest energy and benefits from resonantly stabilized QOOH

- Resonance stabilization of secondary radical
- RO_2-well ~ 26 kcal/mol – shallow!
- $R + O_2 \rightleftharpoons RO_2$ shifted to reactants
- All cyclic ether, HO_2-elimination and bond breaking pathways above entrance channel

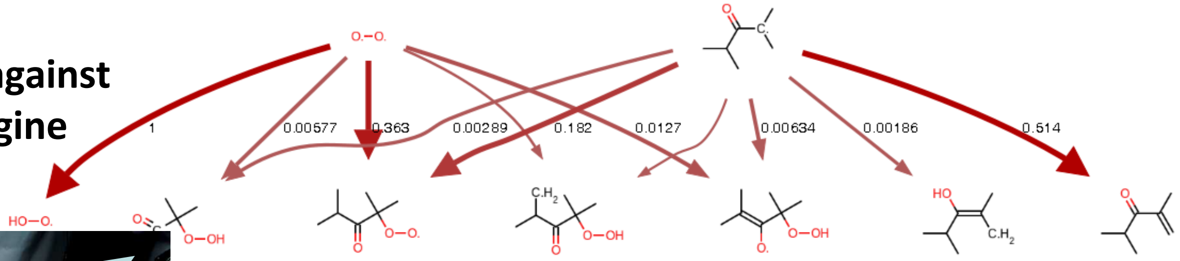
Combination of experiment and theory allows assignment of dominant cyclic ether channel



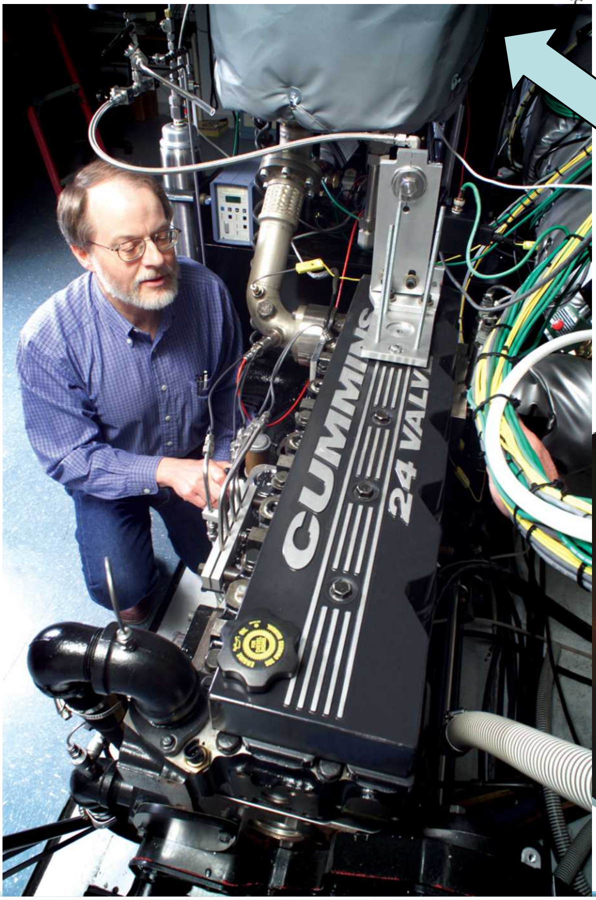


Reaction proceeds through the resonance stabilized QOOH

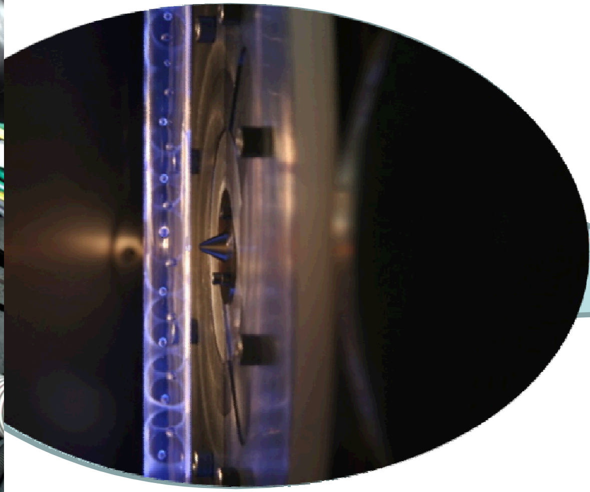
Combustion Chemistry Studies Build From Elementary Reactions to Engine Models



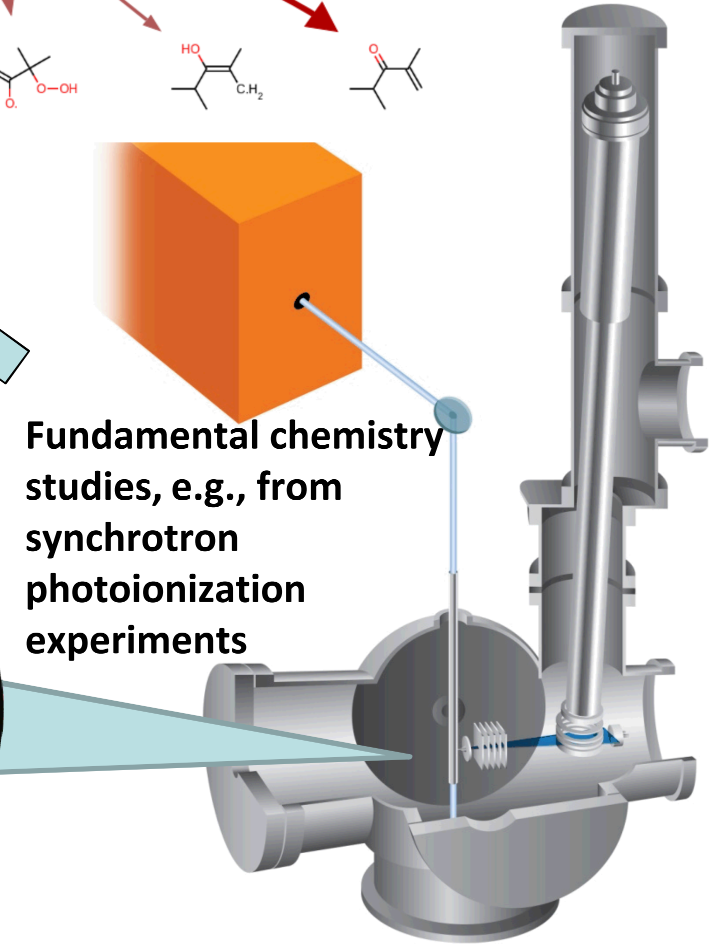
Which are validated against ignition delay and engine measurements



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

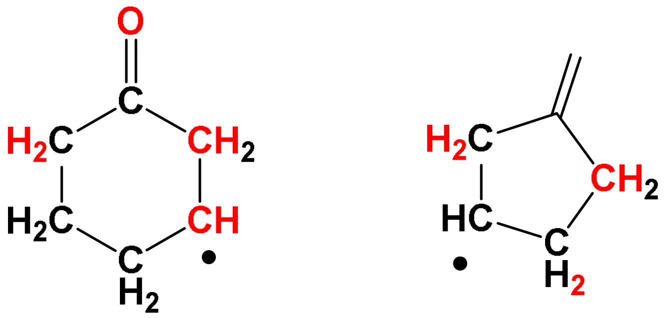


Fundamental chemistry studies, e.g., from synchrotron photoionization experiments



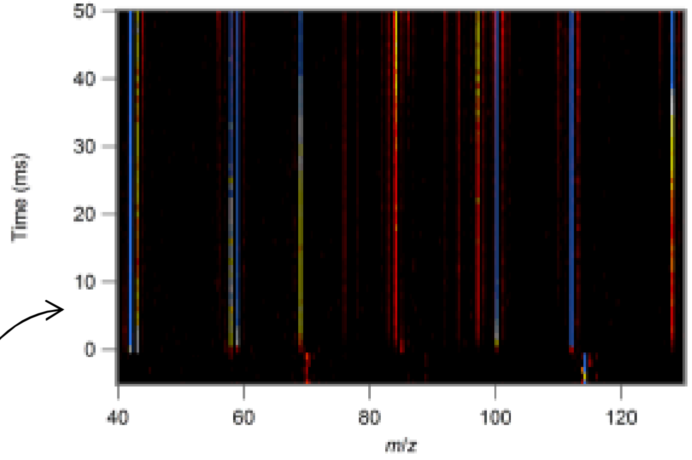
Vinoxylic Stabilization is an Important Determinant for Ketone Oxidation

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?



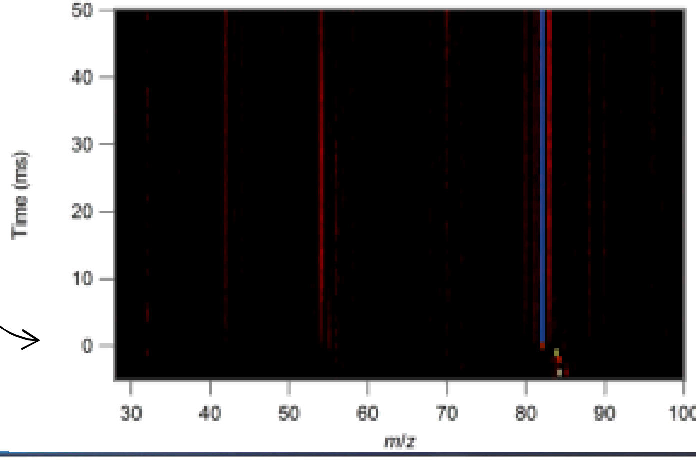
Di-isopropyl ketone: shows species associated with chain-propagating OH formation.

Expect some intermediate temperature heat release (ITHR) in engine



Cyclopentanone: almost exclusively cyclopentenone formation, associated with chain-terminating HO_2 formation.

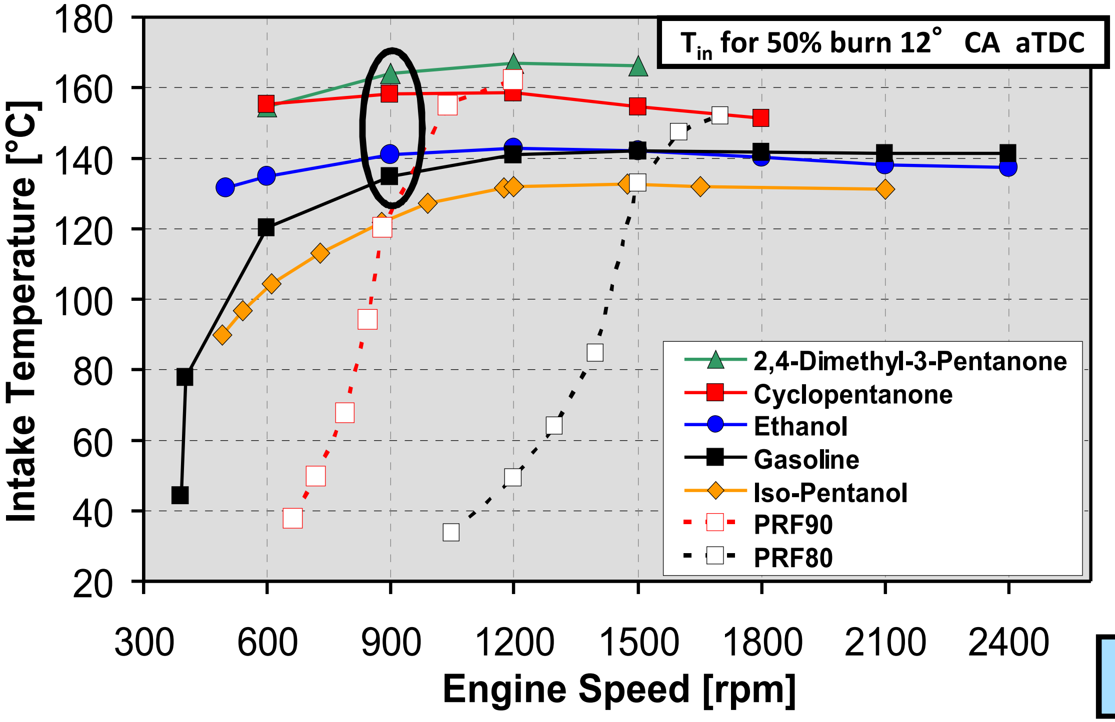
Expect very little ITHR in engine.



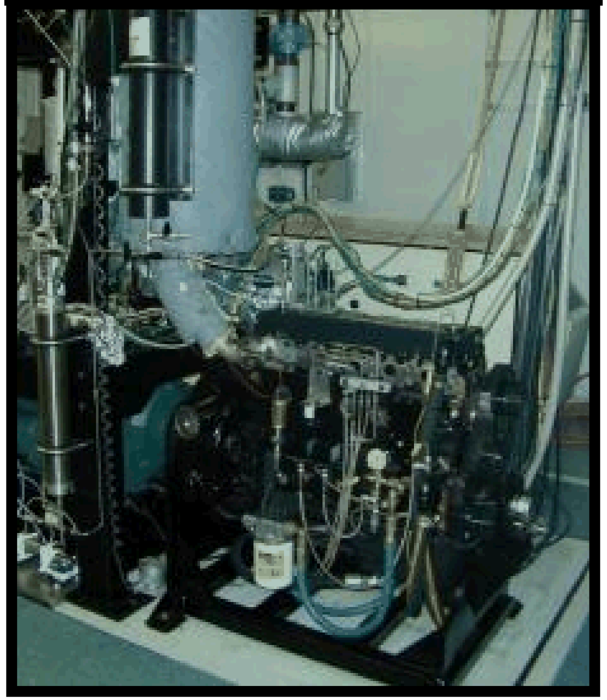
Engine Tests on Ketone Fuels (John Dec)

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.**

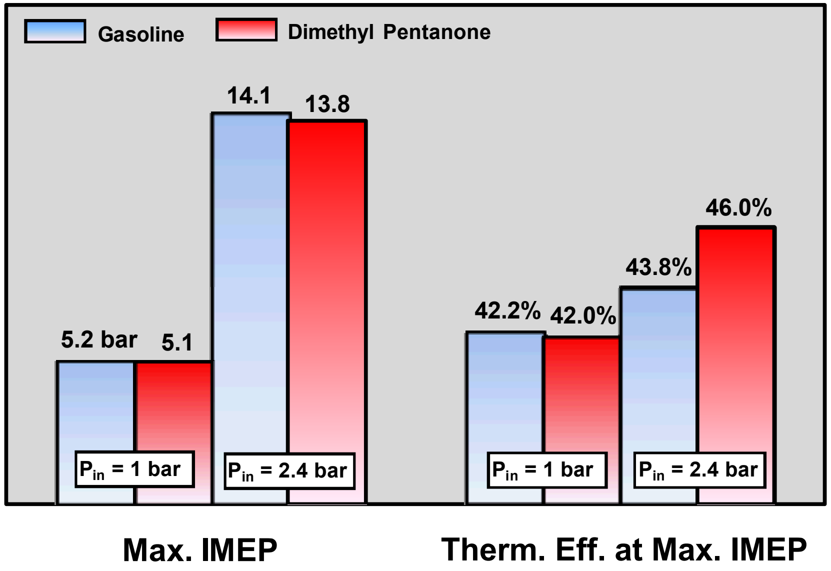
Ketones could raise octane no. of gasoline.

John Dec and Yi Yang, *SAE paper* **2013-01-2627** (2013)

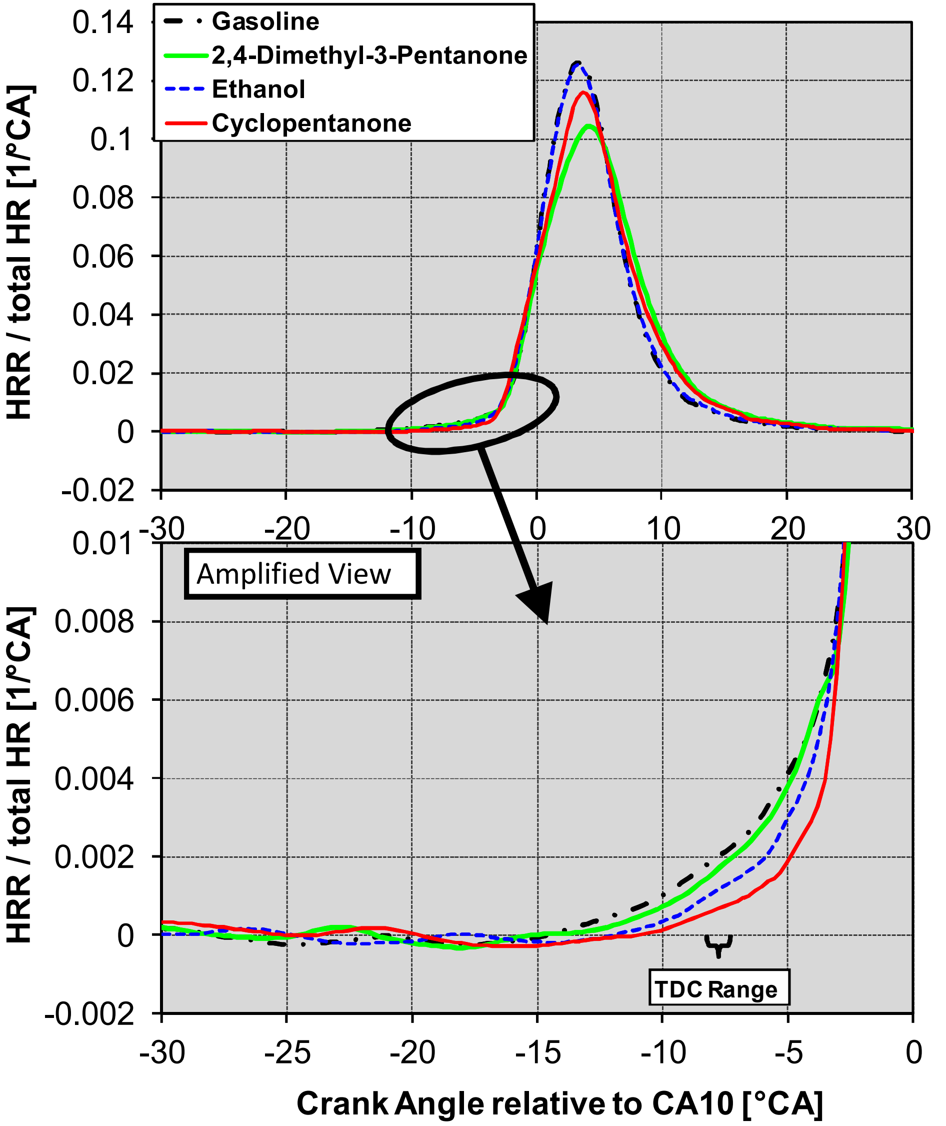
Pre-Ignition Activity of Ketone Fuels in Engines Qualitatively Follows Kinetics Prediction

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.

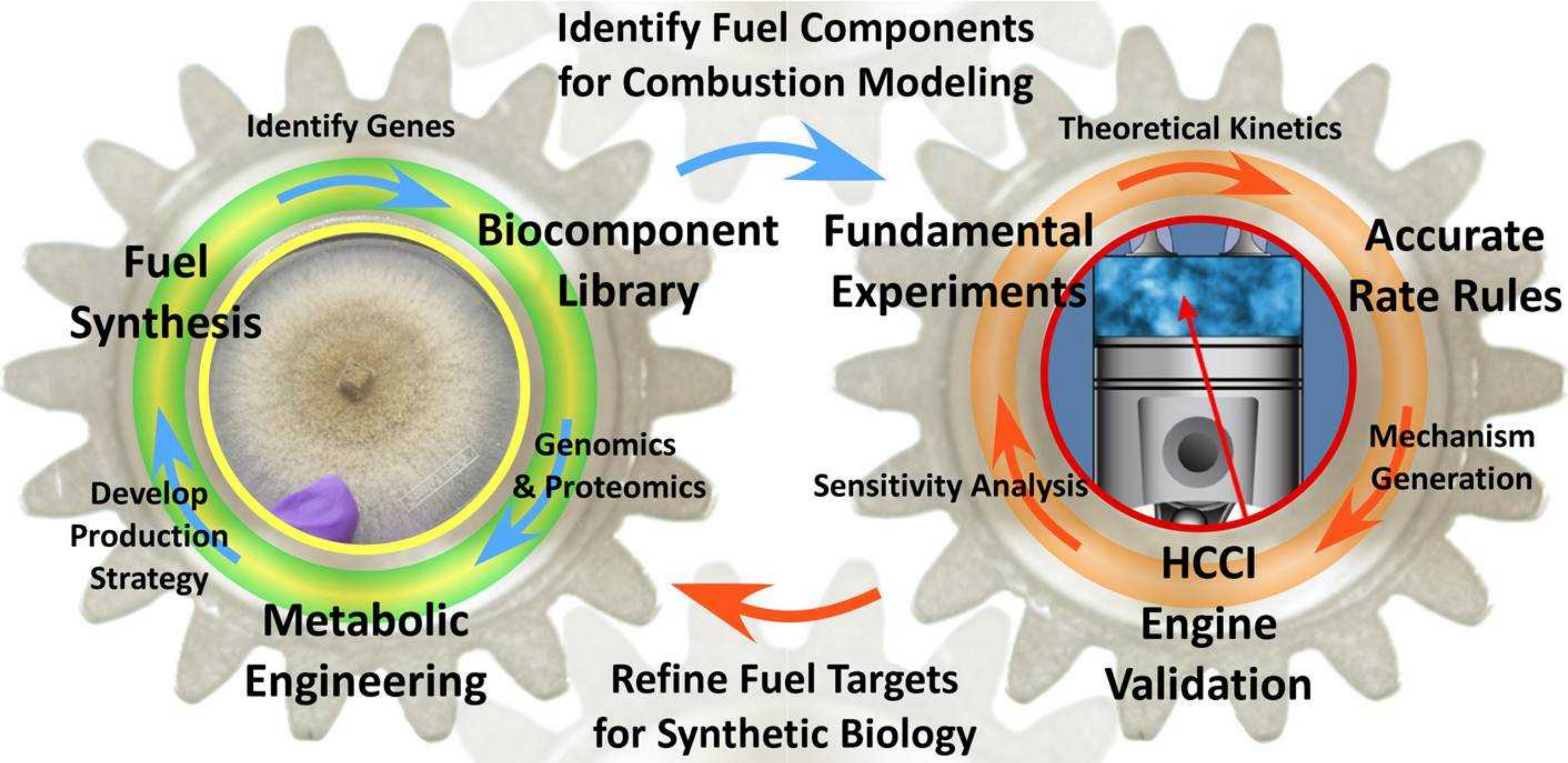


In fact, DIPK shows higher efficiency than gasoline at high load



John Dec and Yi Yang, *SAE paper* **2013-01-2627** (2013)

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

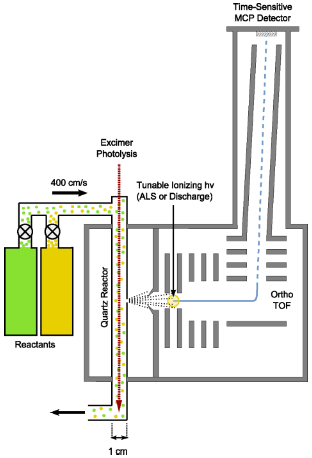
HCCI Engine Validation

Sensitivity Analysis

Fundamental Experiments

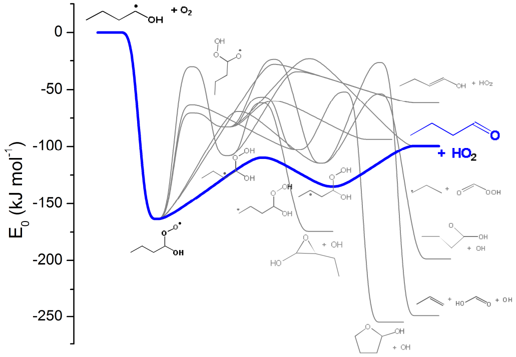
Refine Fuel Targets for Synthetic Biology

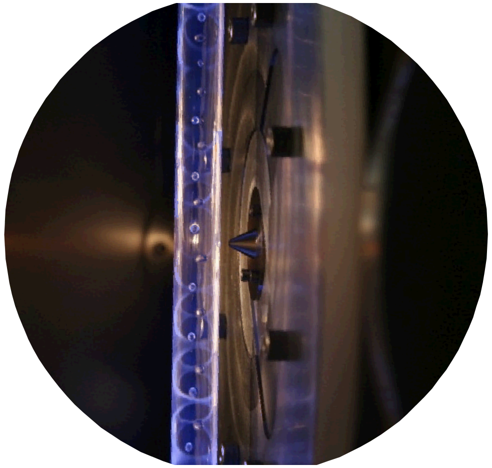
Summary



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

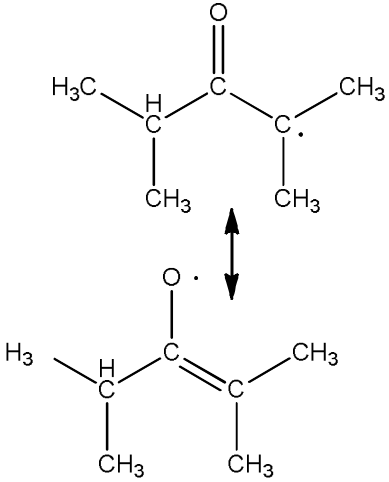
O





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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