SAND2014-16279PE

Working Inside the Box

2014 Polanyi Lecture Szeged, Hungary

Craig A. Taatjes

Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551

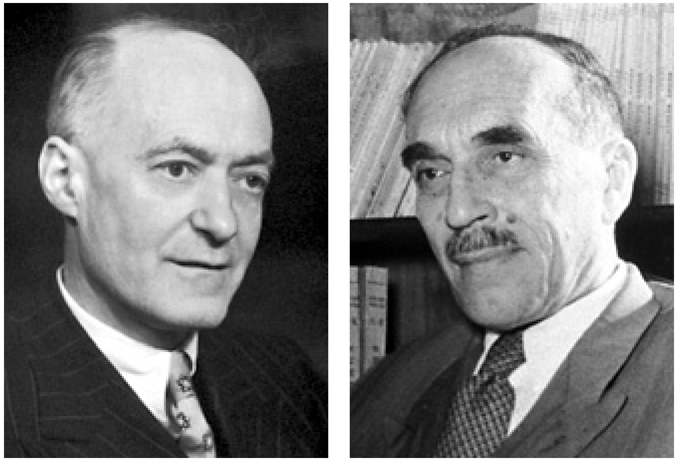
How Does Someone Get the Polanyi Medal?

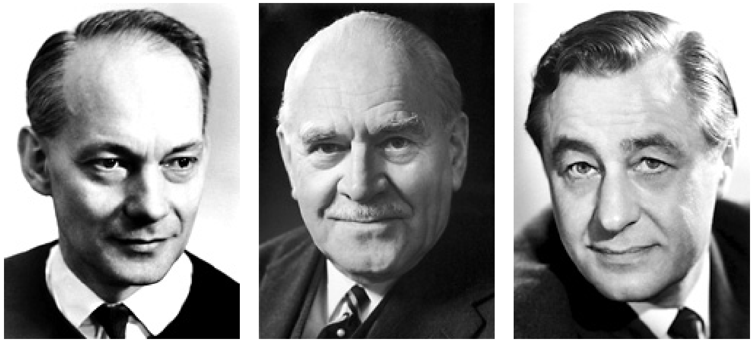
- "someone who has made outstanding contributions to the field of Gas Kinetics"
- What is Gas Kinetics and what is it good for?

- When I was in graduate school –
- goal was understanding details of how molecules interact

- Postdoctoral work – controlling orientation of molecules
- Finer detail and greater control?
- "Dynamics" or "Kinetics"?

There are more frontiers than one …





1967

1986

1995

14	1996	Leeds, UK

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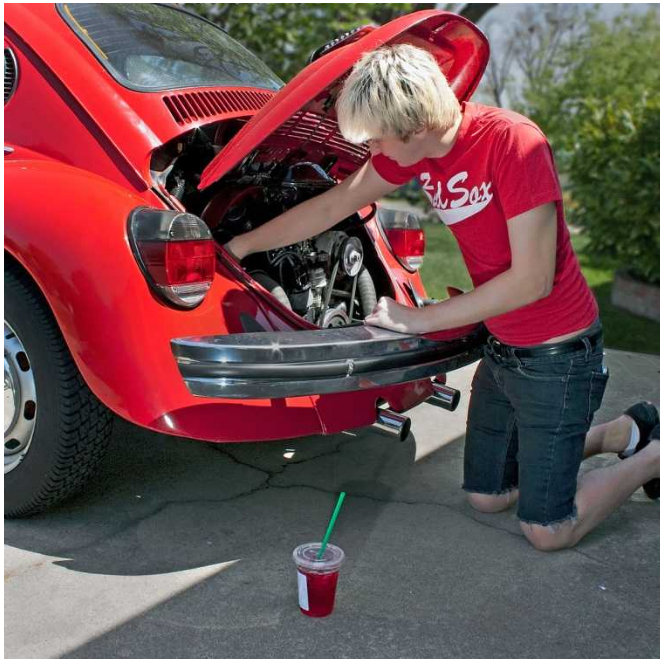
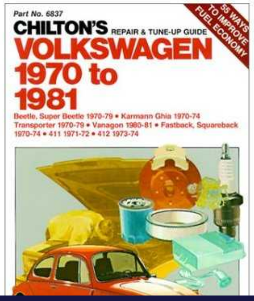
Why do people do chemical kinetic modeling?



Robert Couse-Baker



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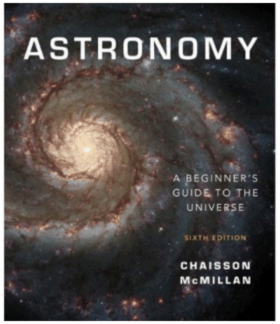
55 WAYS TO IMPROVE FUEL ECONOMY



ASTRONOMY
A BEGINNER'S GUIDE TO THE UNIVERSE
SIXTH EDITION
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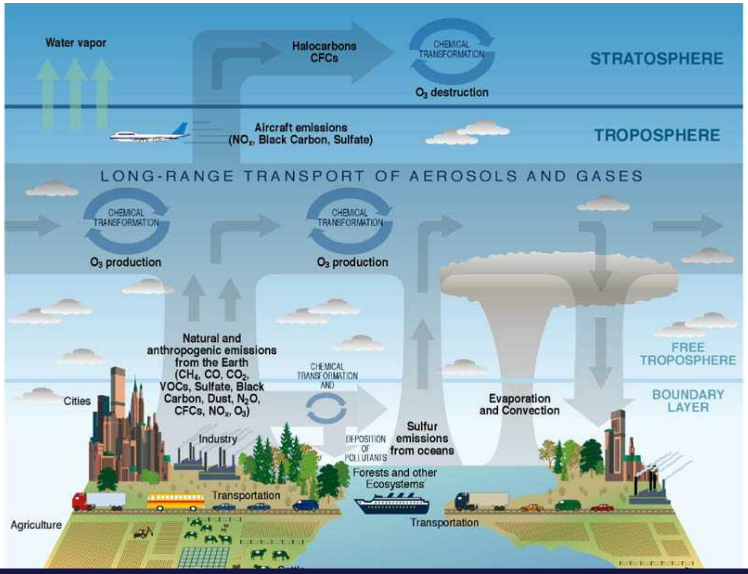


ATE CHANGE SCIENCE PROGRAM OFFICE

?

Predict what will happen as the boundary conditions are changed

What will make a model *predictive*?

6. Wechselgetriebe für vier Geschwindigkeiten und Rücklauf:

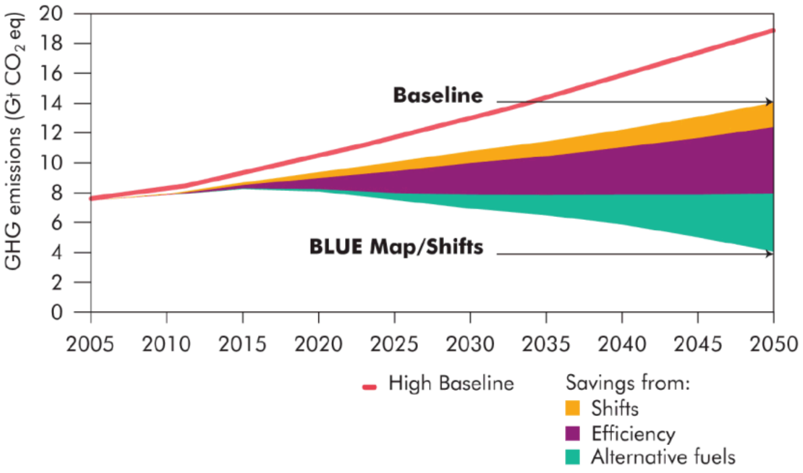
M Angriff der Motorwelle, *C* Angriff der Cardanwelle; Geschwindigkeitsräder *I*, *II*, *III*, *IV*, durch Verschiebung mit *1*, *2*, *3*, *4* in Eingriff gebracht; Rücklaufrad *R*, durch Linksschiebung mit *IV* und *4* in Eingriff gebracht.

Need to understand the *intermediate* steps

Hydrocarbon Oxidation Powers Our Society and Is a Key Process in Earth's Atmosphere

Combustion produces ~ 85% of the world's energy

- Hydrocarbon combustion provides nearly all of the energy for transportation
- Clean, efficient combustion is part of global energy strategies



Musahid Ahmed

Tropospheric Chemistry:

- Oxidation "cleanses" the troposphere
- Oxidation also produces aerosols, smog, other unwanted byproducts

Tropospheric and Engine Oxidation Processes Both Run on Radical Chain Chemistry

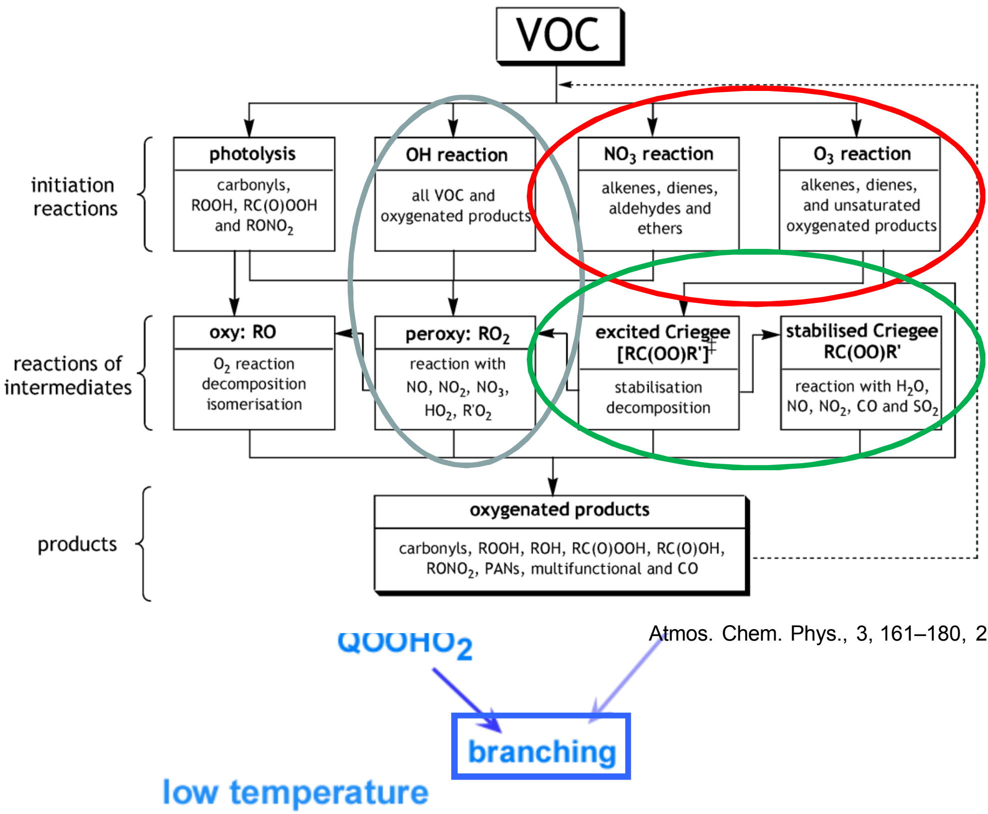
Ignition Chemistry:

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

Tropospheric Chemistry:

- Alkyl + O_2 reactions from OH-initiated oxidation also important in troposphere
- NO_3 and O_3 species are also important oxidation initiators
- *Criegee intermediates* are important species for OH, aerosol formation, NO_x, SO_x

General Alkyl Radical Oxidation Scheme



Atmos. Chem. Phys., 3, 161–180, 2003

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

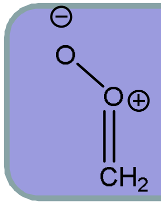
Kinetic Models for Oxidation Chemistry Require Knowing Reactions of "Intermediates"

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

Criegee intermediates also appear in QOOH + O_2 reactions Andersen and Carter, *J Phys. Chem. A.* 107, 9463-9478 (2003); Asatryan and Bozzelli, *J Phys. Chem. A.* 114, 7693-7708 (2010)

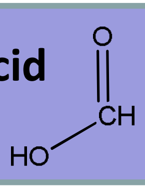
Criegee intermediates are *isomers* of more stable products, organic acids or esters

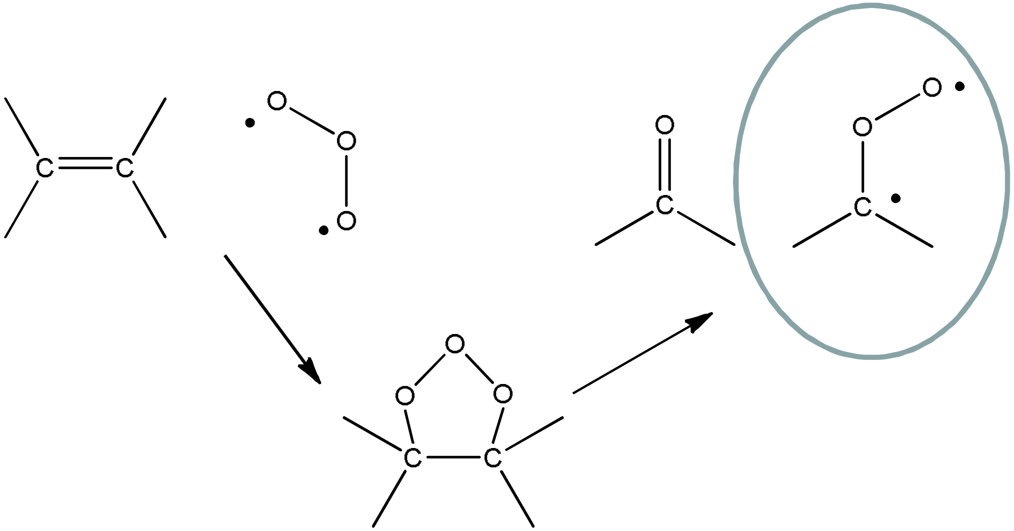
Until 2012, no one had directly measured a Criegee reaction



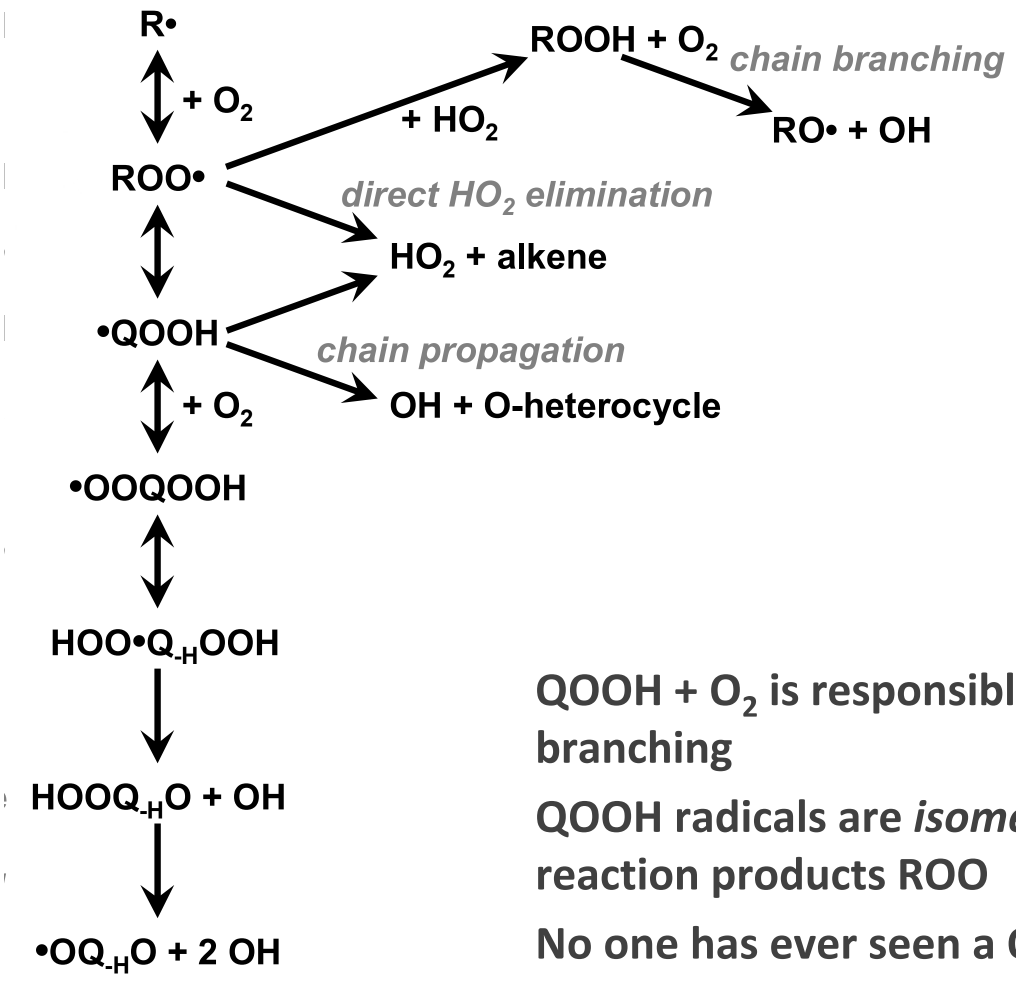
Criegee Intermediate

Formic Acid





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



R•

$+ O_2$

ROO•

$+ HO_2$

$ROOH + O_2$

chain branching

RO• + OH

direct HO_2 elimination

HO_2 + alkene

•QOOH

chain propagation

OH + O-heterocycle

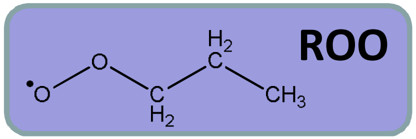
$+ O_2$

•OOQOOH

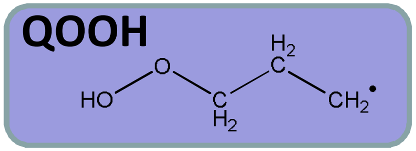
$HOO•Q_{-H}OOH$

$HOOQ_{-H}O + OH$

$•OQ_{-H}O + 2\ OH$



ROO



QOOH

$QOOH + O_2$ is responsible for chain branching

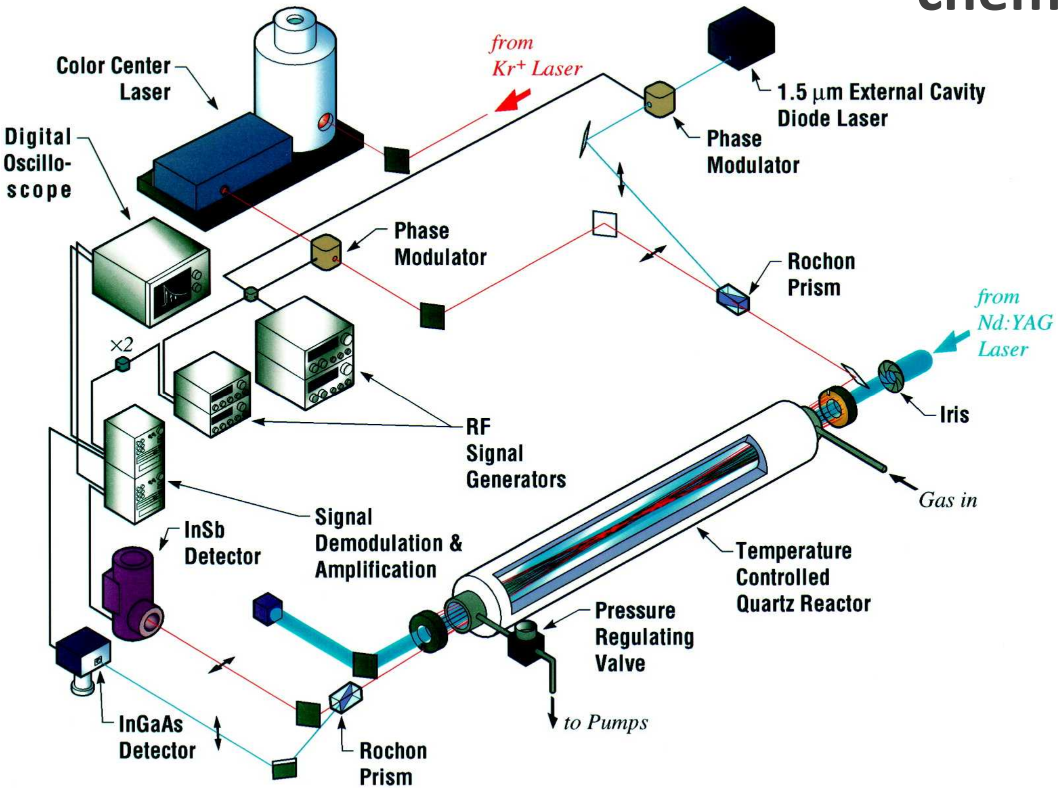
QOOH radicals are *isomers* of the major reaction products ROO

No one has ever seen a QOOH by any means

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

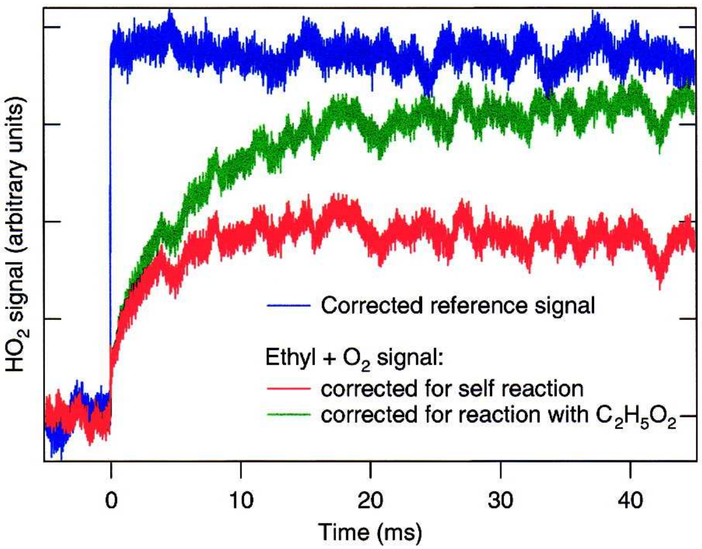
So what can we do?

Alkyl + O_2 reactions – Detect the HO_2 reaction product



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

Phenomenological analysis

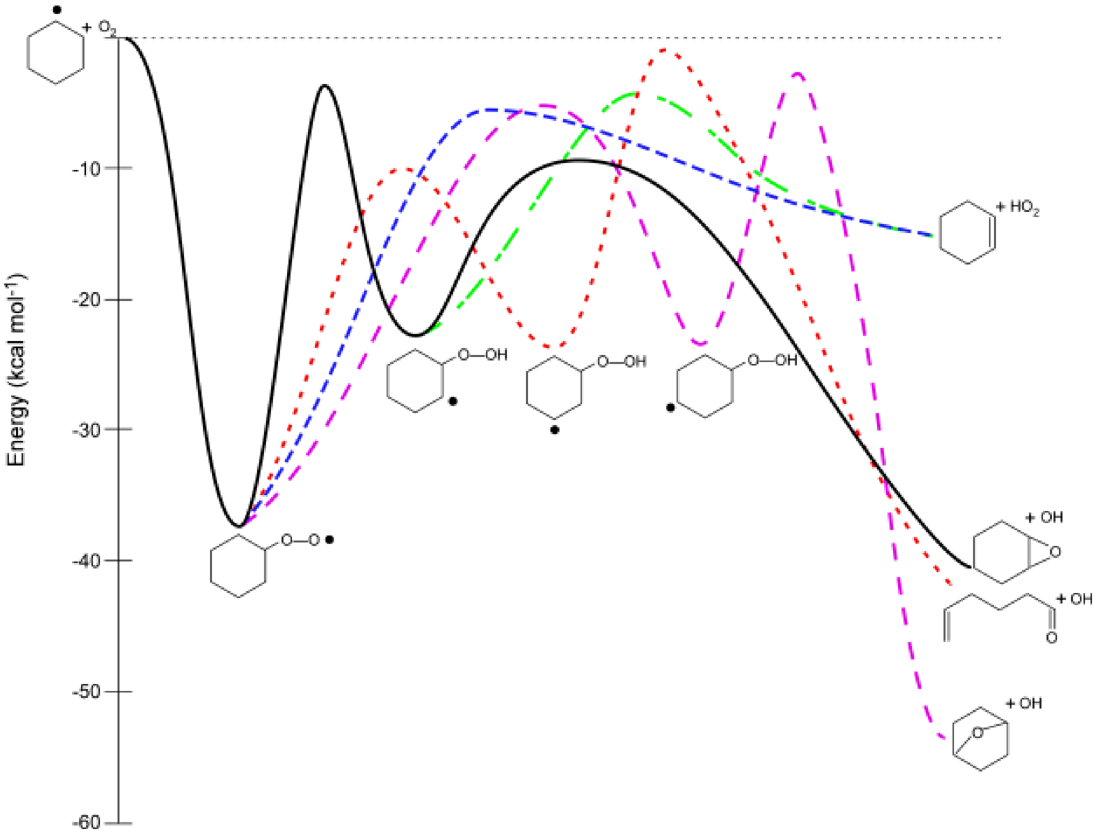


Eileen P. Clifford; John T. Farrell; John D. DeSain; Craig A. Taatjes; *J. Phys. Chem. A* **2000,** 104, 11549-11560

Coupling with Theory Turns Phenomenology into Chemical Insight

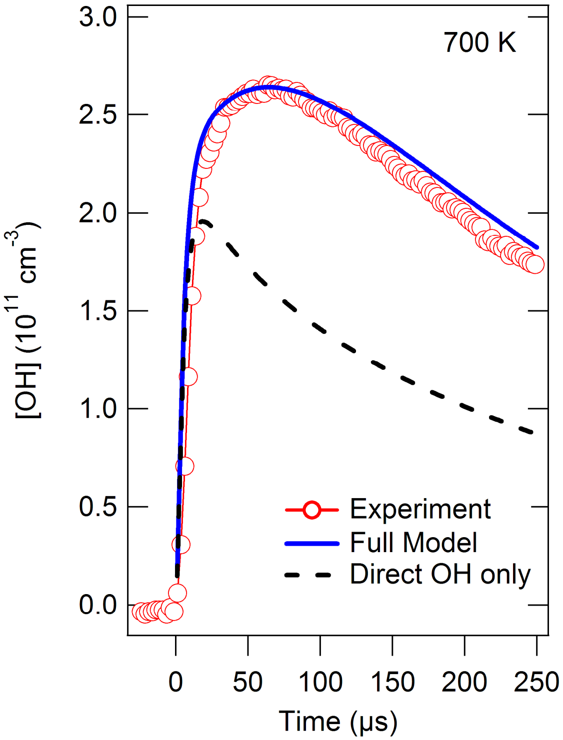
Everything changed when I started working with this guy

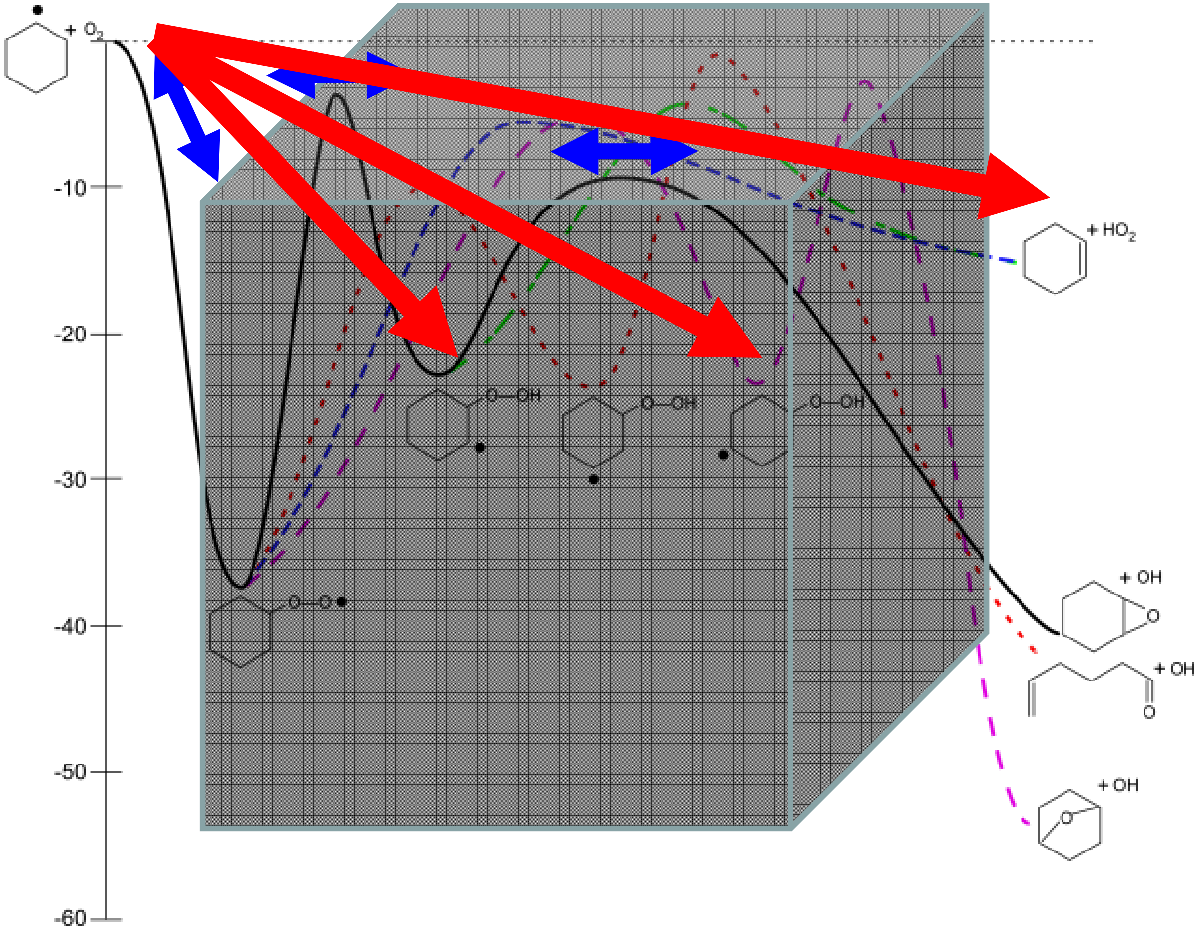
Measurements constrain stationary points on the PES



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

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



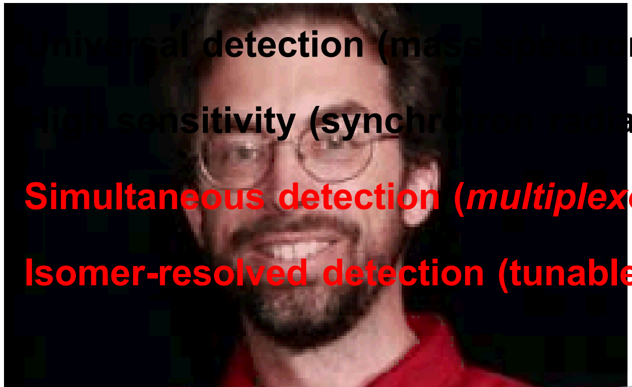


Experimental ambiguity: e.g., OH measurements don't tell *which* QOOH contributes

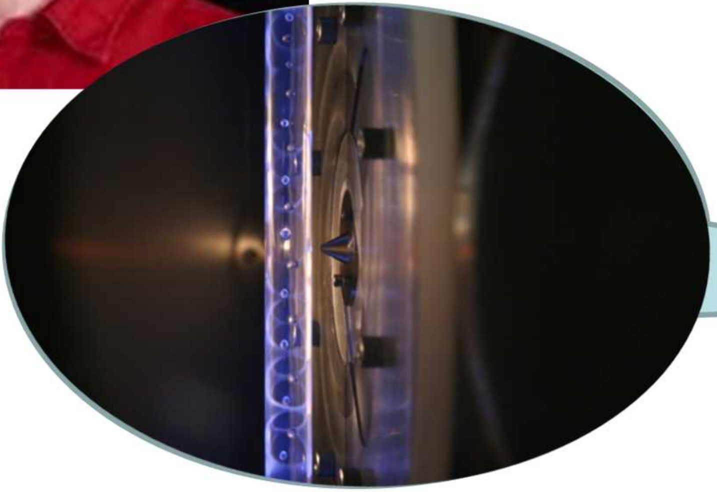
Need as much detail as we can get – really would like to measure all the species all the time

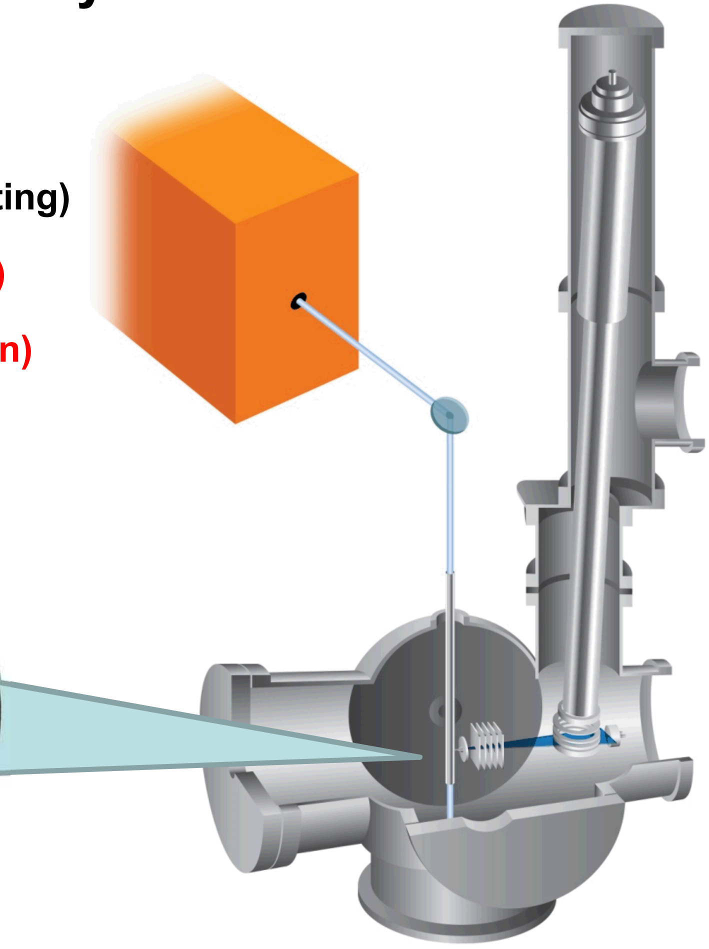
Everything changed again because of this guy

Multiplexed photoionization mass spectrometry (MPIMS)

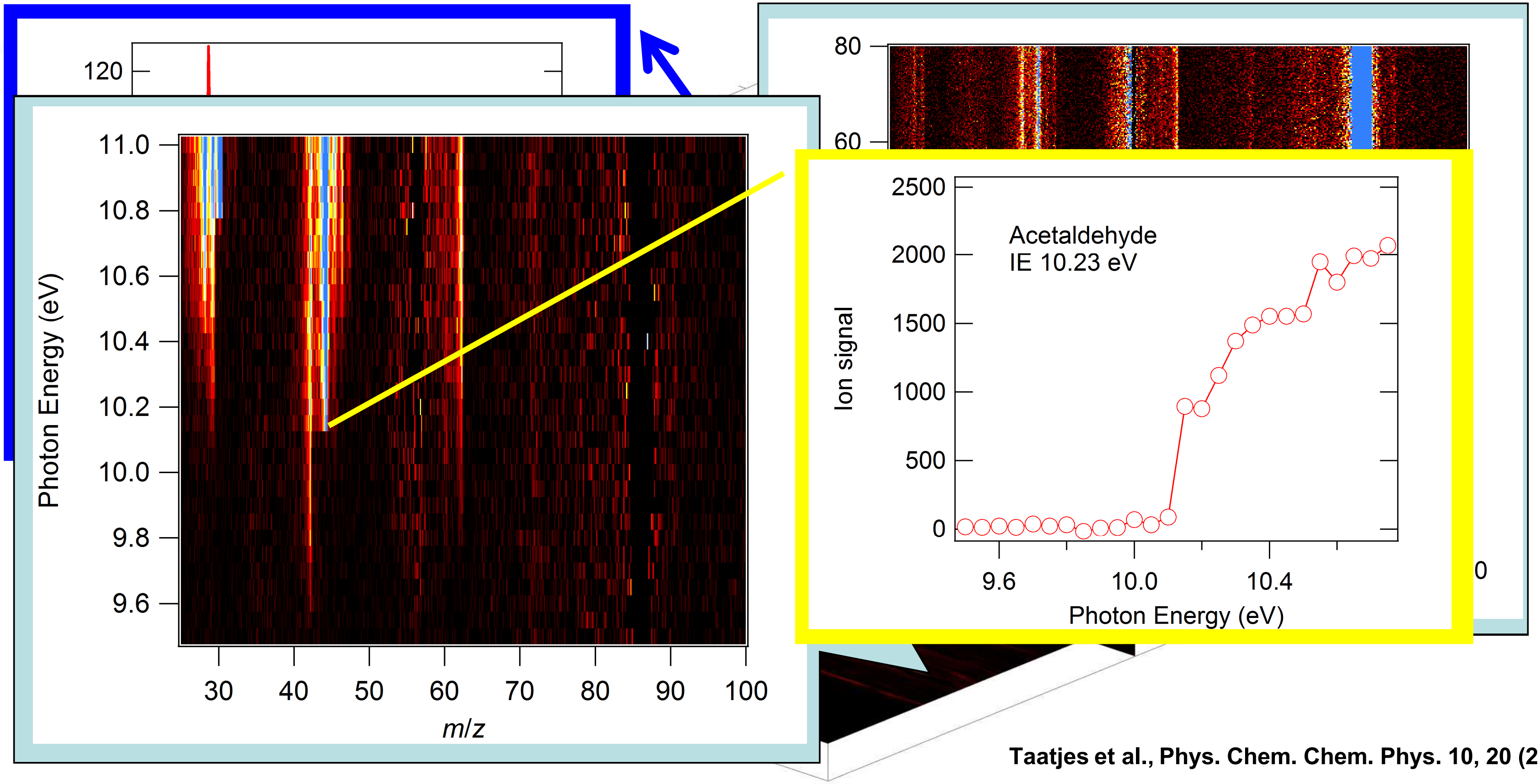


- Universal detection (mass spectrometry)
- High sensitivity (synchrotron radiation + single ion counting)
- Simultaneous detection (*multiplexed* mass spectrometry)
- Isomer-resolved detection (tunable VUV, ALS synchrotron)





Kinetic data is acquired as a function of kinetic time, mass, and photoionization energy

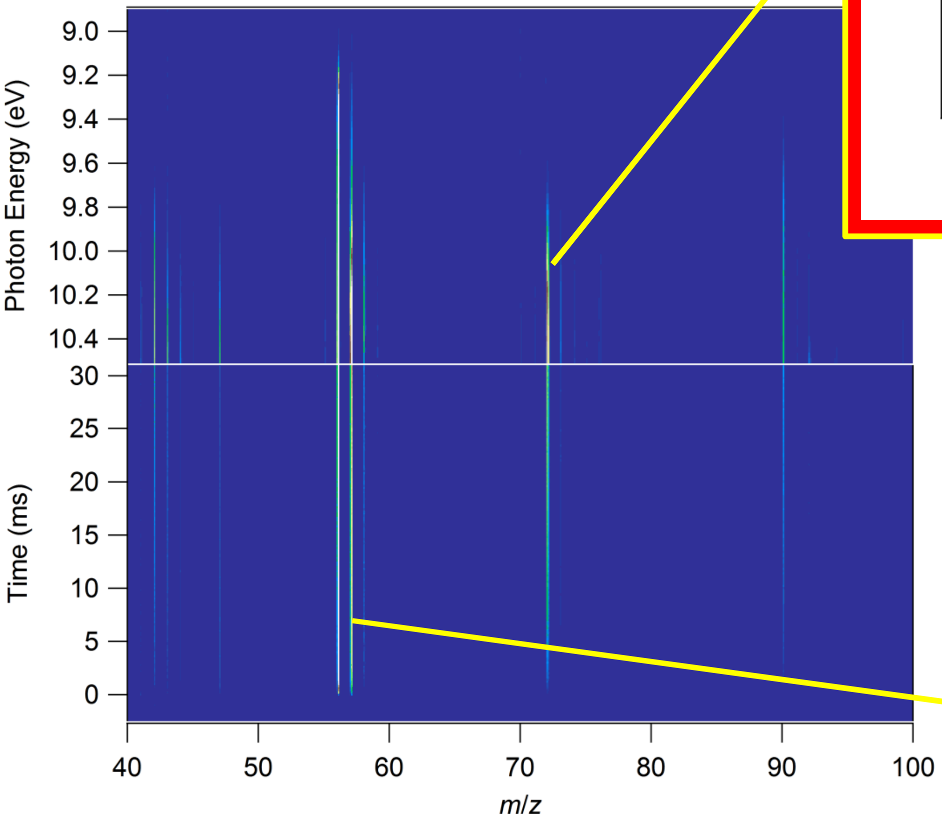


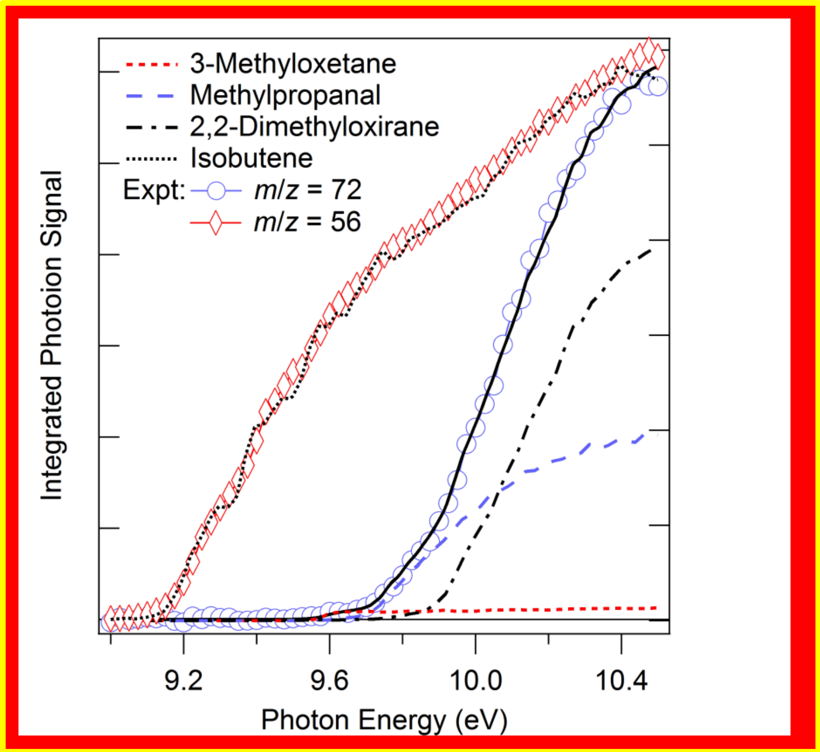
Taatjes et al., Phys. Chem. Chem. Phys. 10, 20 (2008).

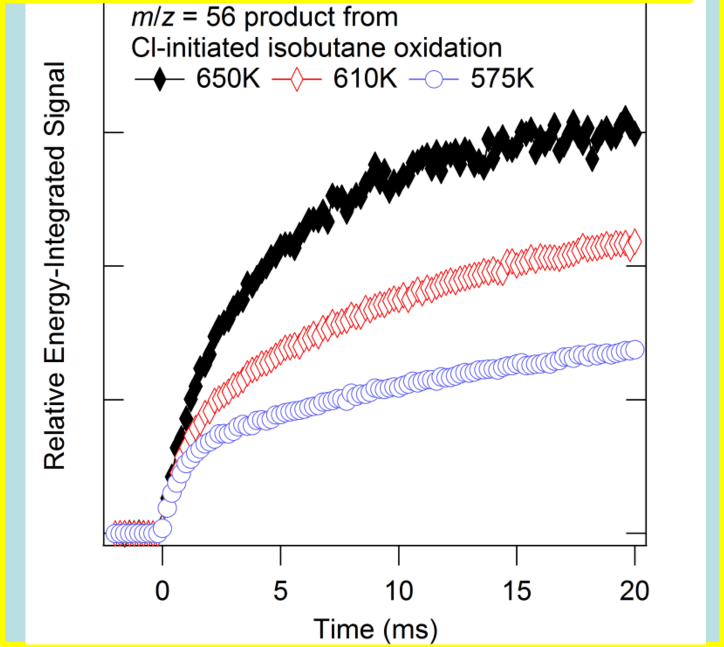
3-D dataset can be "sliced" along different axes to probe different aspects of the reaction

Cl-initiated alkane oxidation

- **Time behavior of product formation – prompt and delayed**
- **Photoionization spectra identify product isomers**

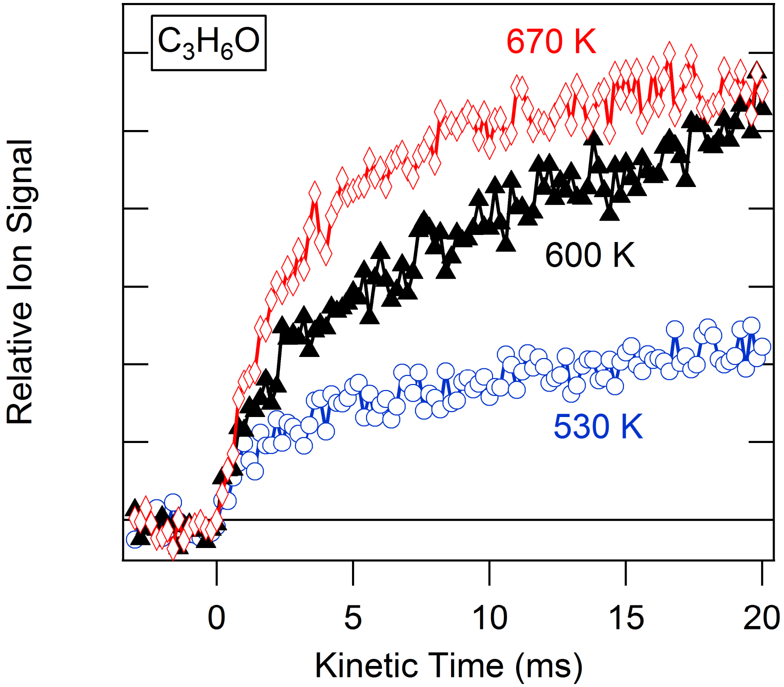




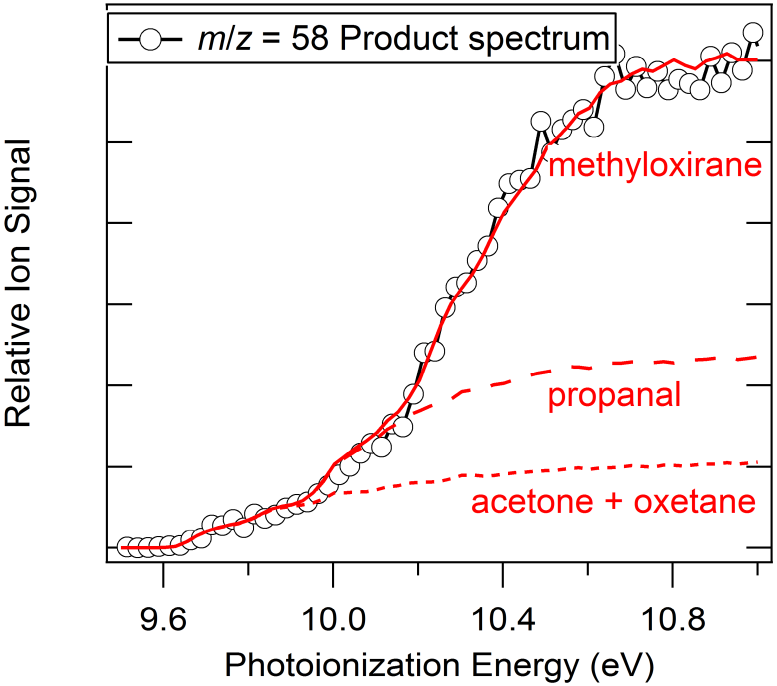


Mass spectroscopic measurements can identify isomeric pathways

Time profiles of stable products reflect same bimodal behavior as radicals



Multiple C_3H_6O isomers are formed in unimolecular reactions of ROO

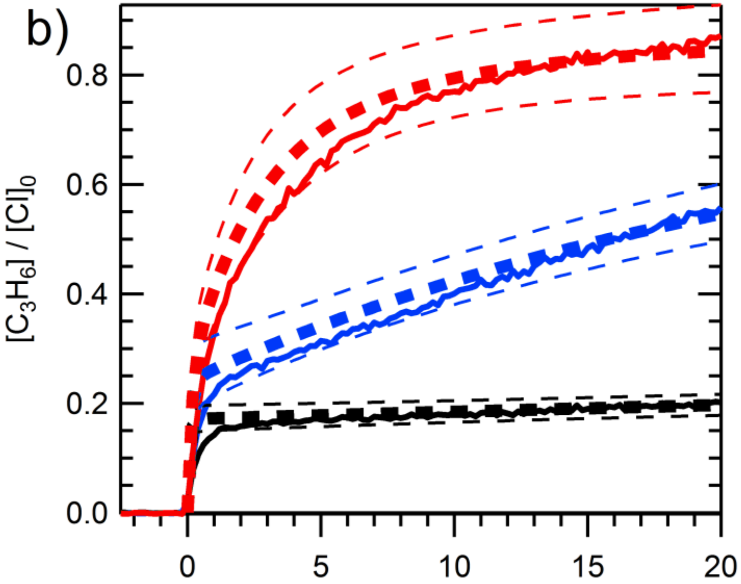


Combine with high-pressure MPIMS (Lenny Sheps), radical product measurements and literature experiments: multi-scale informatics (Mike Burke et al., Argonne)

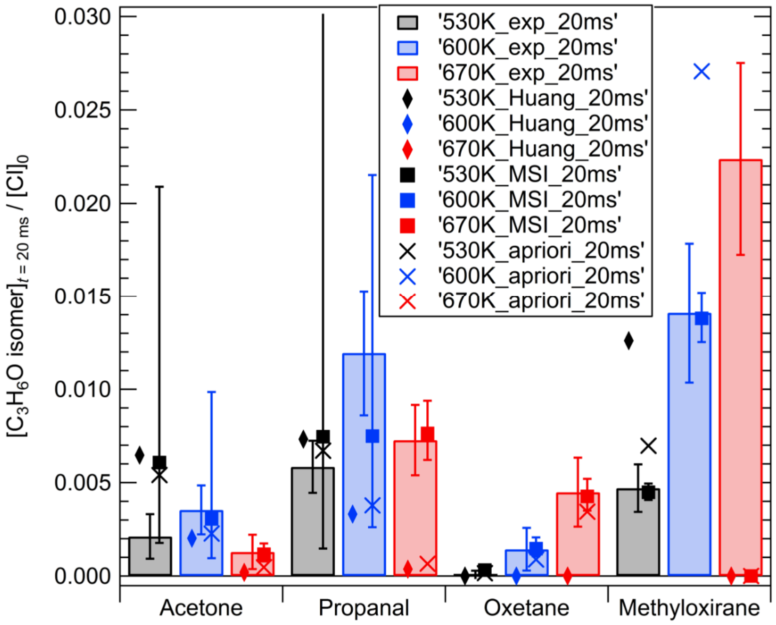
Much better constraints on primary reaction characteristics

"Multiscale Informatics" (Mike Burke) is a powerful way to combine data

Optimized model using rigorous uncertainty bounds



New photoionization experiments constrain model

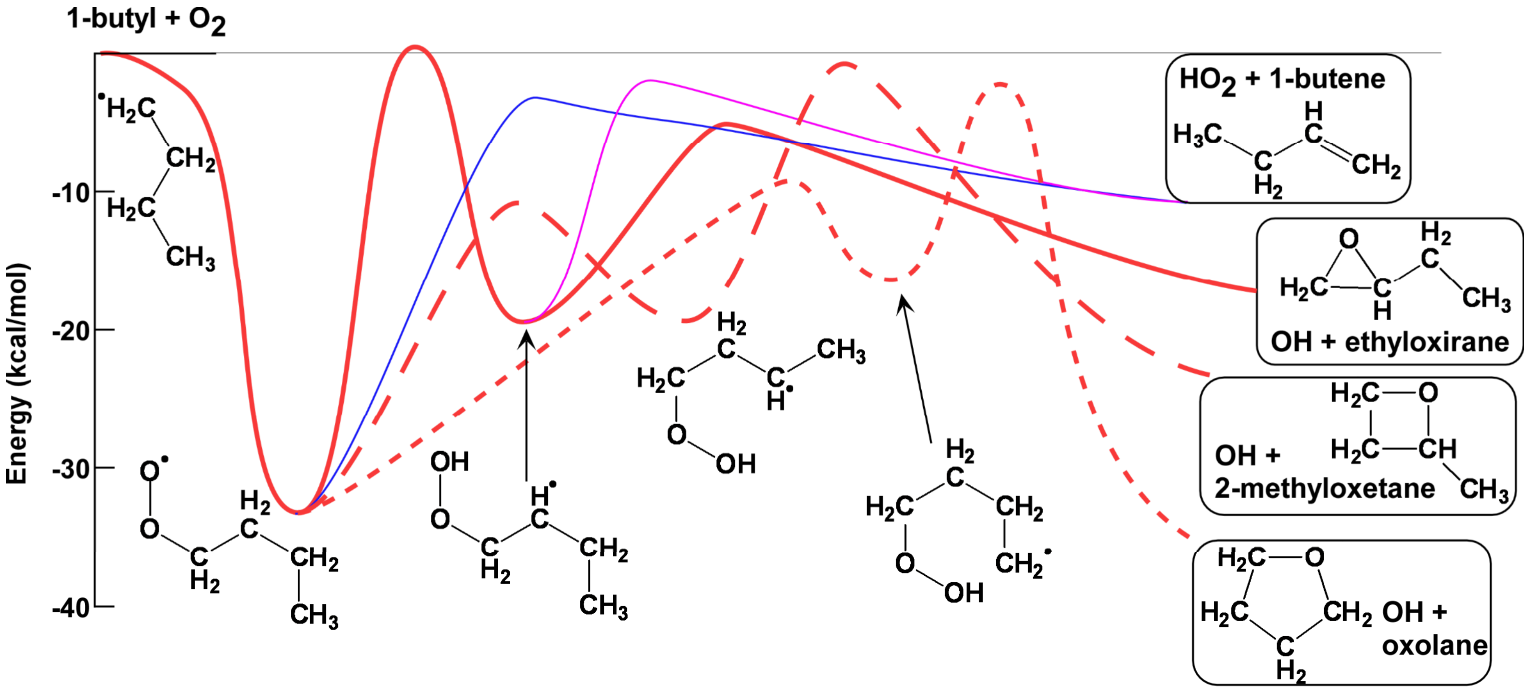


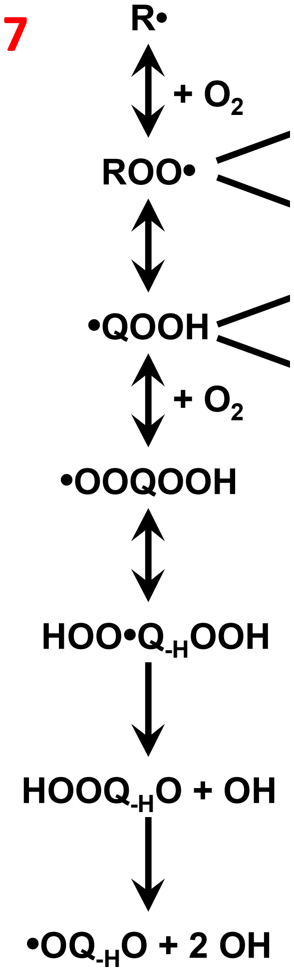
Also includes theoretical kinetics calculations with uncertainties

Monitor time-resolved product formation in pulsed-photolytically initiated oxidation

Butyl radical m/z = 57

Butene m/z = 56




R•

+ O_2

ROO•

•QOOH

+ O_2

•OOQOOH

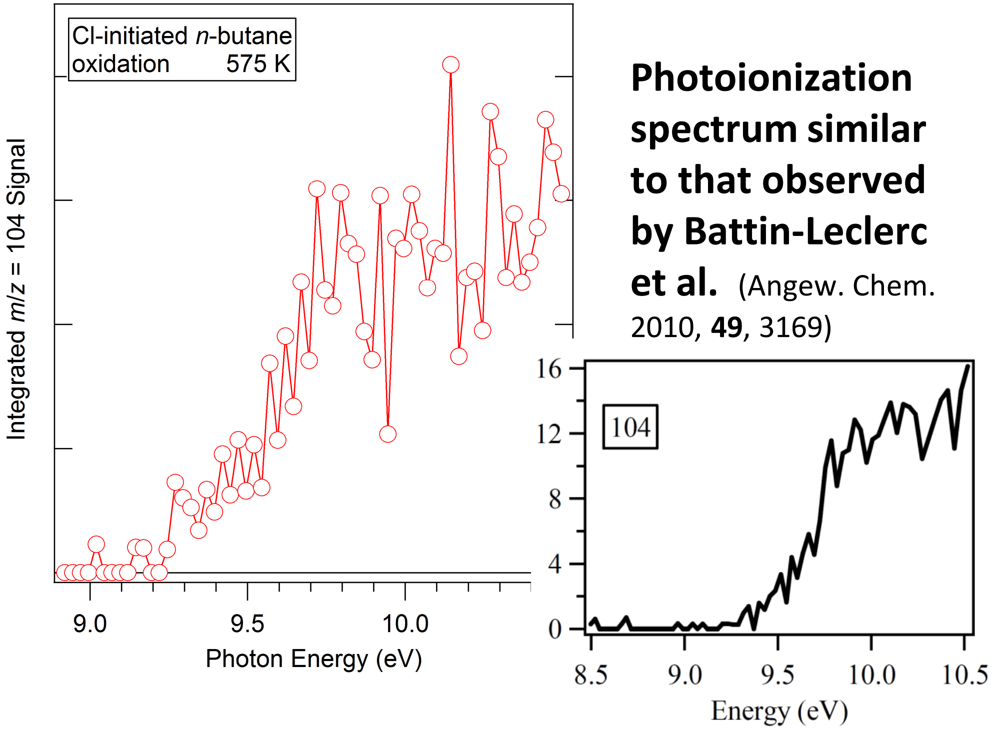
HOO•Q_{-H}OOH

$HOOQ_{-H}O$ + OH

•$OQ_{-H}O$ + 2 OH

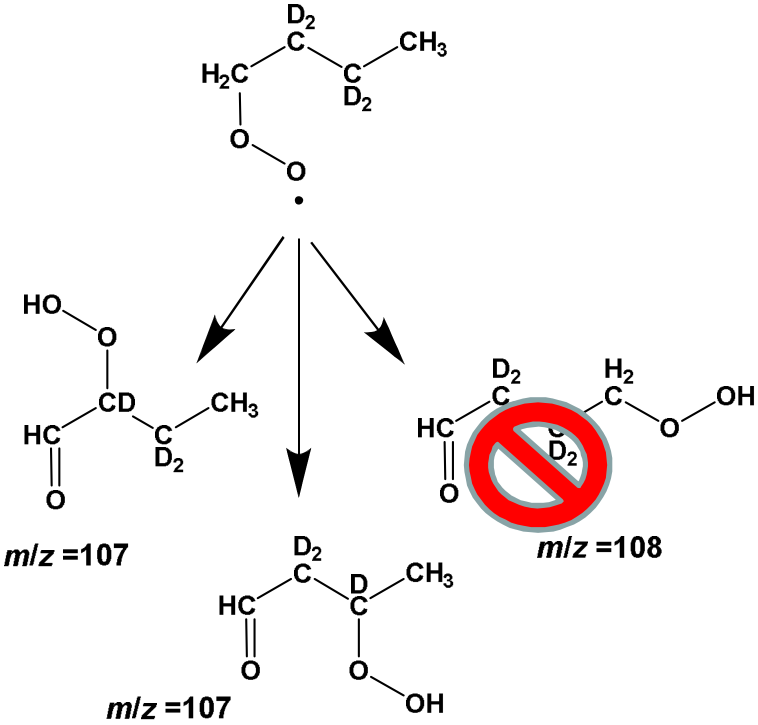
Ketohydroperoxide m/z = 104

Ketohydroperoxide Product at *m/z* = 104 Arises from QOOH + O_2 (but which?)



Photoionization spectrum similar to that observed by Battin-Leclerc et al. (Angew. Chem. 2010, **49**, 3169)

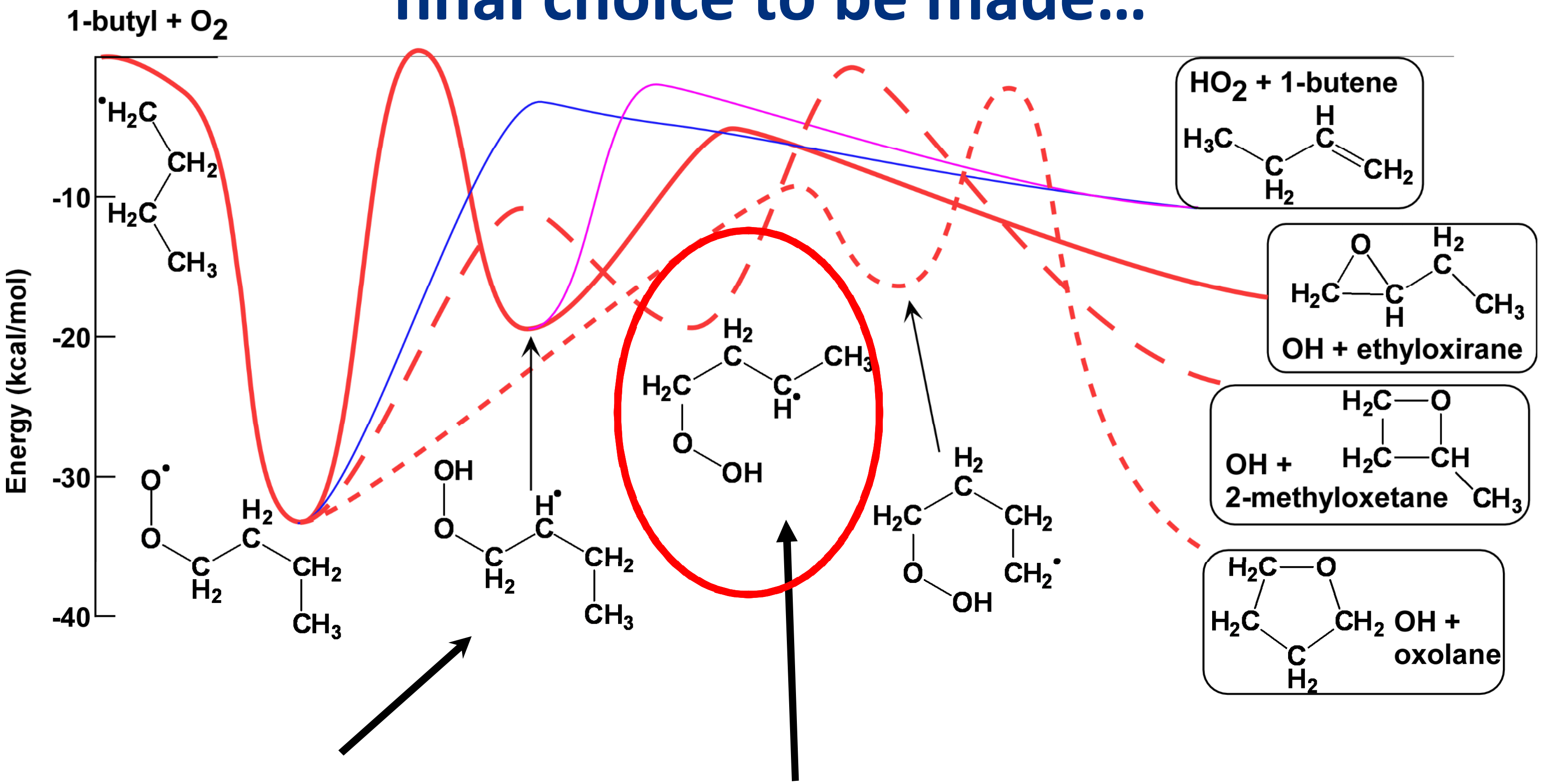
Isotopic labeling further narrows the possible ketohydroperoxide isomers



- At low pressure, the ketohydroperoxide yield 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

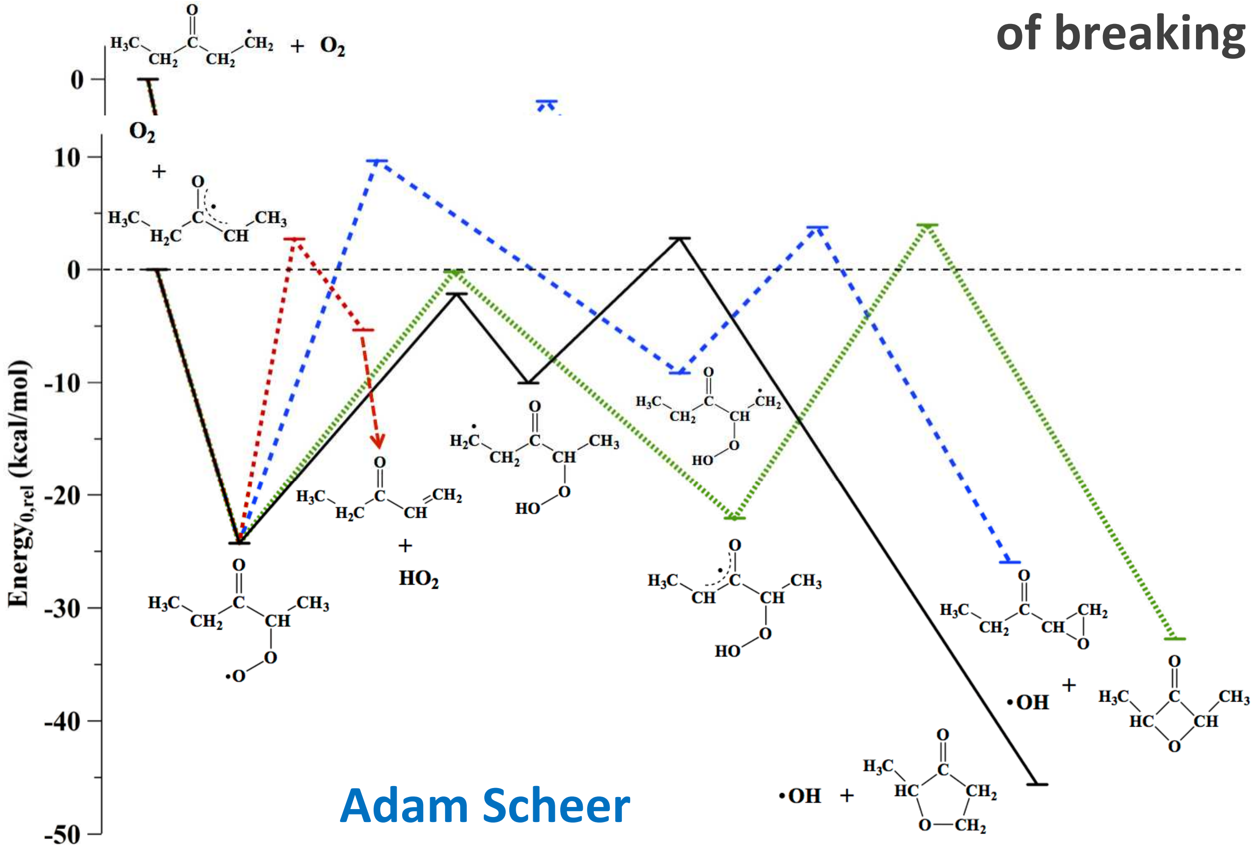
Easy to make, larger barrier to bimolecular products

Thermodynamics Affects the Isomerization and Dissociation of QOOH

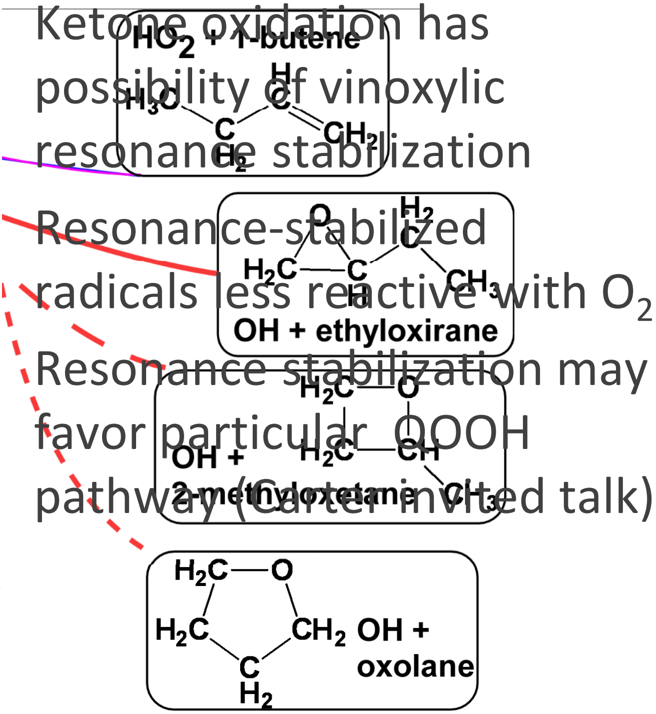
What about systems with unusually stable QOOH?

Ring strain in the transition state for isomerization

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



Adam Scheer



Ketone oxidation has possibility of vinoxylic resonance stabilization

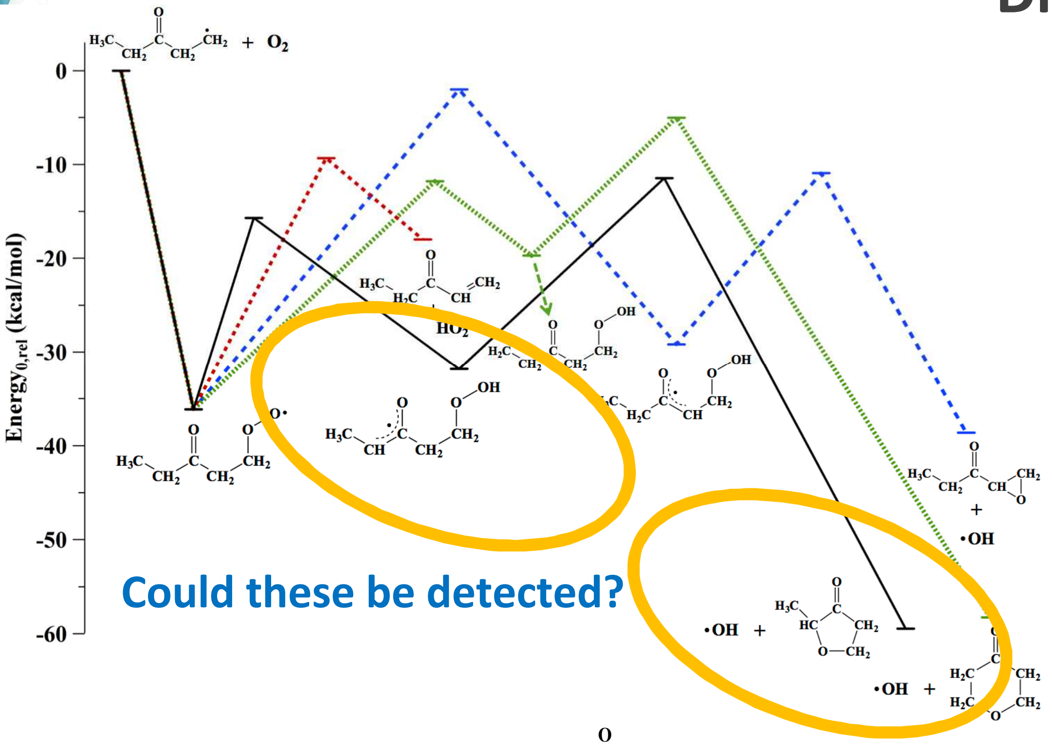
Resonance-stabilized radicals less reactive with O_2

Resonance stabilization may favor particular QOOH pathway (Carter invited talk)

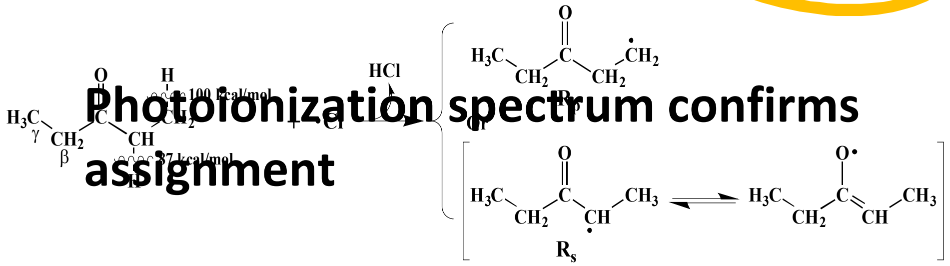
Pathway via resonance-stabilized QOOH dominates cyclic ether formation

Diethyl ketone oxidation

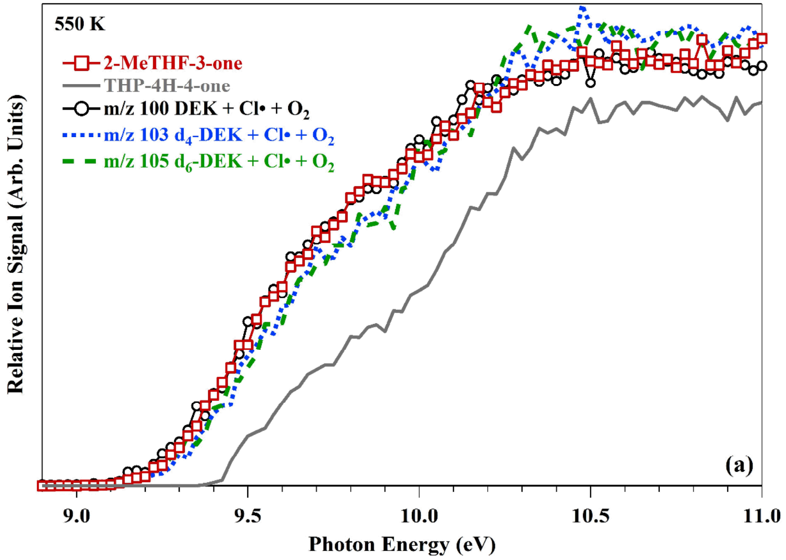
- The vinoxylic initial radical is relatively unreactive
- Selective deuteration suggests formation of five-membered ring from initial primary radical



Could these be detected?



Photoionization spectrum confirms assignment



Why are these things so hard to detect?

People get out of the rain!

They don't stay in their reactive configuration very long – they are made slowly and consumed rapidly

The hole in the bottom of the bucket is bigger than the hole at the top!

We need sensitive and selective detection *and* a way to make intermediates directly

So what about QOOH? Can photoionization detect and characterize the elusive QOOH?

Most ROO have no stable parent cation (Meloni et al., *J. Am. Chem. Soc.* 128, 13559 (2006)), but some $QOOH^+$ are stable

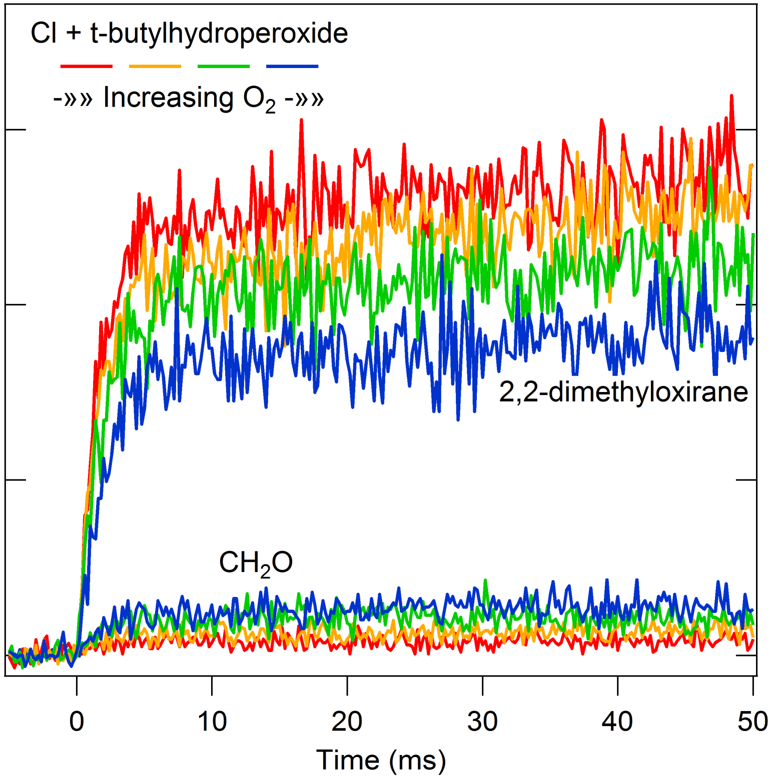
Problem is to make enough!

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

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

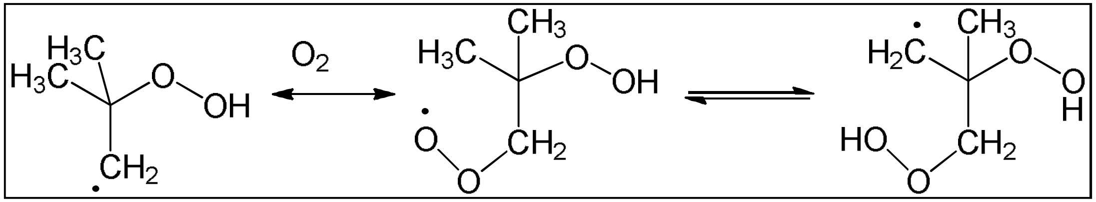
$(CH_3)_2C(CH_2)OOH \rightarrow$ 2,2-dimethyloxirane + OH

Reaction with O_2 competes with dissociation – forms other products



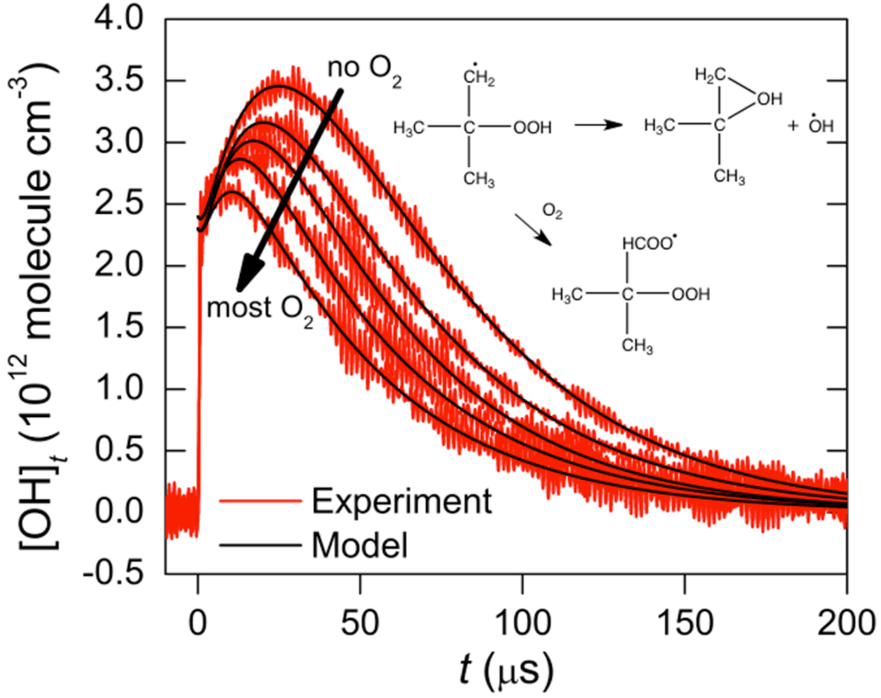
Relative rate can give *direct* measurements of QOOH reactions

Judit Zádor



Measurement of OH directly probes rate constant for QOOH reactions

Haifeng Huang



unknowns w/o O_2

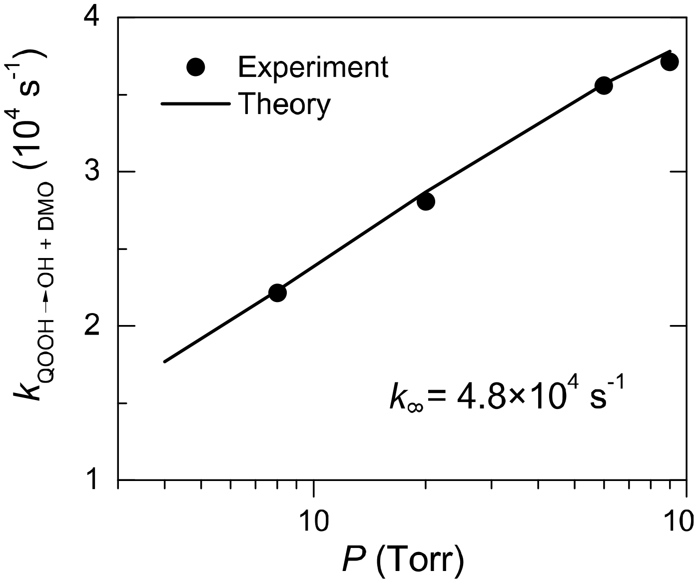
① $k_{QOOH \to OH}$

② chain chlorination (k_{cl})

unknowns w/ O_2, same conditions

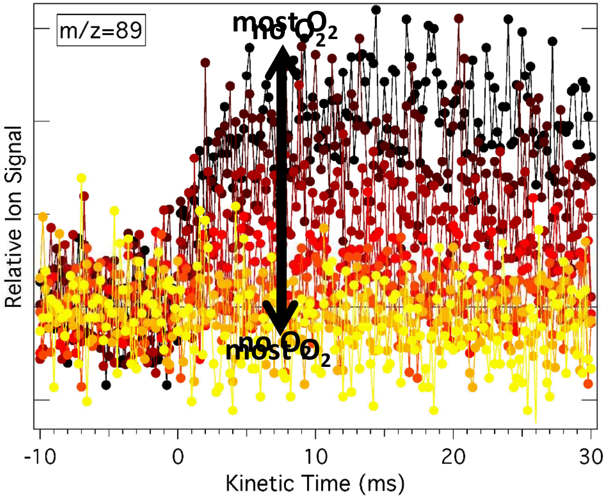
③ loss to ROO in Cl+TBHP (α)

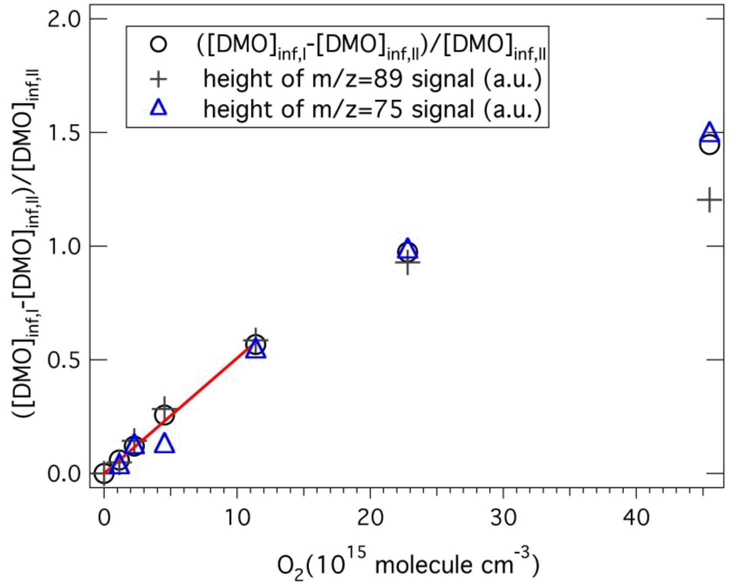
① $k_{QOOH+O2}$



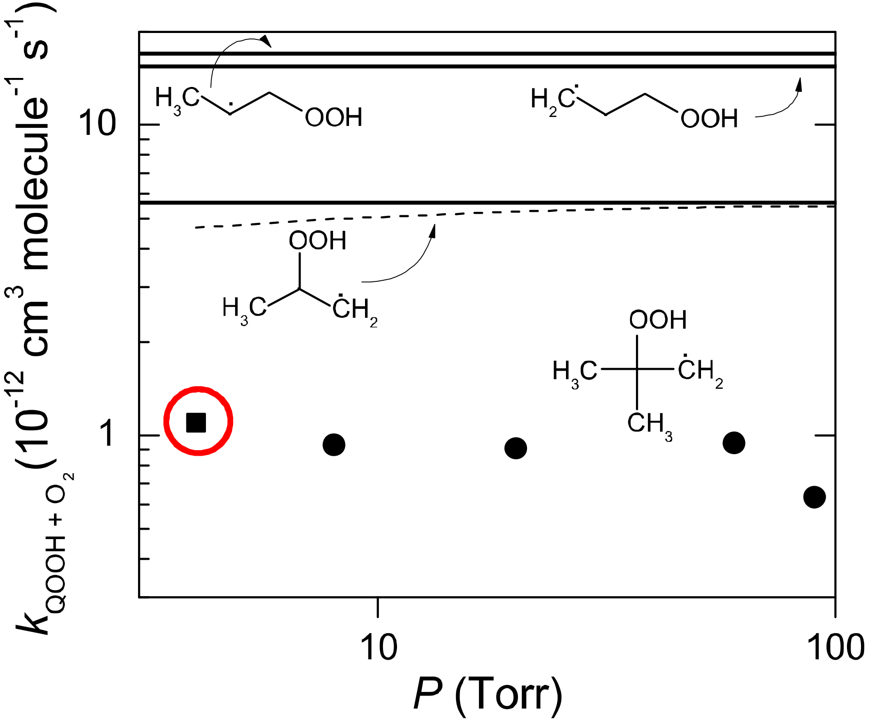
Fit all data -- use competition between QOOH dissociation and addition of O_2 to get $k_{QOOH+O2}$ as well

Direct measurement of QOOH + O_2 reaction rate constant





Comparison of k(QOOH+O_2)
for various QOOH's

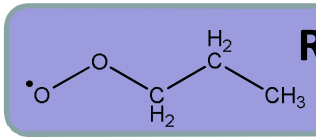


$$k_{QOOH+O2} = \frac{k_{QOOH\text{-->}OH} + L}{[O_2]} \times \frac{[DMO]^0_\infty - [DMO]_\infty}{[DMO]_\infty}$$

C. Franklin Goldsmith, William H. Green, and Stephen J. Klippenstein, J. Phys. Chem A, 2012, *116*, 3325–3346

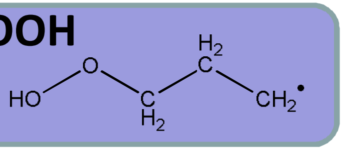
That’s all still pretty indirect – Isn’t there *some* way we can do better?

What are these “intermediates” again?



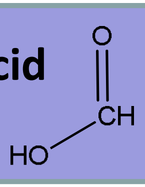
ROO

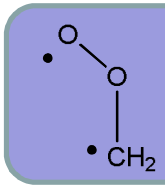
QOOH



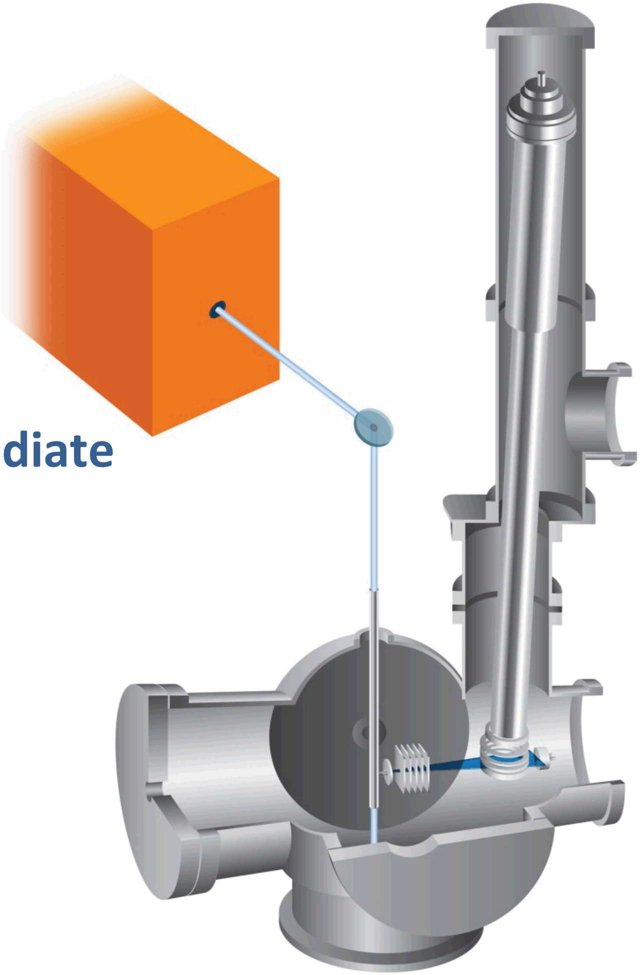
QOOH is an isomer of the more stable ROO intermediate

Formic Acid





Criegee Intermediate



- Criegee intermediates are isomers of more stable tropospheric species
- **But we have a machine that can resolve isomeric chemistry!**

In fact, tunable synchrotron photoionization *can* identify novel isomeric intermediates

Carl Percival, Dudley Shallcross

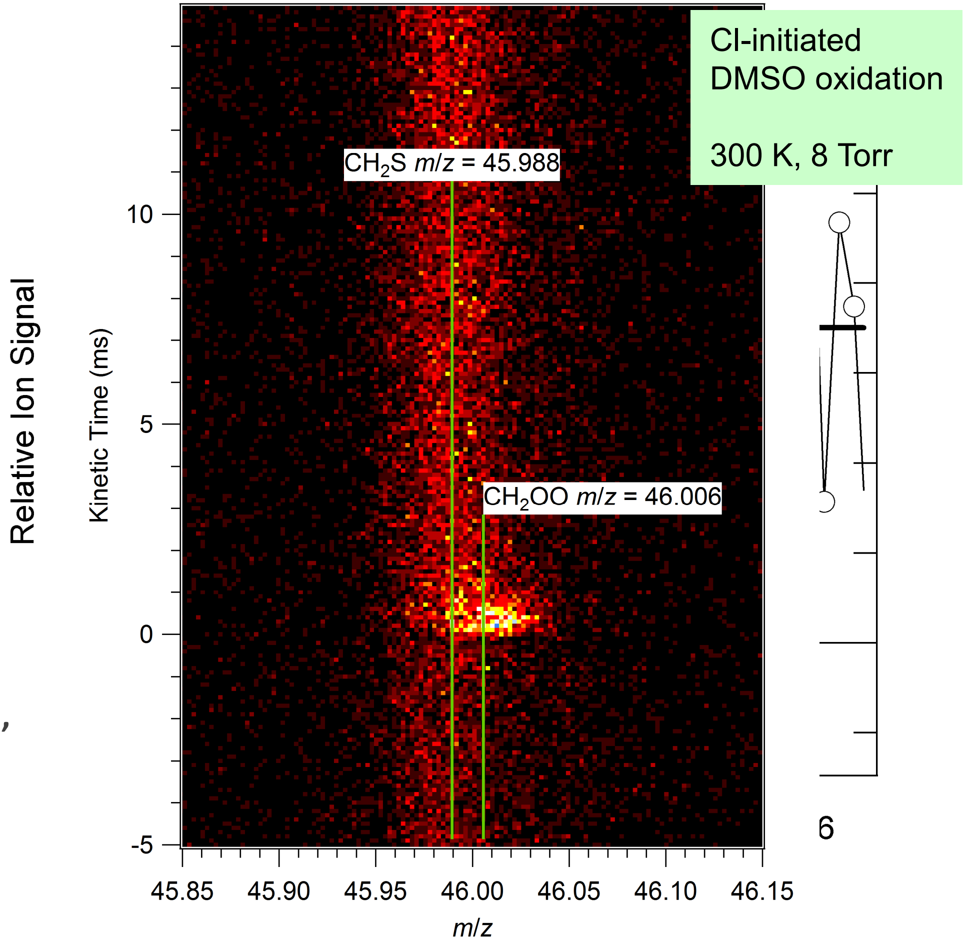
Ozonolysis of alkenes proceeds via a
    carbonyl oxide intermediate
    (“Criegee intermediate”)

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))

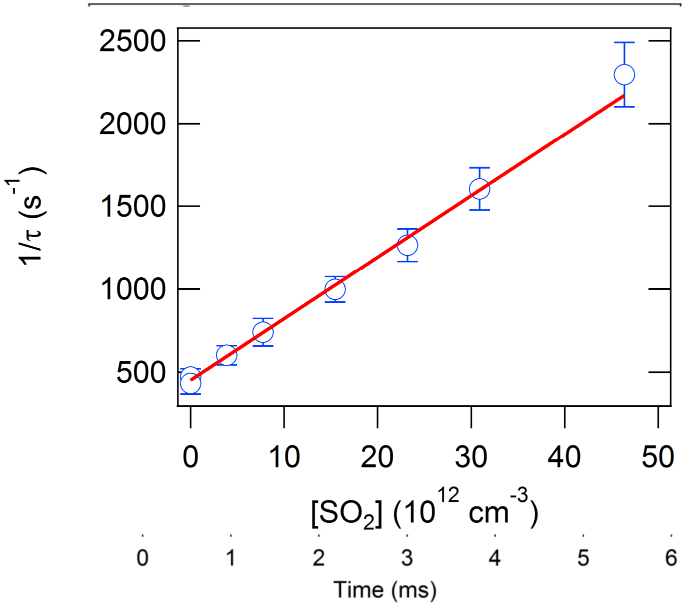
Time-of-flight can resolve CH_2S from
    CH_2O

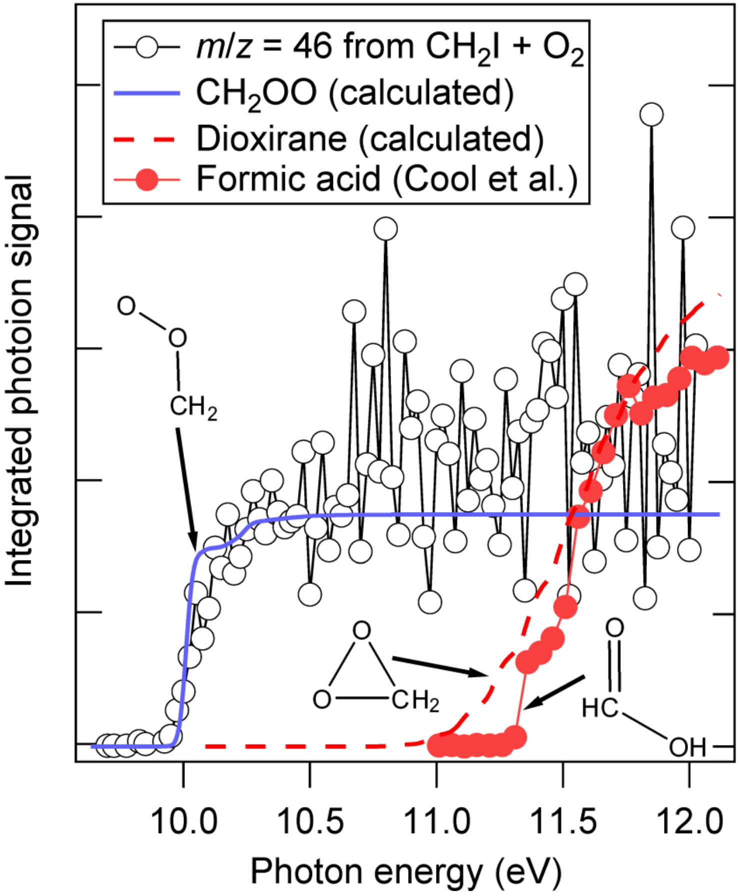


Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008)

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

- **Arkke Eskola et al.** *Phys. Chem. Chem. Phys.* **8**, 1416 (2006) **found that CH_2I reaction with O_2 made I atom – turns out that what's left is Criegee intermediate!**
- **Can make lots of Criegee this way, look at reactions with important tropospheric species**

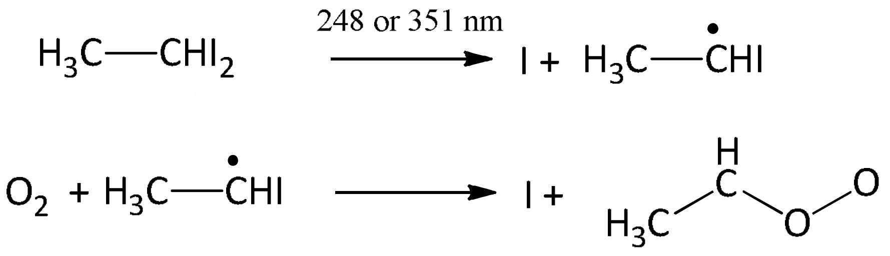




Welz, Savee, et al., *Science* **335**, 204 (2012)

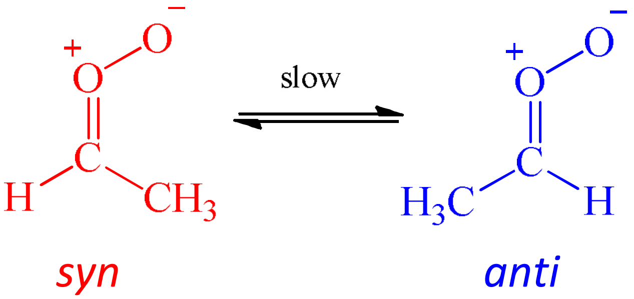
We produced and characterized the next larger Criegee Intermediate: acetaldehyde oxide (CH_3CHOO)

Similar strategy:

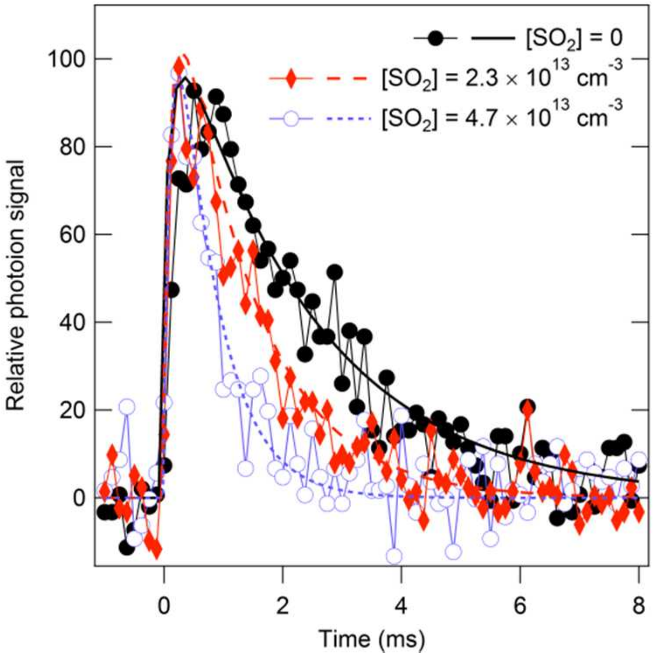


m/z = 60

CH_3CHOO exists in two distinct conformeric forms

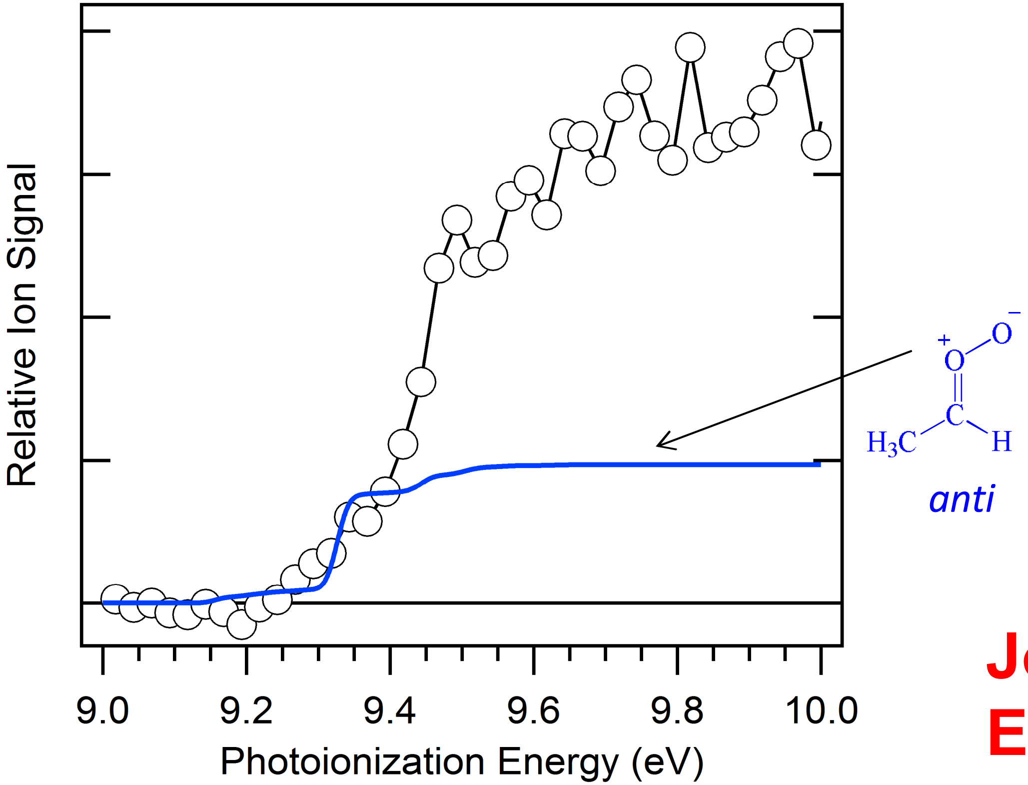


m/z = 60 time profile



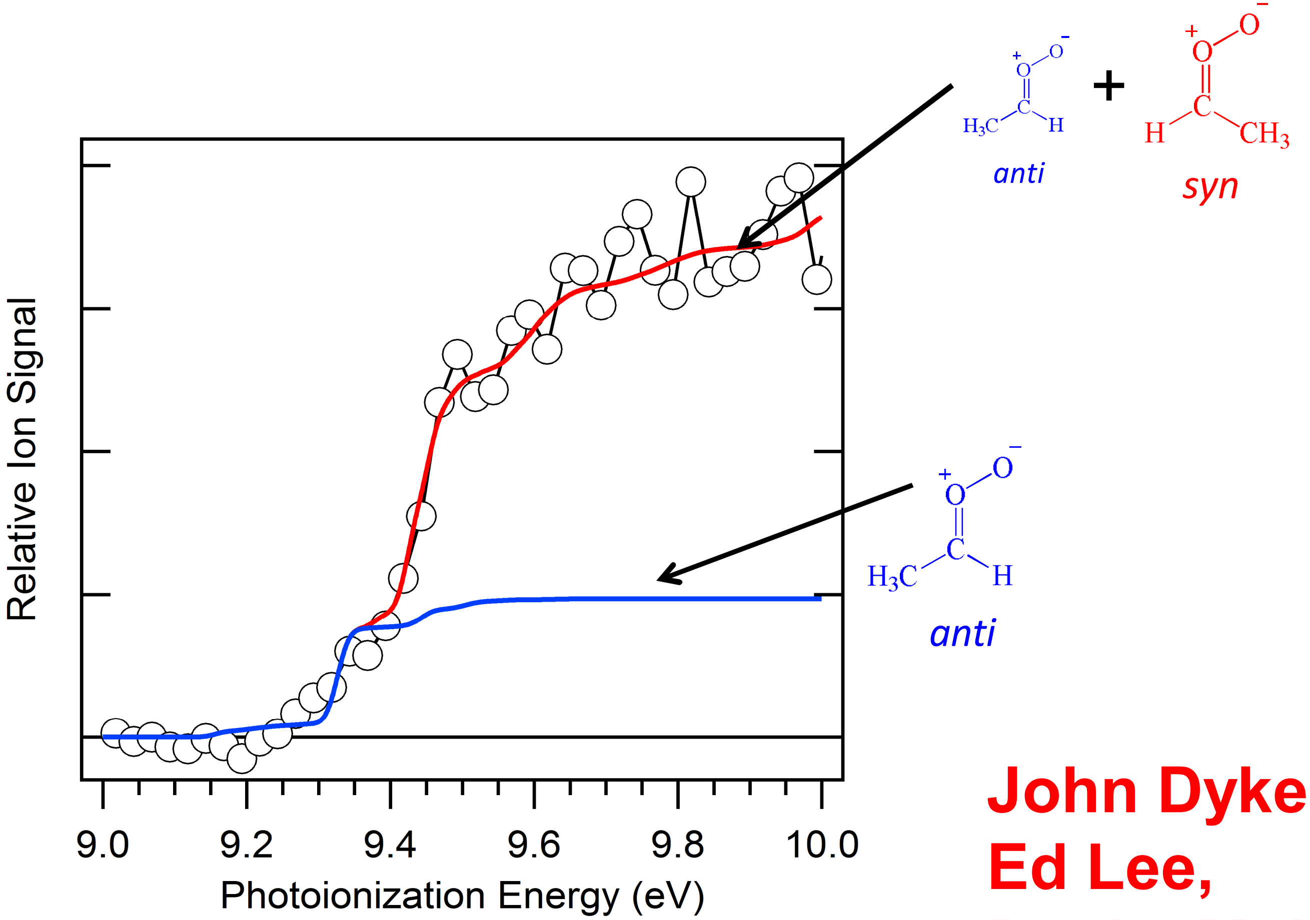
Calculations predict that *anti*-CH_3CHOO reacts with H_2O five orders of magnitude faster than *syn*-CH_3CHOO
(Phys. Chem. Chem. Phys. 13, 13034 (2011))

The *m/z* = 60 photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



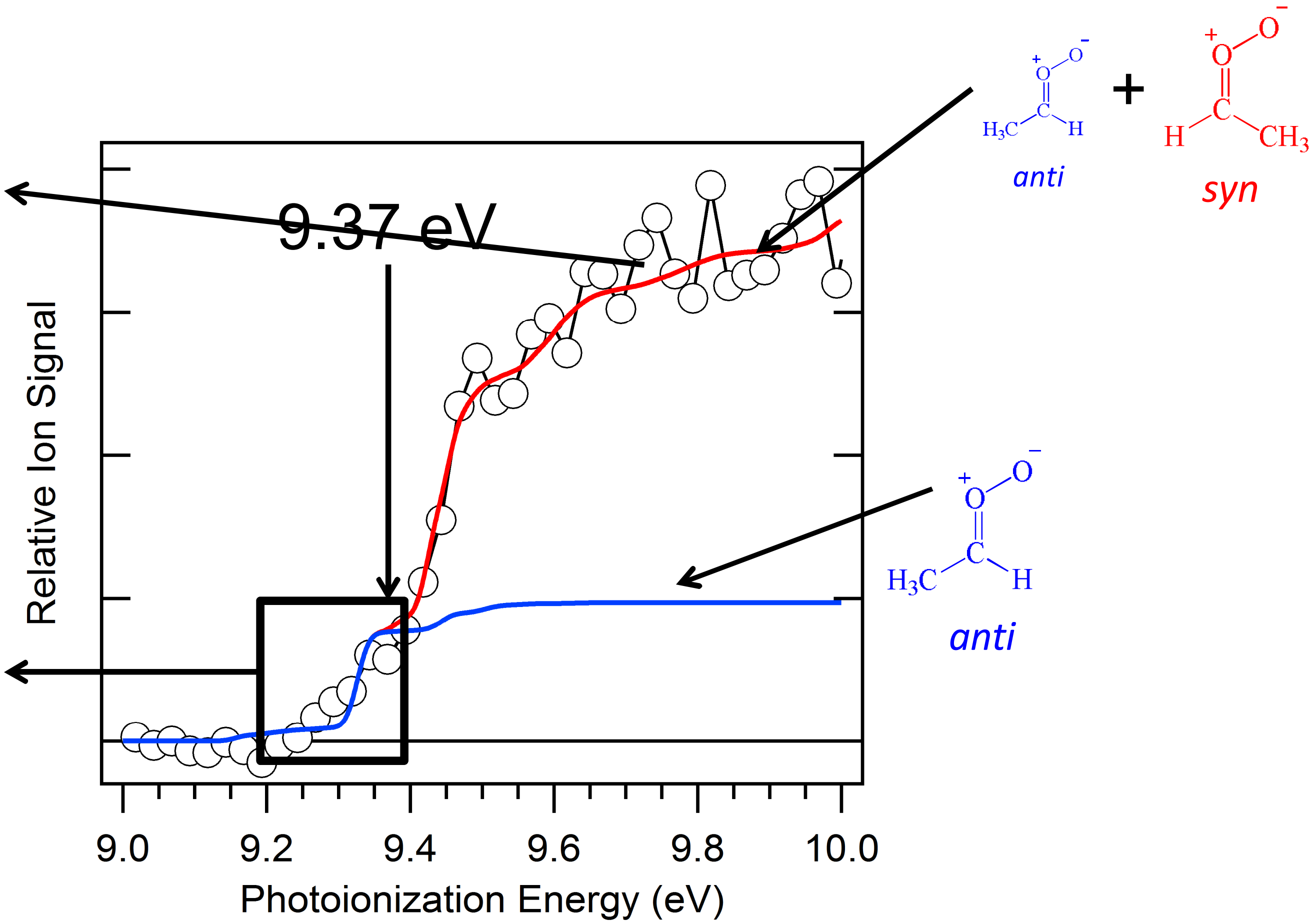
John Dyke, Ed Lee, Daniel Mok

The *m/z* = 60 photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



John Dyke,
Ed Lee,
Daniel Mok

The low-energy part *m/z* = 60 photoionization spectrum is dominated by *anti*-CH_3CHOO

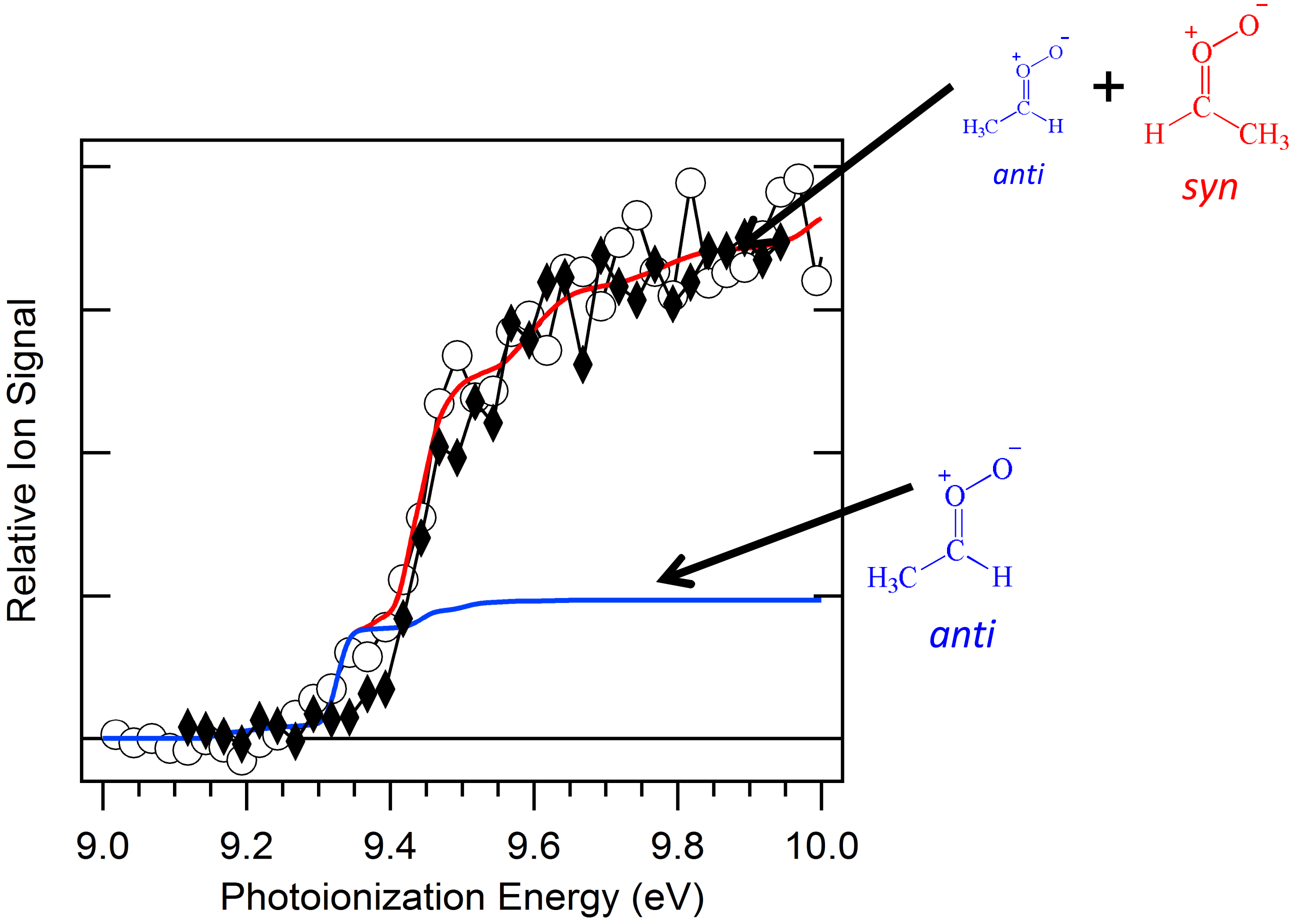


both conformers contribute, but *syn*-dominates

10.5 eV: ~ 85% of the signal is *syn*-

anti- conformer can be probed separately from *syn*-

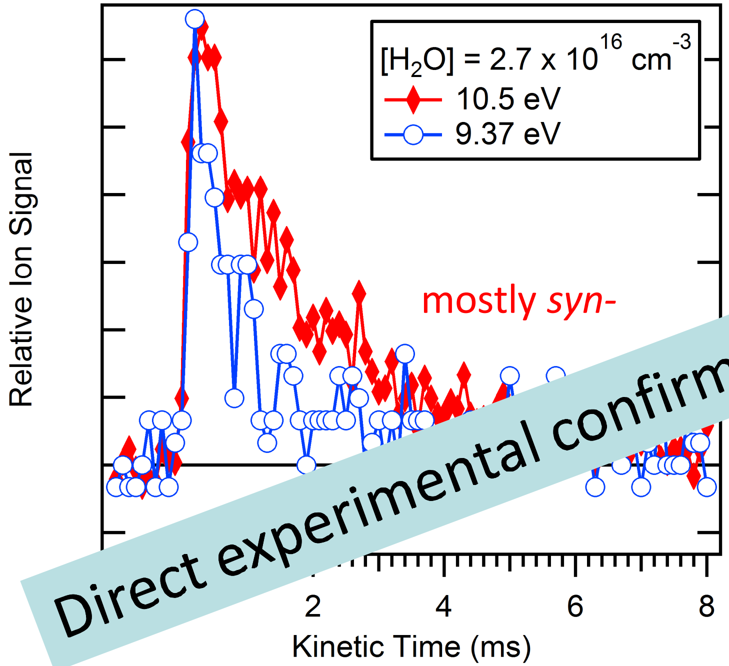
Addition of water preferably removes the *anti*- conformer of CH_3CHOO

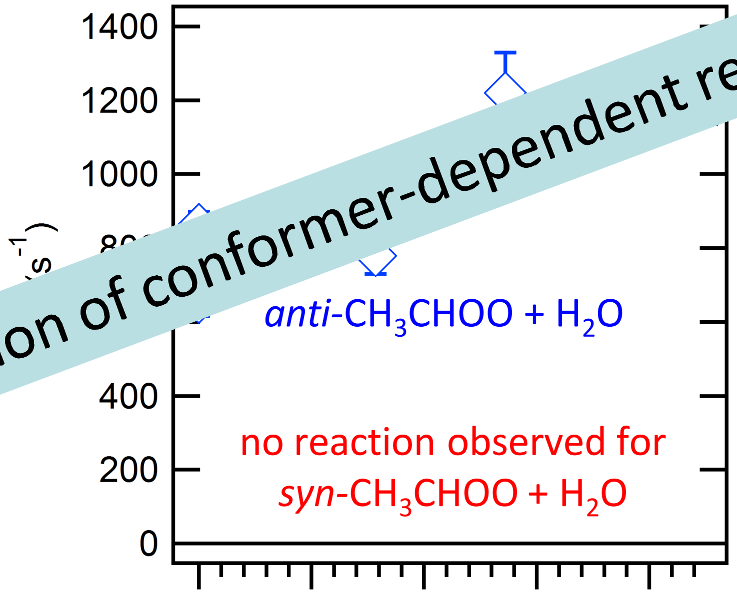


Conformer-dependent reactivity!

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

We measured the rate coefficient of *anti*-CH_3CHOO with H_2O





Direct experimental confirmation of conformer-dependent reactivity

k(*anti*-CH_3CHOO + H_2O) = (1.0 ± 0.4) x 10^{-14} cm^3 s^{-1} ⇨

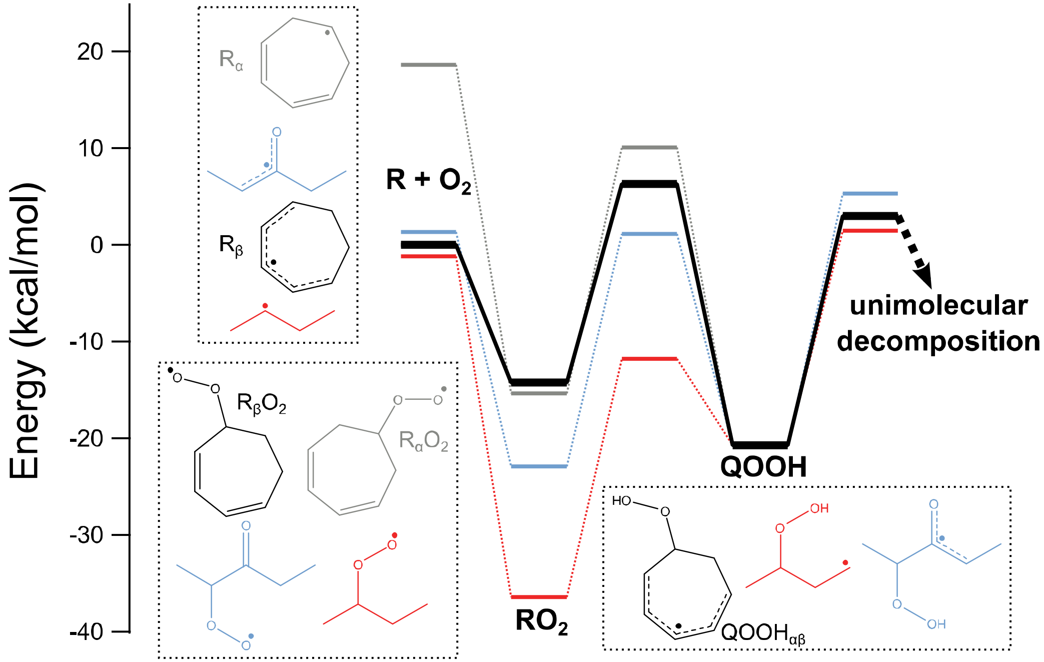
k(*syn*-CH_3CHOO + H_2O) ≤ 4 x 10^{-15} cm^3 s^{-1}

- 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

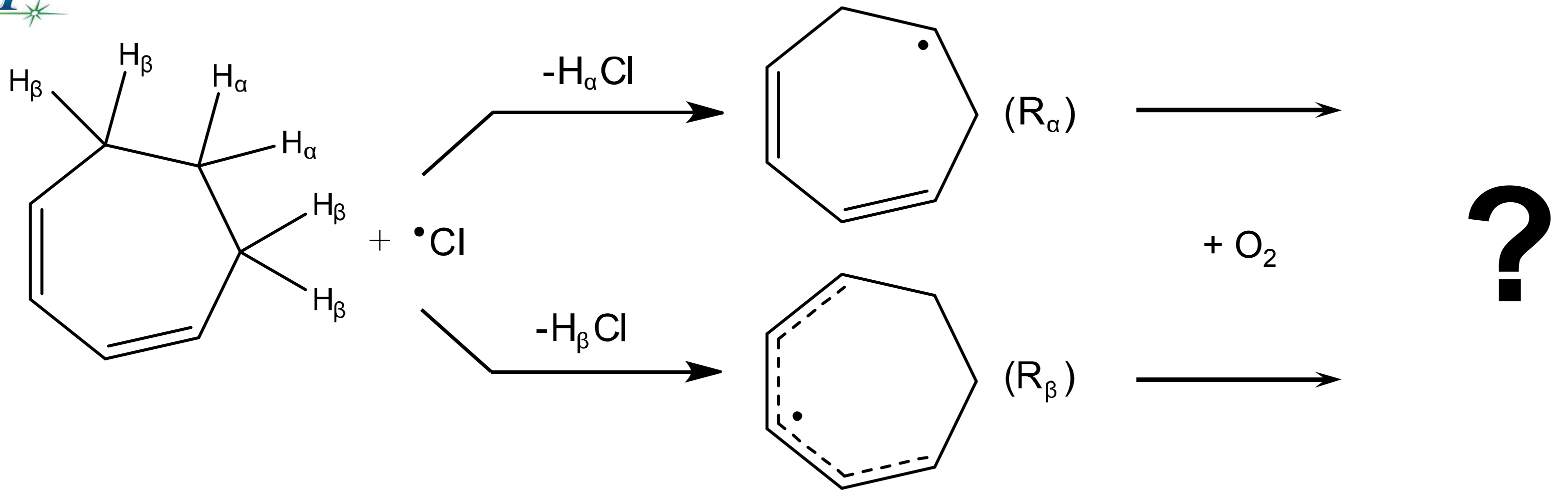
What about QOOH? Don't forget QOOH!

- Cycloheptadiene oxidation (**David Osborn**) -- $QOOH_{\alpha\beta}$ is resonance stabilized (doubly allylic), and below ROO
- ROO well is shallow, inhibiting stabilization
- Both R_α and R_β lead to $QOOH_{\alpha\beta}$

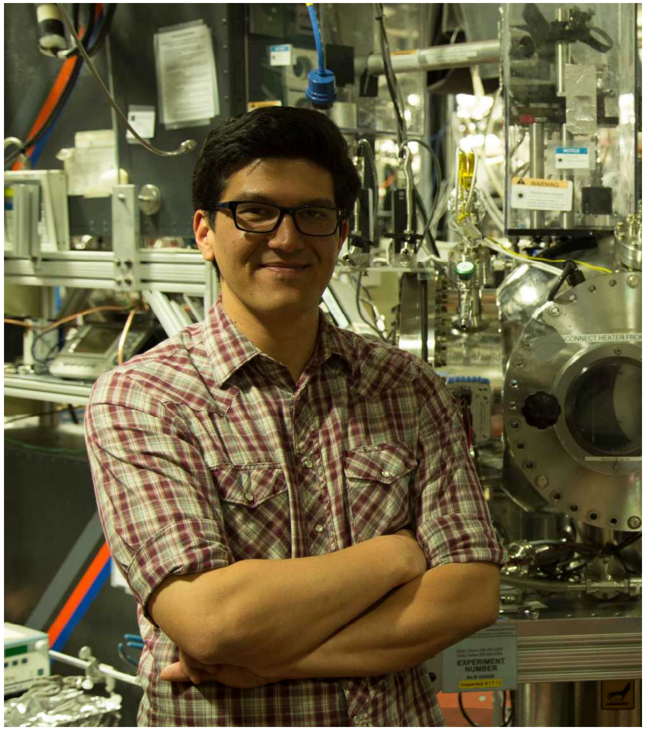
- Butane oxidation – ketohydroperoxides observed
- Ketone oxidation – resonance stabilized QOOH are preferred
- What about more stable QOOH?



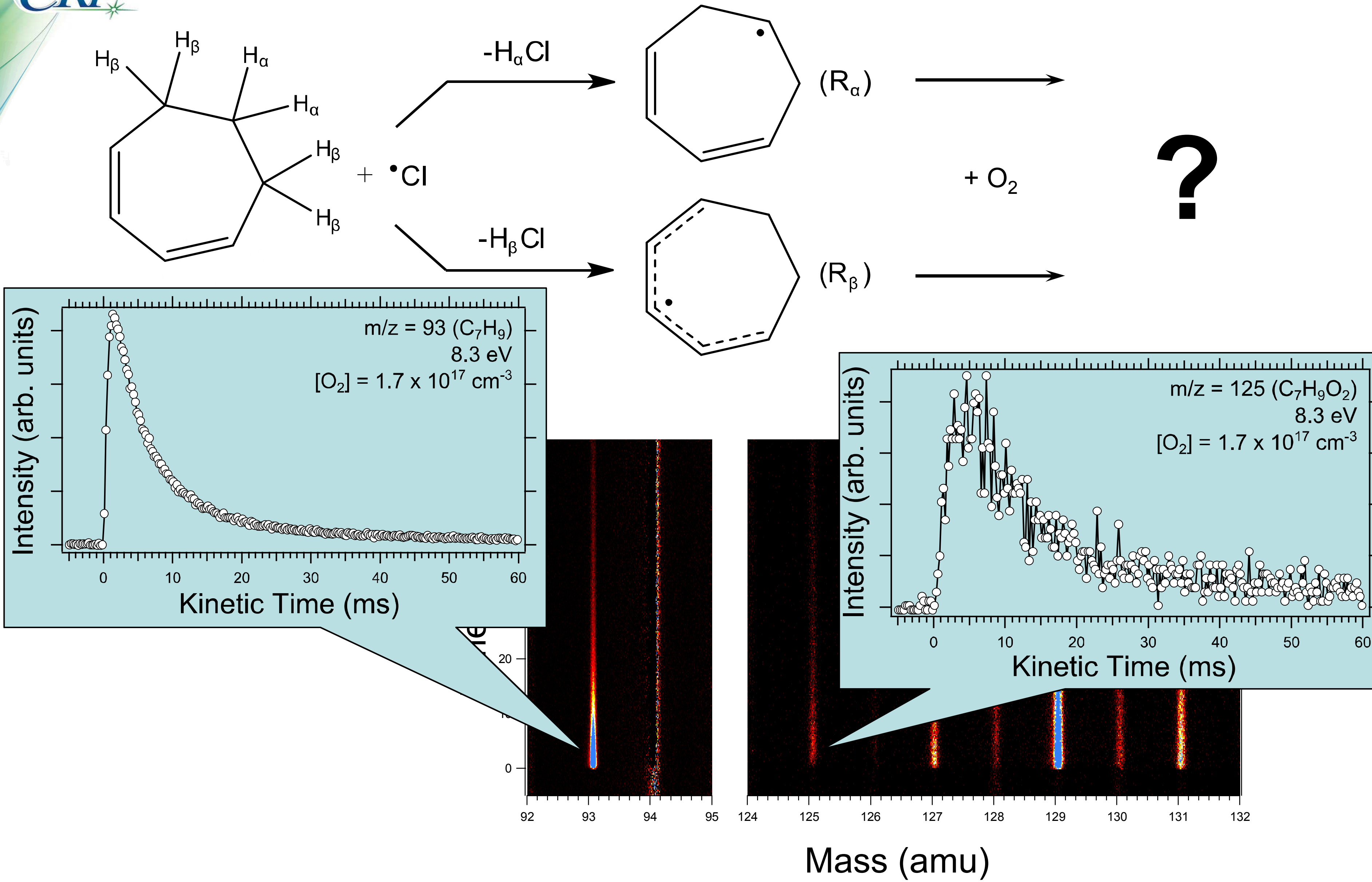
Cycloheptadienyl + O_2



John Savee



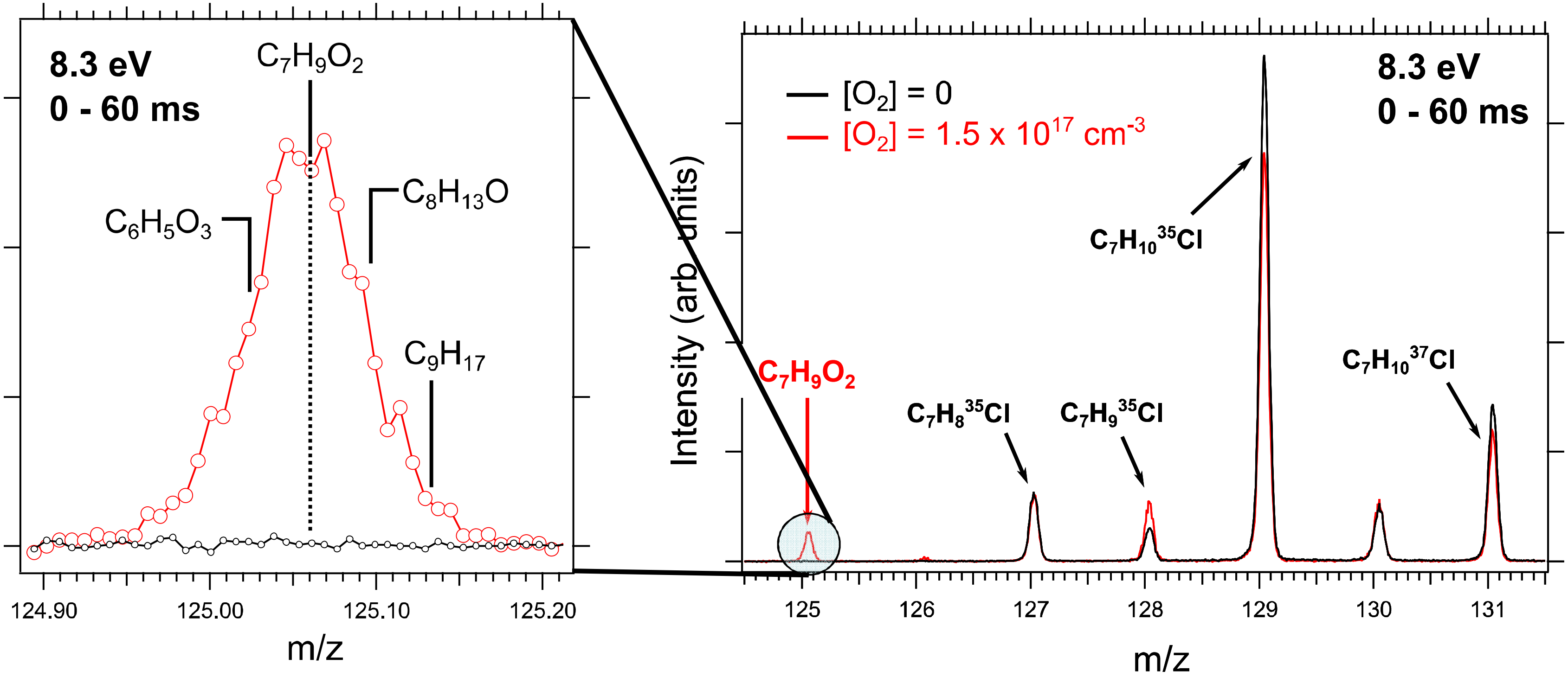
Cycloheptadienyl + O_2



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 $C_7H_9O_2$



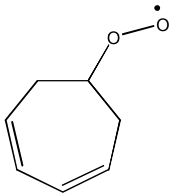
Mass Resolution ~ 1600

Evidence for QOOH

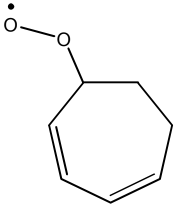
Photoionization Spectrum

- Calculated ionization energy perfect match to QOOH, not ROO

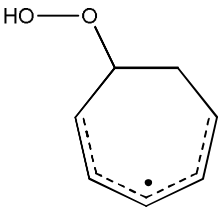
Ab Initio Adiabatic Ionization Energies [M06-2X/6-311+G(2df,2p)]



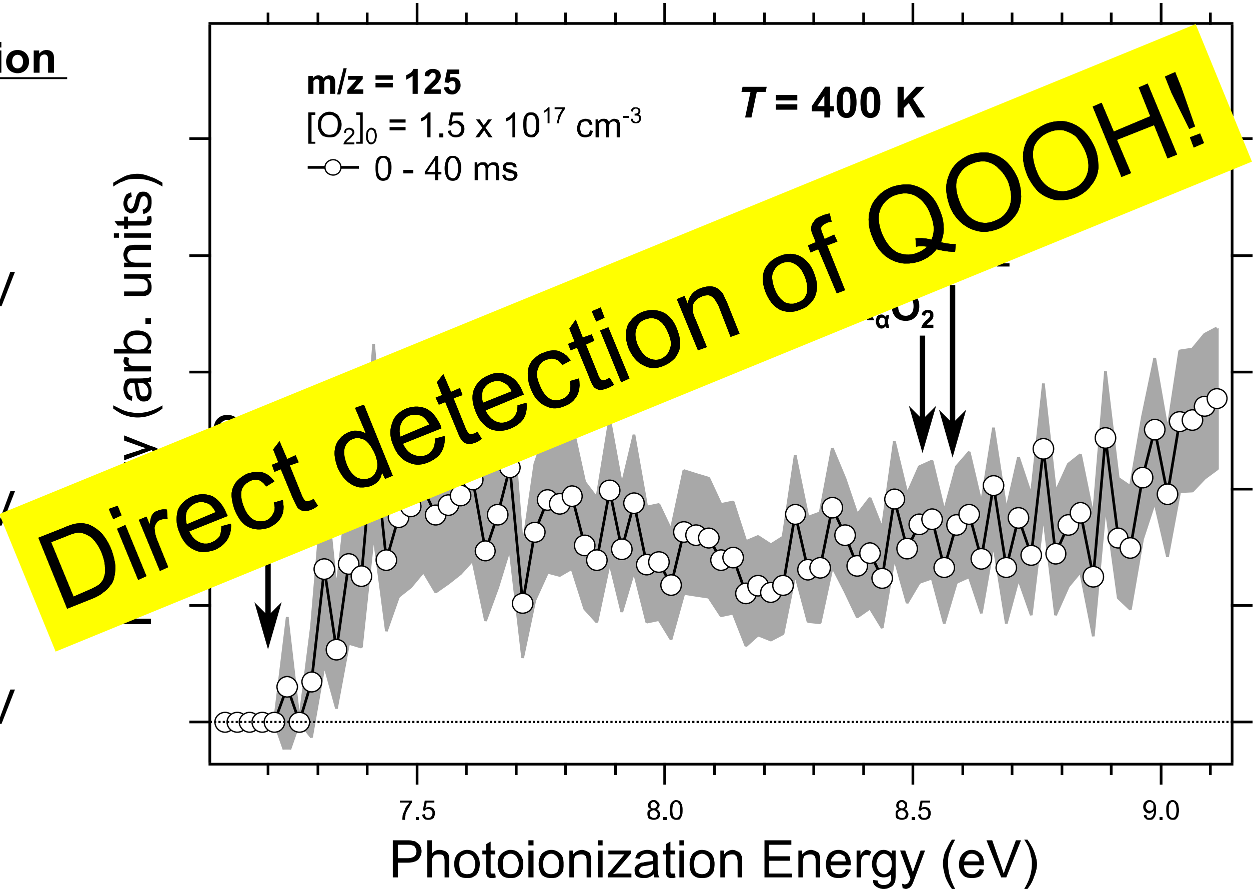
AIE = 8.52 eV



AIE = 8.58 eV



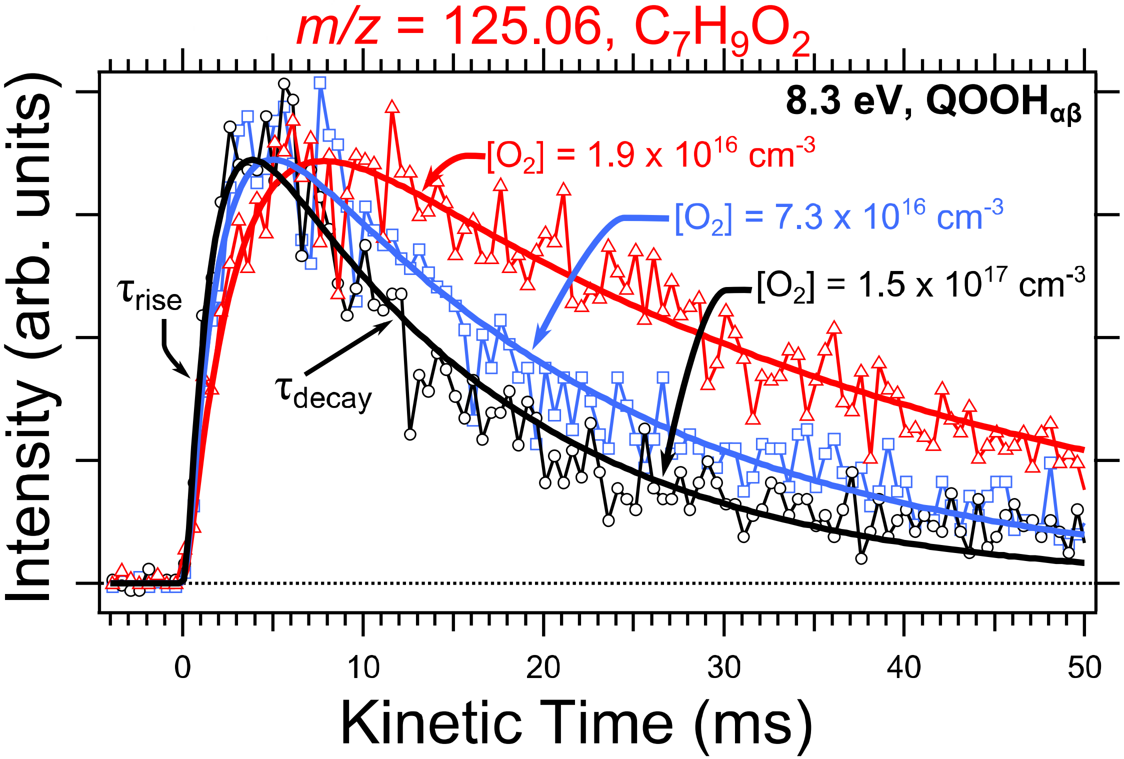
AIE = 7.20 eV

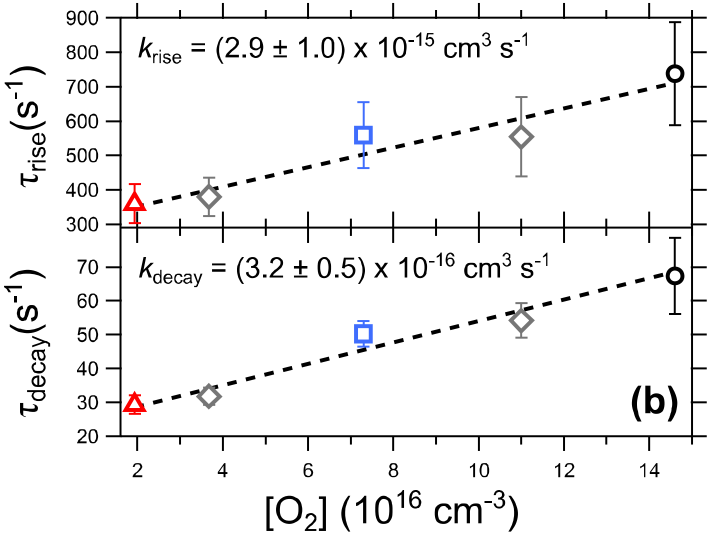


Reaction of QOOH with O_2

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}**

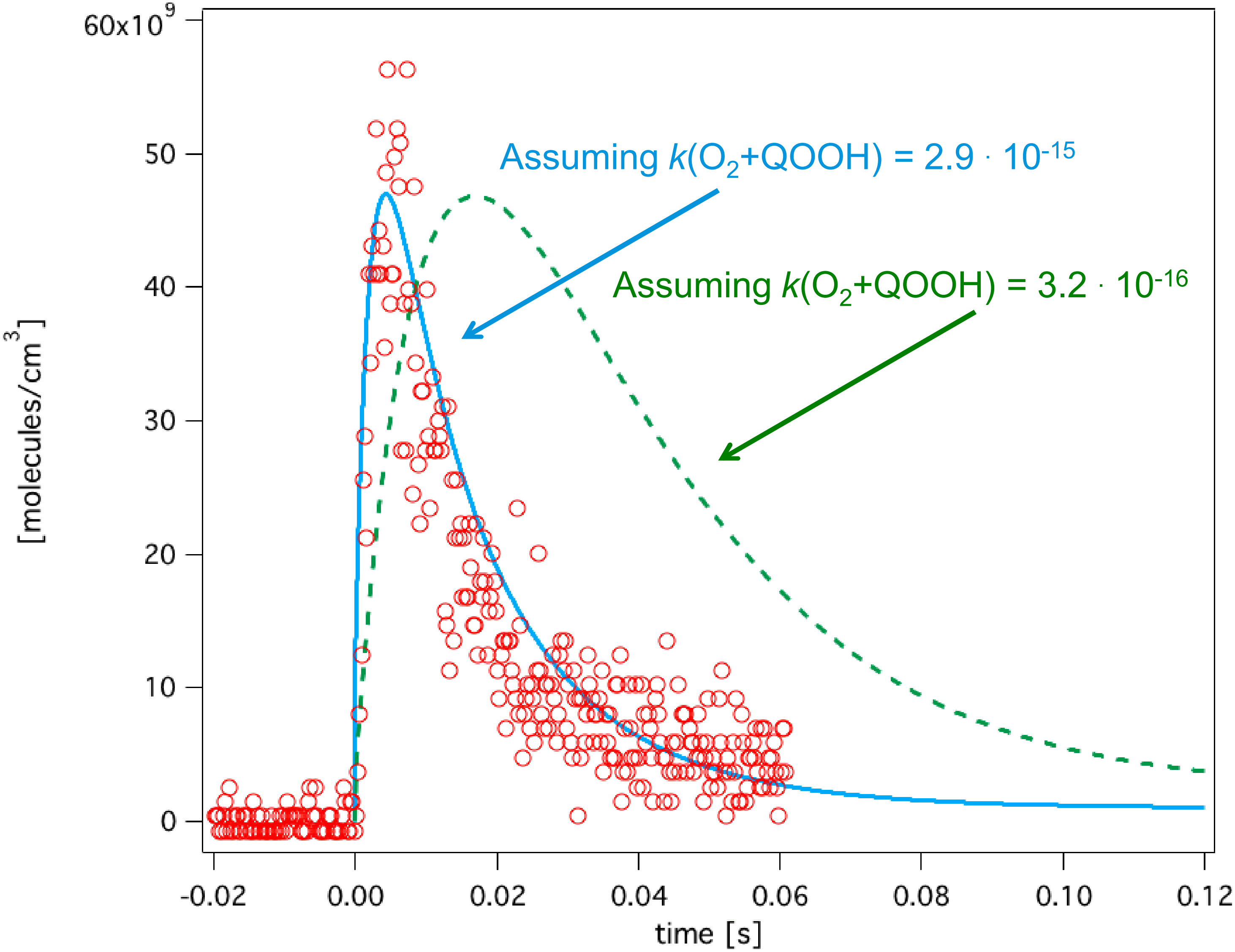




Direct Detection and Kinetics of QOOH Reaction with O_2

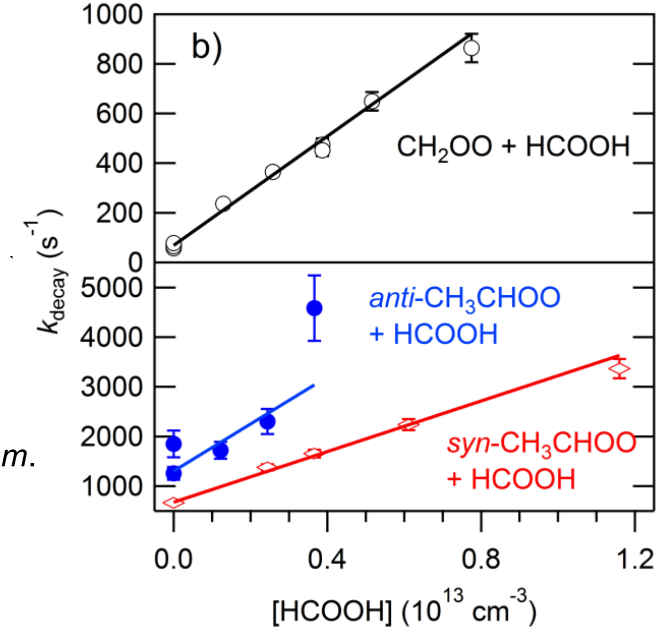
$k(QOOH + O_2) = (2.9 \pm 1.0) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} is much slower than the other second O_2 addition rate coefficients.

Long lifetimes of resonance stabilized QOOHs.

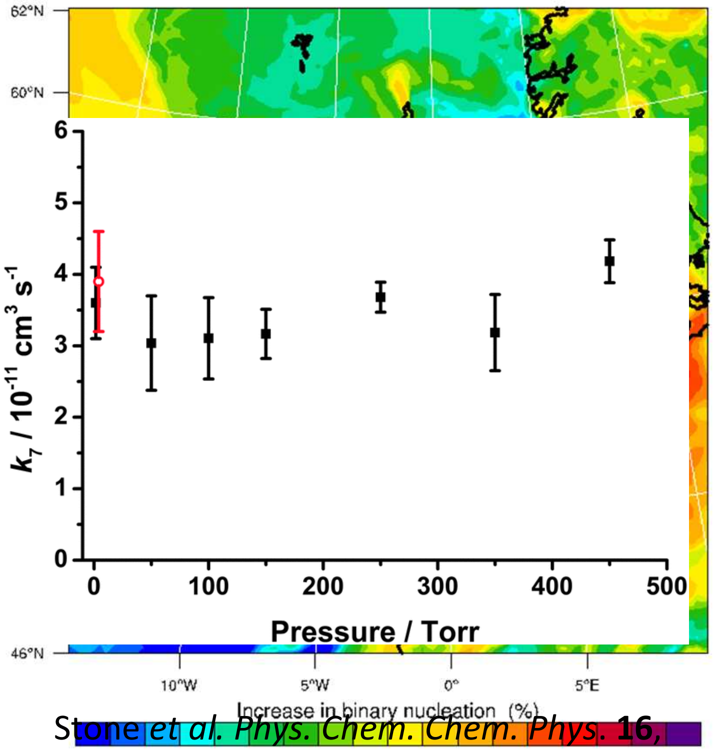


What does all this mean?

- **Sulfate chemistry makes aerosols**
  - Aerosols tend to reflect radiation
    - Criegee chemistry connected to "cooling"
  - Biggest Criegee contribution where there is a lot of ozone and alkenes



Welz et al., *Angew. Chem.* **2014**, 53, 4547 –4550



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

- **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
  - Really need to know *products* of reactions

Percival, Welz, *et al. Faraday Discuss.* **165**, 45-73 (2013)

No really… what does all this mean?

What happens if an important reaction in the model is changed by orders of magnitude?

- Or maybe… nothing happens?

Models of Complex Chemical Systems … They're not so Simple

Criegee reacts faster with SO_2 -- So we must oxidize a lot more SO_2?

- Depends on how much Criegee there is, which (o.a.)
- Depends on what *else* reacts with Criegee intermediates

Sulfate makes aerosols – so we must make a lot more aerosols?

- In some places, but
- Depends on what *else* makes aerosol

Aerosols are cooling, so there must be a change in predicted radiative forcing?

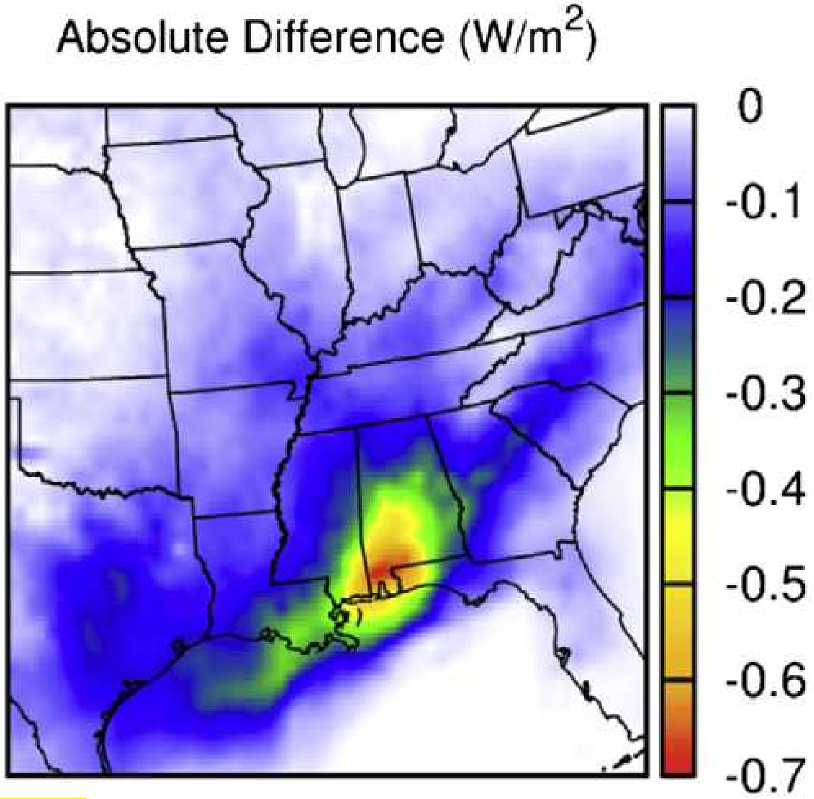
- Maybe in some places
- But global average may still be small

Stone et al. (PCCP **16**, 1139-1149 (2

$k_{CH2OO + water} < 0.9 \times 10^{-16}$ cm^3 s^{-1}

k_{water} = 2.4 × 10 cm s k_{water} s^{-1}

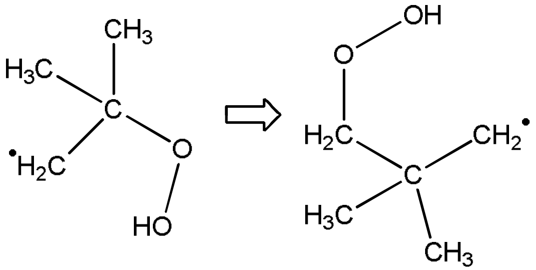
G. Sarwar et al. Atmos. Environ. **68** 186-197 (2013)



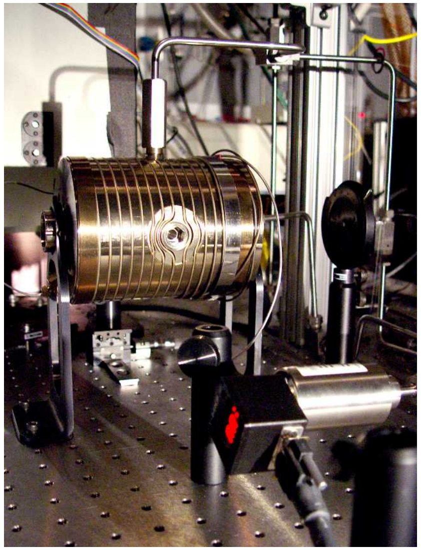
J. Li et al. *Atmos. Environ.* **79** 442-447 (2013)

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

CRF

ZOTS

Judit Zádor, David Osborn, CAT, Lenny Sheps

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Brandon Rotavera, John Savee, Adam Scheer, Oliver Welz
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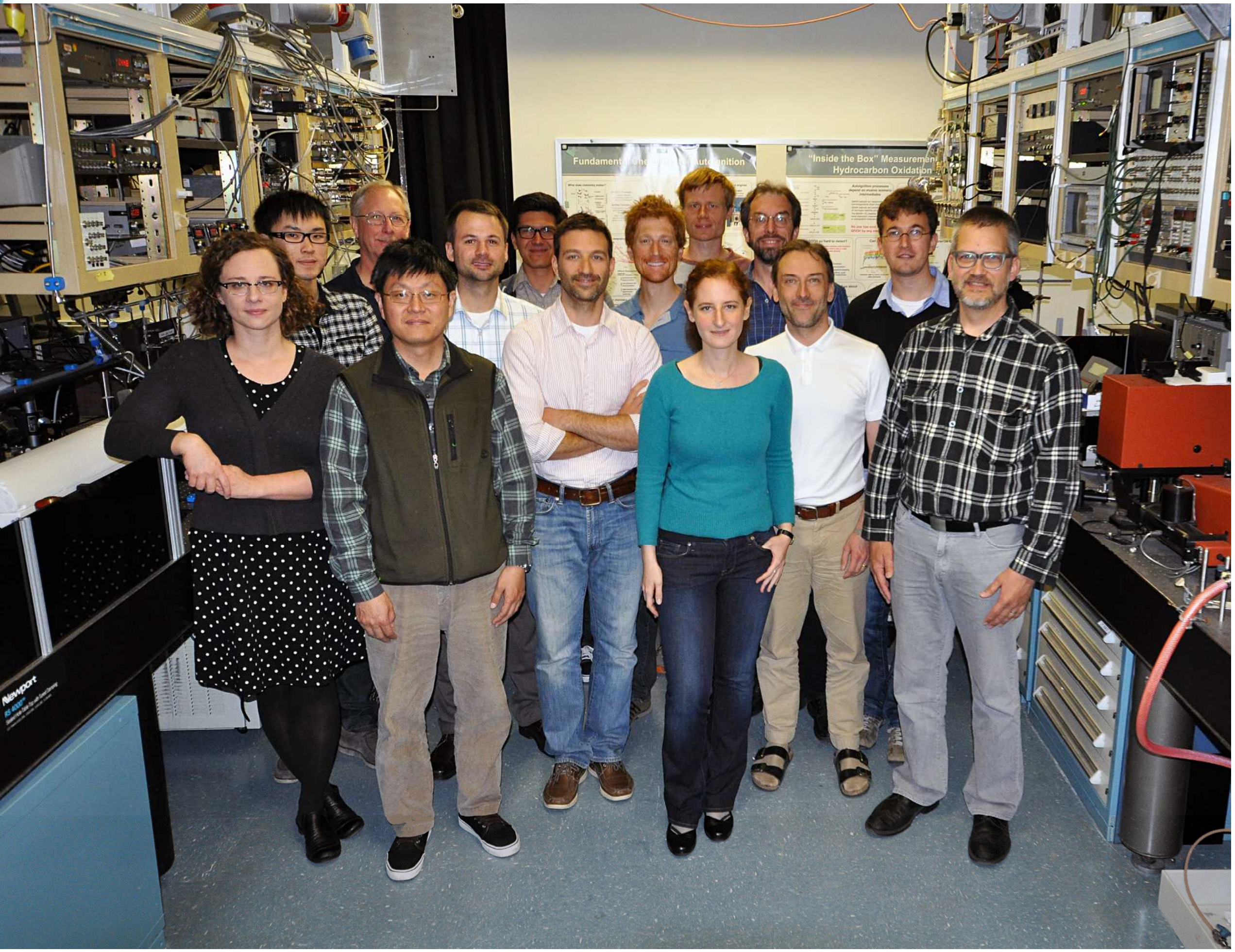

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Carl Percival (Manchester) Dudley Shallcross (Bristol) Stephen Klippenstein (Argonne)

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