SAND2012-2869P

Connecting Theory and Experiment in "Inside the Box" Studies of Hydrocarbon Oxidation Chemistry

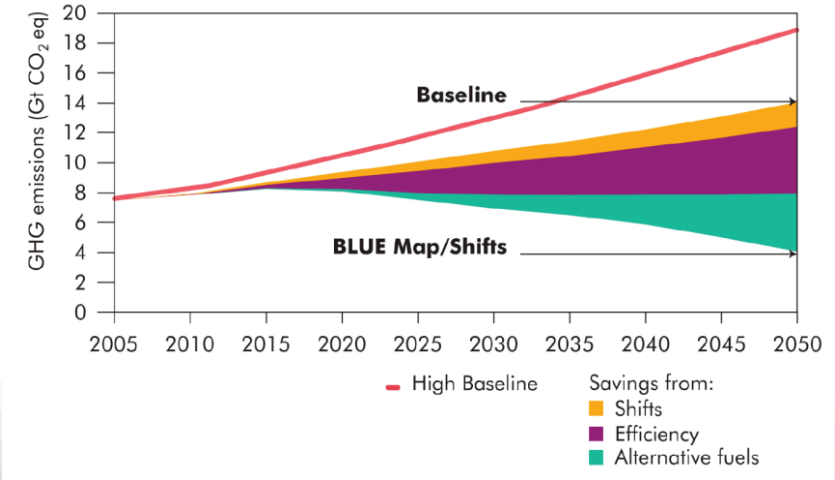
Investigations of Hydrocarbon Oxidation

Craig A. Taatjes

Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551

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

- Combustion produces ~ 85% of the United States' energy
  - Hydrocarbon combustion provides nearly all of the energy for transportation
  - Clean, efficient combustion is part of global energy strategies



Karol M Wikimedia commons

Tropospheric Chemistry:

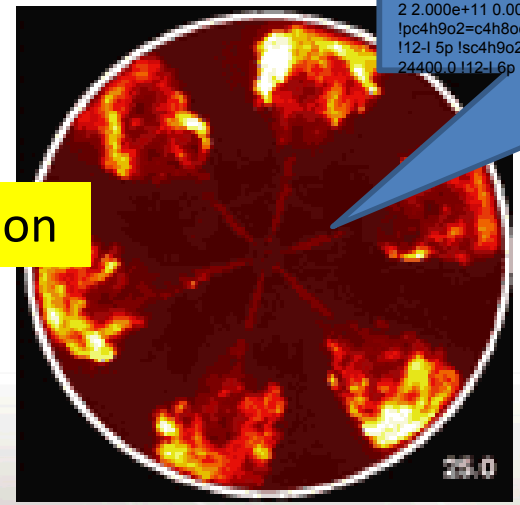
- **Oxidation "cleanses" the troposphere**
- **Oxidation also produces aerosols, smog, other unwanted byproducts**

Combustion is a Complicated Mix of Chemistry and Fluid Dynamics

Comprehensive Kinetic Mechanism

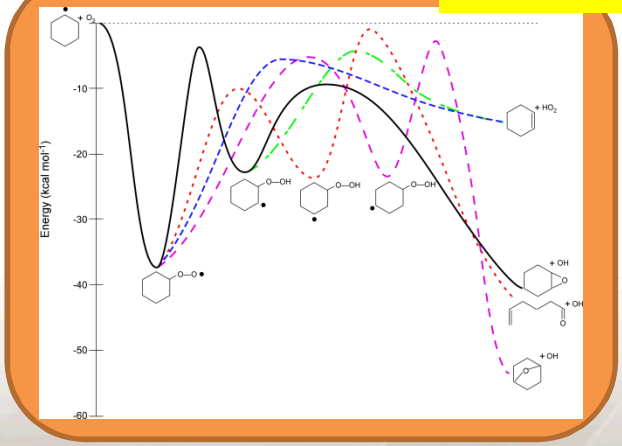
Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Turbulent, multiphase flows interact with the chemistry

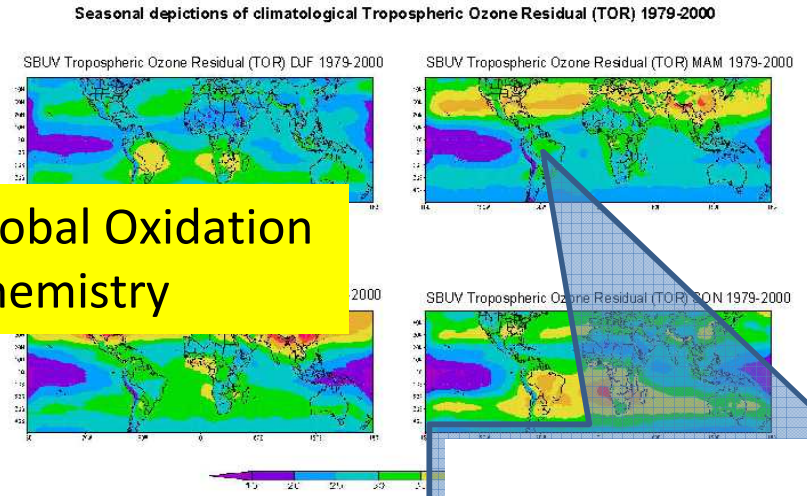


Autoignition

$R + O_2$ reactions



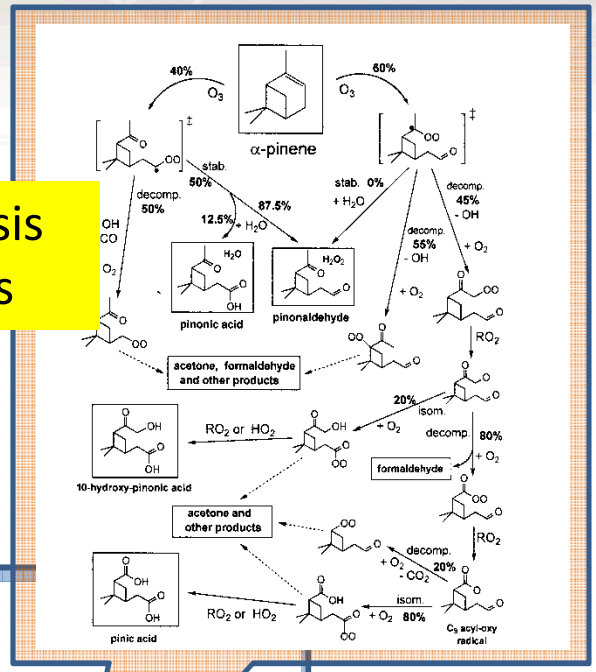
Tropospheric Hydrocarbon Oxidation Depends on Chemistry and Transport



Atmos. Chem. Phys. Discuss., 3, 1453–1476, 2003

Global Oxidation Chemistry

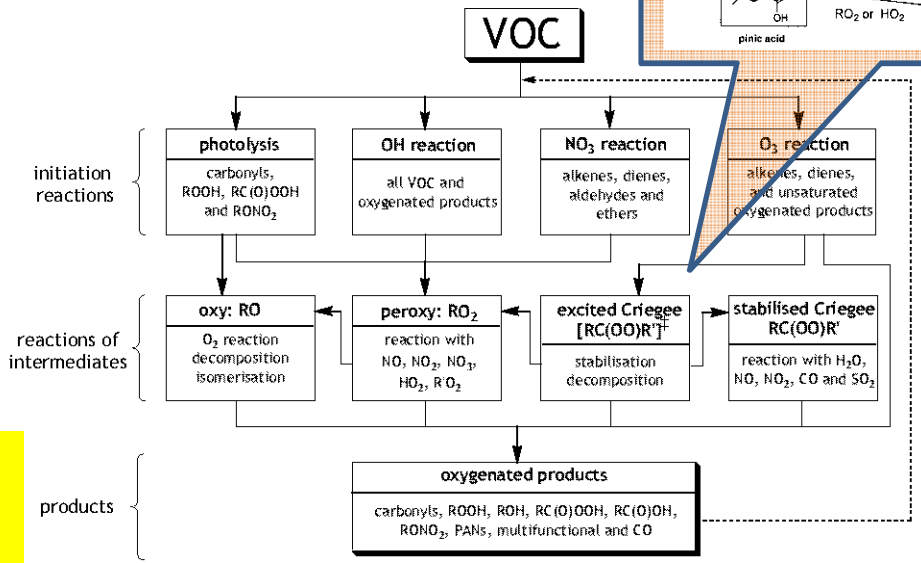
Ozonolysis reactions



Time and length scales are much different than in combustion

Transport changes chemistry

Comprehensive Kinetic Mechanism



Atmos. Chem. Phys., 3, 161–180, 2003

Detailed oxidation mechanism of a single compound is a complicated network of reactions

Jenkin et al., Atmospheric Environment 34 (2000) 2837-2850

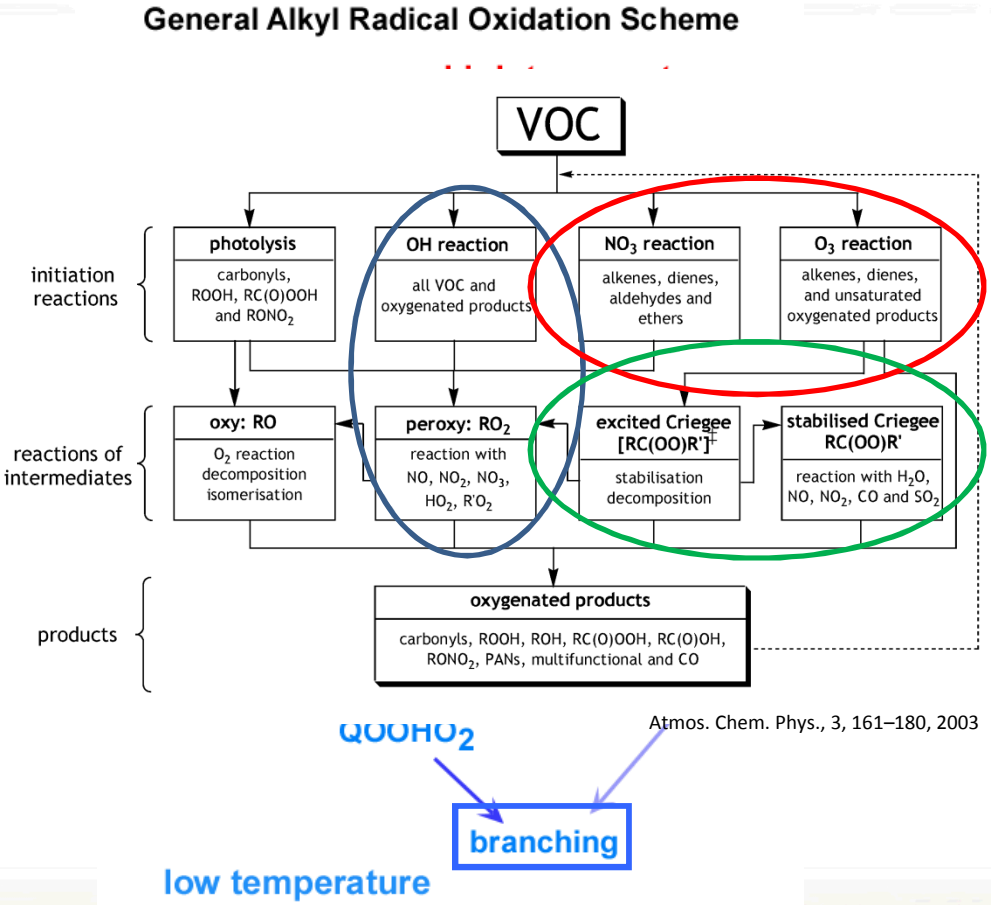
Tropospheric and Engine Oxidation Processes Both Run on Radical Chain Chemistry

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 biradical intermediates* are important species for OH, aerosol formation, NO_x, SO_x

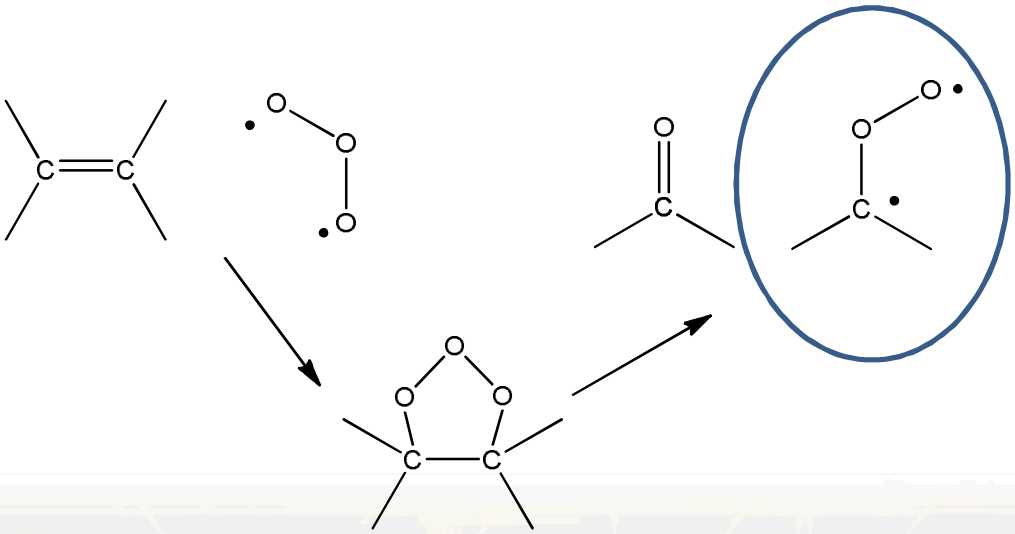


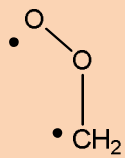
Atmos. Chem. Phys., 3, 161–180, 2003

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

Predicting Oxidation Chemistry Requires Knowing Reactions of "Intermediates"

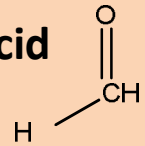
- Ozonolysis is a major component in tropospheric removal of hydrocarbons – makes Criegee biradicals
- Criegee intermediates also appear in QOOH + O_2 reactions Andersen and Carter, *J Phys. Chem. A.* 107, 9463-9478 (2003); Asatryan and Bozzelli, *J Phys. Chem. A.* 114, 7693-7708 (2010)
- Criegee intermediates are *isomers* of more stable products, organic acids or esters
- No one has directly measured a Criegee reaction



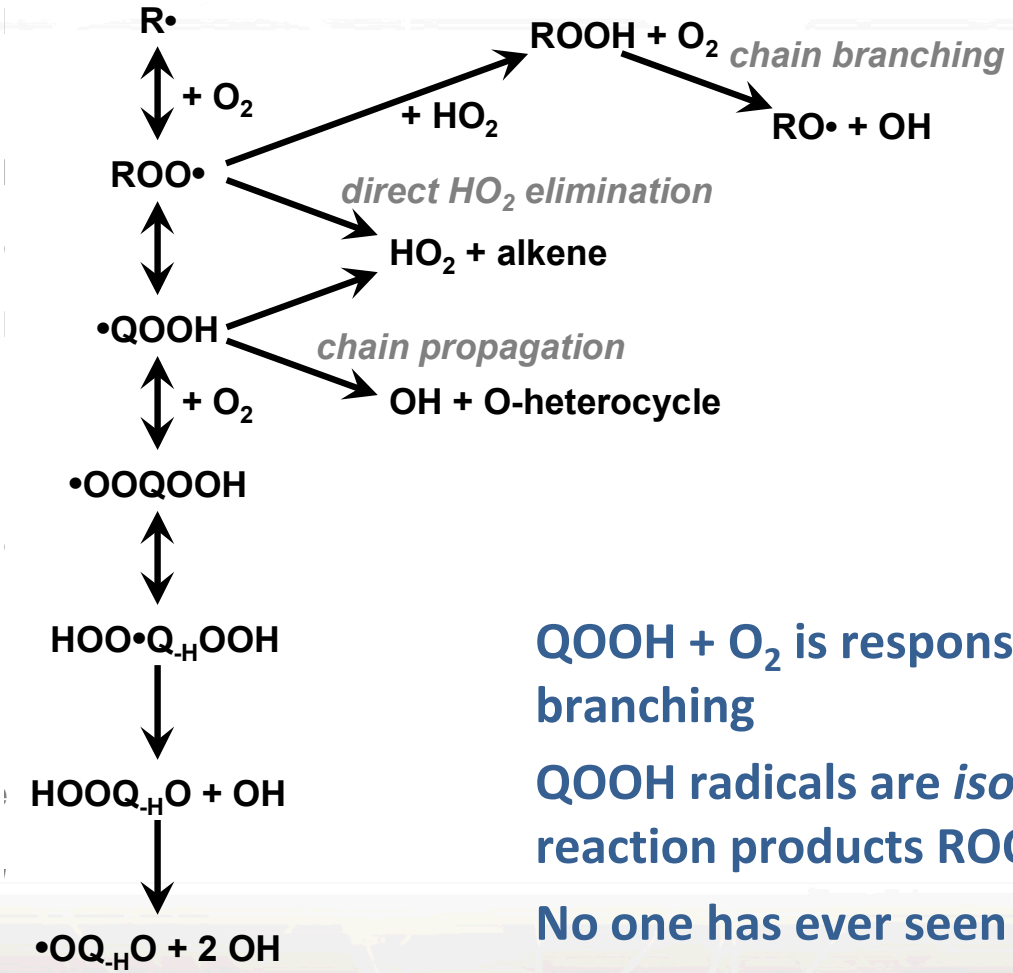


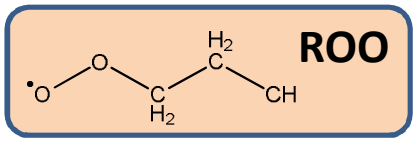
Criegee Intermediate

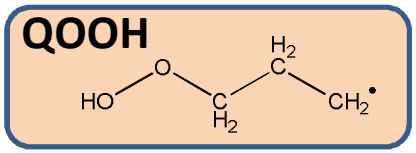
Formic Acid



Predicting Oxidation Chemistry Requires Knowing Reactions of "Intermediates"







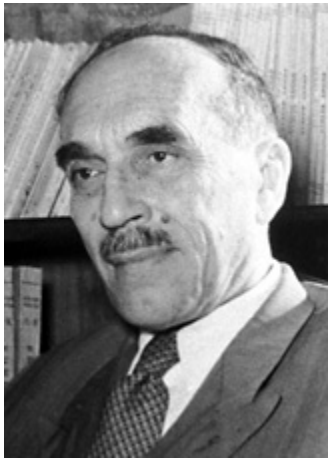
- QOOH + O_2 is responsible for chain branching
- QOOH radicals are *isomers* of the major reaction products ROO
- No one has ever seen a QOOH by any means

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

You Don't Need to Know Much Chemistry to Make an Engine!

Nikolaus August Otto (1832-1891)

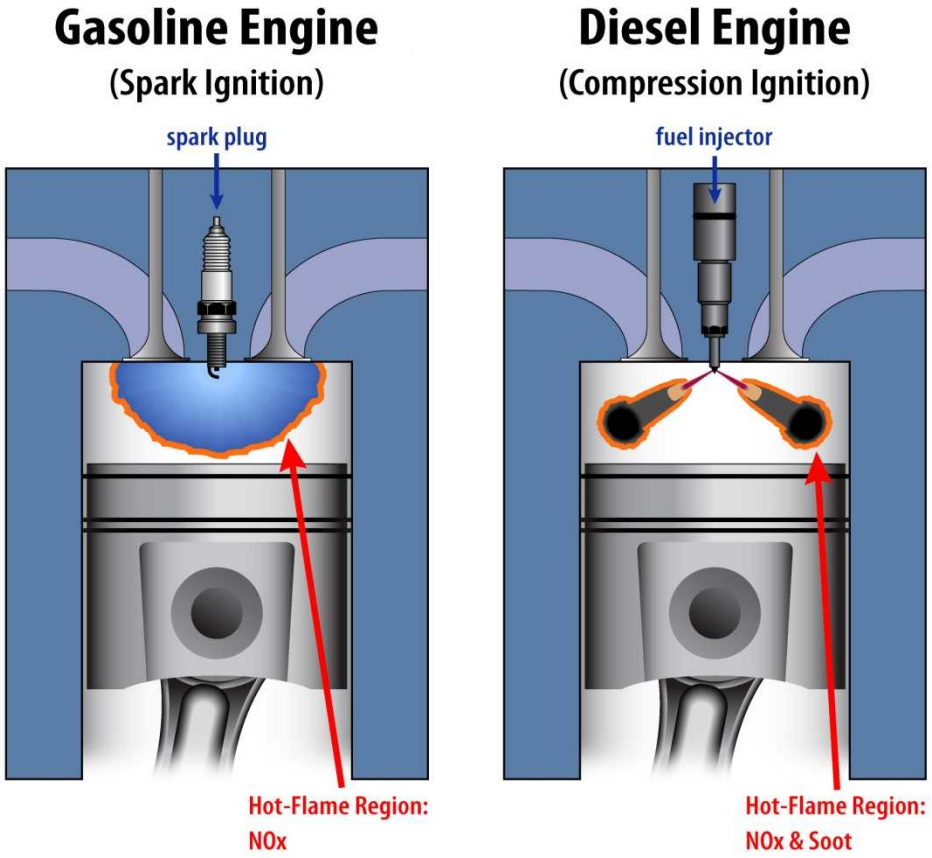
Rudolf Christian Karl Diesel (1858 –1913)



Nikolai Nikolaevic Semenov (Chemistry Nobel, 1956)

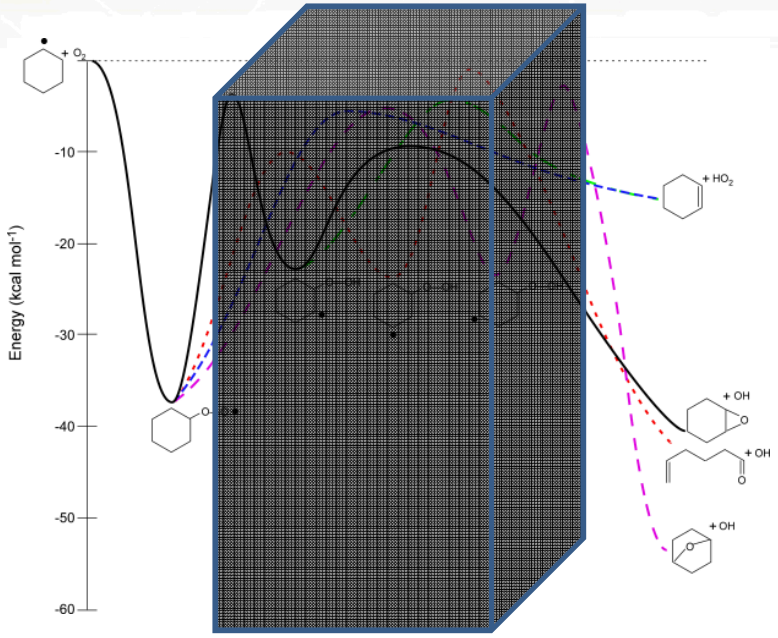
"Some problems relating to chain reactions and to the theory of combustion"

Advanced Engines Rely on Autoignition Chemistry to an Unprecedented Degree



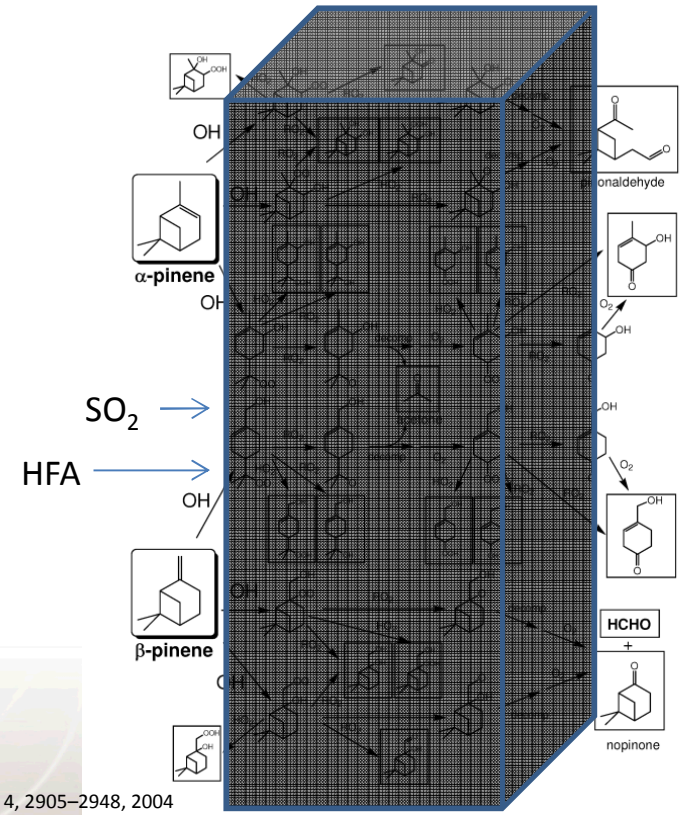
Manley et al., Physics Today, November 2008, 47–52

How Can We Tell Anything about the Reactions of These Intermediates? Deal with the Black Box!



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



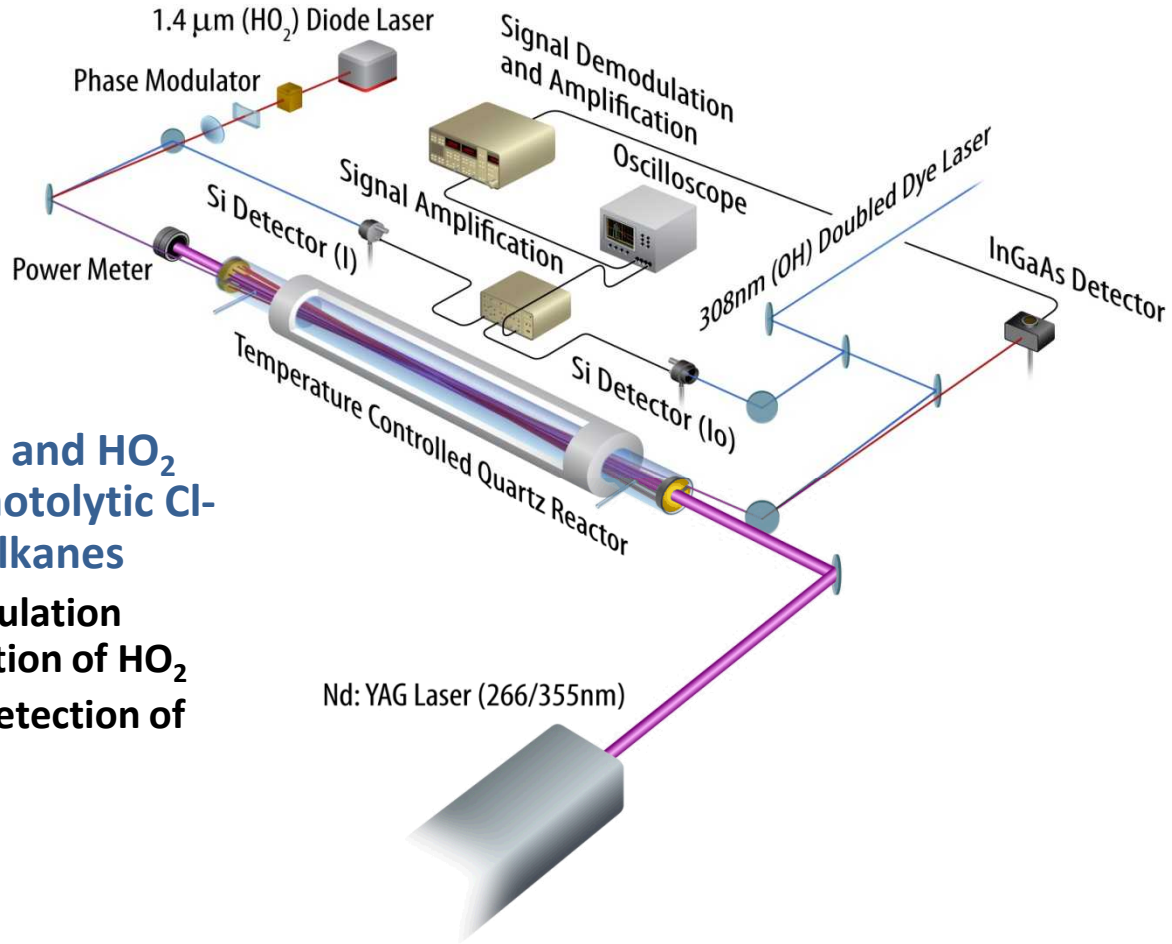
Measure products of R + O_2 reactions and compare to theory

Rigorous theoretical kinetics (Stephen Klippenstein, Jim Miller, Judit Zádor)

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

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

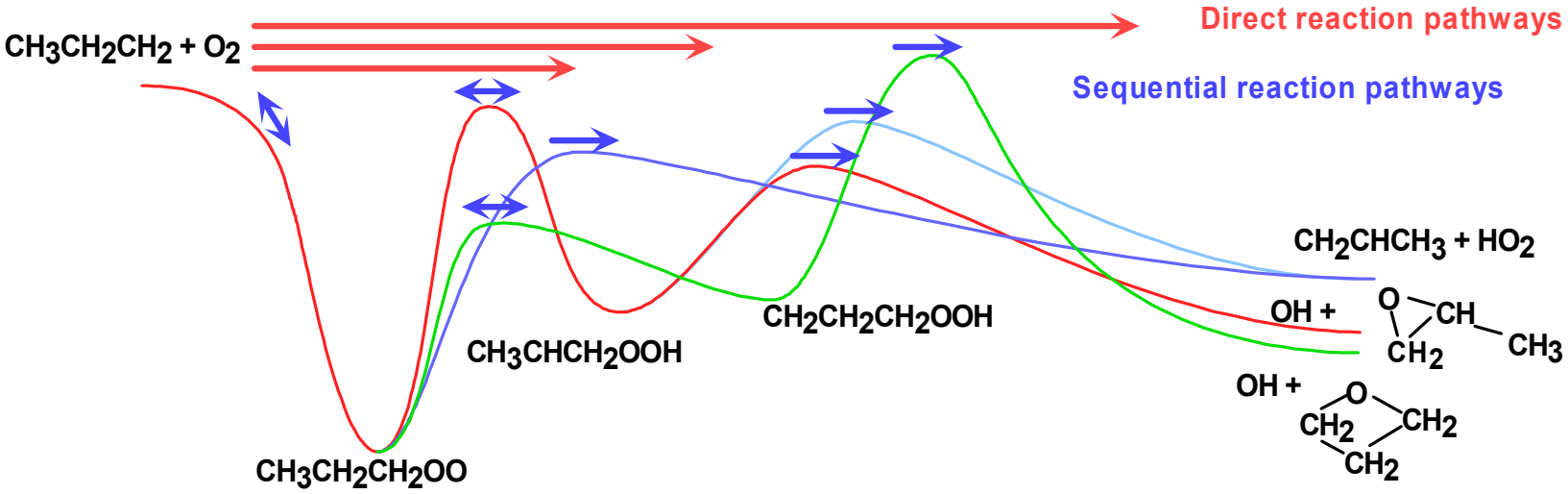
Basis of our strategy: Comparison of experiment and detailed calculations can reveal mechanisms



Experiment: Measure OH and HO_2 formation in pulsed-photolytic Cl-initiated oxidation of alkanes

- **Infrared frequency-modulation spectroscopic detection of HO_2**
- **Ultraviolet absorption detection of OH radicals**

Basis of our strategy: Comparison of experiment and detailed calculations can reveal mechanisms



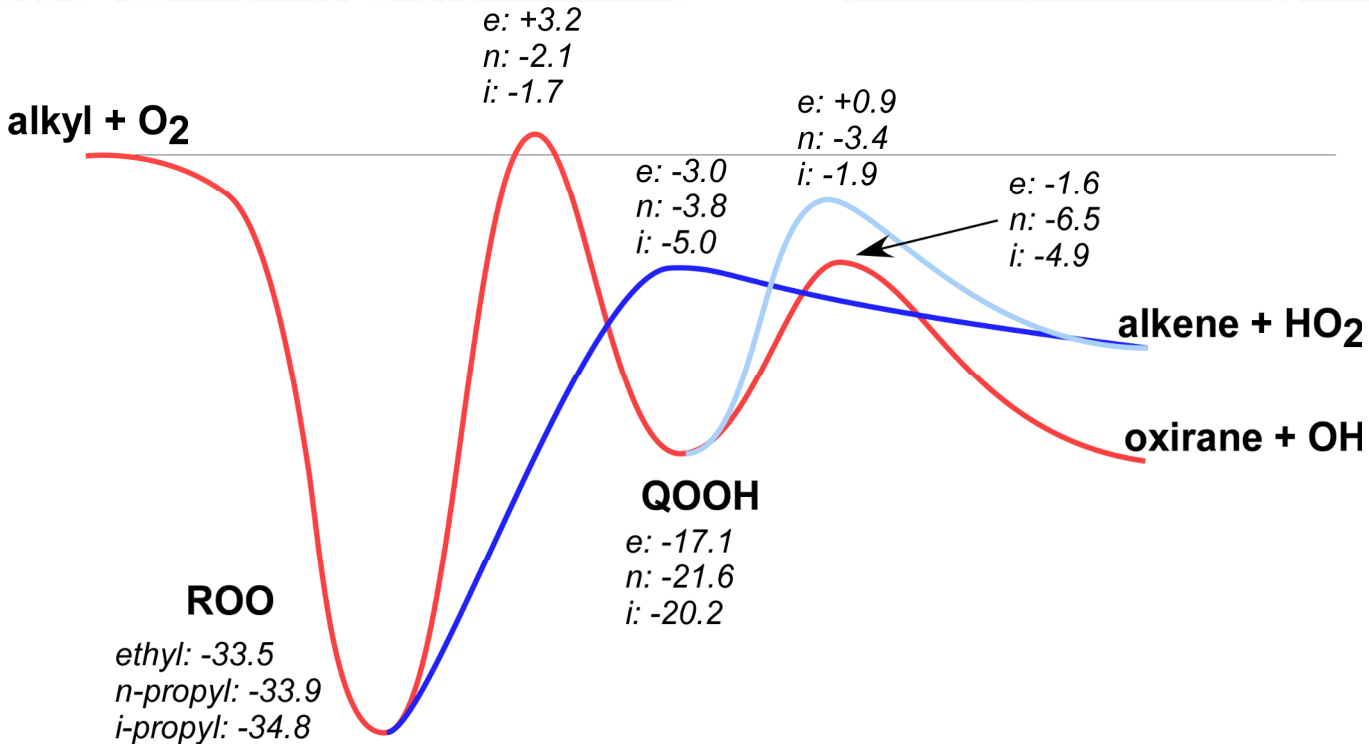
Compare to time-dependent multiple-well master equation solutions

- ***Ab initio*** **characterization of stationary points on the potential surface (Stephen Klippenstein, Jim Miller, Judit Zádor)**
- **Parameterization of ME solution (SJK / JAM/ JZ) input to kinetic models**
- **Includes formally direct pathways for isomer and product formation**

Adjust **stationary point** ***energies*** **to reproduce body of experimental evidence**

We have reinvestigated OH production in ethyl + O_2 and propyl + O_2 reactions

Ethyl and propyl radical reactions with O_2 are prototypical

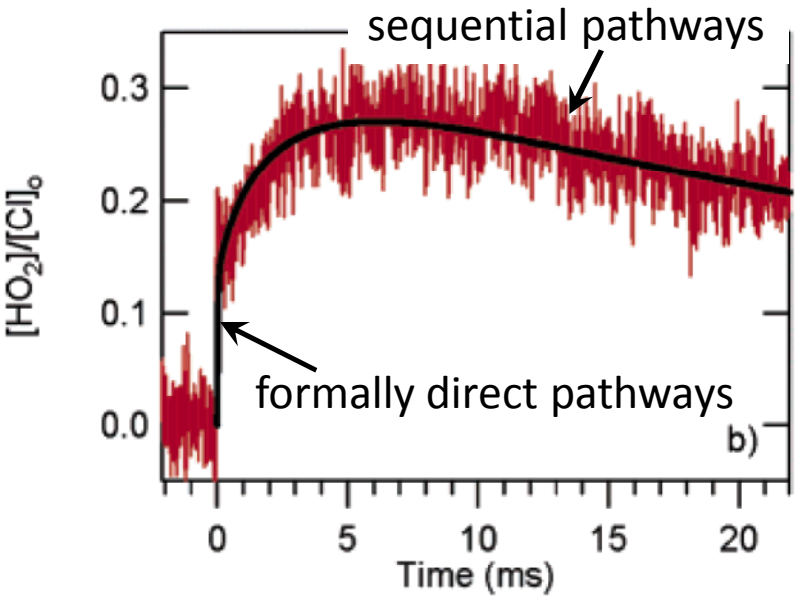


Although the PES's are similar, ethyl + O_2 reaction has barriers for OH formation above reactants while for the propyl + O_2 reactions barriers are below reactants

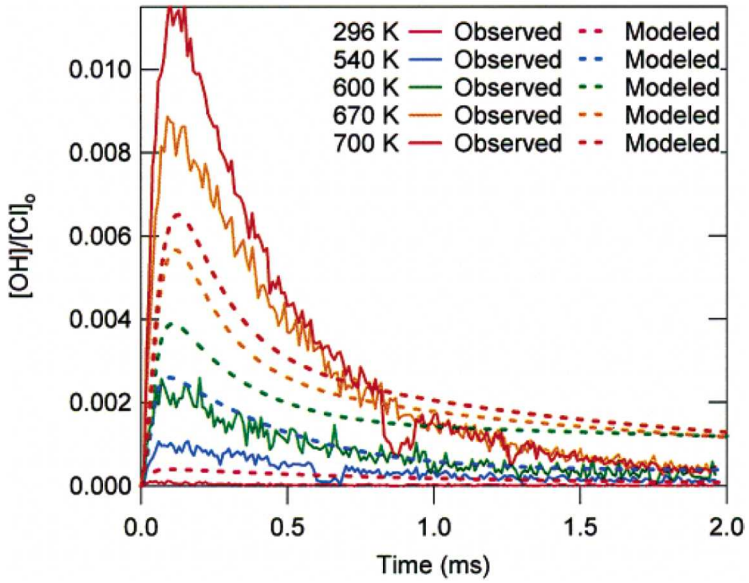
DeSain, J. D.; Taatjes, C. A.; Miller, J. A.; Klippenstein, S. J.; Hahn, D. K. *Faraday Discuss.* **2001**, *119*, 101.
DeSain, J. D.; Klippenstein, S. J.; Miller, J. A.; Taatjes, C. A. *J. Phys. Chem. A* **2003**, *107*, 4415.
Huang, H.; Merthe, D.; Zádor, J.; Jusinski, L. E.; Taatjes, C. A. *Proc. Combust. Inst.* **2010**, *33*, 293.

In previous work, HO_2 profiles were modeled perfectly, but OH profiles could not be reconciled

Model using best R + O_2 rate coefficients from rigorous ME treatment



Estupiñán, E. G.; Klippenstein, S. J.; Taatjes, C. A. *J. Phys. Chem. B* **2005**, *109*, 8374.

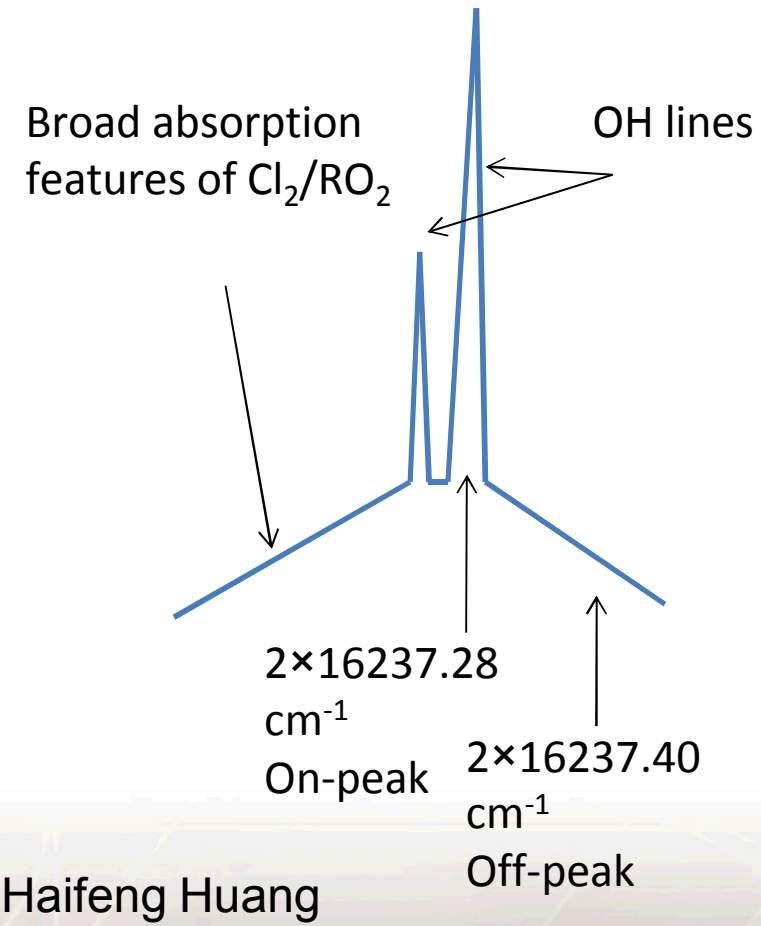


DeSain, J. D.; Klippenstein, S. J.; Miller, J. A.; Taatjes, C. A. *J. Phys. Chem. A* **2003**, *107*, 4415.

Validation of the Master Equation calculations for the OH channels requires more accurate experimental results.

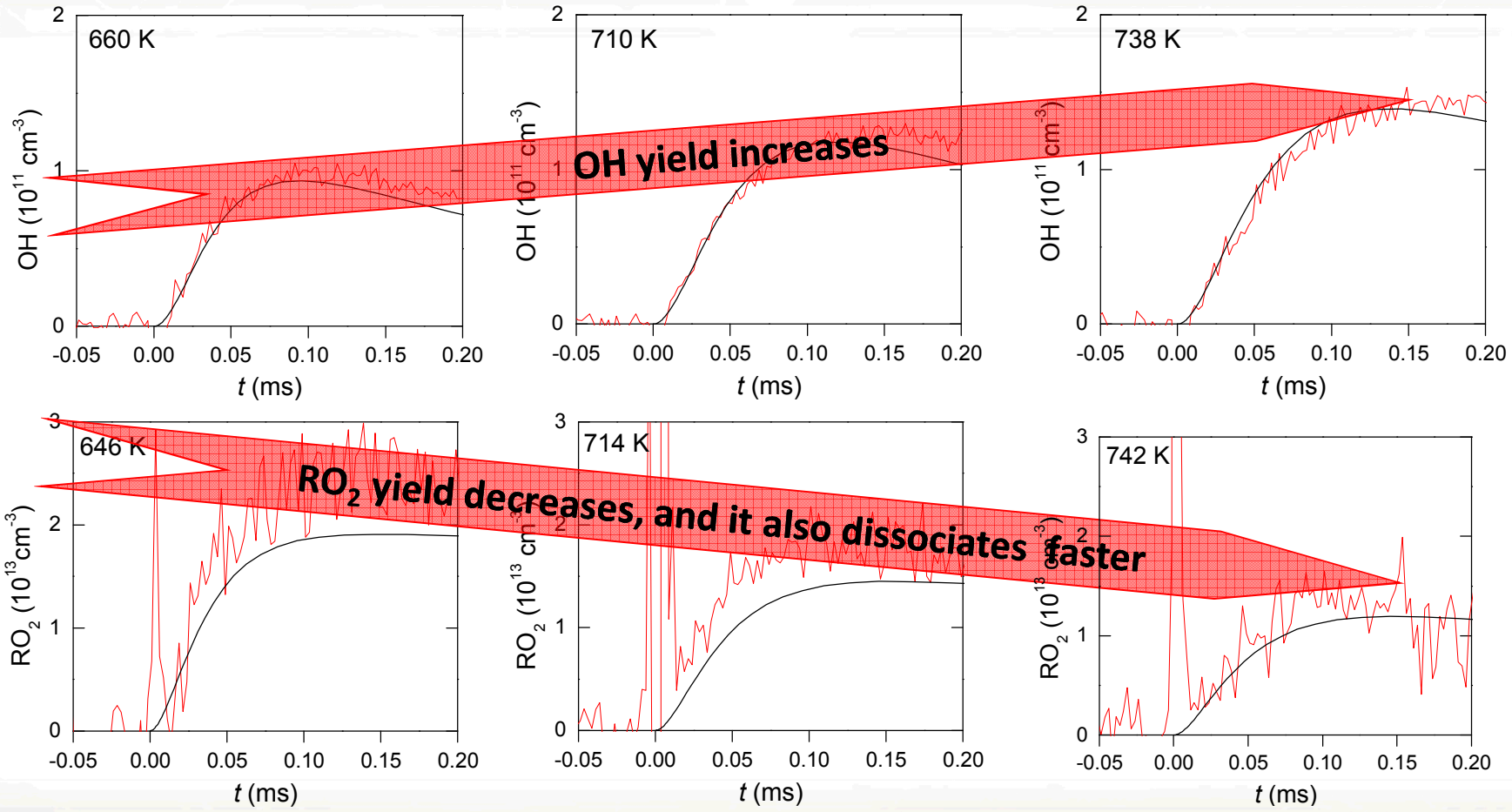
New OH experiments improved upon the previous measurements in two very important aspects.

- **Cl_2 or $(COCl)_2$ radical source**
  - ➔ Few unwanted side-reactions (chain-chlorination is negligible).
- Detection by **differential direct long-path absorption at 308 nm** (frequency doubled 616 nm CW ring dye laser)
  - ➔ Yields OH concentrations directly.
  - ➔ Detection limit is ~10^{10} cm^{-3} (total density is ~10^{17} cm^{-3}).
  - ➔ Absorption spectroscopy also allows the measurement of other species.



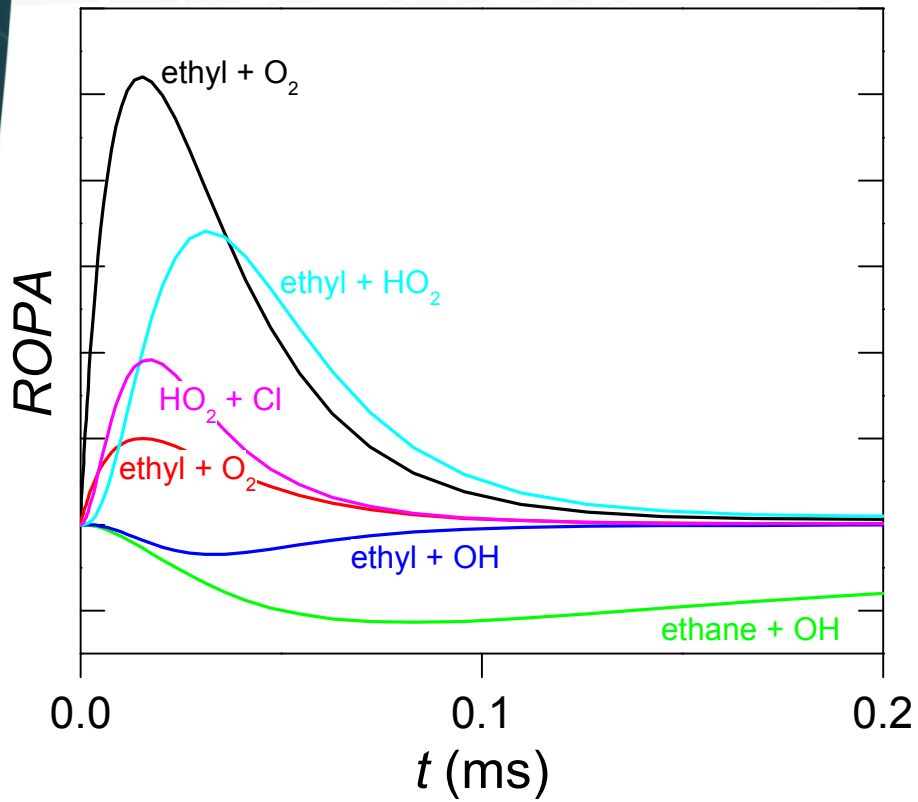
Haifeng Huang

RO_2 and OH production in Cl-initiated ethane oxidation has been remeasured from 660-740 K



Measured and calculated OH concentrations agree very well up to 200 μs.
Note that all curves are **unscaled absolute concentrations**!

Experimental kinetics determinations depend on more than the single reaction of interest



OH is formed principally via "formally direct" pathways.
➔ These experiments probe (and confirm) $RO_2 \leftrightarrow$ QOOH barrier height

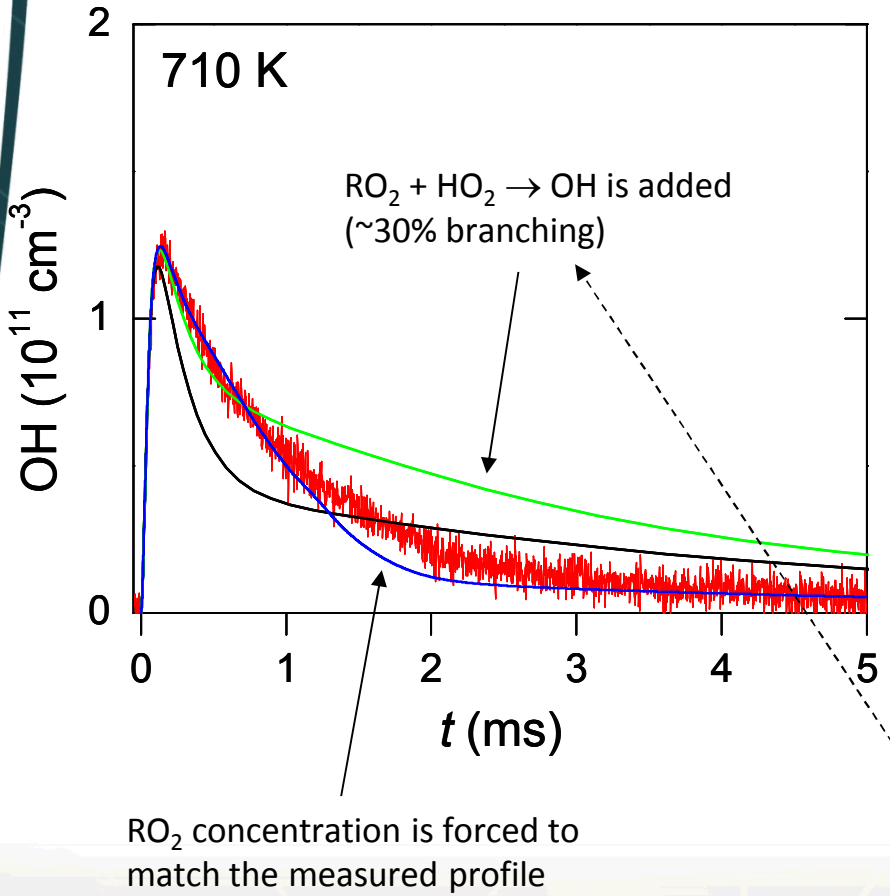
A significant contribution comes from ethyl + HO_2. The rate coefficient is based on methyl + HO_2 (Jasper et al. 2009 PCI).

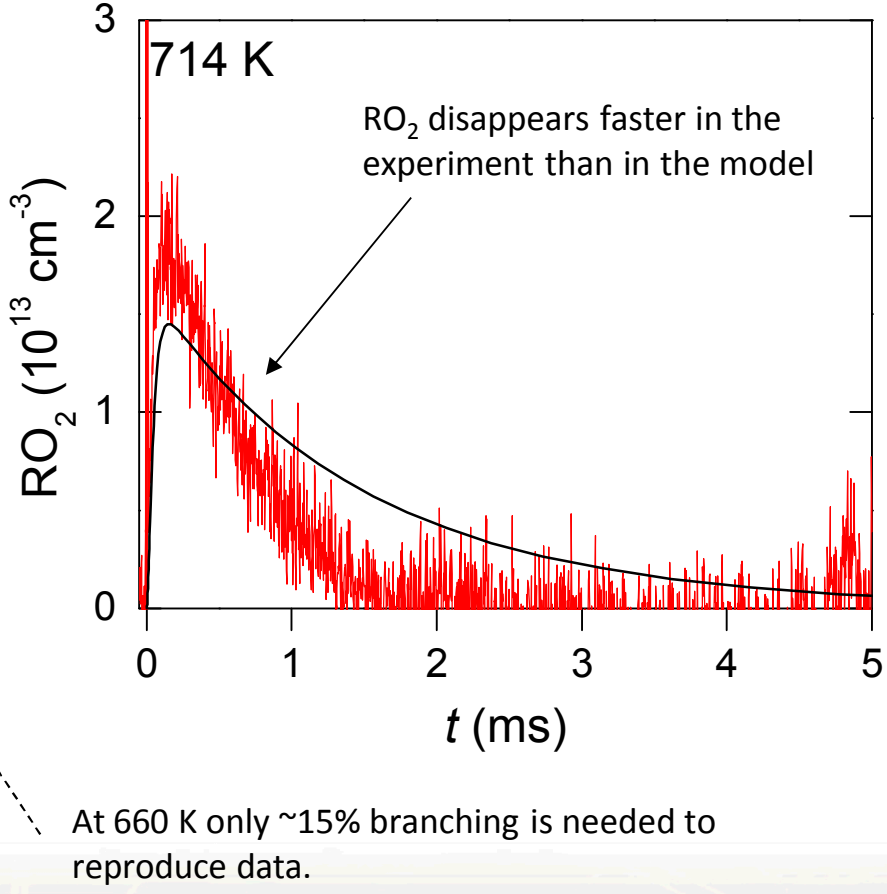
Also, HO_2 + Cl produces some OH, but it is a relatively well-characterized reaction.

After 200 μs ethane + OH is expected to dominate OH profile with a small contribution from $C_2H_5 + O_2 \rightarrow$ OH induced by RO_2 backdissociation.

Concentration profiles on the longer time-scales reveal important secondary reactions.

Ethyl + O_2 contribution takes place in first ~200 µs based on our model.





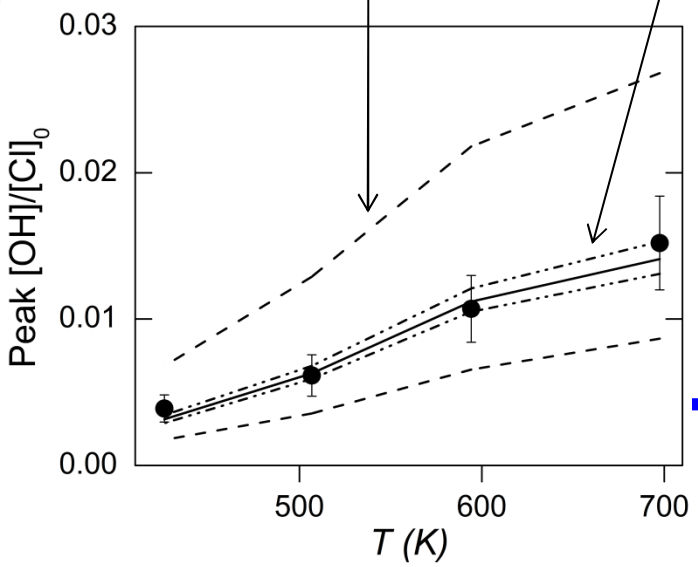
Judit Zádor

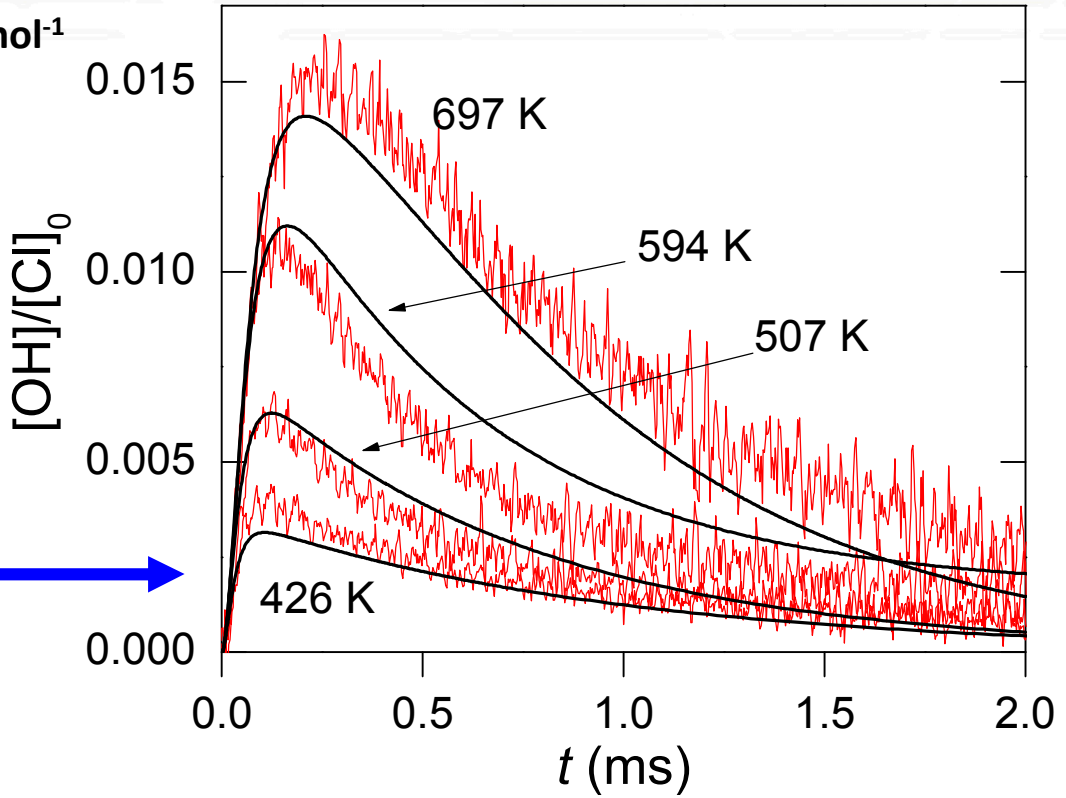
Constraining RO_2 to its measured values and adding $RO_2 + HO_2 \rightarrow OH$ eliminates almost all discrepancies on the whole 5 ms timescale.

OH production in Cl-initiated propane oxidation (426-697 K) is also well-modeled

ΔE (QOOH→OH + *c*-C_3H_6O) = ± 1 kcal mol^{-1}

ΔE ($RO_2 \leftrightarrow$ QOOH) = ± 1 kcal mol^{-1}





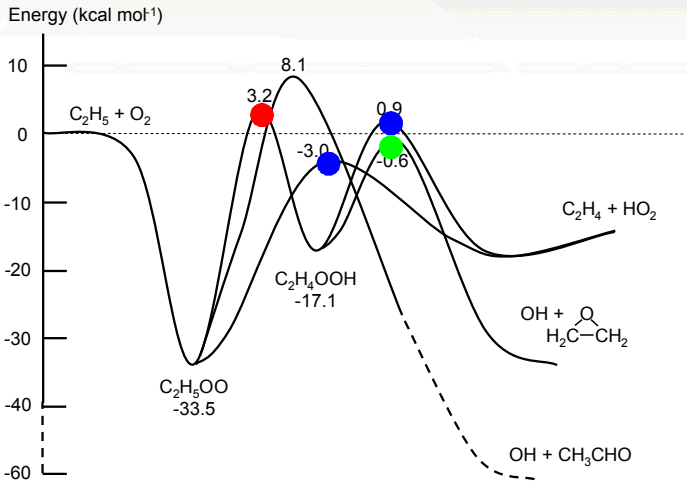
The propyl + O_2 reaction produces more OH, therefore, secondary chemistry is relatively less important than for ethane, even at longer times.

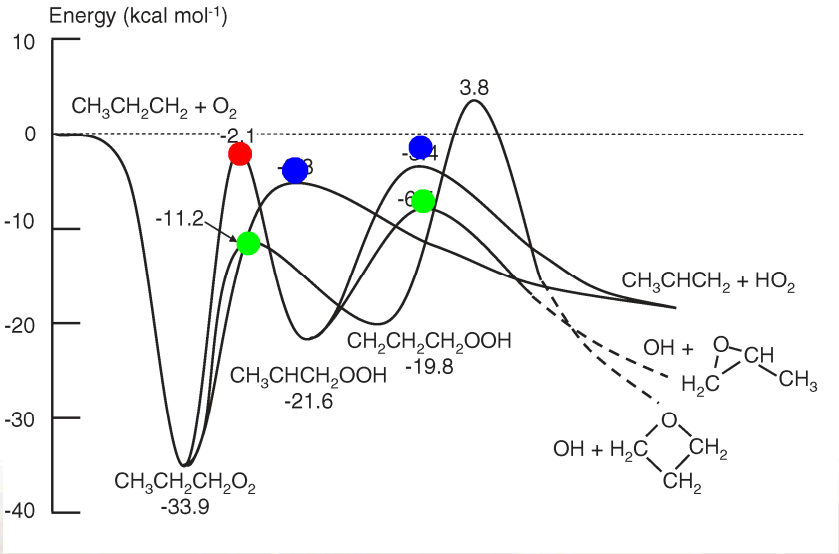
The OH formation is very sensitive to the ROO $\leftrightarrow$ QOOH transition state

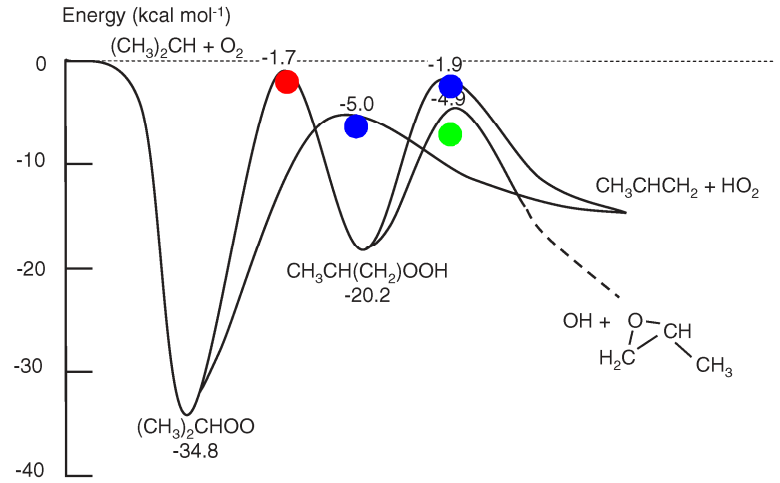
Huang, H.; Merthe, D.; Zádor, J.; Jusinski, L. E.; Taatjes, C. A. *Proc. Combust. Inst.* **2011**, *33*, 293.

Experiments validate stationary points on the ethyl + O_2 and propyl + O_2 potential energy surfaces

- Previous HO_2 measurements at Sandia
- Current OH measurements
- High-pressure experiments are underway **Lenny Sheps**

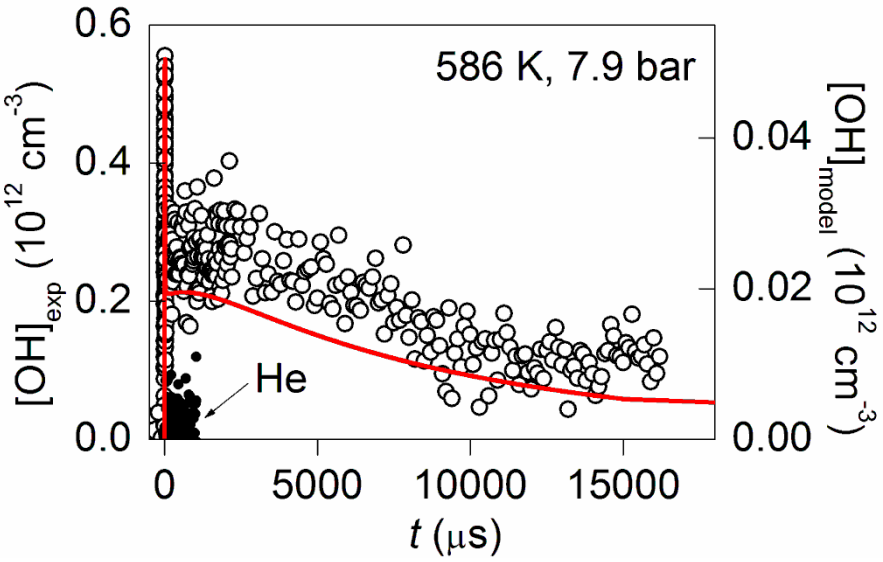






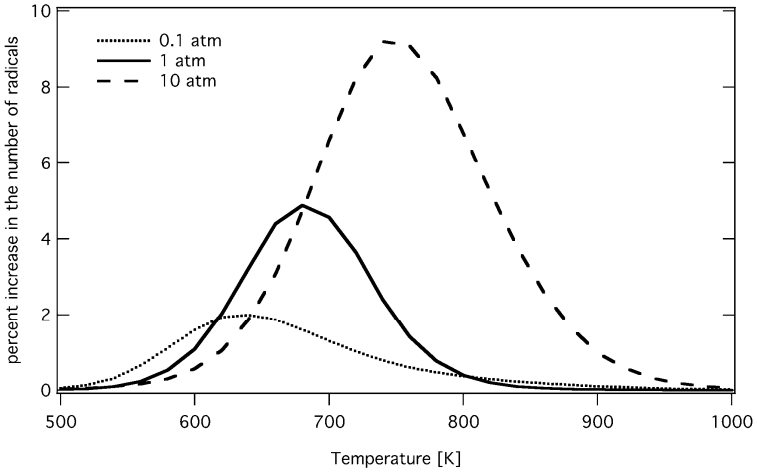
High-pressure experiments will help refine the potential energy surface.

Models for all conditions must use the same stationary points



Cyclohexane oxidation – high-pressure experiments

- Shape predicted from master equations
- Amplitude all wrong, but R + O_2 already validated at low pressure
- Attribute difference to QOOH + O_2 reactions



Propane oxidation – what will high-pressure experiments tell us?

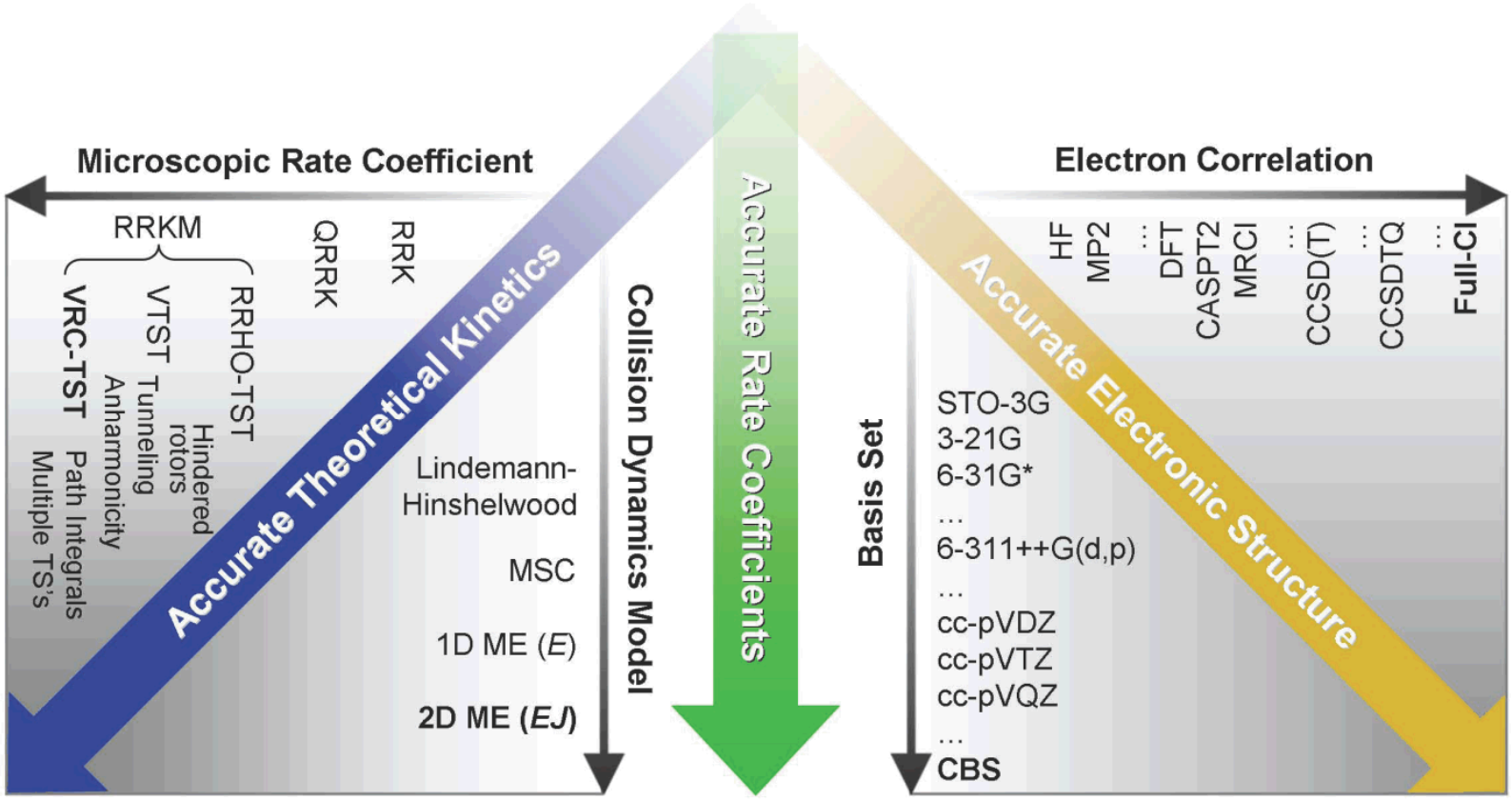
- Increased stabilization is predicted to drastically reduce OH from R + O_2
- Is OH mostly from QOOH + O_2 at high pressure?

Can these experiments get at QOOH?

Role of O_2 + QOOH in Low-Temperature Ignition of Propane. 1. Temperature and Pressure Dependent Rate Coefficients

C. Franklin Goldsmith, William H. Green, and Stephen J. Klippenstein, J. Phys. Chem A, doi:10.1021/jp210722w

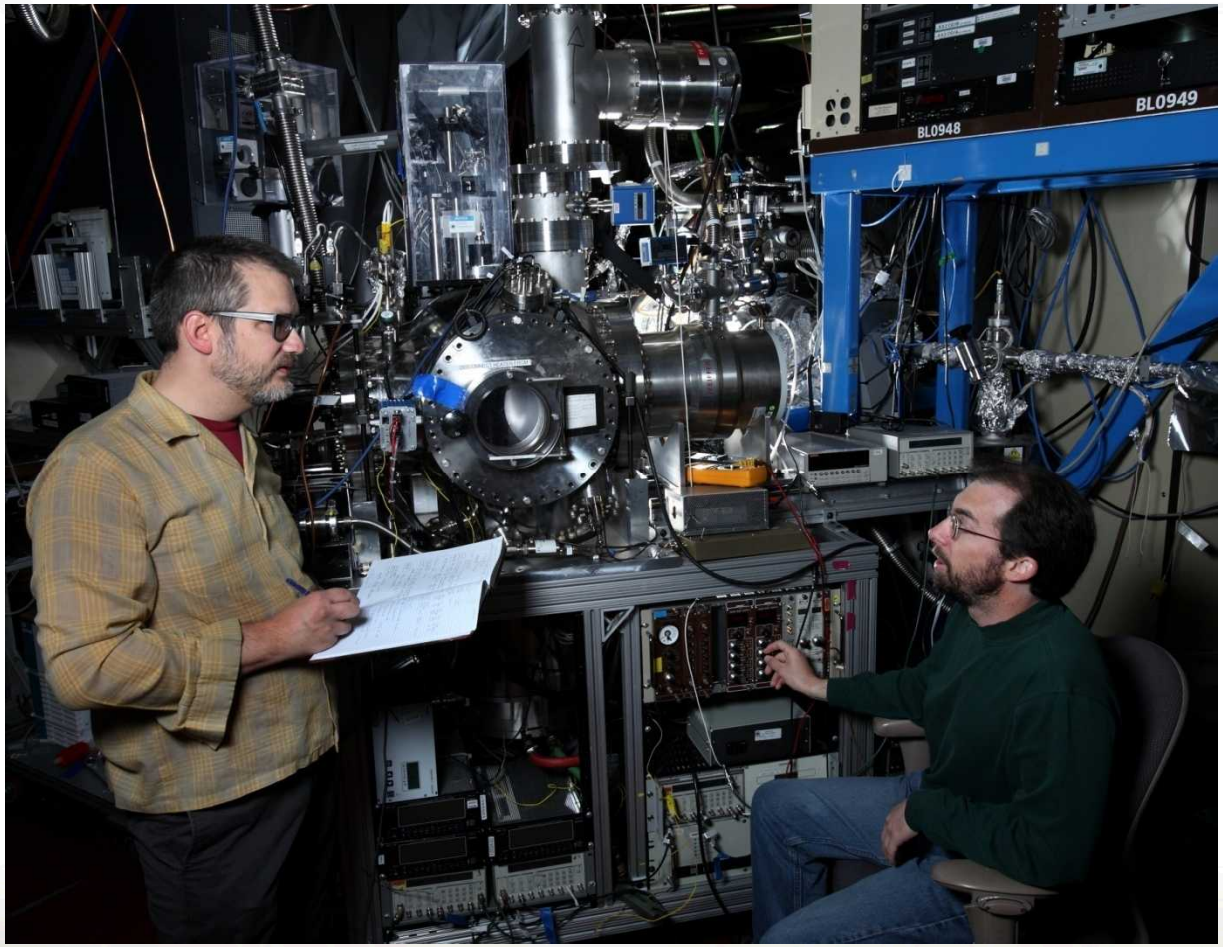
Experimental kinetics *indirectly* relates to physical characteristics of the potential energy surface



Experimental constraints on the stationary point characteristics rely on the accuracy of the theoretical kinetics method

More accurate quantum chemistry may highlight inadequacies in the kinetics!

Can't we do better? – Maybe detecting two products (OH and HO_2) isn't enough?



Tunable synchrotron photoionization mass spectrometry

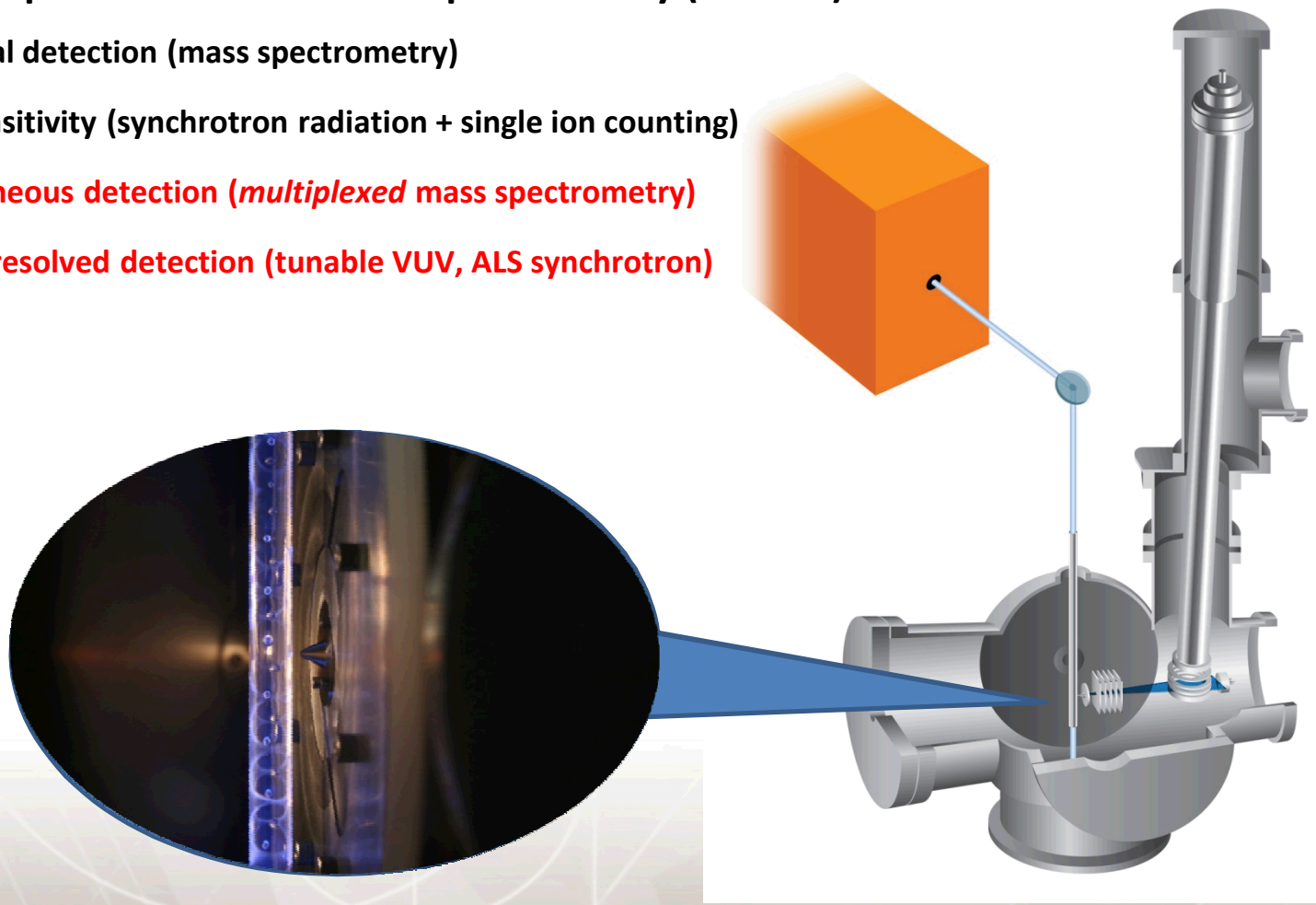
Collaboration between Sandia CRF (**David Osborn**, C.A.T.) and LBNL (Musa Ahmed, Kevin Wilson, Steve Leone)

Osborn et al., *Rev. Sci. Instrum.* **79**, 104103 (2008)

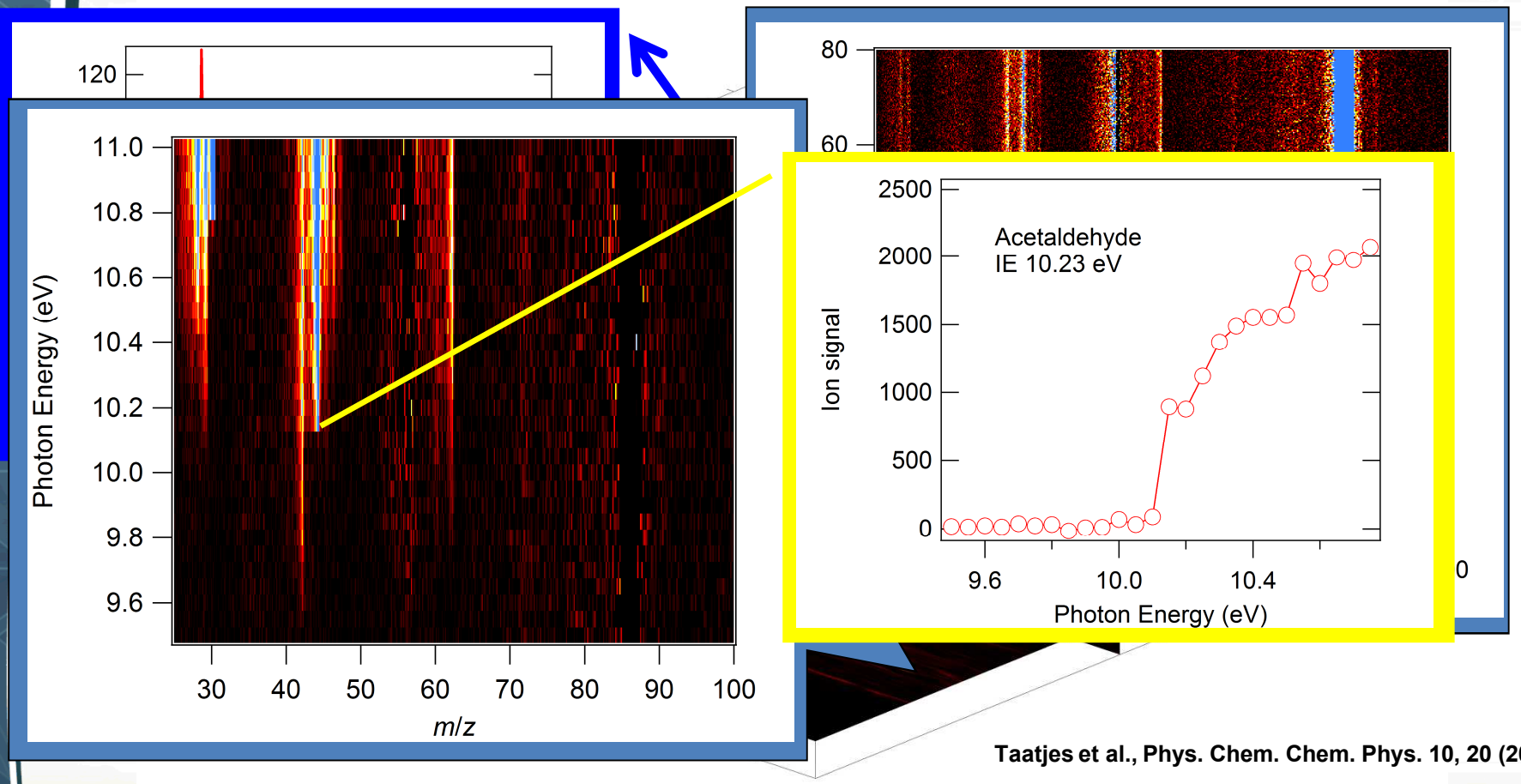
Laser photolysis reactor is coupled to time-of-flight mass spectrometer with synchrotron photoionization

Multiplexed photoionization mass spectrometry (MPIMS)

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



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



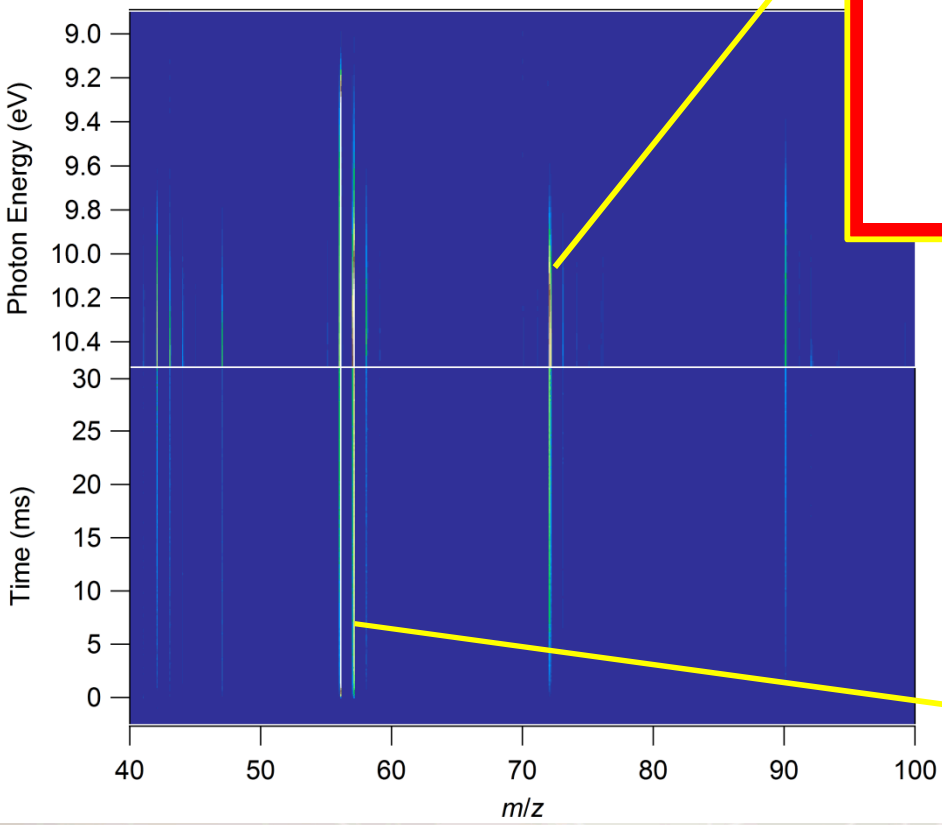
Taatjes et al., Phys. Chem. Chem. Phys. 10, 20 (2008).

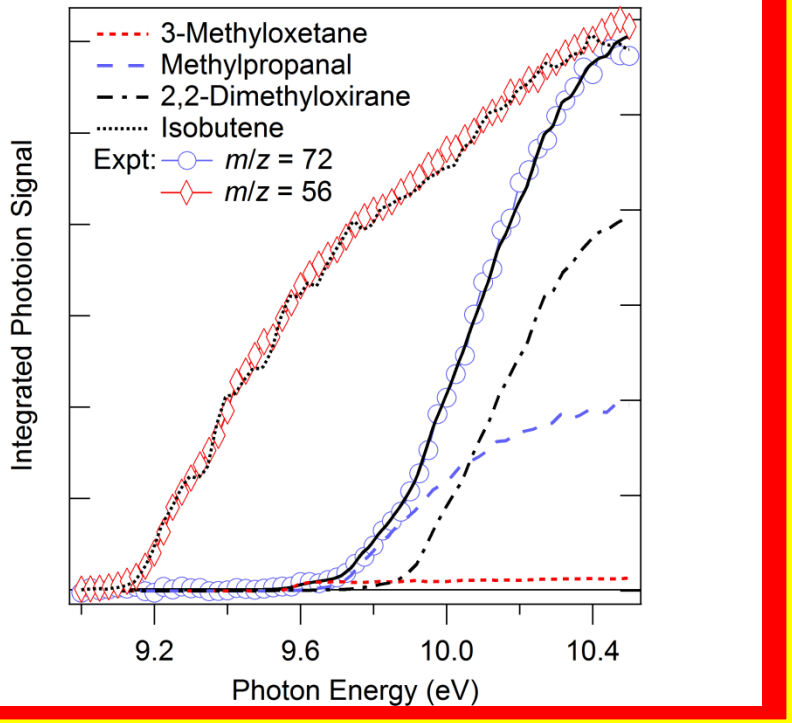
3-D dataset can be "sliced" along different axes to probe different aspects of the reaction

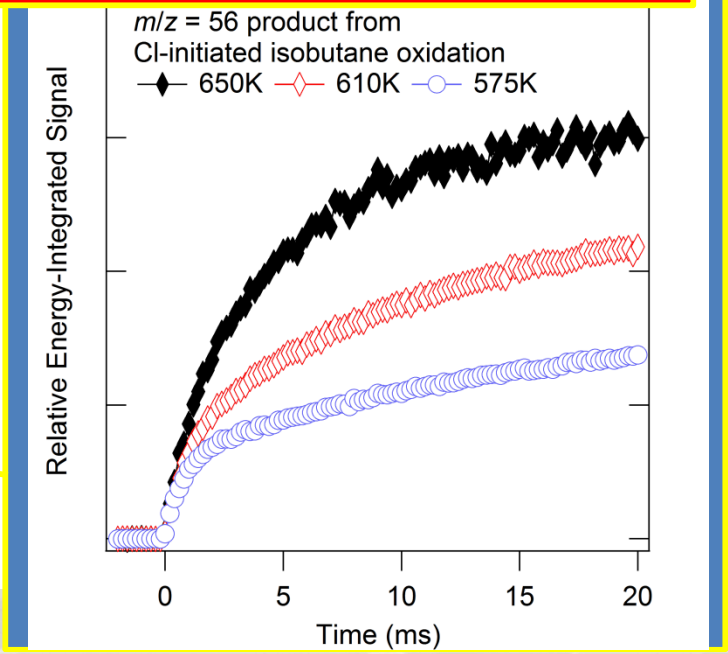
Cl-initiated isobutane oxidation

Time behavior of product formation – prompt and delayed

Photoionization spectra identify product isomers





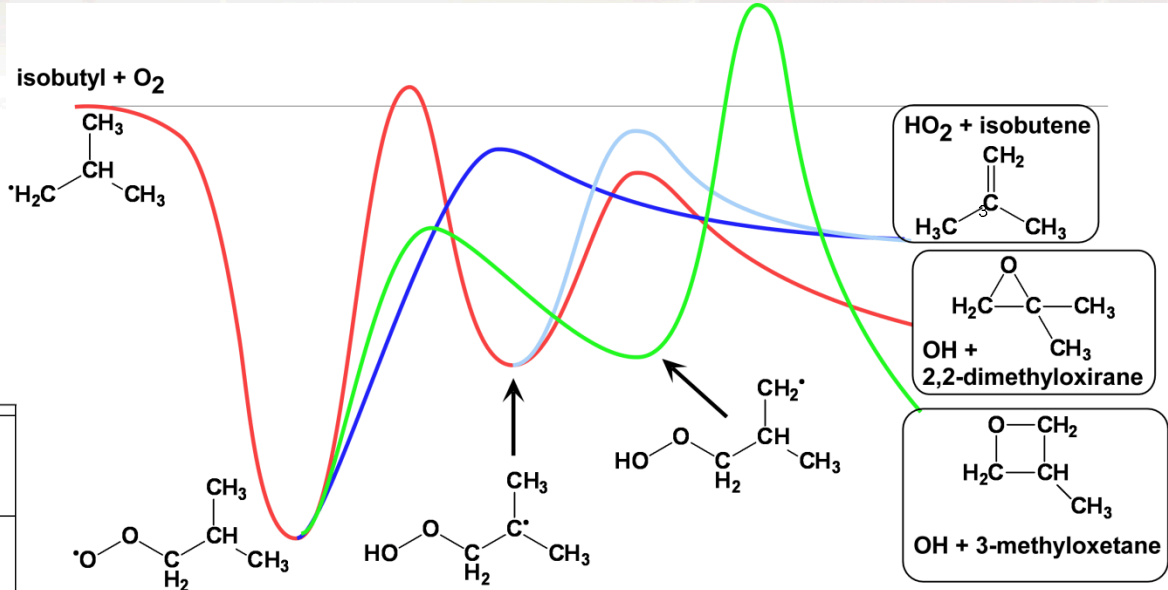


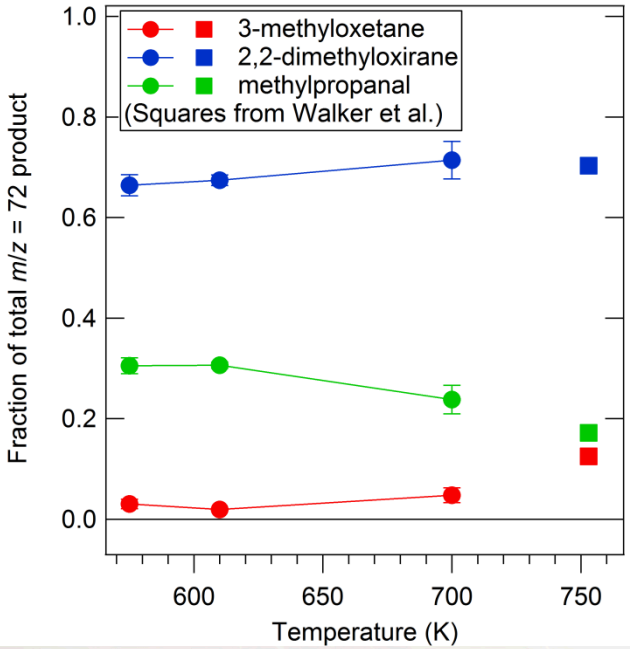
Arkke Eskola, Oliver Welz et al., submitted to Combustion Symposium

How do these experiments constrain theory?

Methylpropanal is a prominent initial product in the oxidation

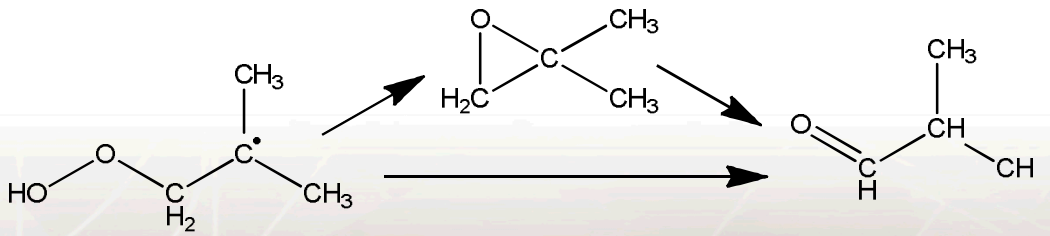
Where does it come from?



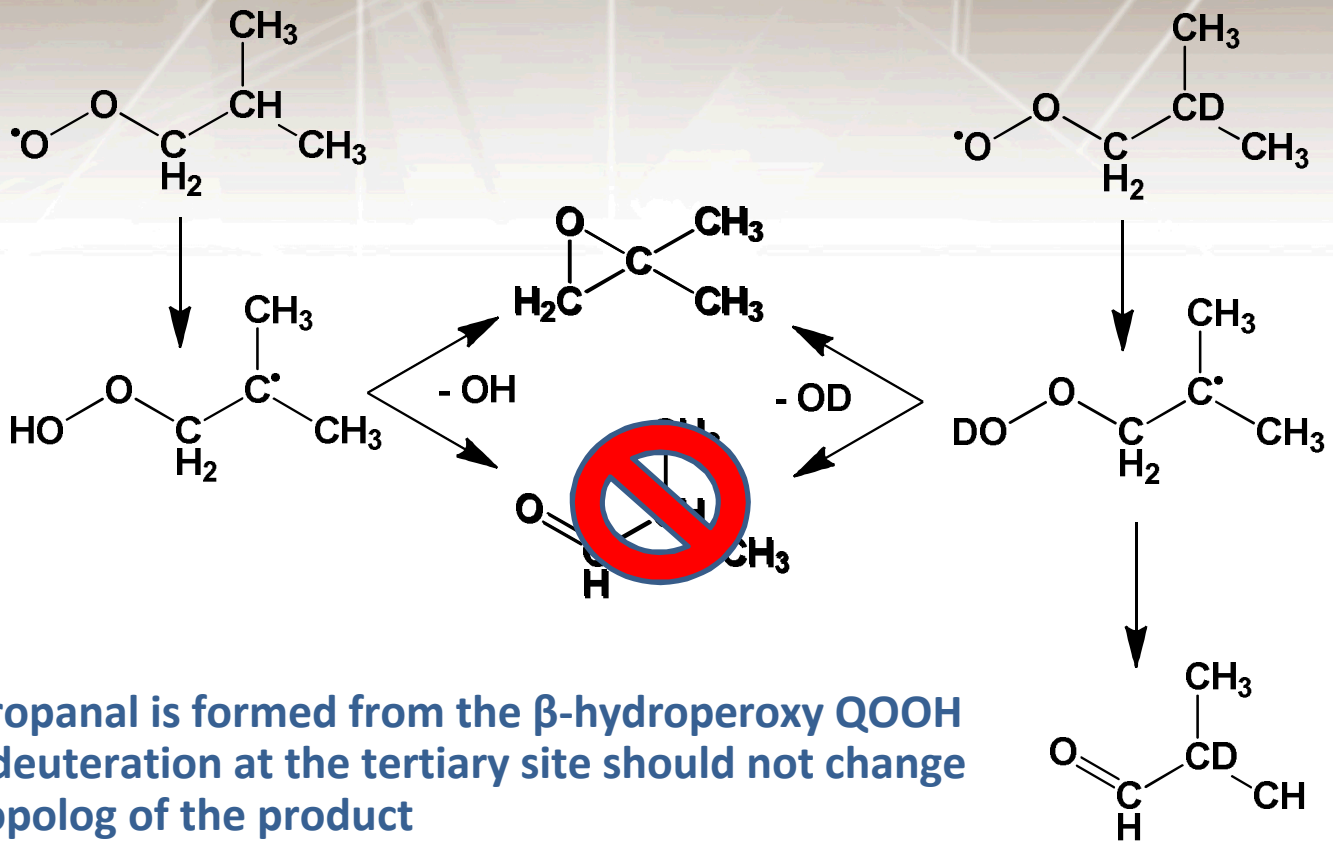


Direct formation? CBS-QB3 – "has a high barrier and is unimportant" Miyoshi, *J. Phys. Chem A* 115, 3301–3325 (2011)

Walker proposed formation from QOOH:



J. Chem. Soc. Faraday Trans. 1, 74 (1978) 2229-2251



If methylpropanal is formed from the β-hydroperoxy QOOH radical, deuteration at the tertiary site should not change the isotopolog of the product

Measure products of $(CH_3)_3CD$ oxidation --

Find singly deuterated methylpropanal

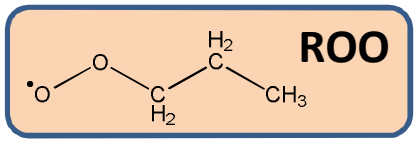
Why?

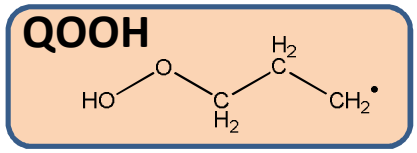
Does methylpropanal form from the other QOOH? – could make a difference in models of autoignition

Or is direct formation by 1,3 isomerization easier than we thought?

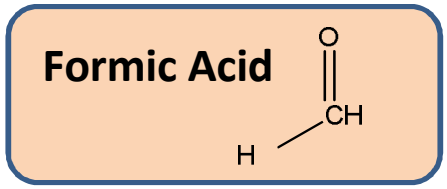
That's all still pretty indirect – Isn't there *some* way we can do better?

What are these "intermediates" again?



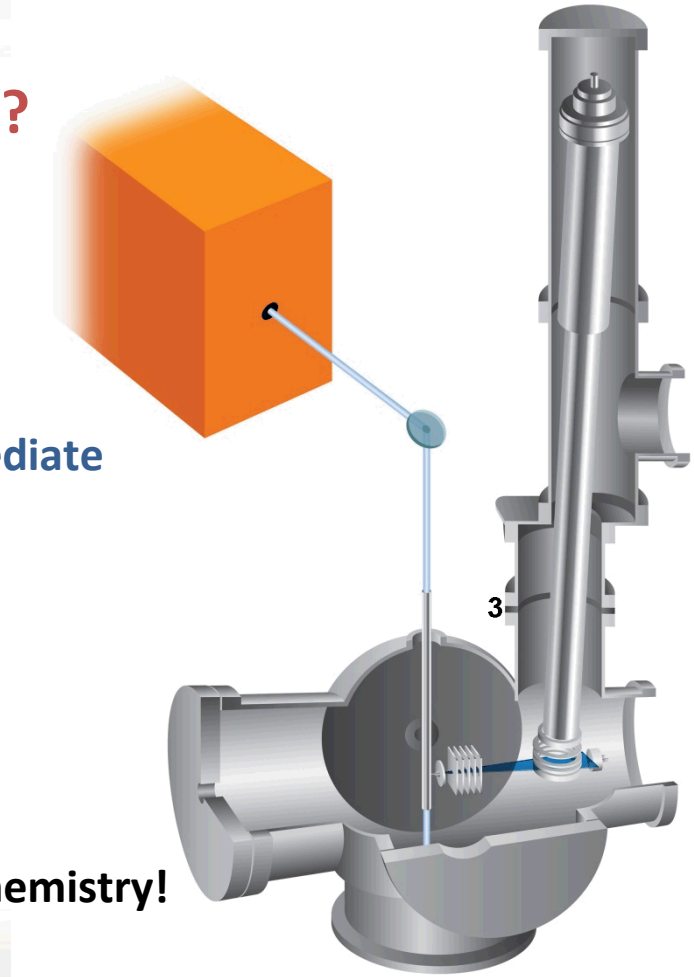


QOOH is an isomer of the more stable ROO intermediate



Criegee intermediates are isomers of more stable tropospheric species

But we have a machine that can resolve isomeric chemistry!



Why are these things so hard to detect?

People get out of the rain!

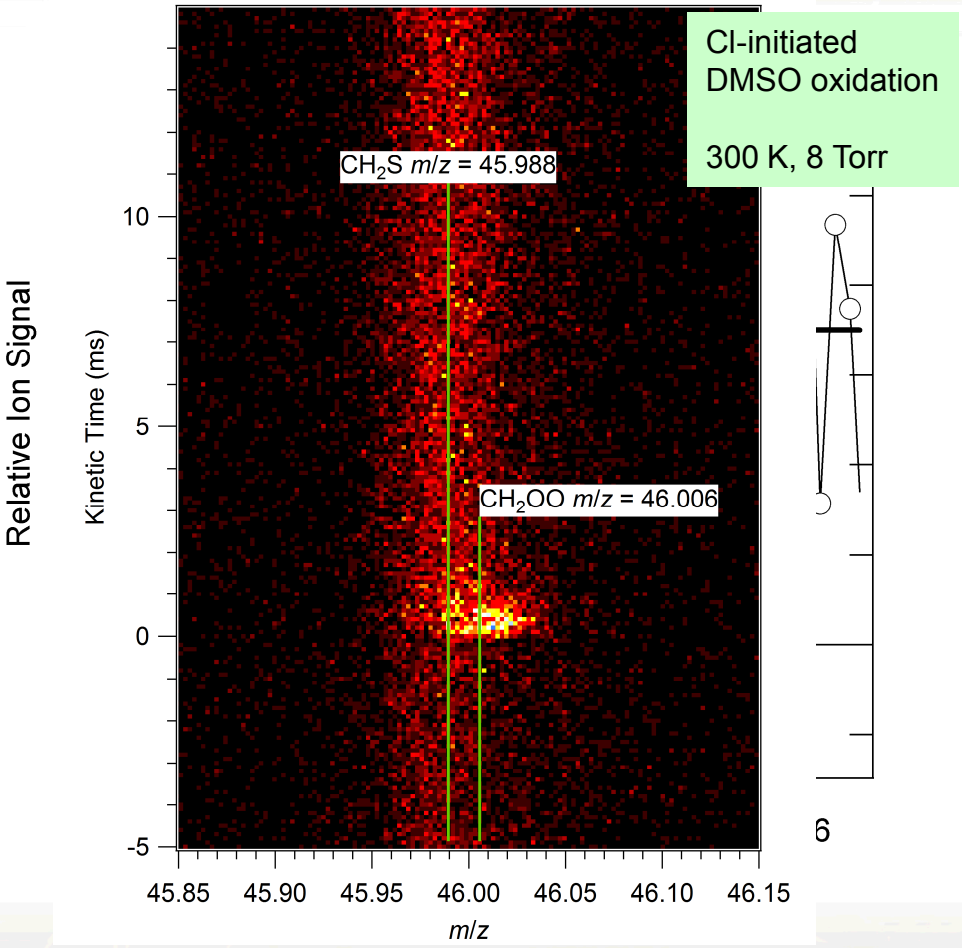
The hole in the bottom of the bucket is bigger than the hole at the top!

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

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

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

- Ozonolysis of alkenes proceeds via a carbonyl oxide intermediate ("Criegee intermediate")
- They are important tropospheric reactants but only indirect measurements exist
- **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_2OO



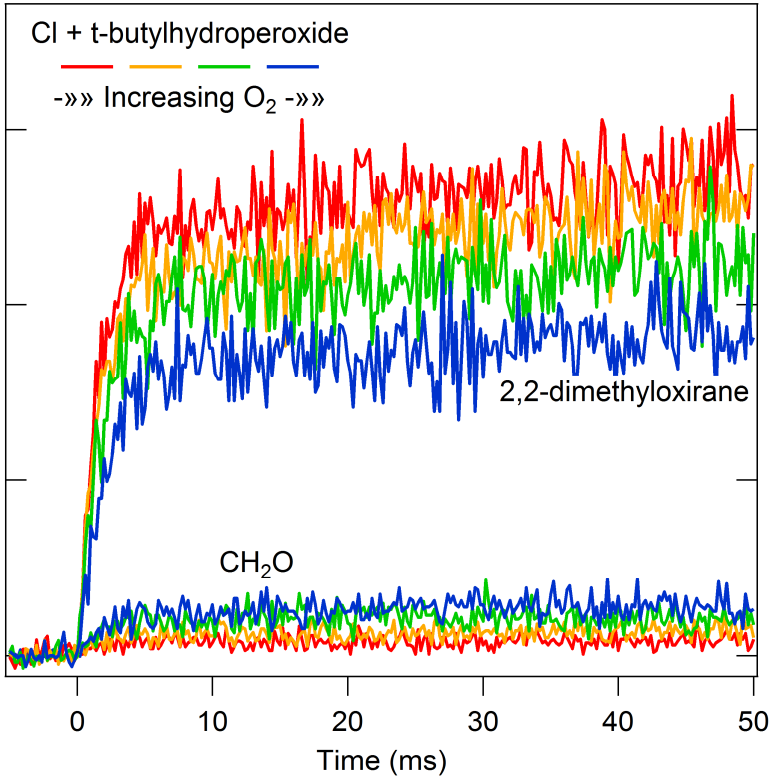
had

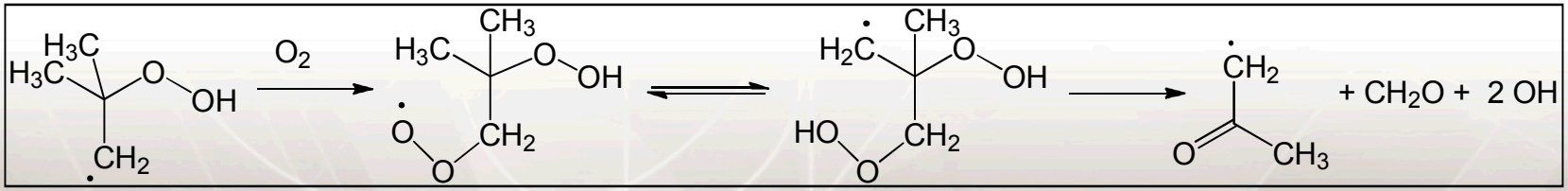
No one ~~has~~ ever seen a gas phase Criegee intermediate

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

Can photoionization directly detect and characterize the elusive QOOH?

- QOOH reactions are critical for autoignition but only indirect measurements exist
- 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





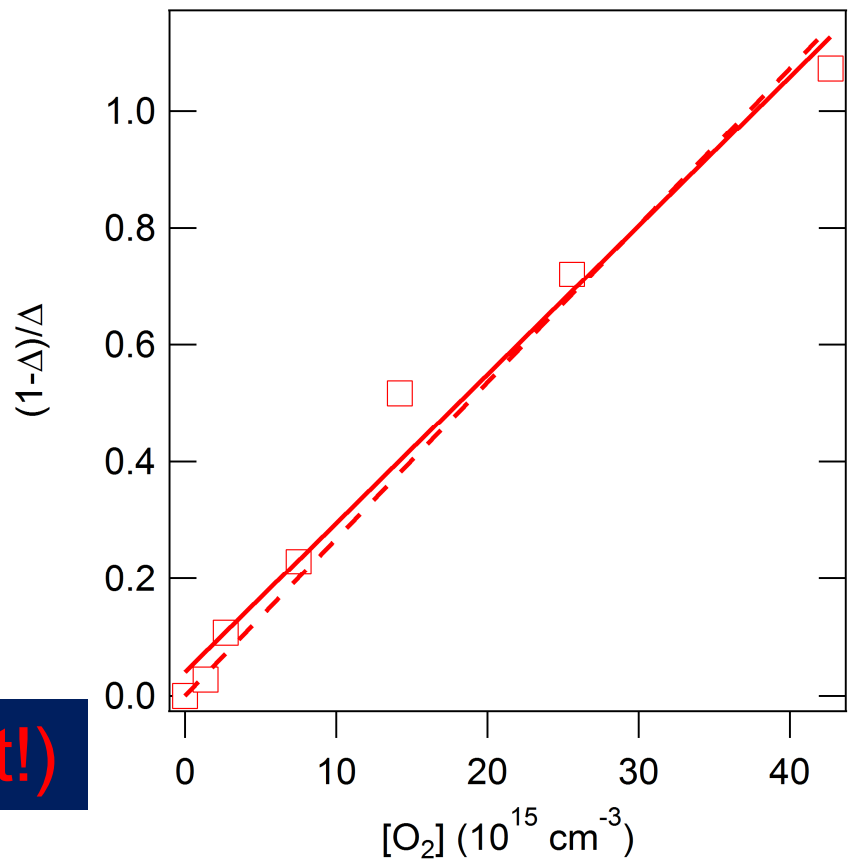
Detection of Reaction Products Can Give Direct Kinetics Measurements

- Correctly scaled change in dimethyloxirane is linear in $[O_2]$
- Direct measurement of QOOH + O_2 rate coefficient relative to thermal dissociation

- **Problem is we don't know the absolute k of either process!**
- Fix this by doing experiments with better time resolution

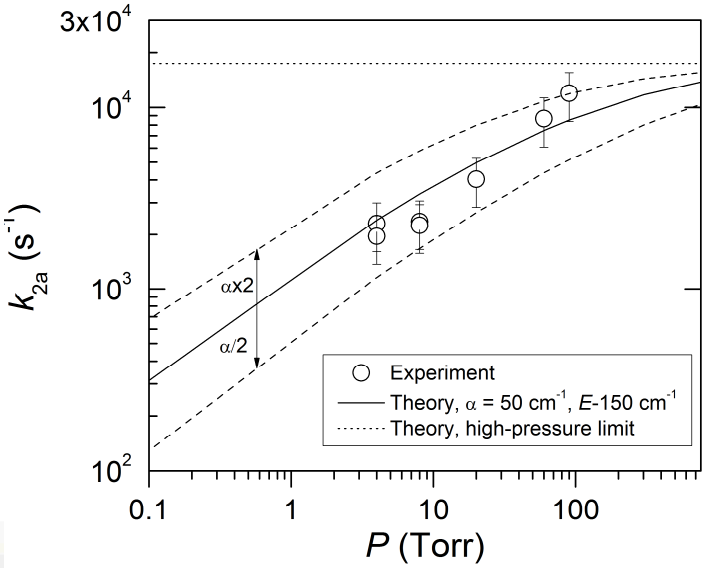
However, no $QOOH^+$ (yet!)

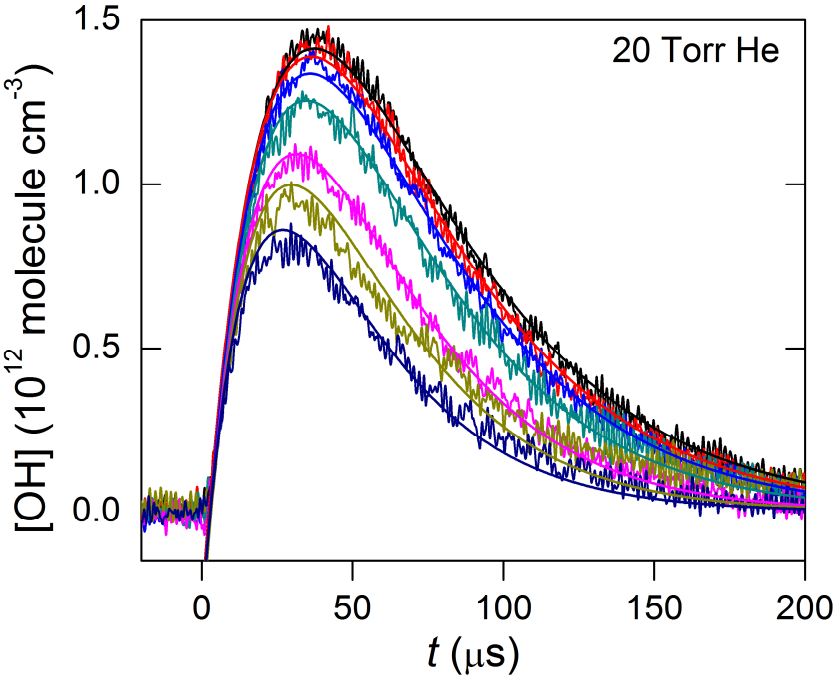
$k(QOOH+O_2)/k(dissociation) = (2.5 +/- 0.4) \times 10^{-17}\ cm^3$



Measurement of OH Formation from QOOH Probes the Dissociation Rate Coefficient

- Photoionization experiments show that QOOH is formed
- OH profiles can be modeled and compared to theory

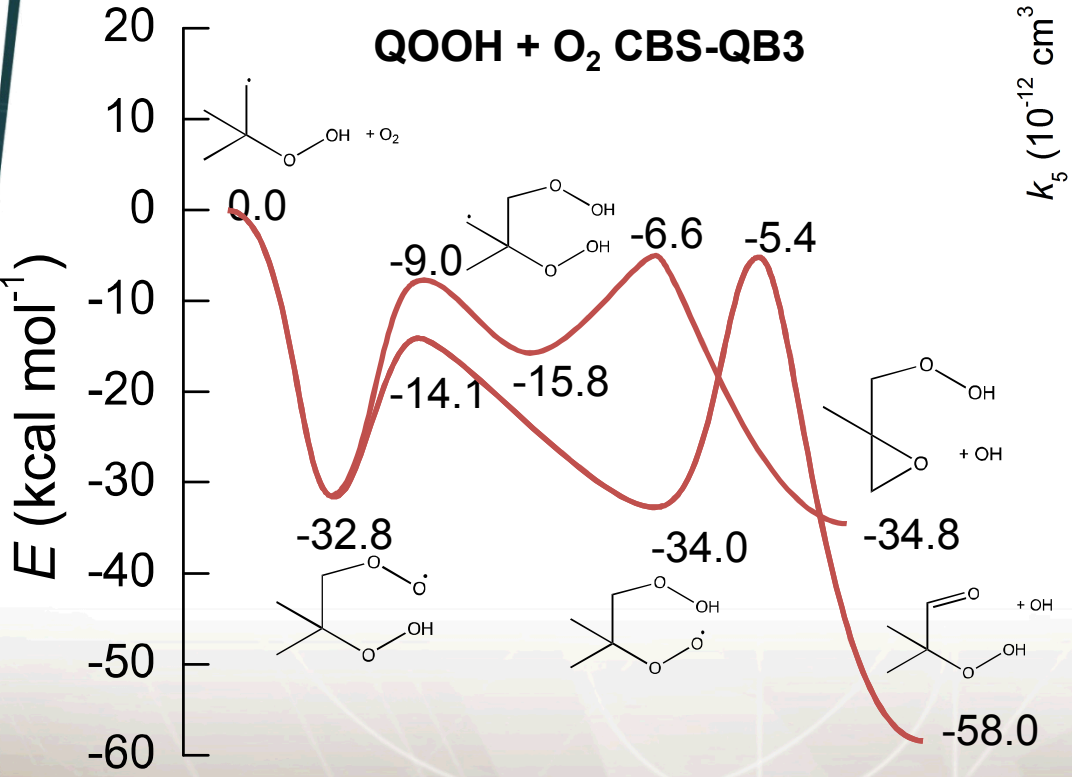


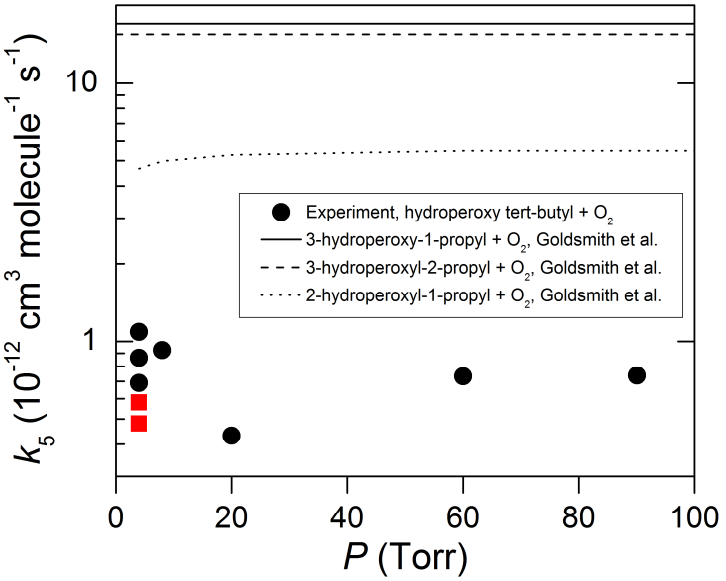


- Dissociation of QOOH shows falloff that is in reasonable agreement with (adjusted!) theory (barrier height reduced by 0.4 kcal mol^{-1} from CBS-QB3)

Modeling the Dependence on O_2 Concentration Now Provides Absolute Rate Coefficient

- Rate coefficient is similar to the calculated rate constant for similar hydroperoxypropyl radical reaction with O_2 (Goldsmith, Green, and Klippenstein)



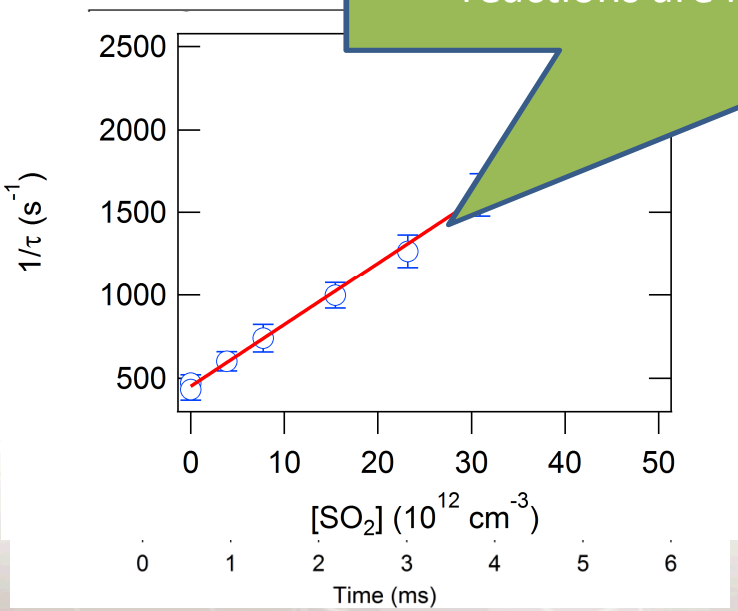


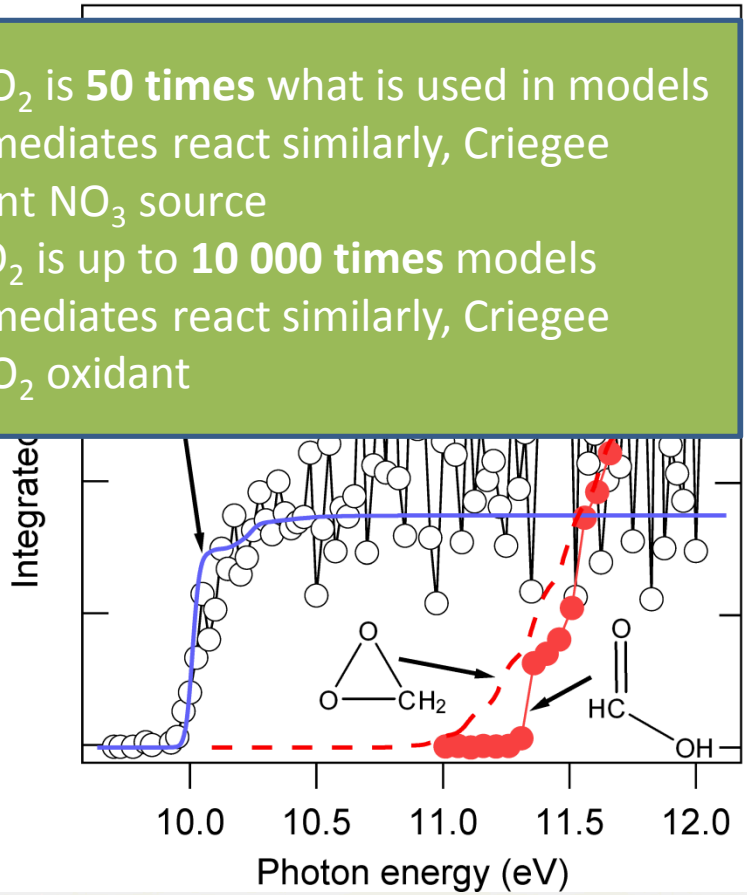
- Stabilization is main channel at room temperature
- No discernible pressure dependence
- More work – other products? Temperature dependence?

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

- **Arkke Eskola et al.** (2006) **found that CH**
  atom – turns out th
  intermediate!
- **Can make lots of C**
  reactions with imp

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** models
If other Criegee intermediates react similarly, Criegee reactions are major SO_2 oxidant



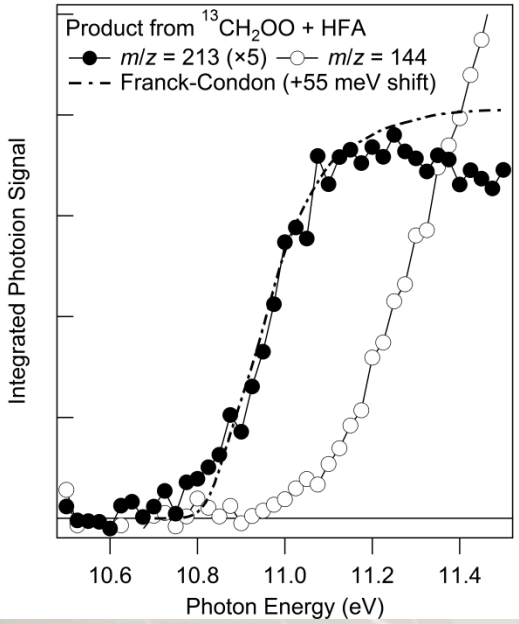


Welz, Savee, et al., *Science* **335**, 204 (2012)

What does all this mean?

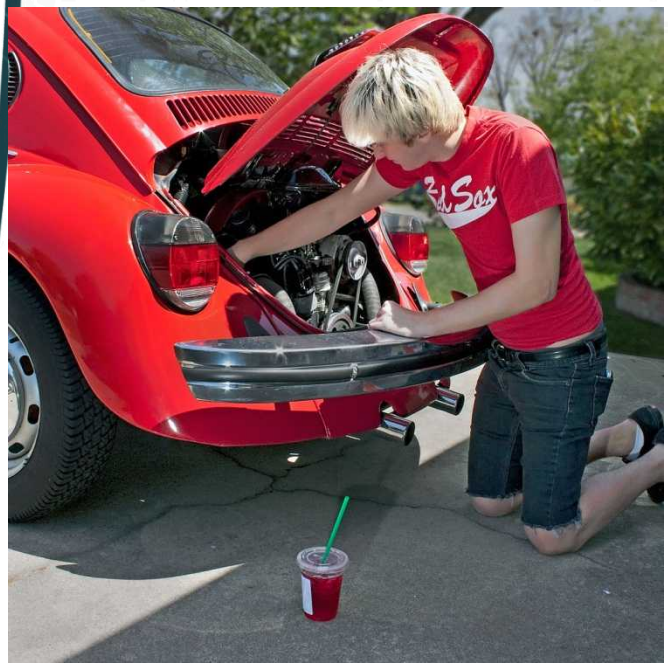
- **Sulfate chemistry makes aerosols**
  - Aerosols tend to reflect radiation
    - Criegee chemistry connected to "cooling"
  - Biggest Criegee contribution where there is a lot of ozone and alkenes

Photo: Christian von Wissel

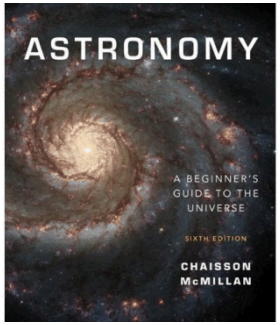


- **We are *just beginning* to understand how Criegee biradicals react**
  - Need to understand larger Criegee molecules
  - Need to understand more reactions: e.g., reactions with carbonyls make secondary ozonides
  - Need to understand reactions at different conditions

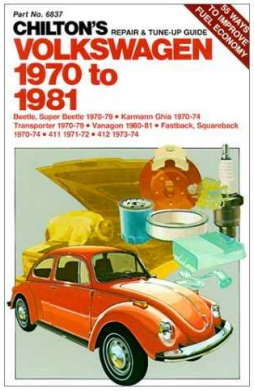
What is the philosophy of our research?

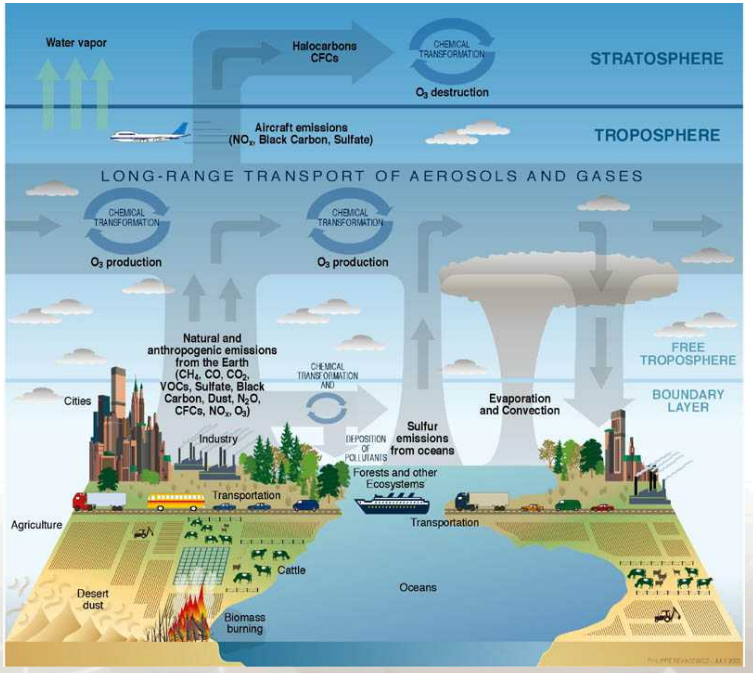


Robert Couse-Baker



Mbz1 Wikimedia commons



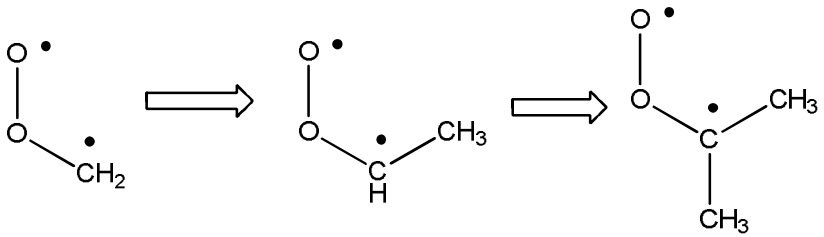


US CLIMATE CHANGE SCIENCE PROGRAM OFFICE

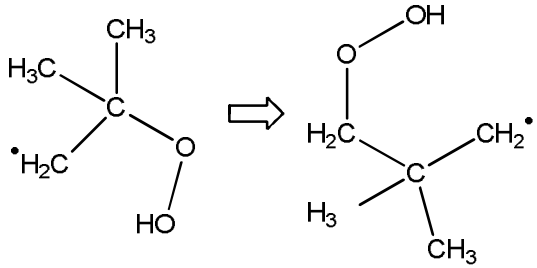
?

Opening the "black box" is just the beginning for studies of these ephemeral intermediates

- Studies so far investigated conditions unlike actual combustion or troposphere



- Measurements of only the simplest or most convenient examples of intermediates



- "Trailblazing" measurements give others tools to investigate these species

David Osborn, Oliver Welz, Judit Zádor, John Savee, Haifeng Huang, Arkke Eskola, Lenny Sheps, Howard Johnsen, Subith Vasu

Carl Percival (Manchester); Dudley Shallcross (Bristol); Henry Curran (Galway); Stephen Klippenstein (Argonne)

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