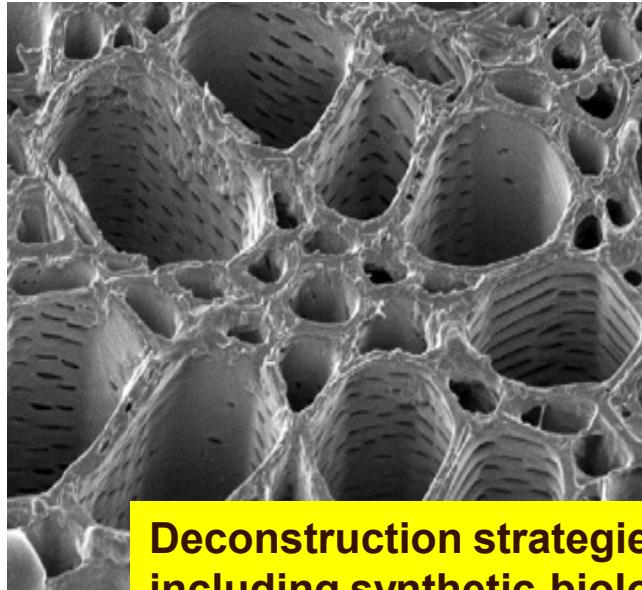


Autoignition chemistry of oxygenated molecules: Linking biofuel development with advanced engine combustion

Craig A. Taatjes
Combustion Research Facility
Sandia National Laboratories

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*



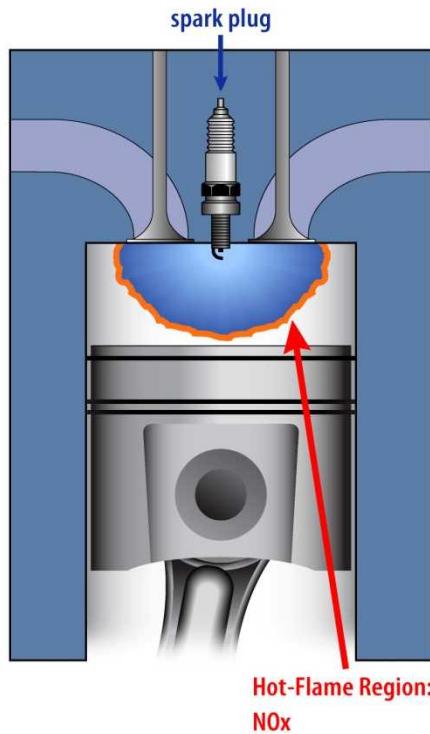
Deconstruction strategies – including synthetic biology – may produce some novel fuel compounds

- **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

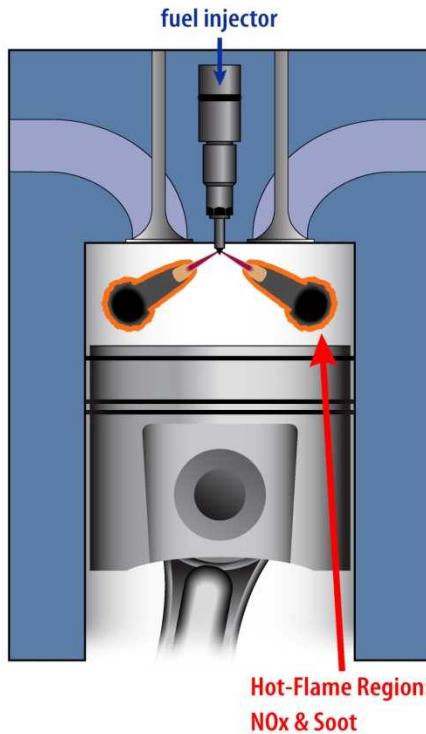
Gasoline Engine

(Spark Ignition)



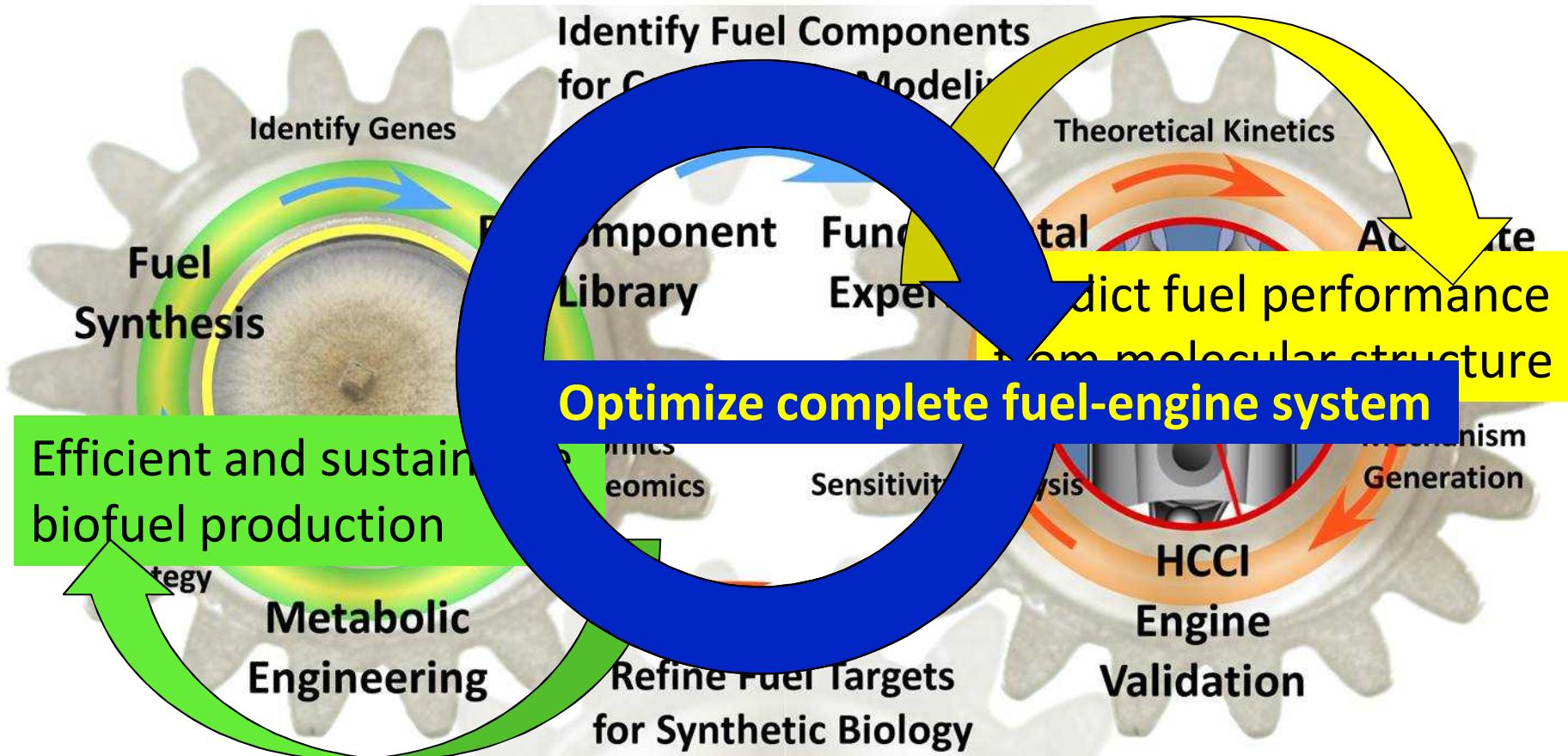
Diesel Engine

(Compression Ignition)



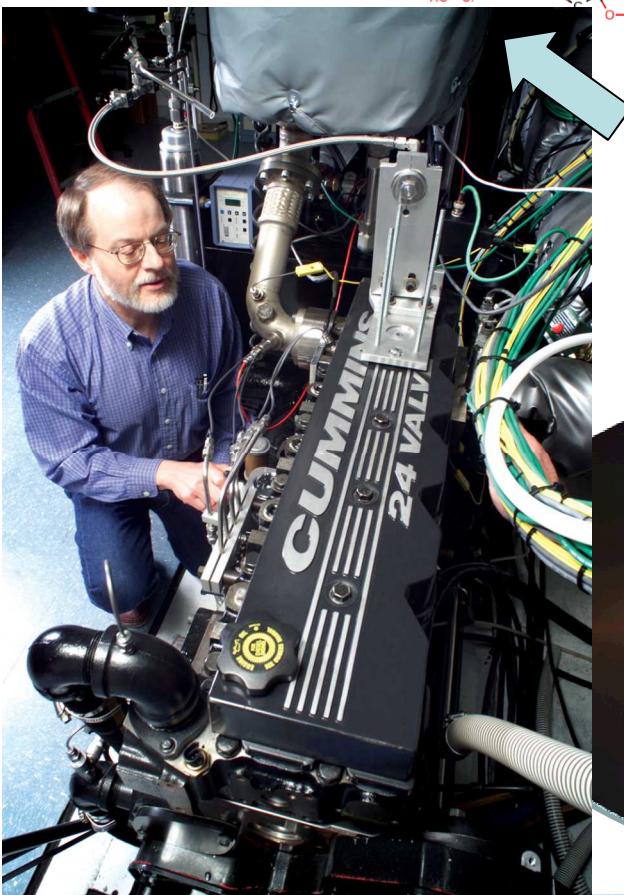
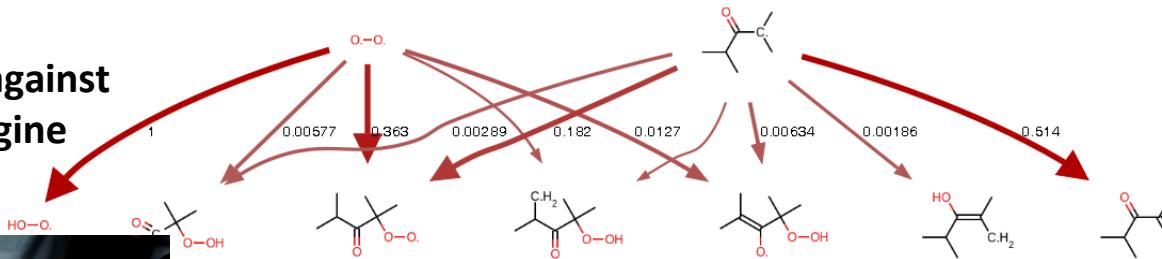
**Fuel chemistry is important – but fuel stream is already changing!
New fuels can be disruptive, but they can also be enabling
How can combustion studies mesh with new fuel development?**

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

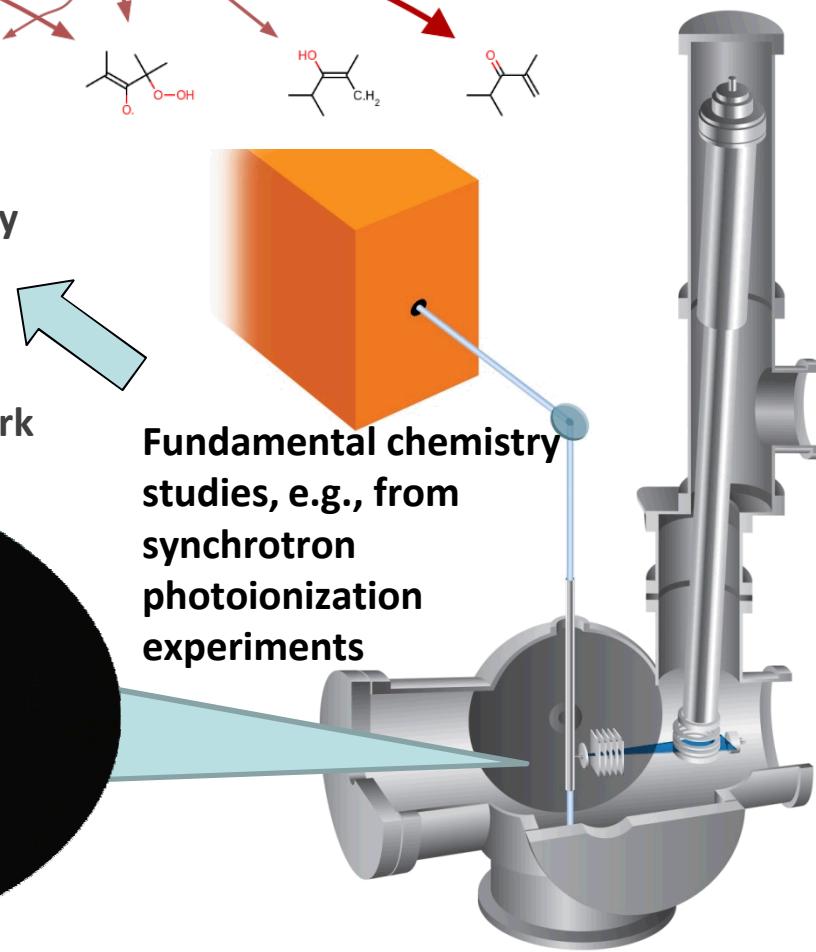
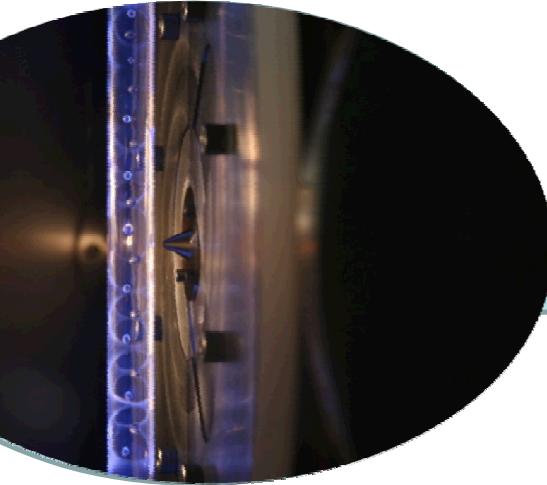


Combustion Chemistry Studies Build From Elementary Reactions to Engine Models

Which are validated against ignition delay and engine measurements

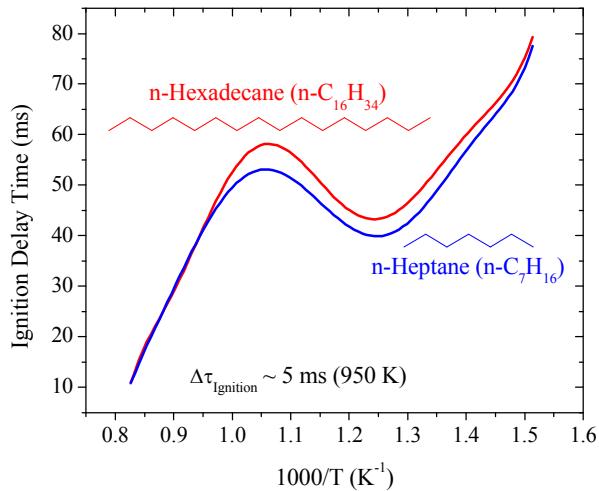


Inform new chemistry models, such as produced by MIT's Reaction Mechanism Generation framework



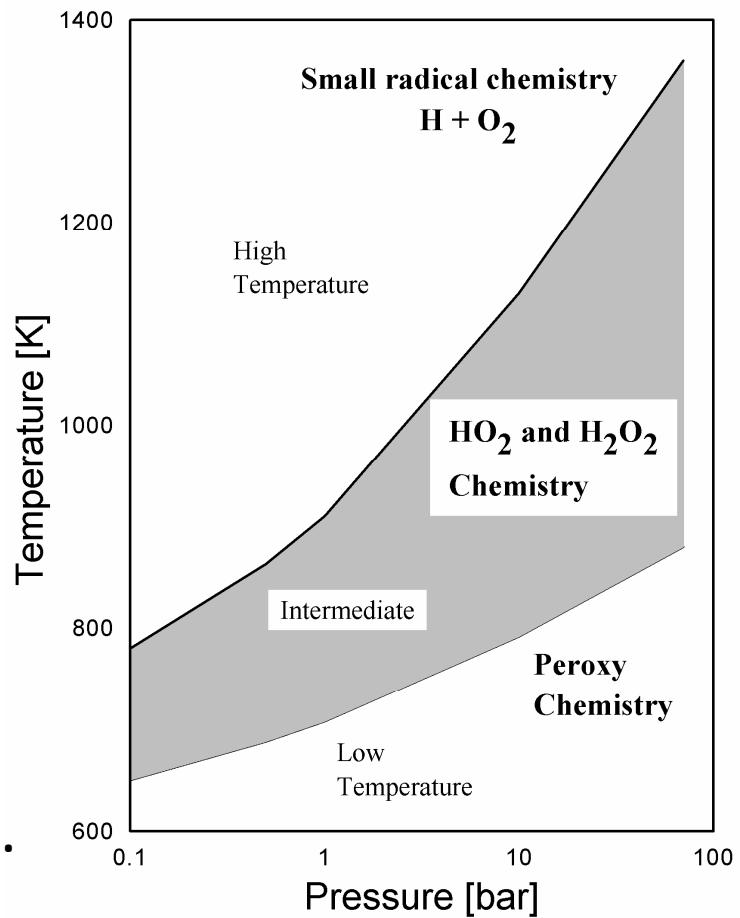
Fuel Effects on Ignition are Dominated by Low-Temperature Oxidation Chemistry

Ignition behavior of different fuels tend to coincide at high temperature



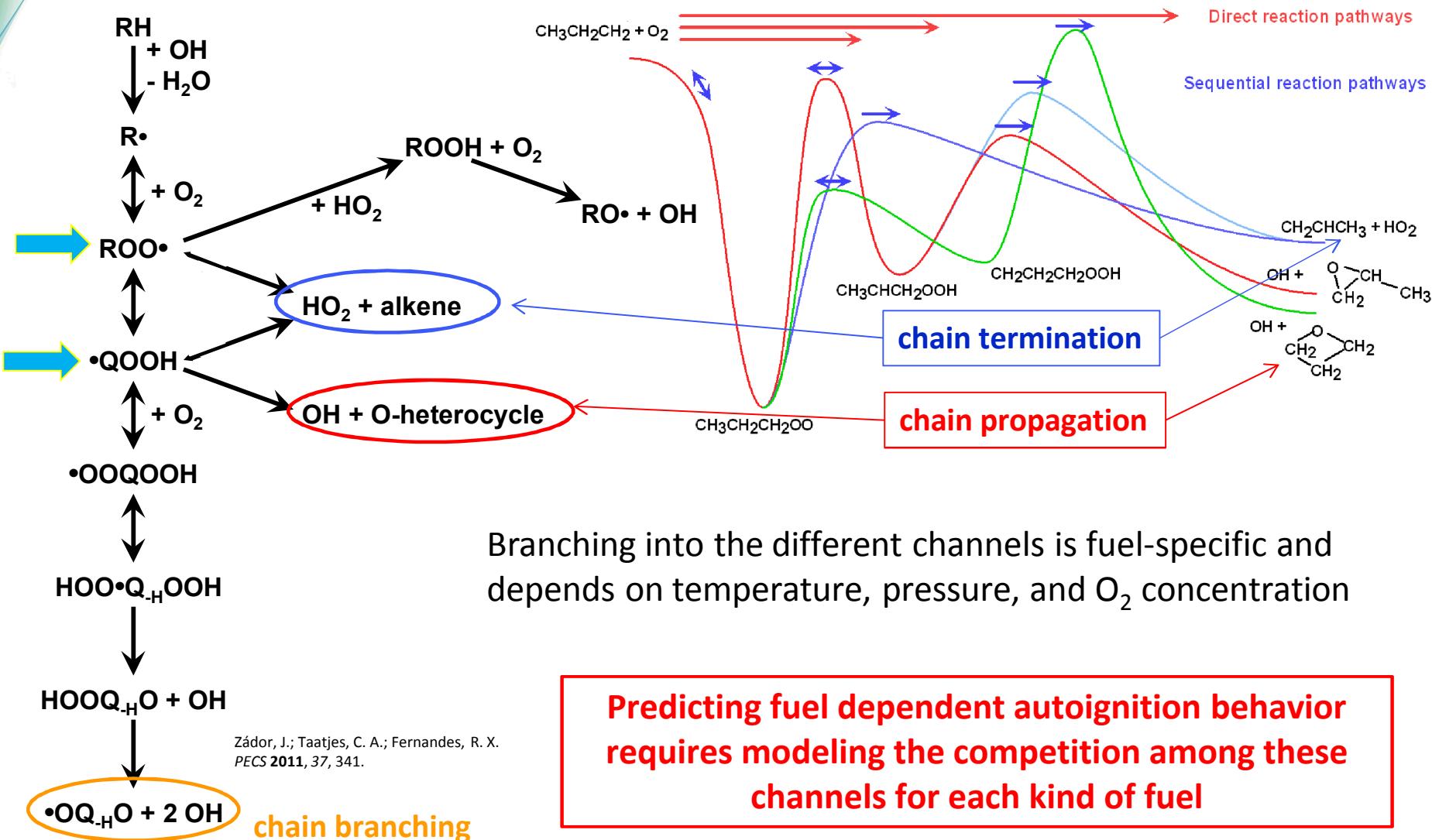
Westbrook et al., *Combust. Flame*, 156 (2009)

Fuel-chemistry effects on autoignition behavior appear in negative temperature coefficient region.
 → Fundamental kinetic studies in the low-temperature regime are critical



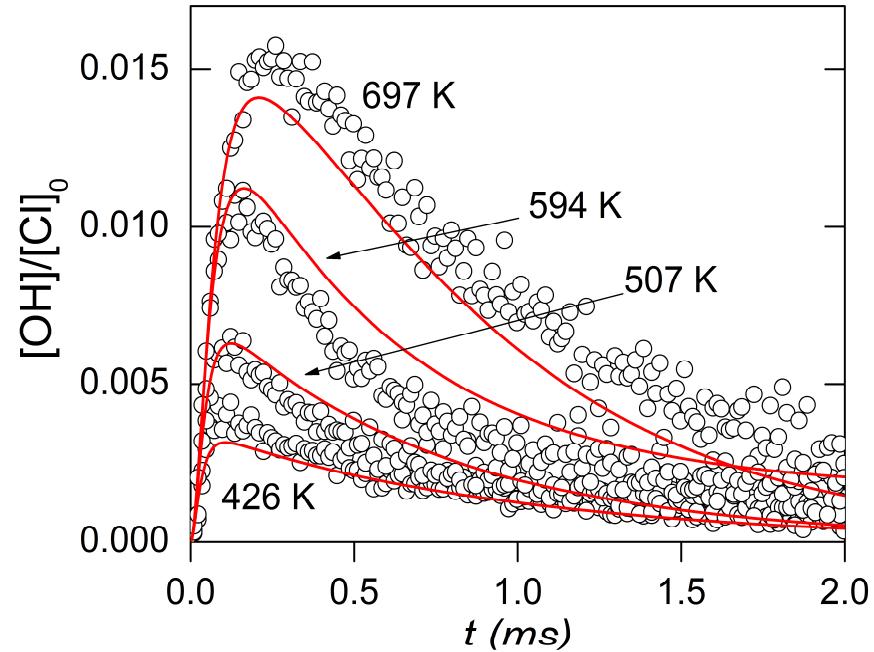
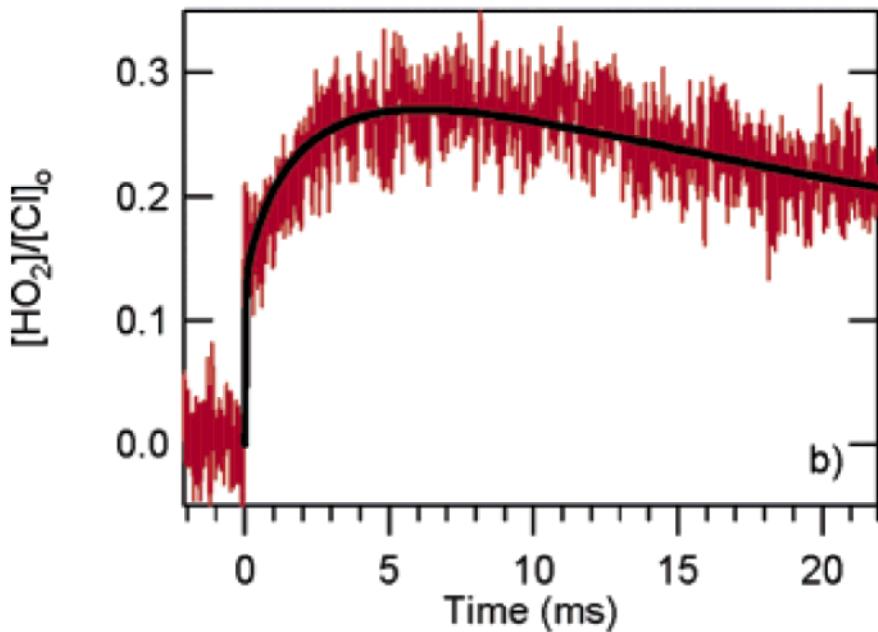
Vranckx et al., *Combust Flame* 2011, 148, 1444 (1-butanol)

Predicting Low-Temperature Oxidation Requires Understanding Chemistry of Intermediates



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

Measurements of the important radical products HO_2 and OH constrain calculations

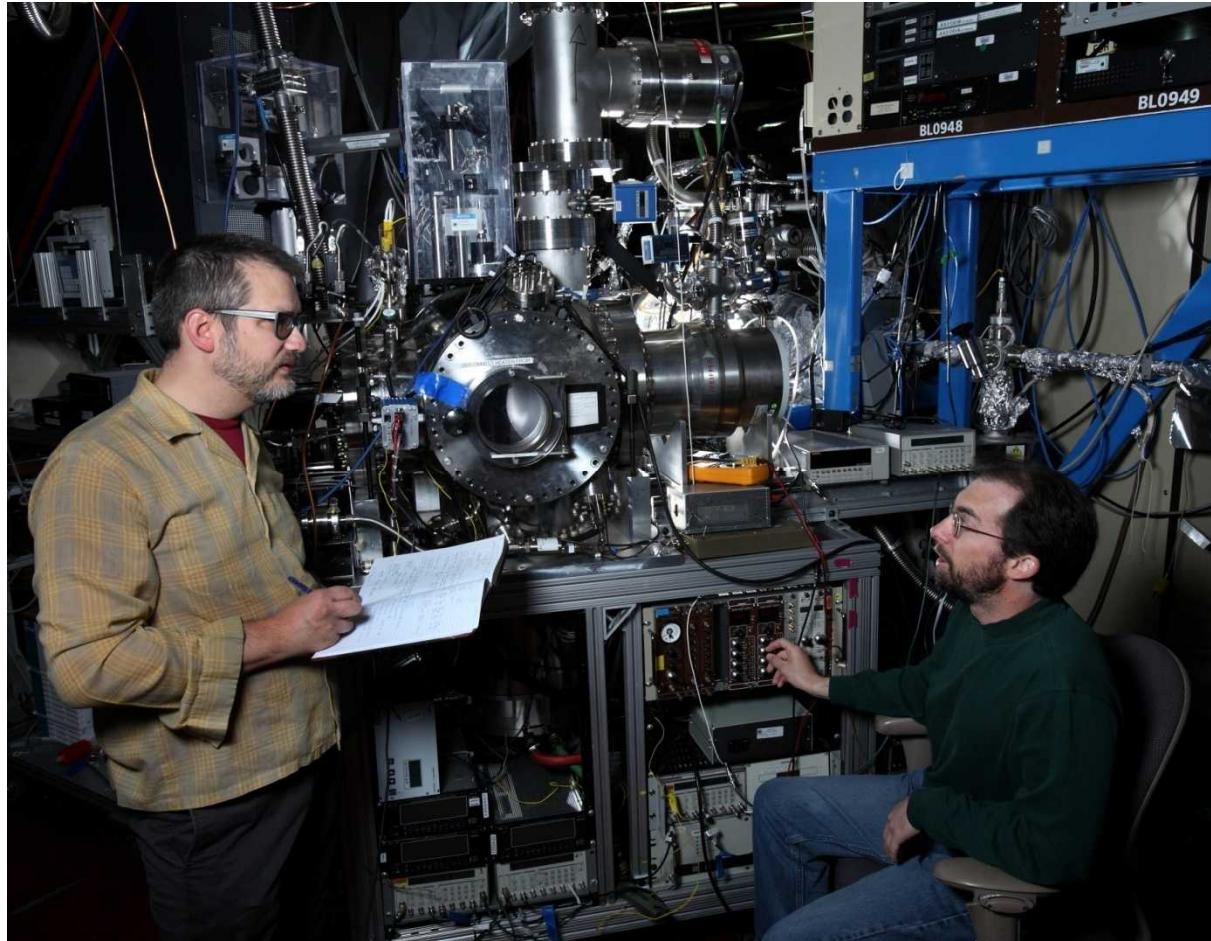


Pulsed photolytic Cl-initiated oxidation, with absorption detection of radicals

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 HO₂) *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

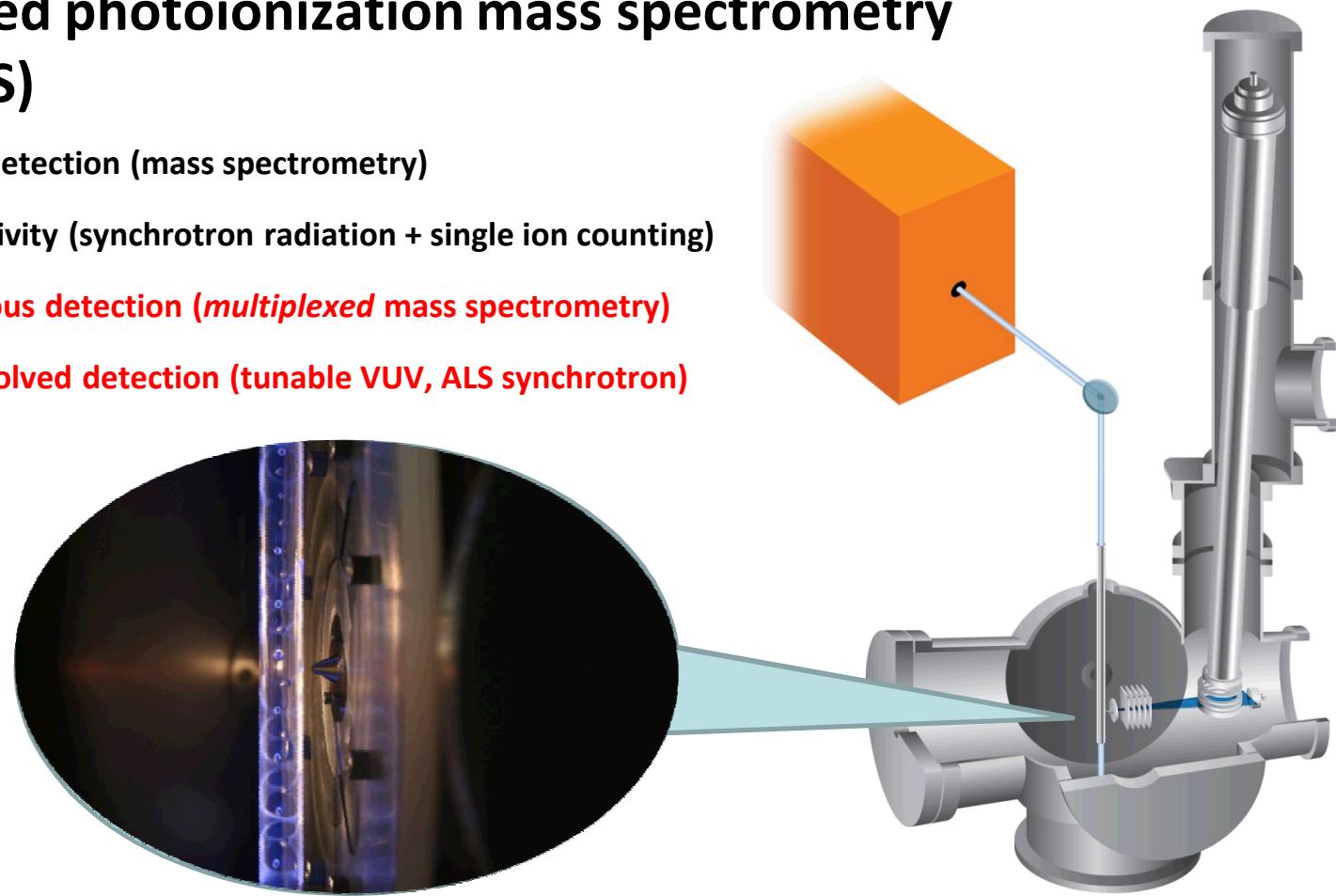
Multiplexed photoionization mass spectrometry (MPIMS)

Universal detection (mass spectrometry)

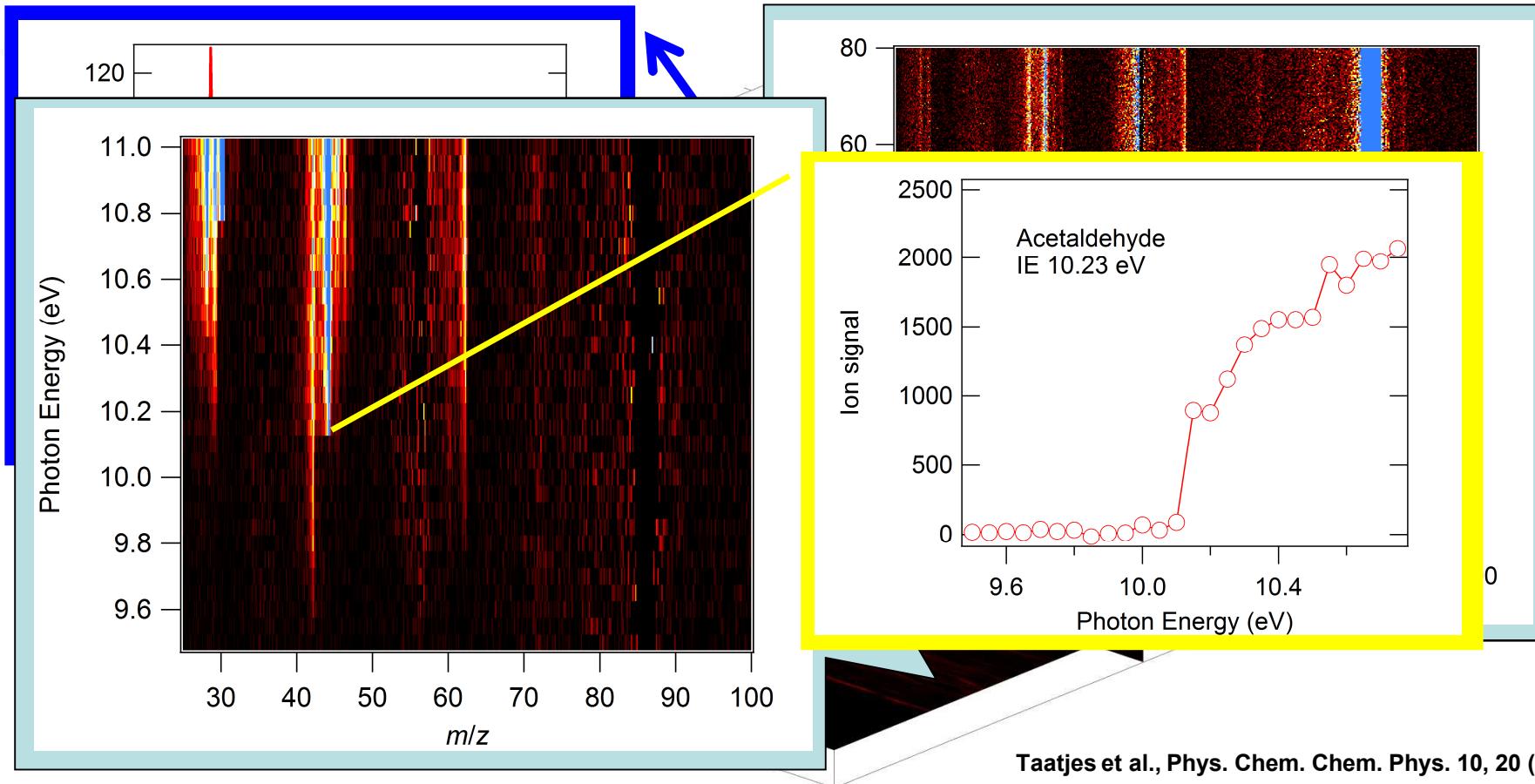
High sensitivity (synchrotron radiation + single ion counting)

Simultaneous detection (*multiplexed* mass spectrometry)

Isomer-resolved detection (tunable VUV, ALS synchrotron)



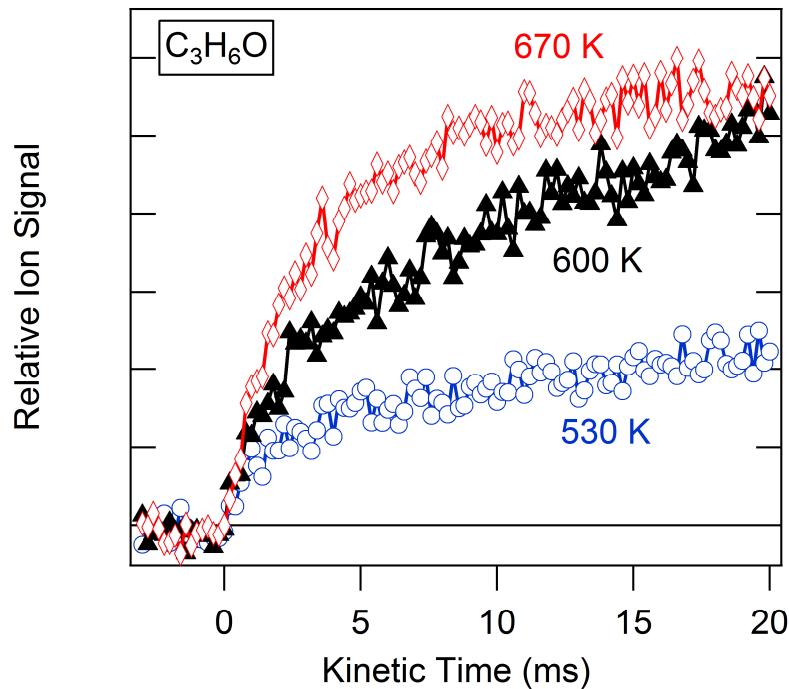
Kinetic Data is Acquired as a Function of Time, Mass, and Photoionization Energy



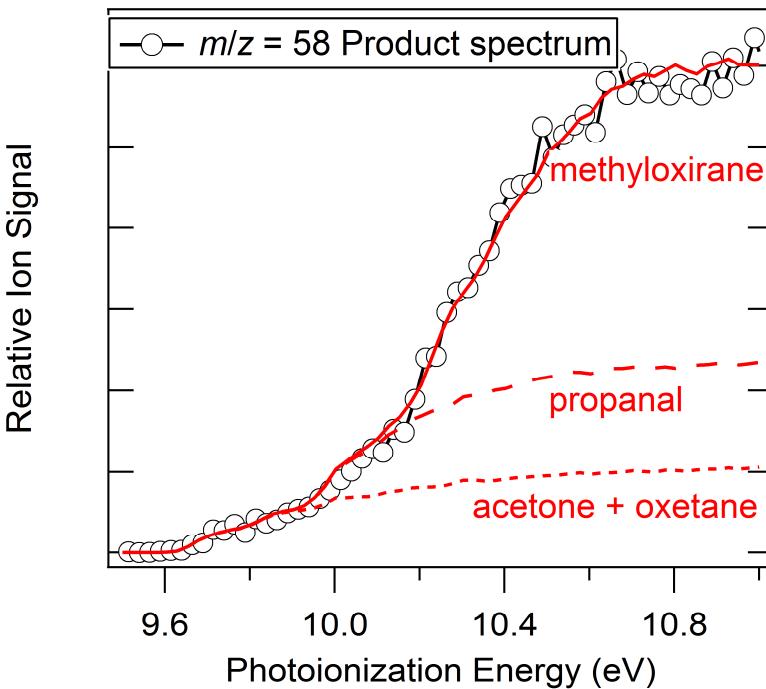
3-D dataset can be “sliced” along different axes to probe different aspects of the reaction

Mass spectroscopic measurements can identify isomeric pathways

Time profiles of stable products reflect same bimodal behavior as radicals



Multiple $\text{C}_3\text{H}_6\text{O}$ isomers are formed in unimolecular reactions of ROO

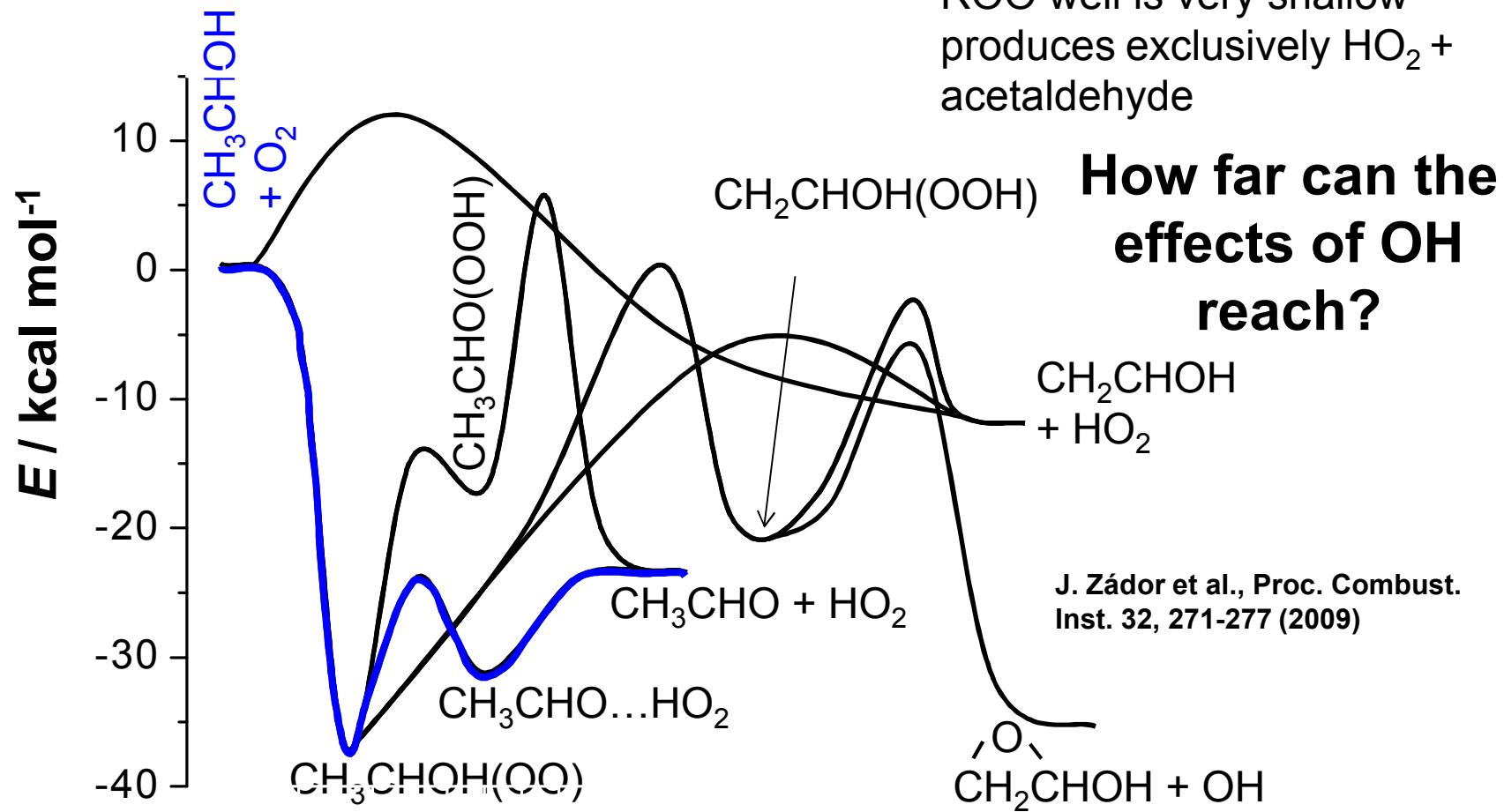


Combination of high-pressure MPIMS, radical product measurements and literature experiments with application of “multi-scale informatics” (Mike Burke et al., Argonne)

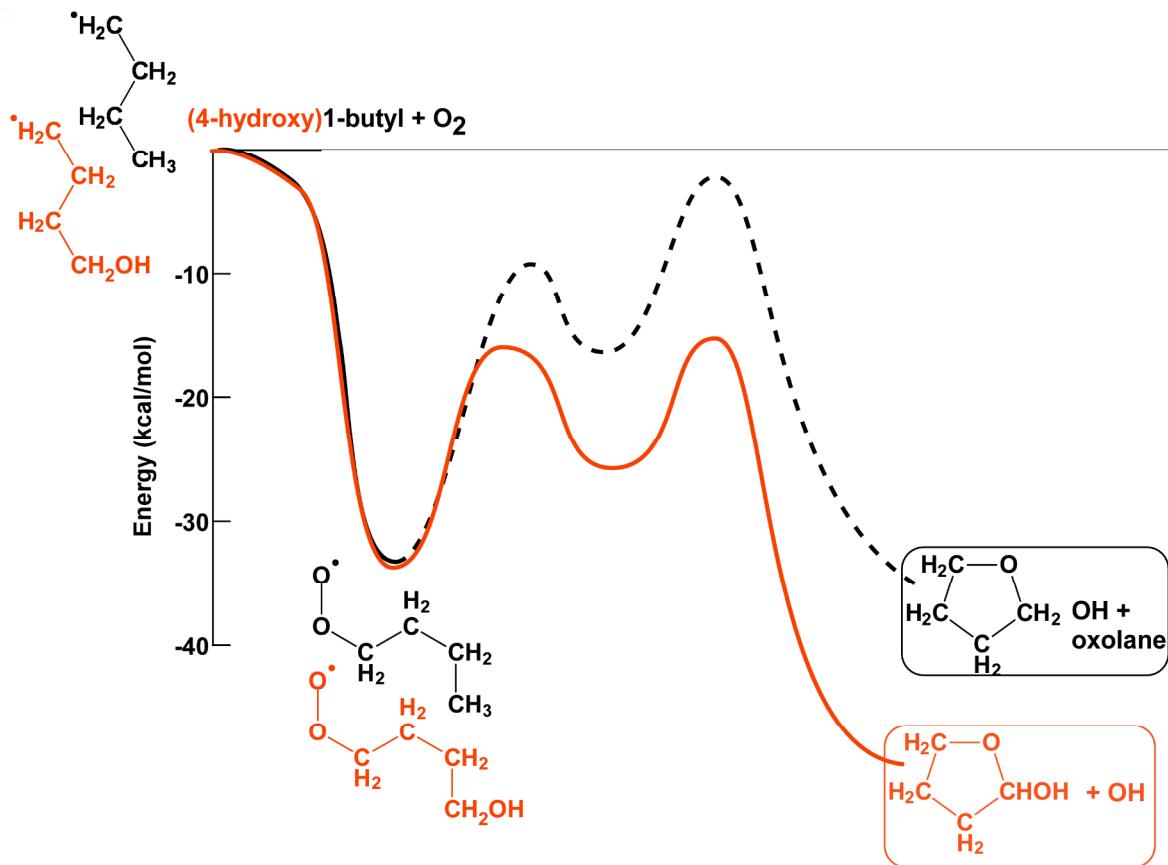
Much better constraints on primary reaction characteristics

How Might Functionalization Affect Ignition Chemistry? Alcohols Give One Example

OH group changes the **thermochemistry**



In n-butanol oxidation, all hydroxybutyl + O₂ reactions are affected by OH group

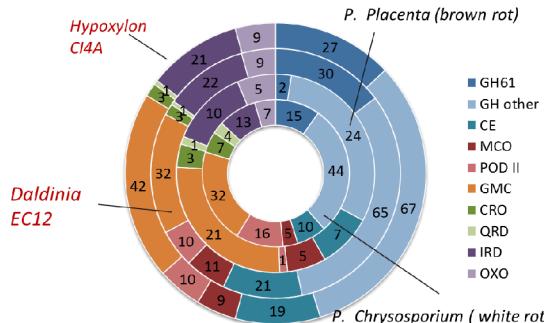
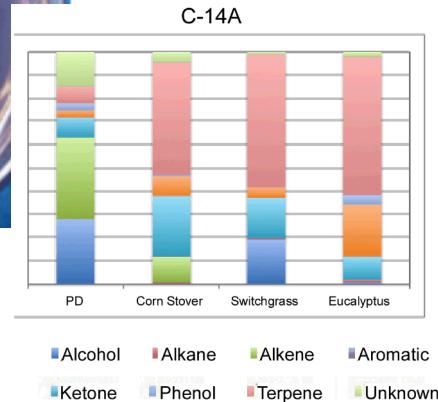
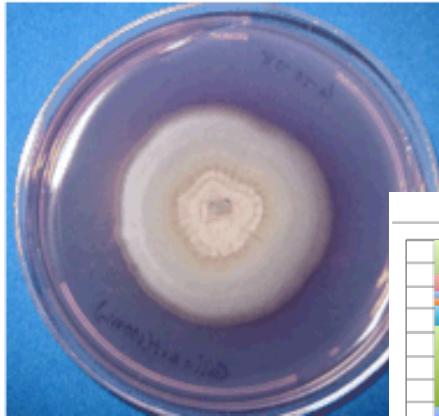


α -hydroxyalkyl reaction
forms HO₂

β -hydroxyalkyl reaction
Waddington mechanism

Weaker α -C—H bond
favors OH formation

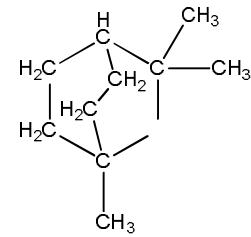
What might other “next-generation” biofuel production platforms offer?



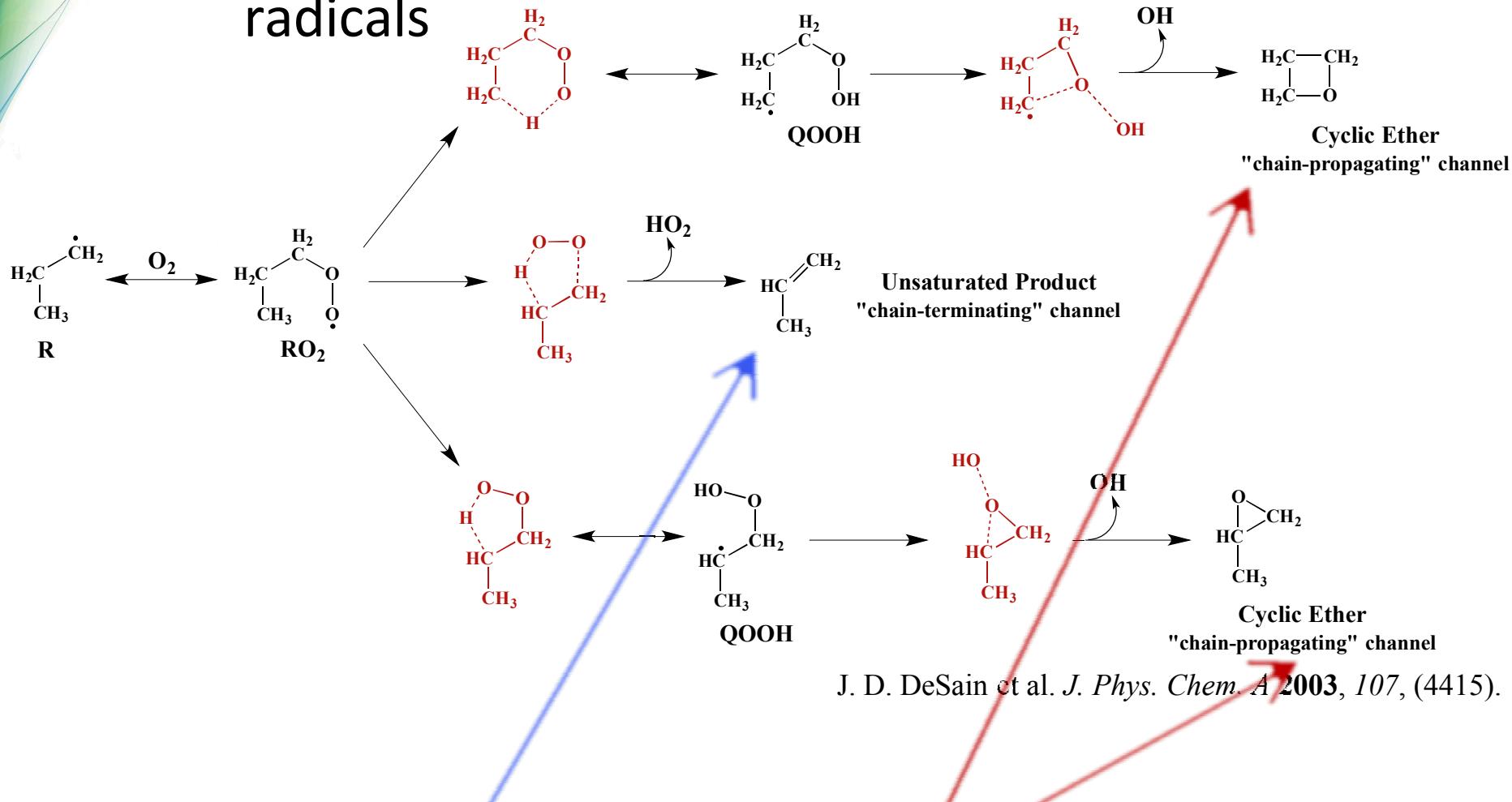
Endophytic fungi can degrade cellulose directly and produce a spectrum of potentially useful organic compounds

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



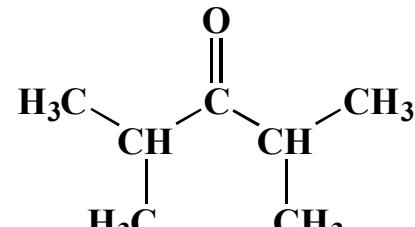
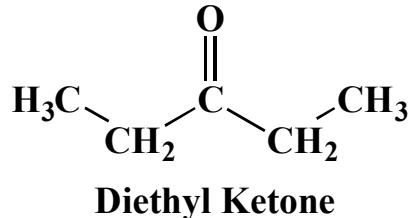
Recall the oxidation mechanism of *n*-propyl radicals



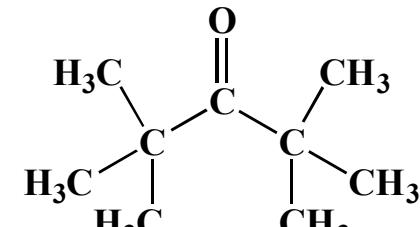
J. D. DeSain et al. *J. Phys. Chem. A* 2003, 107, (4415).

- 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

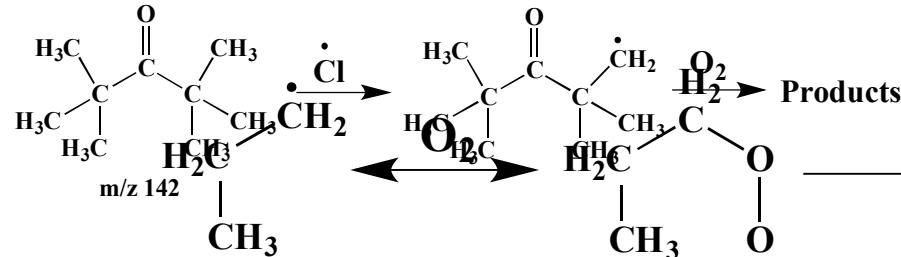


Diisopropyl Ketone

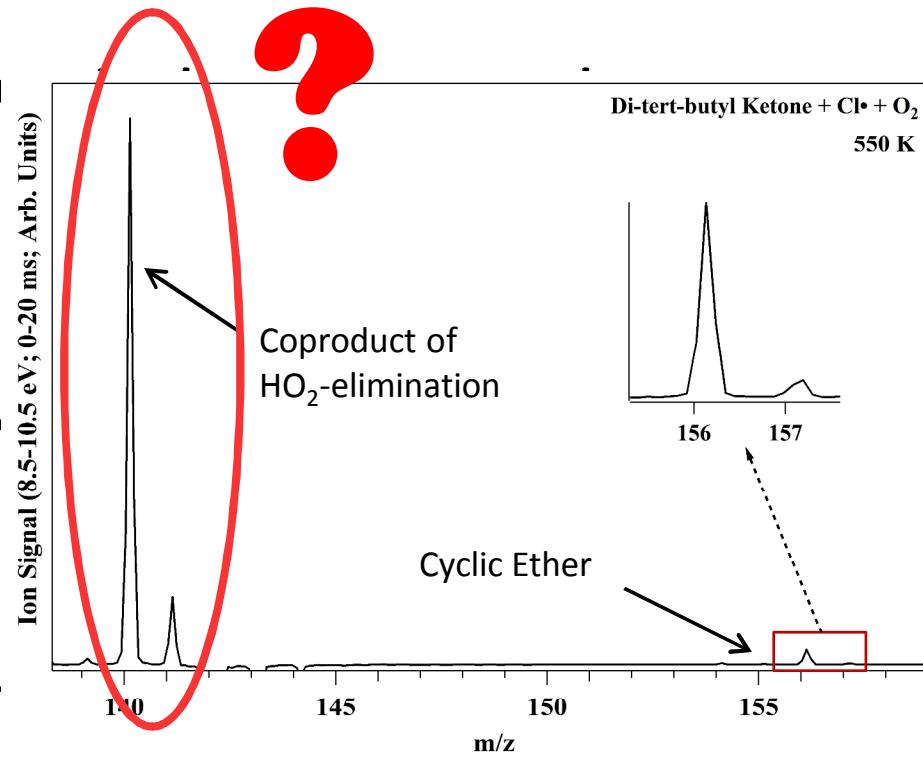


Di-tert-butyl Ketone

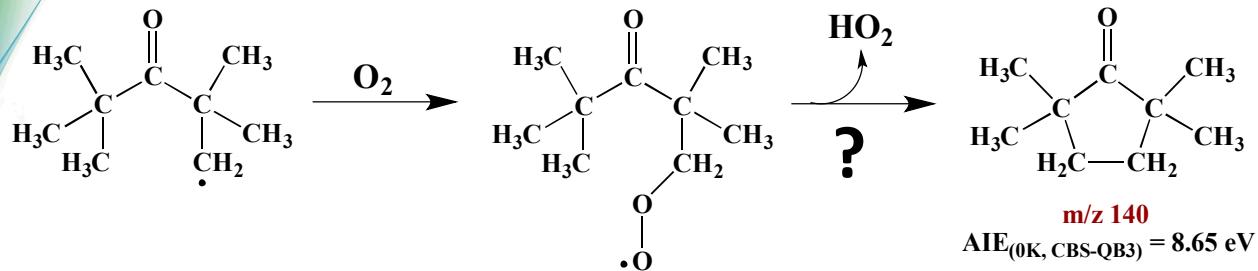
Di-tert-butyl ketone is the largest and most possible initial radical; no expected HO_2 -



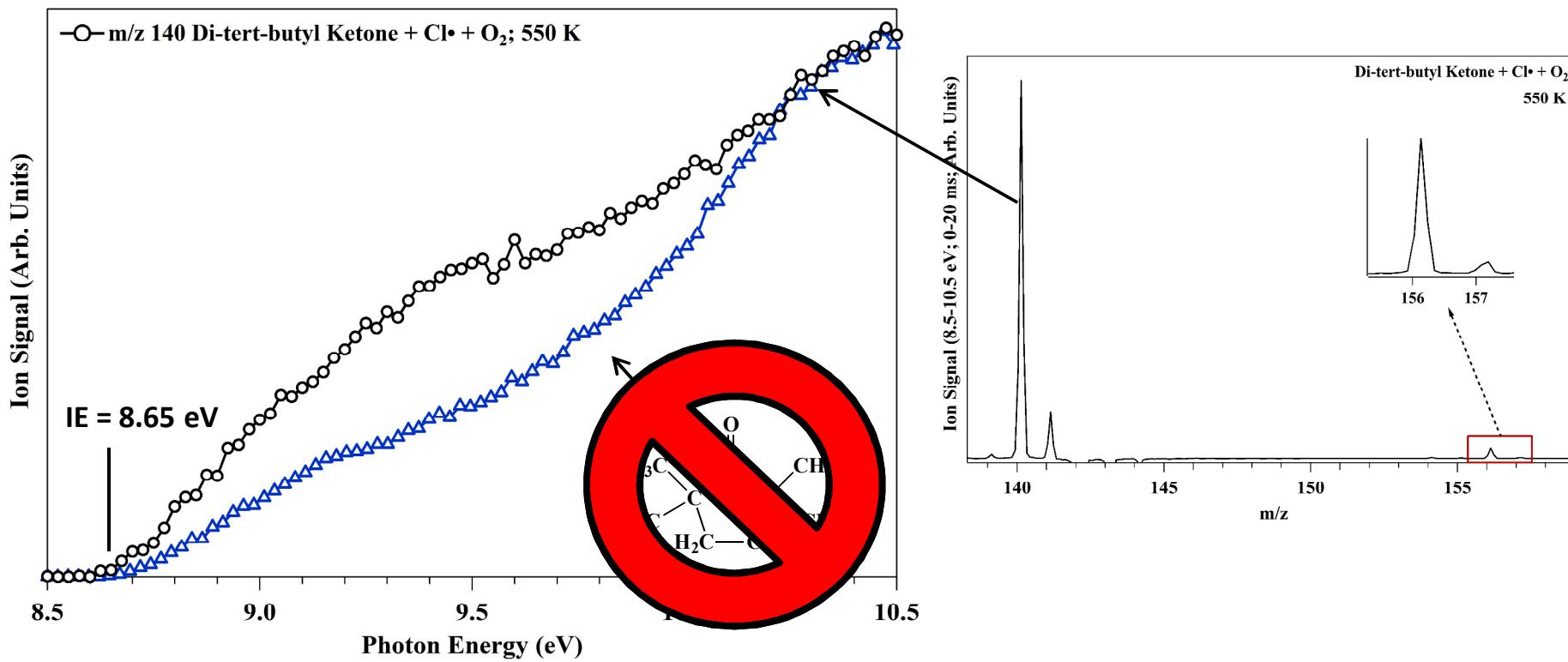
Structure requirement for HO_2 -elimination: each also bound to at least one H atom



Could this be Ring Closure with HO₂ Elimination?

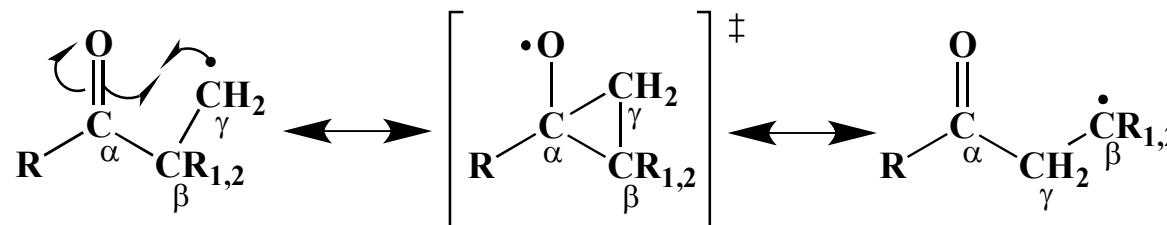


Calculated ionization energy matches experimental onset.



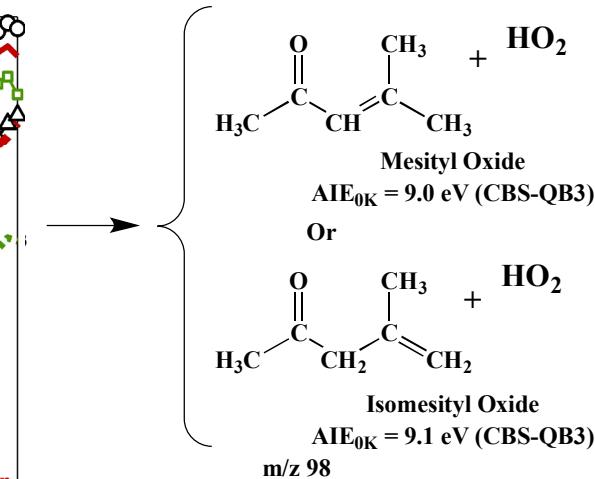
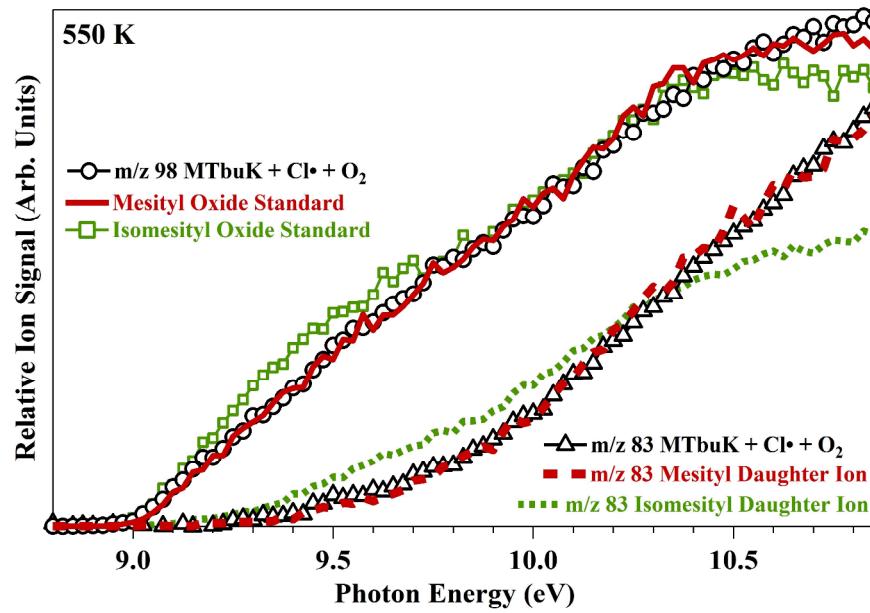
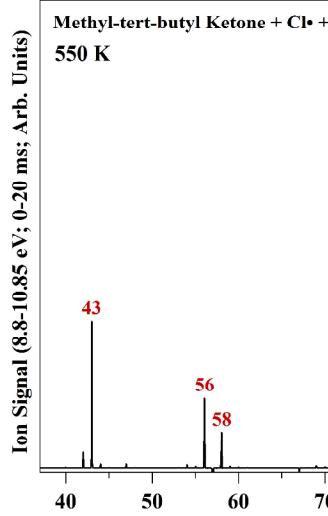
Instead, the initial radical isomerizes rapidly

Known in
solution-
phase
chemistry

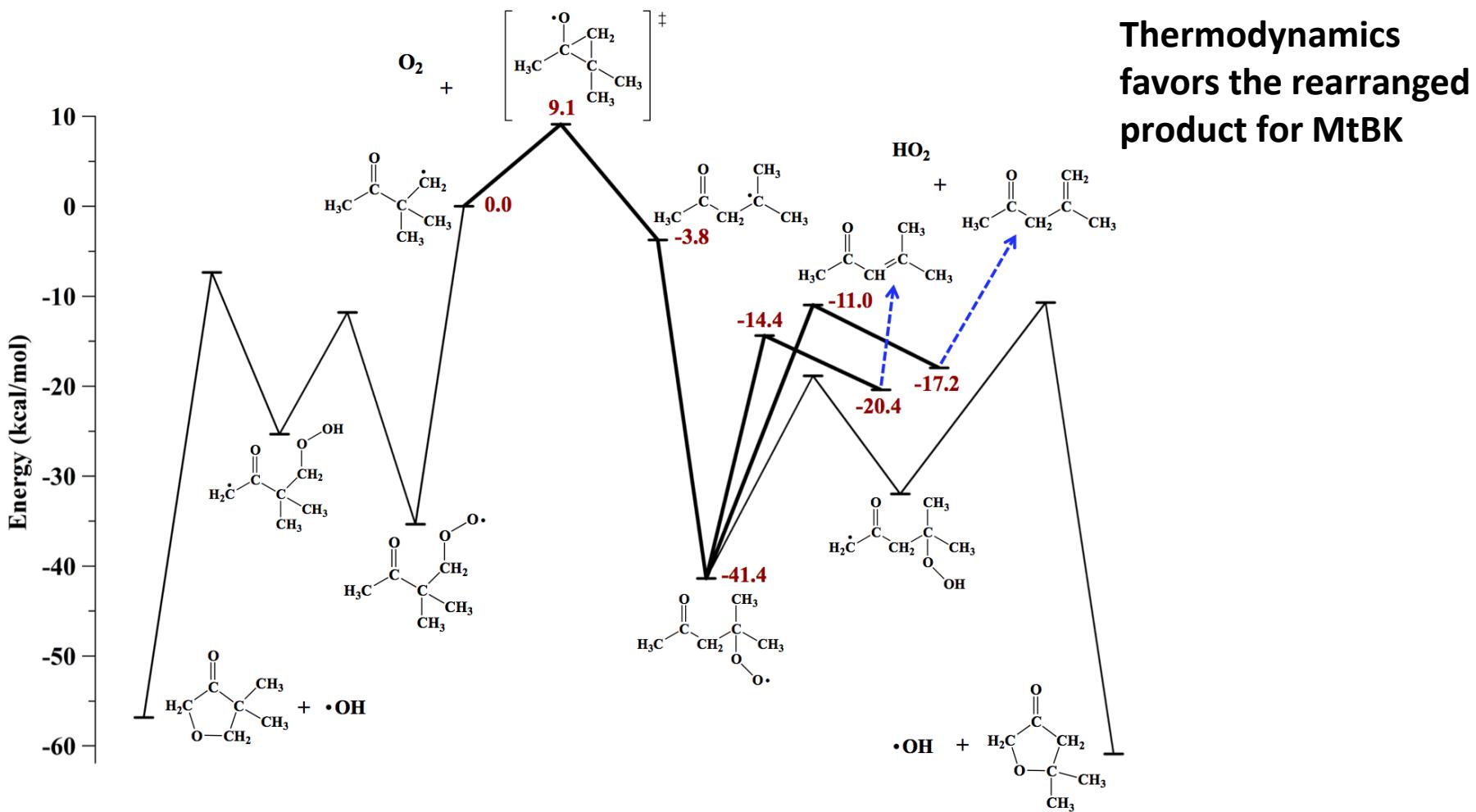


Karl et al. *J. Org. Chem.* **37**, 2834 (1972)

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



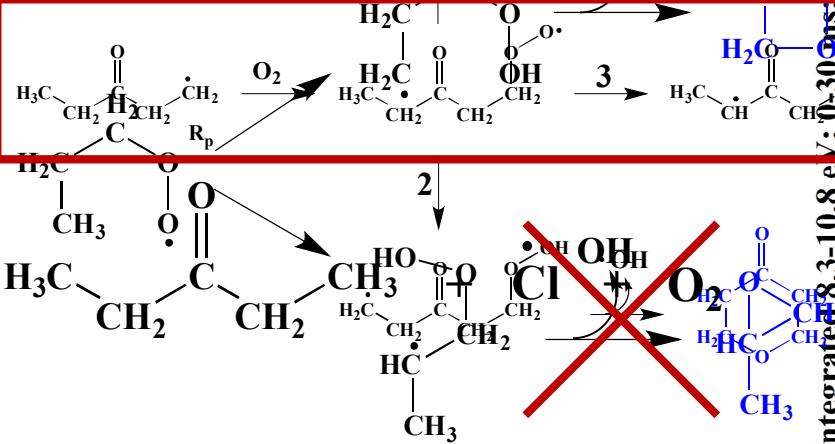
Rearrangement over a small barrier is rapid enough to compete with O_2 addition



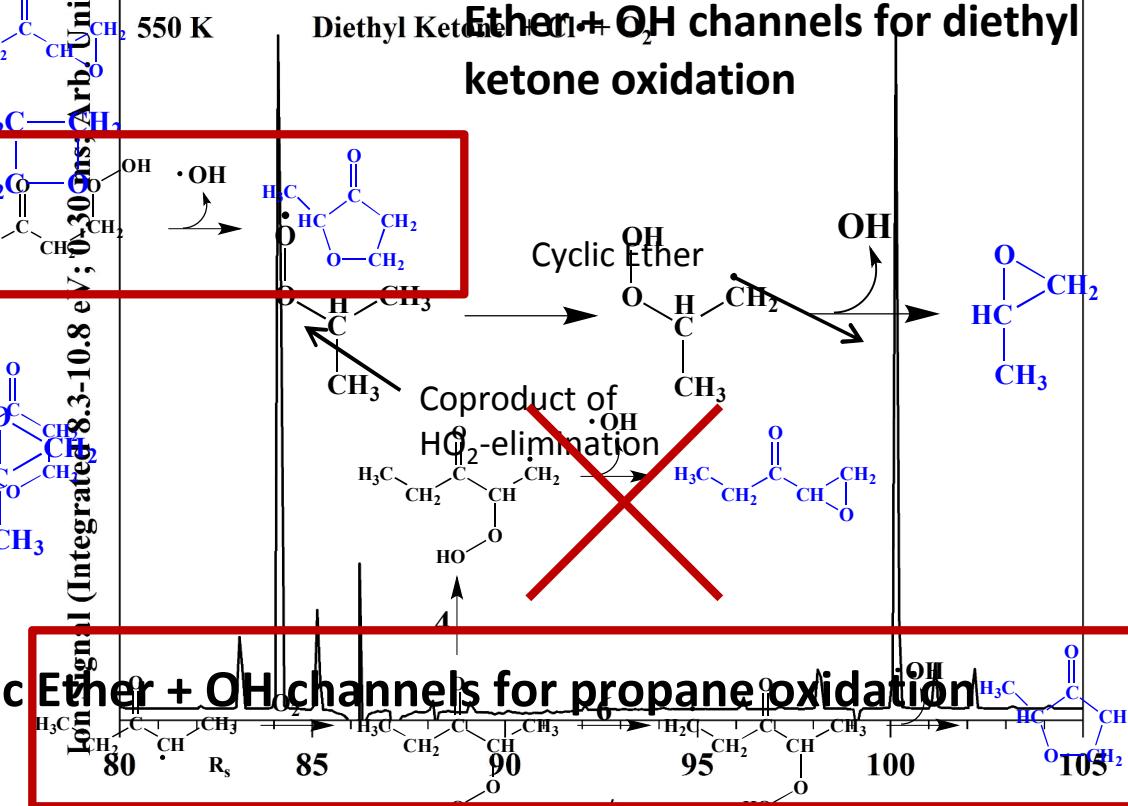
Isomerization changes amount of chain propagation and termination

Now Consider Cyclic Ether Formation Possibilities in Ketone Oxidation

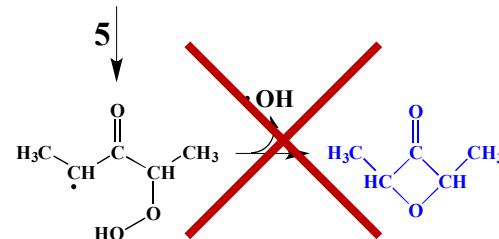
Recall propyl radical pathways



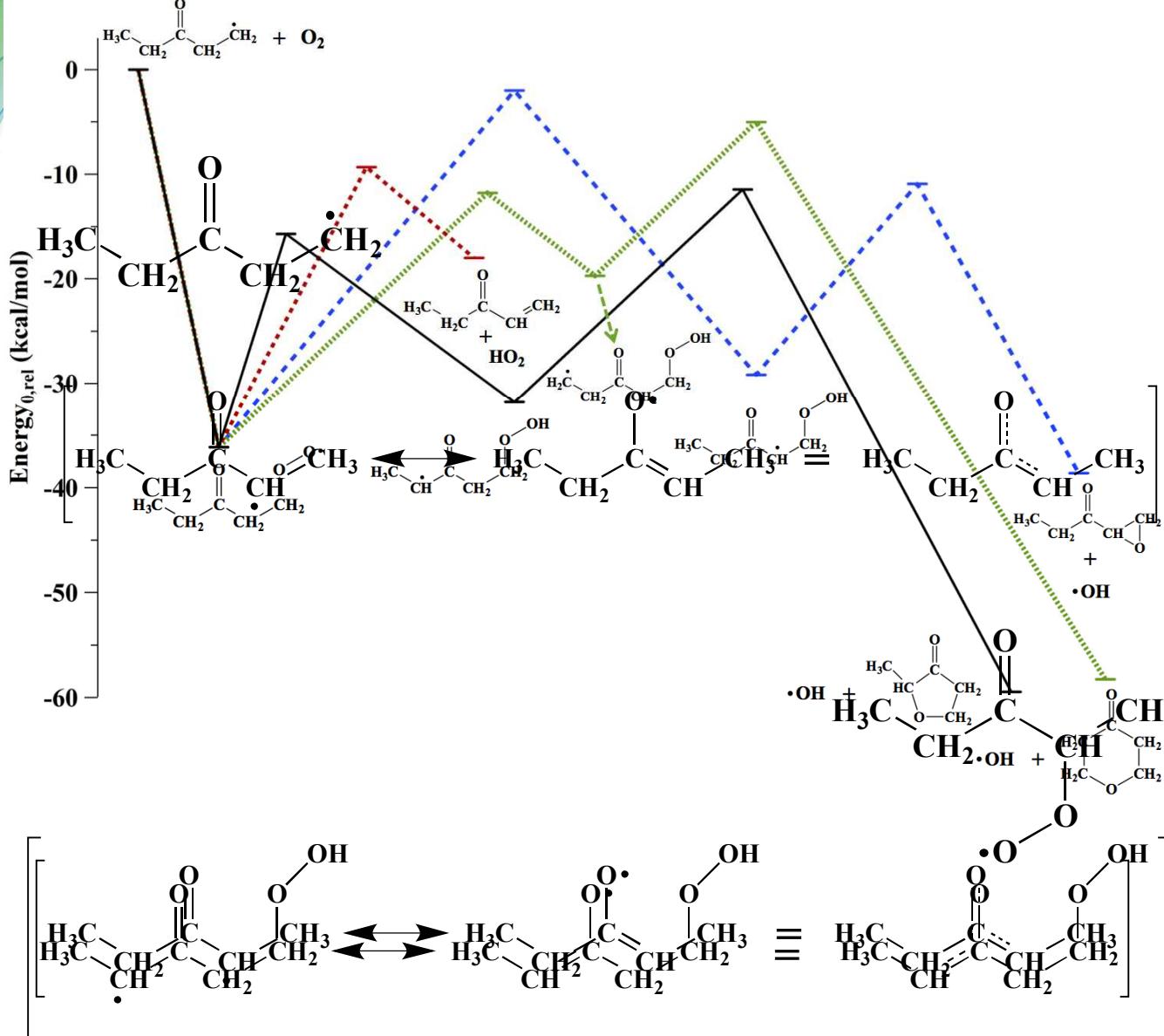
- 6 distinct $\text{RO}_2 \rightarrow \text{QOOH} \rightarrow \text{Cyclic Ether} + \text{OH}$ channels for diethyl ketone oxidation



- 3 distinct $\text{RO}_2 \rightarrow \text{QOOH} \rightarrow \text{Cyclic Ether} + \text{OH}$ channels for propane oxidation
- 2 possible cyclic ether products
 - 2 channels possible to produce 5-membered ring cyclic ether + OH

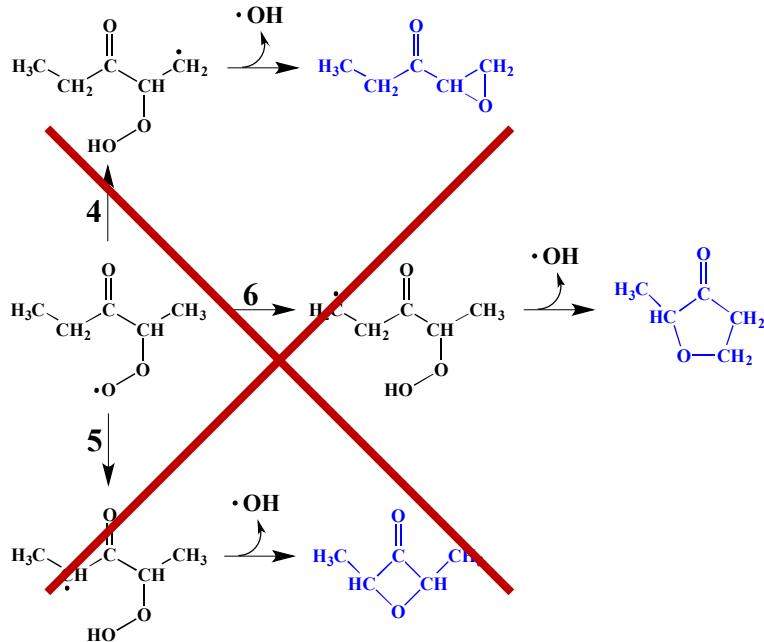
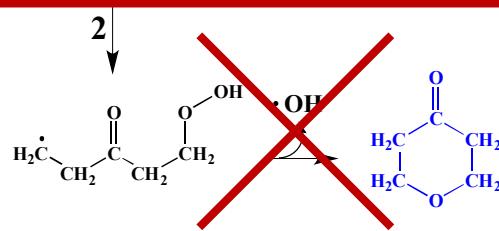
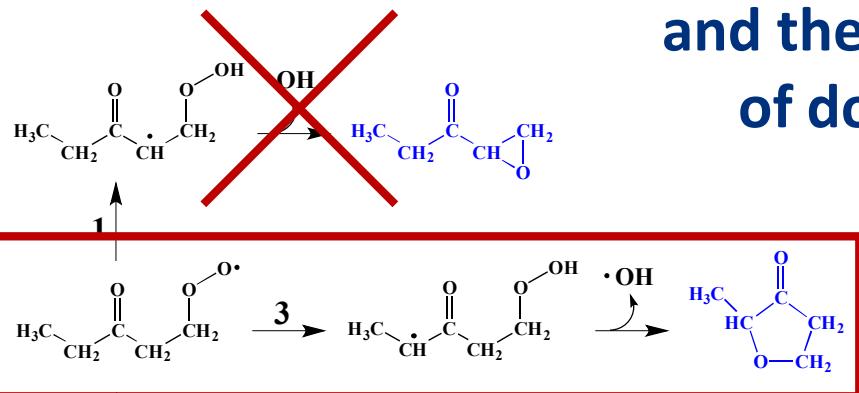


Thermodynamics Drives Cyclic Ether Selectivity in Diethyl Ketone Oxidation



- Response stabilization of primary radical
- RO_2 -well ~ 26 kcal/mol – shallow!
- $\text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2$ shifted to products
- Alkyls ether HO_2- platination and bond breaking pathways above entrance stabilized OOH

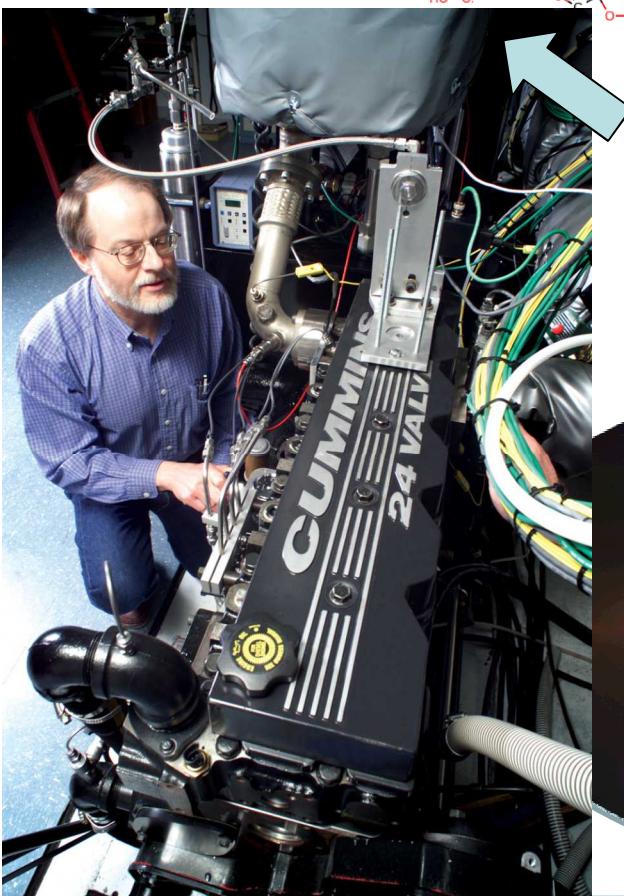
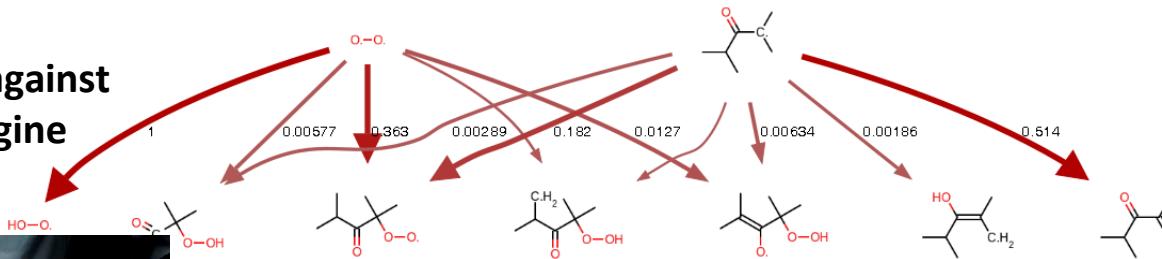
**Combination of experiment
and theory allows assignment
of dominant cyclic ether
channel**



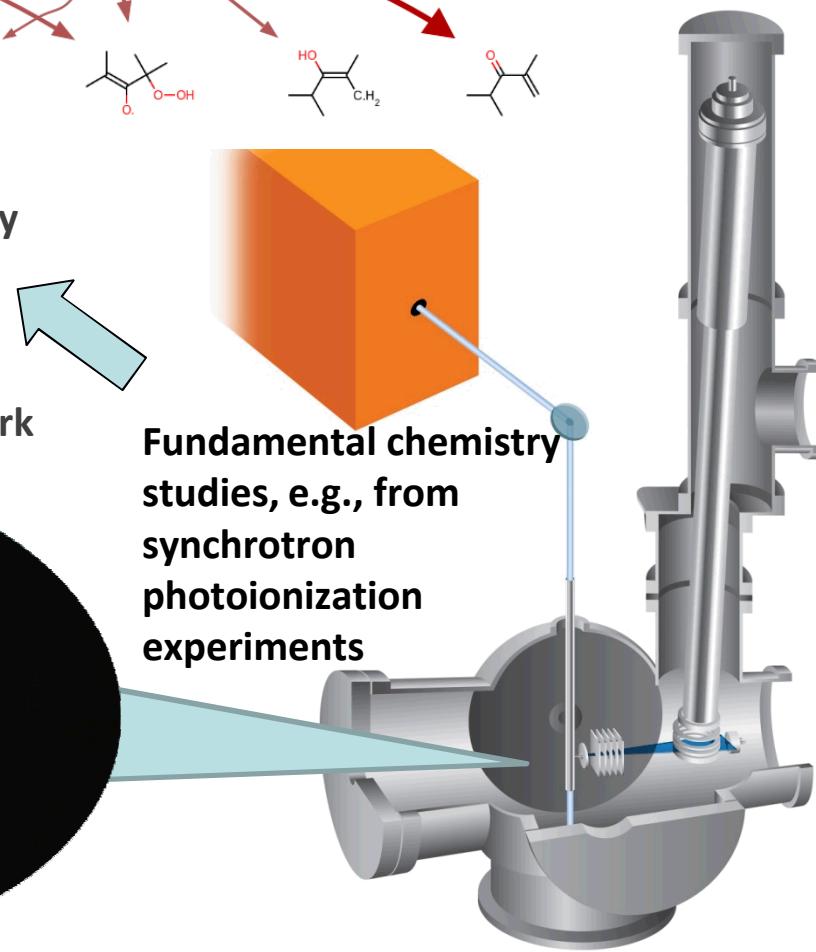
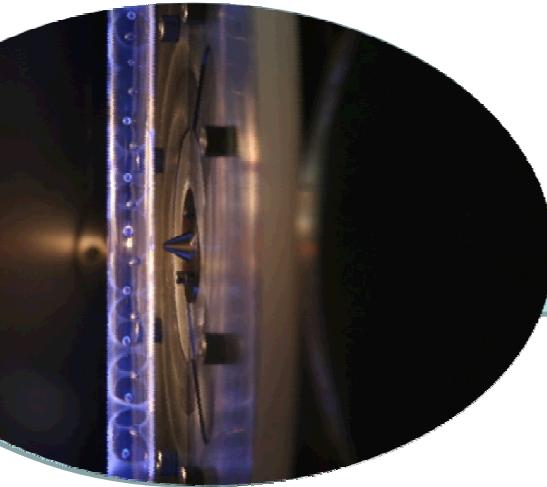
Reaction proceeds through the resonance stabilized QOOH

Combustion Chemistry Studies Build From Elementary Reactions to Engine Models

Which are validated against ignition delay and engine measurements

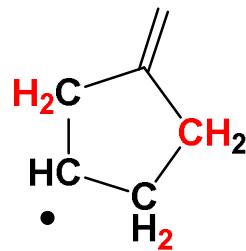
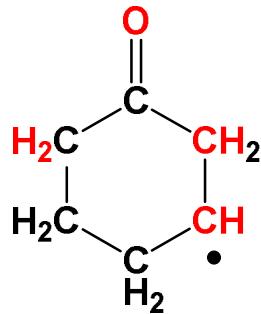


Inform new chemistry models, such as produced by MIT's Reaction Mechanism Generation framework



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?

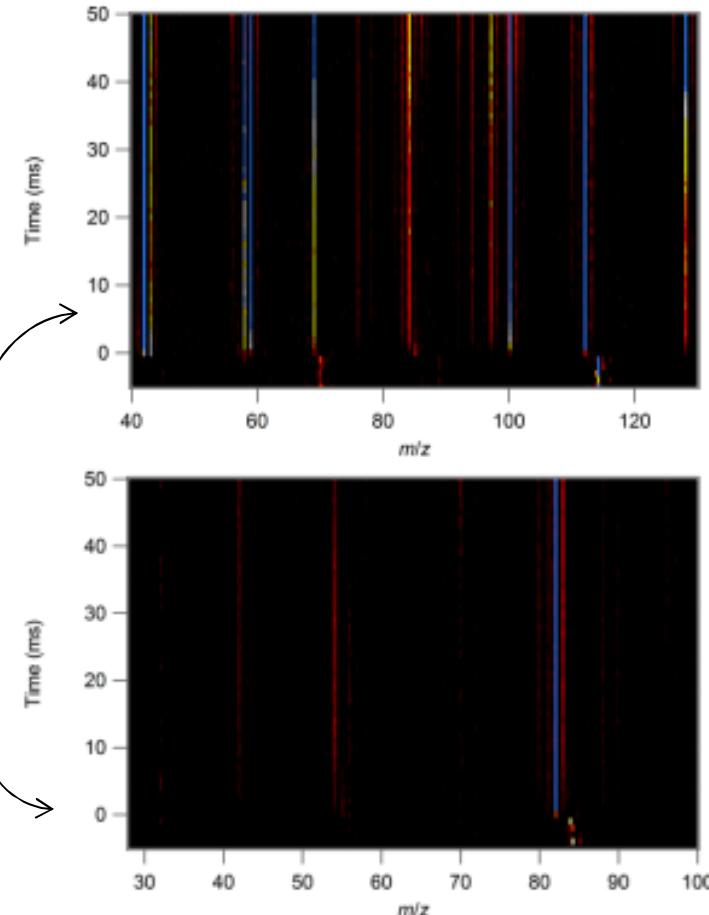


Di-isopropyl ketone: shows species associated with chain-propagating OH formation.

Expect some intermediate temperature heat release (ITHR) in engine

Cyclopentanone: almost exclusively cyclopentenone formation, associated with chain-terminating HO₂ formation.

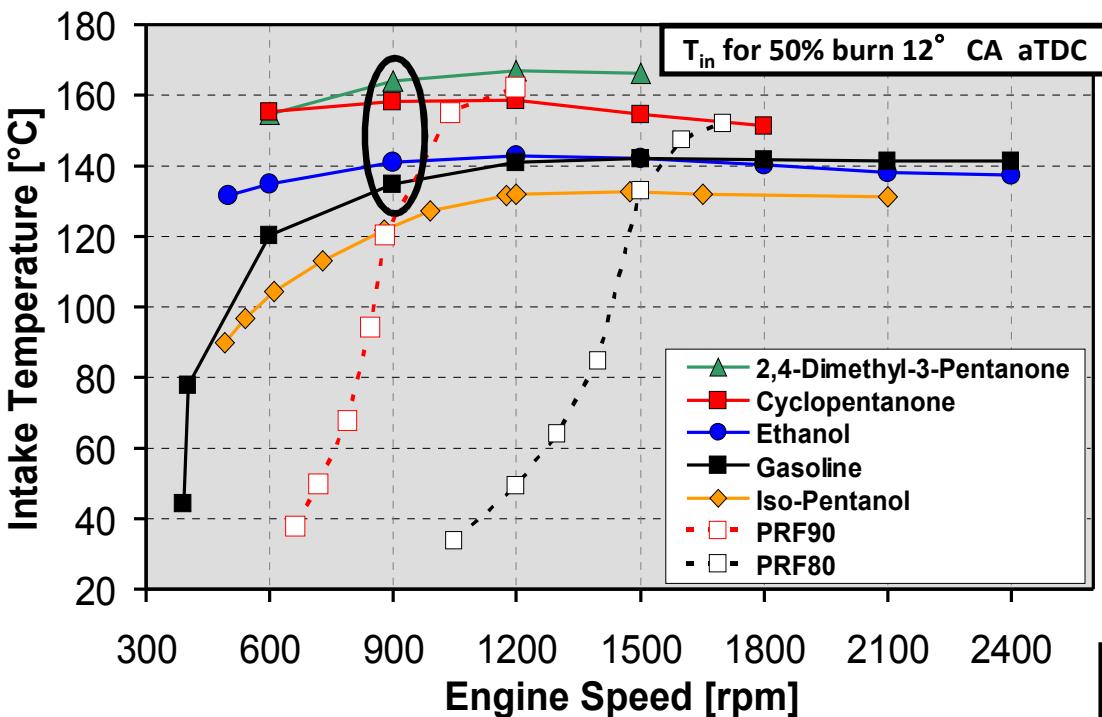
Expect very little ITHR in engine.



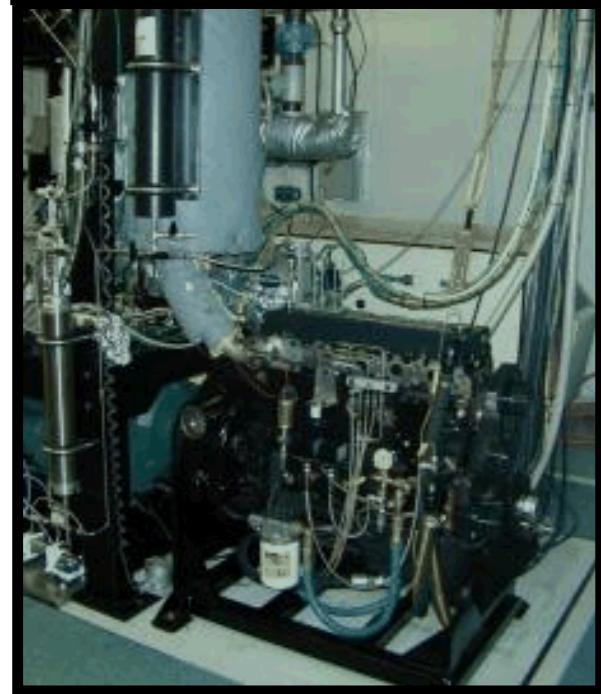
Engine Tests on Ketone Fuels (John Dec)

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.

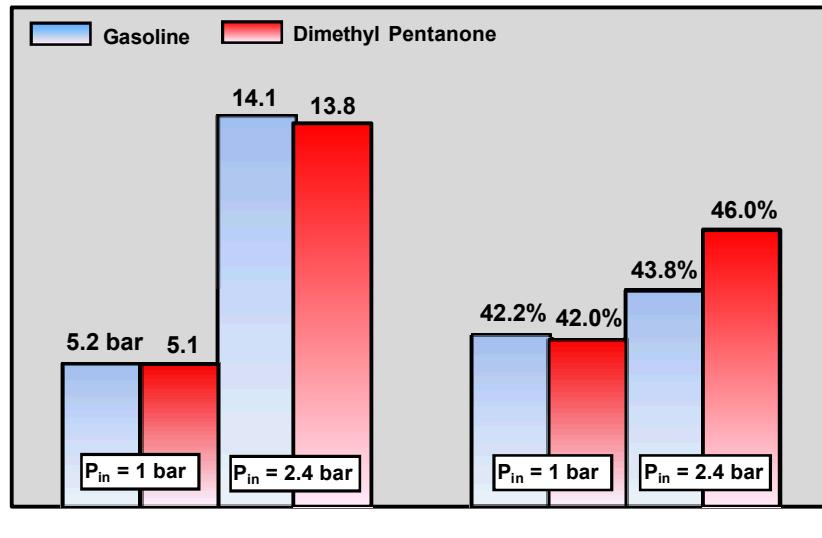
Ketones could raise octane no. of gasoline.

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

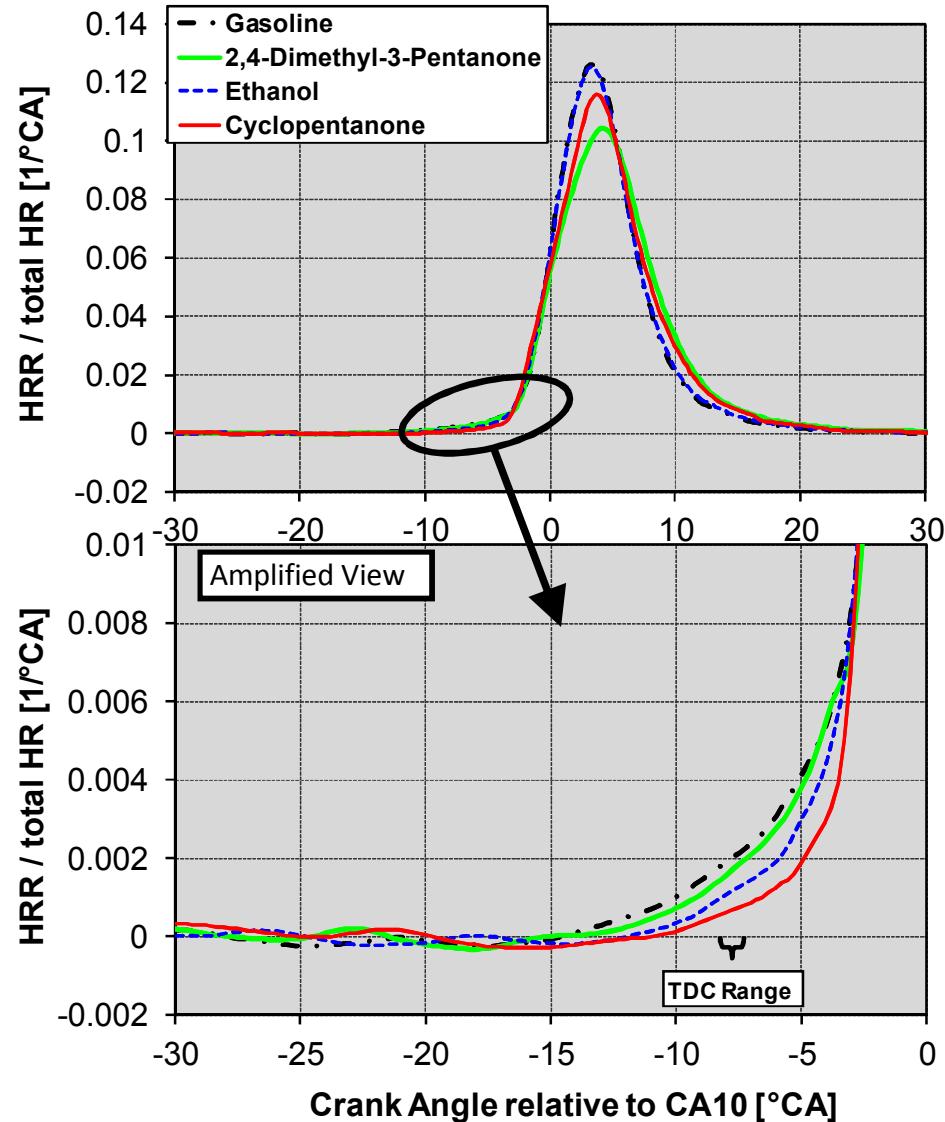
Pre-Ignition reactions are key to performance differences in fuels.

Low-temp. heat release (LTHR), 760 K – 880 K.

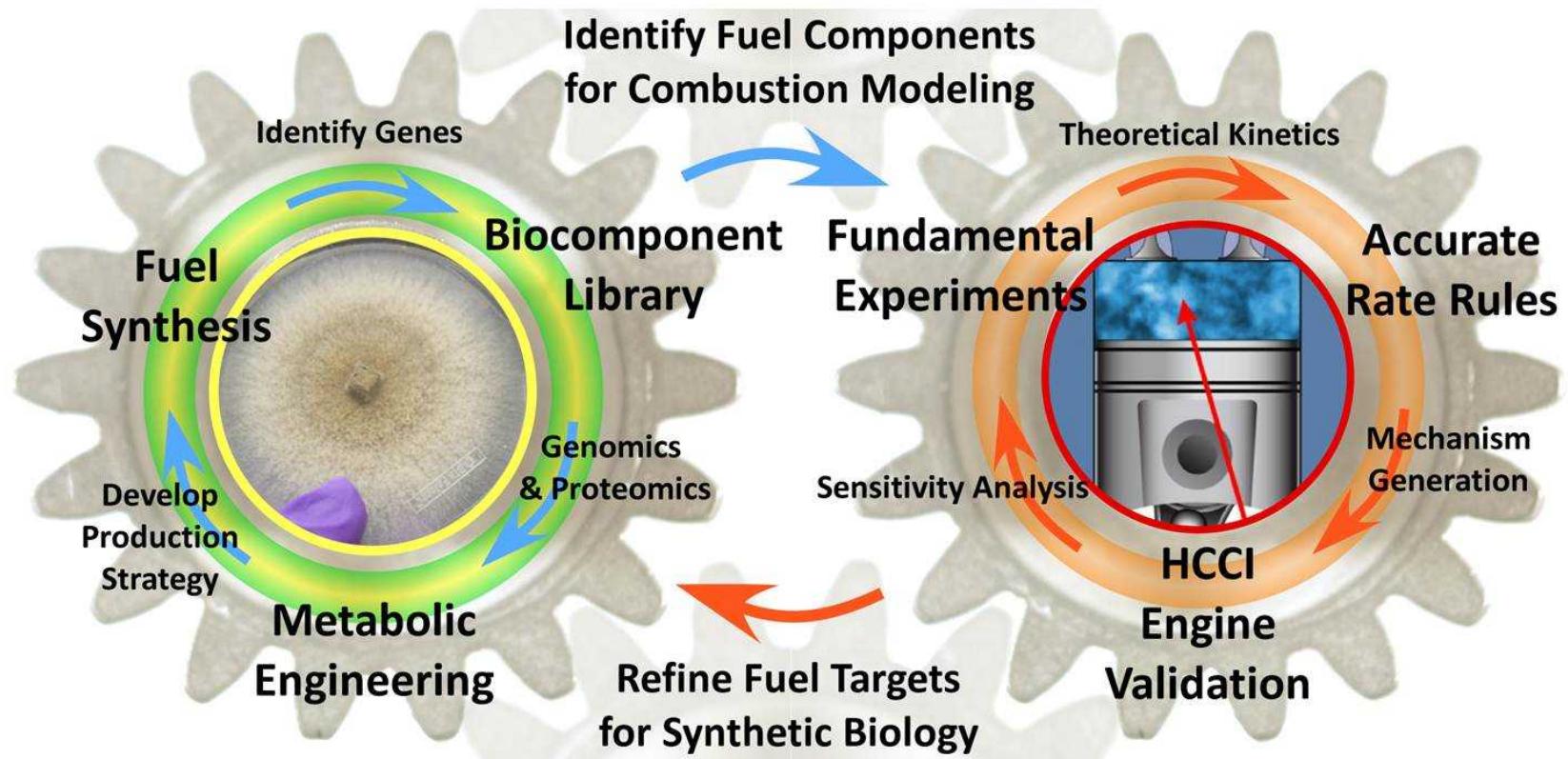
Intermediate-temp. heat release (ITHR), 950 K – 1050 K.



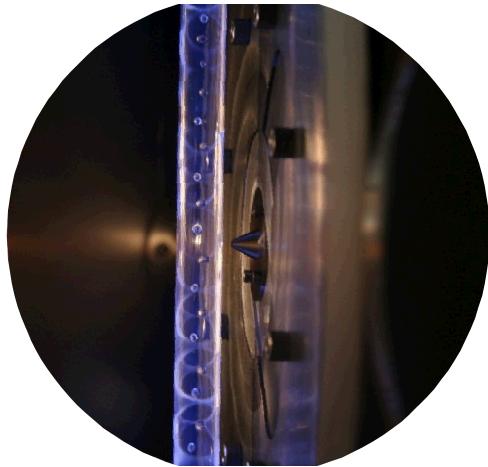
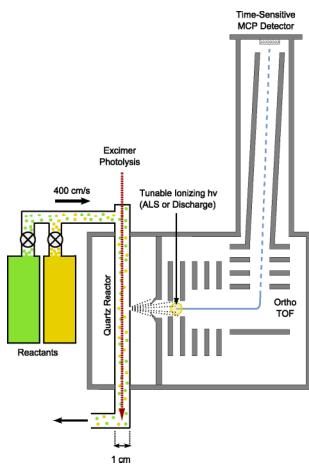
In fact, DIPK shows higher efficiency than gasoline at high load



What is next?



Summary

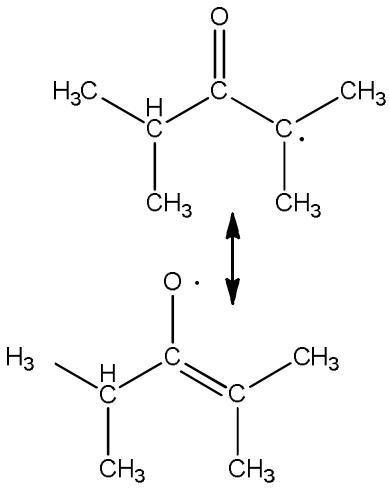
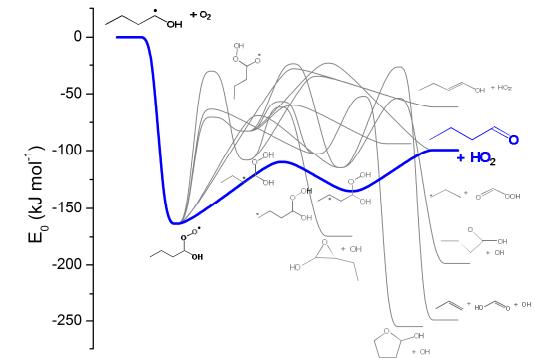


Combination of QM/ME and MPIMS studies on the low-temperature oxidation is a powerful means for understanding mechanisms

0

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





Acknowledgements

Subith S. Vasu (now at U. Central Florida), Yi Yang, John Dec,
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National
Laboratories**

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(Sandia Biomass Conversion Technologies Department)



Bill Green, Josh Allen, Connie Gao, Shamel Merchant (MIT)

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