

Probing the Chemistry of Elusive Intermediates in Hydrocarbon Oxidation

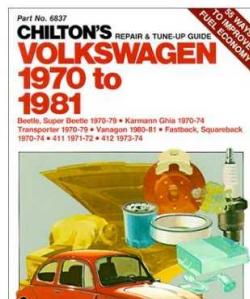
Craig A. Taatjes

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

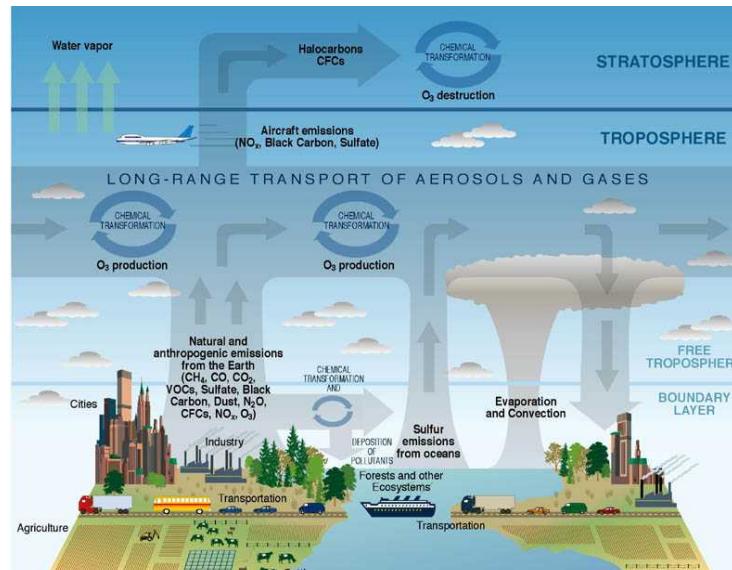
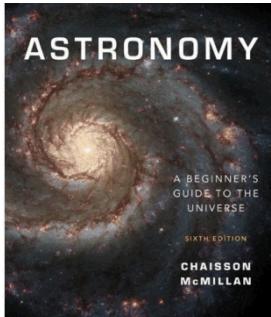
Why do people do chemical kinetic modeling?



Robert Couse-Baker



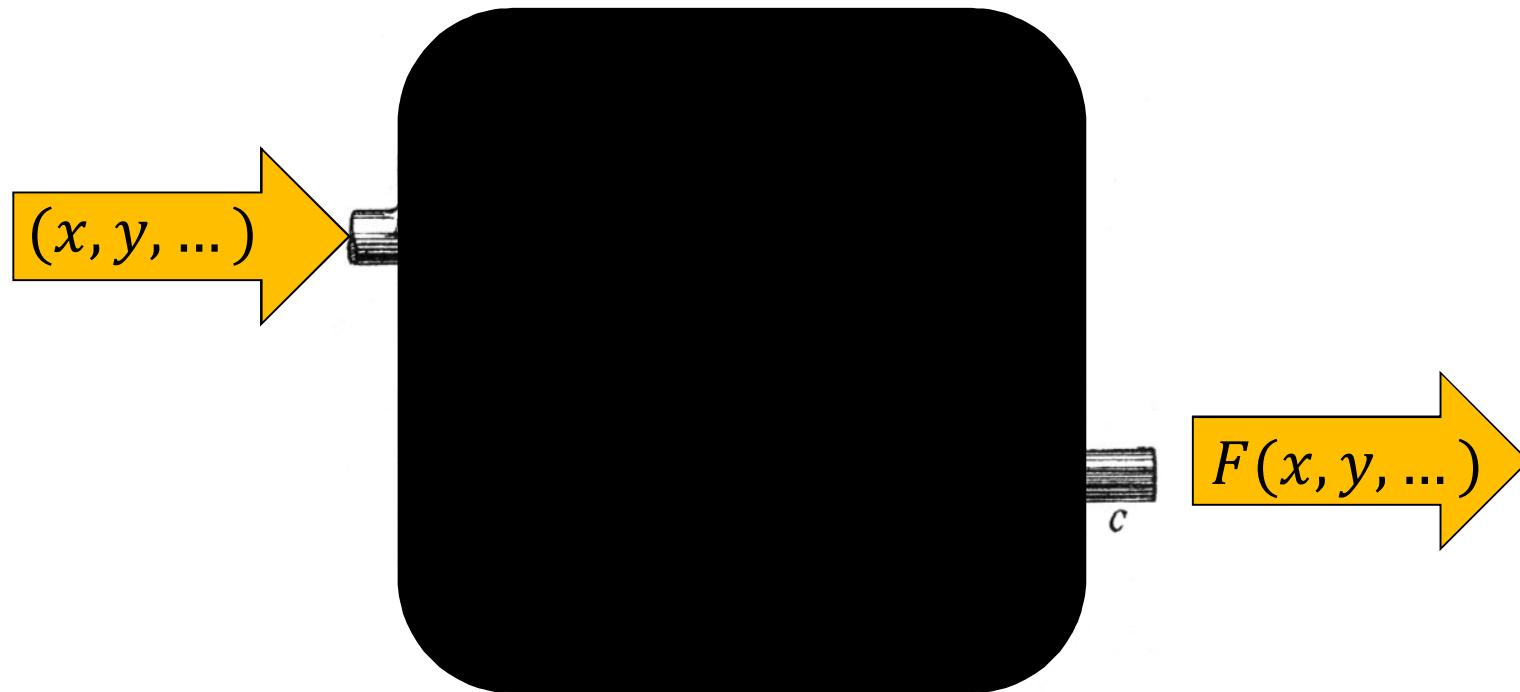
Predict what will happen as the boundary conditions are changed



CLIMATE CHANGE SCIENCE PROGRAM OFFICE



What will make a model *predictive*?



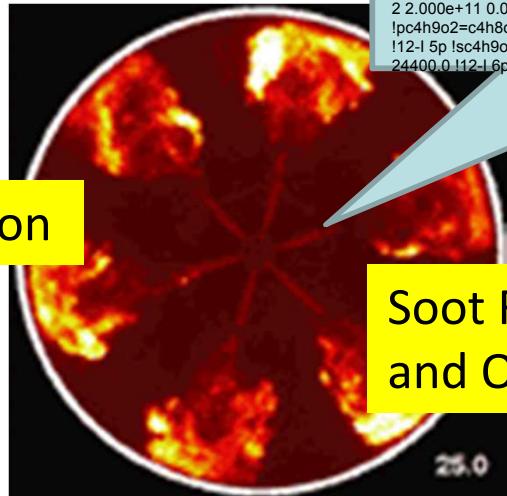
6. Wechselgetriebe für vier Geschwindigkeiten und Rücklauf:

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

Turbulent,
multiphase flows
interact with the
chemistry



Comprehensive Kinetic Mechanism

c7h15o2-1=c7h14oho1-2 2.000e+11 0.000 26850.0 !12-l 5s c7h15o2-1=c7h14oho1-3 2.500e+10 0.000
c7h14oho1-4 3.125e+09 0.000 19050.0 !12-l 7s c7h15o2-1=c7h14oho1-5
2-l 8s c7h15o2-2=c7h14oho1-3 3.000e+11 0.000 29400.0 !12-l 5p c7h15o2-1
0.000 26850.0 !12-l 5s c7h15o2-2=c7h14oho2-4 2.500e+10 0.000 20850.0
h2-5 3.125e+09 0.000 19050.0 !12-l 7s c7h15o2-2=c7h14oho2-6 3.912e+0
5o2-3=c7h14oho3-1 3.750e+10 0.000 24400.0 !12-l 6p c7h15o2-1
0.000 26850.0 !12-l 5s c7h15o2-3=c7h14oho3-4 2.000e+11 0.000 26850.0
h3-5 2.500e+10 0.000 20850.0 !12-l 6s c7h15o2-3=c7h14oho3-6 3.125e+0
5o2-3=c7h14oho3-7 5.860e+08 0.000 25550.0 !12-l 8p c7h15o2-4=c7h14oho4-1
1 9.376e+09 0.000 22350.0 !12-l 7p c7h15o2-4=c7h14oho4-2 5.000e+10 0.000 20850.0 !12-l 6s c7h15o2-1
4=c7h14oho4-3 4.000e+11 0.000 26850.0 !12-l 5s !c6h13o2-1=c6h12oho1-2 2.000e+11 0.000 26850.0
!12-l 5s c6h13o2-1=c6h12oho1-3 2.500e+10 0.000 20850.0 !12-l 6s c6h13o2-1=c6h12oho1-4 3.125e+0
0.000 19050.0 !12-l 7s c6h13o2-1=c6h12oho1-5 3.912e+08 0.000 22050.0 !12-l 8s c6h13o2-2
=c6h12oho2-1 3.000e+11 0.000 29400.0 !12-l 5p c6h13o2-2=c6h12oho2-3 2.000e+11 0.000 26850.0
!12-l 5s c6h13o2-2=c6h12oho2-4 2.500e+10 0.000 20850.0 !12-l 6s c6h13o2-2=c6h12oho2-5 3.125e+0
0.000 19050.0 !12-l 7s c6h13o2-2=c6h12oho2-6 5.860e+08 0.000 25550.0 !12-l 8p c6h13o2-3
=c6h12oho3-1 3.750e+10 0.000 24400.0 !12-l 6p c6h13o2-3=c6h12oho3-2 2.000e+11 0.000 26850.0
!12-l 5s c6h13o2-3=c6h12oho3-4 2.000e+11 0.000 26850.0 !12-l 5p c6h13o2-3=c6h12oho3-5 2.500e+0
0.000 20850.0 !12-l 6s c6h13o2-3=c6h12oho3-6 4.688e+09 0.000 25550.0 !12-l 7p !c5h11o2-1
=c5h11o0h1-2 2.000e+11 0.000 26850.0 !12-l 5s c5h11o2-1=c5h11o0h1-3 2.500e+10 0.000 20850.0
!12-l 6s c5h11o2-1=c5h10oho1-4 3.125e+09 0.000 19050.0 !12-l 7s c5h11o2-1=c5h10oho1-5 5.860e+0
0.000 25550.0 !12-l 8p c5h11o2-2=c5h10oho2-1 3.000e+11 0.000 29400.0 !12-l 5p c5h11o2-2
=c5h10oho2-3 2.000e+11 0.000 26850.0 !12-l 5s c5h11o2-2=c5h10oho2-4 2.500e+10 0.000 20850.0
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0.000 24400.0 !12-l 6p c5h11o2-3=c5h10oho3-2 4.000e+11 0.000 26850.0 !12-l 7s c5h11o2-3=c5h10oho3-1
2 2.000e+11 0.000 26850.0 !12-l 5s !pc4h9o2=c4h8oho1-3 2.500e+10 0.000 20850.0 !12-l 6s
!pc4h9o2=c4h8oho1-4 4.688e+09 0.000 22350.0 !12-l 7p !sc4h9o2=c4h8oho2-1 2.000e+11 0.000 29400.0
!12-l 5p !sc4h9o2=c4h8oho2-3 3.2000e+11 0.000 26850.0 !12-l 5s !sc4h9o2=c4h8oho2-4 2.000e+11 0.000
24400.0 !12-l 6p !

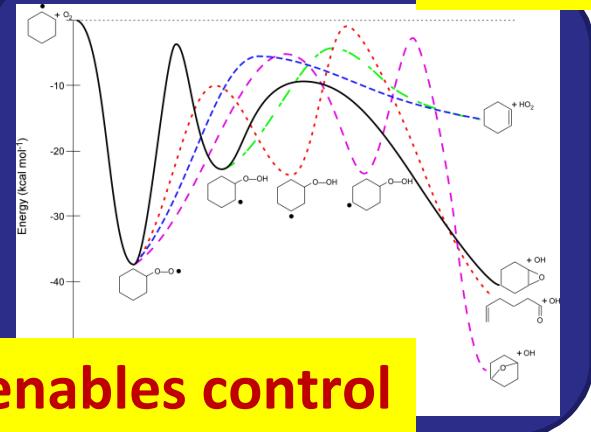
Autoignition

Soot Formation and Oxidation

Prediction enables control

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

R + O₂ reactions



Tropospheric and Engine Oxidation Processes Both Run on Radical Chain Chemistry

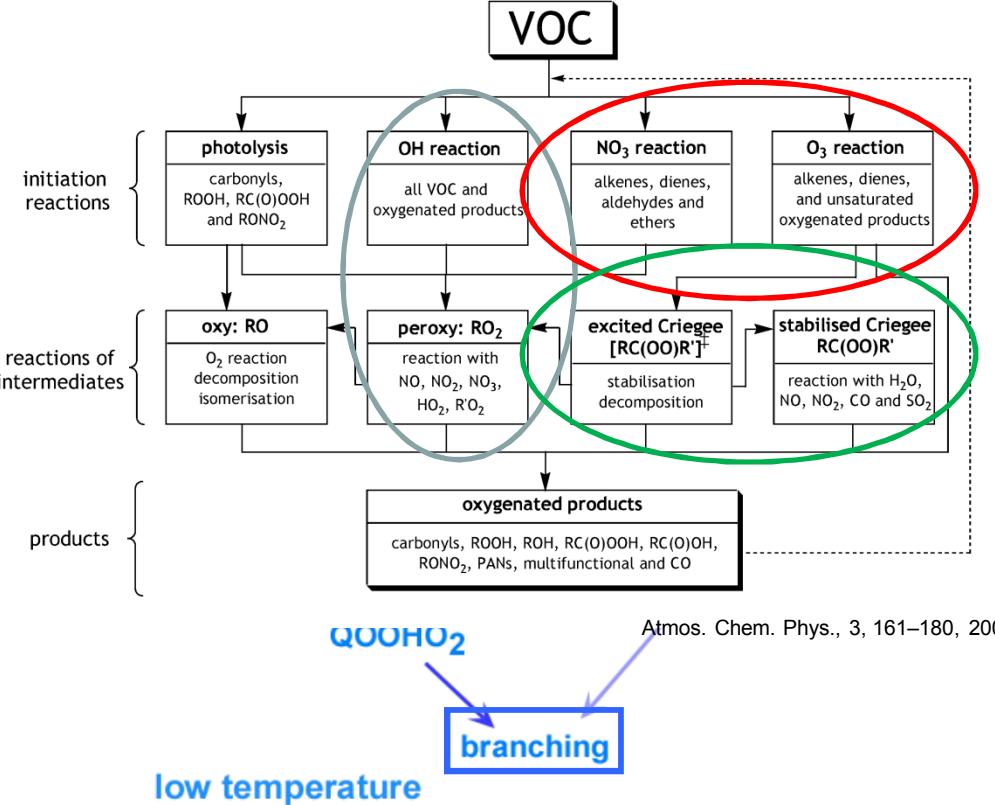
Ignition Chemistry:

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

Tropospheric Chemistry:

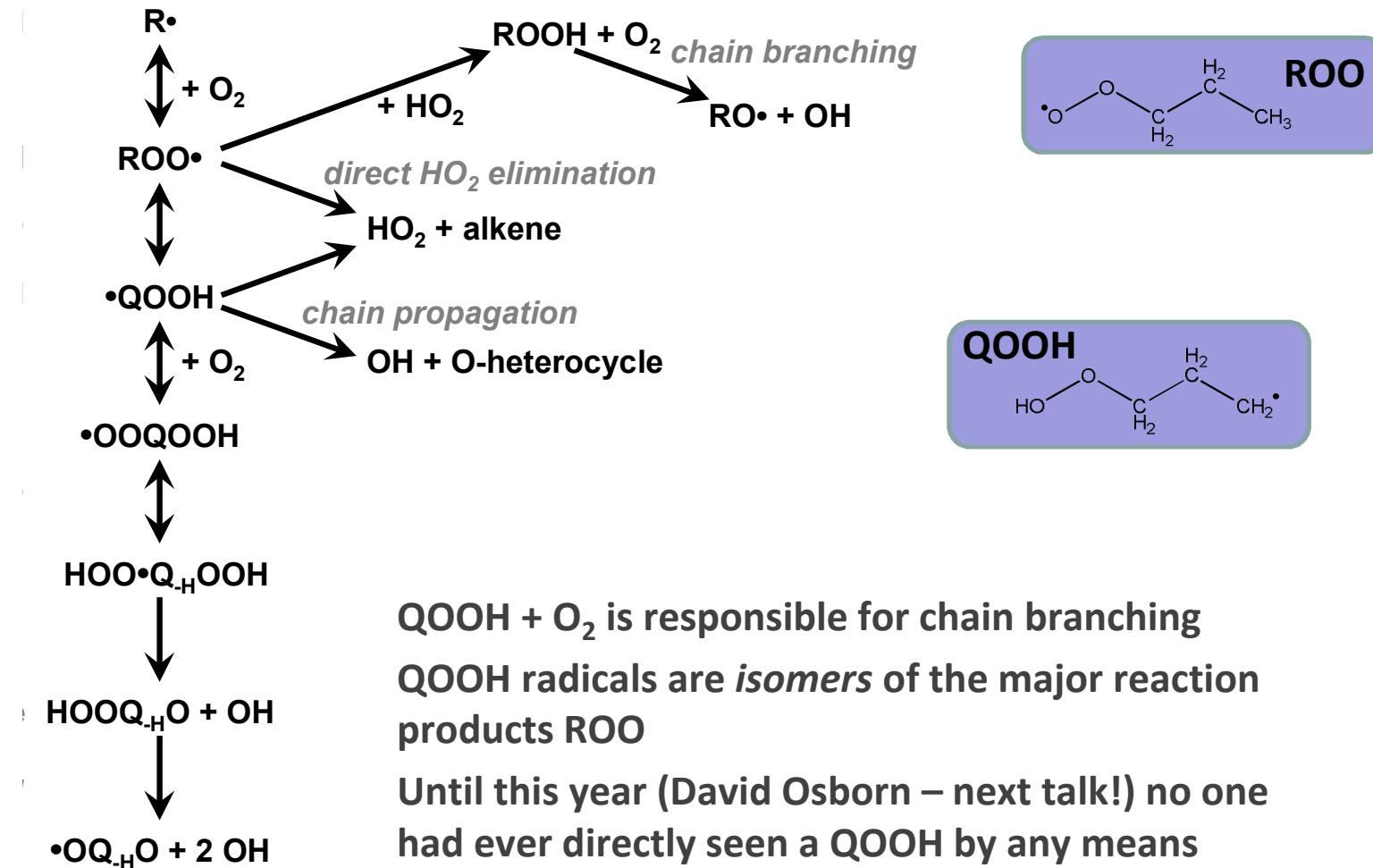
- Alkyl + O₂ reactions from OH-initiated oxidation also important in troposphere
- NO₃ and O₃ species are also important oxidation initiators
- Criegee intermediates* are important species for OH, aerosol formation, NO_x, SO_x

General Alkyl Radical Oxidation Scheme



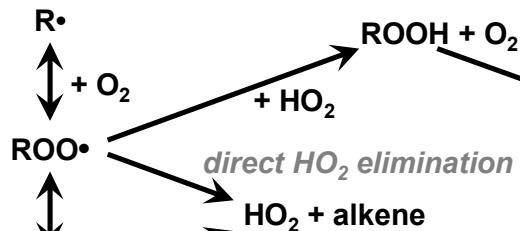
Adapted from Walker and Morley, "Basic Chemistry of Combustion," in *Low Temperature Combustion and Autoignition*, Ed. M. J. Pilling, (Comprehensive Chemical Kinetics Vol. 35) Elsevier, 1997

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

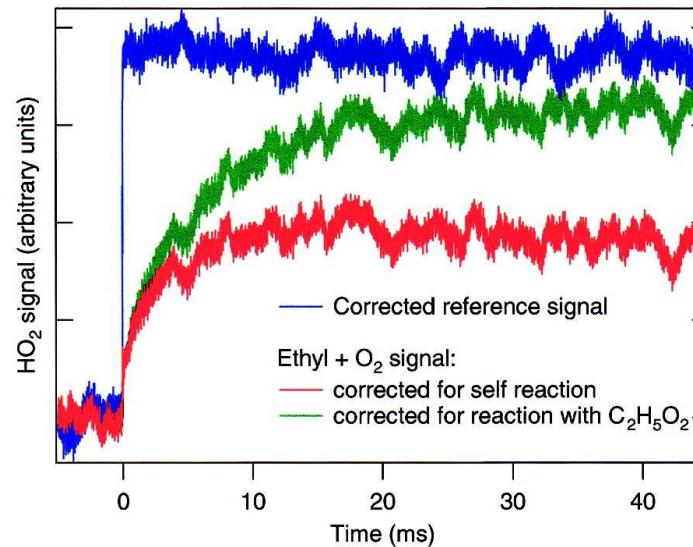


So what can we do? Take one step at a time?

Alkyl + O_2 reactions – Detect the HO_2 reaction product



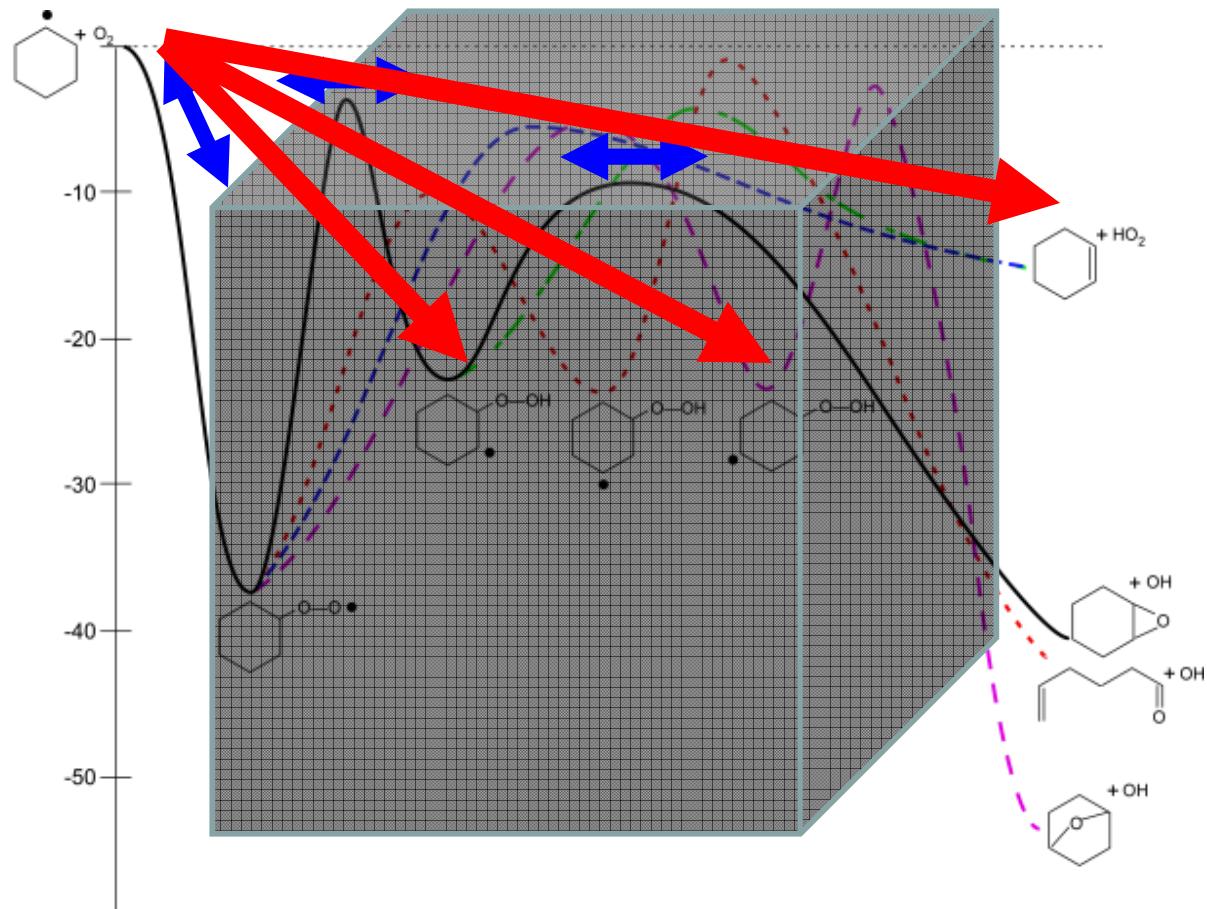
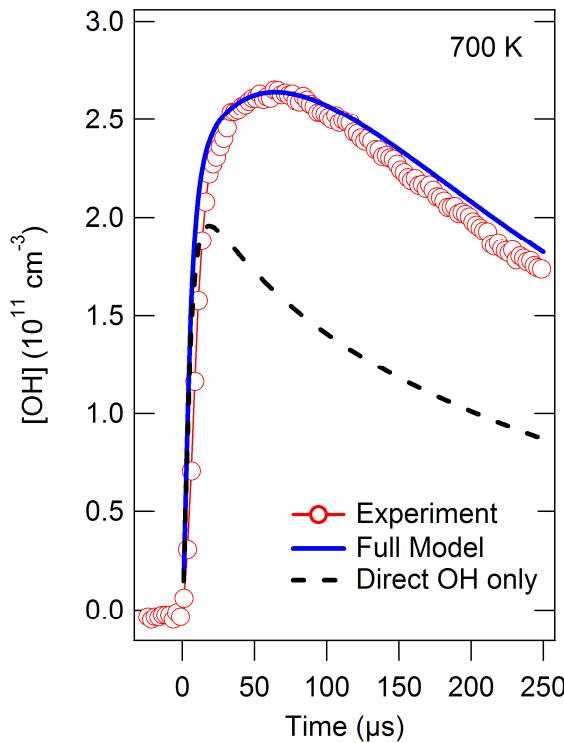
Product appears on two timescales -- kinetically separate chemical activation contribution



Phenomenological analysis

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

Measured products from
pulsed photolytically
initiated $R + O_2$ 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

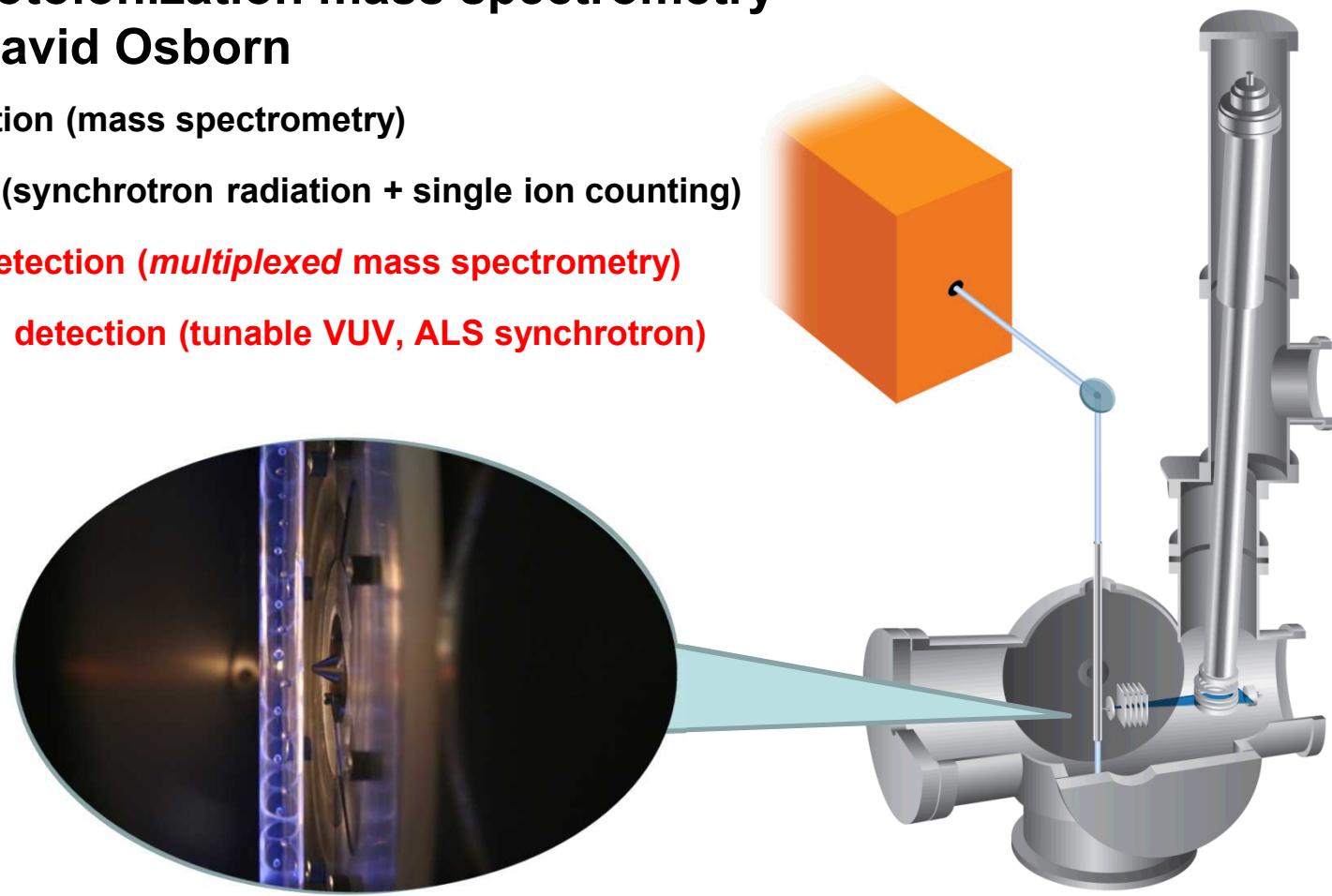
Multiplexed photoionization mass spectrometry (MPIMS) – David Osborn

Universal detection (mass spectrometry)

High sensitivity (synchrotron radiation + single ion counting)

Simultaneous detection (*multiplexed* mass spectrometry)

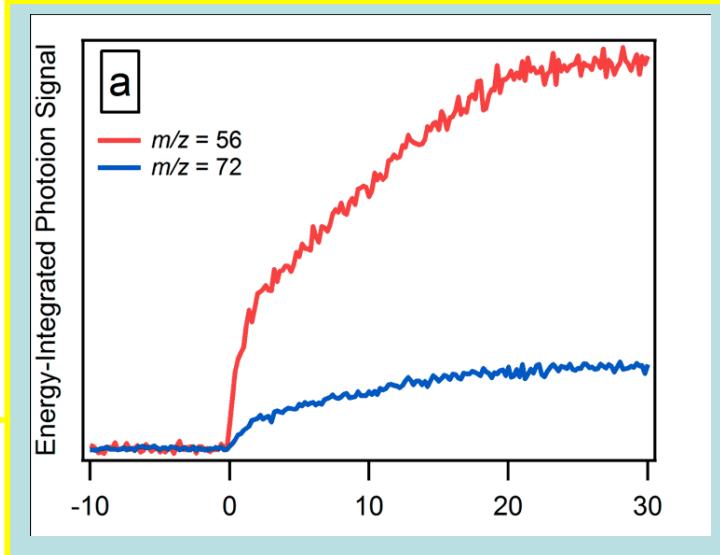
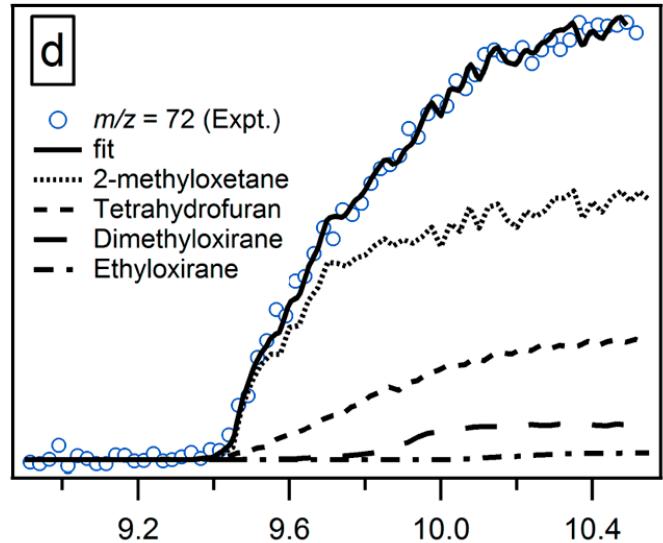
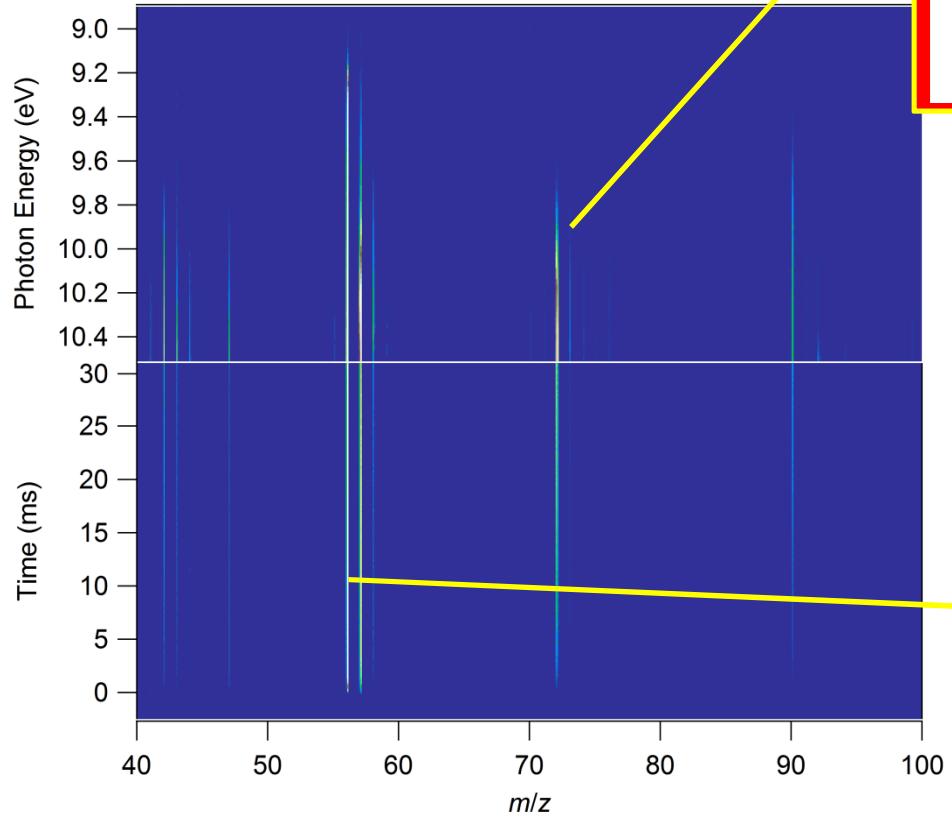
Isomer-resolved detection (tunable VUV, ALS synchrotron)



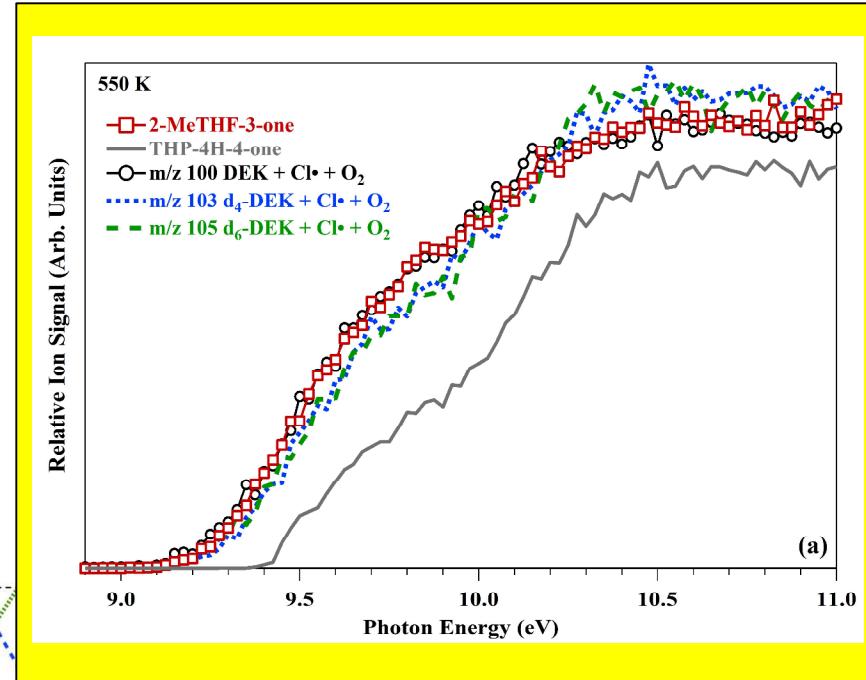
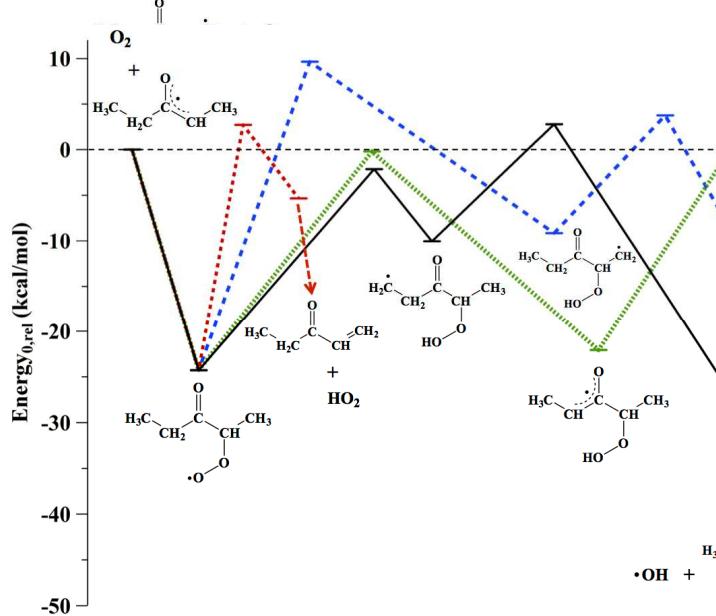
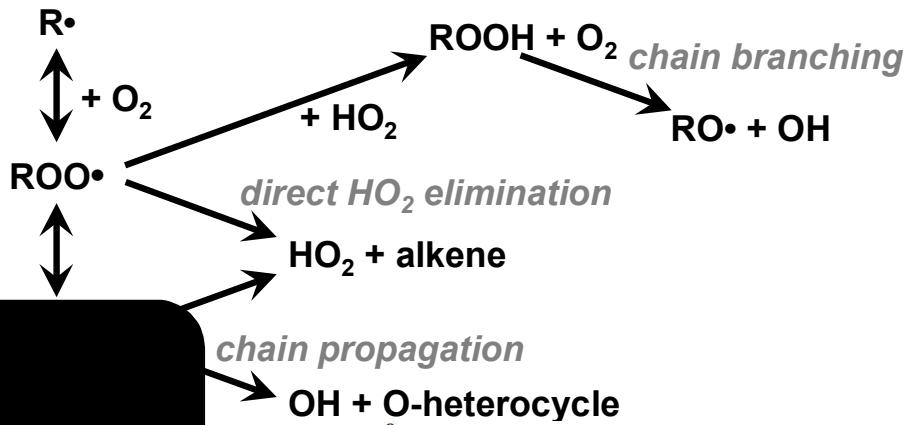
Cl-initiated oxidation

Time behavior of product formation – prompt and delayed

Photoionization spectra identify product isomers



Thermodynamics Affects the Isomerization and Dissociation of QOOH



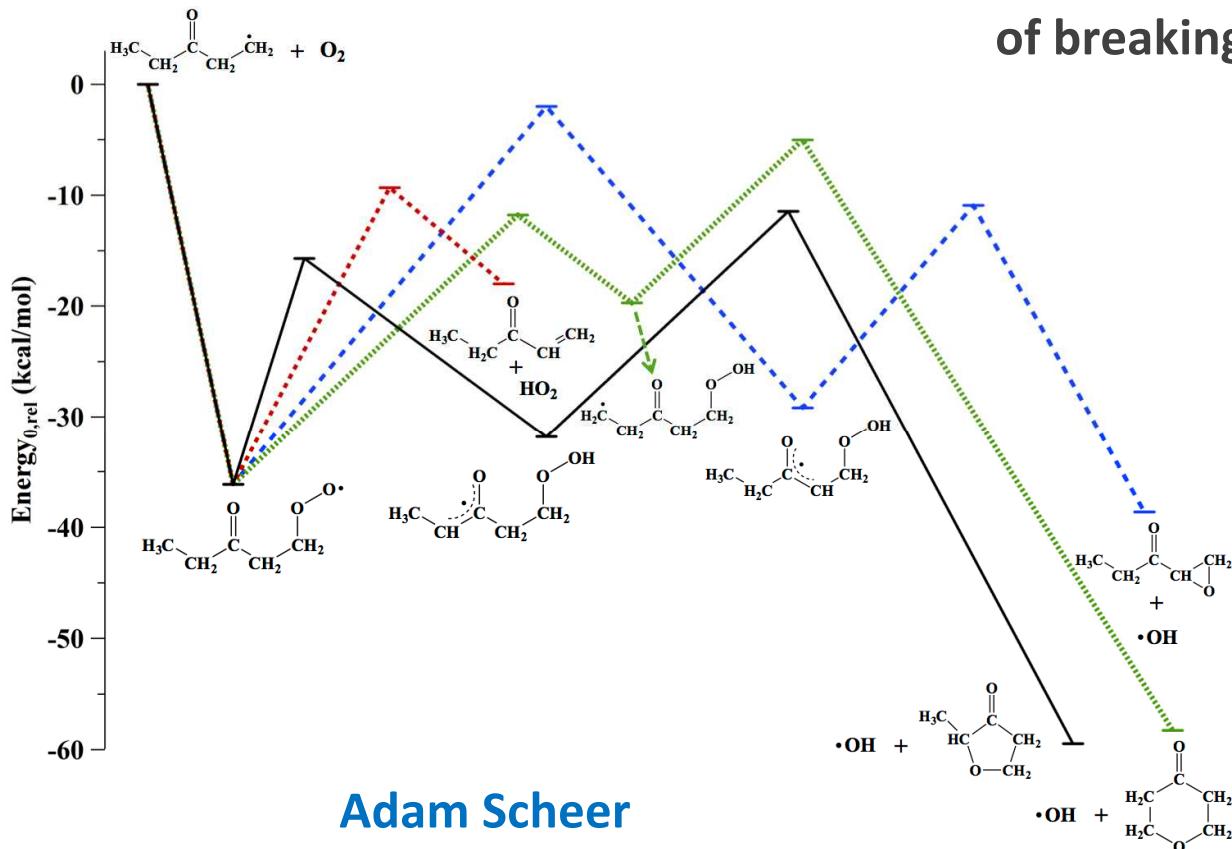
Resonance stabilization
may favor particular QOOH
pathway

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?



Adam Scheer

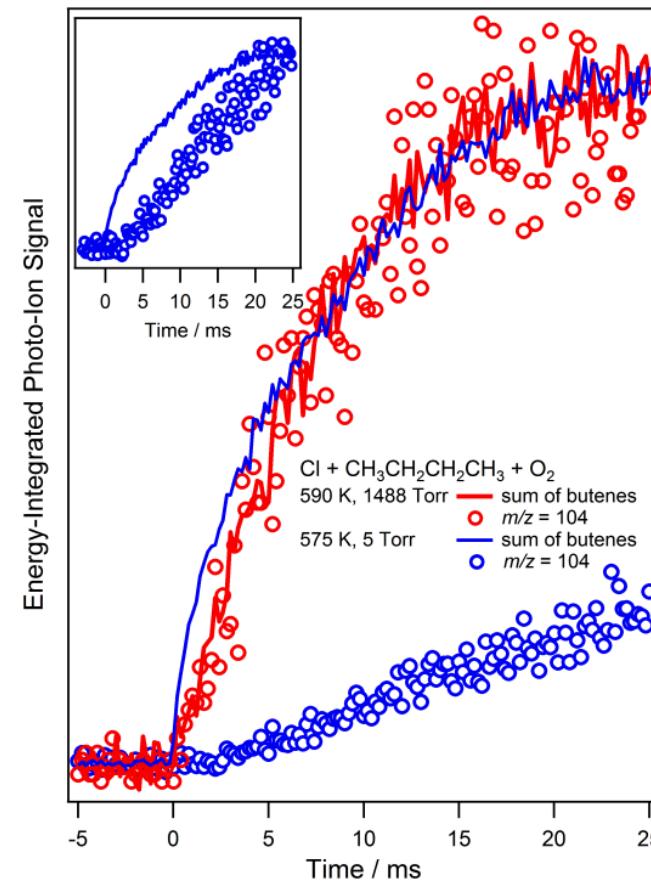
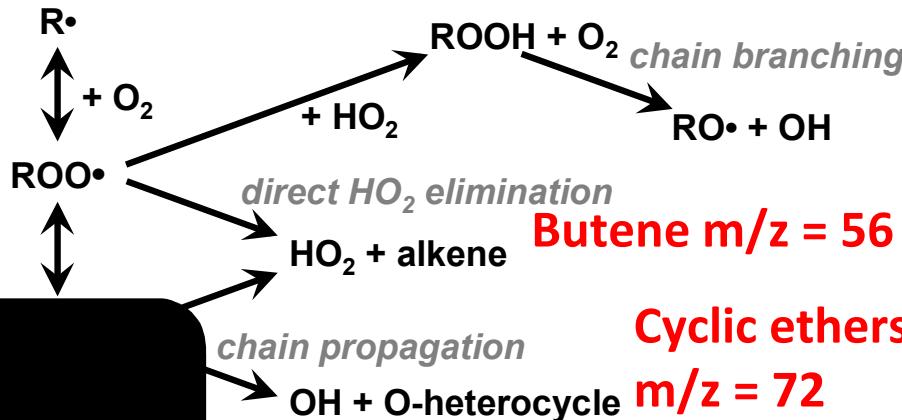
Ring strain in the transition state for isomerization

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

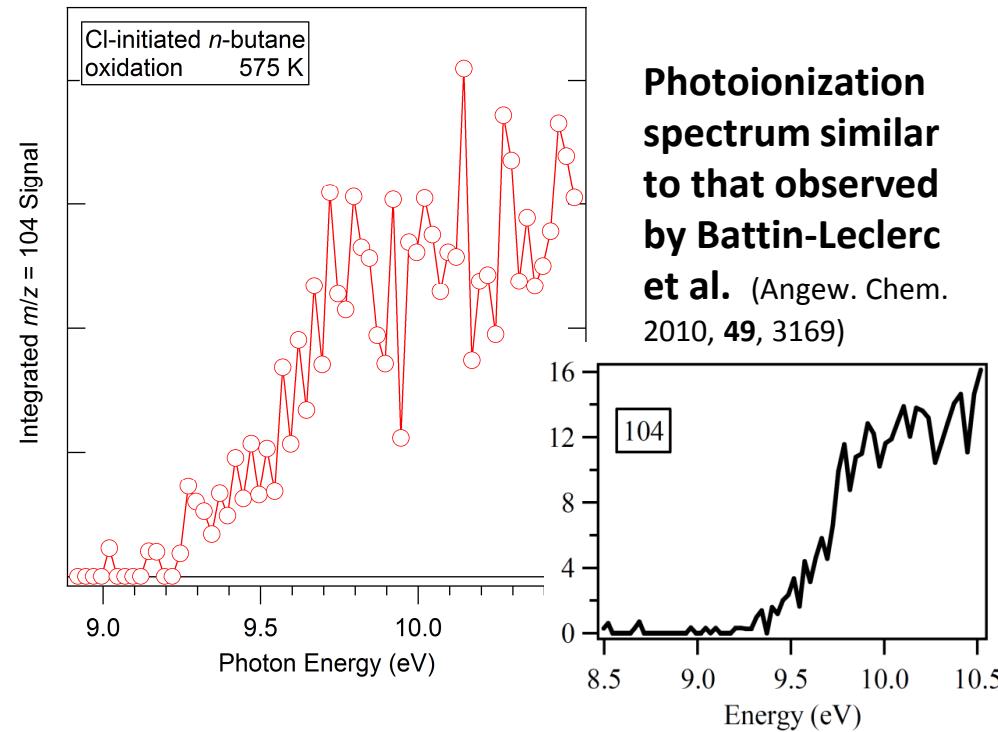
Photoionization mass spectrometry can also follow the subsequent oxidation steps

Butyl radical
 $m/z = 57$



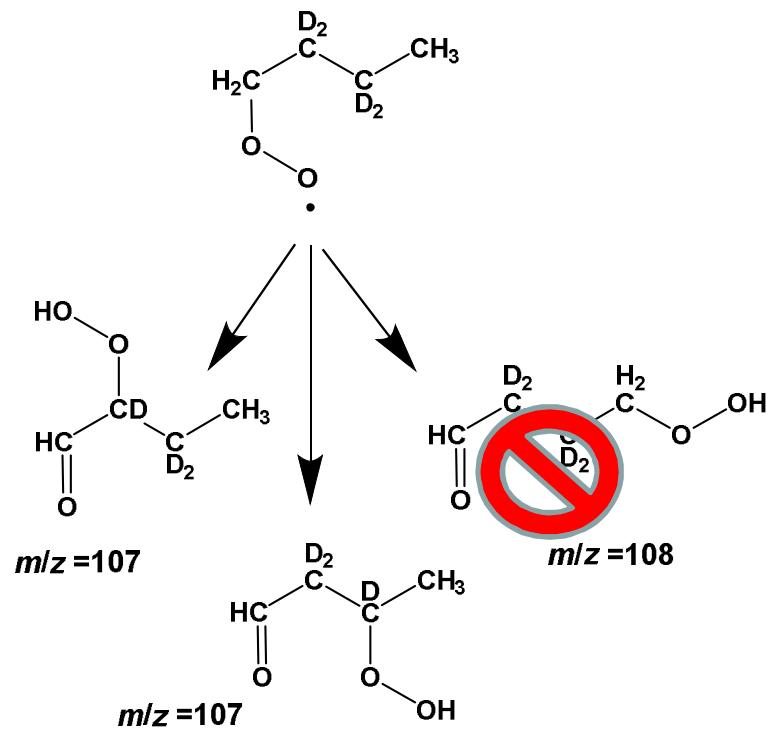
Arkke Eskola et al. *Proc. Combust. Inst.* in press
doi:10.1016/j.proci.2014.05.011

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



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

Isotopic labeling further narrows the possible ketohydroperoxide isomers

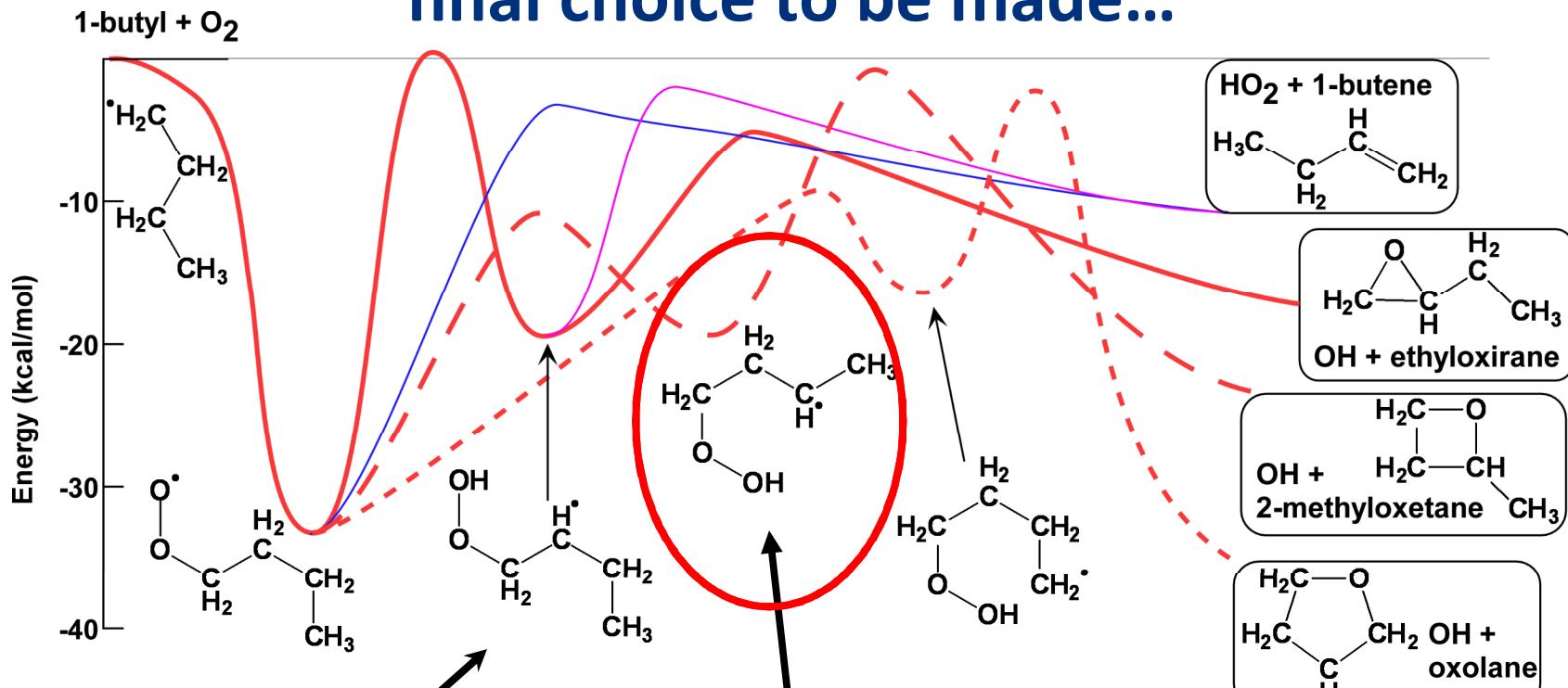


At low pressure, the ketohydroperoxide yield relative to ROO is linear with $[O_2]$

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

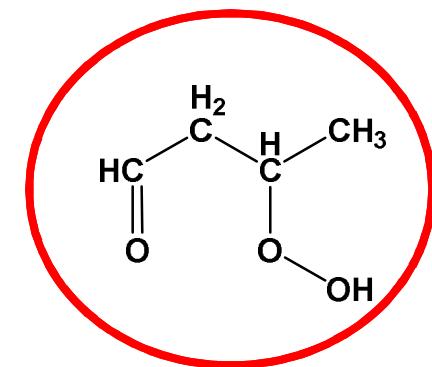
Arkke Eskola

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



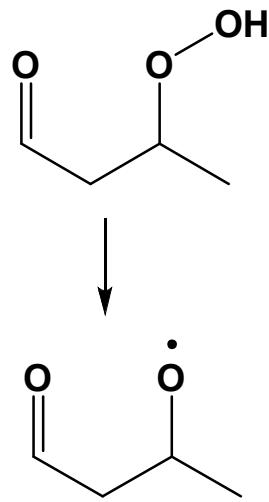
Difficult to make, rapidly dissociates to bimolecular products

Easy to make, larger barrier to bimolecular products



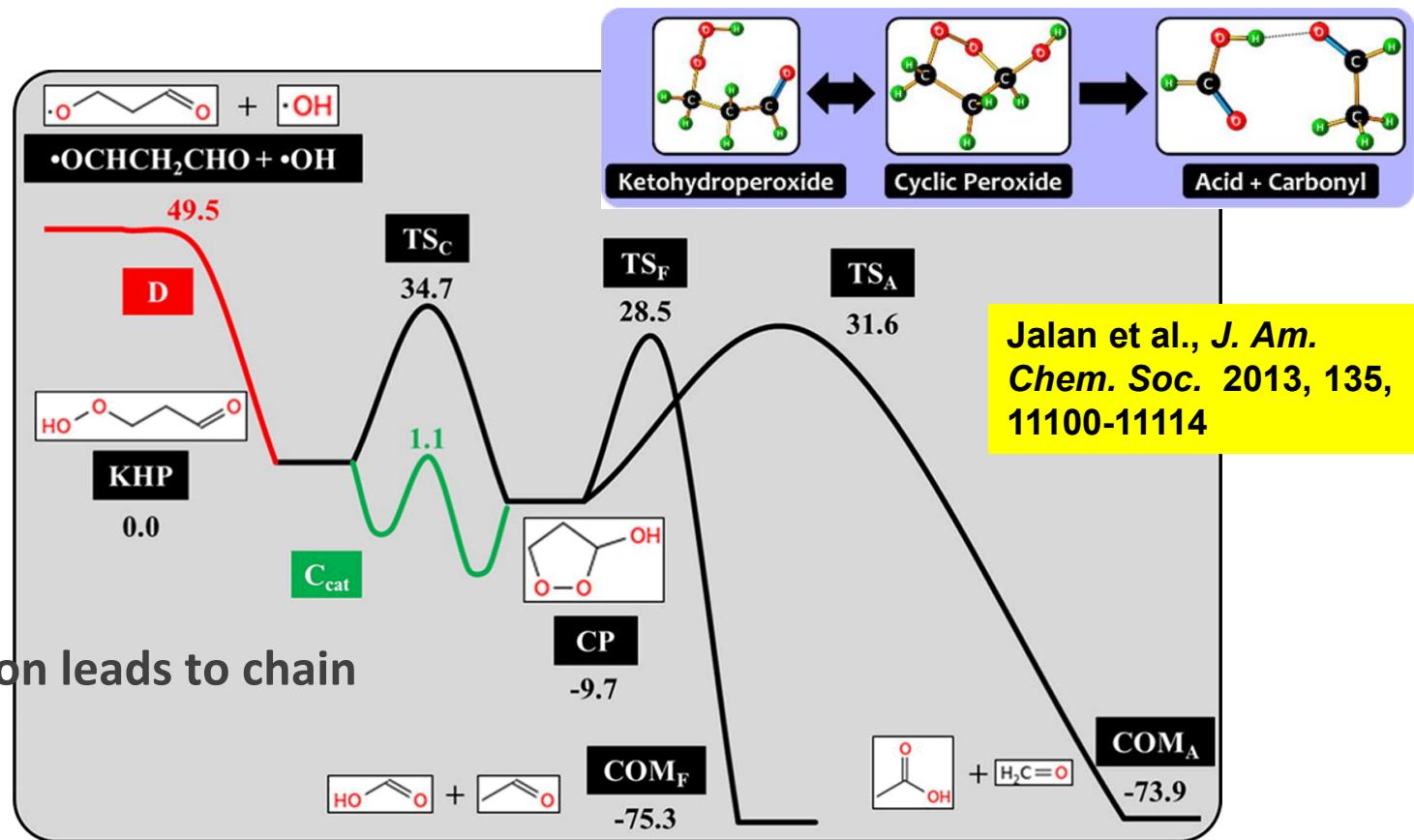
What happens to γ -ketohydroperoxides?

The observed species is a gamma-ketohydroperoxide



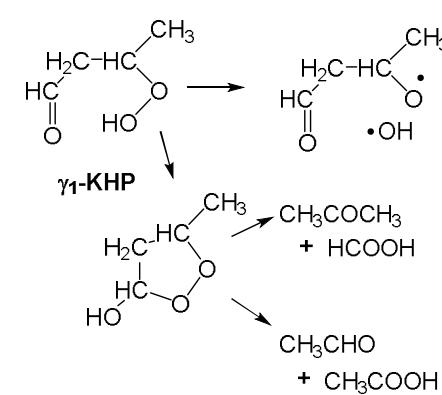
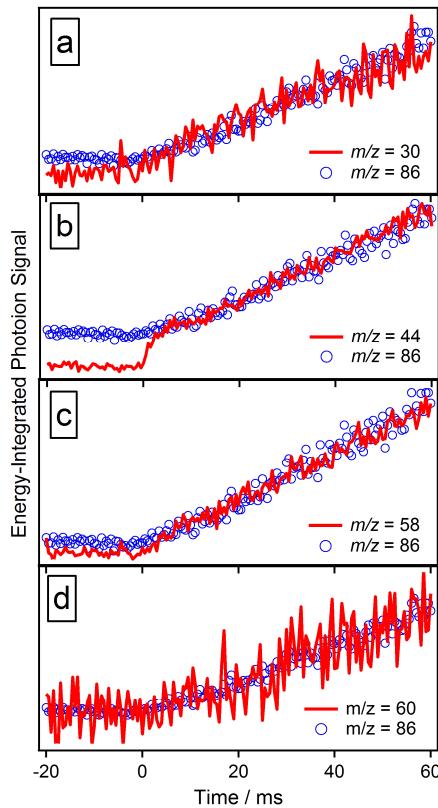
O-O bond fission leads to chain branching

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

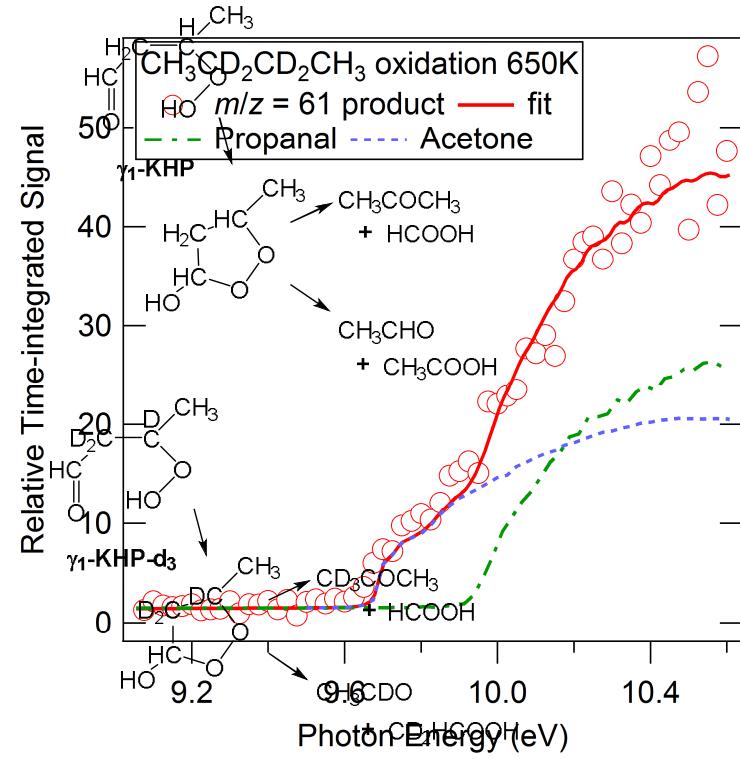


Observed products in Cl-initiated butane oxidation include organic acids

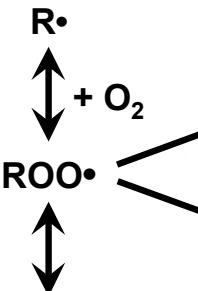
Timescale suggests formation from ketohydroperoxide



Acetone isotopic signature could signal isomerization



But we still haven't measured the intermediate QOOH steps



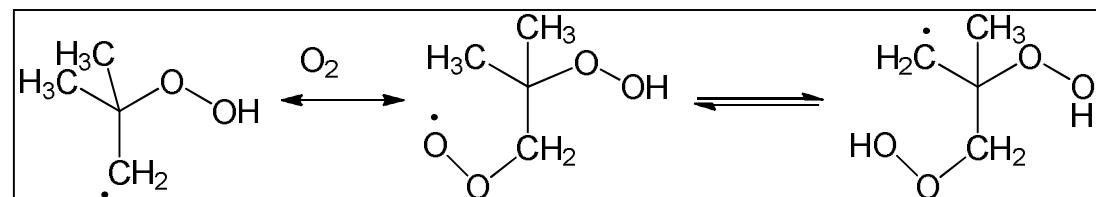
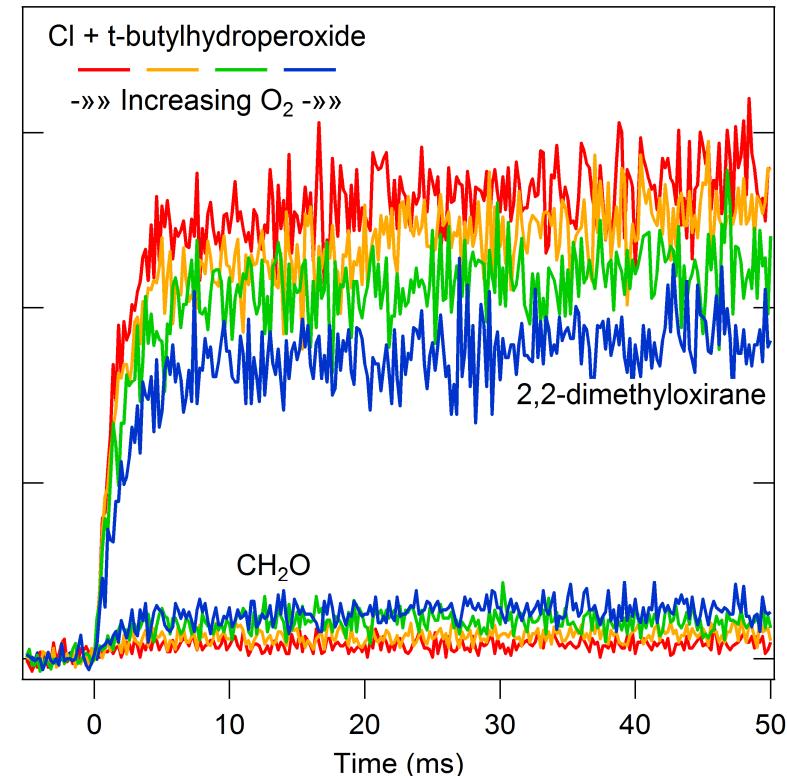
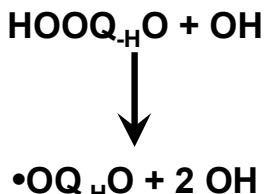
Problem is to make enough!

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



Reaction with O₂ competes with dissociation – forms other products

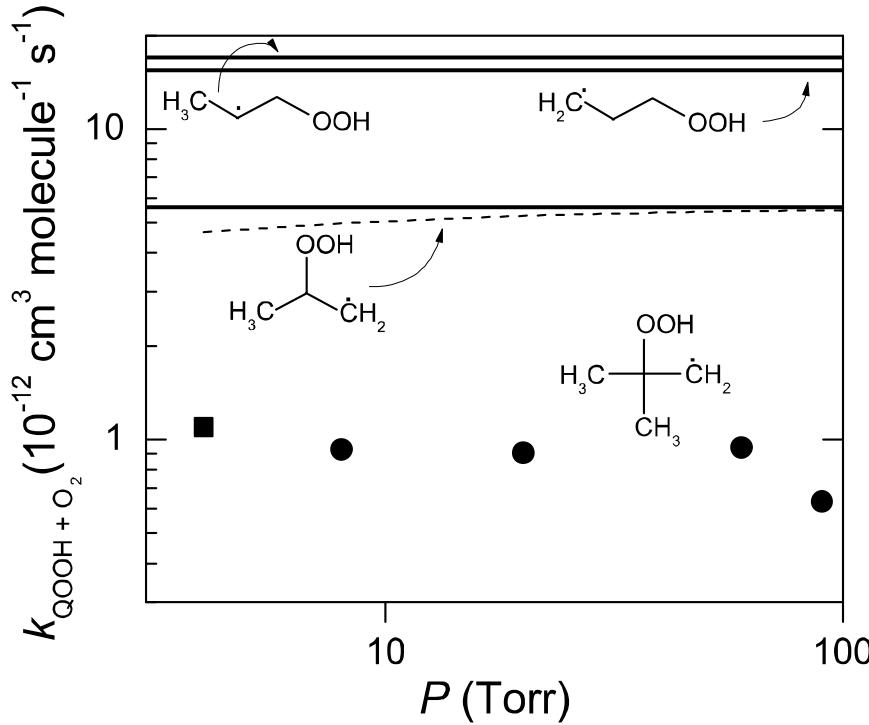
Relative rate can give *direct* measurements of QOOH reactions
Judit Zádor



Measurement of OH directly probes rate constant for QOOH reactions

Haifeng Huang

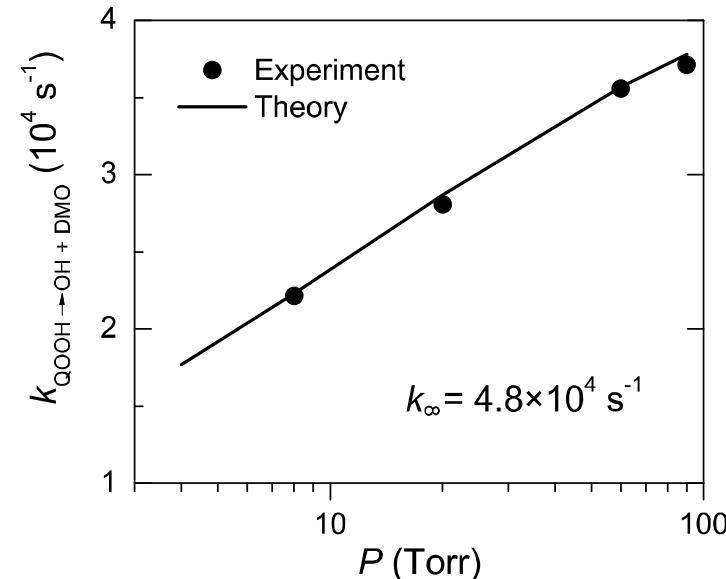
C. F. Goldsmith, W. H. Green, and S. J. Klippenstein,
J. Phys. Chem. A, 2012, 116, 3325–3346



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

unknowns w/o O_2

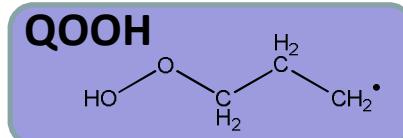
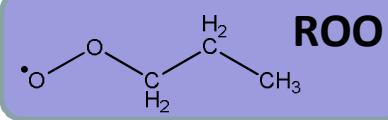
- 1 $k_{\text{QOOH} \rightarrow \text{OH}}$
- 2 new chain chlorination (k_{Cl})
- 3 loss to ROO in $\text{Cl} + \text{TBHP}$ (α)



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?

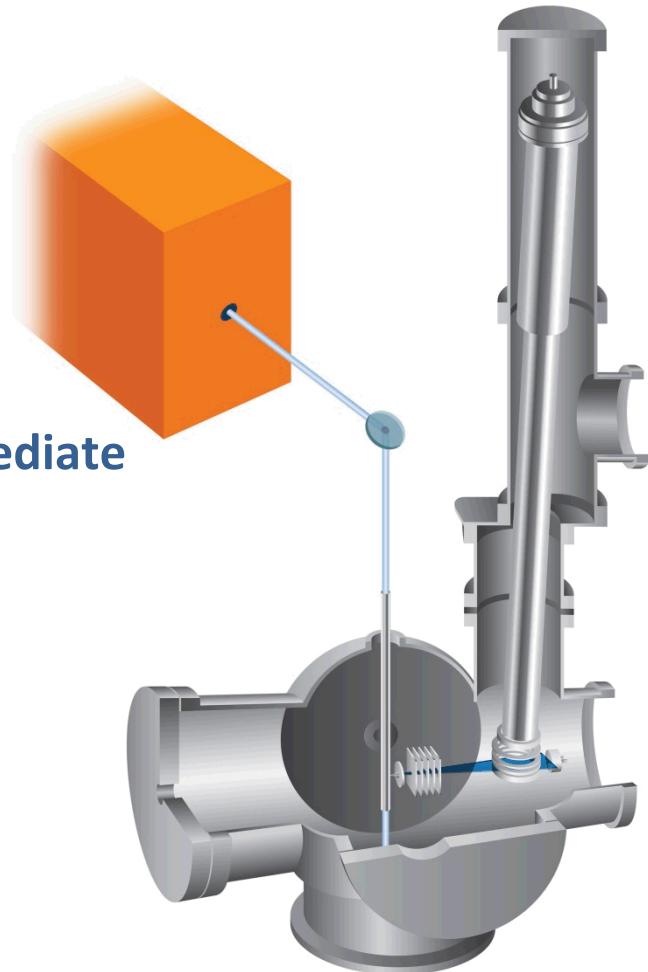


QOOH is an isomer of the more stable ROO intermediate

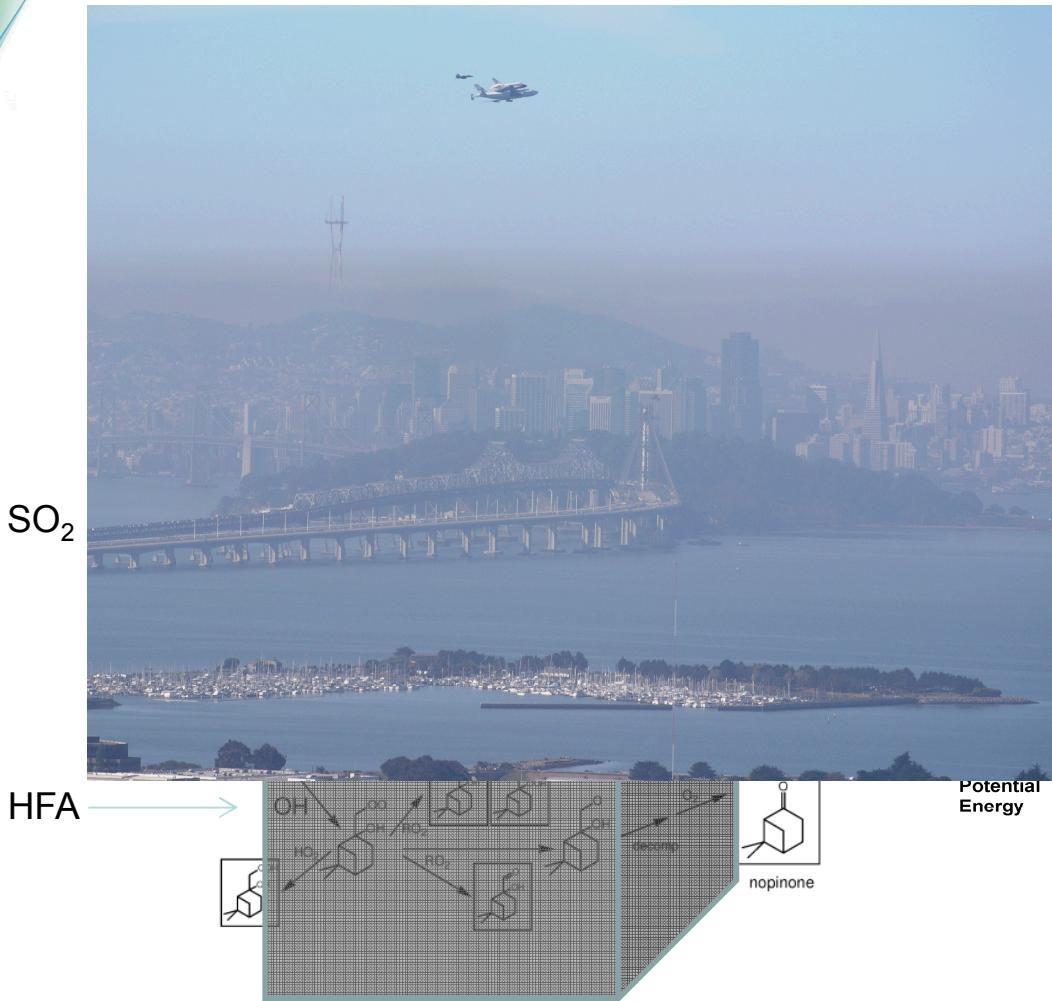


Criegee intermediates are isomers of more stable tropospheric species

But we have a machine that can resolve isomeric chemistry!



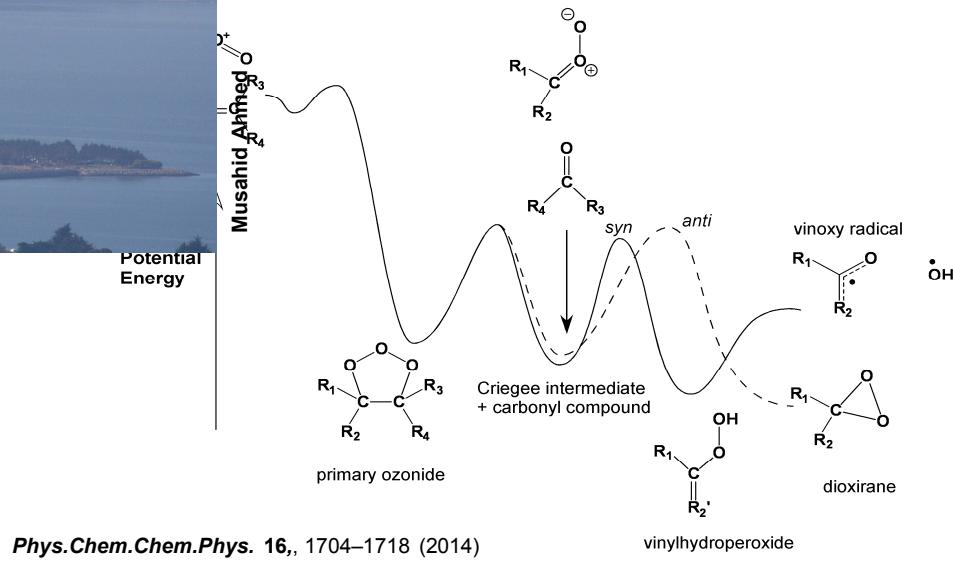
Other systems have their own black boxes...



Modeling ozonolysis has long been the 'black box' of atmospheric chemistry. It is very difficult 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!

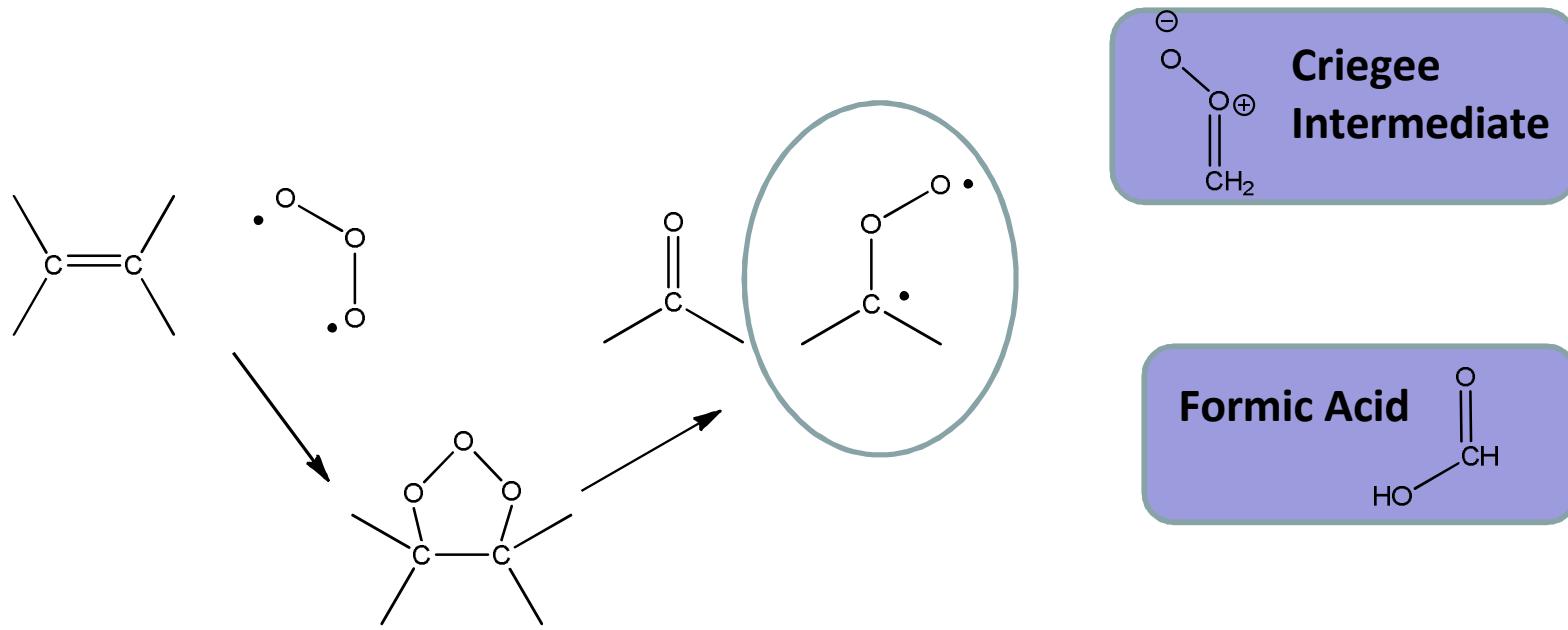


Kinetic Models for Oxidation Chemistry Require Knowing Reactions of “Intermediates”

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



Tunable synchrotron photoionization *can* identify novel isomeric intermediates

Carl Percival, Dudley Shallcross

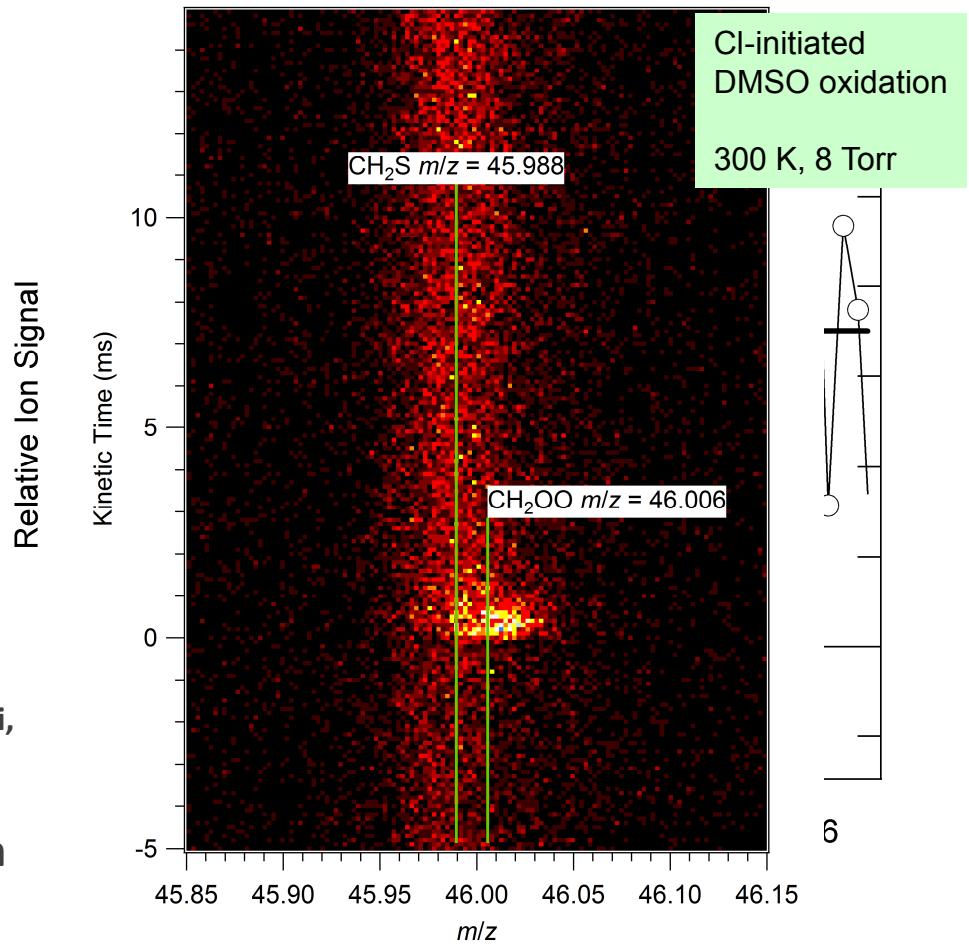
Ozonolysis of alkenes proceeds via a carbonyl oxide intermediate (“Criegee intermediate”)

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))

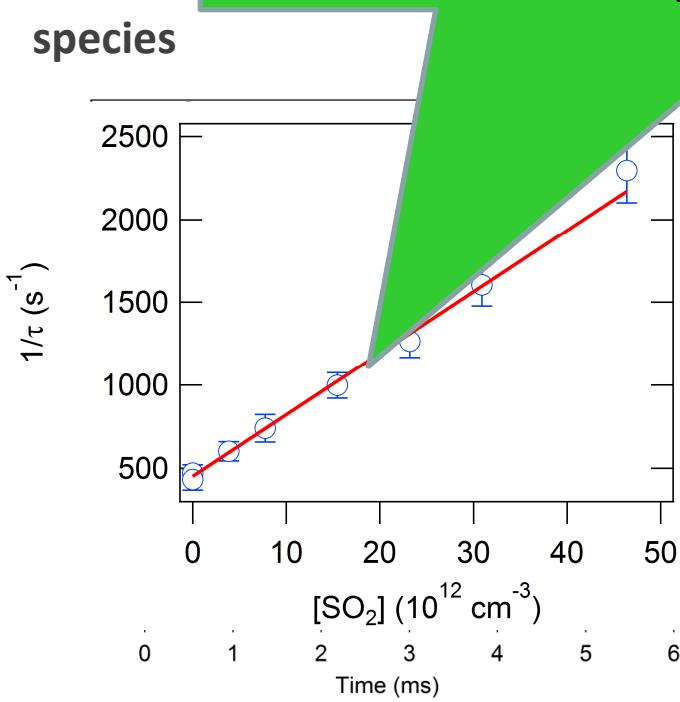
Time-of-flight can resolve CH_2S from CH_2O



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

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

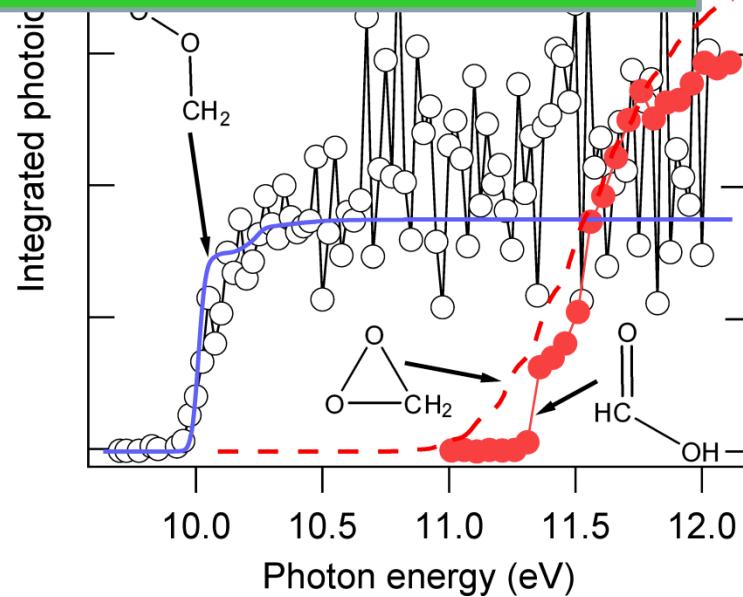
- Arkke Es 1416 (2006) made I a Criegee i
- Can make reaction species



Reaction of CH₂OO with NO₂ is **50 times** what is used in models
 If other Criegee intermediates react similarly, Criegee reactions are significant NO₃ source

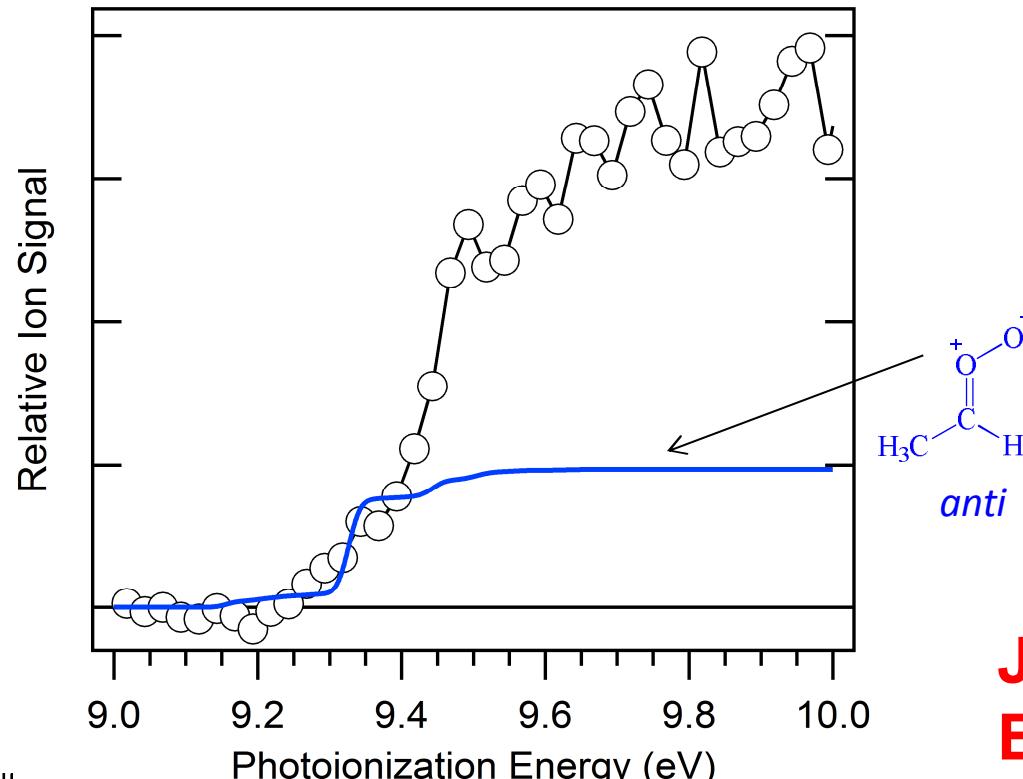
Reaction of CH₂OO with SO₂ is up to **10 000 times** values inferred from ozonolysis modeling

If other Criegee intermediates react similarly, Criegee reactions are major SO₂ oxidant

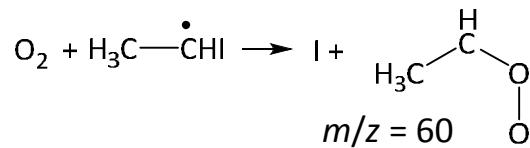
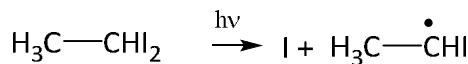


Welz, Savee, et al., *Science* **335**, 204 (2012)

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

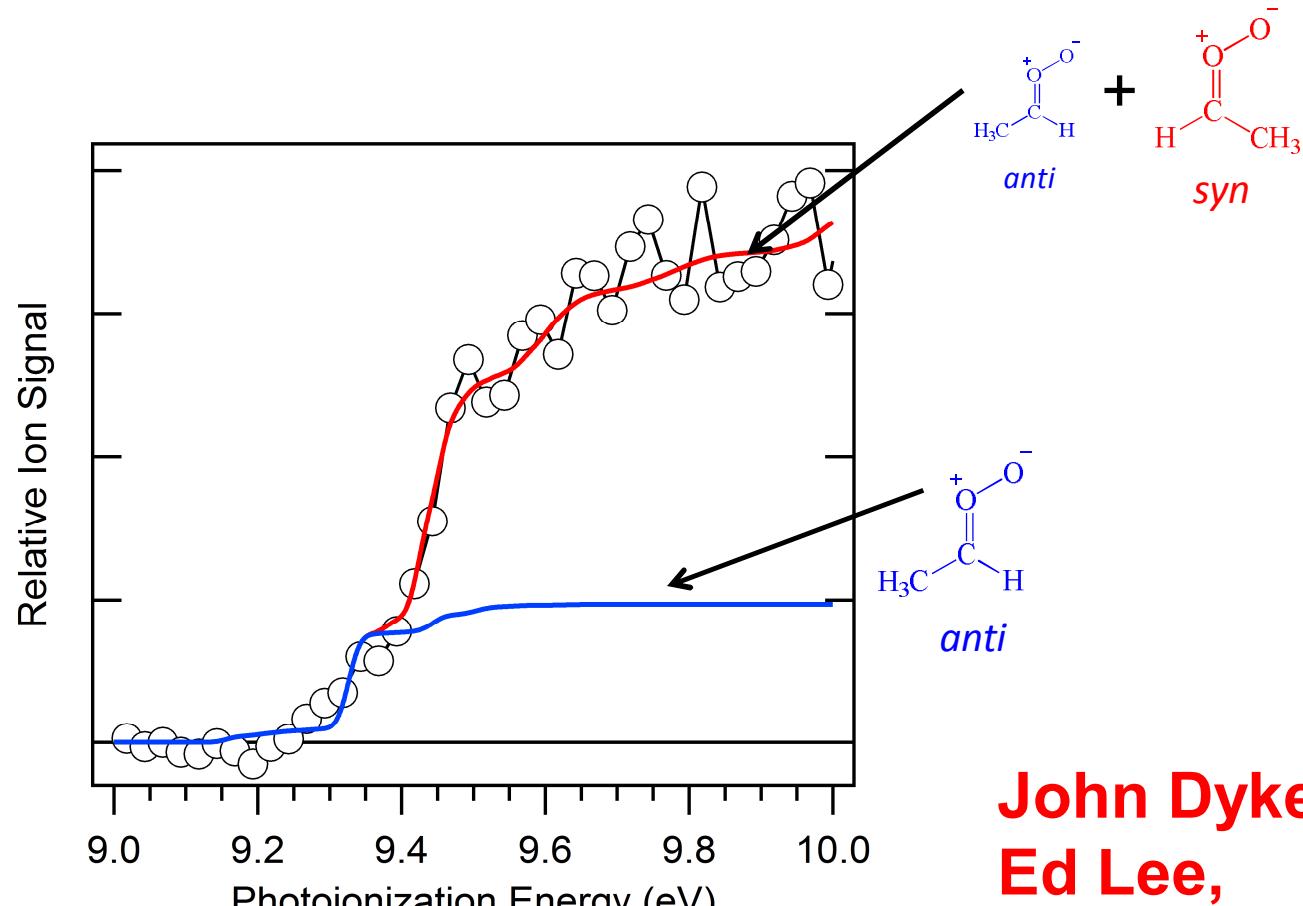


Similar strategy:



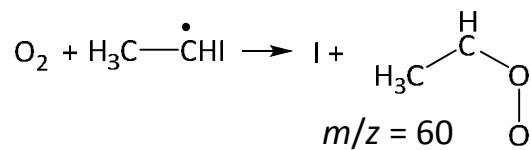
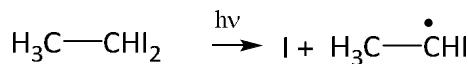
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Can also make larger Criegee Intermediates like acetaldehyde oxide (CH_3CHOO)

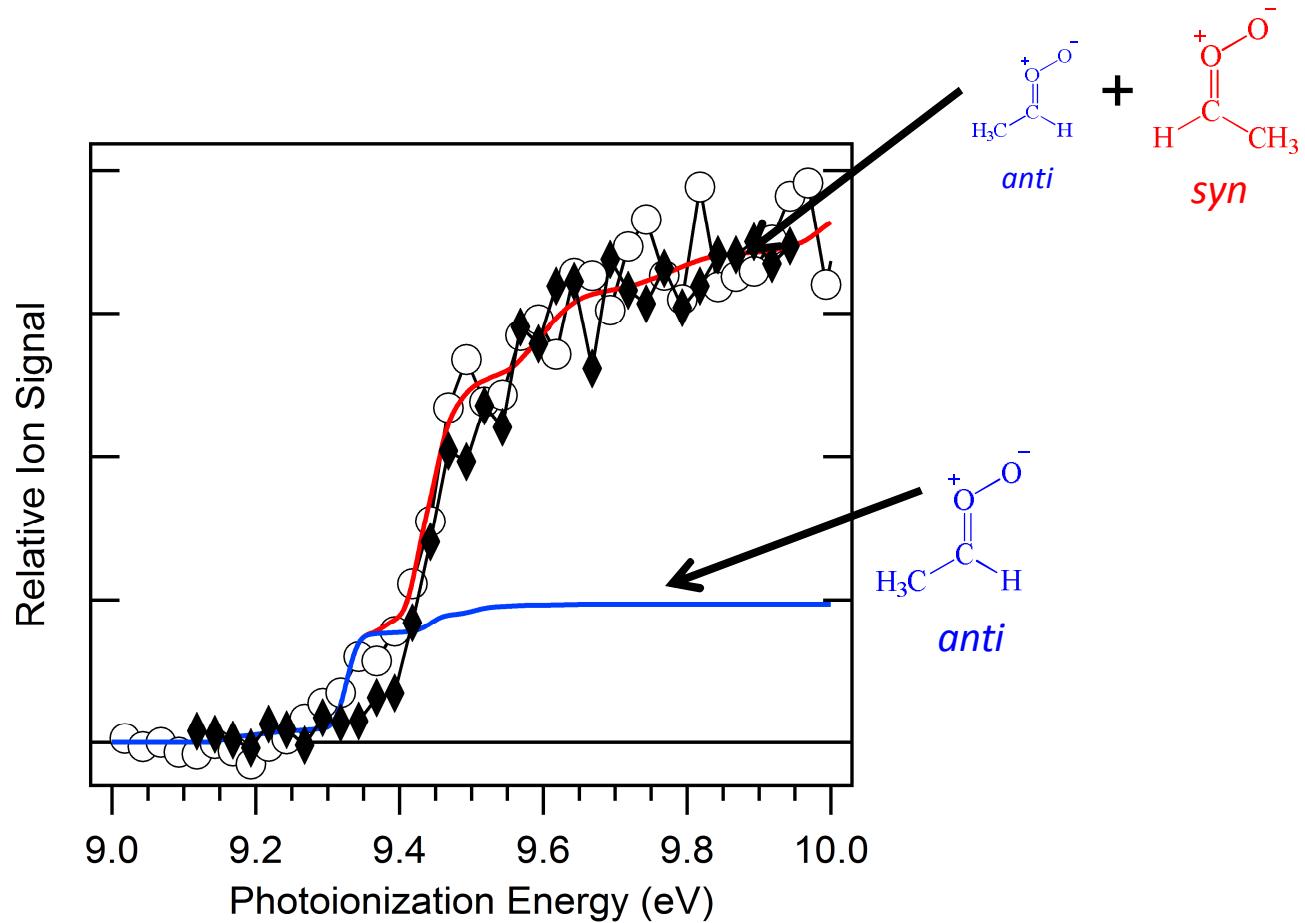


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Similar strategy:



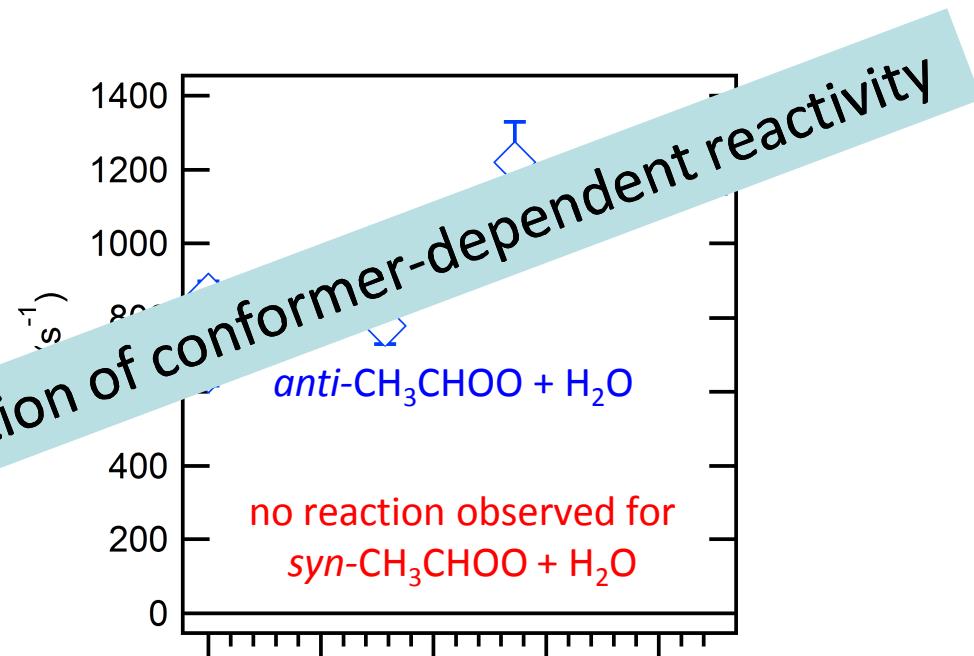
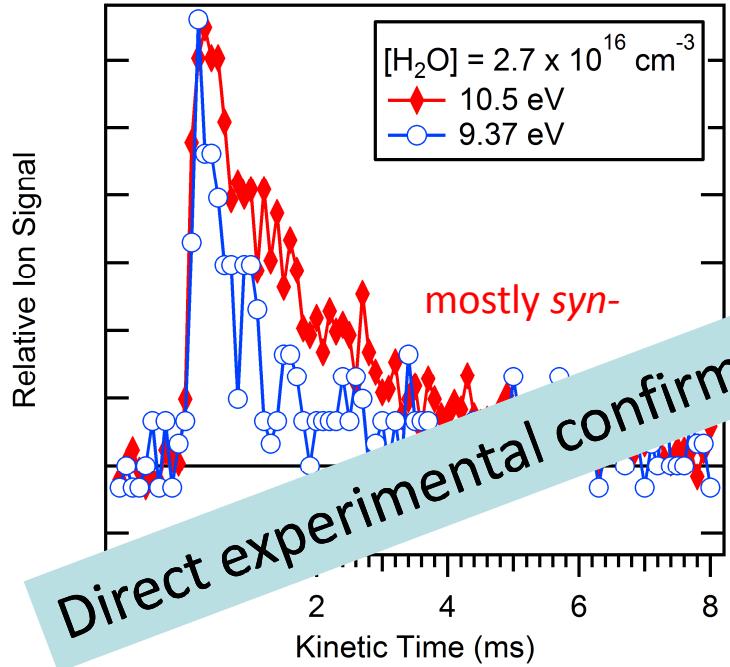
Addition of water preferably removes the *anti*- conformer of CH_3CHOO



Conformer-dependent reactivity!

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

We measured the rate coefficient of *anti*-CH₃CHO with H₂O



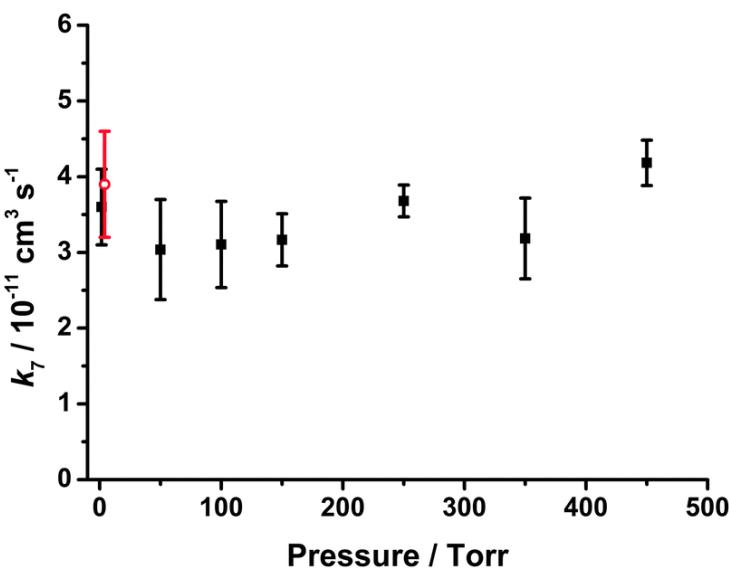
$$k(\text{*anti*-CH}_3\text{CHO} + \text{H}_2\text{O}) = (1.0 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \rightarrow$$

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

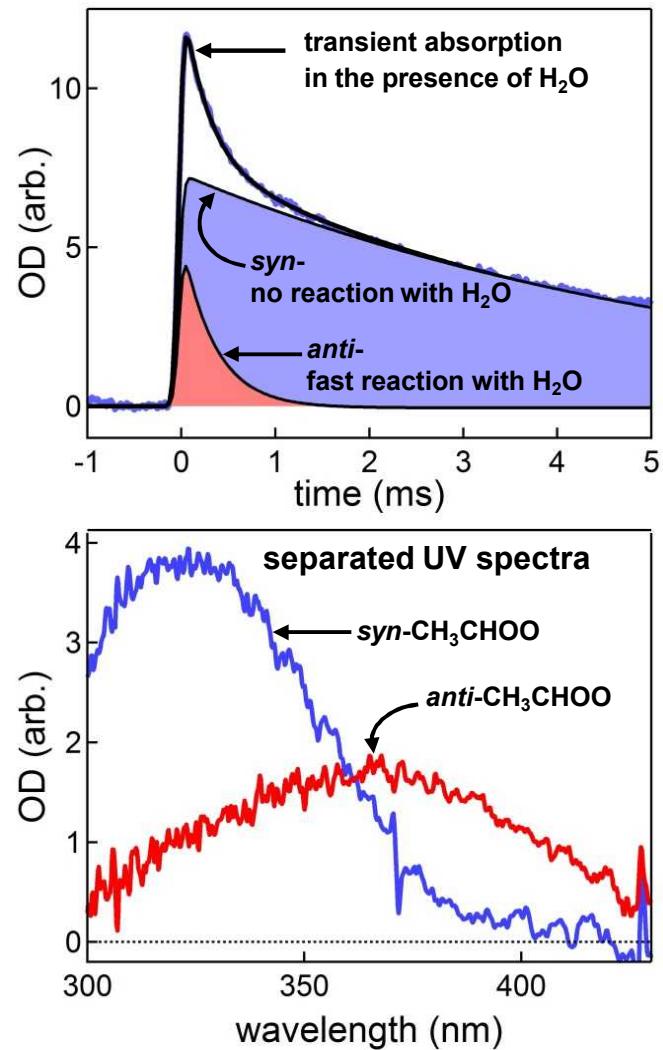
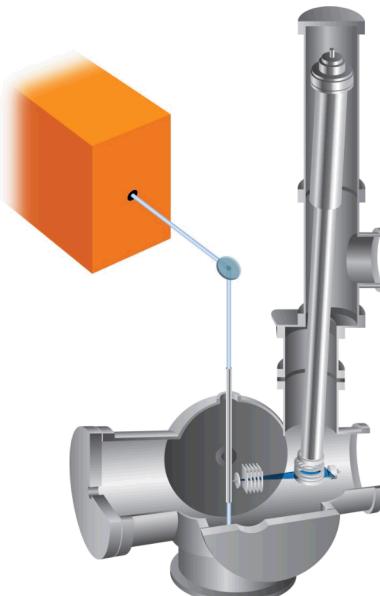
- A factor of 10 lower than predictions for the high-pressure limit from Anglada et al. (Phys. Chem. Chem. Phys. 13, 13034 (2011)), but larger than other calculations
- Substantially larger than prediction for other Criegee Intermediates

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)

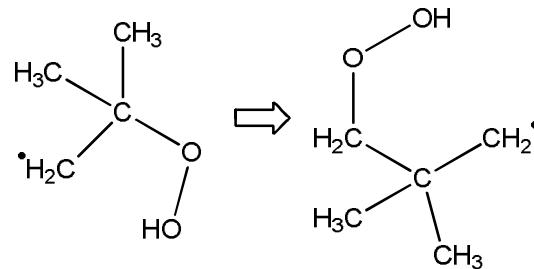


Leonid Sheps, Ashley M. Scully, Kendrew Au
Phys. Chem. Chem. Phys. **16**, 26701-26706

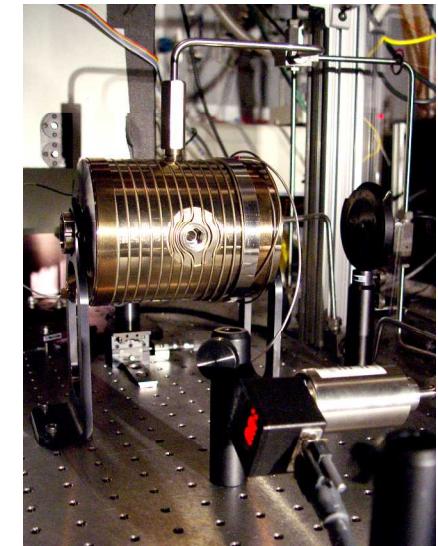
Working inside the “black box” connects fundamental kinetics to complex models



- 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



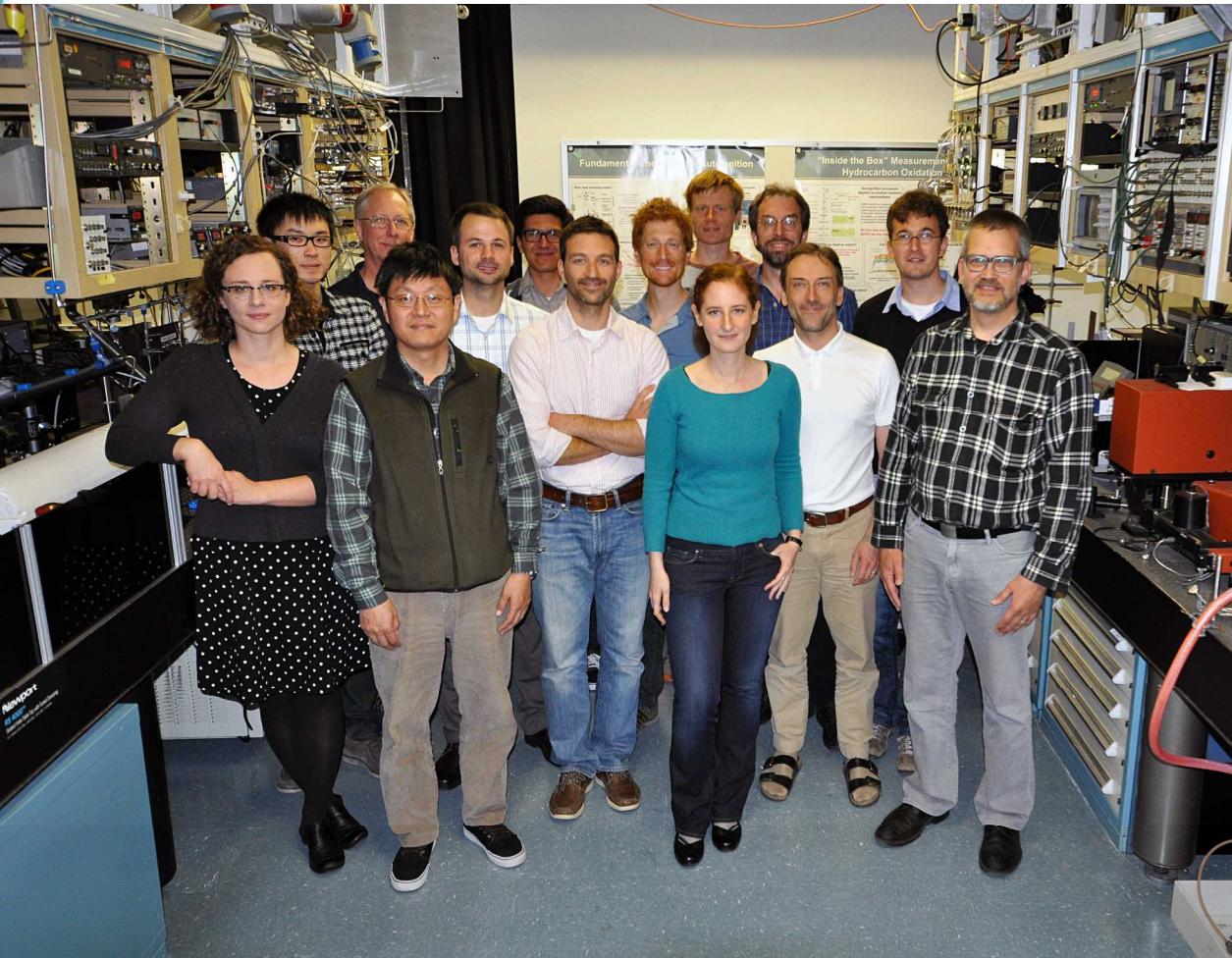
- New measurement methods are opening things up -- others are developing new tools to investigate these species

Judit Zádor, David Osborn, CAT, Lenny Sheps

Ewa Papajak, Ivan Antonov, Arkke Eskola, Haifeng Huang,

Brandon Rotavera, John Savee, Adam Scheer, Oliver Welz

Kendrew Au, Howard Johnsen





Judit Zádor, David Osborn, CAT, Lenny Sheps

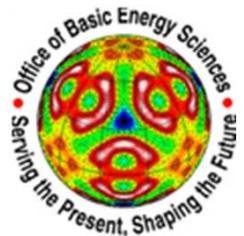
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Carl Percival (Manchester) Dudley Shallcross (Bristol)

Stephen Klippenstein (Argonne)



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