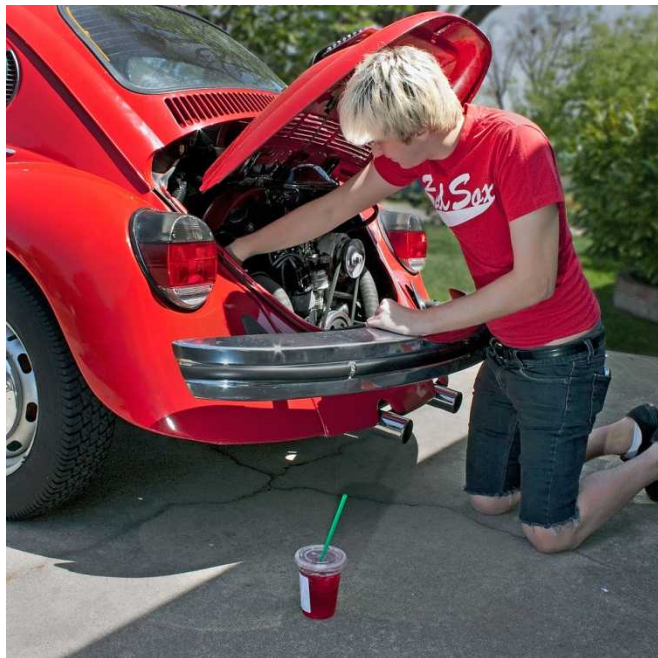


Probing the Chemistry of Elusive Intermediates in Hydrocarbon Oxidation

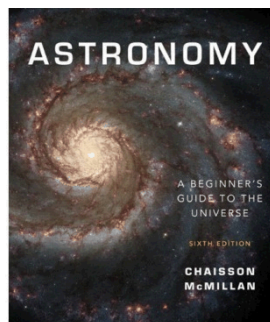
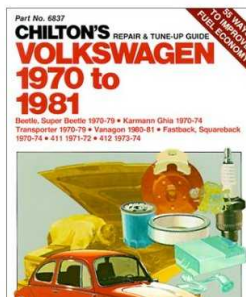
Craig A. Taatjes

*Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551*

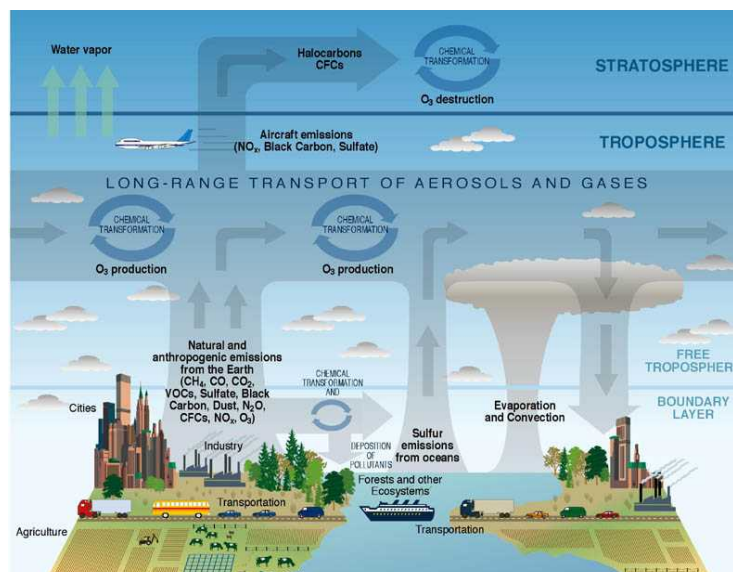
Why do people do chemical kinetic modeling?



Robert Couse-Baker



Mbz1 Wikimedia commons

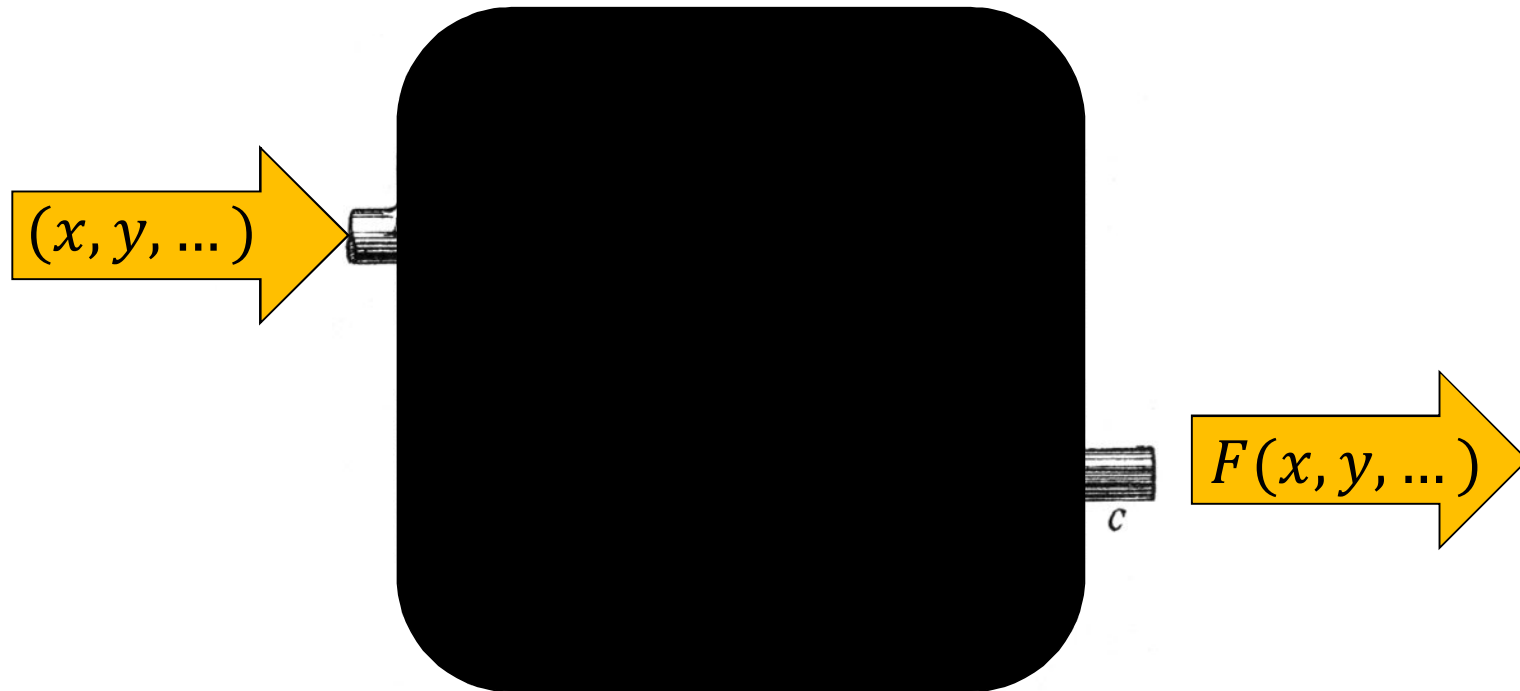


CLIMATE CHANGE SCIENCE PROGRAM OFFICE



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

“Decision points” that determine the outcome of the process

A Longstanding Fundamental Challenge – Predictive Models of Complex Systems

Comprehensive Kinetic Mechanism

Turbulent, multiphase flows interact with the chemistry

nsive
chanism

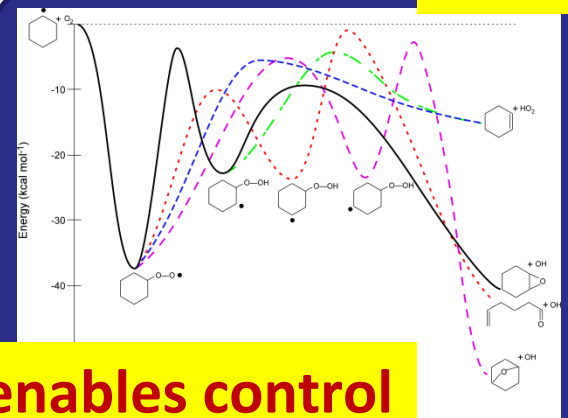
Detailed chemistry
of single elementary
fuel may have
thousands of
reactions and
hundreds of species

R + O₂
reactions

Autoignition

Soot Formation and Oxidation

Prediction enables control



Charles Mueller, CRF

Tropospheric and Engine Oxidation Processes Both Run on Radical Chain Chemistry

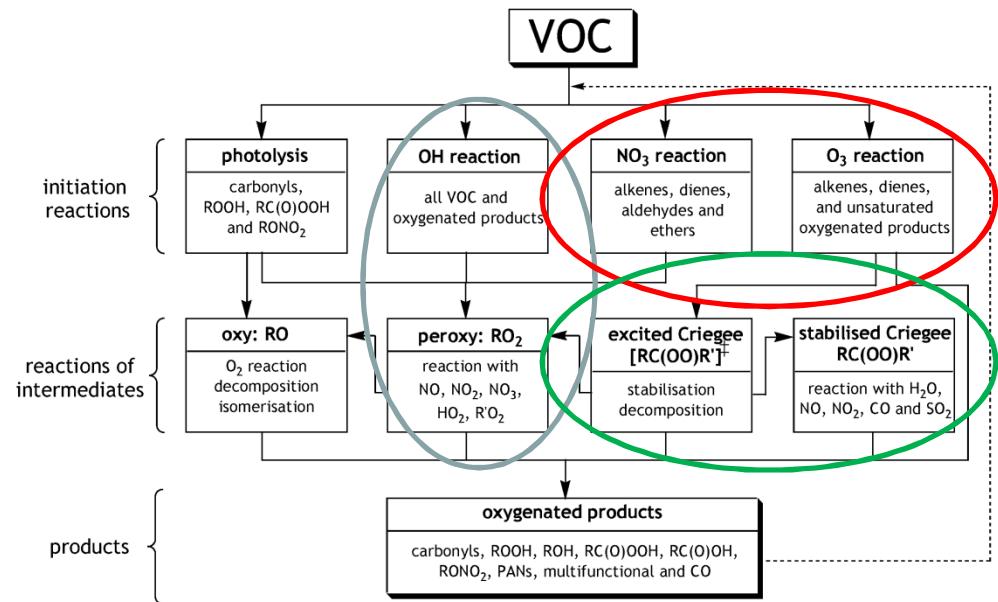
Ignition Chemistry:

- Chain-branching pathways are a “nonlinear feedback” for autoignition
- Alkyl + O₂ reactions and “QOOH” intermediates are central to low-temperature chain branching

Tropospheric Chemistry:

- Alkyl + O₂ reactions from OH-initiated oxidation also important in troposphere
- NO₃ and O₃ species are also important oxidation initiators
- Criegee intermediates are important species for OH, aerosol formation, NO_x, SO_x

General Alkyl Radical Oxidation Scheme



QOOHO₂

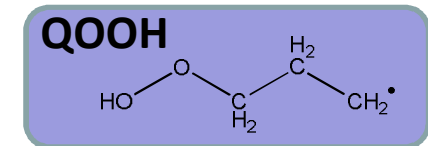
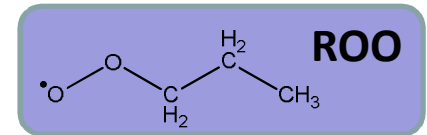
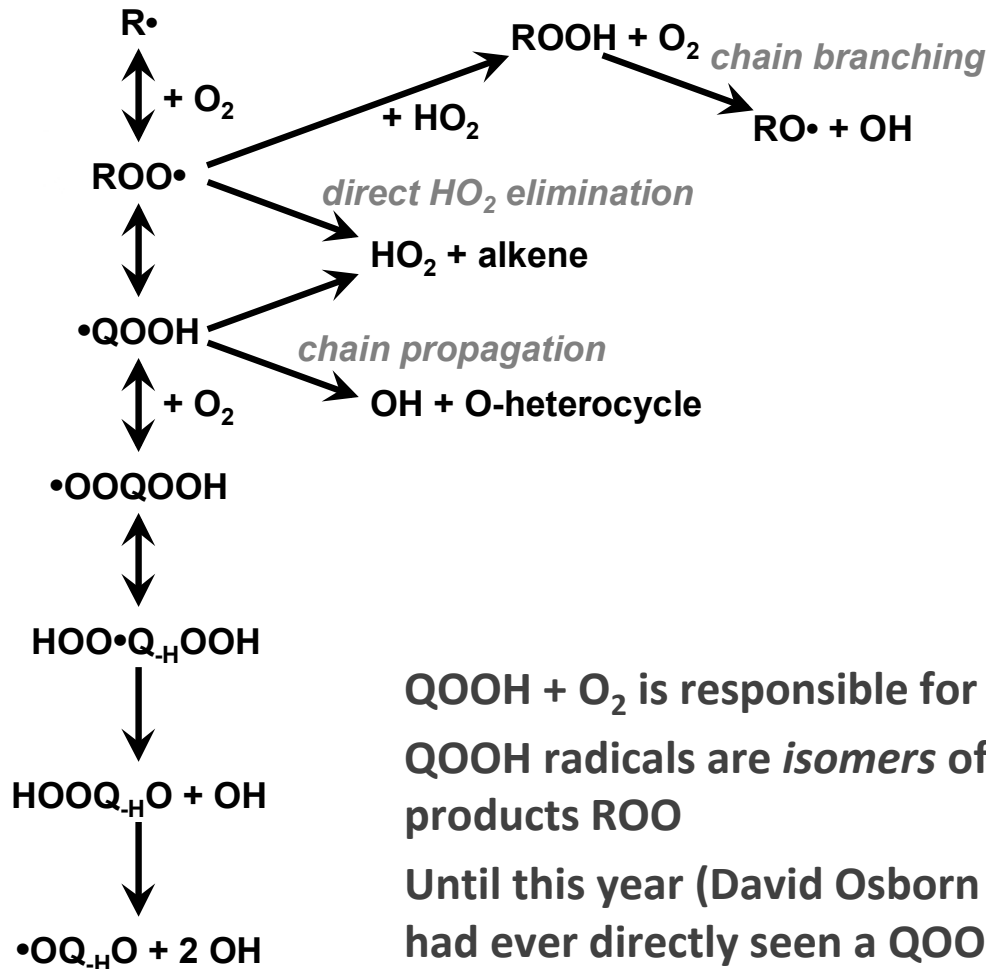
Atmos. Chem. Phys., 3, 161–180, 2003

branching

low temperature

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

Kinetic Models for Oxidation Chemistry Require Knowing Reactions of “Intermediates”



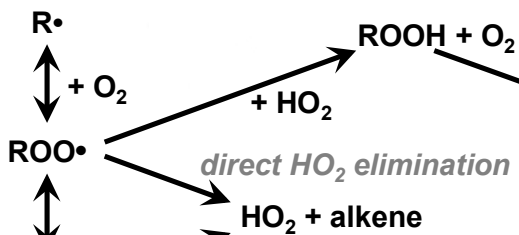
QOOH + O₂ is responsible for chain branching
QOOH radicals are *isomers* of the major reaction products ROO

Until this year (David Osborn – next talk!) no one had ever directly seen a QOOH by any means

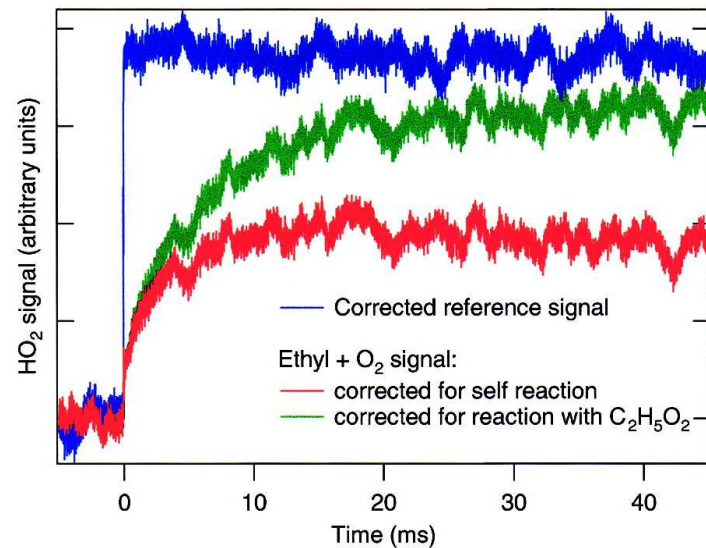
So what can we do?

Take one step at a time?

Alkyl + O₂ reactions – Detect the HO₂ reaction product



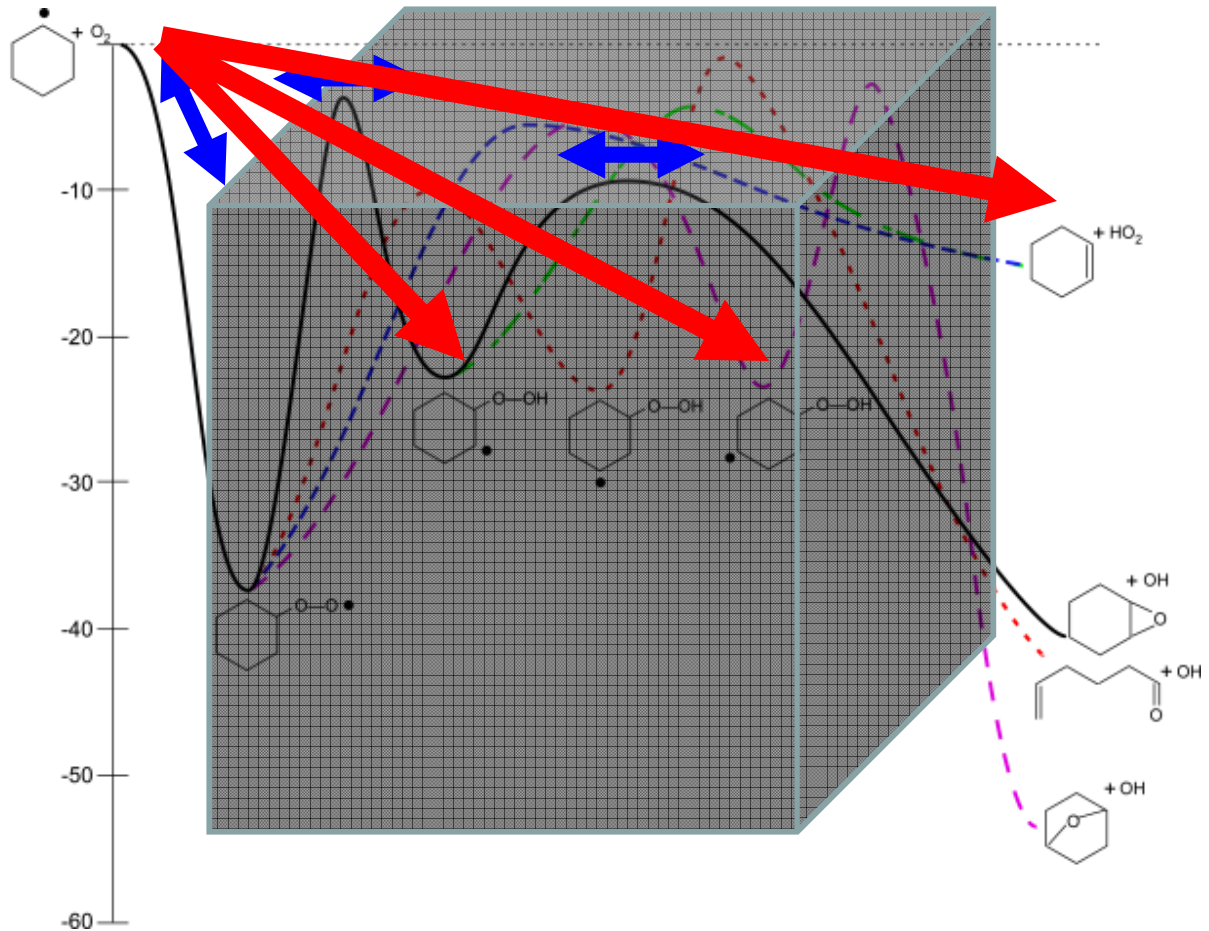
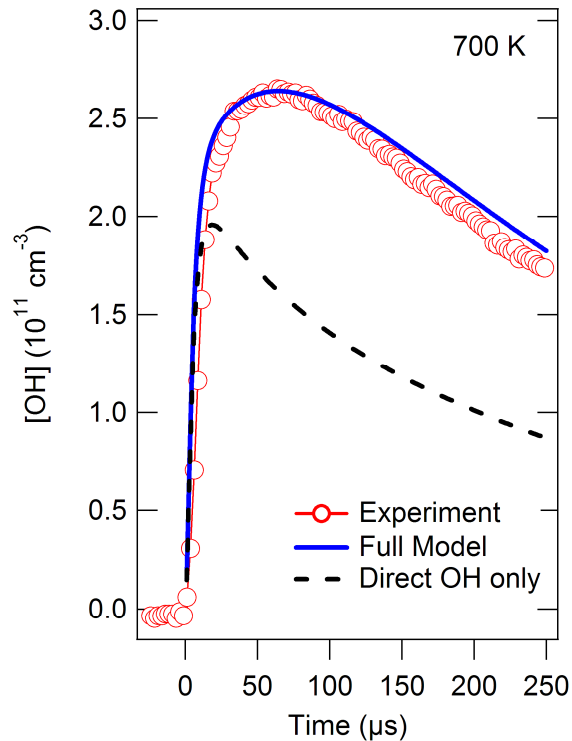
Product appears on two timescales -- kinetically separate chemical activation contribution



Phenomenological analysis

How Does This Tell Us Anything about the Intermediates? Theory opens the Black Box!

Measured products from pulsed photolytically initiated R + O₂ reactions compared to theory



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

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

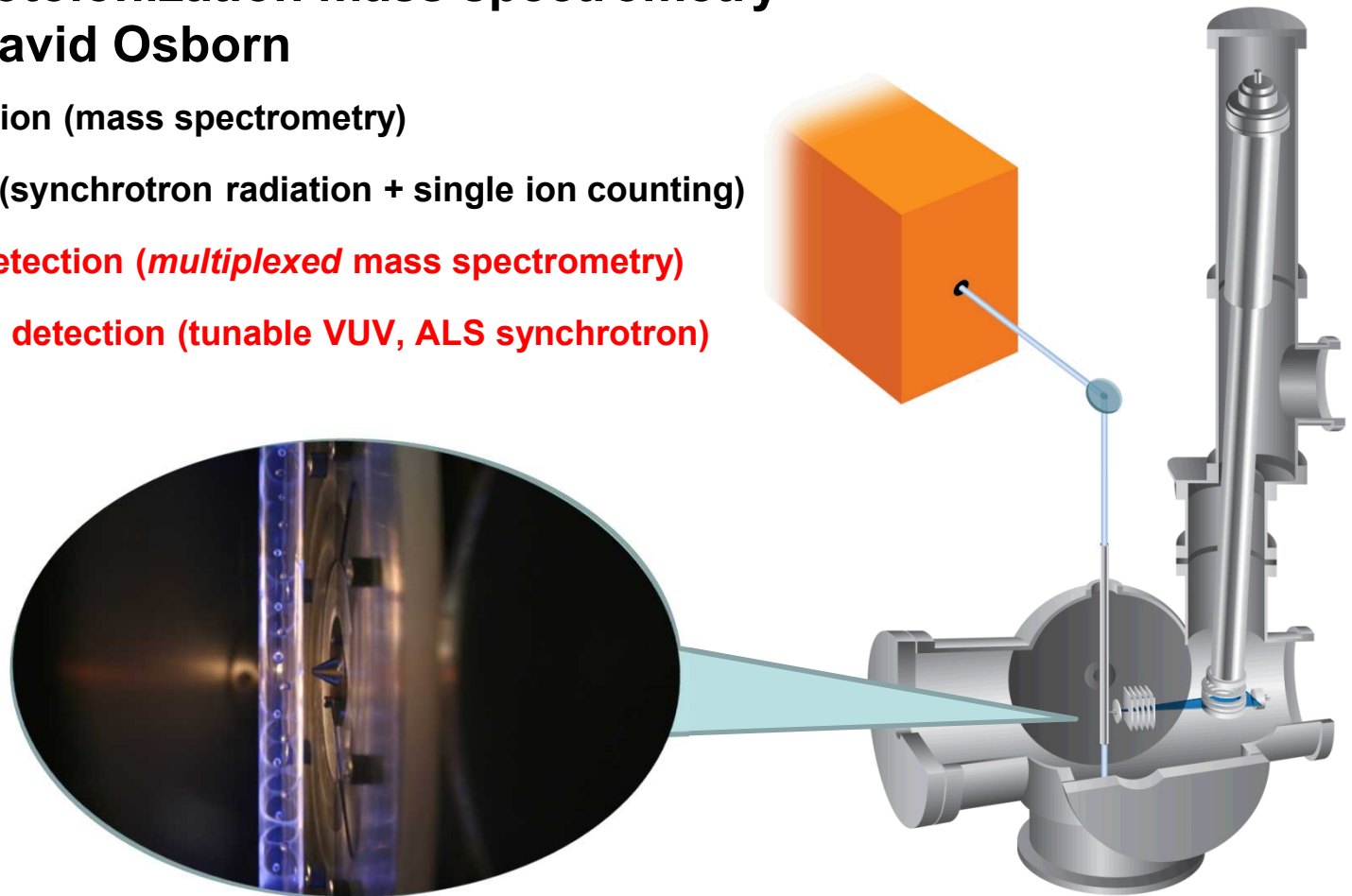
Multiplexed photoionization mass spectrometry (MPIMS) – David Osborn

Universal detection (mass spectrometry)

High sensitivity (synchrotron radiation + single ion counting)

Simultaneous detection (*multiplexed* mass spectrometry)

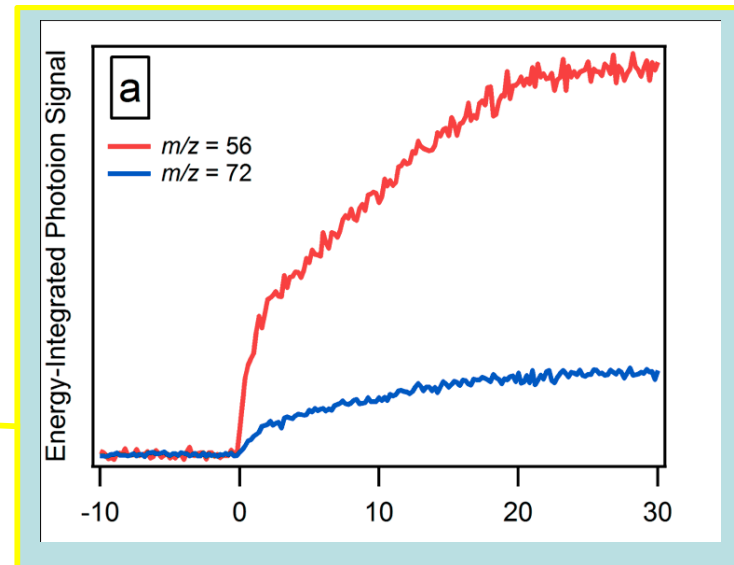
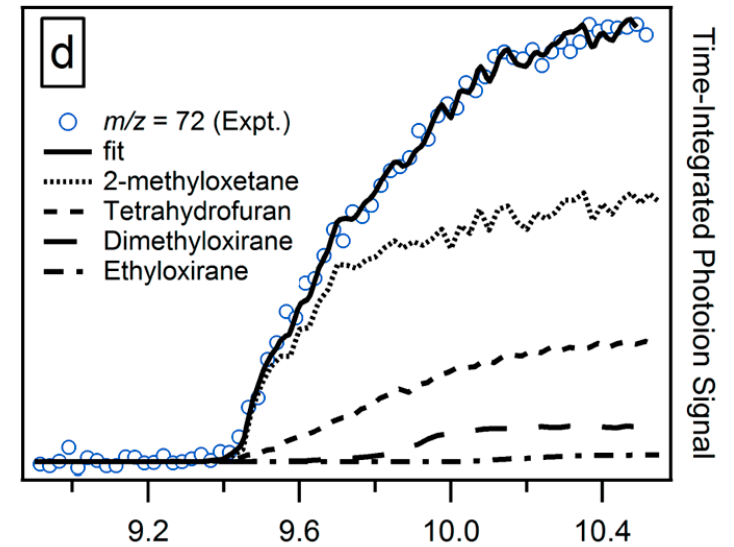
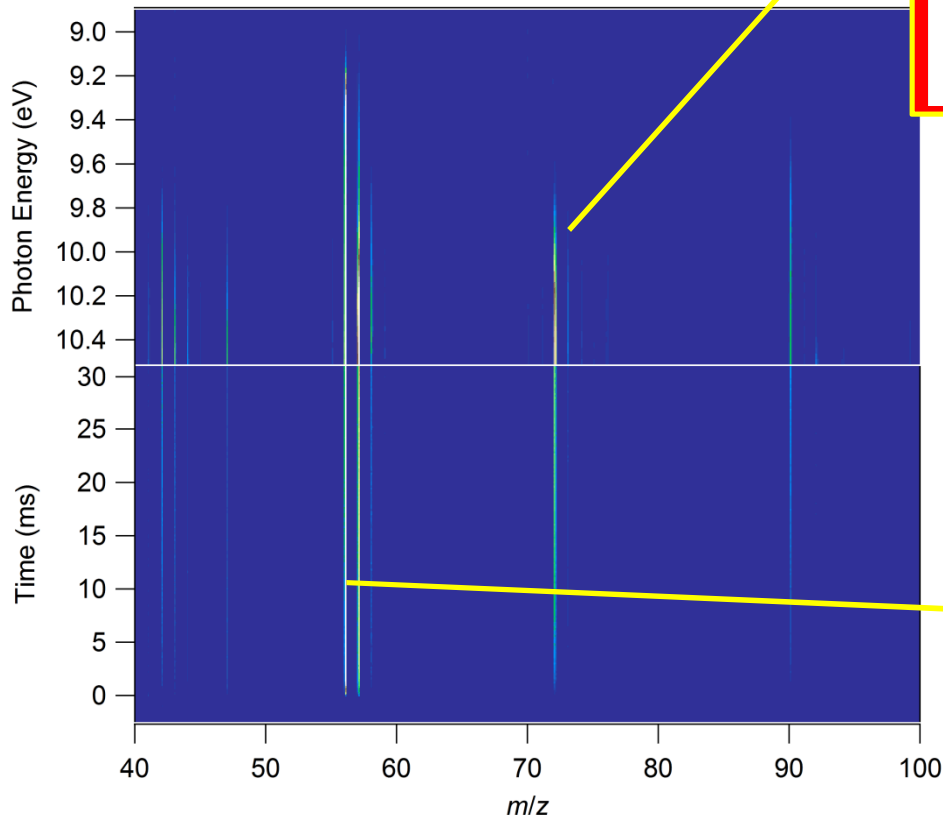
Isomer-resolved detection (tunable VUV, ALS synchrotron)



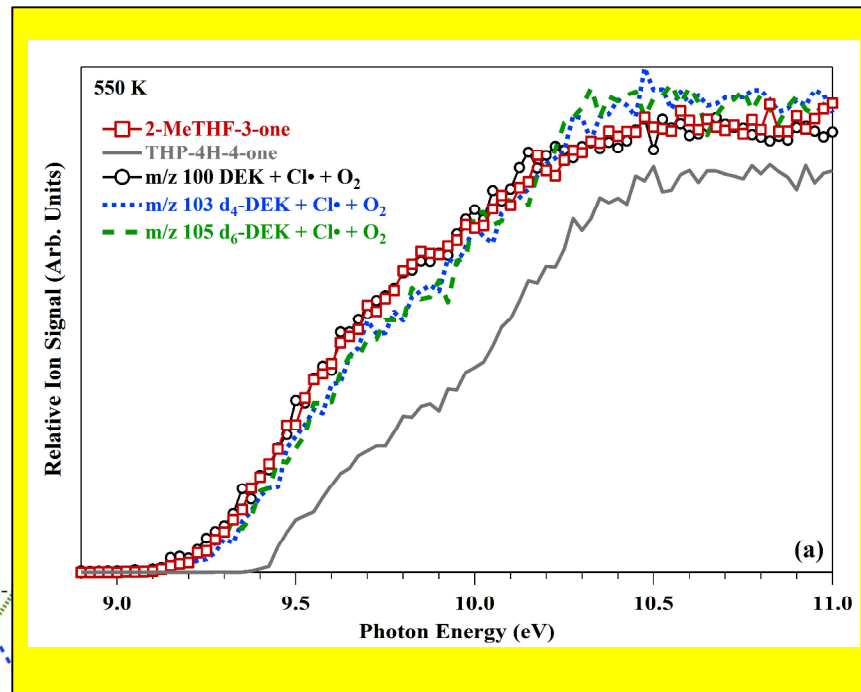
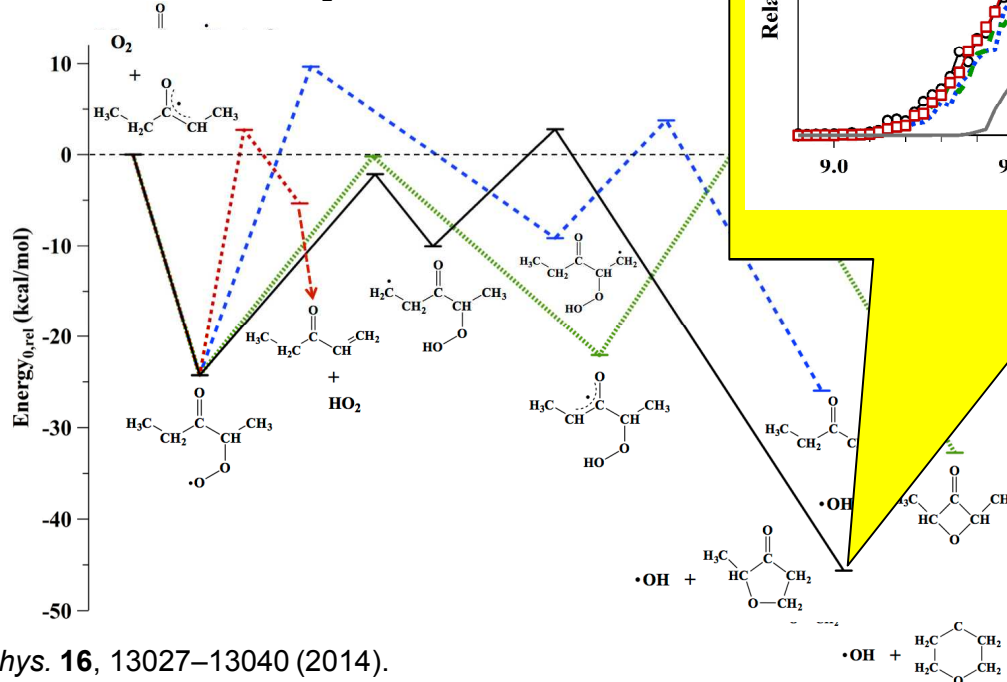
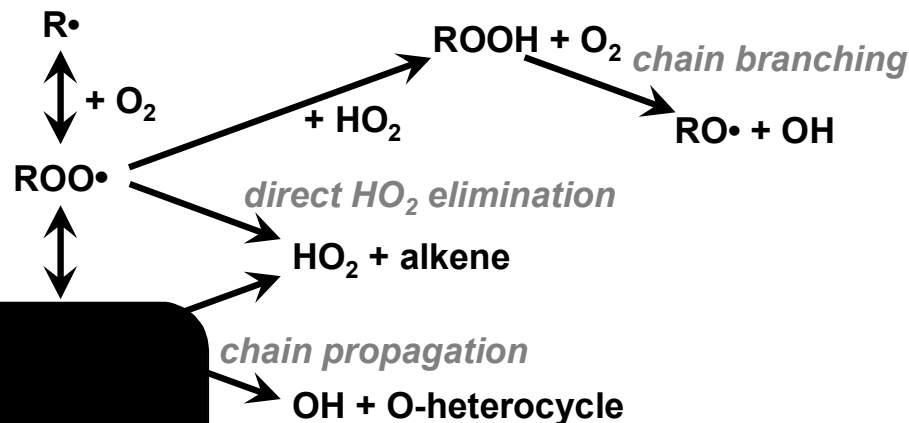
Cl-initiated oxidation

Time behavior of product
formation – prompt and
delayed

Photoionization spectra identify
product isomers



Thermodynamics Affects the Isomerization and Dissociation of QOOH



Resonance stabilization may favor particular QOOH pathway

Adam Scheer

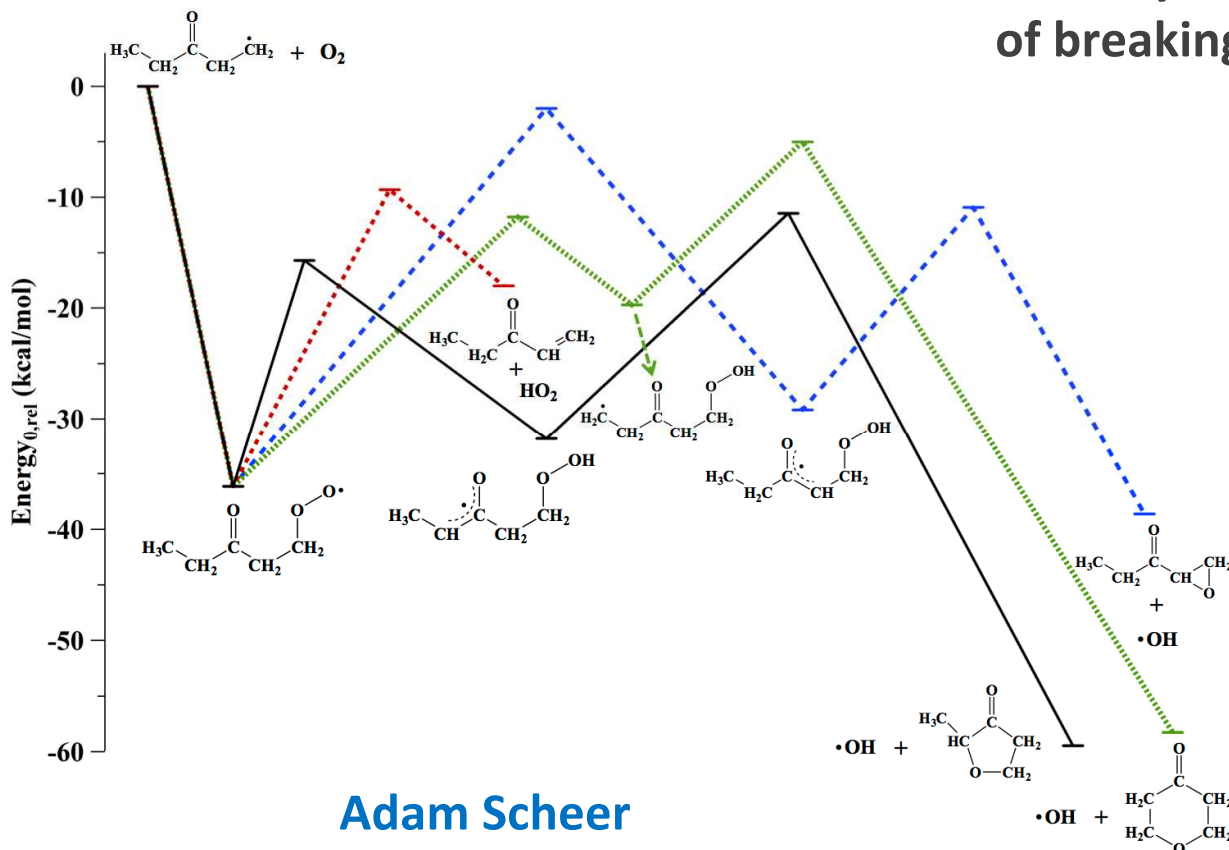
Phys. Chem. Chem. Phys. **16**, 13027–13040 (2014).

Thermodynamics Affects the Isomerization and Dissociation of QOOH

What about systems with unusually stable QOOH?

Ring strain in the transition state for isomerization

Stability of QOOH radical (strength of breaking C-H bond)



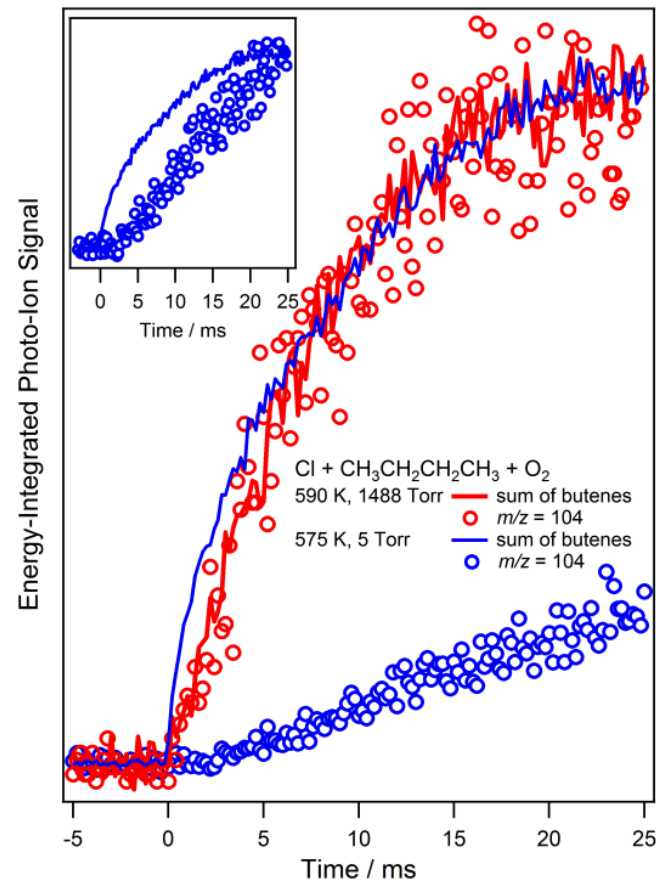
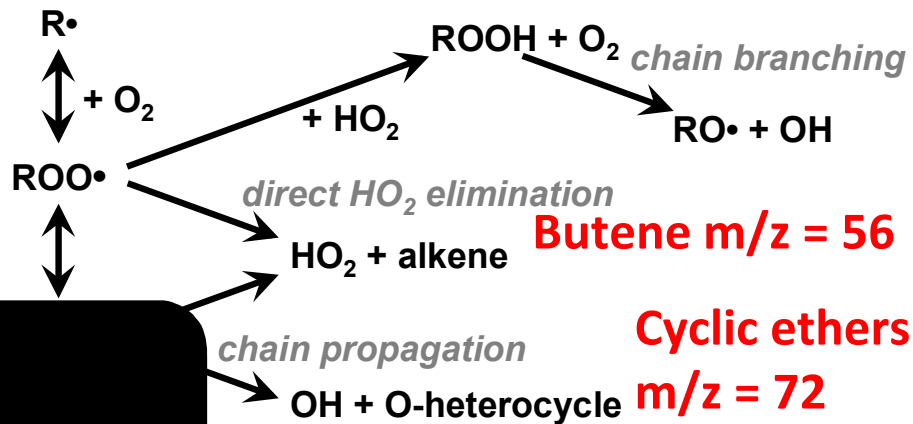
Ketone oxidation has possibility of vinylic resonance stabilization

Resonance-stabilized radicals less reactive with O₂

Resonance stabilization may favor particular QOOH pathway

Photoionization mass spectrometry can also follow the subsequent oxidation steps

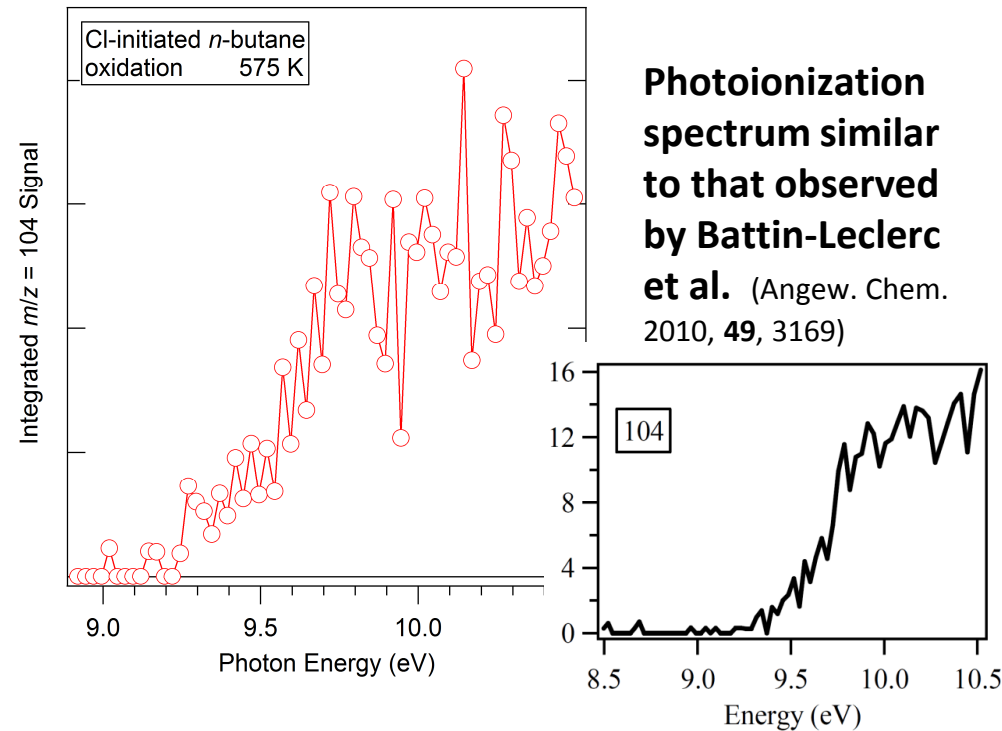
Butyl radical
 $m/z = 57$



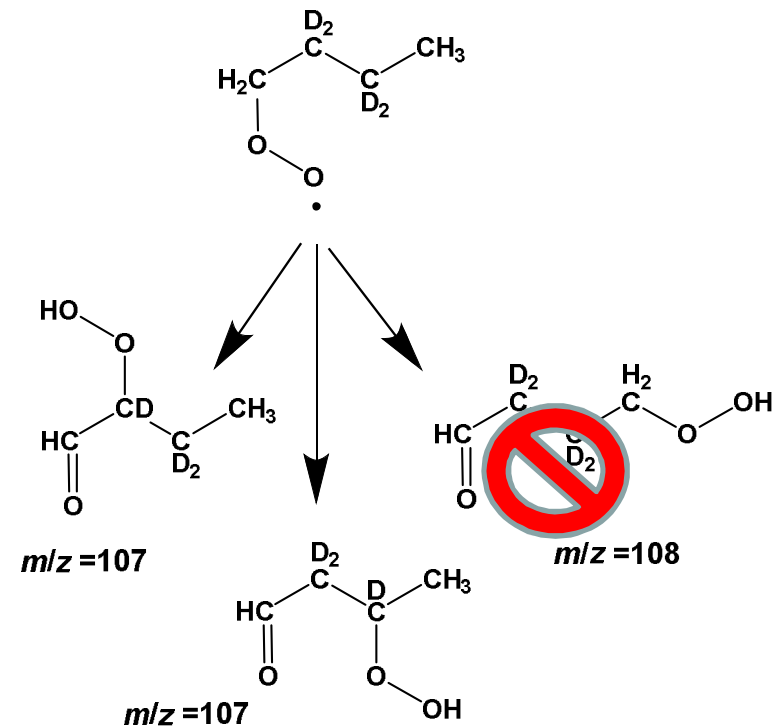
Ketohydroperoxide $m/z = 104$

Arkke Eskola et al. *Proc. Combust. Inst.* in press
doi:10.1016/j.proci.2014.05.011

Observed ketohydroperoxide product at $m/z = 104$ arises from $O_2 + QOOH$ (but which?)



Isotopic labeling further narrows the possible ketohydroperoxide isomers

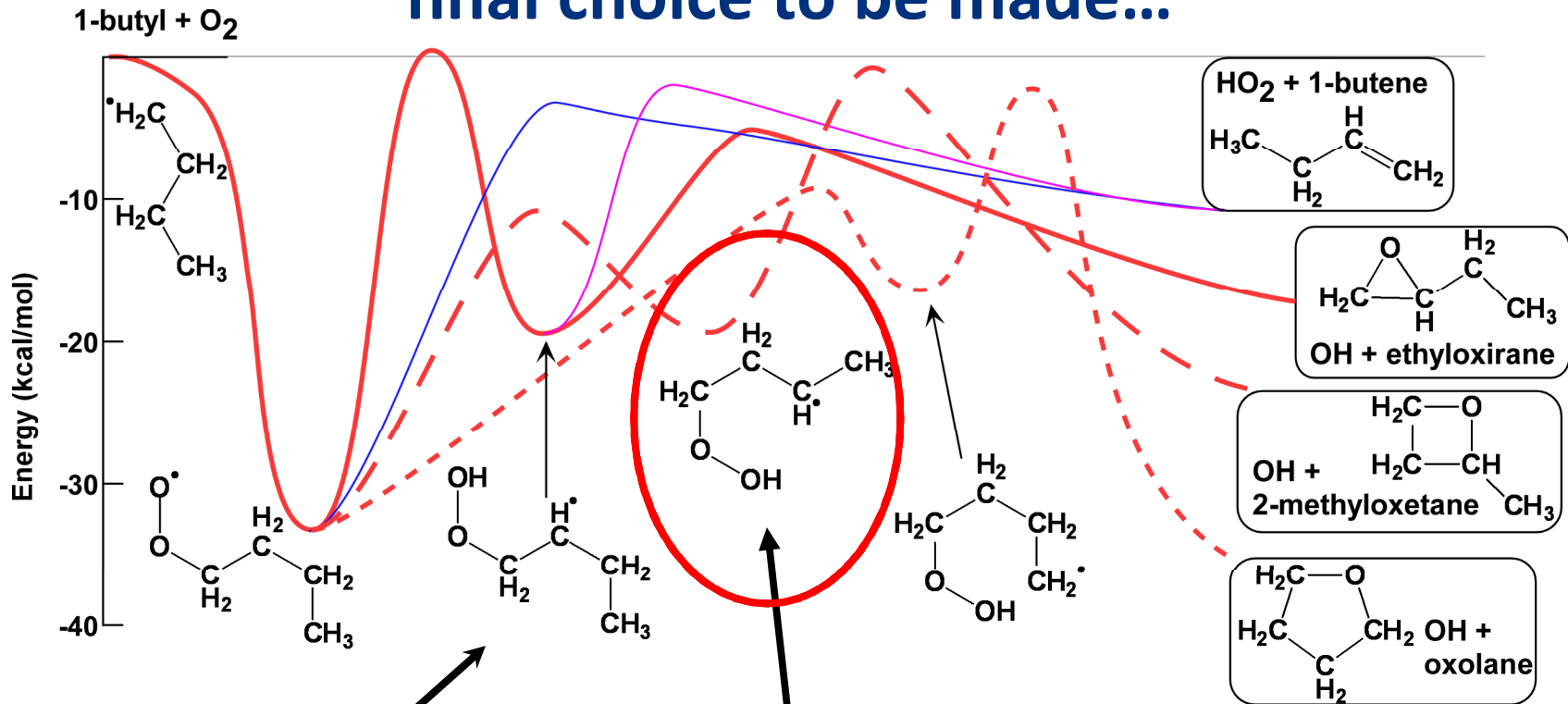


At low pressure, the ketohydroperoxide yield relative to ROO is linear with $[O_2]$

Measurements with specific butyl isomers show ketohydroperoxide from 1-butyl oxidation but **not** from 2-butyl oxidation

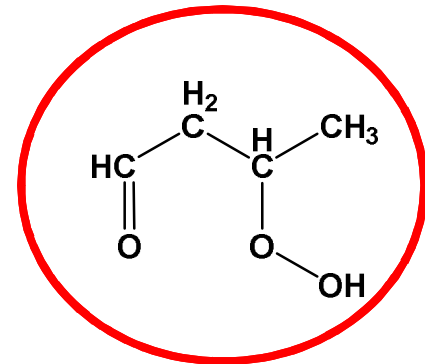
Arkke Eskola

Considering the potential surface allows the final choice to be made...



Difficult to make, rapidly dissociates to bimolecular products

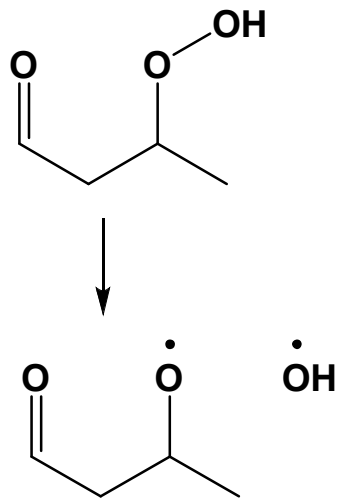
Easy to make, larger barrier to bimolecular products



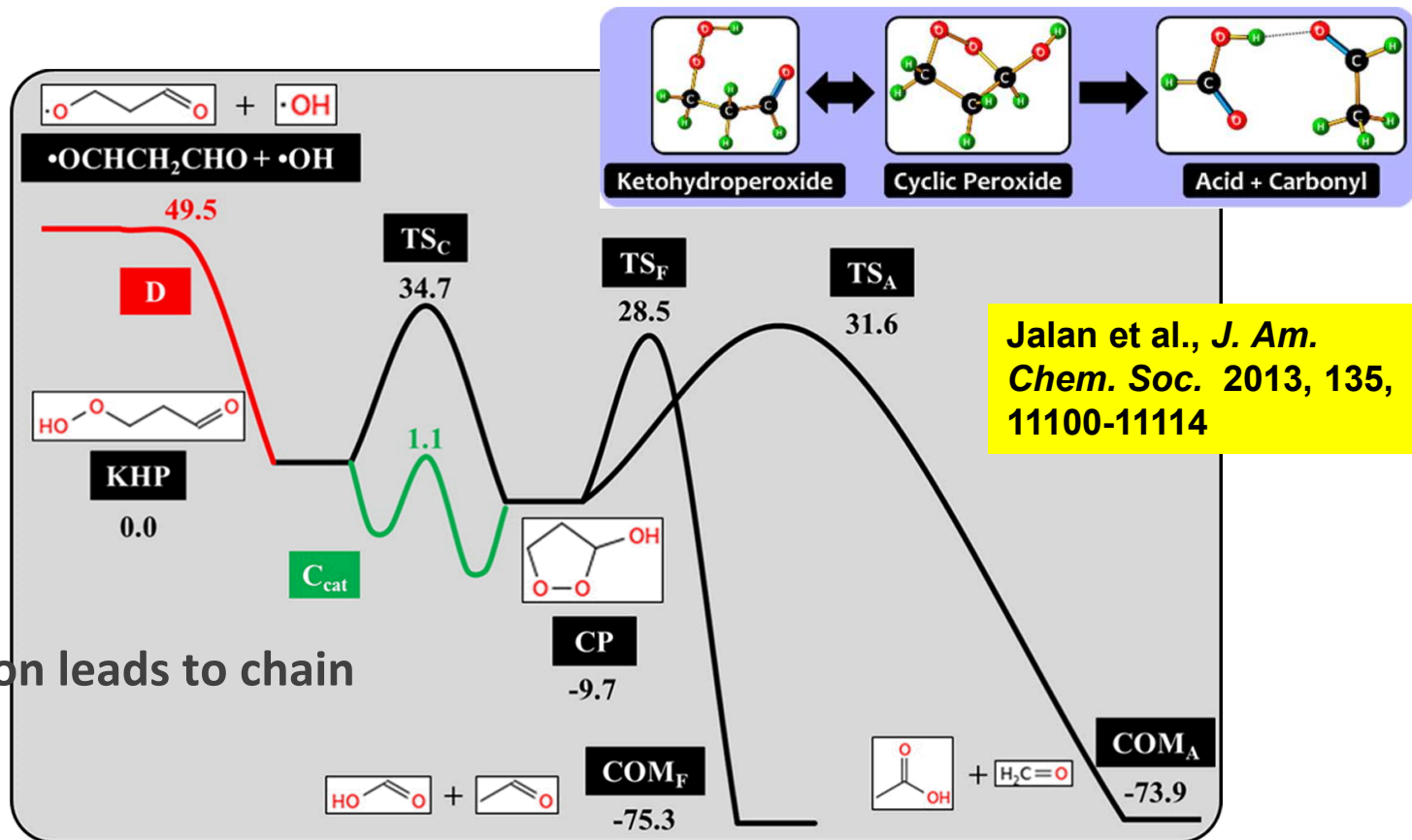
What happens to γ -ketohydroperoxides?

The observed species is a gamma-ketohydroperoxide

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



O-O bond fission leads to chain branching

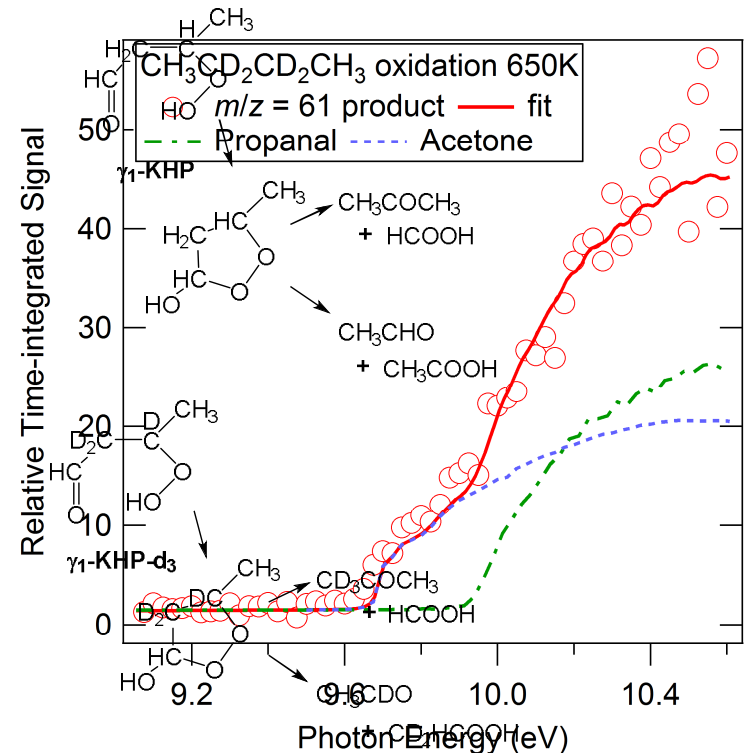
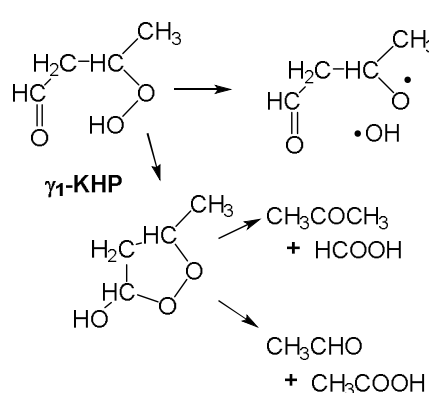
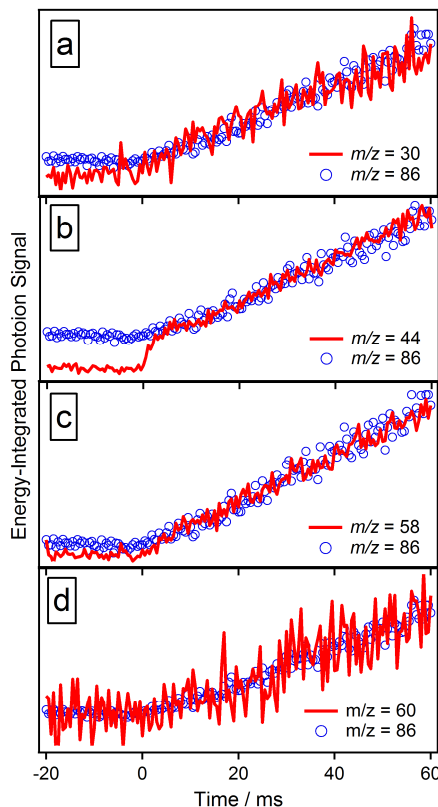


Jalan et al., *J. Am. Chem. Soc.* 2013, 135, 11100-11114

Observed products in Cl-initiated butane oxidation include organic acids

Timescale suggests formation from ketohydroperoxide

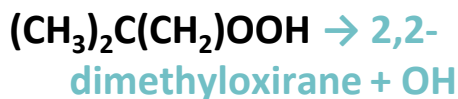
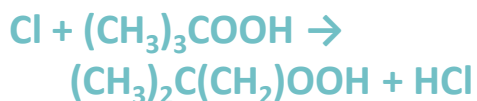
Acetone isotopic signature could signal isomerization



But we still haven't measured the intermediate QOOH steps

Problem is to make enough!

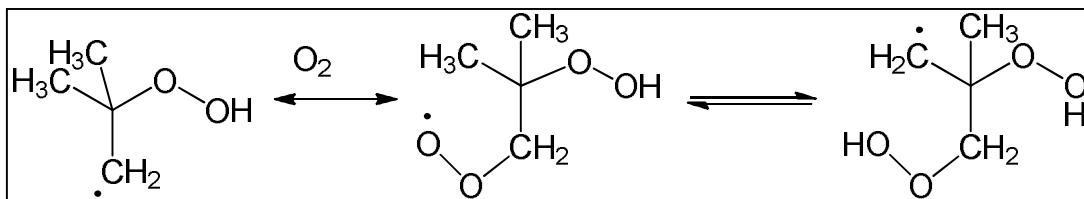
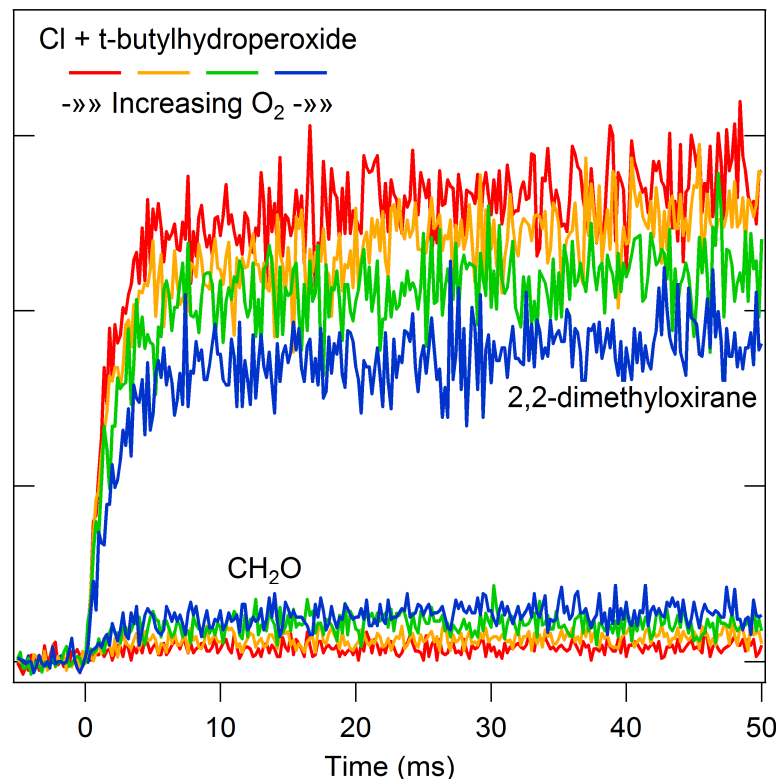
Cl + alkylhydroperoxide reactions make QOOH: e.g.,



Reaction with O_2 competes with dissociation – forms other products

Relative rate can give *direct* measurements of QOOH reactions

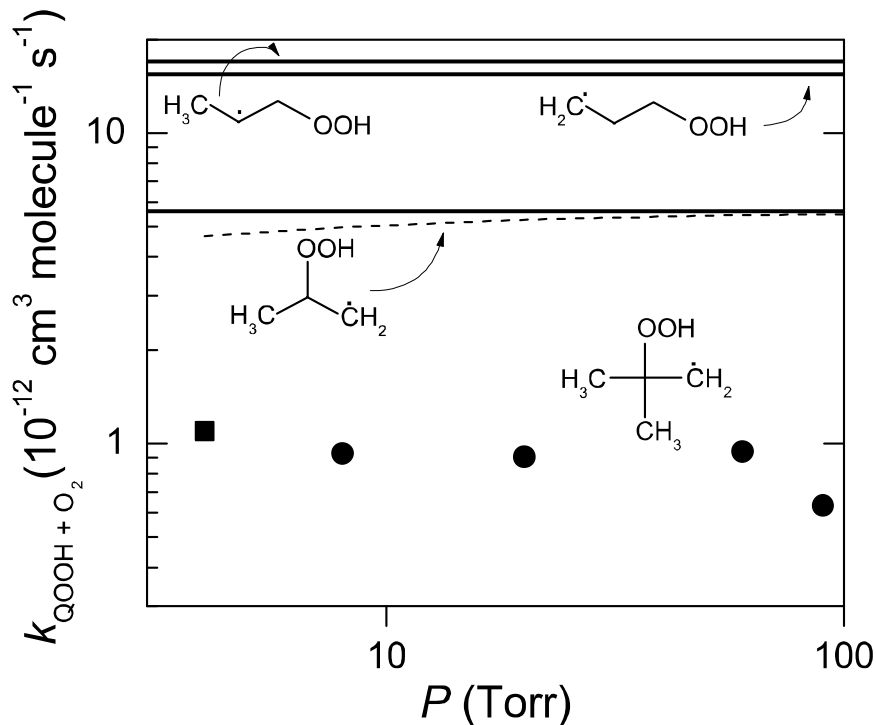
Judit Zádor



Measurement of OH directly probes rate constant for QOOH reactions

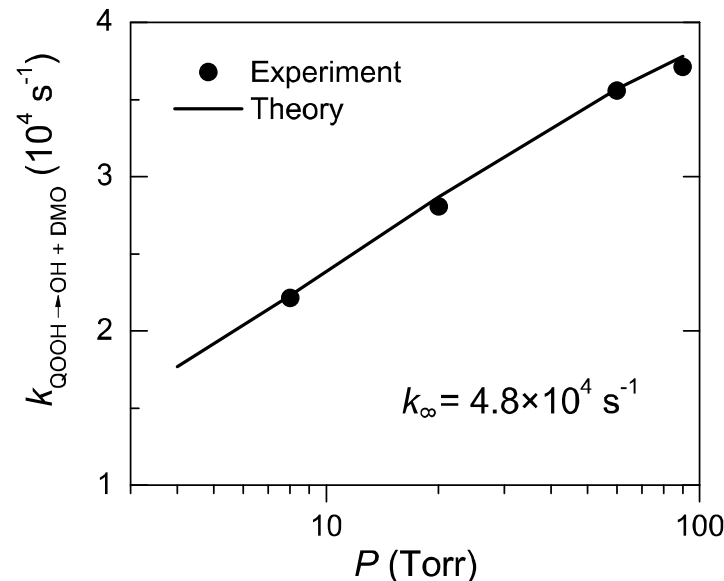
Haifeng Huang

C. F. Goldsmith, W. H. Green, and S. J. Klippenstein,
J. Phys. Chem A, 2012, 116, 3325–3346



unknowns w/o O_2

- ① $k_{\text{QOOH} \rightarrow \text{OH}}$
- ② chain chlorination (k_{cl})
- ③ new unknowns w/ O_2 , same conditions
- ④ loss to ROO in Cl+TBHP (α)
- ⑤ $k_{\text{QOOH} + \text{O}_2}$

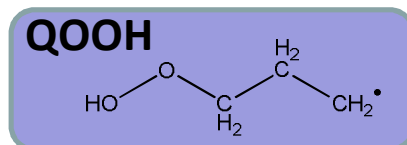
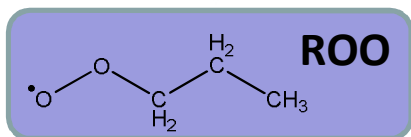


Fit all data -- use competition between
QOOH dissociation and addition of O_2 to
get $k_{\text{QOOH} + \text{O}_2}$ as well

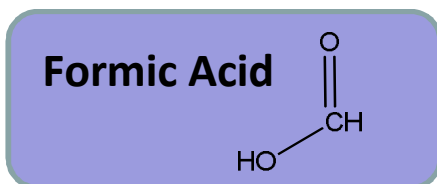
Zador, Huang et al., Phys. Chem. Chem. Phys. **15**, 10753-10760 (2013)

That's pretty close – Is there some way we can do even better?

What are these “intermediates” again?

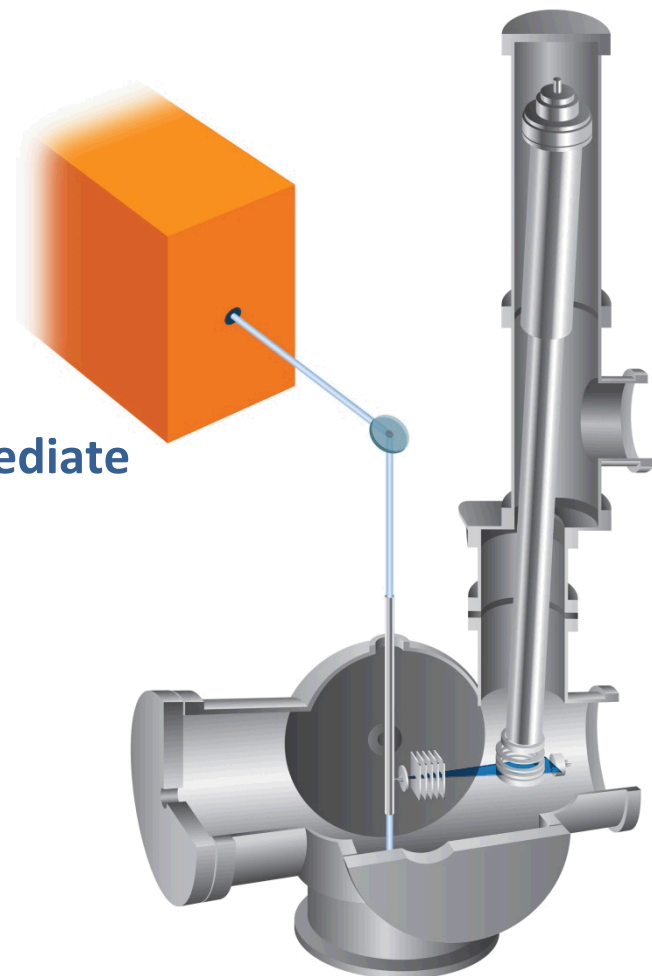


QOOH is an isomer of the more stable ROO intermediate

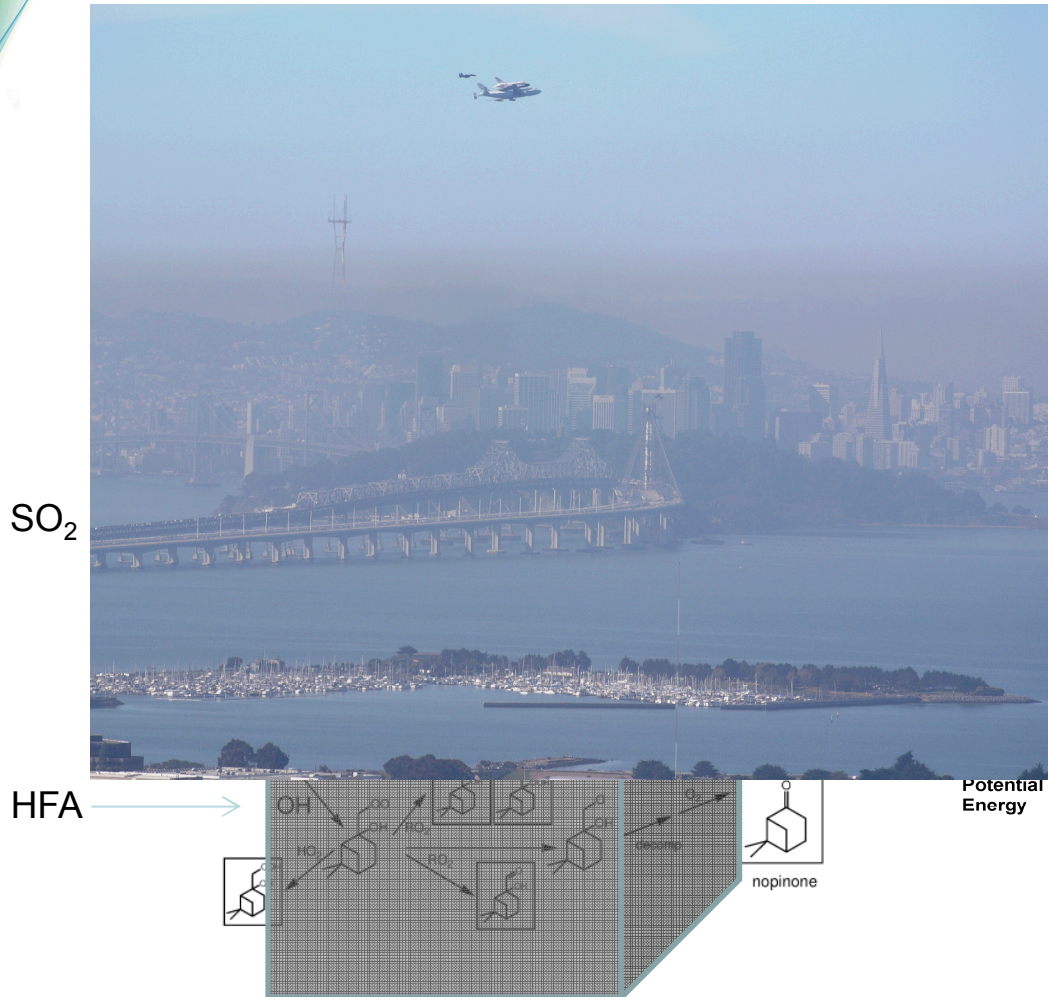


Criegee intermediates are isomers of more stable tropospheric species

But we have a machine that can resolve isomeric chemistry!



Other systems have their own black boxes...

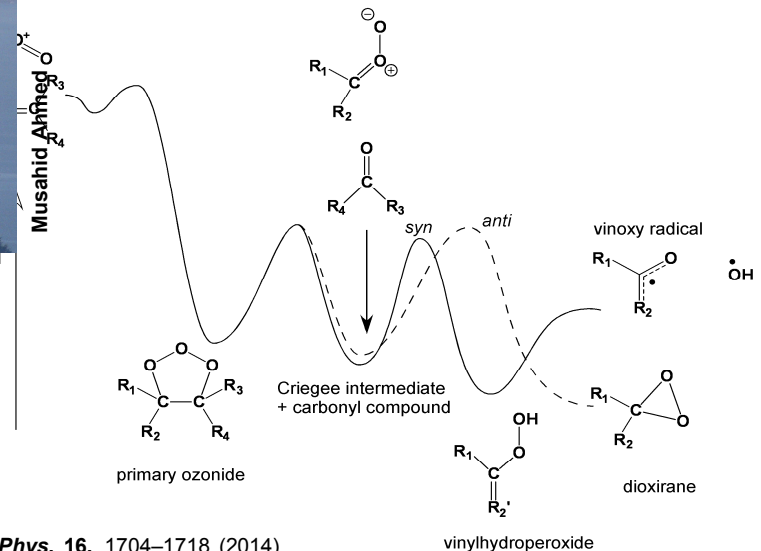


Atmos. Chem. Phys. Discuss., 4, 2905–2948, 2004

Modeling ozonolysis has long been the
to determine reactions of Criegee
intermediates

Measure products of ozonolysis and
compare to theory and models

- Add scavengers that are thought to remove Criegee intermediates, see what happens to stable product yields
- Lots of other intermediates possible!



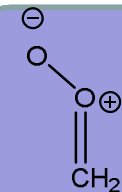
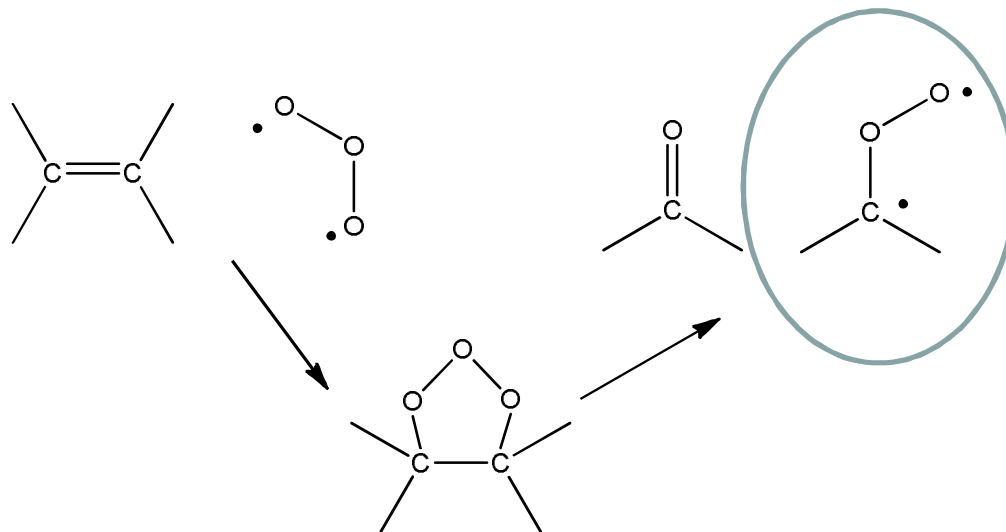
Phys.Chem.Chem.Phys. 16,, 1704–1718 (2014)

Kinetic Models for Oxidation Chemistry Require Knowing Reactions of “Intermediates”

Ozonolysis is a major component in tropospheric removal of hydrocarbons – makes carbonyl oxides, often known as Criegee intermediates

Criegee intermediates are *isomers* of more stable products, organic acids or esters

Until 2012, no one had directly measured a Criegee reaction



Criegee Intermediate



Formic Acid

Tunable synchrotron photoionization *can* identify novel isomeric intermediates

Carl Percival, Dudley Shallcross

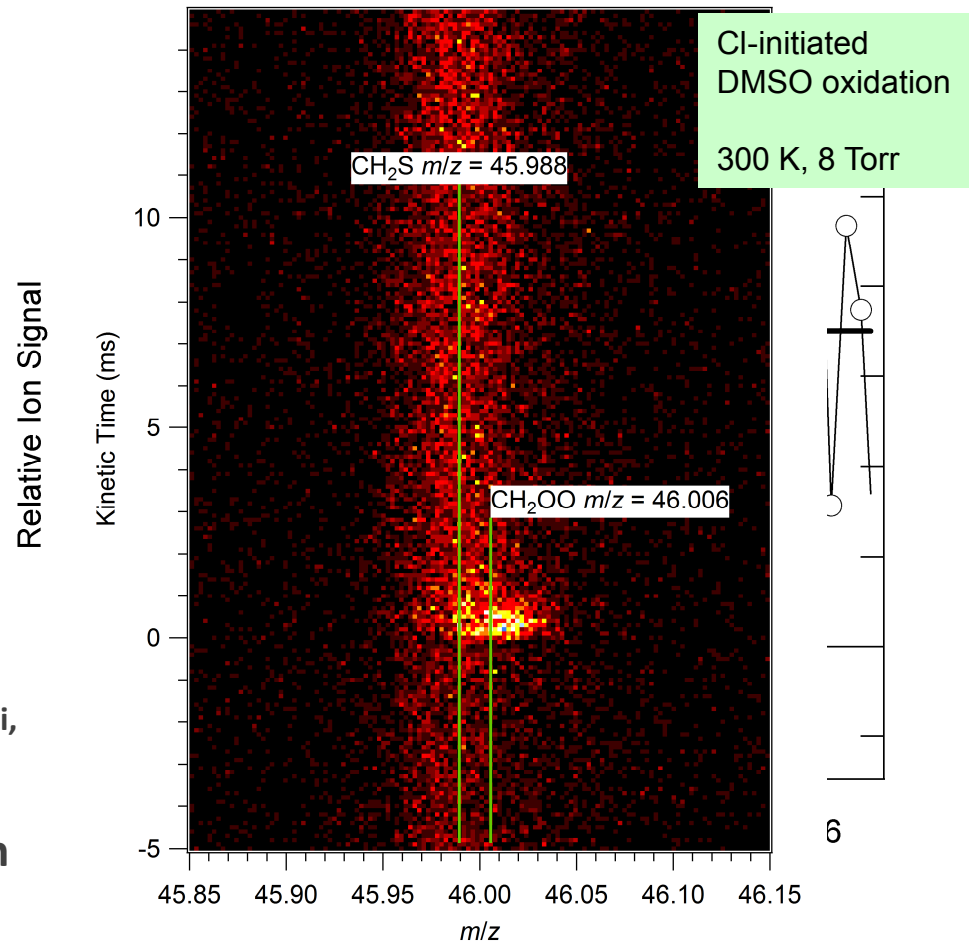
Ozonolysis of alkenes proceeds via a carbonyl oxide intermediate (“Criegee intermediate”)

They are important tropospheric reactants but only indirect measurements existed

Problem is to make enough

Dimethyl Sulfoxide (DMSO) oxidation may form CH_2OO (Asatryan and Bozzelli, PCCP 10, 1769 (2008))

Time-of-flight can resolve CH_2S from CH_2O



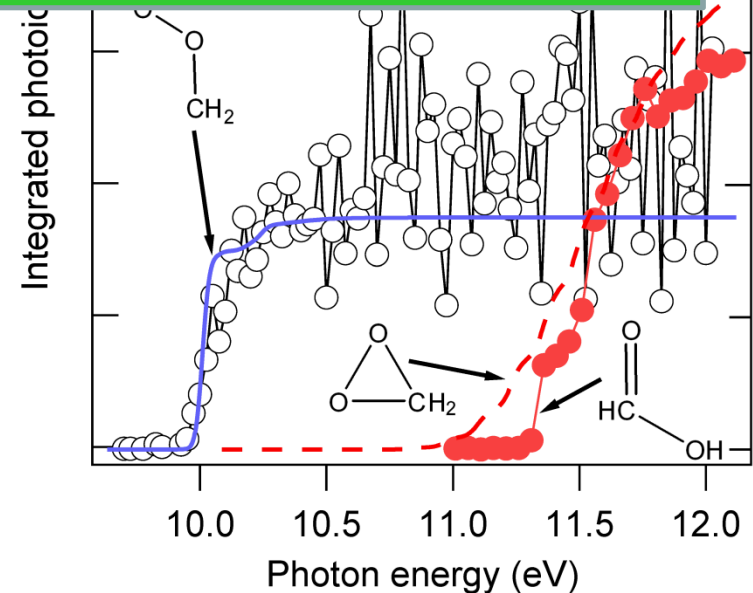
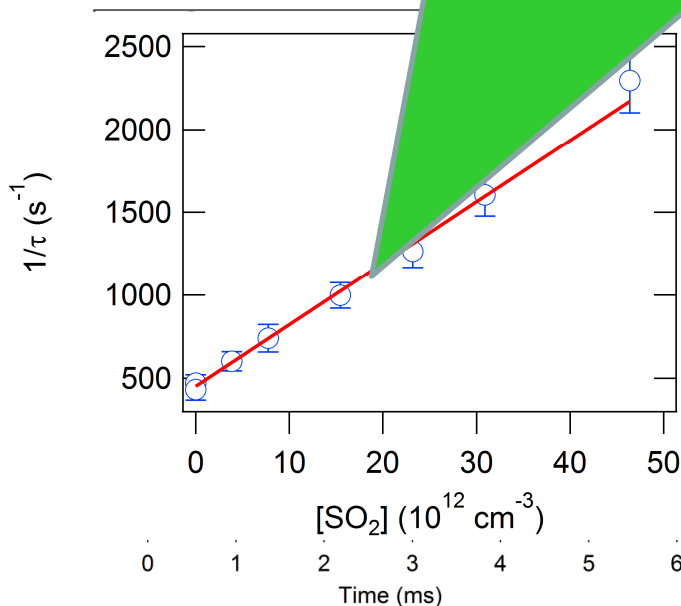
Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008)

Detection Is One Thing, Kinetics Is Another: Make More Criegee to Measure Reactions

- Arkke Es
1416 (2006)
made I a
Criegee i
Can mak
reaction
species

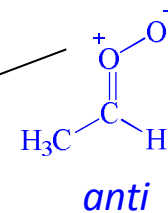
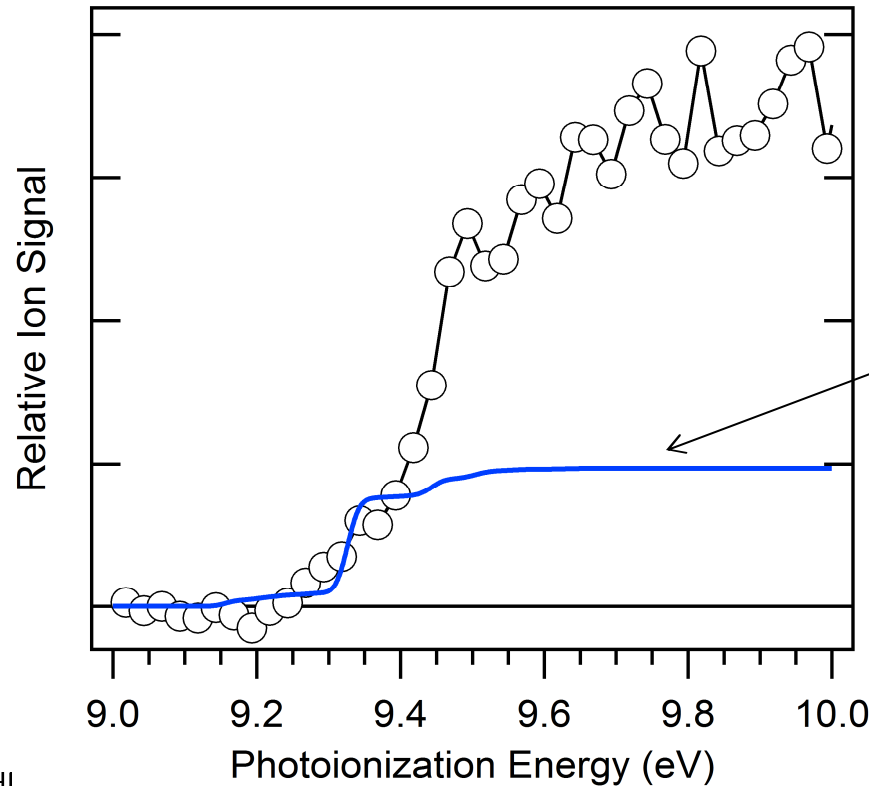
Reaction of CH_2OO with NO_2 is **50 times** what is used in models
If other Criegee intermediates react similarly, Criegee reactions are significant NO_3 source

Reaction of CH_2OO with SO_2 is up to **10 000 times** values inferred from ozonolysis modeling
If other Criegee intermediates react similarly, Criegee reactions are major SO_2 oxidant



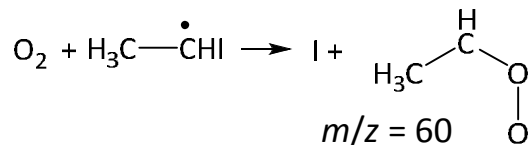
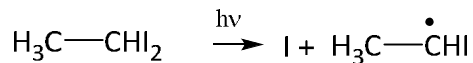
Welz, Savee, et al., *Science* **335**, 204 (2012)

Can also make larger Criegee Intermediates like acetaldehyde oxide (CH_3CHOO)

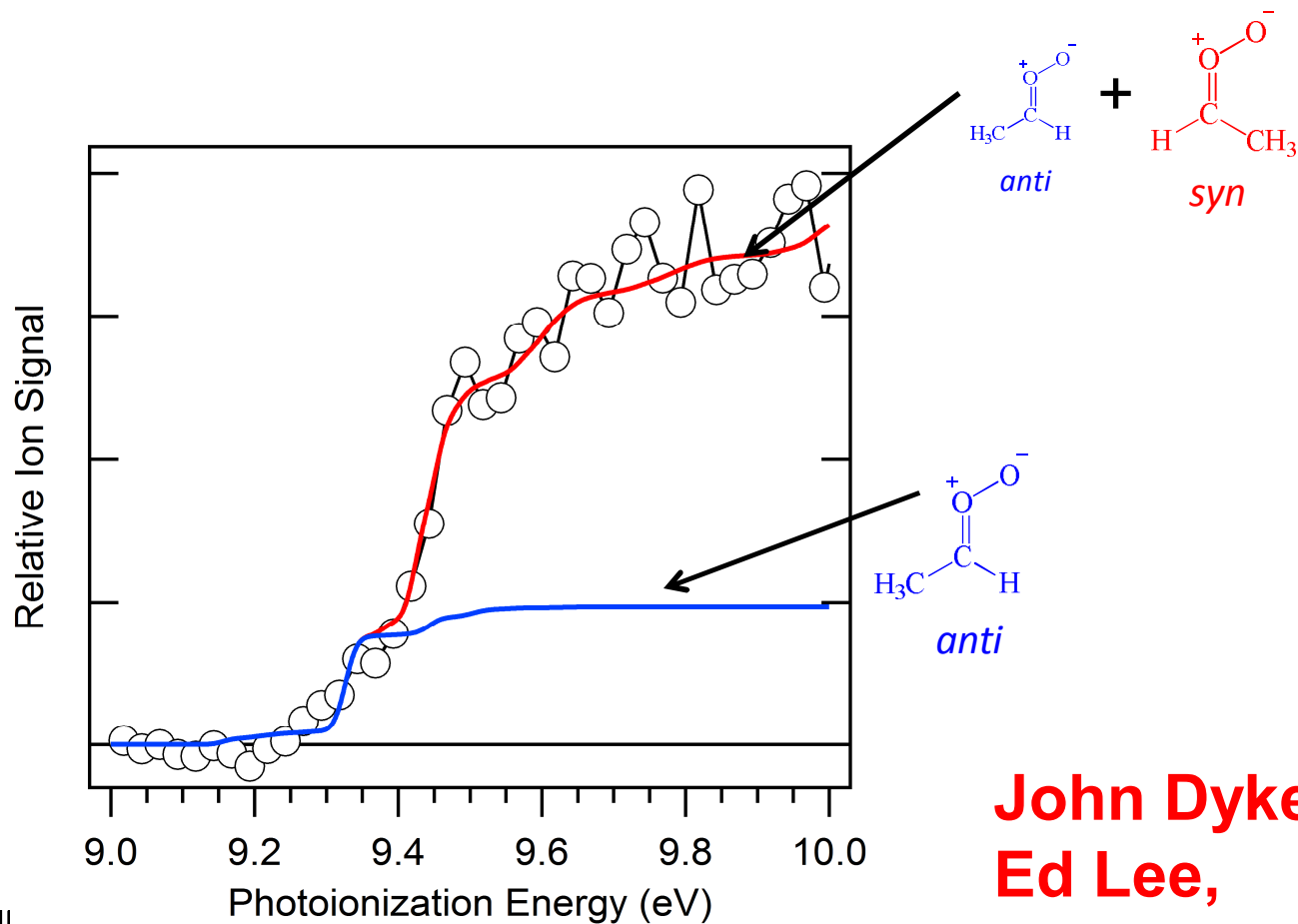


**John Dyke,
Ed Lee,
Daniel Mok**

Similar strategy:

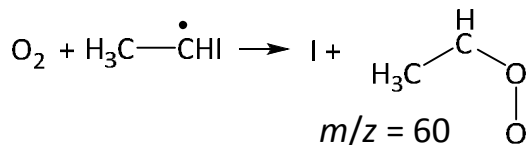
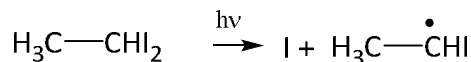


Can also make larger Criegee Intermediates like acetaldehyde oxide (CH_3CHOO)

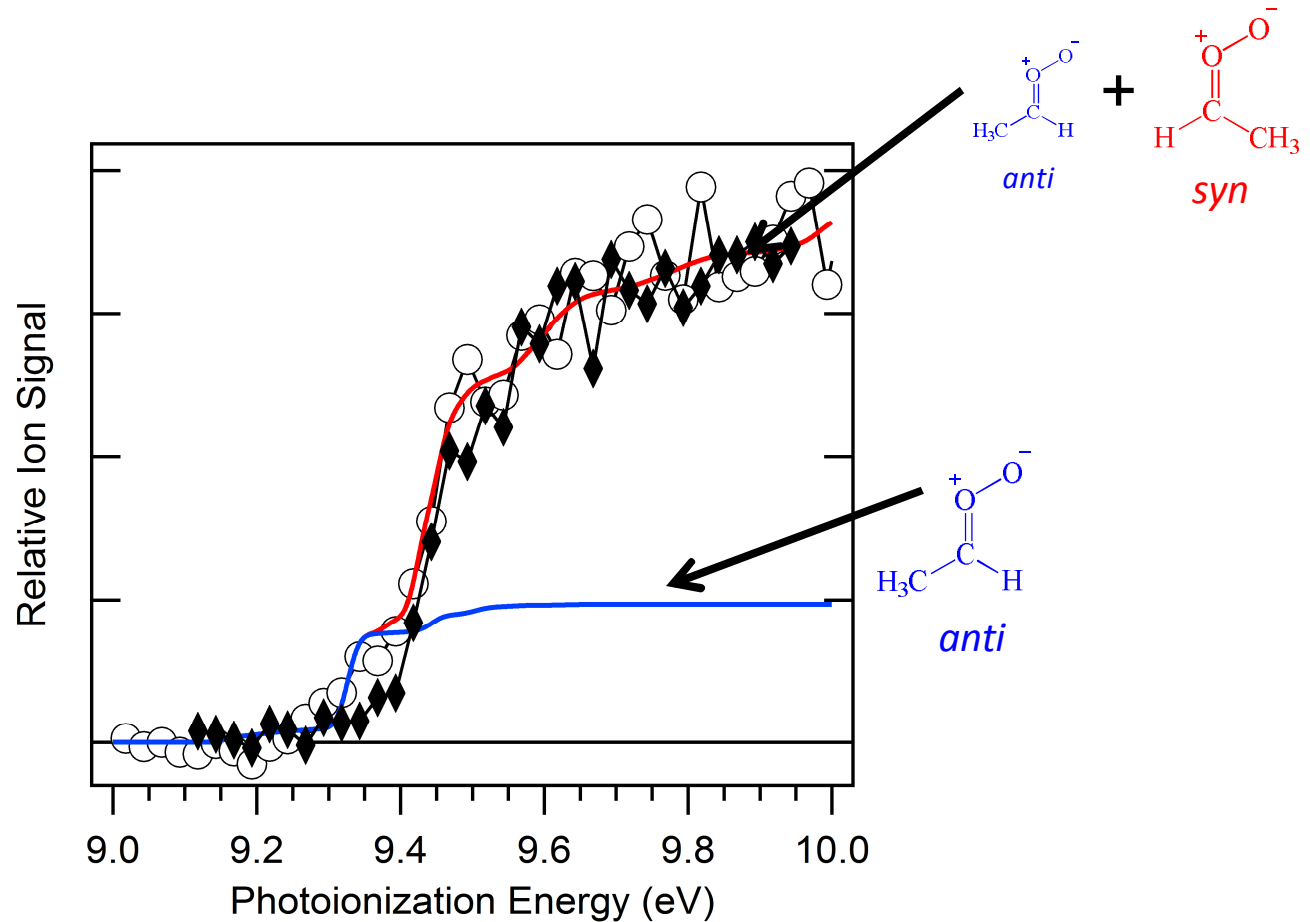


**John Dyke,
Ed Lee,
Daniel Mok**

Similar strategy:



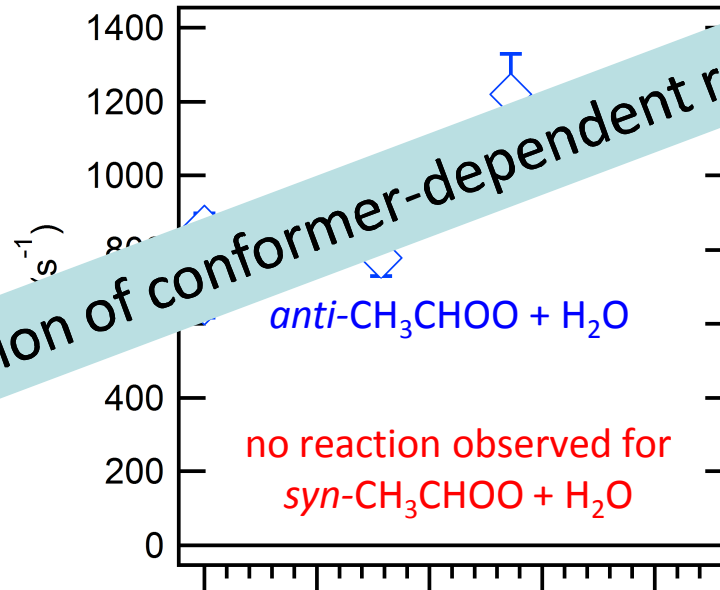
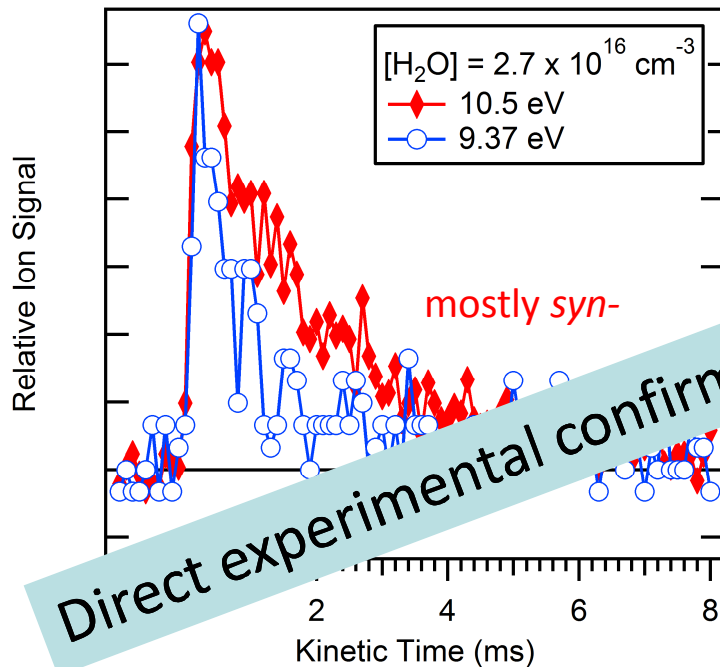
Addition of water preferably removes the *anti*- conformer of CH_3CHOO



Conformer-dependent reactivity!

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

We measured the rate coefficient of *anti*-CH₃CHOO with H₂O



Direct experimental confirmation of conformer-dependent reactivity

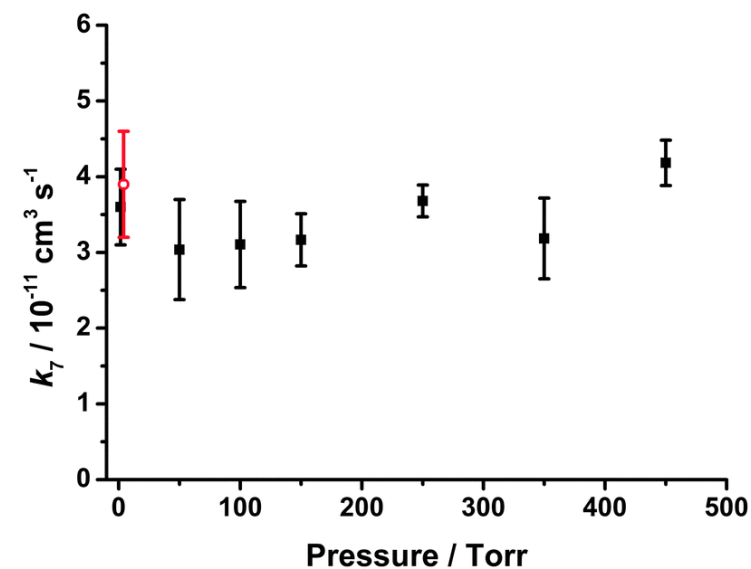
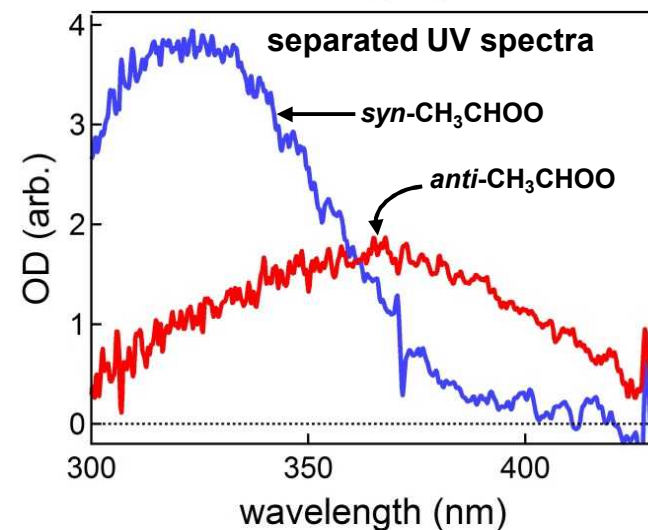
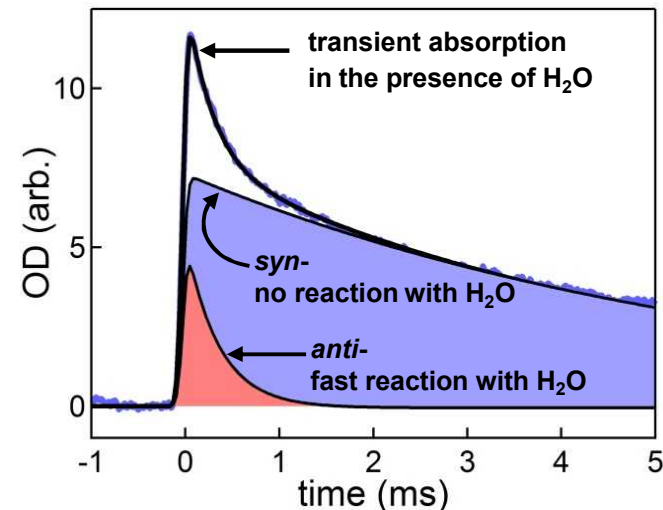
$$k(\text{anti-CH}_3\text{CHOO} + \text{H}_2\text{O}) = (1.0 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \rightarrow$$

$$k(\text{syn-CH}_3\text{CHOO} + \text{H}_2\text{O}) \leq 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$$

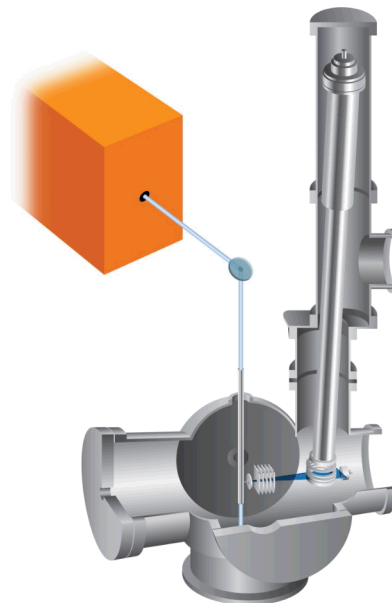
- A factor of 10 lower than predictions for the high-pressure limit from Anglada et al. (Phys. Chem. Chem. Phys. 13, 13034 (2011)), but larger than other calculations
- Substantially larger than prediction for other Criegee Intermediates

What are the next steps?

- We are just beginning to understand how Criegee intermediates react
 - Need to understand larger Criegee molecules
 - Need to understand more reactions
 - Need to understand reactions at different conditions, measure with different methods
 - Really need to know *products* of reactions

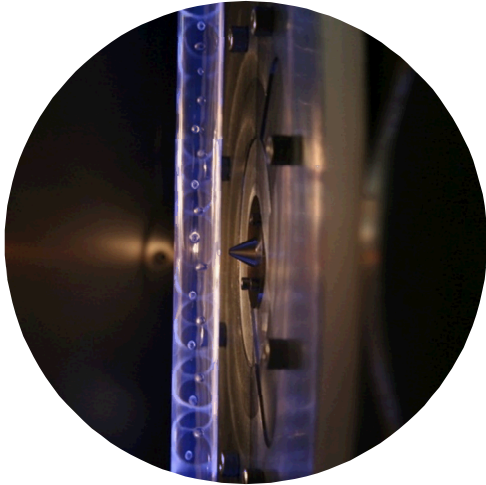


Stone *et al.* *Phys. Chem. Chem. Phys.* **16**, 1139-1149 (2014)

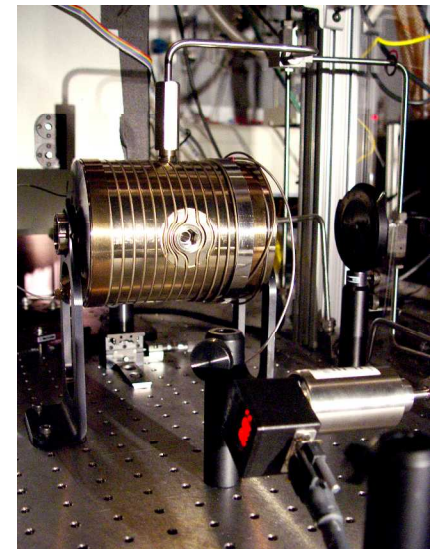
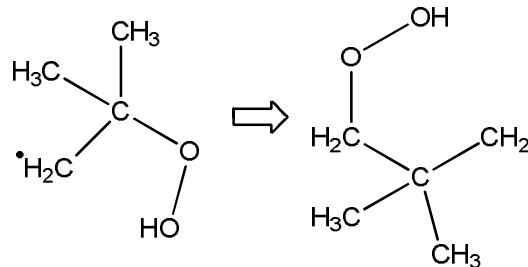


Leonid Sheps, Ashley M. Scully, Kendrew Au
Phys. Chem. Chem. Phys. **16**, 26701-26706

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



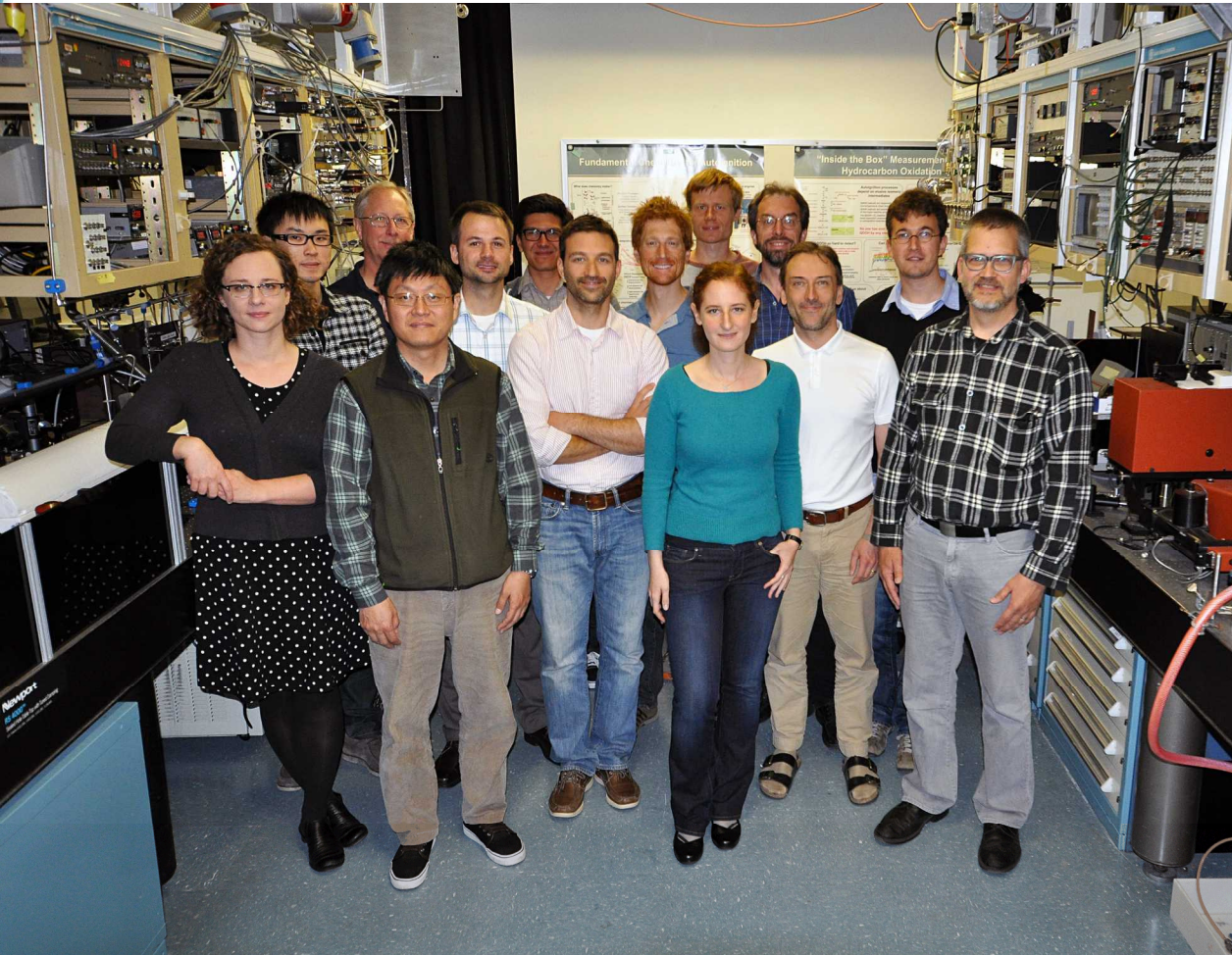
- Begin to investigate conditions more like troposphere and real combustion devices



- 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, CAT, Lenny Sheps
Ewa Papajak, Ivan Antonov, Arkke Eskola, Haifeng Huang,
Brandon Rotavera, John Savee, Adam Scheer, Oliver Welz
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Carl Percival (Manchester) Dudley Shallcross (Bristol)

Stephen Klippenstein (Argonne)



Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the United States Department of Energy (DOE).

Laboratory-Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

Butane oxidation studies have been funded as part of the Saudi Aramco “Kinetics Cluster of Excellence” under a cooperative research and development agreement (CRADA) between Sandia National Laboratories and Aramco Services Company, a U.S.-based subsidiary of Saudi Aramco, the state-owned national oil company of Saudi Arabia (CRADA SC10/01773.00, ASC Contract No. 6500007287).

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the DOE under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.



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