SAND2018-1701PE

Direct Measurement of Elusive Intermediates

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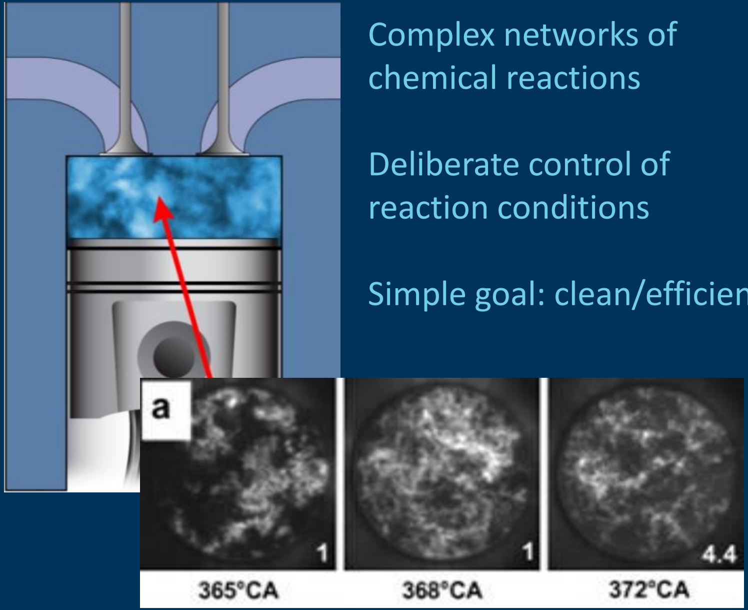
NOAA-CSD February 15, 2018

Sandia National Laboratories

Comparing different (but related) chemical systems

Autoignition chemistry



Complex networks of chemical reactions

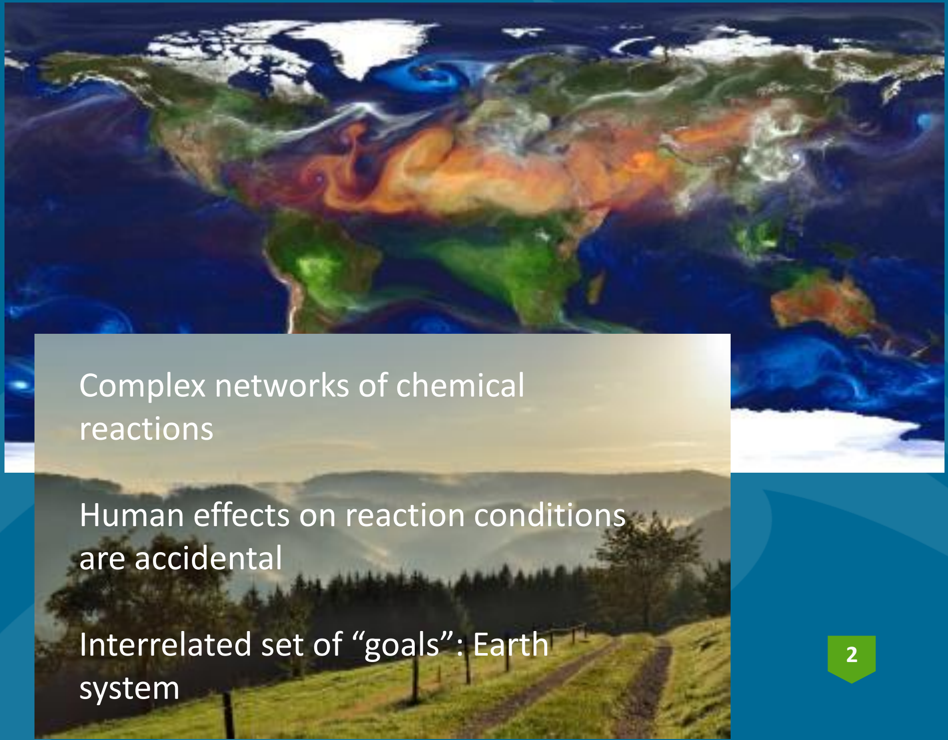
Deliberate control of reaction conditions

Simple goal: clean/efficient

John Dec, Sandia

Tropospheric oxidation

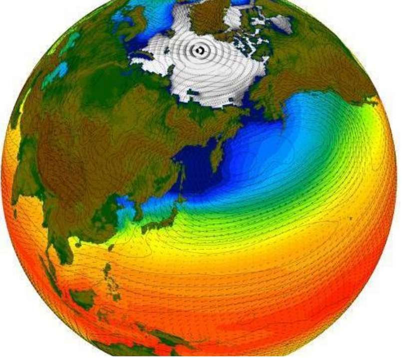
William Putman, NASA/Goddard

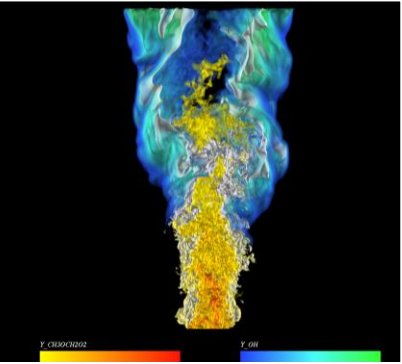


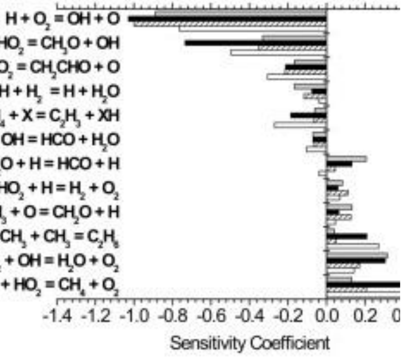
Complex networks of chemical reactions

Human effects on reaction conditions are accidental

Interrelated set of “goals”: Earth system







Combust. Flame **153**, 2-32 (2008)

How do we handle complex networks of reactions?

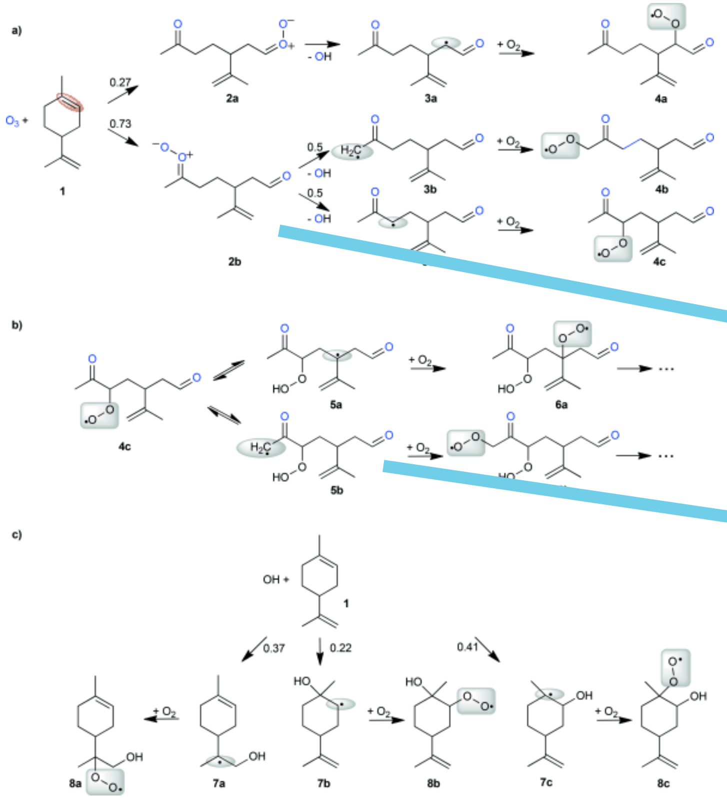
- Control of model and parametric uncertainties
- “Comprehensive” chemical models not always feasible
- Targeted reduced models

Are laboratory kineticists a modelers’ friend?

- (don’t necessarily have the same motivations!)

How can kineticists

- Choose reactions that make a difference
- Connect the laboratory work *correctly* to field or device



- Specific investigations target individual reaction types
- Physical understanding allows rigorous generalization

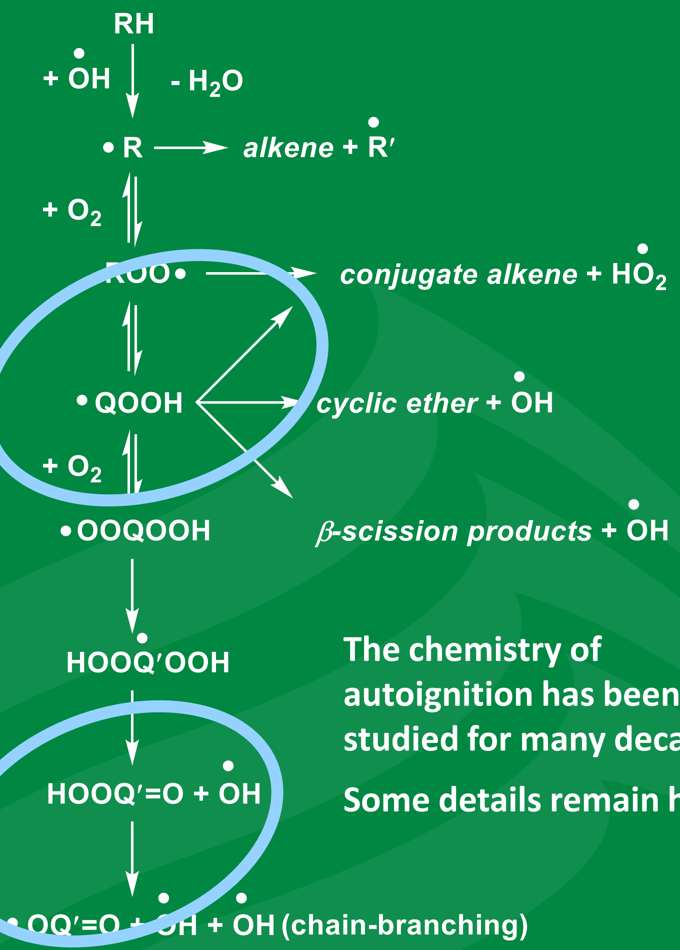
Ozonolysis – can we focus on individual carbonyl oxide channels?

Peroxy radical chemistry – can we isolate specific transformations?

Outcome of reaction systems depend on fate of short-lived intermediates

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

In autoignition chemistry it is easy to specify some key intermediates



RH

$\downarrow + \dot{O}H \quad - H_2O$

$\bullet R \longrightarrow$ *alkene* $+ \dot{R}'$

$+ O_2 \rightleftharpoons$

$ROO\bullet \longrightarrow$ *conjugate alkene* $+ H\dot{O}_2$

$\rightleftharpoons$

$\bullet QOOH \longrightarrow$ *cyclic ether* $+ \dot{O}H$

$\bullet QOOH \longrightarrow$ *β-scission products* $+ \dot{O}H$

$+ O_2 \rightleftharpoons$

$\bullet OOQOOH$

$\downarrow$

$HOO\dot{Q}'OOH$

$\downarrow$

$HOOQ'{=}O + \dot{O}H$

$\downarrow$

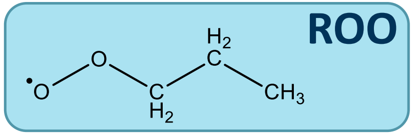
$\bullet OQ'{=}O + \dot{O}H + \dot{O}H$ (chain-branching)

The chemistry of autoignition has been studied for many decades –

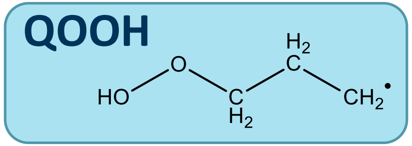
Some details remain hidden

Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *Prog. Energy Combust. Sci.* **2011**, *37*, 341.

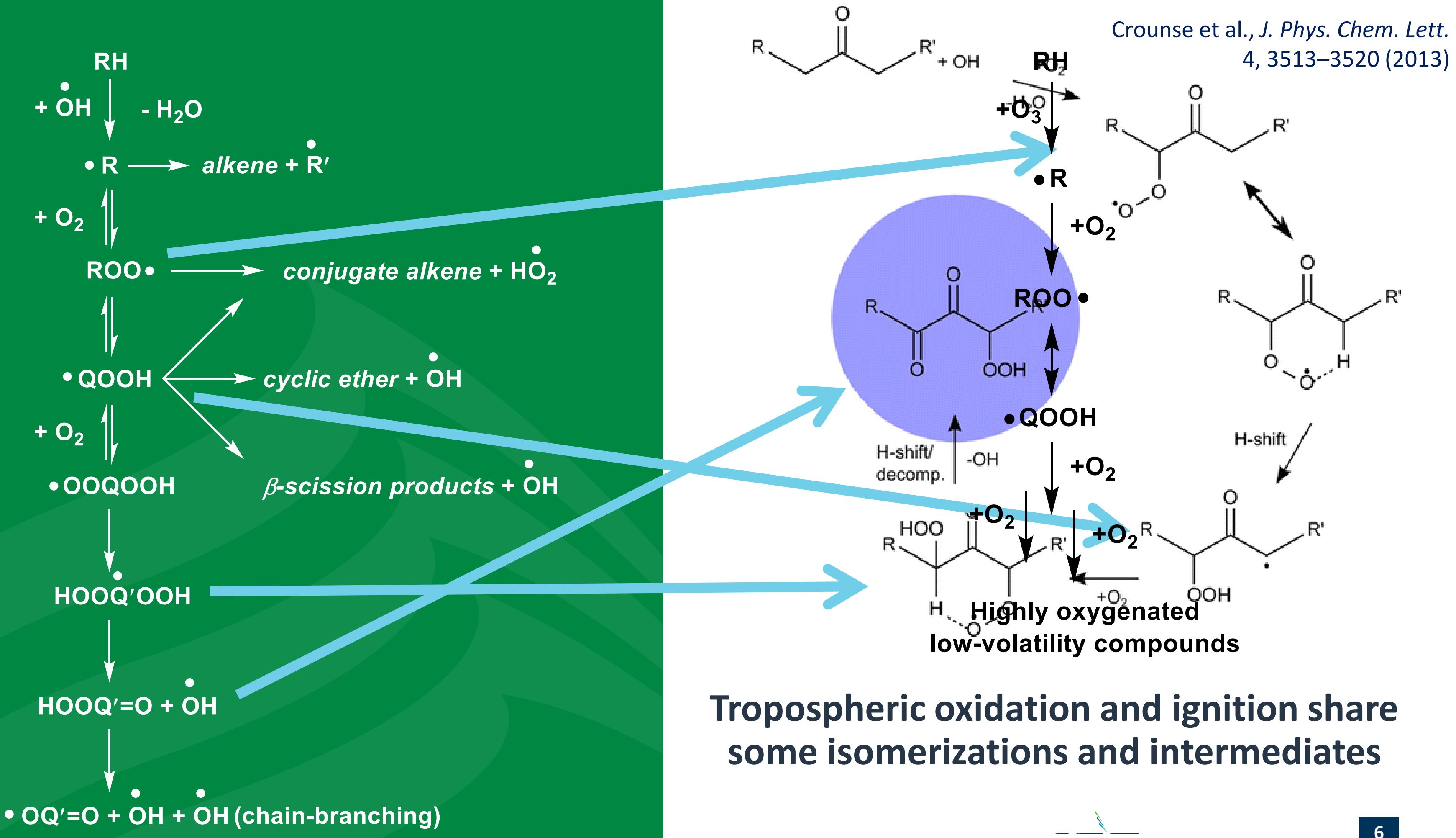
ROO



QOOH



- QOOH + O_2 is responsible for chain branching
- Chain branching step goes through dissociation of a ketohydroperoxide
- Isomers make a difference


RH

$+\ \dot{O}H$ $-\ H_2O$

$\cdot R$ → *alkene* + $\dot{R}'$

$+\ O_2$

$ROO\cdot$ → *conjugate alkene* + $H\dot{O}_2$

$\cdot QOOH$ → *cyclic ether* + $\dot{O}H$

β-scission products + $\dot{O}H$

$+\ O_2$

$\cdot OOQOOH$

$HOO\dot{Q}'OOH$

$HOOQ'{=}O + \dot{O}H$

$\cdot OQ'{=}O + \dot{O}H + \dot{O}H$ (chain-branching)

Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *Prog. Energy Combust. Sci.* **2011**, *37*, 341.

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

RH

$+O_3$

$\cdot R$

$+O_2$

$ROO\cdot$

$\cdot QOOH$

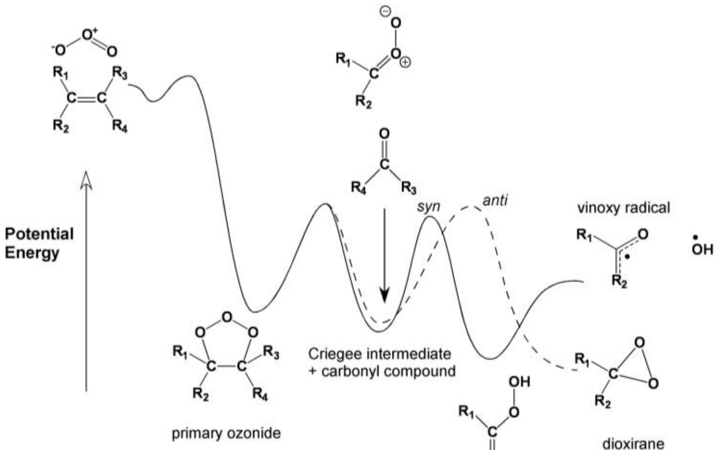
$+O_2$

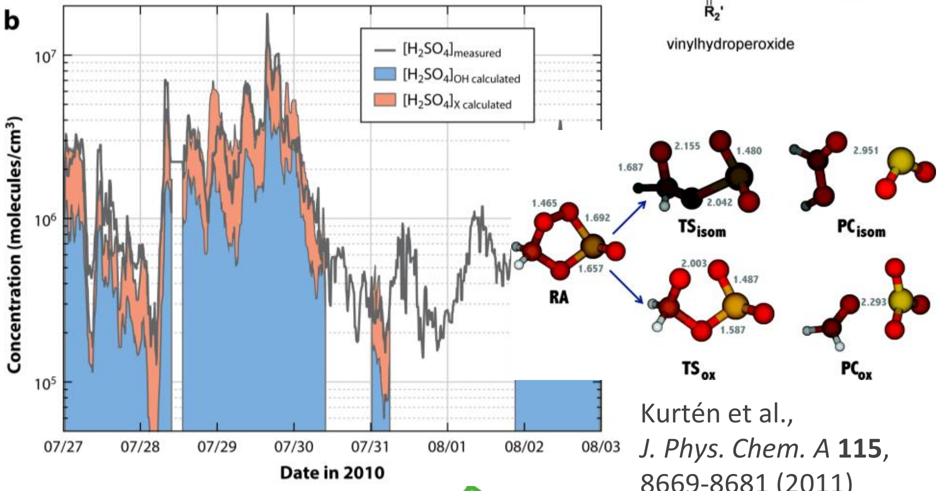
$+O_2$

$+O_2$

Highly oxygenated low-volatility compounds

Tropospheric oxidation and ignition share some isomerizations and intermediates

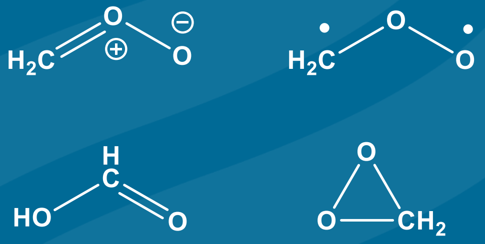




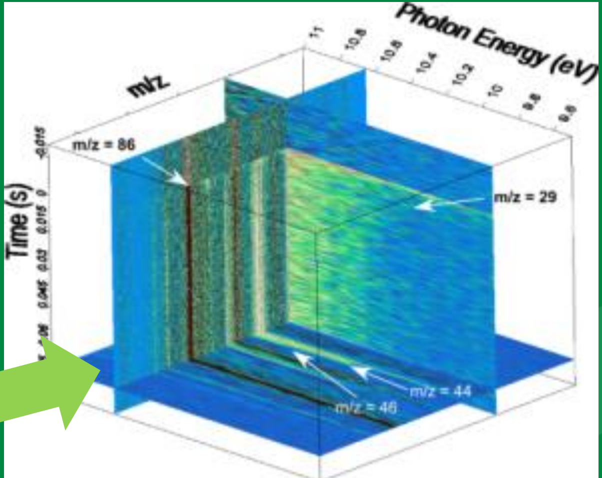
Kurtén et al., *J. Phys. Chem. A* **115**, 8669-8681 (2011)

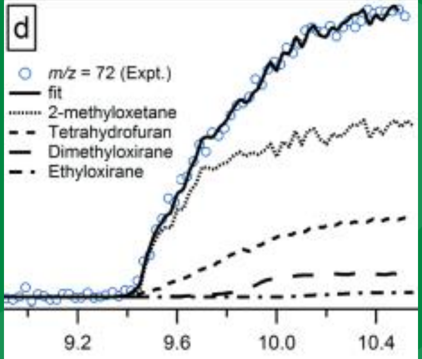
Mauldin et al., *Nature* **488**, 193–196 (2012)

- Kinetic models for tropospheric oxidation require knowing reactions of other intermediates
- Carbonyl oxides (“Criegee intermediates”) are formed in ozonolysis
- Criegee intermediates are potential tropospheric reactants
- Key intermediates are again isomers of other stable or reactive species



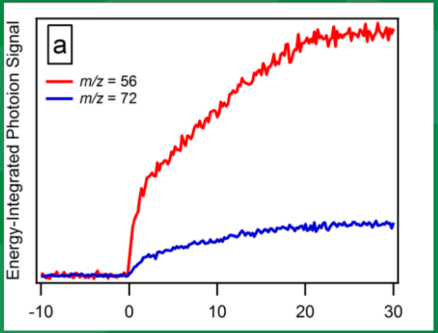
Synchrotron photoionization mass spectrometry can detect and characterize these intermediates





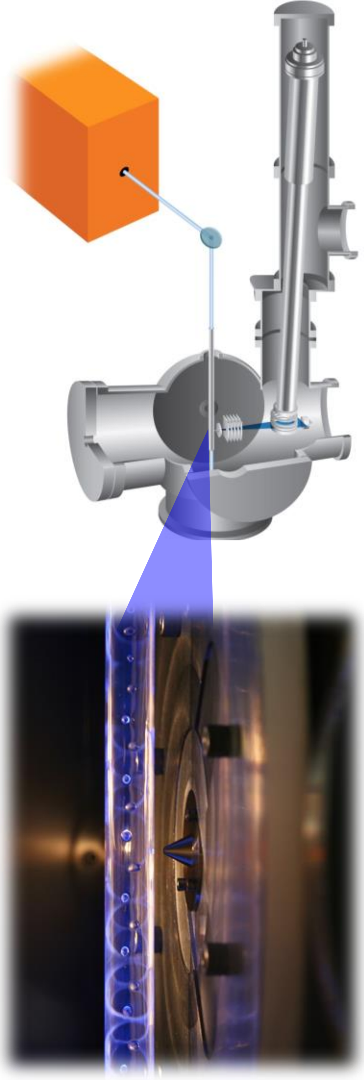
David Osborn

Isomer-Resolved Species Identification



Time-Dependent Chemical Kinetics

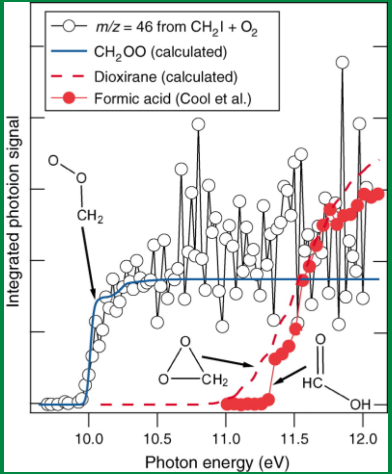
We can detect the intermediates but first we need to make them

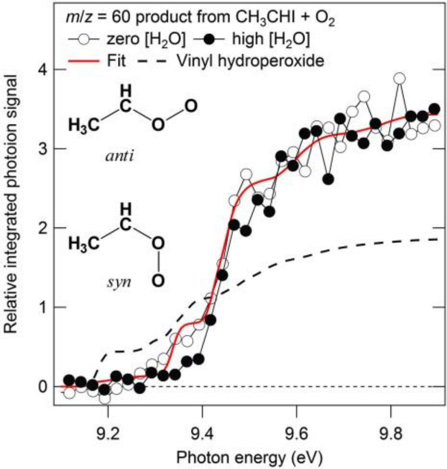


- In the troposphere or in bulk oxidation reactions, these intermediates are difficult to isolate
- They are formed in slow processes like ozonolysis or ROO isomerization, then react relatively rapidly

- Need strategies to form the intermediates in a controlled way

We can detect the intermediates but first we need to make them



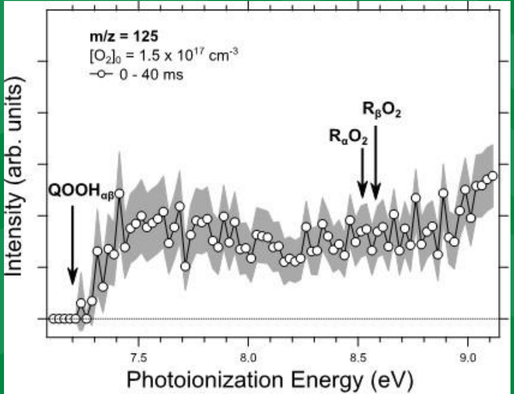


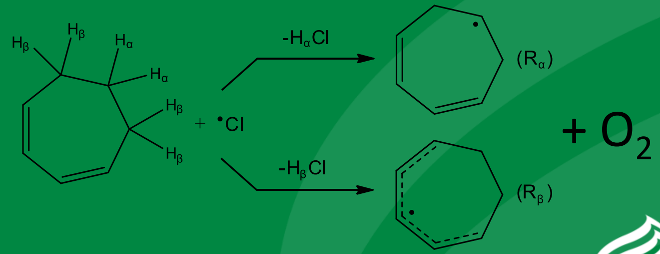
$CH_2I + O_2 \rightarrow CH_2OO + I$

gem-iodoalkyl + $O_2 \rightarrow$

carbonyl oxide + I

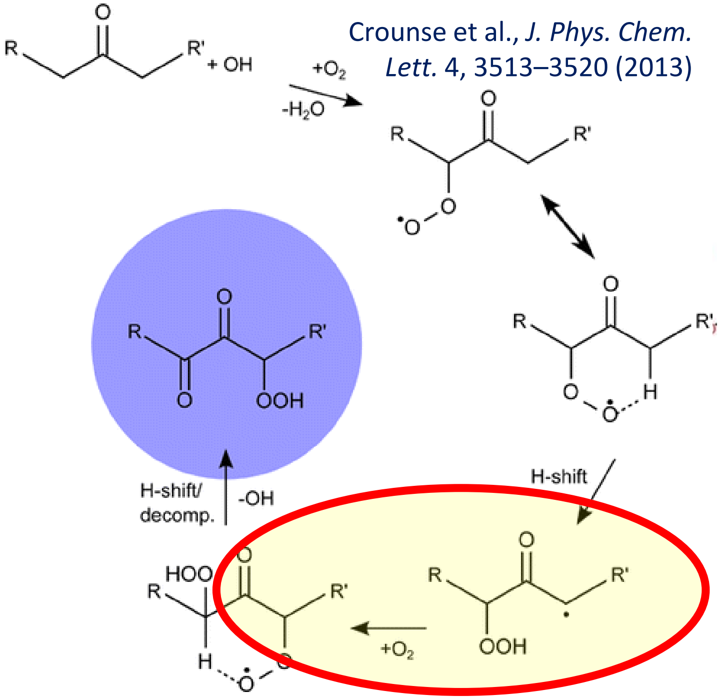
Welz et al., *Science* **335**, 204 – 207 (2012);
Taatjes et al. *Science* **340**, 177–180 (2013)



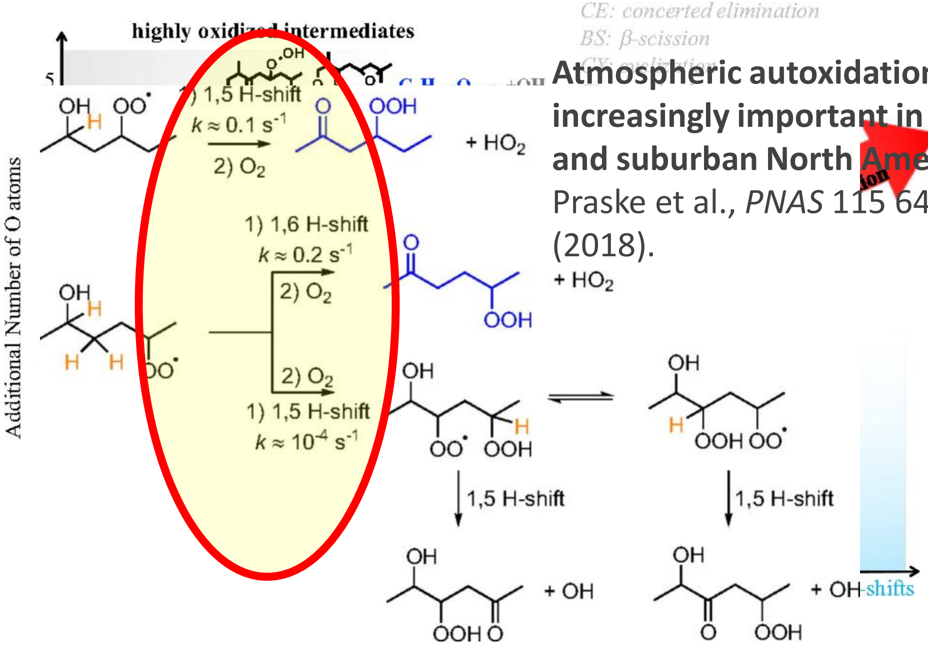


J.D. Savee, E. Papajak, B. Rotavera, H. Huang, A.J. Eskola, O. Welz, L. Sheps, C.A. Taatjes, J. Zádor, **D.L. Osborn**, *Science* **347**, 643-646 (2015).

Additions of QOOH to O_2 are important to complex oxidation submechanisms



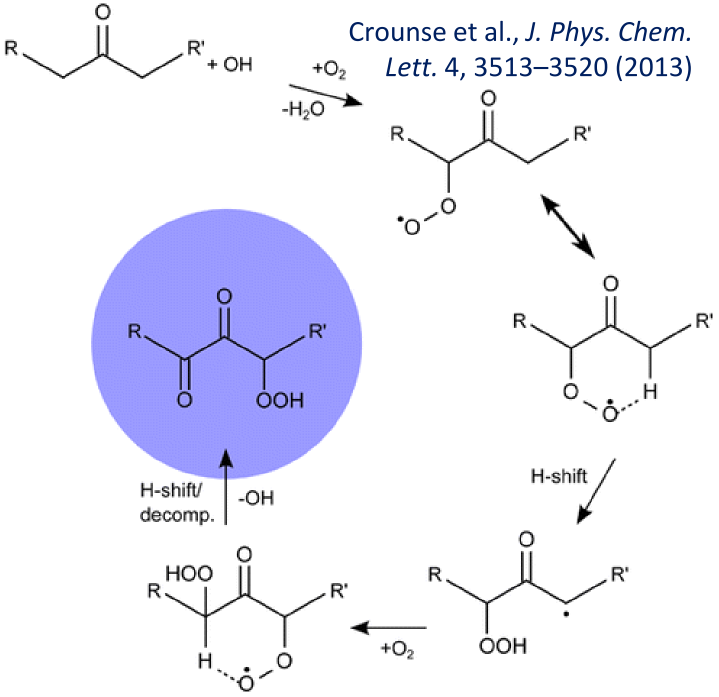
Crounse et al., *J. Phys. Chem. Lett.* 4, 3513–3520 (2013)



Atmospheric autoxidation is increasingly important in urban and suburban North America
Praske et al., *PNAS* 115 64-69 (2018).

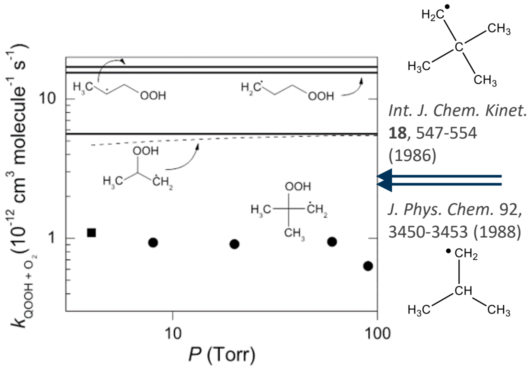
Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds
Wang et al., PNAS 2017 doi: 10.1073/pnas.1707564114

Additions of QOOH to O_2 are important to complex oxidation submechanisms



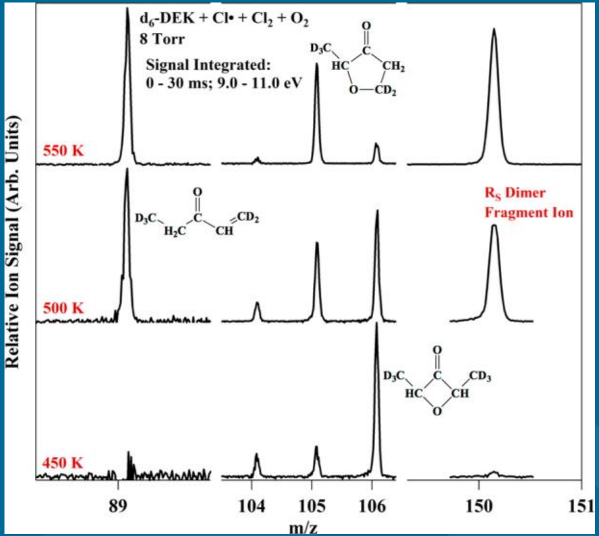
Crounse et al., *J. Phys. Chem. Lett.* 4, 3513–3520 (2013)

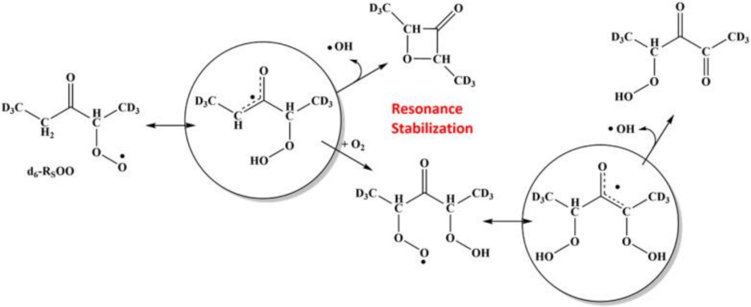
- Can we assume kinetics similar to alkyl + O_2 reactions?
- Preparing QOOH by alternative methods (e.g., Cl + ROOH) allows direct kinetics measurement (Zádor et al. *PCCP* **15**, 10753-10760 (2013))
- Resonance stabilization can dramatically shift dominant product channels in these reactions



Int. J. Chem. Kinet. **18**, 547-554 (1986)

J. Phys. Chem. 92, 3450-3453 (1988)





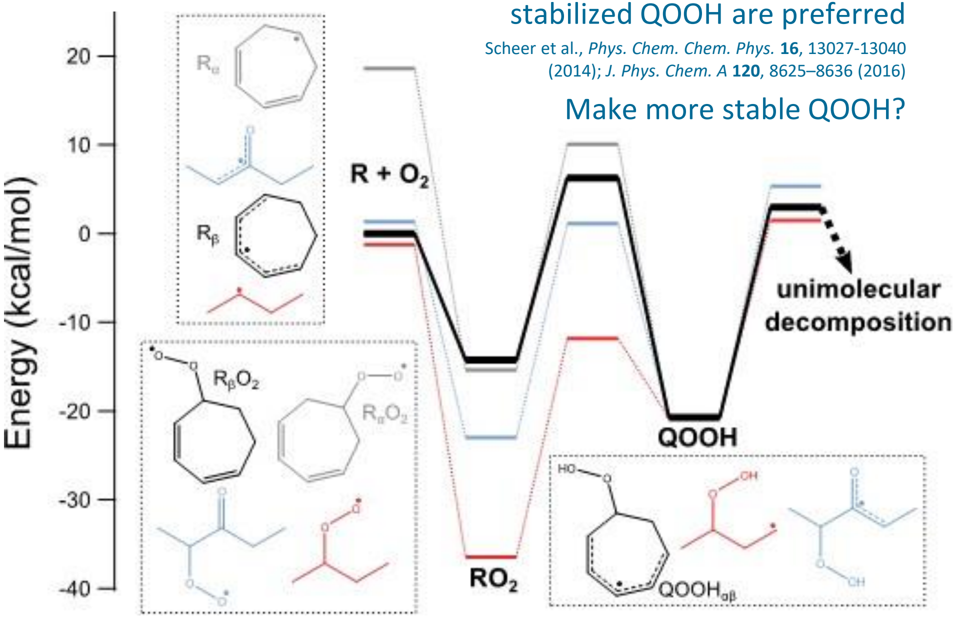
Scheer et al., *J. Phys. Chem. A* **120**, 8625–8636 (2016)

Extreme resonance stabilization

Ketone oxidation – resonance stabilized QOOH are preferred

Scheer et al., *Phys. Chem. Chem. Phys.* **16**, 13027-13040 (2014); *J. Phys. Chem. A* **120**, 8625–8636 (2016)

Make more stable QOOH?

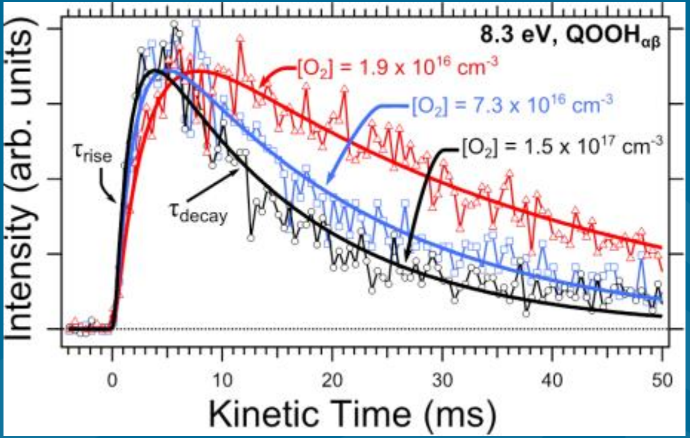


J.D. Savee, E. Papajak, et al., *Science* **347**, 643-646 (2015).

Extreme resonance stabilization

Double resonance stabilization allowed first direct detection of QOOH

Identified by mass, spectrum, and kinetics



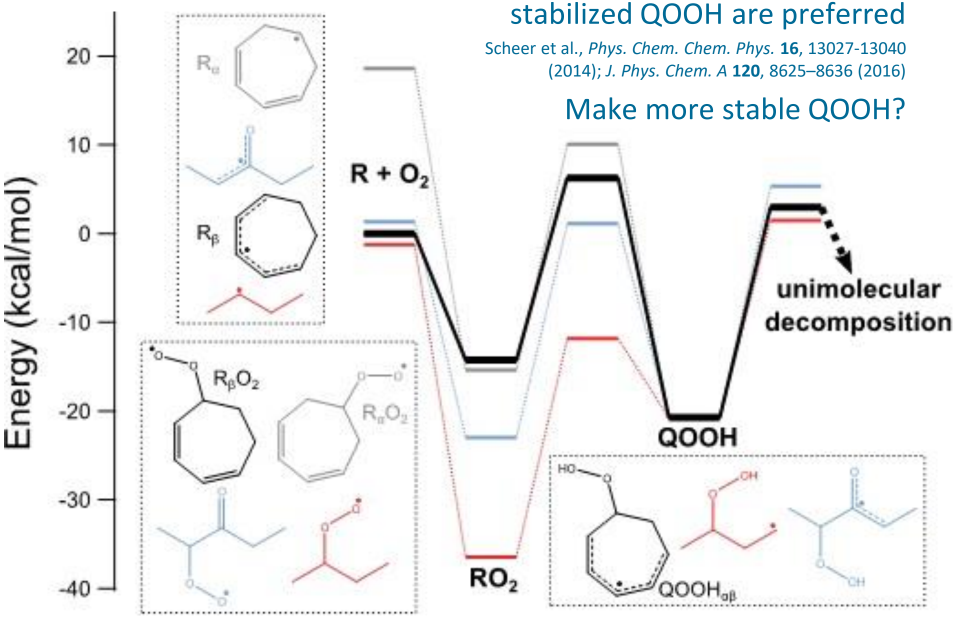
Resonance stabilization dramatically reduces the reactivity with O_2

$k_{QOOH+O2}$ = (2.9 ± 1.0) x 10^{-15} cm^3 s^{-1}
k_{R+O2} = (3.2 ± 0.5) x 10^{-16} cm^3 s^{-1}

Ketone oxidation – resonance stabilized QOOH are preferred

Scheer et al., *Phys. Chem. Chem. Phys.* **16**, 13027-13040 (2014); *J. Phys. Chem. A* **120**, 8625–8636 (2016)

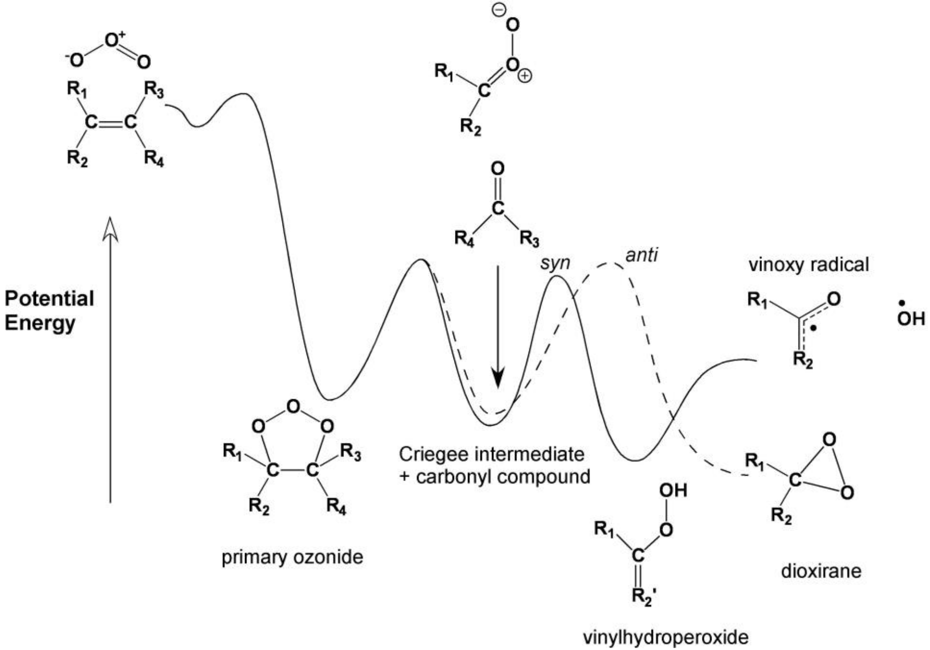
Make more stable QOOH?



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

For Criegee intermediates the strategy is direct synthesis

Verified by mass, kinetics, and spectrum

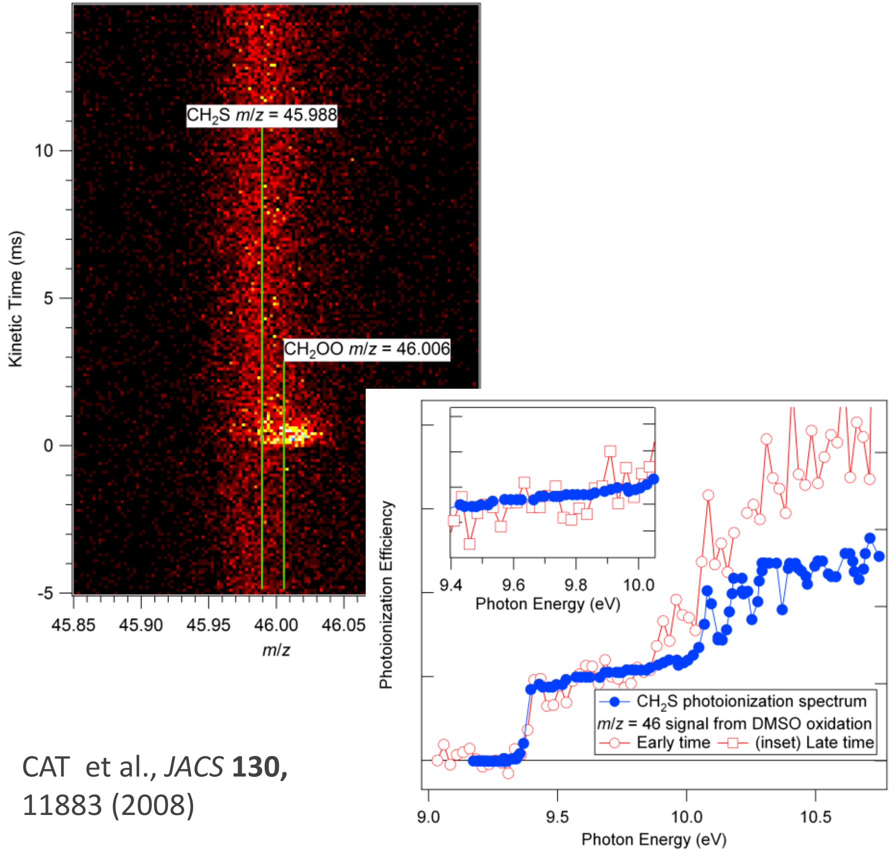


Ozonolysis is too slow and too energetic

For Criegee intermediates the strategy is direct synthesis

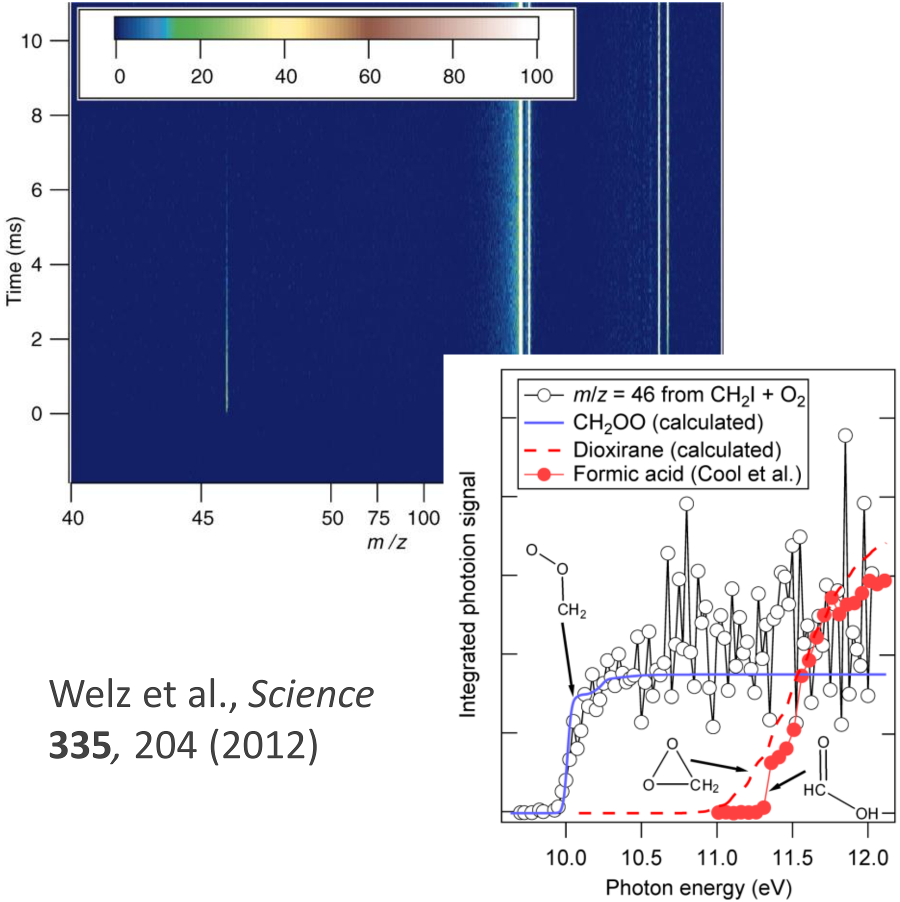
Verified by mass, kinetics, and spectrum

Reaction of CH_3SOCH_2 with O_2 makes CH_2OO



CAT et al., *JACS* **130,** 11883 (2008)

For Criegee intermediates the strategy is direct synthesis



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

Verified by mass, kinetics, and spectrum

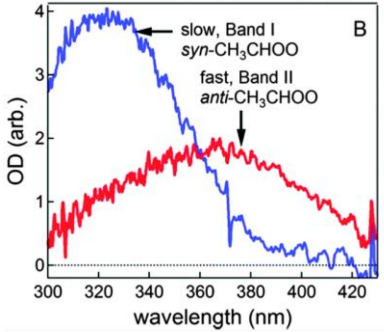
Reaction of CH_3SOCH_2 with O_2 makes CH_2OO

Reaction of gem-iodoalkyl radicals with O_2 makes lots of carbonyl oxides

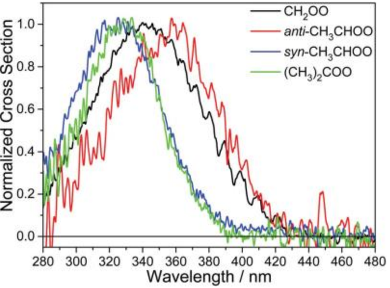
Now can measure carbonyl oxide reaction kinetics directly

Since discovery of the *gem*-iodoalkyl + O_2 synthesis:

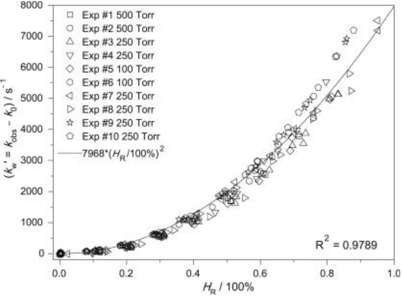
UV, infrared, and microwave spectra for carbonyl oxides have been measured



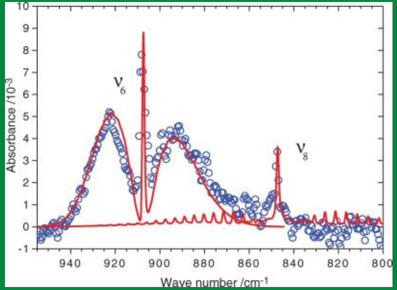
Sheps et al, *Phys Chem. Chem. Phys.* ***16***, 26701-26706 (2014)



Lin and Chao, *Chem. Soc. Rev.* 46, 7483 (2017)

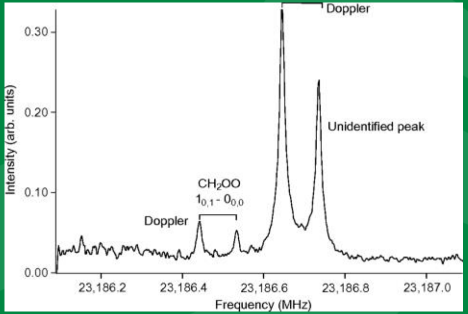


Chao et al, *Science.* ***347***, 751-754 (2014)

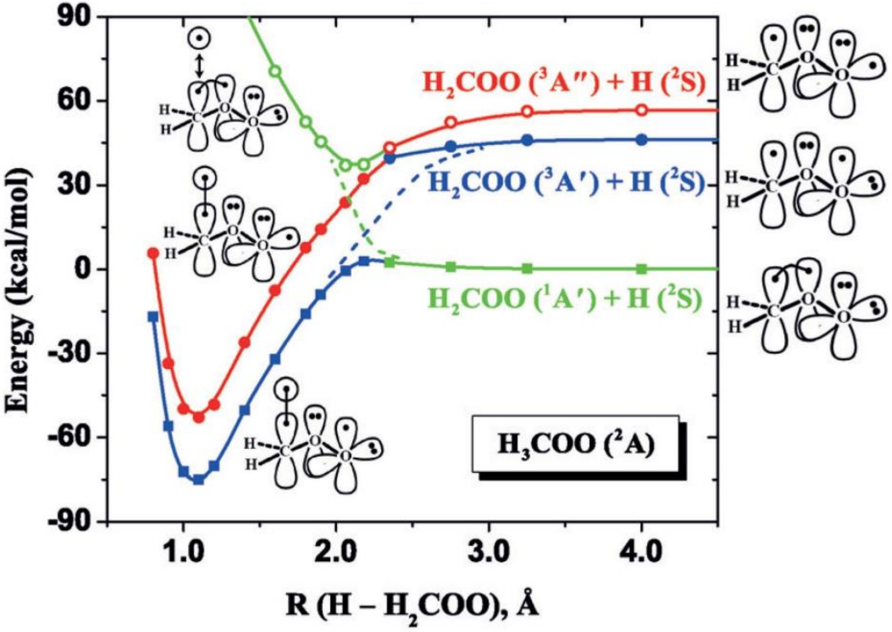


Yu-Te Su et al, *Science* **340**, 174-176 (2013)

Caroline C. Womack et al., *Science Advances* **1**, e1400105 (2015)



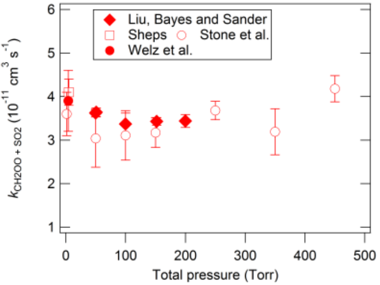
Many groups have begun to measure kinetics of carbonyl oxides: Boering (Cal); Lin (IAMS); Lester (Penn); Blitz/Seakins/Heard (Leeds); Bloss (Cambridge); Orr-Ewing (Bristol); Green (MIT)

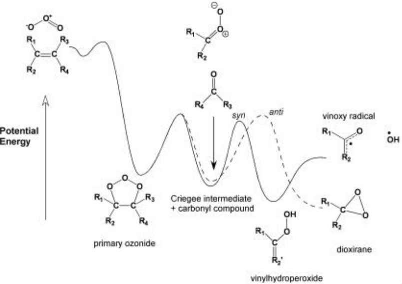


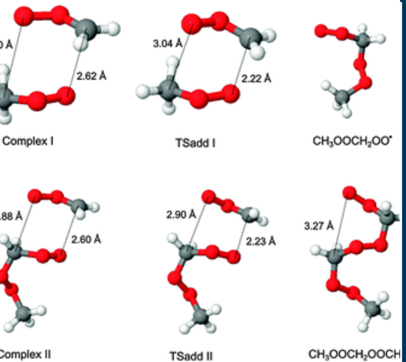
Miliordos and Xantheas, *Angew. Chem. Int. Ed.* **55**, 1015-1019, 2015

- Criegee intermediates have multireference electronic character
  - Ground state is dominantly the closed-shell singlet zwitterion

  - How should they react? … not like radicals!
  - CH_3OO + NO 7.5 × 10^{-12} $cm^3\ s^{-1}$
    Lightfoot et al., *Atmos. Environ. A* **26**, 1805 – 1961 (1992)
  - CH_2OO + NO < 6 × 10^{-14} cm^3 s-1
    Welz et al., *Science* **335**, 204 – 207 (2012)
  - What about reactions with closed-shell species?





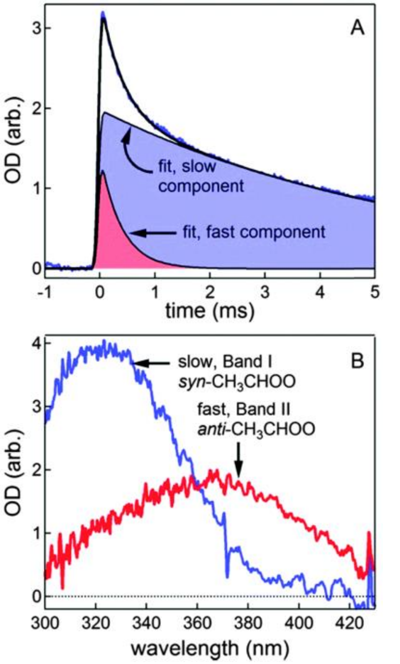


The chemistry of ozonolysis was largely worked out from solution phase – gas phase can be different!

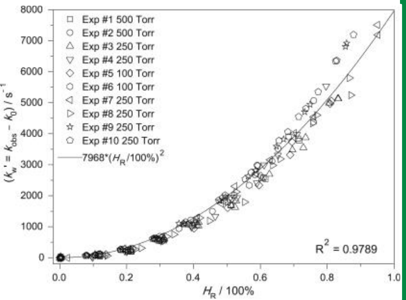
Criegee (1975) outlined four types of reactions that carbonyl oxides undergo: dimerization, reaction with carbonyls, isomerization, and reactions with “proton active substances”

Generalization (CAT, *Annu. Rev. Phys. Chem.* 2017):

- Reactions with other 1,3 bipoles
- Unimolecular reactions
- Cycloadditions
- Insertions
- Addition to radical species



Sheps et al, *Phys Chem. Chem. Phys.* ***16***, 26701-26706 (2014)



Chao et al, *Science.* ***347***, 751-754 (2014)

Most direct studies of Criegee kinetics look at disappearance of the carbonyl oxide

Nature of products can make a difference in troposphere

- Insertions
- Reactions with other 1,3 bipoles
- Unimolecular reactions
- Addition to radical species
- Cycloadditions

Proton active species – insertion

Acids react with carbonyl oxides at supercollisional rates (Welz et al., *Angew. Chem. Int. Ed.* 53, 4547-4550 (2014); Foreman et al., *Angew. Chem. Int. Ed.* 55, 10419-10422 (2016);Chhantyal-Pun et al., *Angew. Chem. Int. Ed.* 56, 9044-9047 (2017))

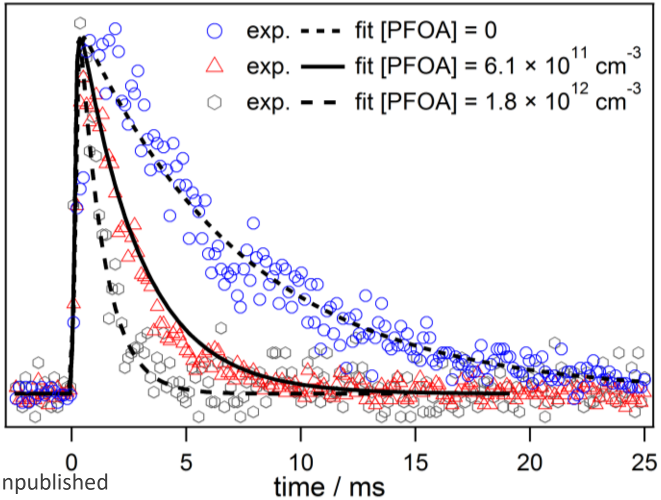
Carbonyl oxide reactions in solution: ROH>H_2O>CH_3CO_2H

In gas phase RCO_2H >> ROH, H_2O

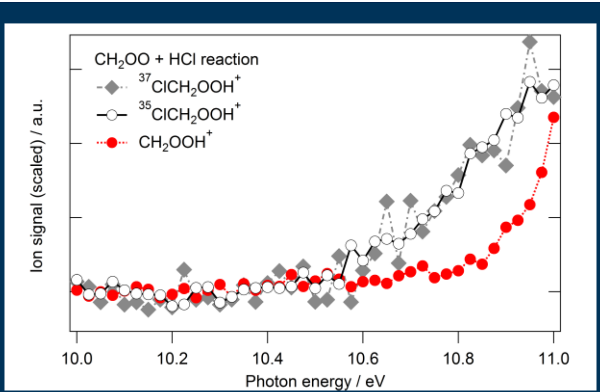
Fast reaction general for all acids

- PFOA reacts slowly with OH
- Reaction with CH_2OO is fast:
  - $(4.7 \pm 0.7) \times 10^{-10}$ cm^3 s^{-1}

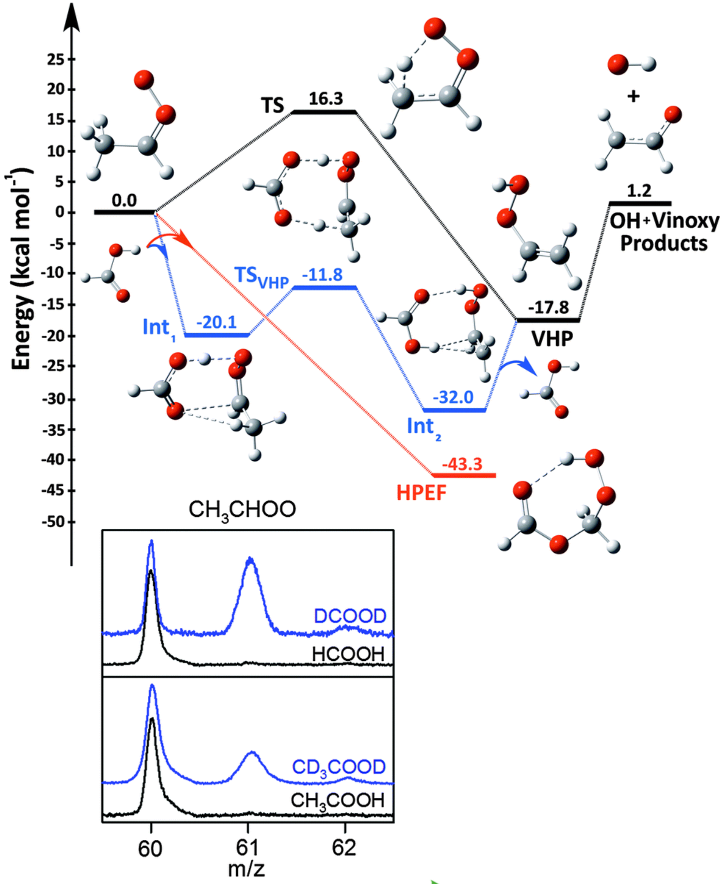
What are the products of reactions with acids?



Eskola et al., unpublished



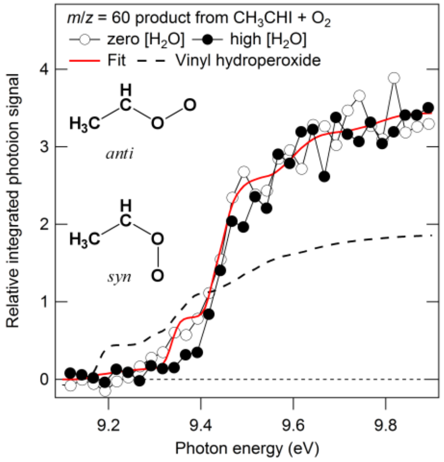
Caravan, Rotavera et al., unpublished

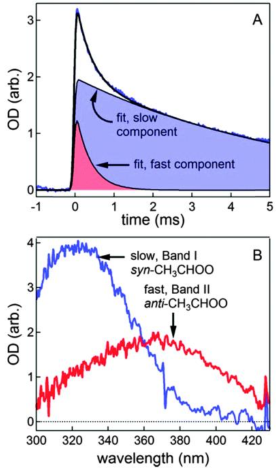


- Reactions with acids appear to form hydroperoxyesters
  - Adduct mass observed
  - Dissociative ionization to protonated carbonyl oxides
- There are other possibilities
  - Acid-assisted tautomerization

    (Kumar et al., Phys. Chem. Chem. Phys., 2014, 16, 22968-22973; Liu et al., Phys. Chem. Chem. Phys., 2015, 17, 20490-20494)

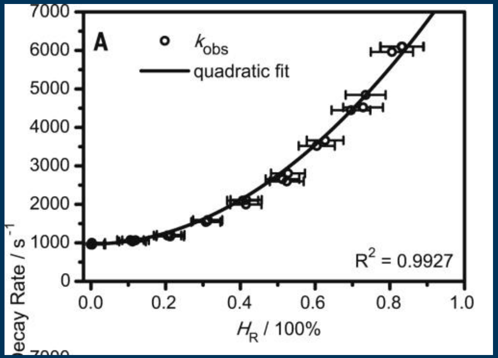
- Most common proton active species – H_2O
- Differences in reactivity among carbonyl oxides:
  - $(CH_3)_2COO < 1.5 \times 10^{-16}$ (Huang et al., *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10857–10862 (2015))
  - CH_2OO $(3.2 \pm 1.2) \times 10^{-16}$ (Berndt et al., *Phys. Chem. Chem. Phys.* **17**, 19862–19873 (2015))
  - *anti*-CH_3CHOO $(2.3 \pm 2.1) \times 10^{-14}$ (Huang et al., *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10857–10862 (2015))
- H_2O monomer reactions have conformer dependence – *syn*-CH_3CHOO unmeasurably slow
- H_2O dimer reaction is the dominant removal mechanism for tropospheric CH_2OO





$CH_2OO + (H_2O)_2$ ~ 5×10^{-14} cm^3 s^{-1}

Chao et al, *Science* **347**, 751-754 (2014); Lewis et al., *Phys. Chem. Chem. Phys.* **17**, 4859–4863 (2015); Smith et al., *J. Phys. Chem. Lett.* **6**, 2708–2713 (2015)



Chao et al, *Science.* ***347***, 751-754 (2014)

Does reaction of CH_2OO and water dimer make formic acid?

Water monomer reaction makes hydroperoxymethanol (hydroxymethyl hydroperoxide)

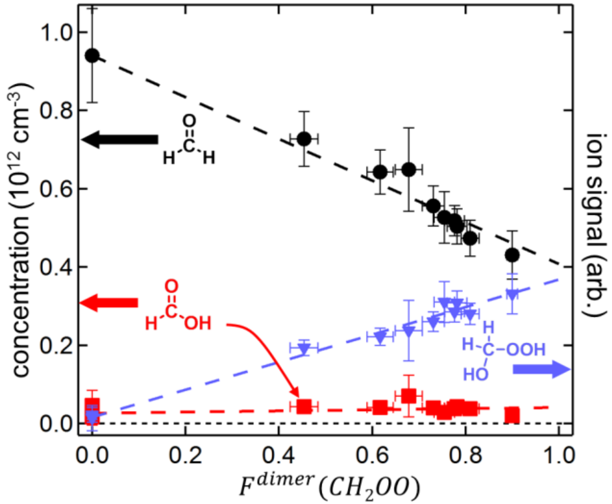
Suggestion that reaction with dimer makes ~ 50% HCOOH (Nguyen et al., *Phys. Chem. Chem. Phys.* **18**, 10241-10254 (2016))

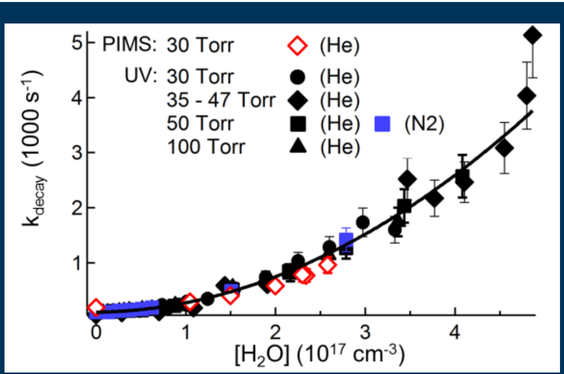
Can confirm rate coefficient with UV absorption, photoionization

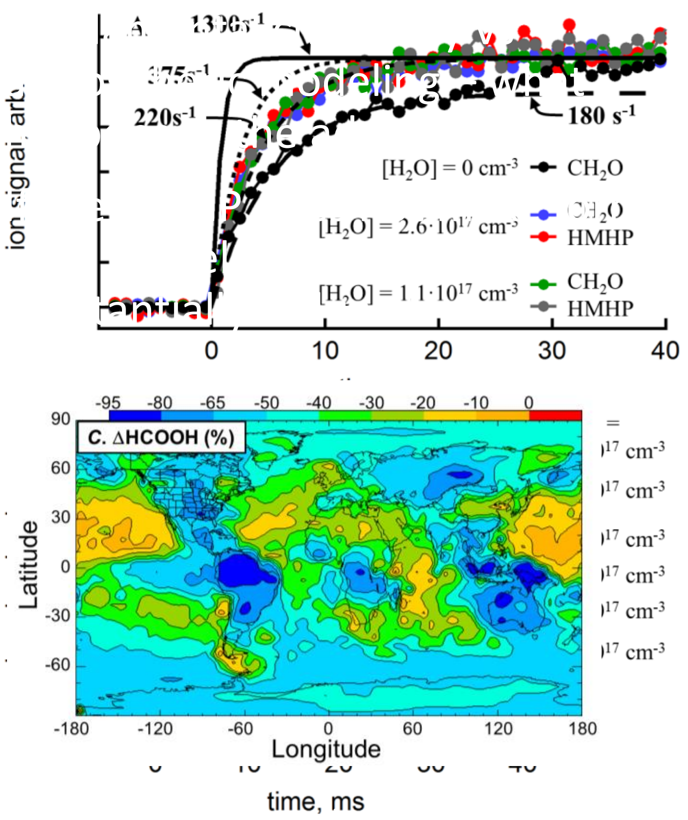
MPIMS measures all products

Sheps et al., *Phys. Chem. Chem. Phys.*, **19**, 21970-21979 (2017)

Lenny Sheps

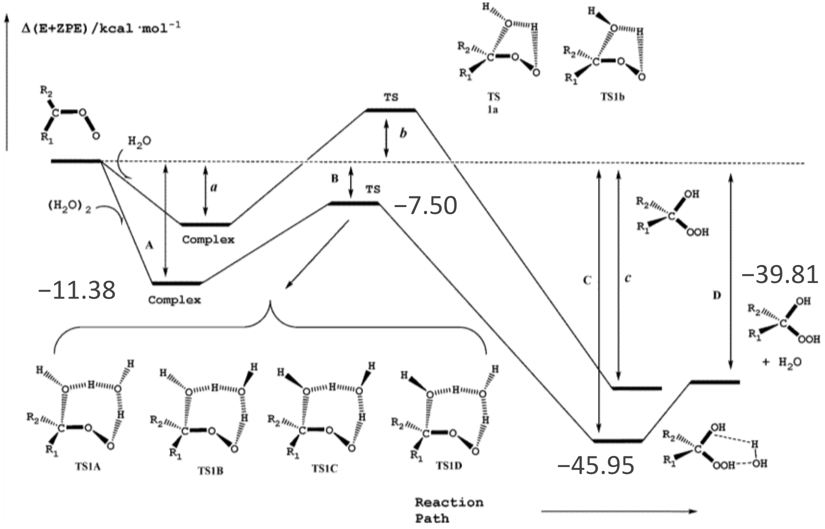






var Khan

More experiments to do



Calculation of $CH_2OO + (H_2O)_2$ reaction suggests entrance complex that dissociates to HMHP and H_2O

Anglada and Solé *Phys. Chem. Chem. Phys.* **18**, 17698-17712 (2016)

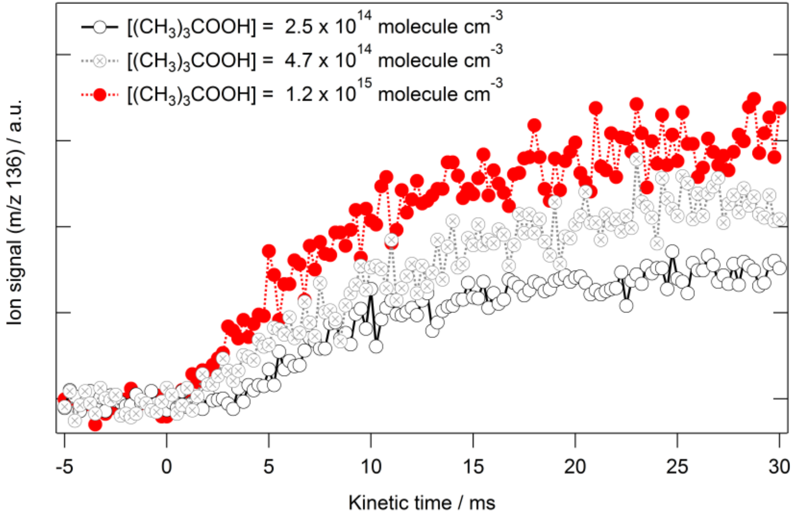
Do other proton-active species in the gas phase also insert?

ROOH – CH_2OO reaction with $(CH_3)_3COOH$ makes adduct

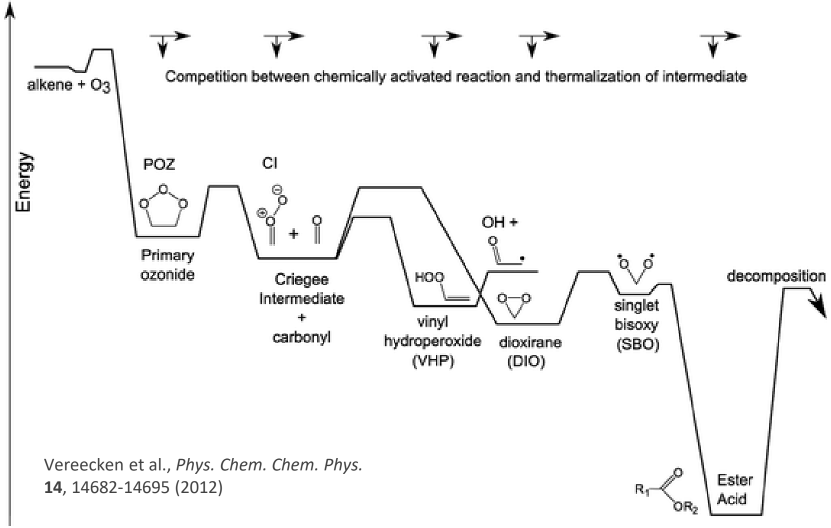
ROH? – reactions with CH_3OH insert in solution phase

Acetone oxide + methanol

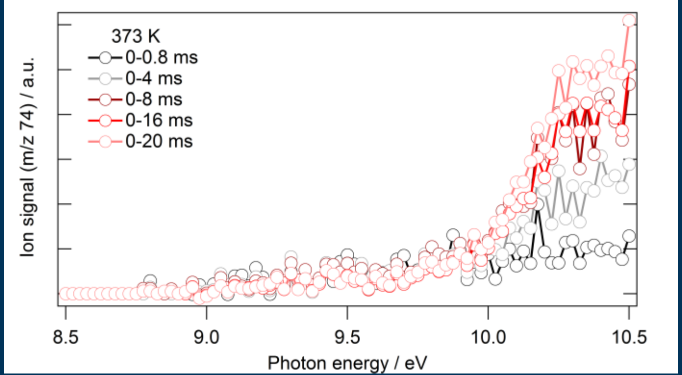
- No observed adduct mass
- Product with CD_3OH is acetone



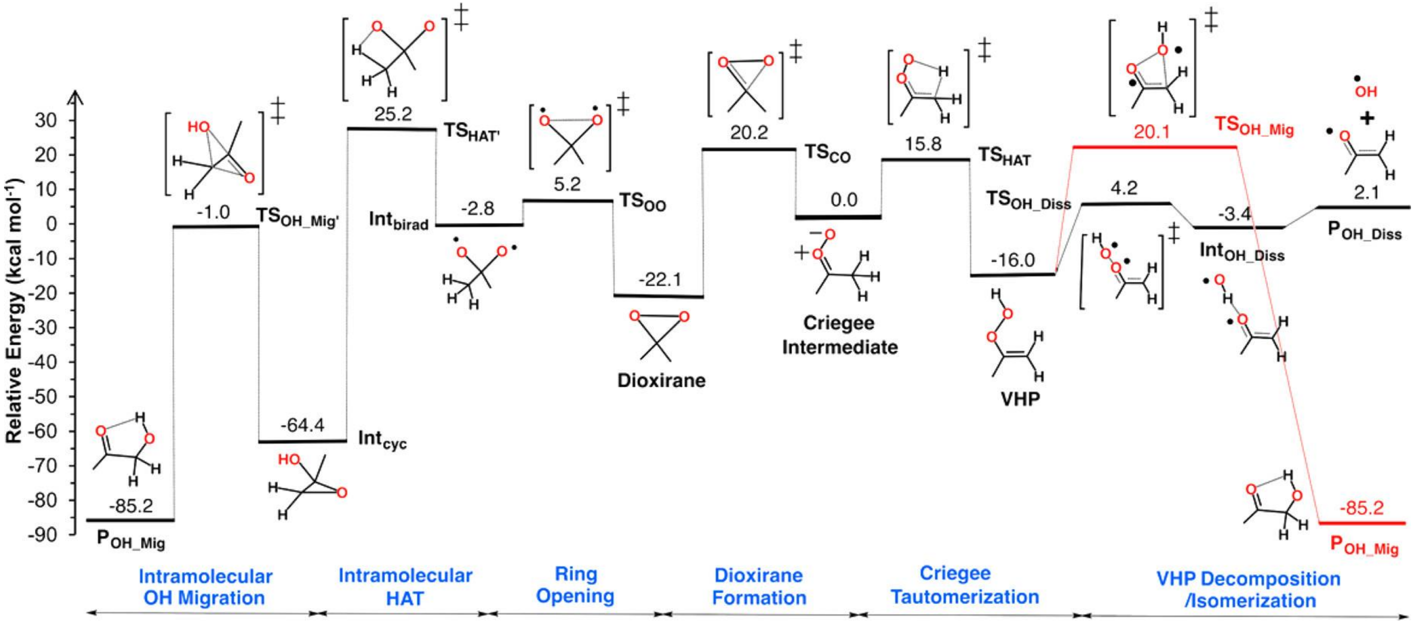
Caravan, Eskola et al., unpublished



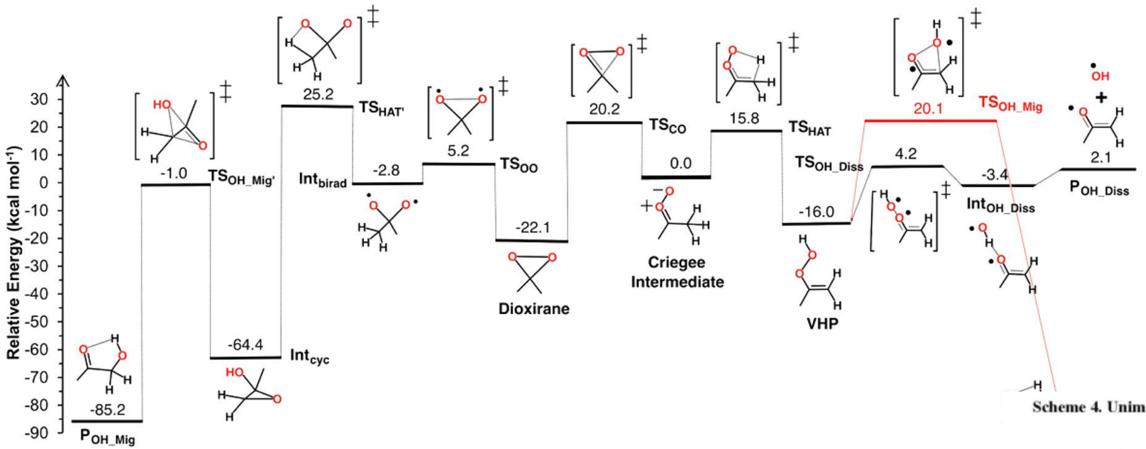
Vereecken et al., *Phys. Chem. Chem. Phys.* **14**, 14682-14695 (2012)



- Isomerization has two basic pathways – dioxirane and vinyl hydroperoxide
- Is it that simple?
- $(CH_3)_2COO$ isomerizes to hydroxyacetone (CAT et al, J. Phys. Chem. A **121** 16–23 (2017))
- Temperature dependence confirms first-order gas phase reaction (Caravan et al., unpublished)
- Observed in solution long ago (P. R. Story and J R. Burgess, *J. Am. Chem. Soc.* **89**, 5726 (1967); **90**, 1094 (1968))
- Proposed to start from VHP

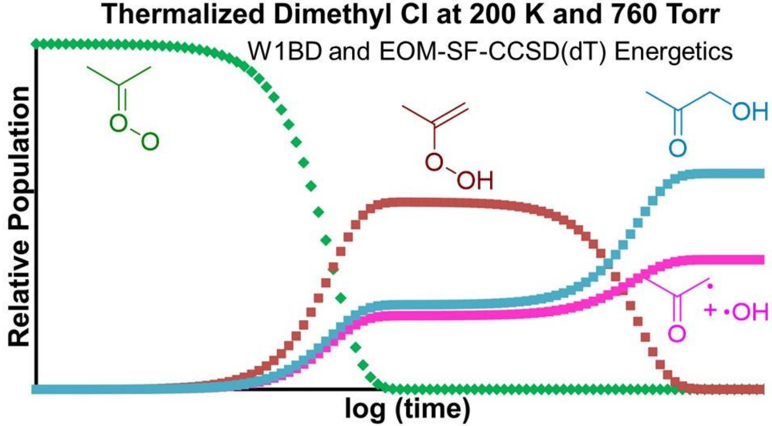


(Ward Thompson, in *J. Phys. Chem. A* **121** 16–23 (2017))

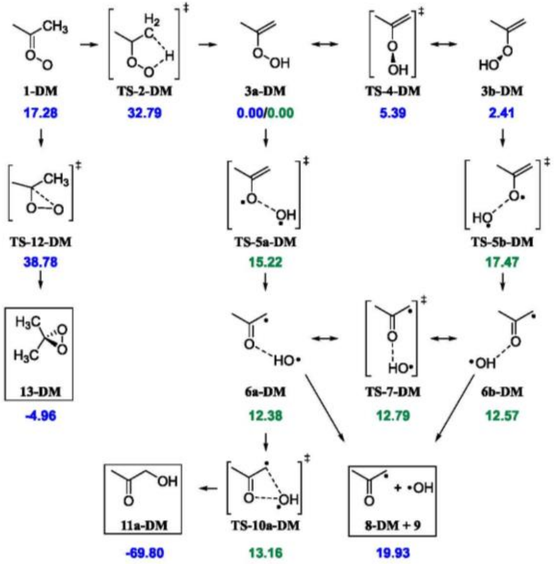


Kuwata et al. recently calculated a roaming style pathway through the vinyl hydroperoxide (*J. Phys. Chem. A* **just accepted DOI:** 10.1021/acs.jpca.8b00287 (2018)) that obviates the high transition state

They also predicted product branching for the acetone oxide decomposition.



Scheme 4. Unimolecular Reactivity of the Dimethyl Criegee Intermediate[a]



Reactions with radicals?

Look at NO_2 – how does this reaction proceed?

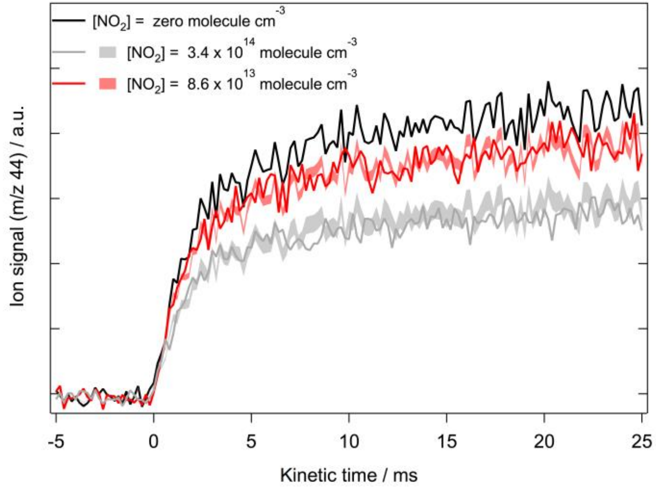
Could be source of NO_3?

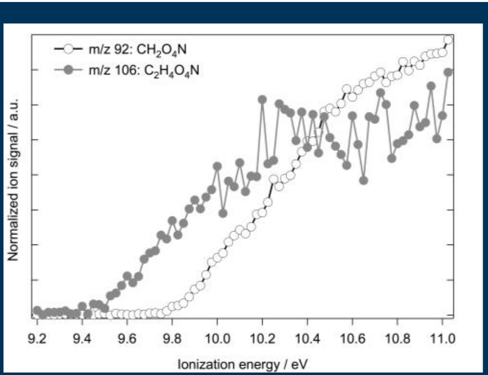
- No NO_3 observed
- See signal at mass of adduct
- See decrease in carbonyl
- Upper limit of 30% NO_3

May limit effect of carbonyl oxides on NO_3 concentrations

Caravan et al., *Faraday Discuss.* **200**, 313-330 (2017)

CH_3CHOO
$+ NO_2$

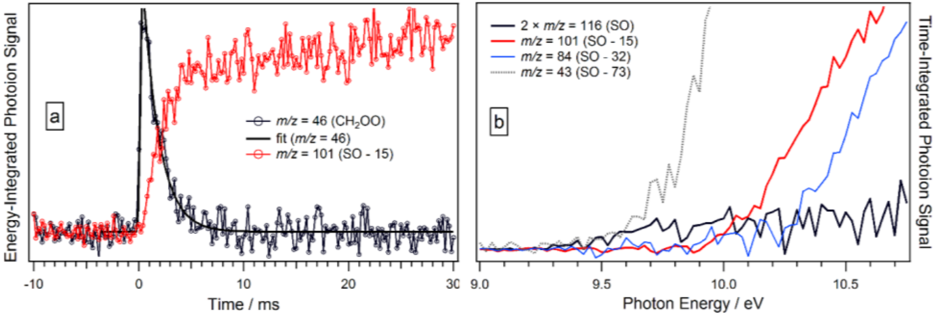




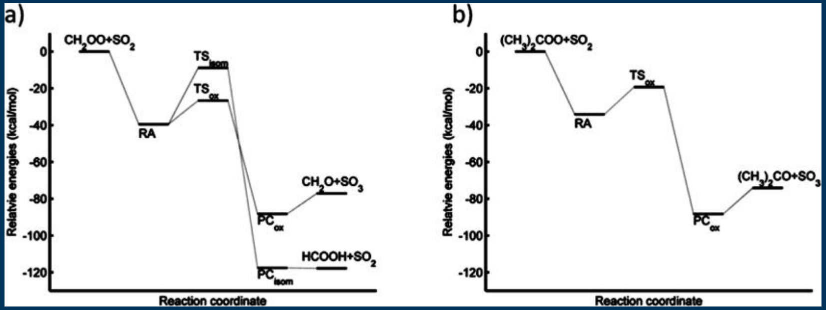
Cycloaddition – reaction with carbonyls is one of the three steps in the Criegee mechanism

Can directly detect secondary ozonide products

Carbonyl oxides can transfer O atom, e.g., to SO_2 – but are these reactions mediated by cycloaddition?



CH_2OO + MVK: Eskola et al., unpublished

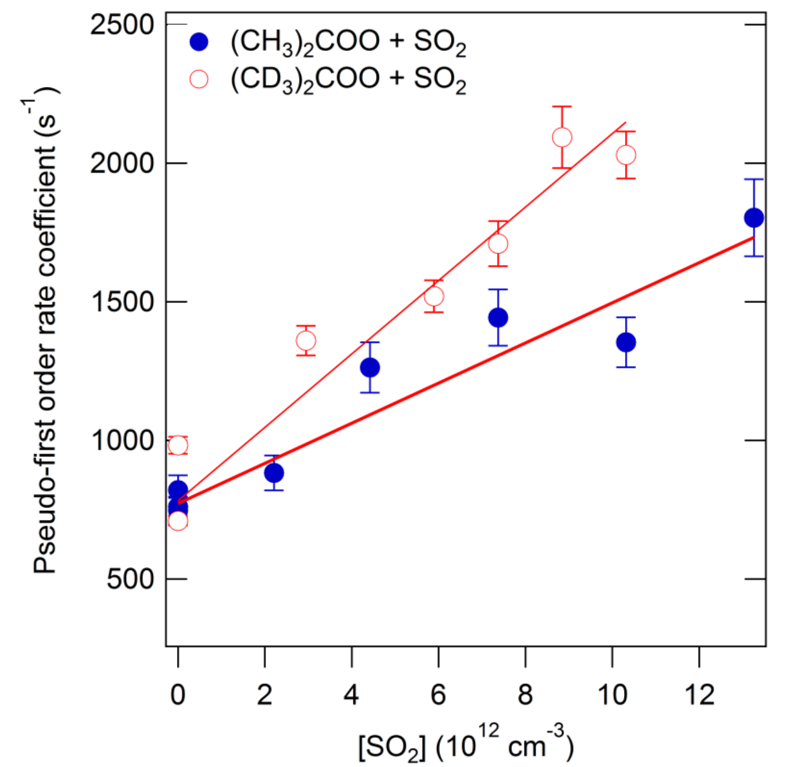


Kurtén et al., *J. Phys. Chem. A* **115**, 8669–8681 (2011)

SO_3 has been directly observed from Criegee intermediate reactions with SO_2 -- but other pathways are possible

Pressure dependence and inverse kinetic isotope effect is observed in reaction of acetone oxide with SO_2 (Chhantyal-Pun et al., *J. Phys. Chem. A* **121** 4–15 (2017); Huang et al., *Proc. Nat. Acad. Sci. USA* **112,** 10857–10862 (2015))

All direct rate coefficient measurements so far have been for total carbonyl oxide removal



- Hydrocarbon structure and resonance stabilization can dramatically affect autoxidation processes

- Importance of carbonyl oxide reactions to the atmosphere depends on fate of adducts

Do these results actually make a difference in complex chemical models?

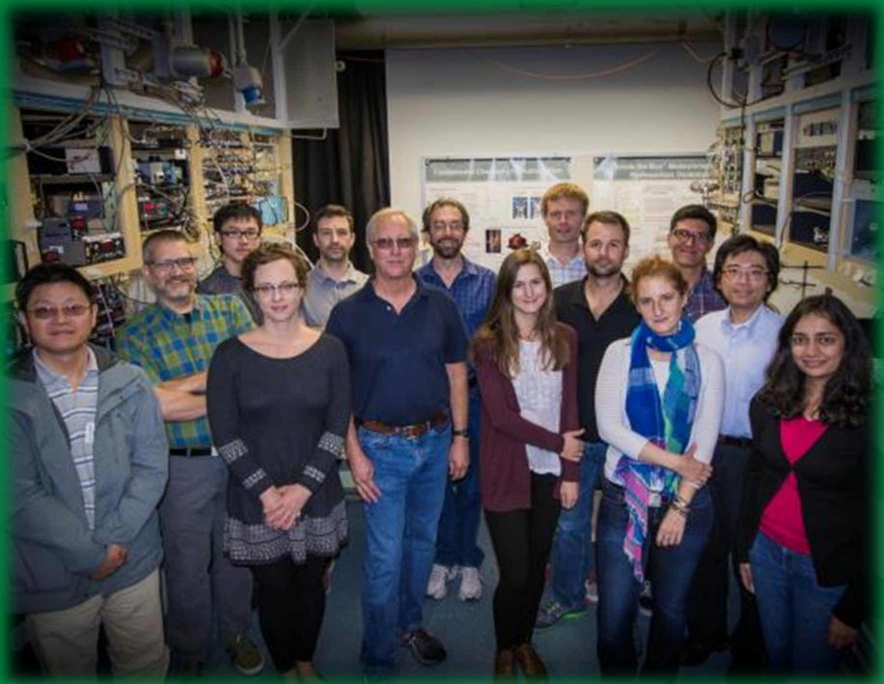
What does it mean to make a difference?

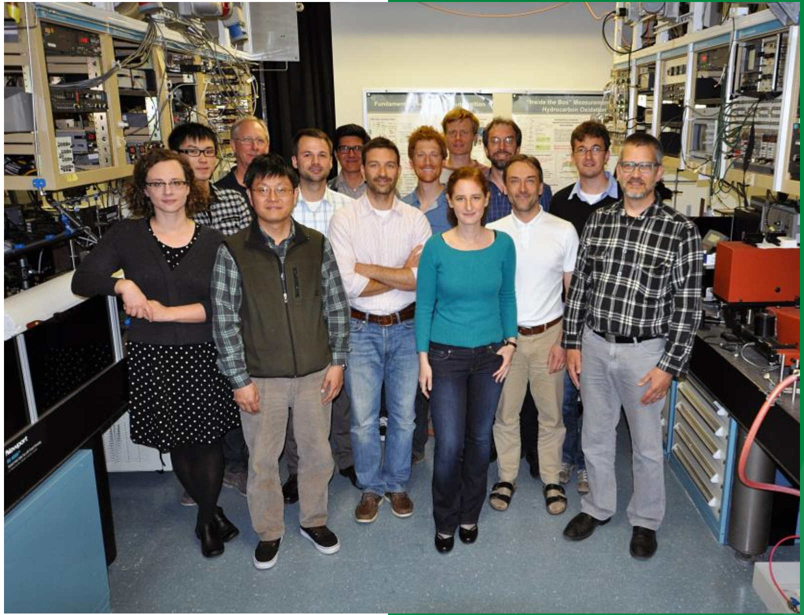
- Models are changed (people use the results)
- New details are revealed as important
- Predictions get better?

Kinetics research in CRF Combustion Chemistry Department

Rebecca Caravan
Arkke Eskola
Brandon Rotavera
John Savee
Kai Moshammer

David Osborn
Howard Johnsen
Lenny Sheps
Nils Hansen
Ahren Jasper
Kendrew Au





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Adam Scheer
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- This material is based on work supported by the Office of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, United States Department of Energy.
- Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Carl Percival (Manchester / JPL); Dudley Shallcross, Anwar Khan, Rabi Chhantyal-Pun, Andrew Orr-Ewing (Bristol); Asan Bacak (Manchester); Marsha Lester, Fang Liu (Penn); Christa Fittschen (Lille); Jim Lin, Wen Chao (IAMS); Ward Thompson (Kansas); Manoj Kumar (Nebraska); John Dyke, Ed Lee (Southampton); Stan Sander (JPL); Mitchio Okumura (Caltech); Zhandong Wang (KAUST); Steve Leone (Berkeley)