COMBUSTION RESEARCH FACILITY

SAND2015-10553C

Chemistry of Reactive Intermediates in Combustion and Tropospheric Oxidation Systems

Reaction Dynamics Symposium commemorating IAMS 20th Anniversary
November 10, 2015

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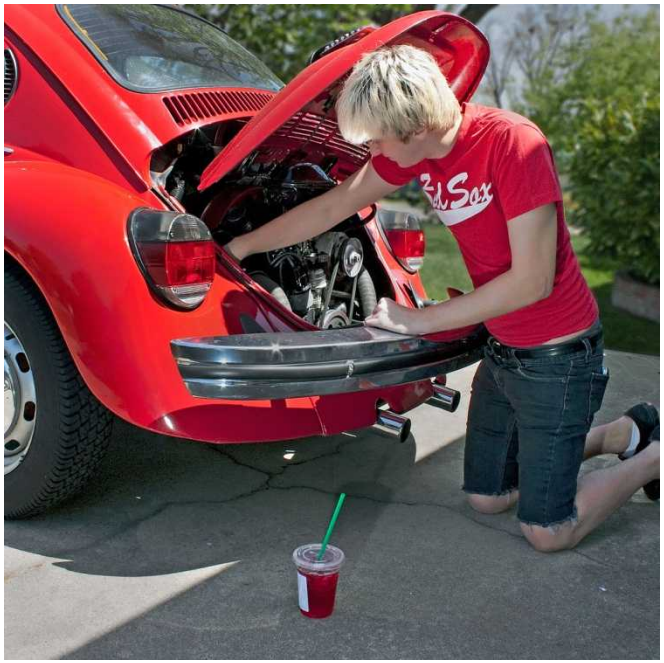
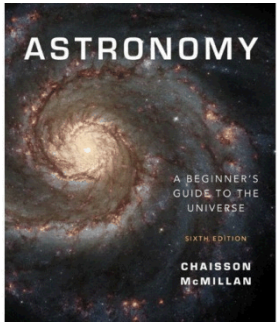
Livermore, CA 94551

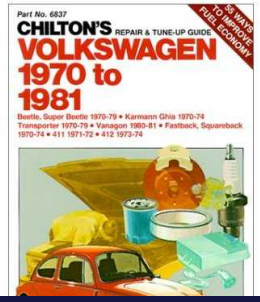
Why do people do chemical kinetic modeling?

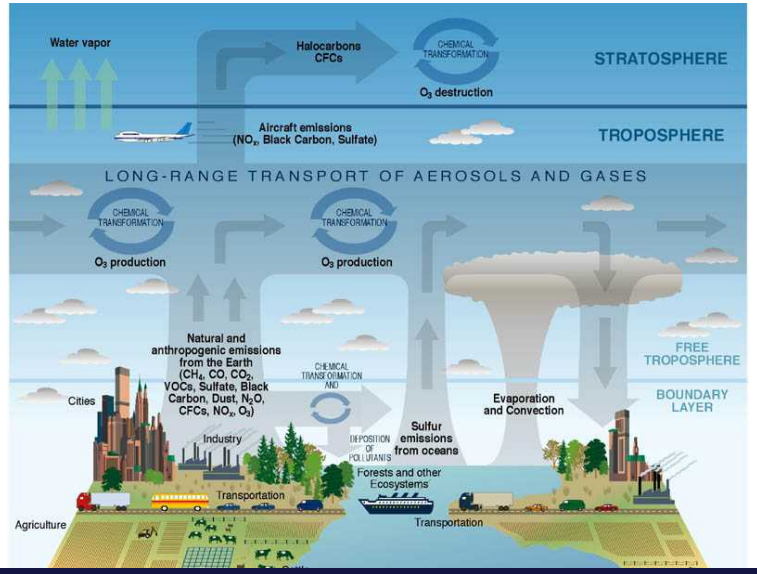


Robert Couse-Baker



Mbz1 Wikimedia commons



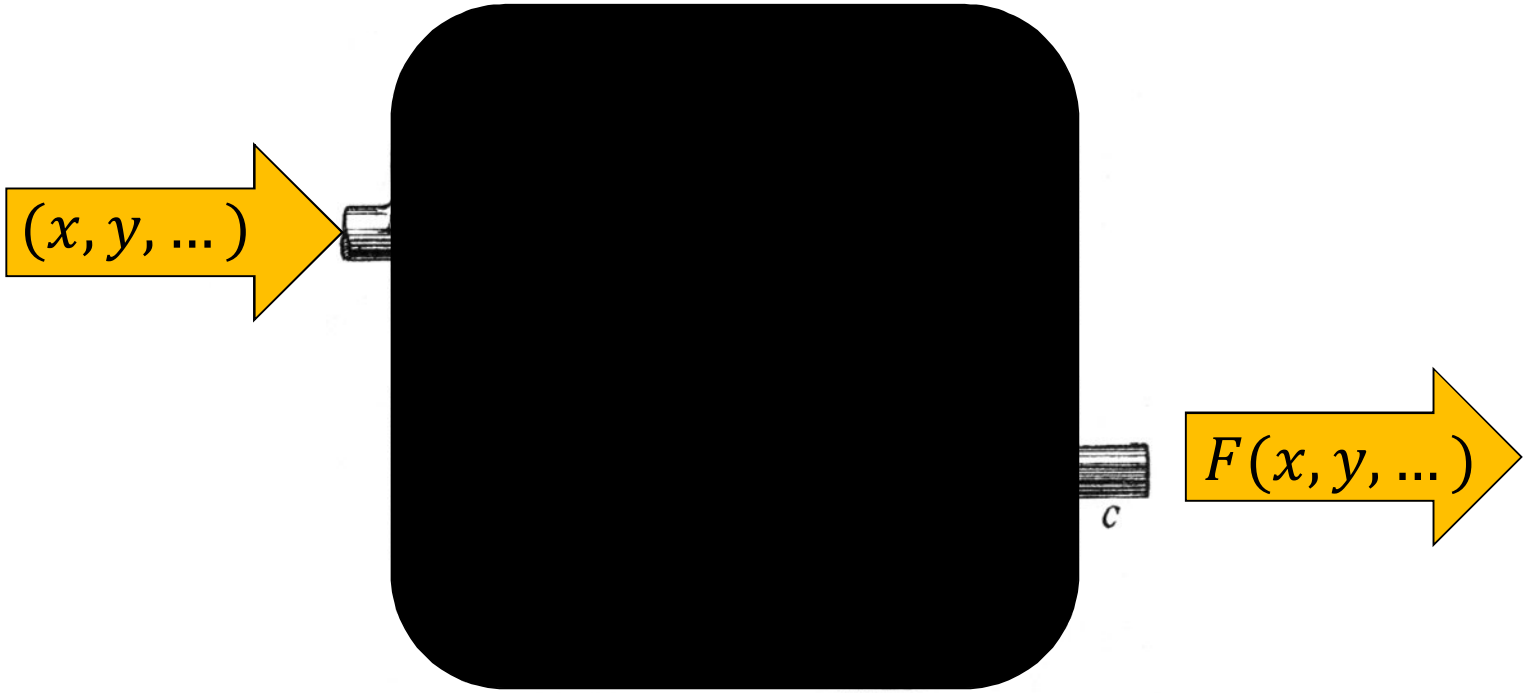


ATE CHANGE SCIENCE PROGRAM OFFICE

?

Predict what will happen as the boundary conditions are changed

What will make a model *predictive*?

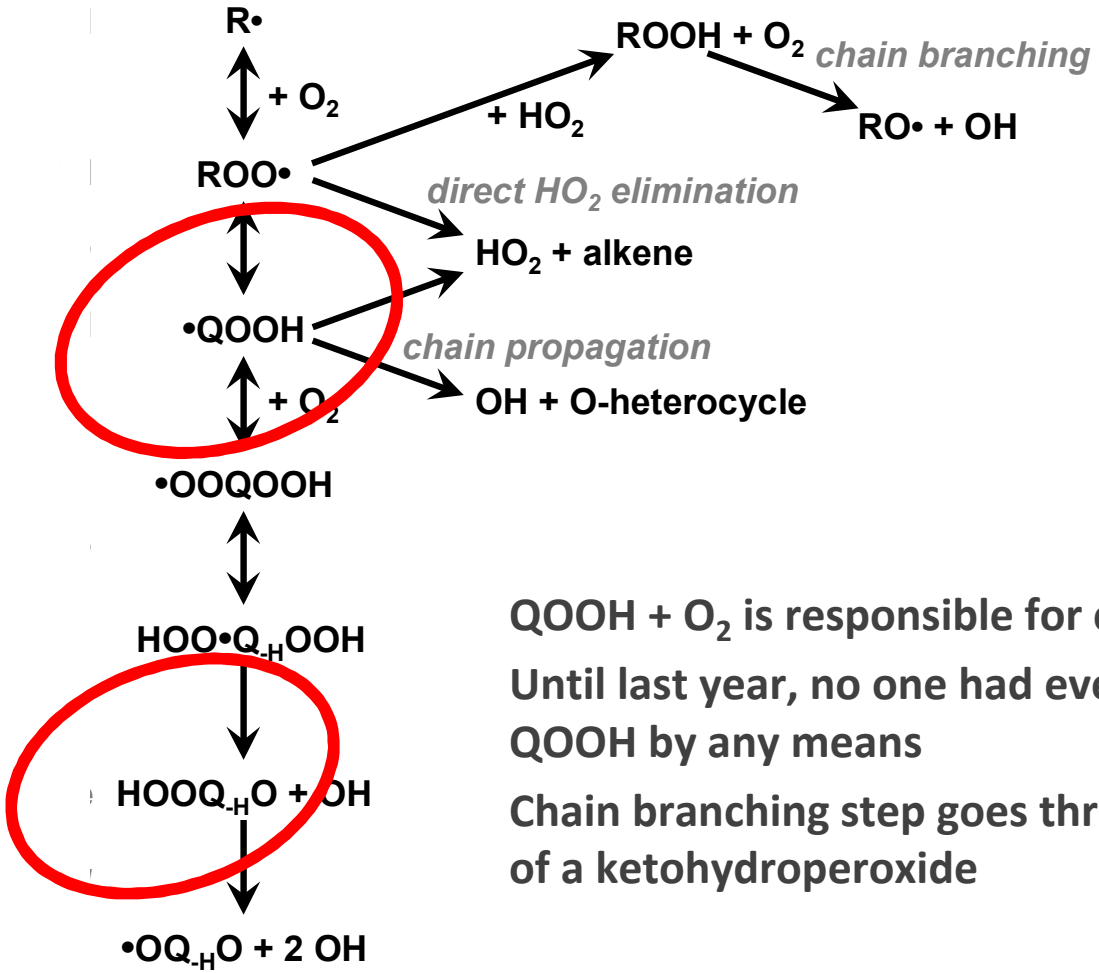


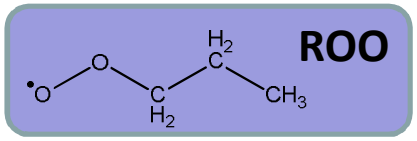
6. Wechselgetriebe für vier Geschwindigkeiten und Rücklauf:

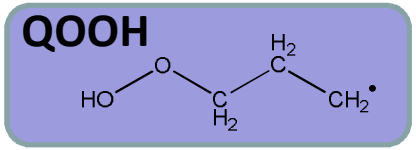
M Angriff der Motorwelle, *C* Angriff der Cardanwelle; Geschwindigkeitsräder *I*, *II*, *III*, *IV*, durch Verschiebung mit *1*, *2*, *3*, *4* in Eingriff gebracht; Rücklaufrad *R*, durch Linksschiebung mit *IV* und *4* in Eingriff gebracht.

Need to understand the *intermediate* steps

Kinetic Models for Oxidation Chemistry Require Knowing Reactions of "Intermediates"







$QOOH + O_2$ is responsible for chain branching

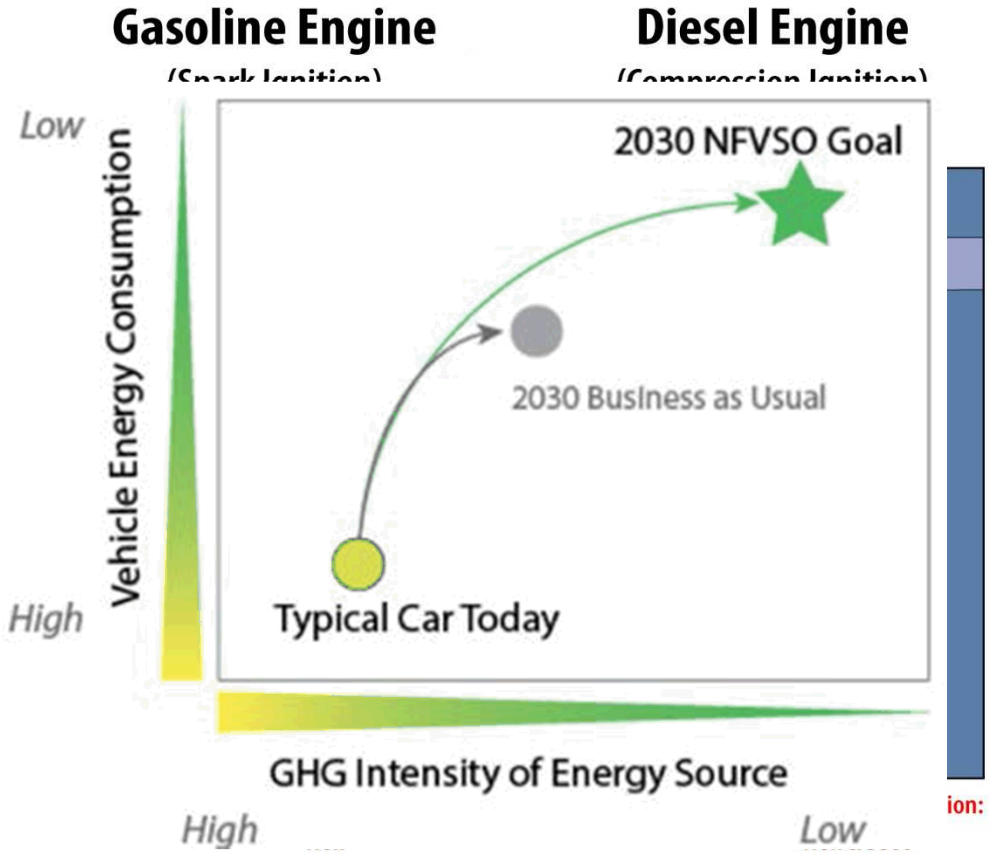
Until last year, no one had ever directly seen a QOOH by any means

Chain branching step goes through dissociation of a ketohydroperoxide

All these steps depend on molecular structure

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

Advanced Engines Rely on Autoignition Chemistry to an Unprecedented Degree

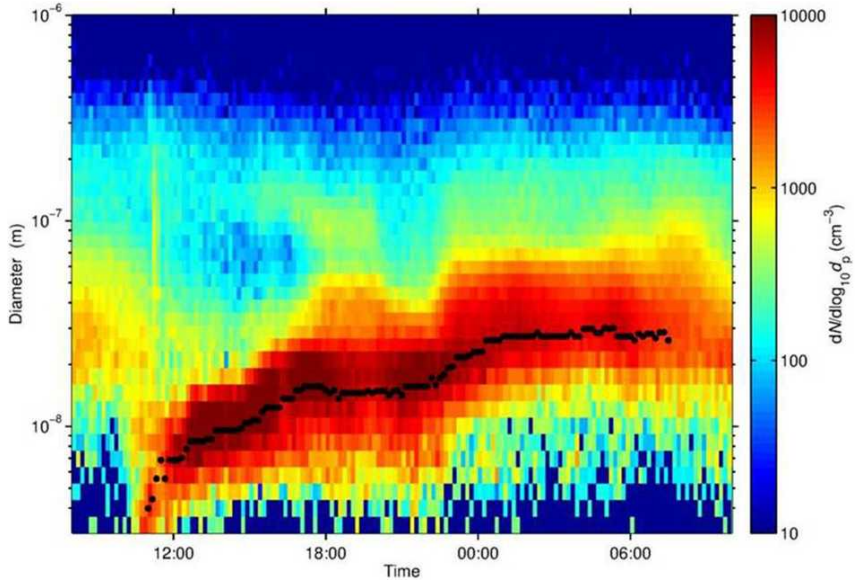


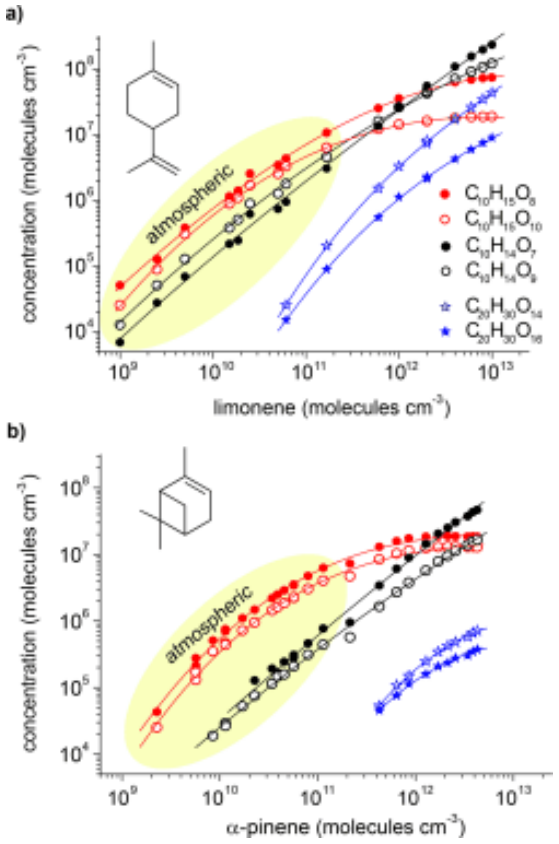
DOE initiative to link alternative fuel and advanced engine developments

Fuel chemistry is important – but fuel stream is already changing!
New fuels = biofuels? can be disruptive, or they can be enabling

Tropospheric Autoxidation Forms Highly Oxygenated Molecules

M. Ehn et al., *Nature* 506, 476–479 (2014)





- **Forest emission of VOCs can lead to secondary aerosol formation** through condensation of low-volatility oxygenated species
- **QOOH chemistry is involved** Vereecken et al., *PCCP* **9**, 5241-5248 (2007) showed reaction pathway for α-pinene; recently others expanded to, e.g., ozonolysis of other hydrocarbons.

T. Jokinen et al., *Angew. Chem. Int. Ed.* **53,** 14596-14600 (2014)

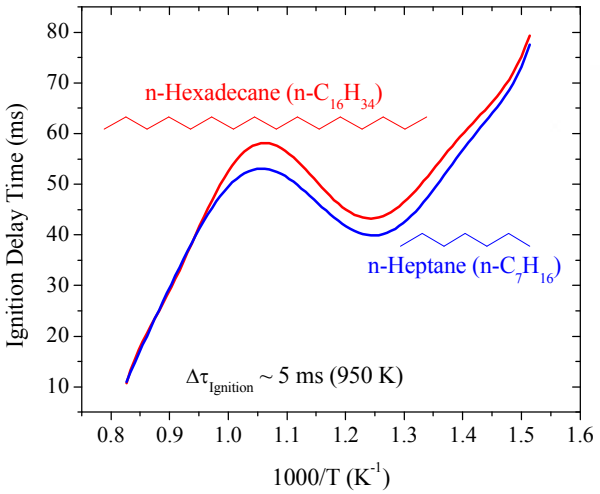
So what can we do?

First approach – Global oxidation experiments (e.g., ozonolysis or ignition delay)

$(x, y, \ldots)$

Will that ever really tell us about what's in this box??

$F(x, y, \ldots)$



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

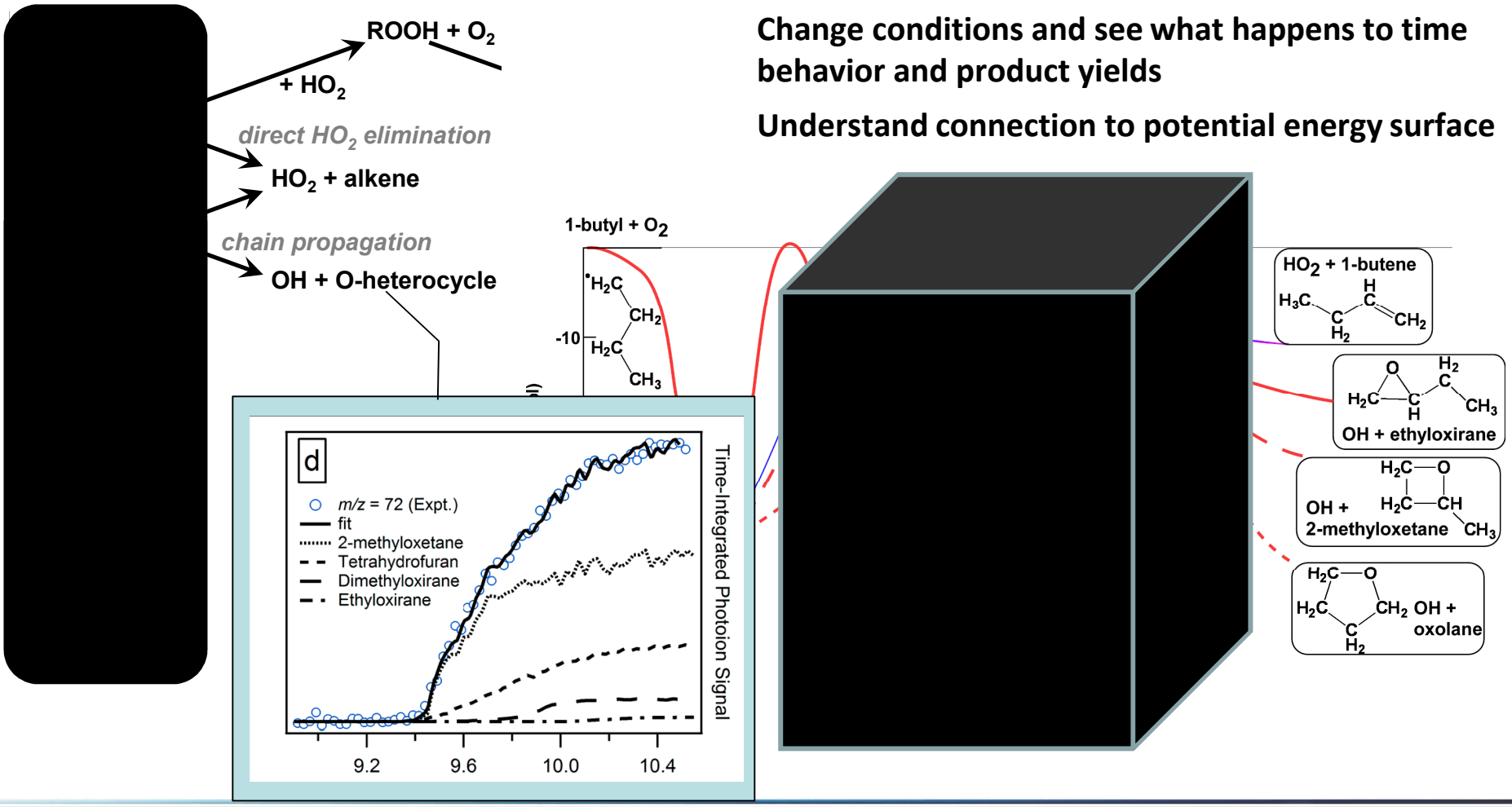
Probes overall process: modeling and theory fill in

So what can we do?
Take one step at a time?

Measure products from pulsed photolytically initiated R + O_2 reactions

Change conditions and see what happens to time behavior and product yields

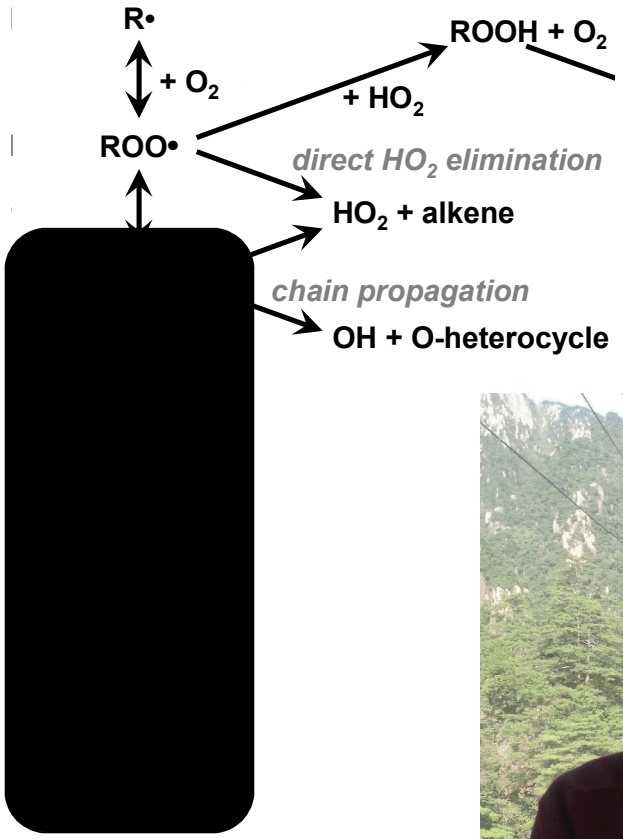
Understand connection to potential energy surface



So what can we do?
Take one step at a time?

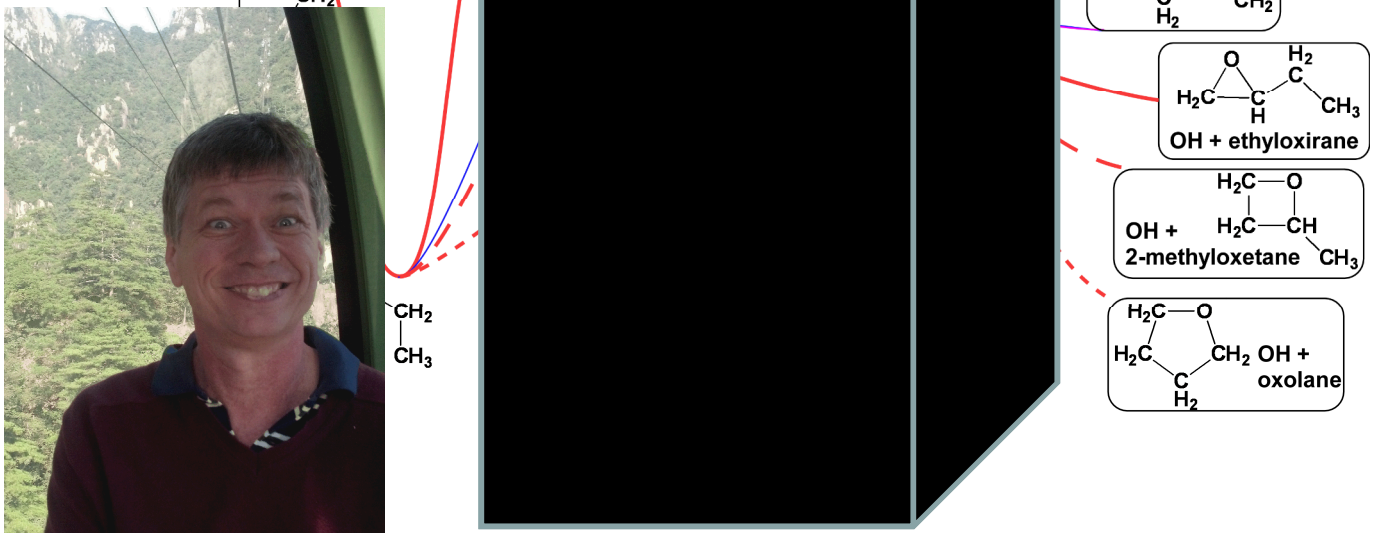
Theory can help open the black box
-- if experiments are detailed enough

Measure products from pulsed photolytically initiated R + O_2 reactions



Change conditions and see what happens to time behavior and product yields

How do we connect to the underlying potential?

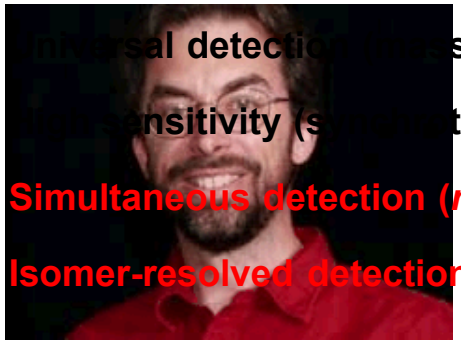


Stephen Klippenstein

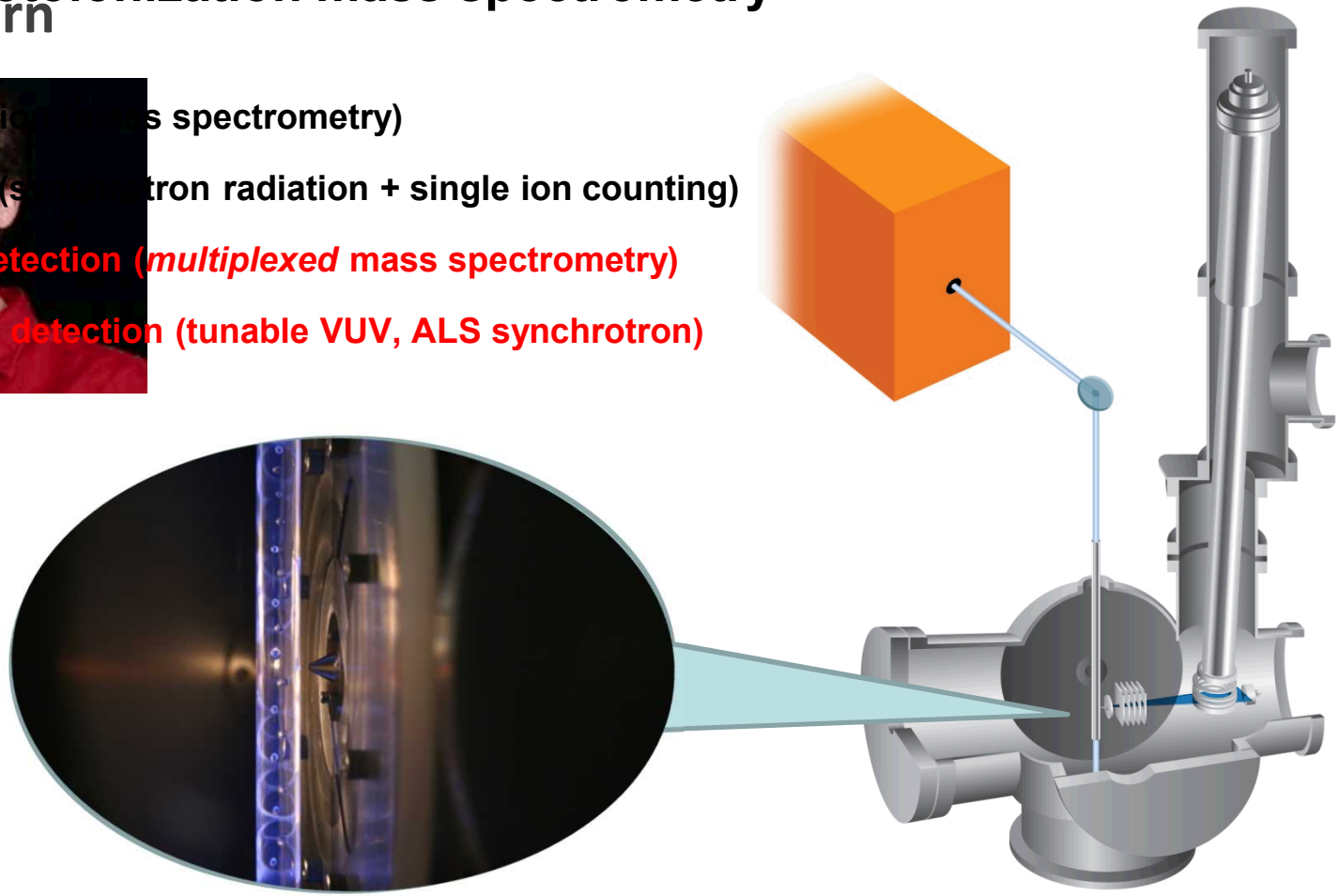
Need as much detail as we can get – really would like to measure all the species all the time

Multiplexed photoionization mass spectrometry (MPIMS)

David Osborn



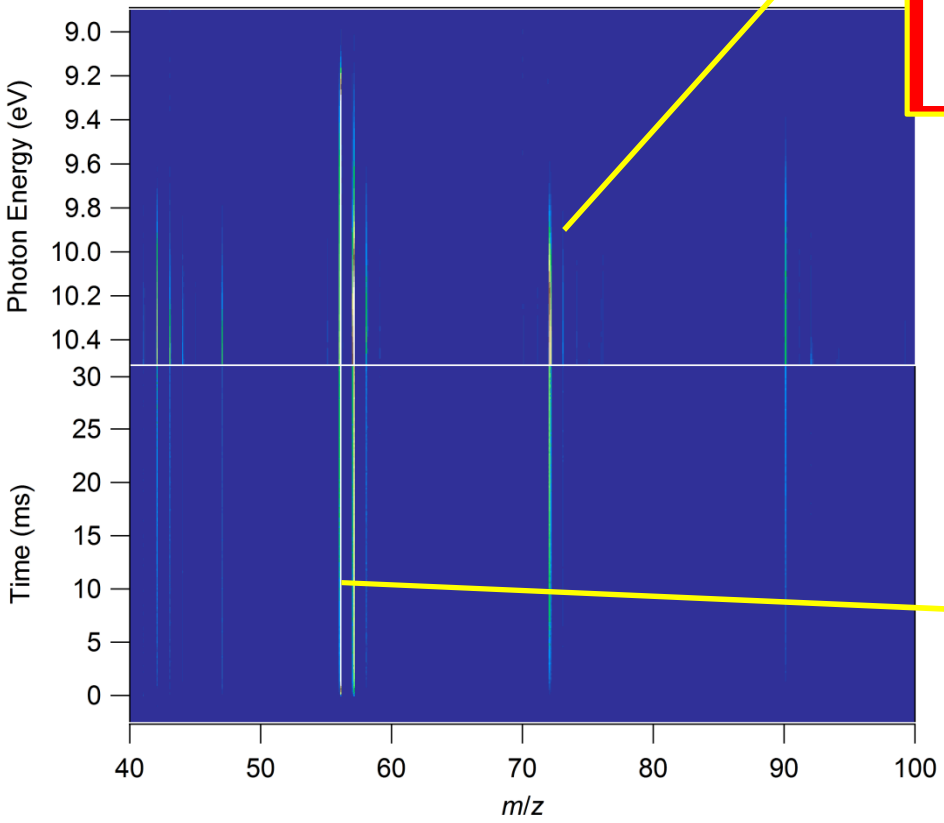
- Universal detection (mass spectrometry)
- High sensitivity (synchrotron radiation + single ion counting)
- Simultaneous detection (*multiplexed* mass spectrometry)
- Isomer-resolved detection (tunable VUV, ALS synchrotron)

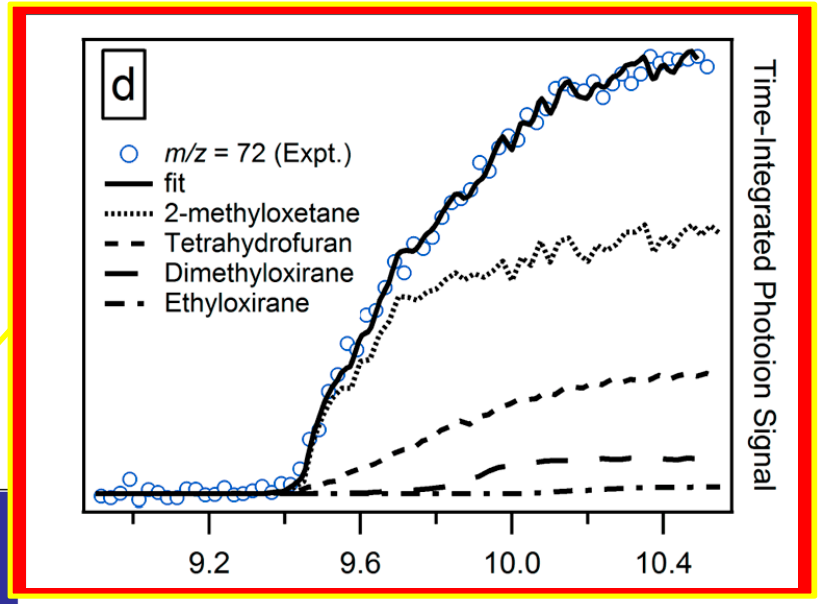


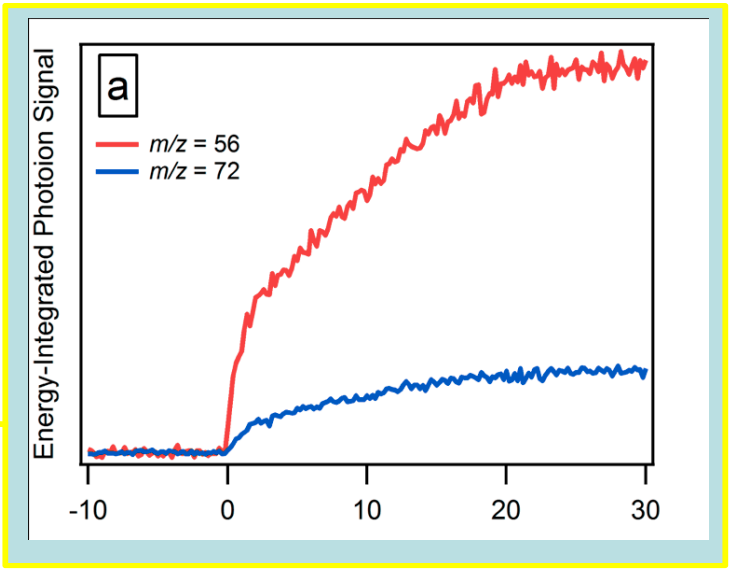
Cl-initiated oxidation

Time behavior of product formation – prompt and delayed

Photoionization spectra identify product isomers

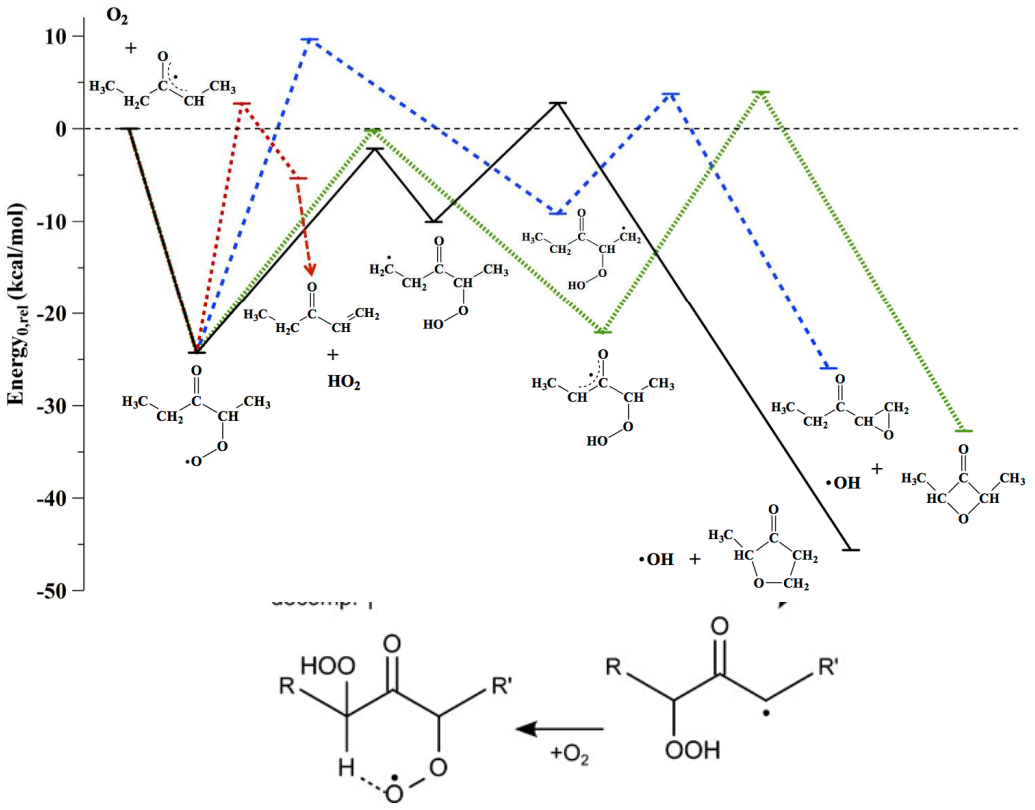






Isomeric product branching can show how molecular structure affects QOOH

- Diethyl ketone prototype for tropospheric autoxidation
- Ketone oxidation has possibility of vinoxylic resonance stabilization
- Resonance-stabilized radicals less reactive with O_2



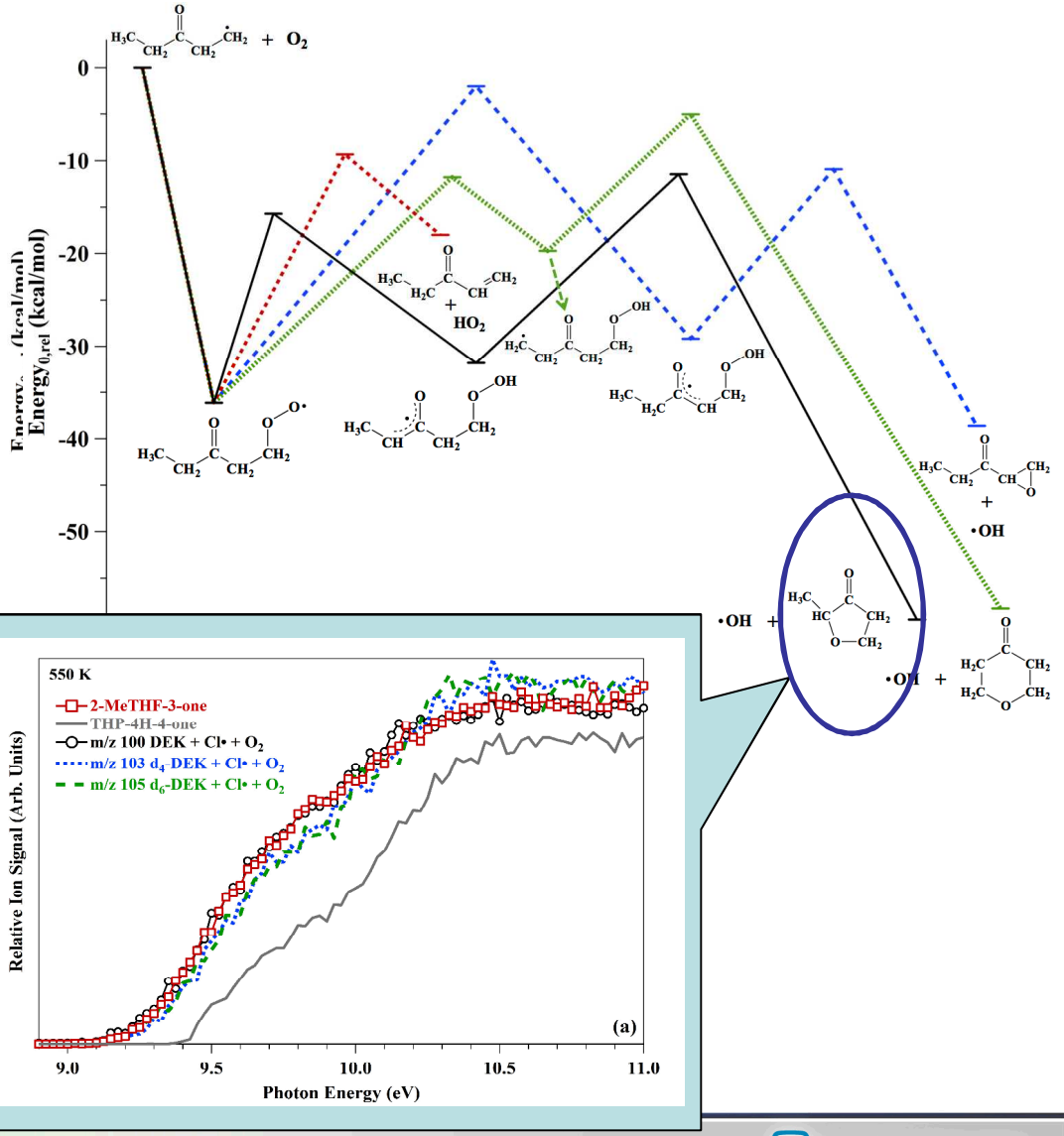
(Crounse et al. *J. Phys. Chem. Lett.* 4, 3513-3520 (2013))

Adam Scheer

Isomeric product branching can show how molecular structure affects QOOH

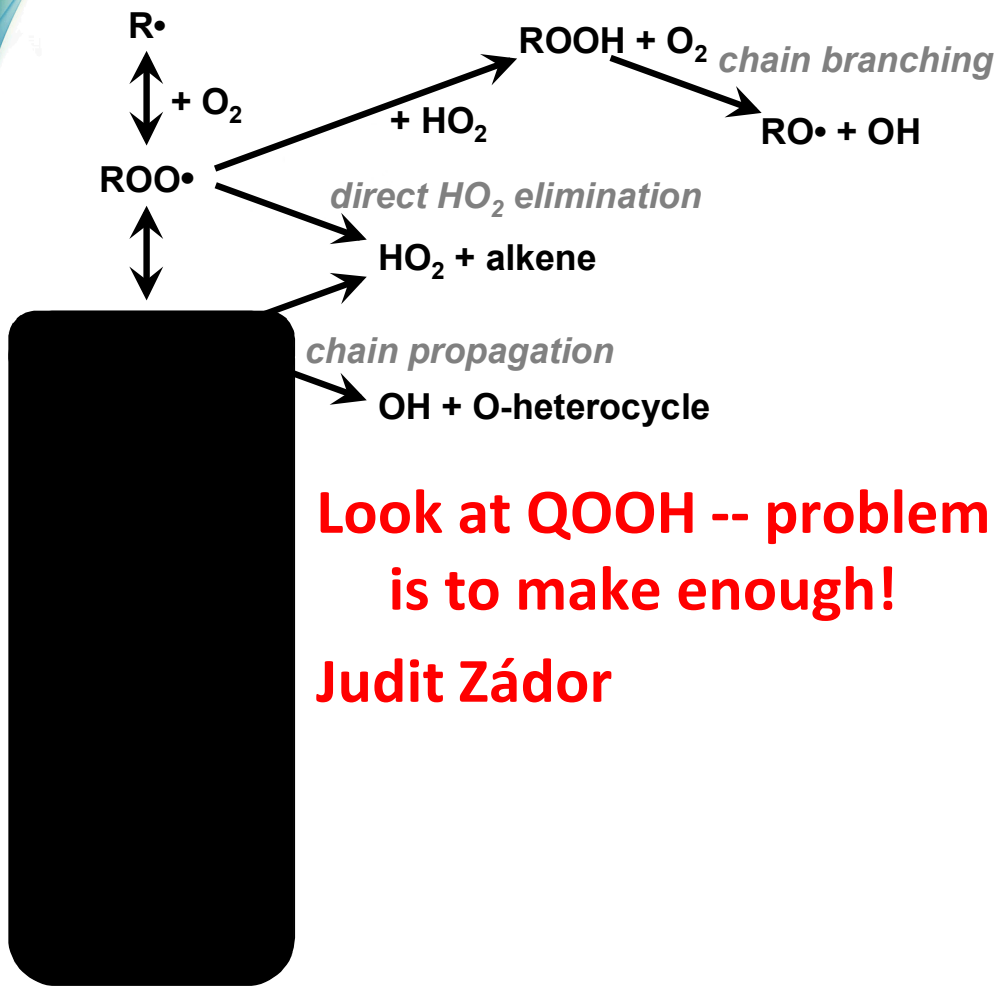
- Diethyl ketone prototype for tropospheric autoxidation
- Ketone oxidation has possibility of vinoxylic resonance stabilization
- Resonance-stabilized radicals less reactive with O_2
- Resonance stabilization may favor particular QOOH pathway

Substitution changes oxidation chemistry – for ignition or for the troposphere



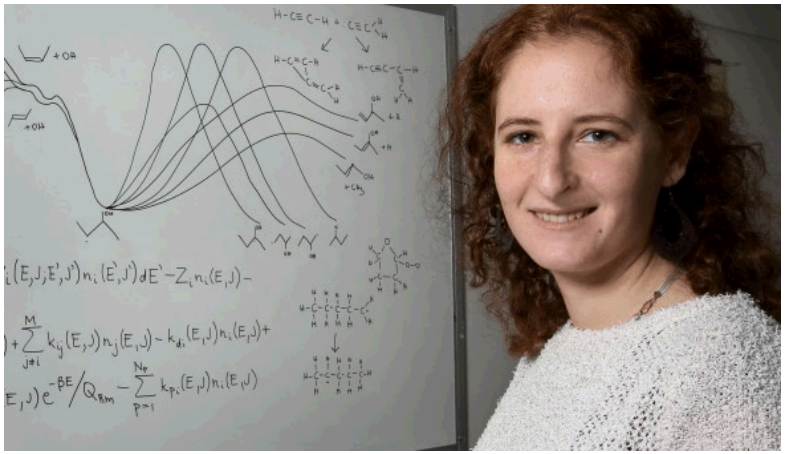
Adam Scheer

So what can we do to learn more about QOOH? Start at the next step?



Look at QOOH -- problem is to make enough!

Judit Zádor



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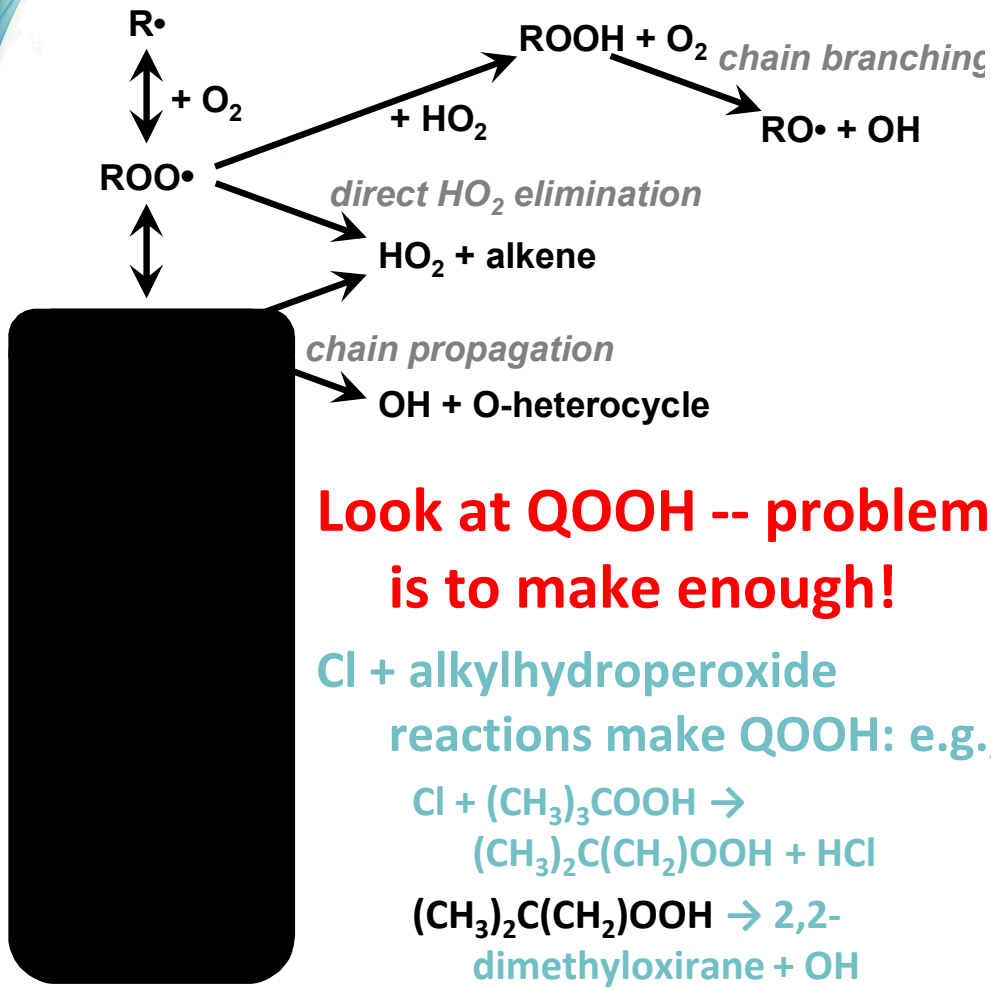
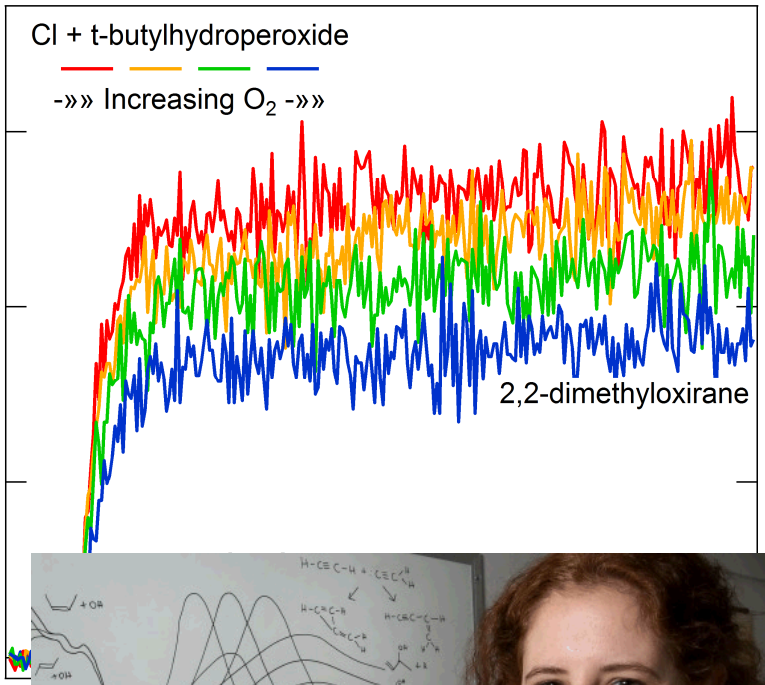


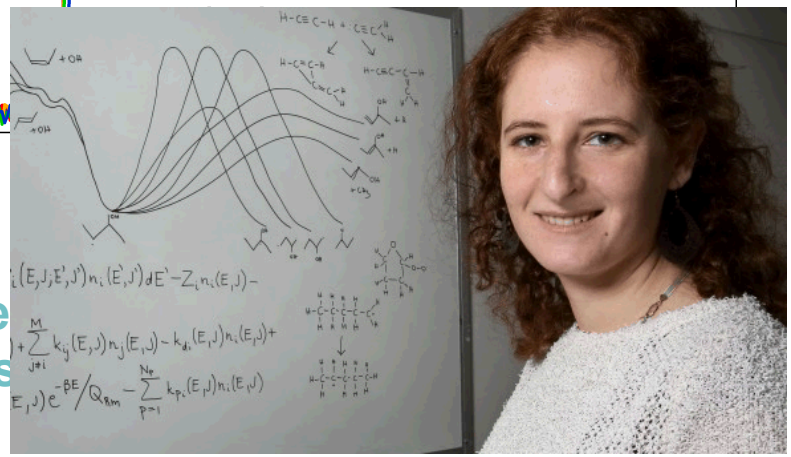
Look at QOOH -- problem is to make enough!

Cl + alkylhydroperoxide reactions make QOOH: e.g.,

$Cl + (CH_3)_3COOH \rightarrow (CH_3)_2C(CH_2)OOH + HCl$

$(CH_3)_2C(CH_2)OOH \rightarrow$ 2,2-dimethyloxirane + OH





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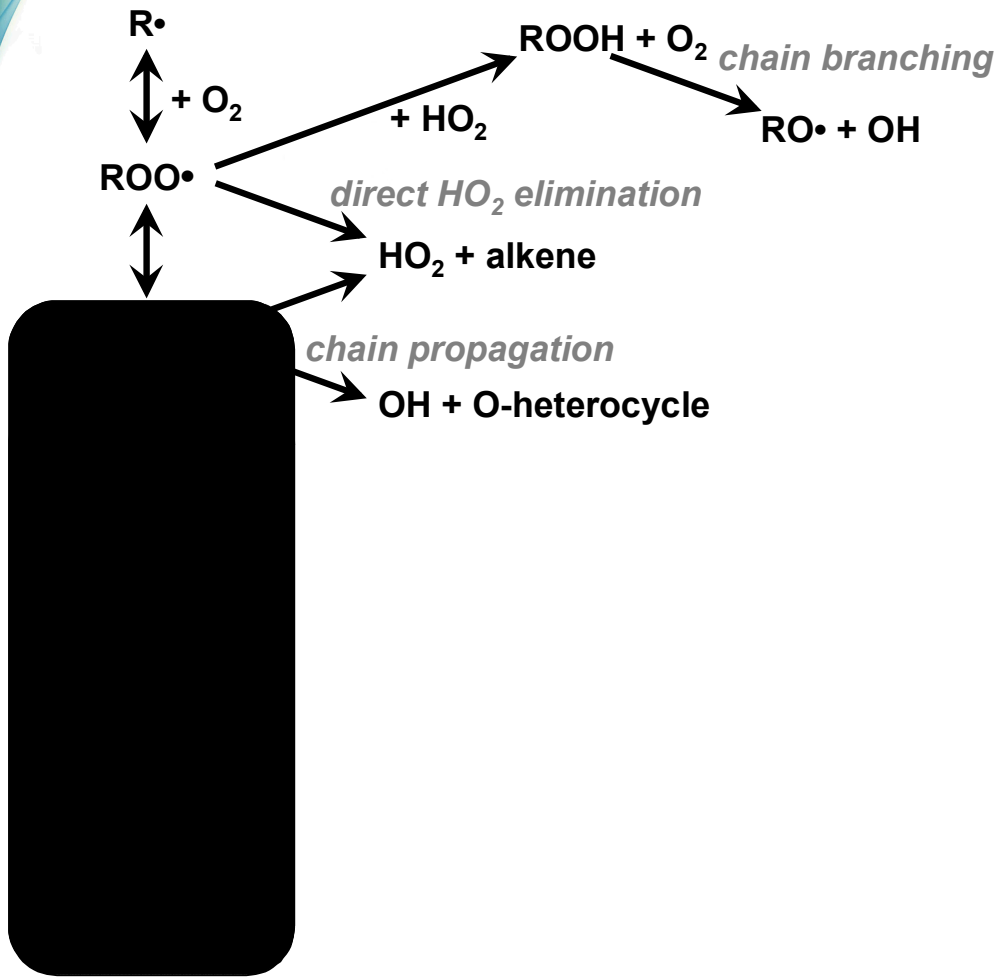

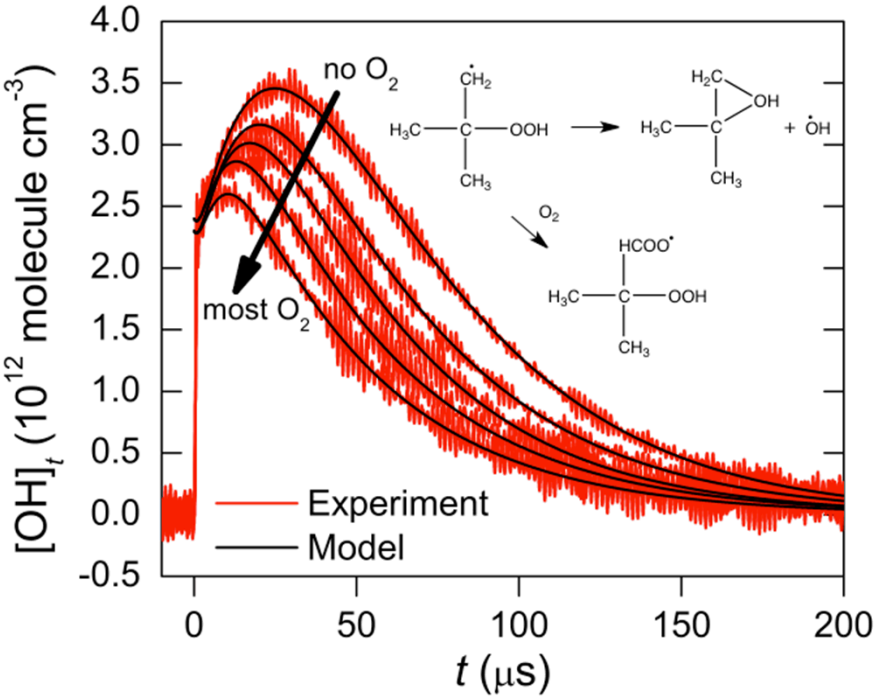

Product measurements can give *direct* measurements of QOOH reactions

Zador, Huang et al., Phys. Chem. Chem. Phys. **15**, 10753-10760 (2013)

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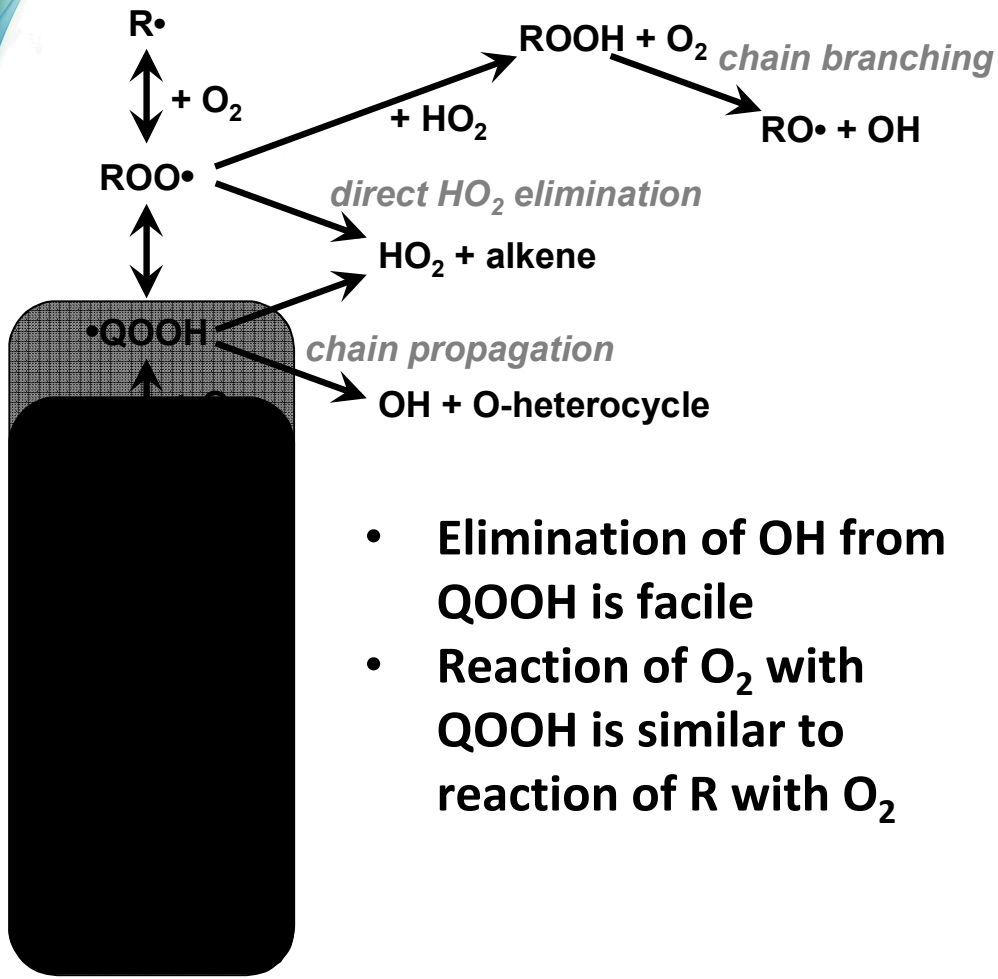
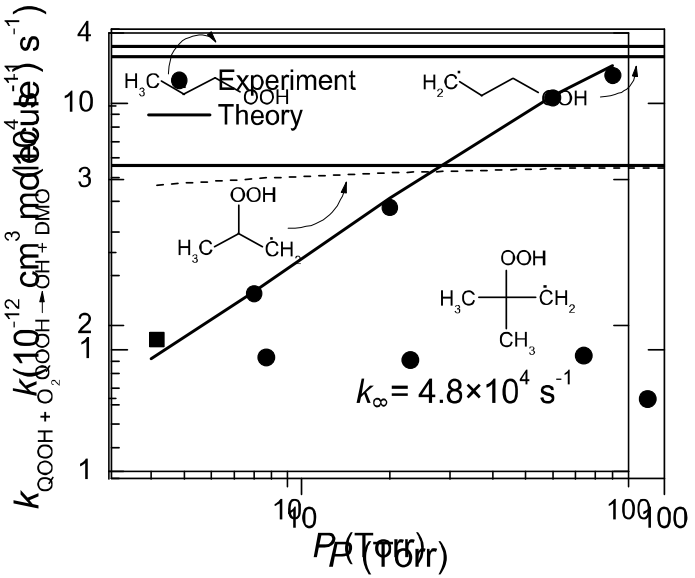


- Elimination of OH from QOOH is facile
- Reaction of O_2 with QOOH is similar to reaction of R with O_2



C. F. Goldsmith, W. H. Green, & S. J. Klippenstein, *J. Phys. Chem A* 116, 3325–3346 (2012)

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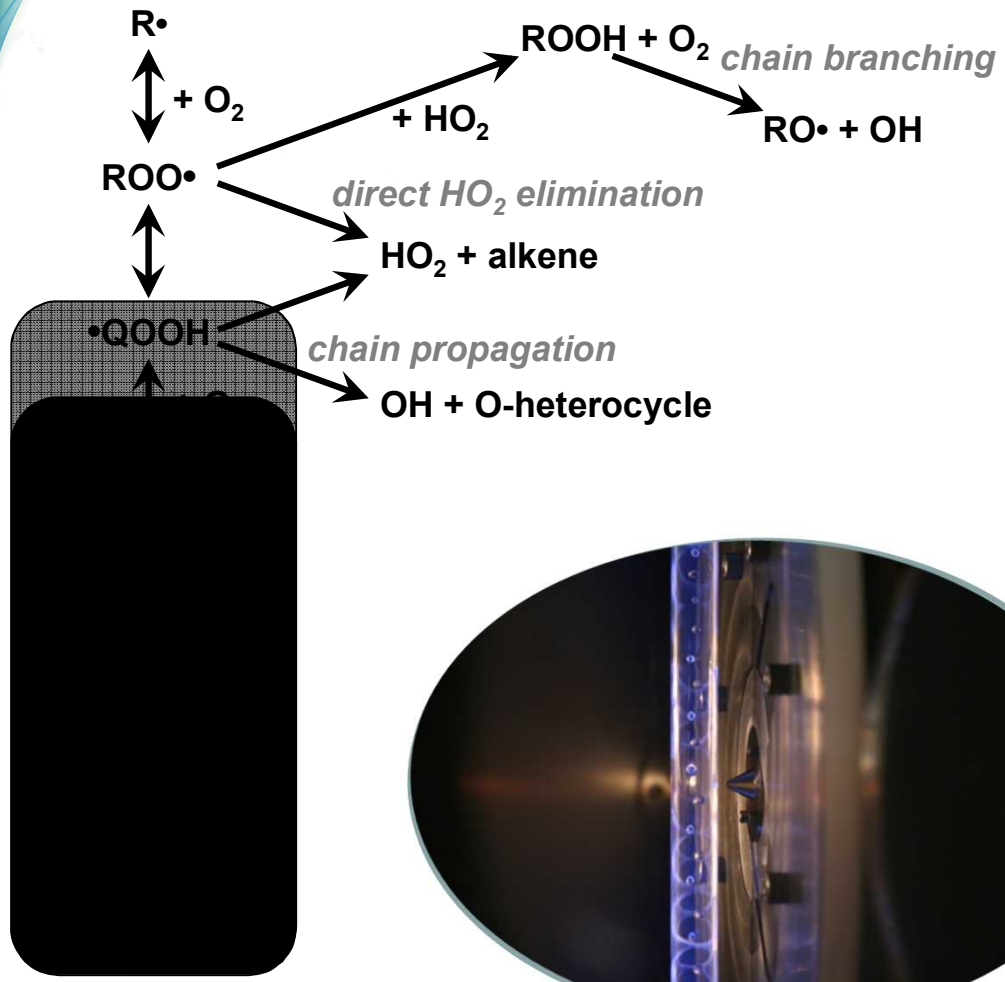
Zador, Huang et al., Phys. Chem. Chem. Phys. **15**, 10753-10760 (2013)

But can we directly measure QOOH itself?

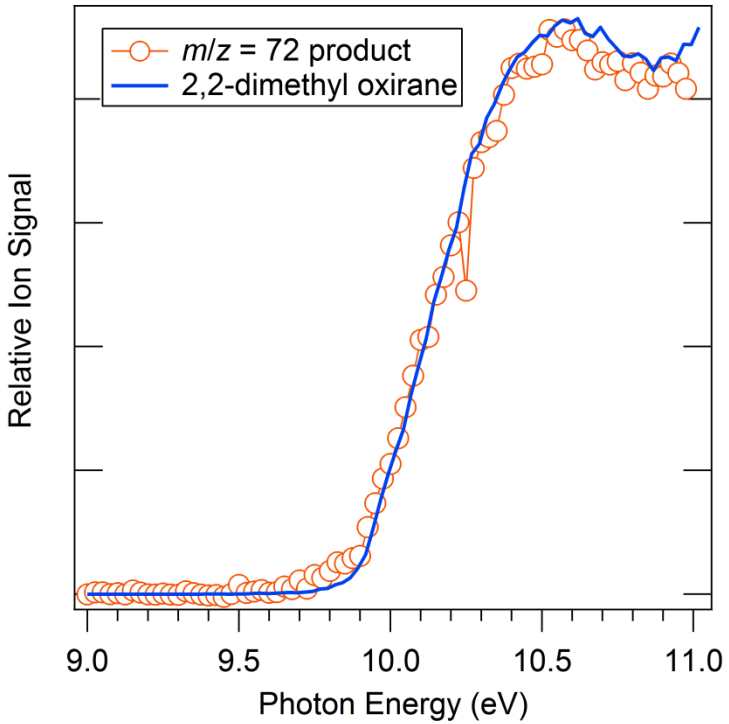


We have a machine that can discriminate isomers!

Identification of isomers in MPIMS machine relies on photoionization spectra

For stable products we can buy or make calibrants

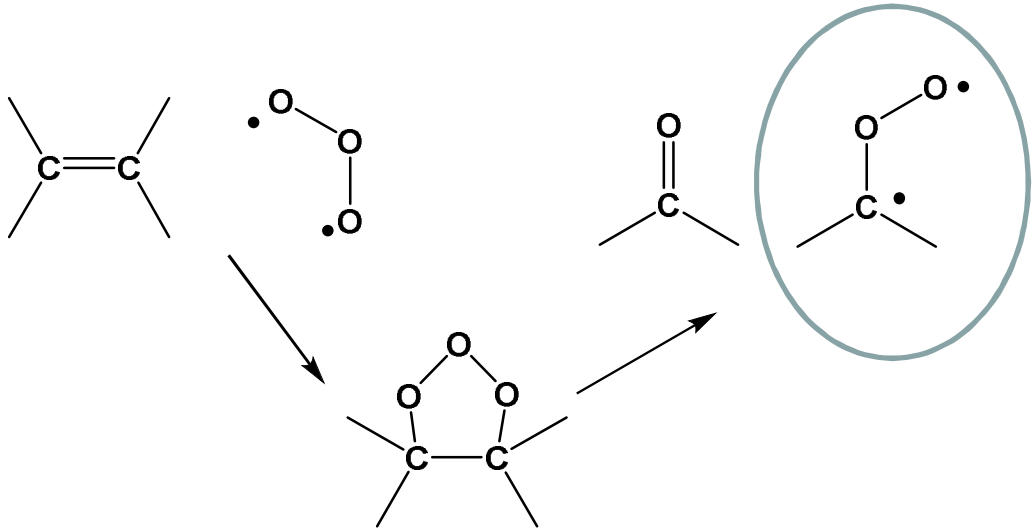
What do we do for something that has never been seen?

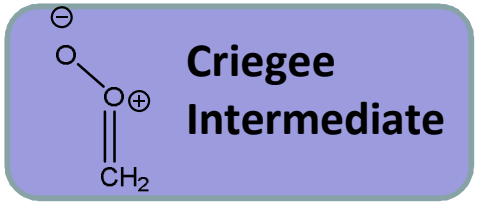


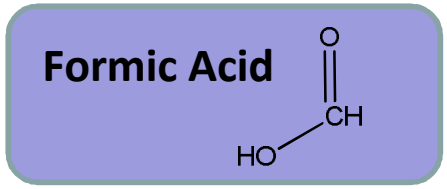
Theory, of course!

An illustrative digression on another set of oxidation "intermediates"

- Ozonolysis makes carbonyl oxides, often known as Criegee intermediates
- Criegee intermediates also appear in QOOH + O_2 reactions
- Until 2012, no one had directly measured a Criegee intermediate reaction







Problem was to make enough

Tunable synchrotron photoionization *can* identify Criegee intermediates if we make them

Carl Percival, Dudley Shallcross

Dimethyl Sulfoxide (DMSO) oxidation forms CH_2OO (Asatryan and Bozzelli, PCCP 10, 1769 (2008), Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008))

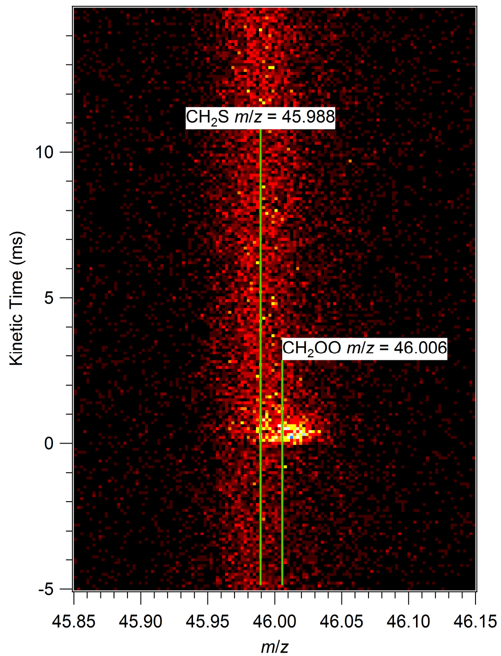
Time-of-flight can resolve CH_2S from CH_2OO

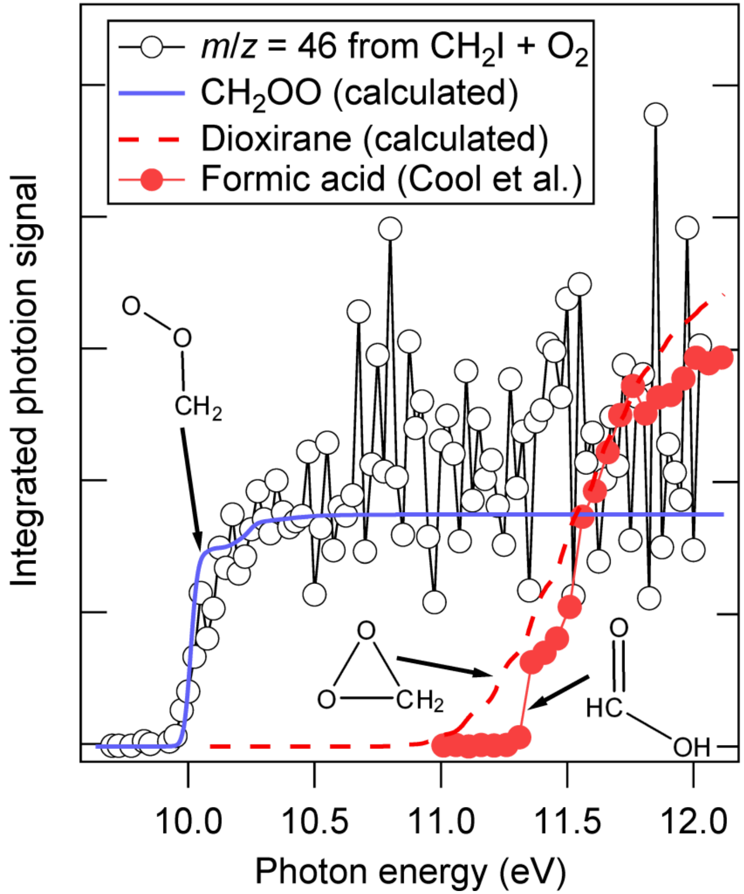
et (2(wit turns out tha Criegee inte

Cl-initiated DMSO oxidation

300 K, 8 Torr

Can make lots o look at react tropospheri





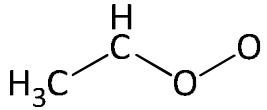
Calculated photoionization spectra

Welz *et al.*, *Science* **335** 204-207 (2012)

We produced and characterized larger Criegee Intermediates, e.g. acetaldehyde oxide (CH_3CHOO)

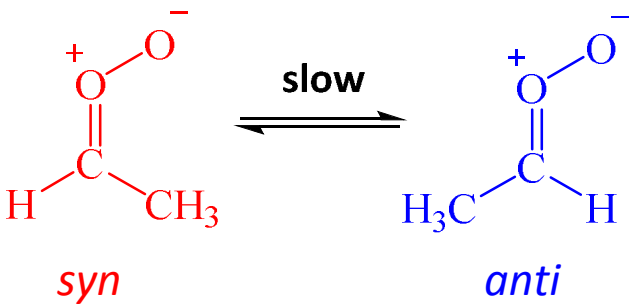
Similar strategy:

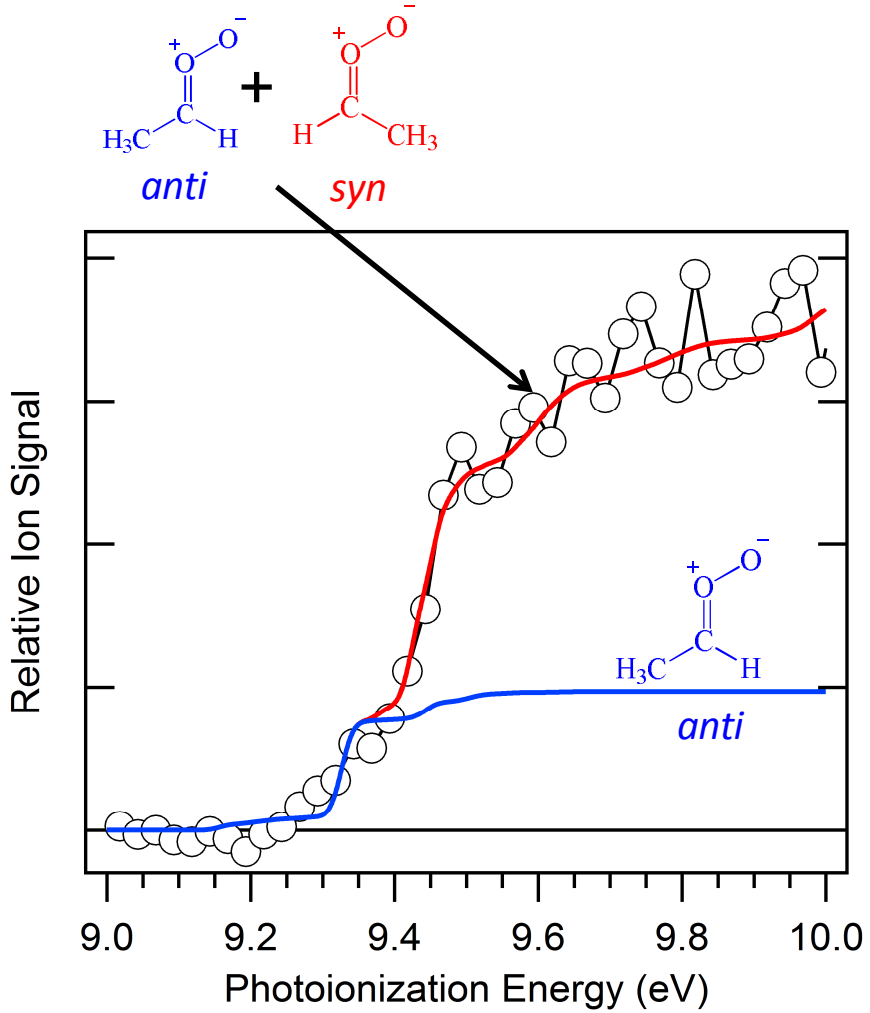
$H_3C—CHI_2 \xrightarrow{248 \text{ or } 351 \text{ nm}} I + H_3C—\dot{C}HI$

$O_2 + H_3C—\dot{C}HI \longrightarrow I +$ 

$m/z = 60$

CH_3CHOO exists in two distinct conformeric forms

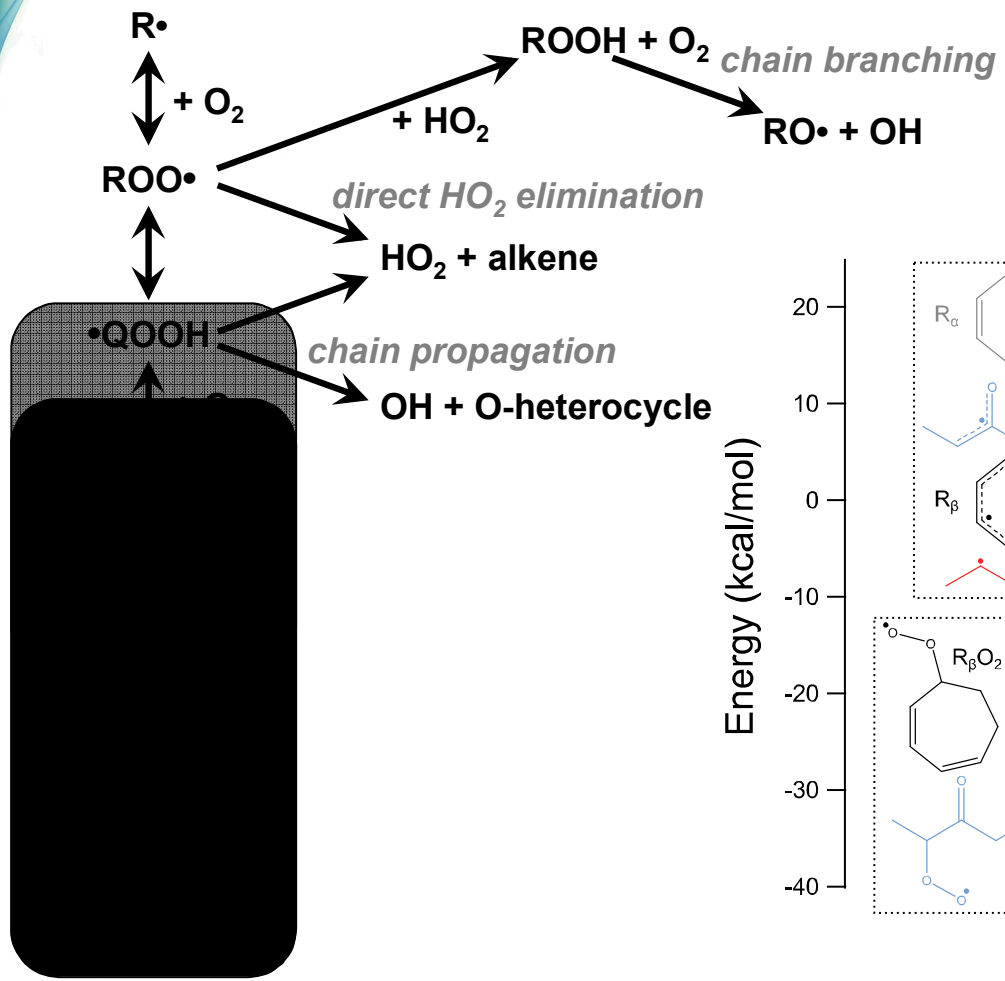




Taatjes, Welz *et al.*, *Science* **340**, 171-180 (2013)

John Dyke, Ed Lee, Daniel Mok

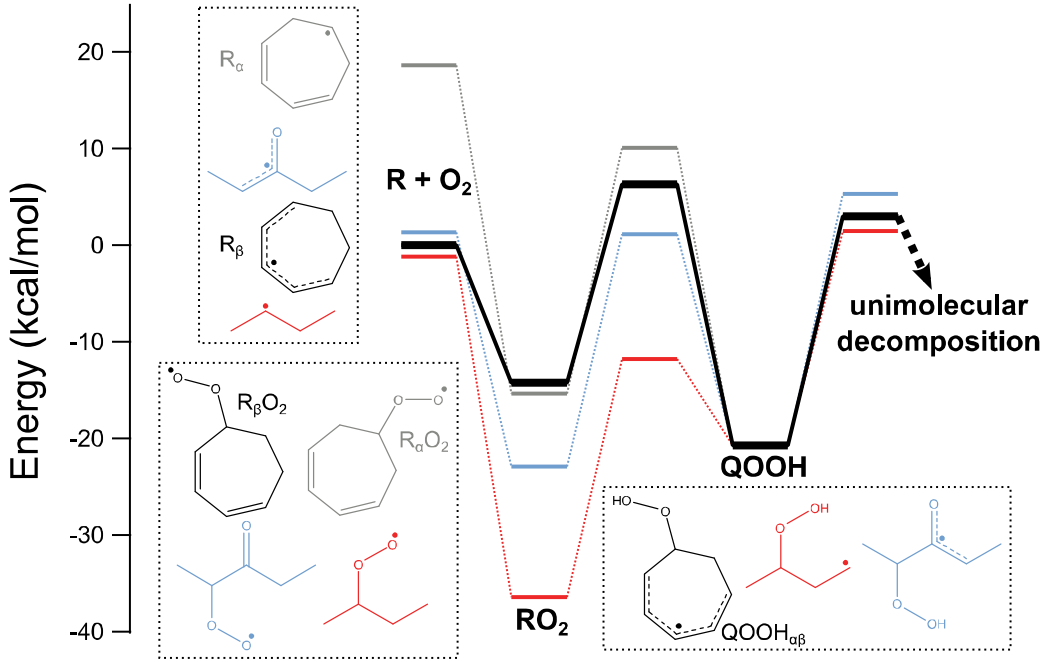
But can we directly measure QOOH itself?



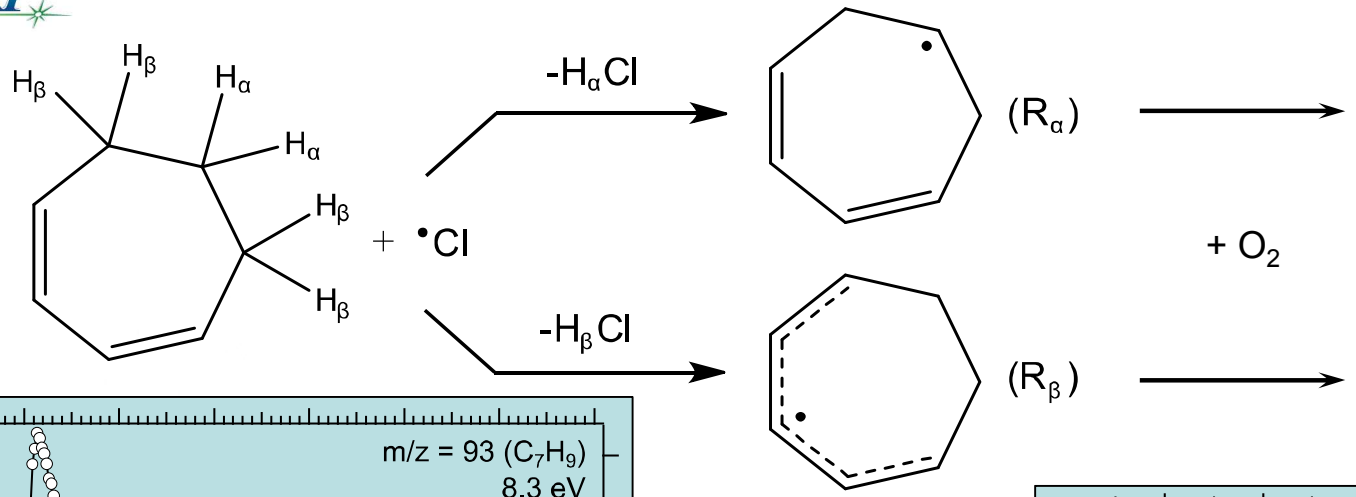
Butane oxidation – ketohydroperoxides observed (Battin-Leclerc et al., *Angew. Chem.* 49, 3169 (2010); Eskola et al. *Proc. Combust. Inst.* 35, 291-298 (2015))

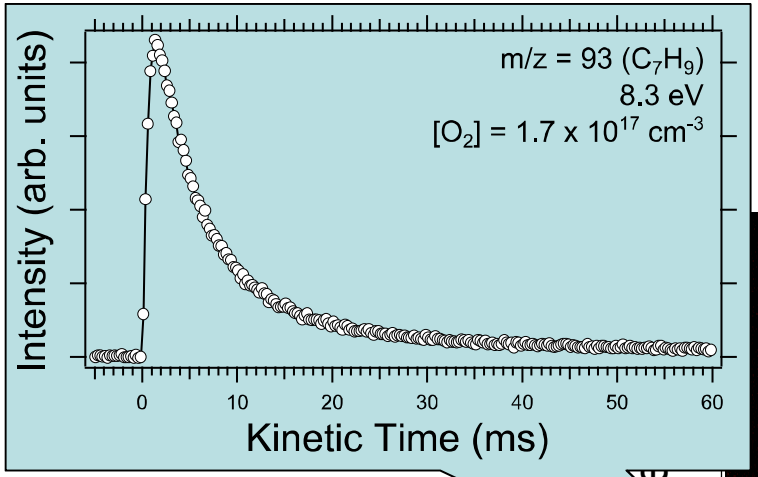
Ketone oxidation – resonance stabilized QOOH are preferred

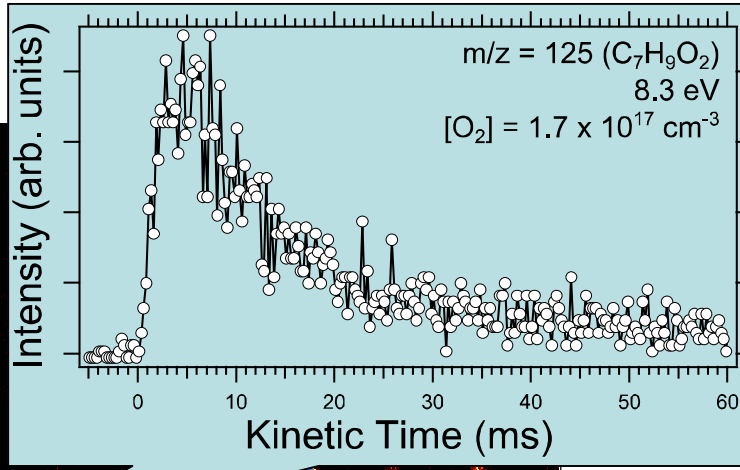
What about more stable QOOH?



Cycloheptadienyl + O_2



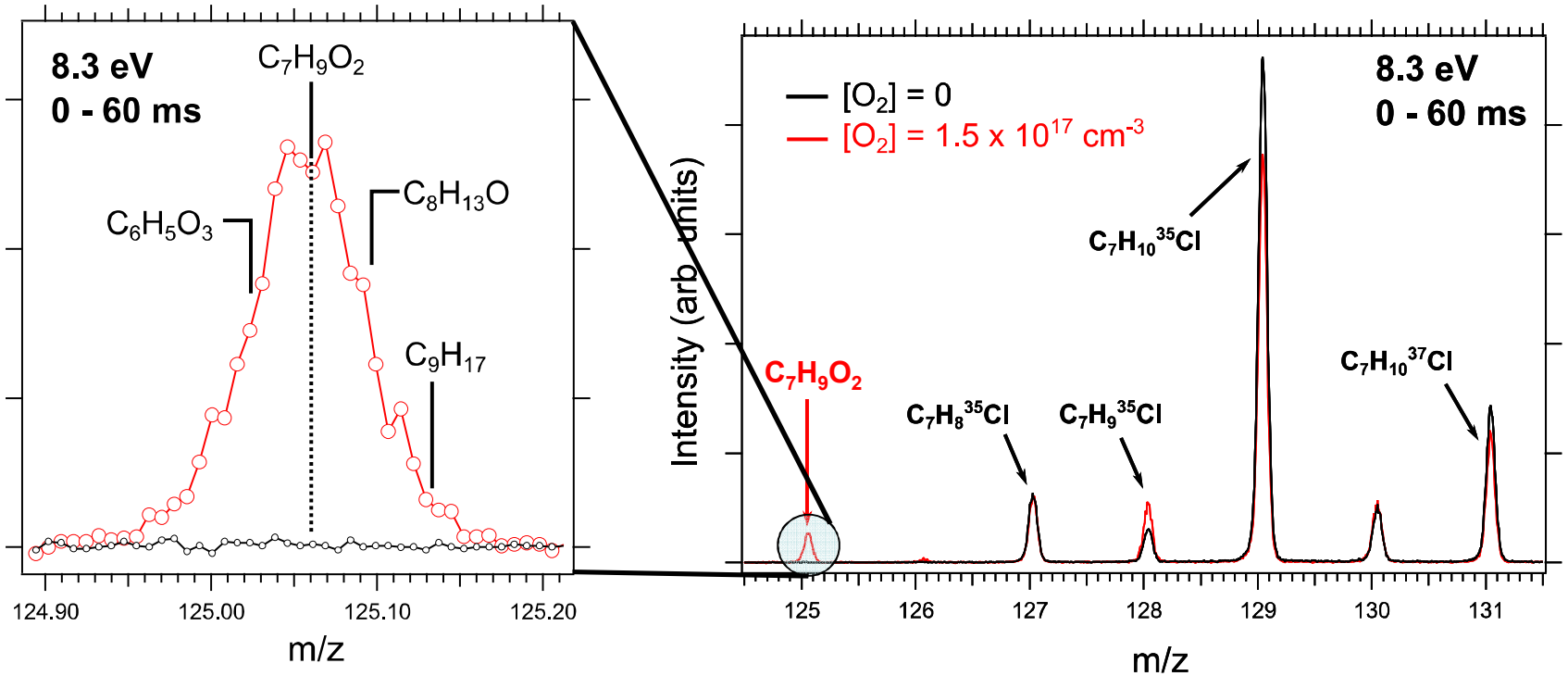




John Savee
Ewa Papajak

Evidence for QOOH
Oxygen Dependence, Exact Mass

- m/z = 125 amu only present when O_2 is present
- Exact m/z = 125.06 amu confirms formula of $C_7H_9O_2$

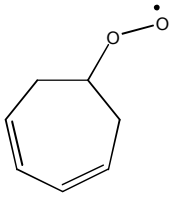


Mass Resolution ~ 1600

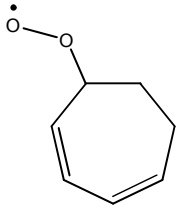
Evidence for QOOH
Photoionization Spectrum

- Calculated ionization energy perfect match to QOOH, not ROO

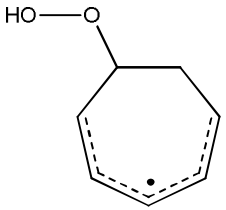
Ab Initio Adiabatic Ionization Energies
[M06-2X/6-311+G(2df,2p)]



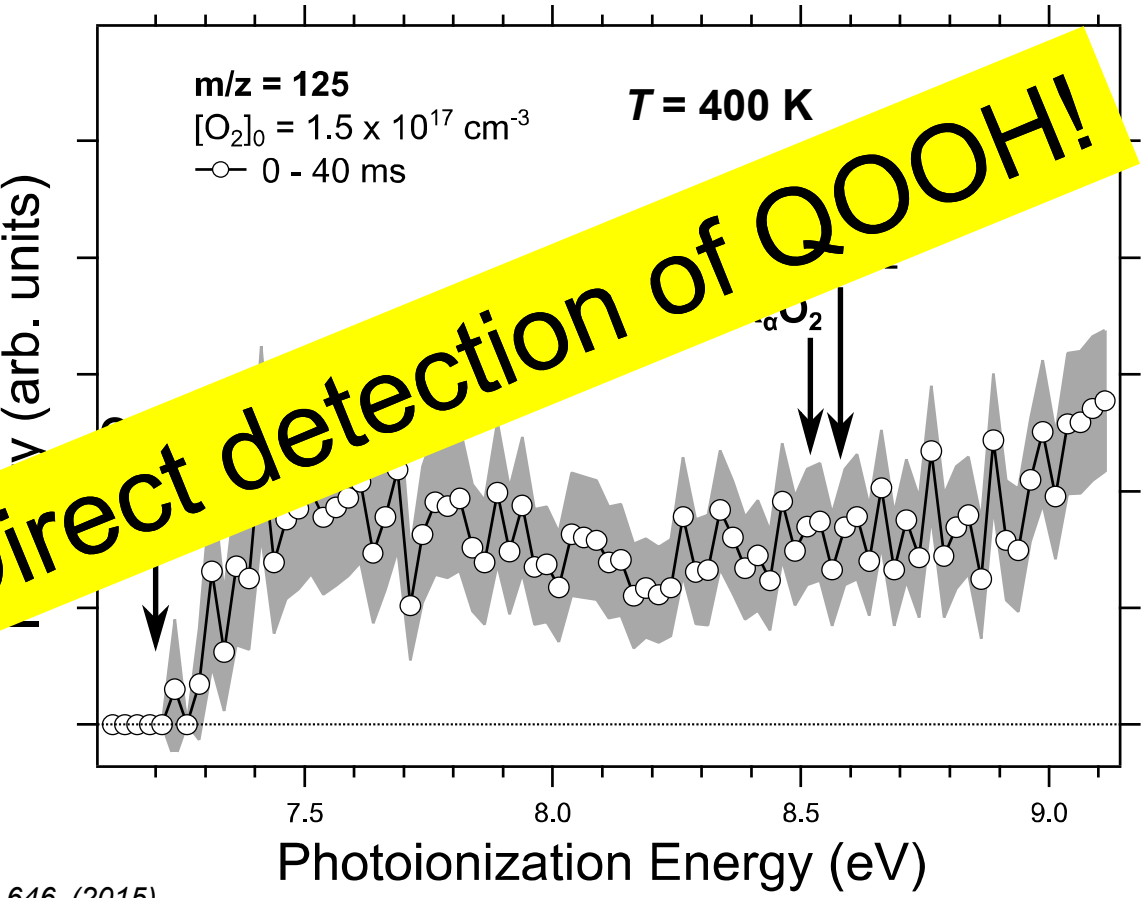
AIE = 8.52 eV



AIE = 8.58 eV



AIE = 7.20 eV

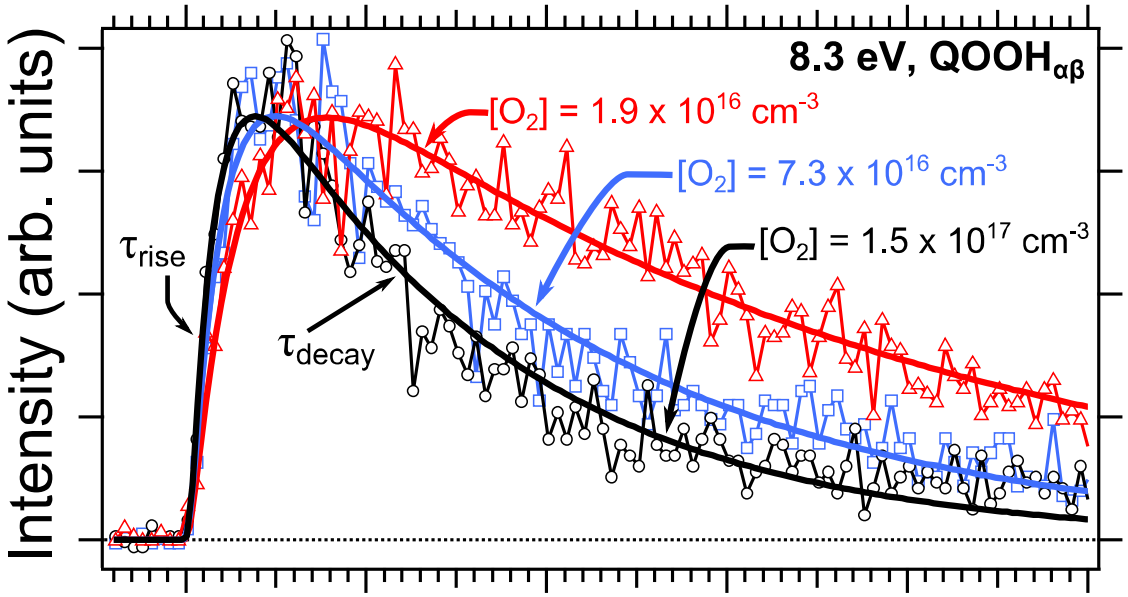


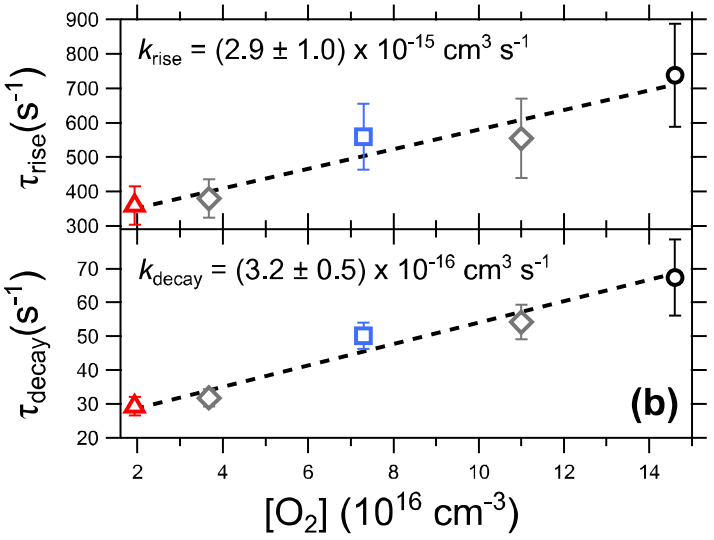
Direct detection of QOOH!

J.D. Savee, E. Papajak, et al.,, *Science 347, 643-646 (2015).*

Reaction of QOOH with O_2
Kinetic Time Profiles

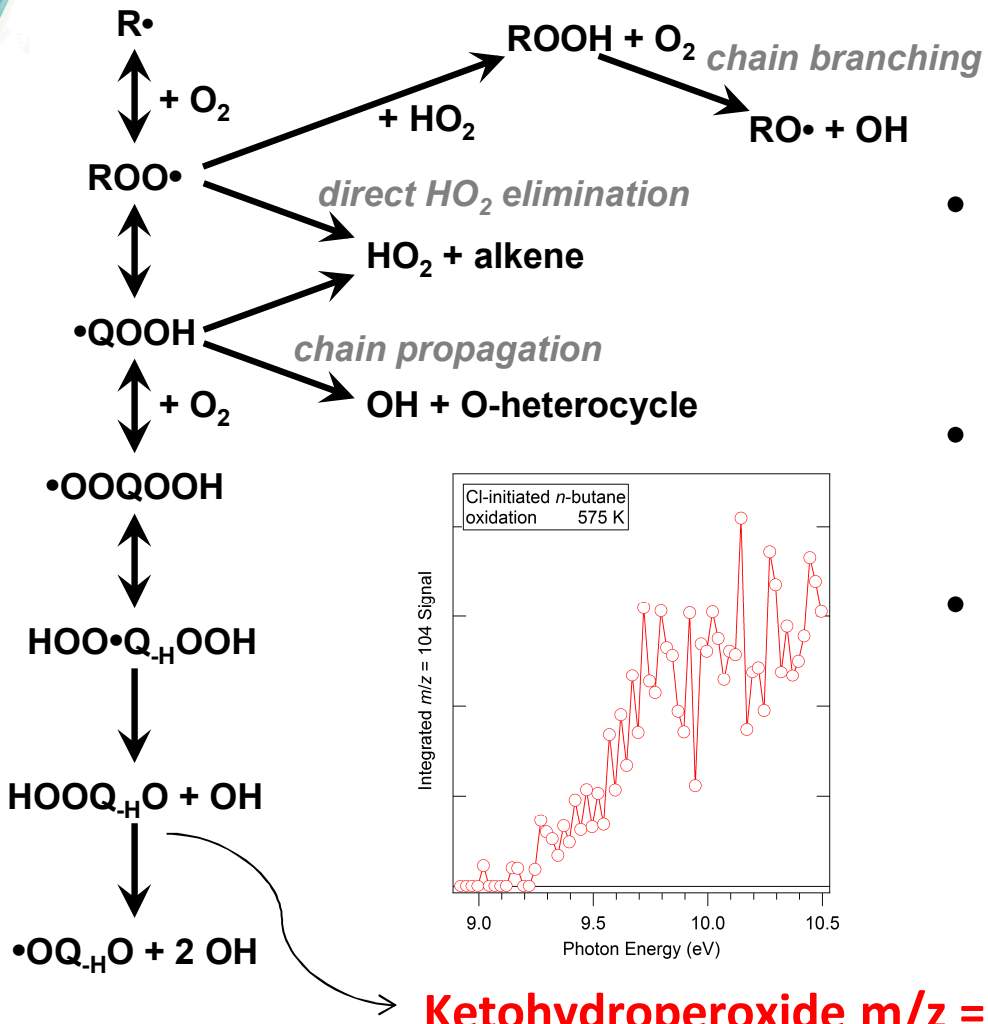
- Both rise and decay of $C_7H_9O_2$ faster as $[O_2]$ increases
- $k_{rise} = (2.9 \pm 1.0) \times 10^{-15}$ cm^3 s^{-1}, $k_{decay} = (3.2 \pm 0.5) \times 10^{-16}$ cm^3 s^{-1}





k(QOOH + O_2) is much smaller than other "second O_2 additions"
Dissociation of resonance stabilized QOOH is slow
- ➢ Long lifetimes for resonance-stabilized QOOH.

What does this tell us about oxidation? What about that last step?

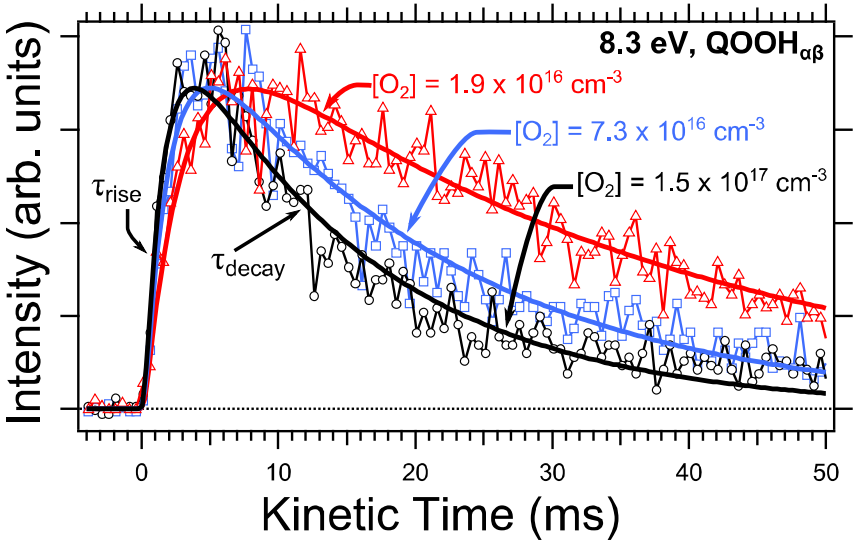


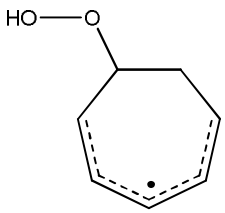
- "Normal" autoignition chemistry has OOQOOH forming ketohydroperoxide
- Ketohydroperoxide falls apart to two radicals
- Substitution can make the chemistry "not normal"!

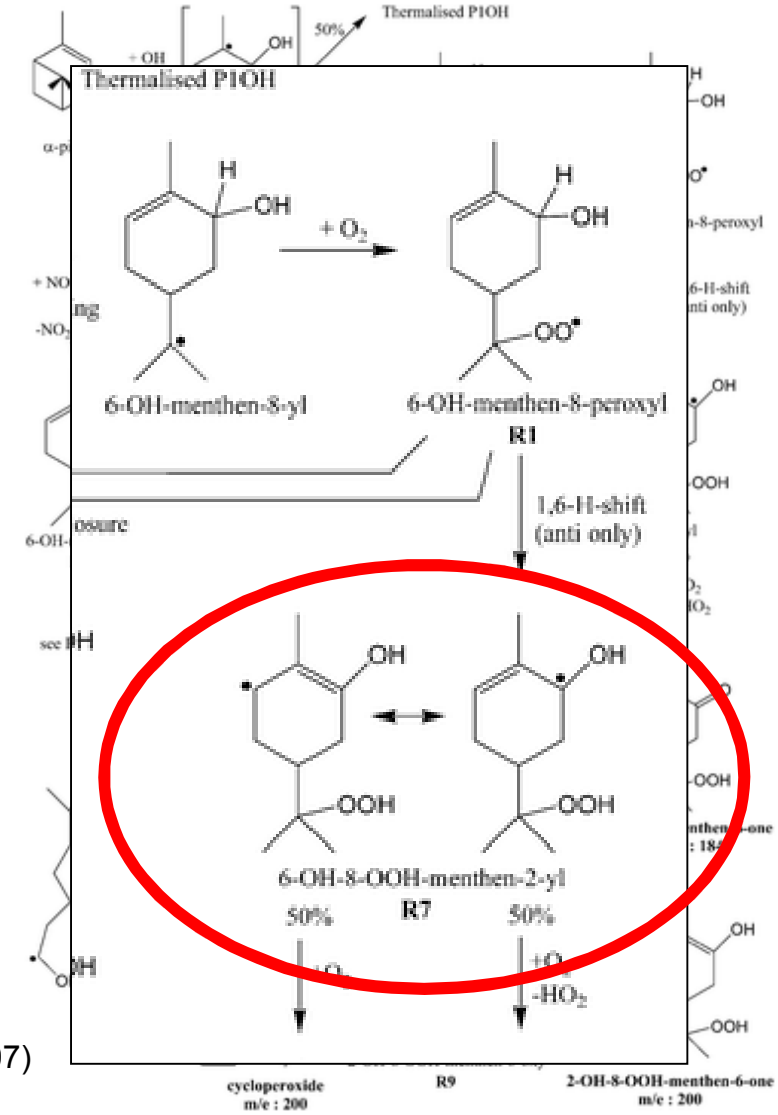
Ketohydroperoxide m/z = 104

What if QOOH doesn't make a ketohydroperoxide?

Resonance stabilization can make QOOH less reactive





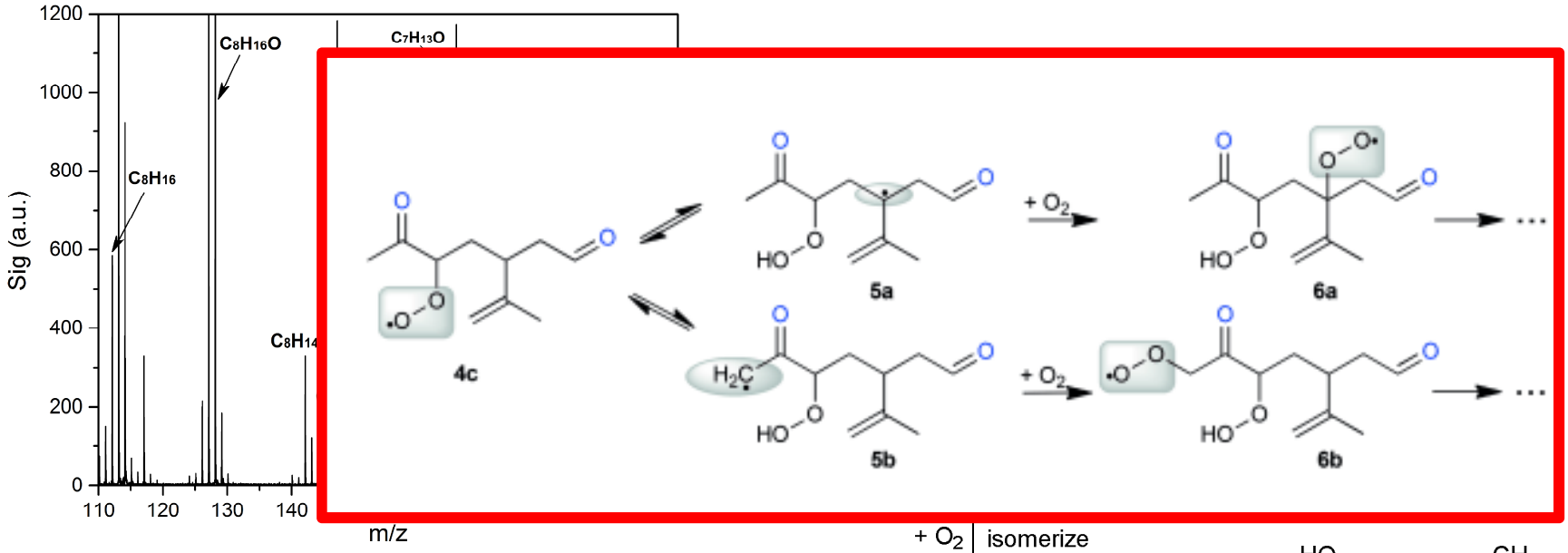


Vereecken et al., *Phys. Chem. Chem. Phys*. **9**, 5241-5248 (2007)

What if QOOH doesn't make a ketohydroperoxide?

Tertiary carbons can prevent "normal" OOQOOH reaction

T. Jokinen et al., *Angew. Chem. Int. Ed.* 53, 14596-14600 (2014)

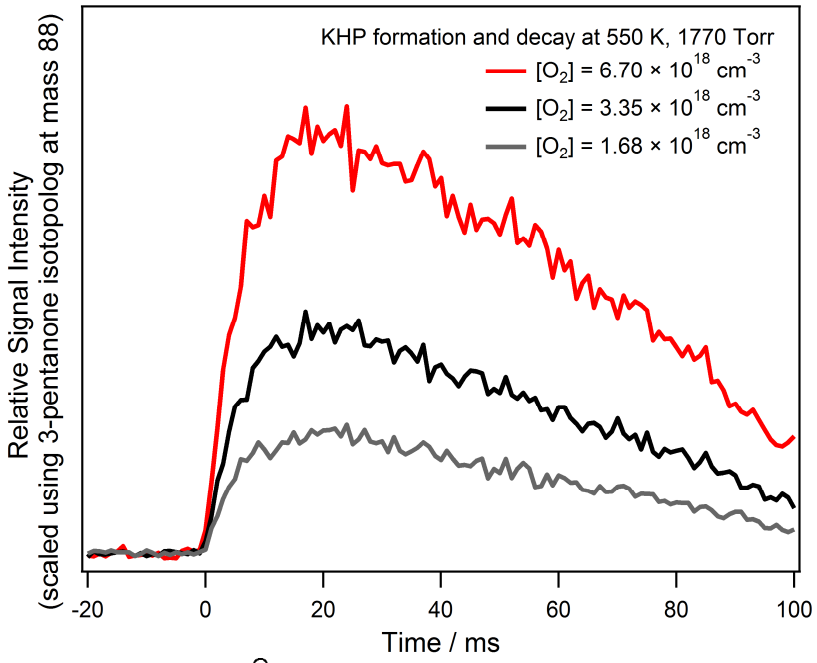


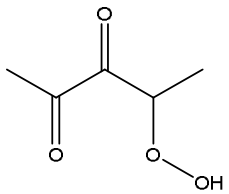
Oxidation of 2,5-dimethylhexane makes highly oxygenated species

Z. Wang et al., *Combust. Flame,* in press.

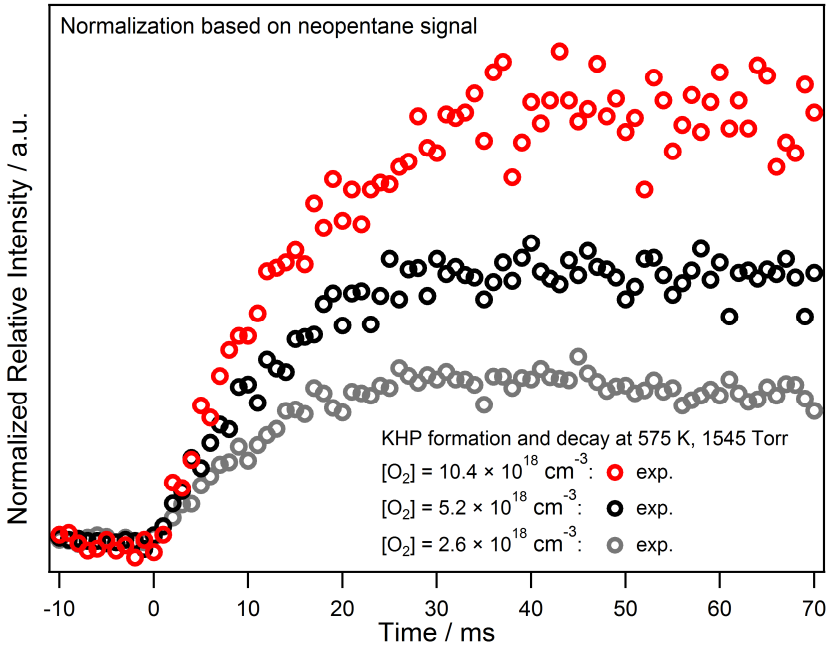
Ketohydroperoxides have now been observed in many kinetic systems

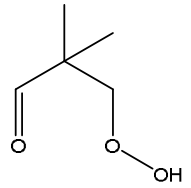
Oxidation of 3-pentanone shows KHP formation





Neopentane oxidation also shows KHP formation



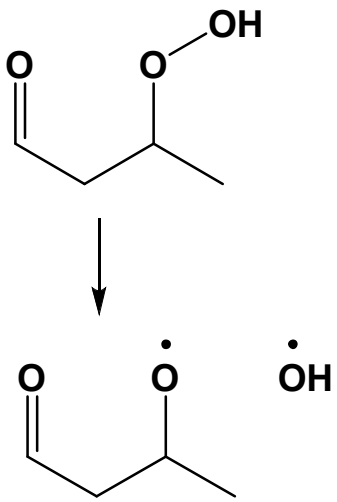


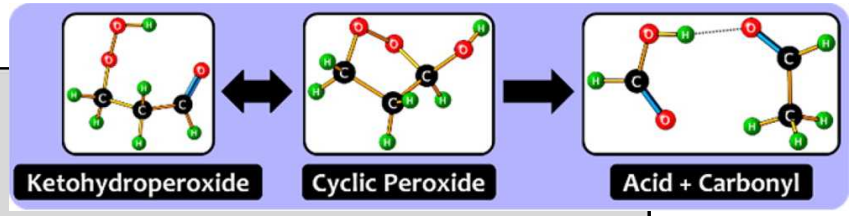
We know where they come from – where do they go?

What happens to γ-ketohydroperoxides?

So far observed species are gamma-ketohydroperoxides

Jalan et al. pointed out that gamma-KHP can isomerize



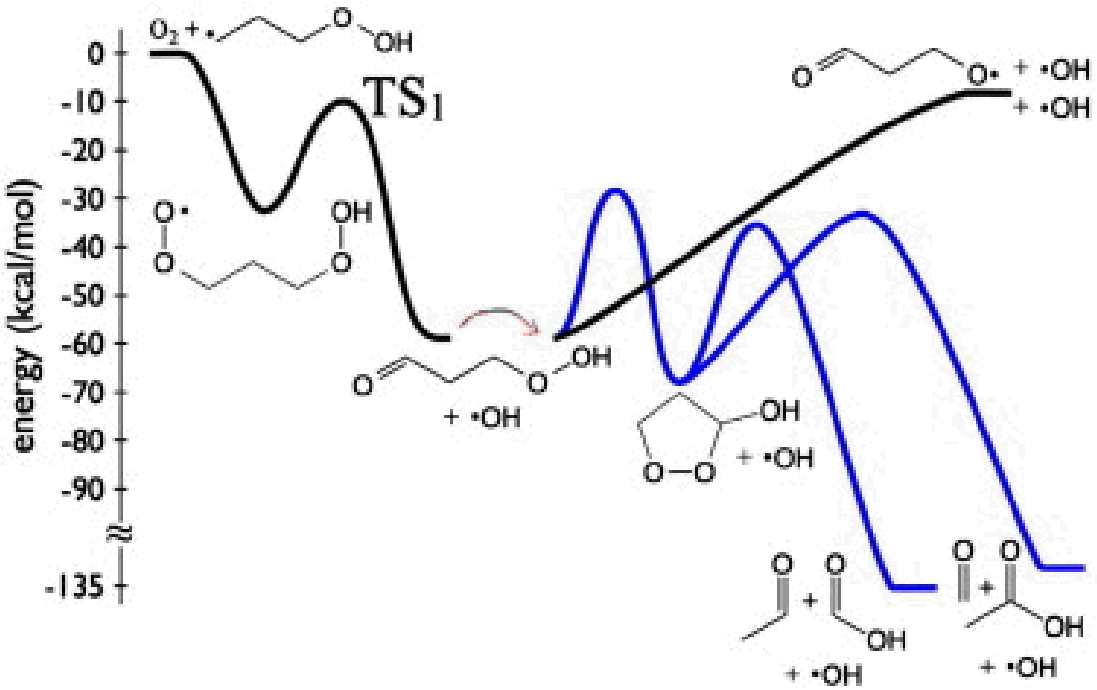


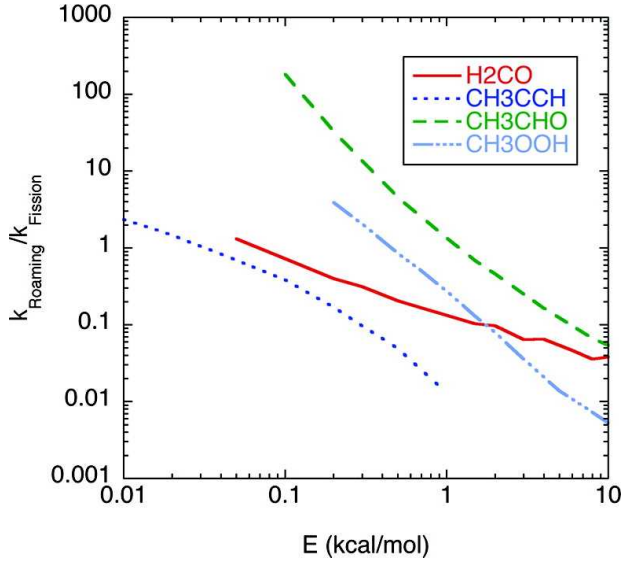
Jalan et al., *J. Am. Chem. Soc.* 2013, 135, 11100-11114

O-O bond fission leads to chain branching

Dynamics and beyond -- could excited products play a role?

Klippenstein et al. predicted substantial roaming in dissociation of methyl hydroperoxide (Klippenstein, Georgievskii and Harding; *J. Phys. Chem. A* **2011,** 115, 14370-14381)

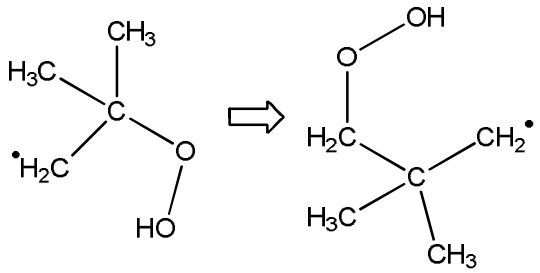


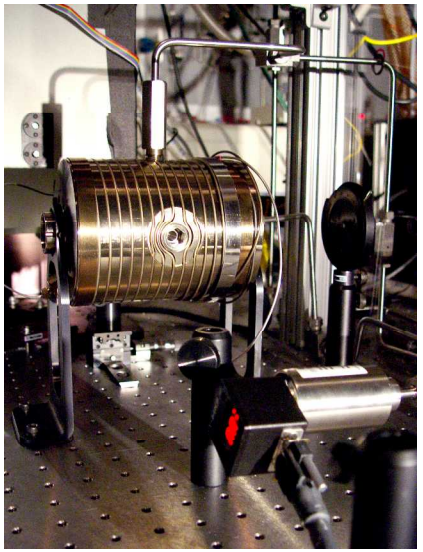


"Effect of non-thermal product energy distributions on ketohydroperoxide decomposition kinetics"
Goldsmith, C. Franklin; Burke, Michael P.; Georgievskii, Yuri; Klippenstein, Stephen J.
Proc. Combust. Inst. 35, 283-290 (2015)

Working inside the “black box” connects fundamental kinetics to complex models

- Begin to investigate conditions more like real combustion devices





- So far only the simplest or most convenient examples of intermediates -- try harder problems
  - New measurement methods are opening things up -- others are developing new tools to investigate these species

Judit Zádor, David Osborn, Lenny Sheps, Nils Hansen

Ewa Papajak, Ivan Antonov, Arkke Eskola, Haifeng Huang

Brandon Rotavera, John Savee, Adam Scheer, Oliver Welz

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Kendrew Au, Howard Johnsen

Stephen Klippenstein (Argonne)

Carl Percival (Manchester), Dudley Shallcross (Bristol)

Ed Lee, John Dyke (Southampton)

Denisia Popolan-Vaida (LBNL)

Zhandong Wang, Mani Sarathy (KAUST)

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