SAND2019-9986PE

Fundamental reactions in accidental and intentional oxidation of hydrocarbons

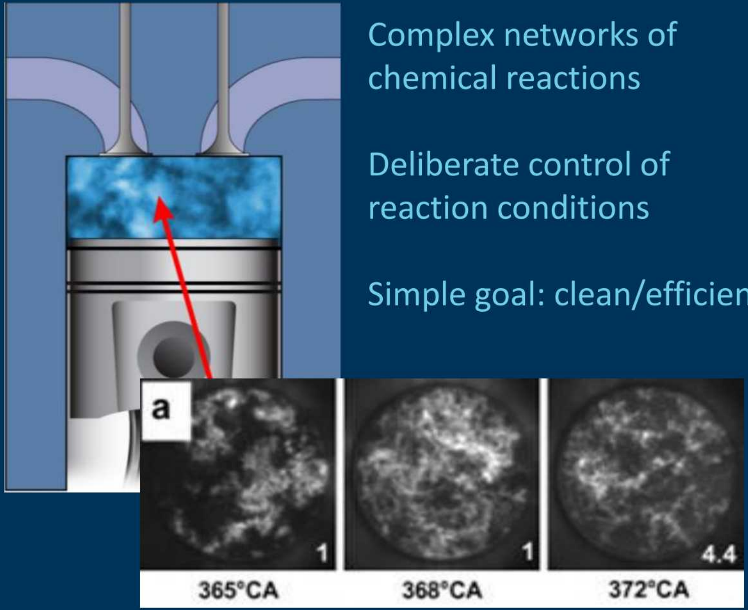
Craig A. Taatjes

Combustion Research Facility, Sandia National Laboratories, Livermore CA

University of Colorado February 16, 2018

Comparing different (but related) chemical systems

Autoignition chemistry



John Dec, Sandia

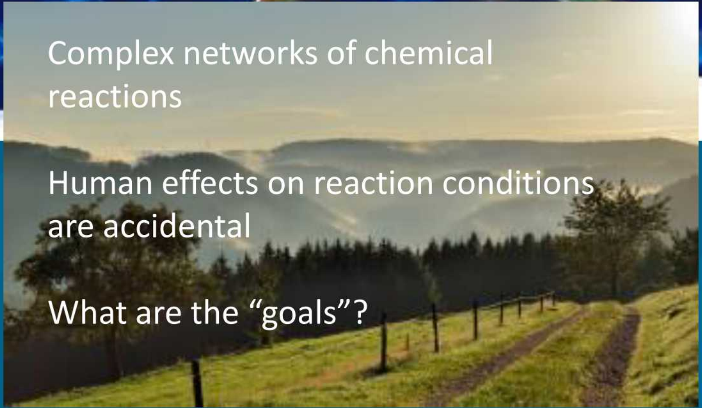
Complex networks of chemical reactions

Deliberate control of reaction conditions

Simple goal: clean/efficient

Tropospheric oxidation

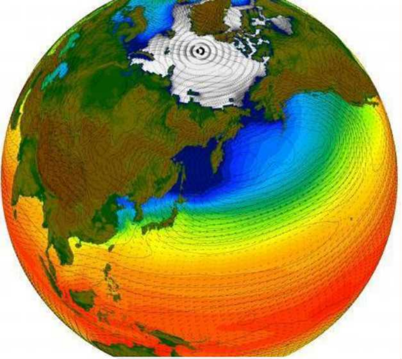
William Putman, NASA/Goddard

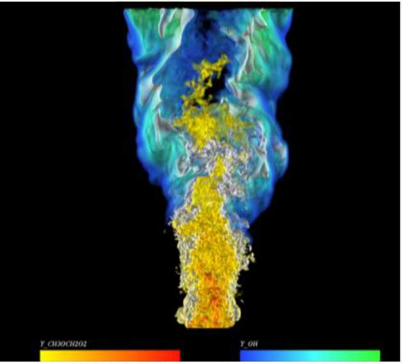


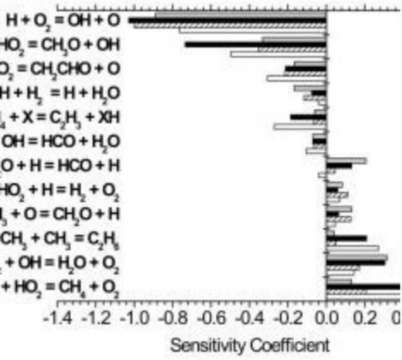
Complex networks of chemical reactions

Human effects on reaction conditions are accidental

What are the “goals”?







How do we handle complex networks of reactions?

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

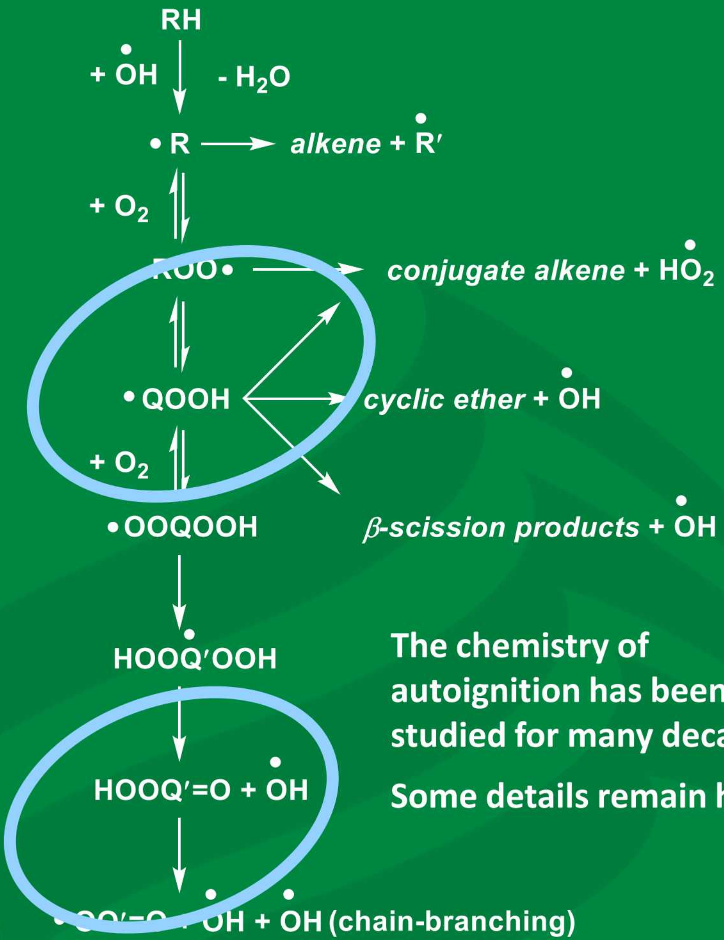
How can kineticists

- Choose reactions that make a difference
- Choose reactions that give fundamental insight

Look at reactions that have multiple possible channels that have different impacts in the complex system

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

In autoignition chemistry it is easy to find reactions that fit these criteria


RH

+ •OH, - H_2O

•R → alkene + R′•

+ O_2

ROO• → conjugate alkene + HO_2•

•QOOH → cyclic ether + •OH

→ *β-scission products* + •OH

+ O_2

•OOQOOH

HOOQ′•OOH

HOOQ′=O + •OH

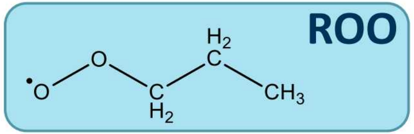
•OQ′=O + •OH + •OH (chain-branching)

The chemistry of autoignition has been studied for many decades –

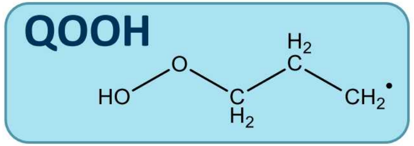
Some details remain hidden

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

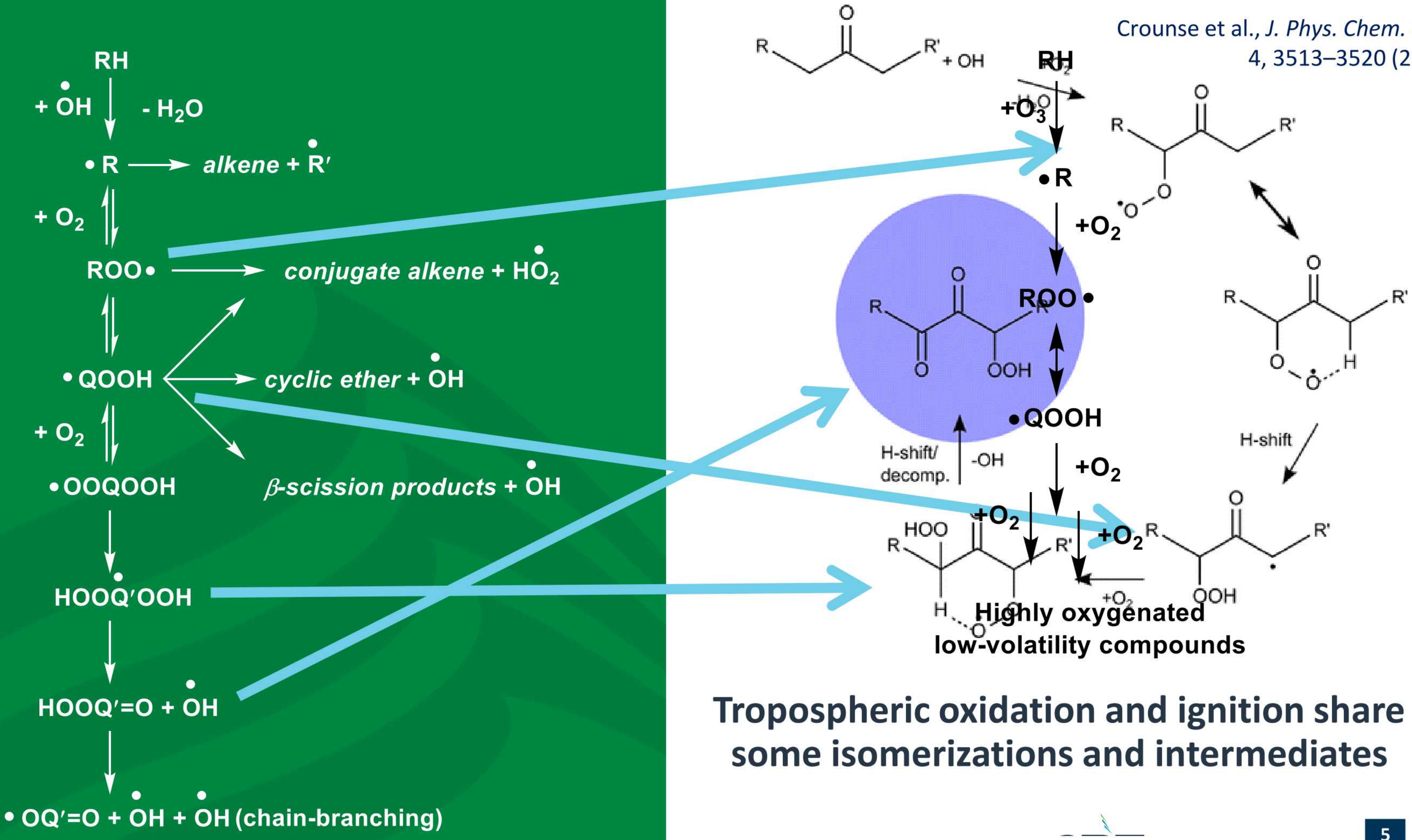
ROO



QOOH



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


RH

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

$\cdot R \rightarrow$ *alkene* $+ \dot{R}'$

$+ O_2$

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

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

$+ O_2$ *β-scission products* $+ \dot{O}H$

$\cdot OOQOOH$

$HOO\dot{Q}'OOH$

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

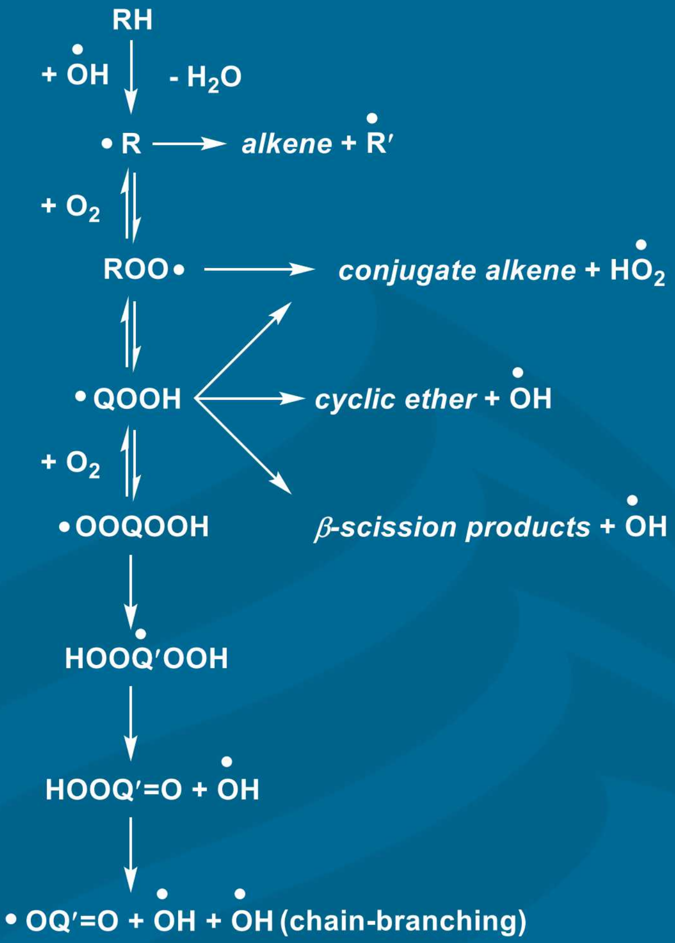
$\cdot OQ'{=}O + \dot{O}H + \dot{O}H$ (chain-branching)

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

Highly oxygenated
low-volatility compounds

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

Tropospheric oxidation and ignition share some isomerizations and intermediates



RH

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

• R → alkene + $\dot{\mathrm{R}}'$

+ O_2

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

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

+ O_2

• OOQOOH   *β-scission products* + $\dot{\mathrm{O}}\mathrm{H}$

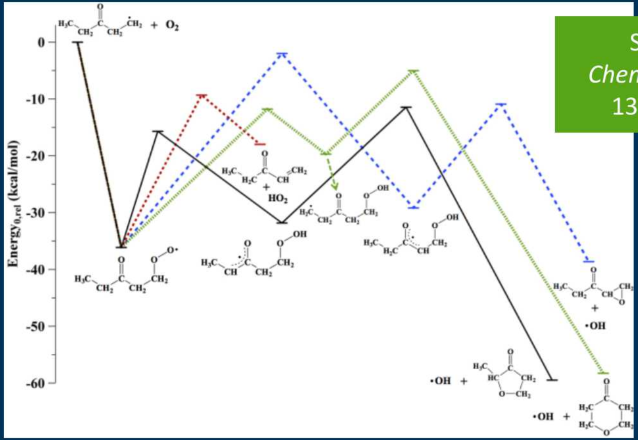
$\mathrm{HOO\dot{Q}'OOH}$

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

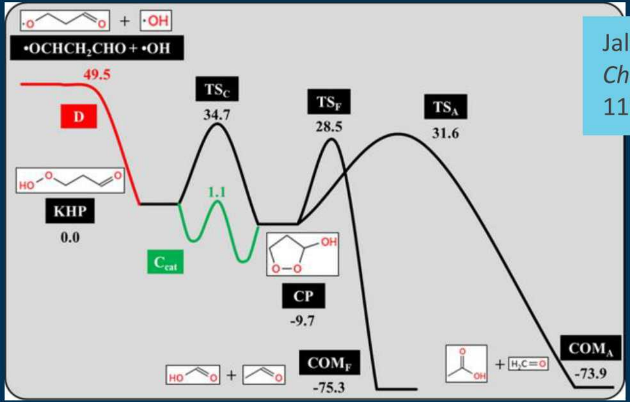
• OQ′=O + $\dot{\mathrm{O}}\mathrm{H}$ + $\dot{\mathrm{O}}\mathrm{H}$ (chain-branching)

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

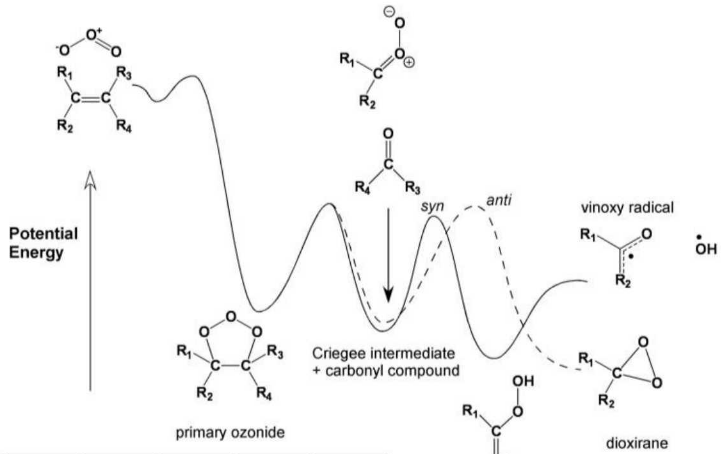
Reactions proceed on surfaces with multiple wells – Isomerization leads to different products

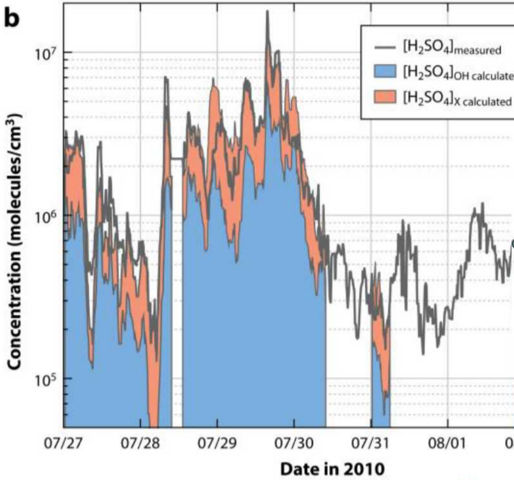


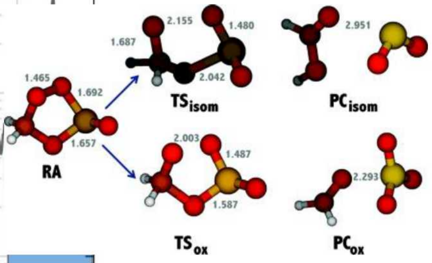
Scheer et al., *Phys. Chem. Chem. Phys.* **16**, 13027-13040 (2014)



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







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

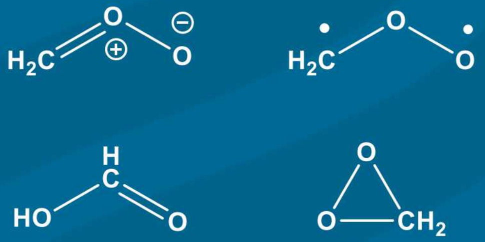
Mauldin et al., *Nature* **488**, 193–196 (2012)

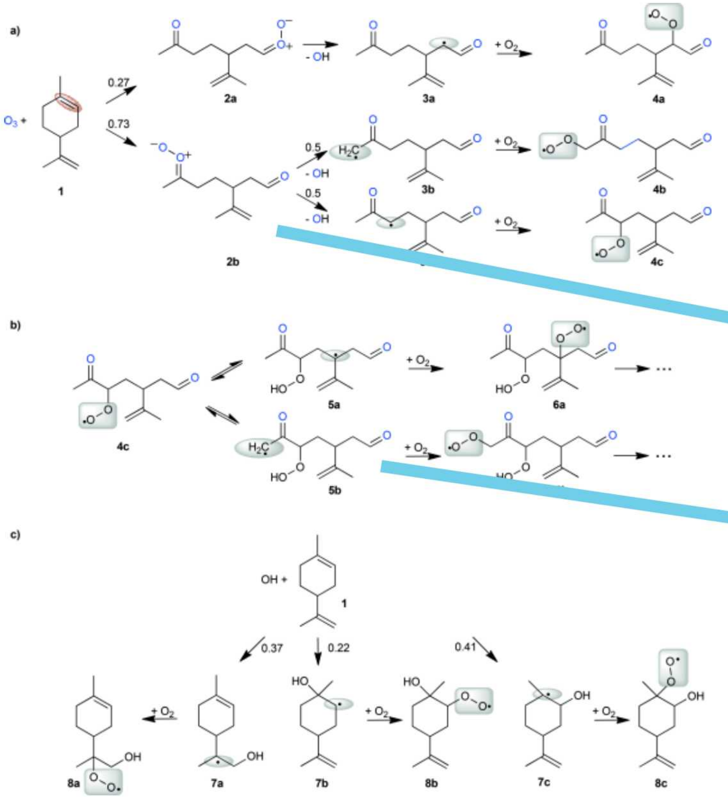
Kinetic models for tropospheric oxidation require knowing reactions of other intermediates

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





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

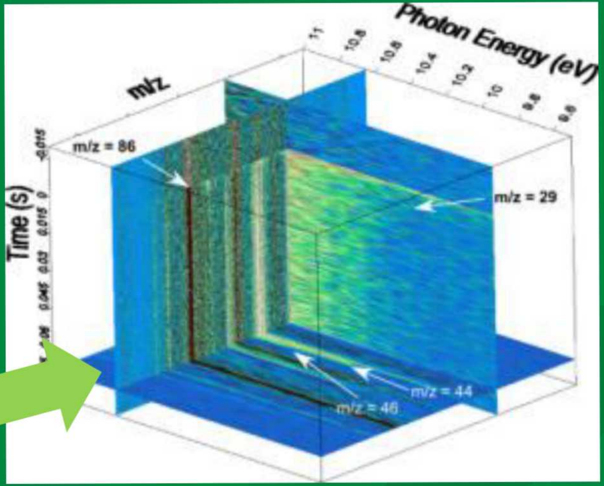
- Specific investigations target individual reaction types
- Physical understanding allows rigorous generalization

Ozonolysis – can we focus on individual carbonyl oxide channels?

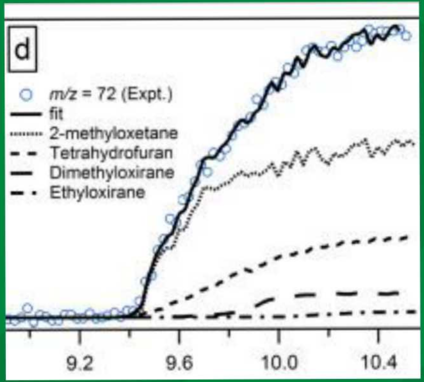
Peroxy radical chemistry – can we isolate specific transformations?

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

Synchrotron photoionization mass spectrometry can detect and characterize these intermediates

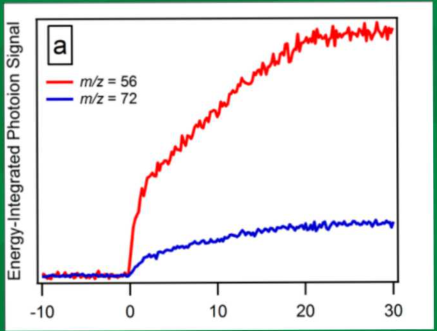


David Osborn



Isomer-Resolved Species Identification

Time-Dependent Chemical Kinetics



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

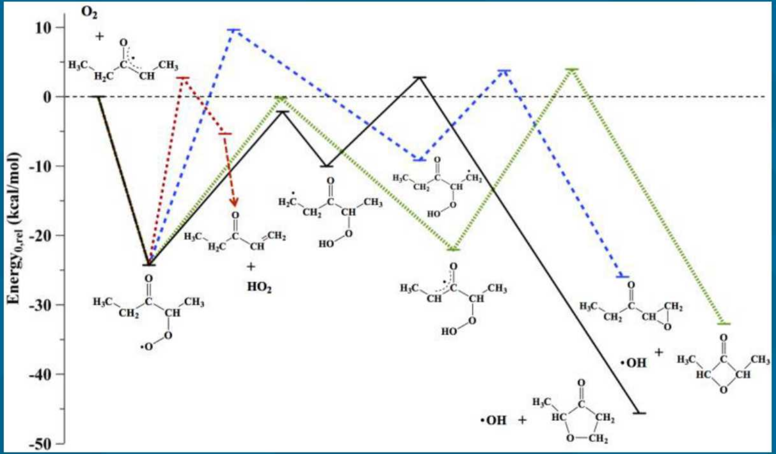
- In the troposphere or in bulk oxidation reactions, these intermediates are difficult to isolate
- They are formed in slow processes like ozonolysis or ROO isomerization, then react relatively rapidly

- Need strategies to form the intermediates in a controlled way
- Pulsed laser photolytic initiation of oxidation

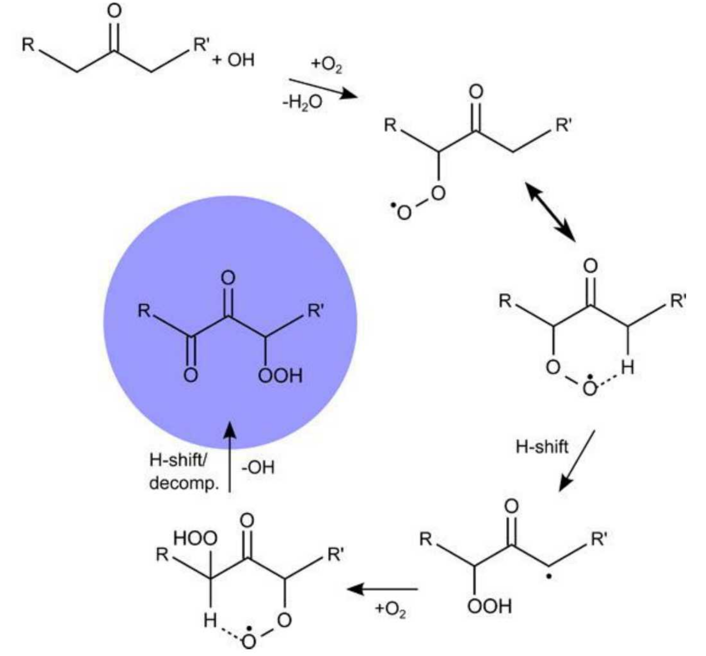
CRF

Isomeric product branching can show how molecular structure affects QOOH

- Diethyl ketone prototype for tropospheric autoxidation
- Ketone oxidation has possibility of vinoxylic resonance stabilization
- Resonance-stabilized radicals less reactive with O_2



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



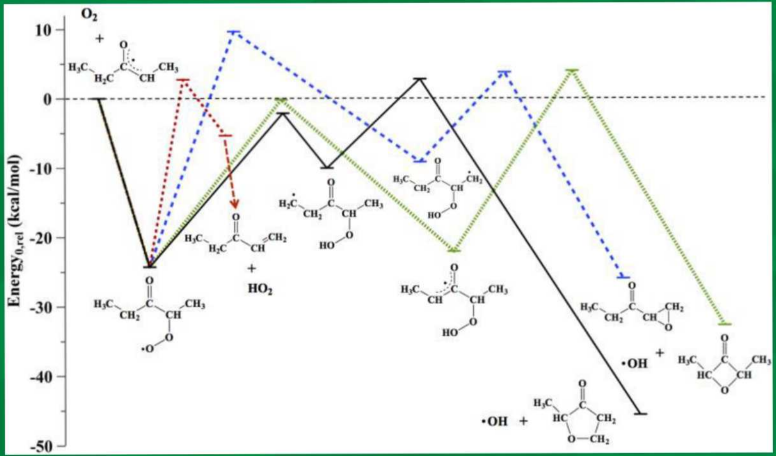
(Crounse et al. *J. Phys. Chem. Lett.* 4, 3513-3520 (2013))

Isomeric product branching can show how molecular structure affects QOOH

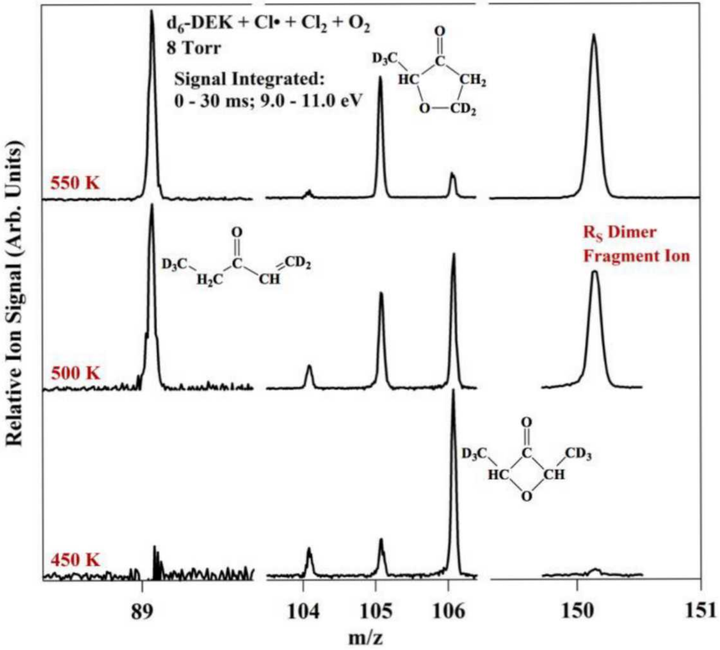
Diethyl ketone prototype for tropospheric autoxidation

Ketone oxidation has possibility of vinoxylic resonance stabilization

Resonance-stabilized radicals less reactive with O_2



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



At low T observe vinoxylic radical R_s oxidation product, no R_s dimer

At higher T see primary radical R_P oxidation product, see R_s dimer

Isomeric product branching can show how molecular structure affects QOOH

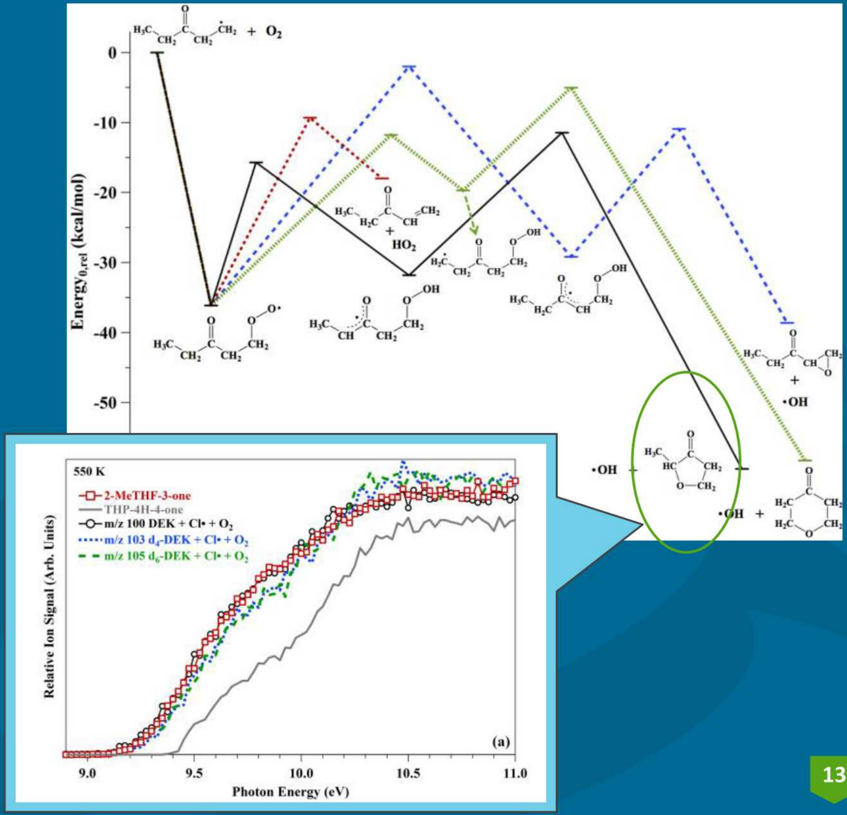
Diethyl ketone prototype for tropospheric autoxidation

Ketone oxidation has possibility of vinoxylic resonance stabilization

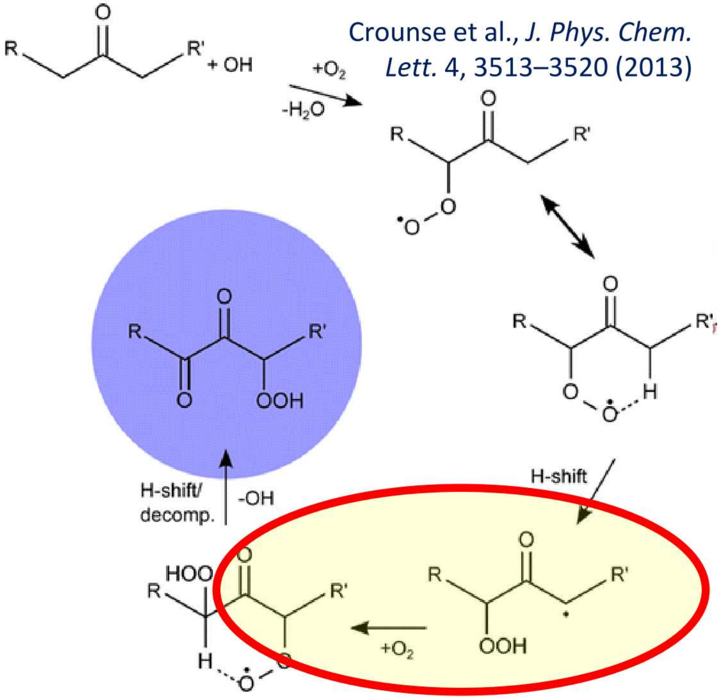
Resonance-stabilized radicals less reactive with O_2

Resonance stabilization may favor particular QOOH pathway

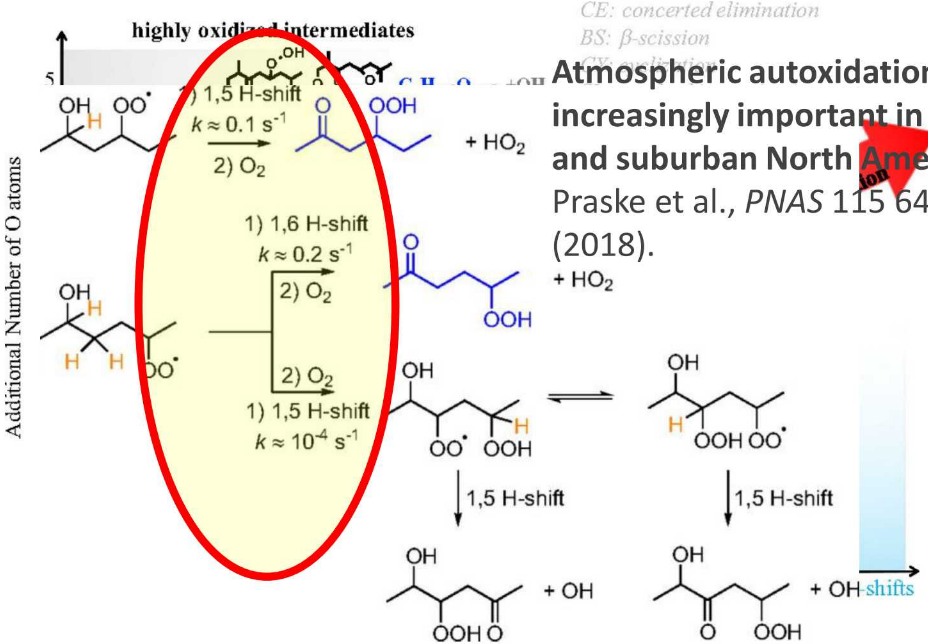
Substitution changes oxidation chemistry – for ignition or for the troposphere



Additions of QOOH to O_2 are important to complex oxidation submechanisms



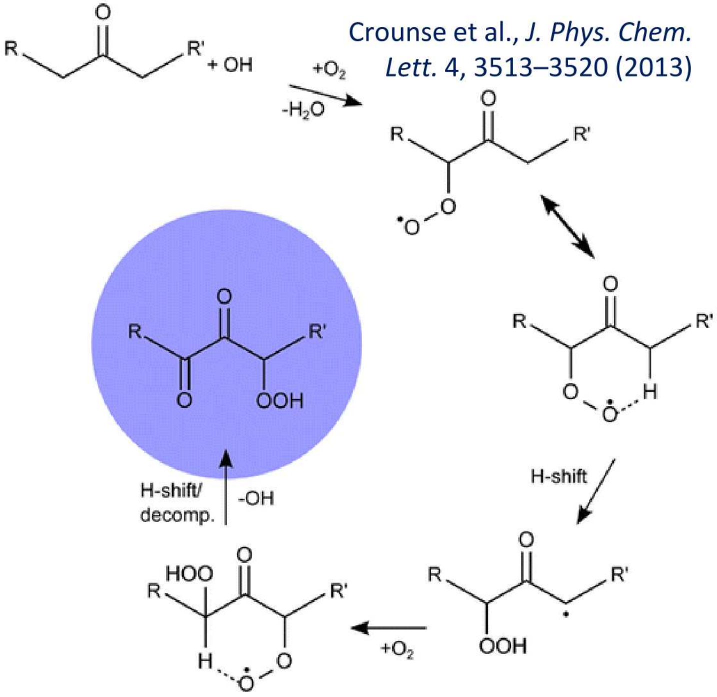
Crounse et al., *J. Phys. Chem. Lett.* 4, 3513–3520 (2013)



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

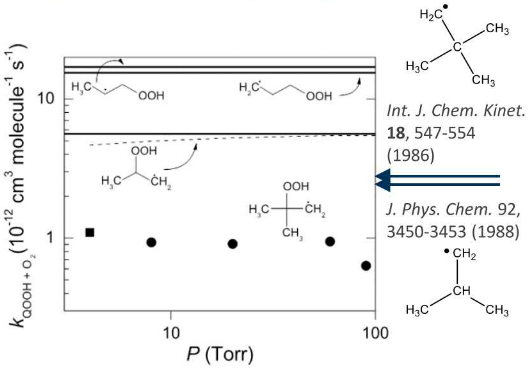
Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds
Wang et al., PNAS 2017 doi: 10.1073/pnas.1707564114

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



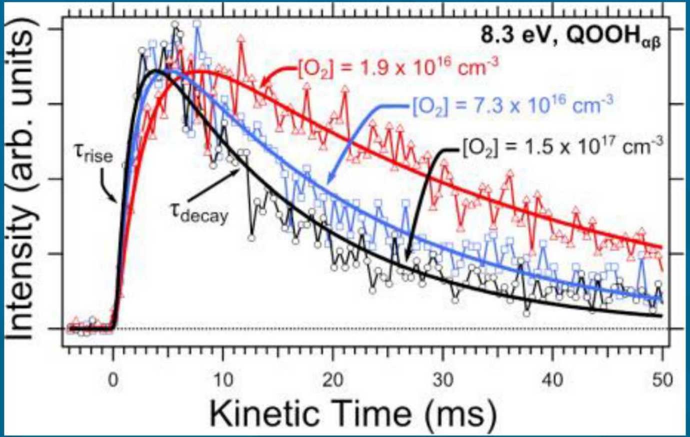
Int. J. Chem. Kinet. **18**, 547-554 (1986)

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

Extreme resonance stabilization

Double resonance stabilization allowed first direct detection of QOOH – photolytic Cl atoms initiate reaction of cycloheptadiene

QOOH verified by mass, spectrum, and kinetics



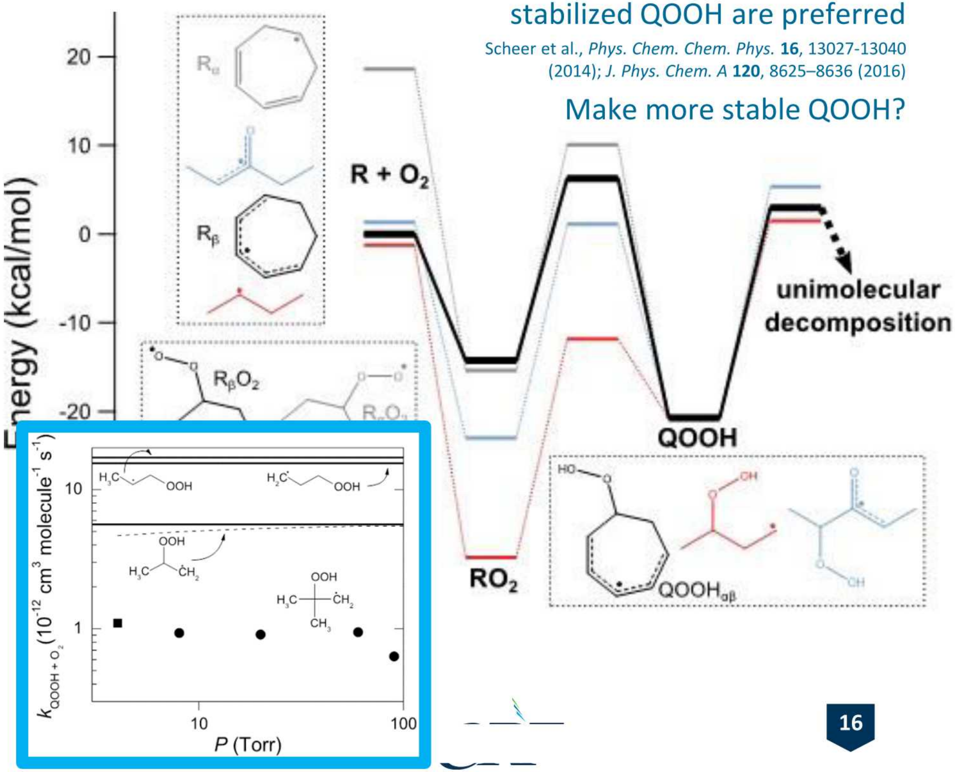
Resonance stabilization dramatically reduces the reactivity with O_2

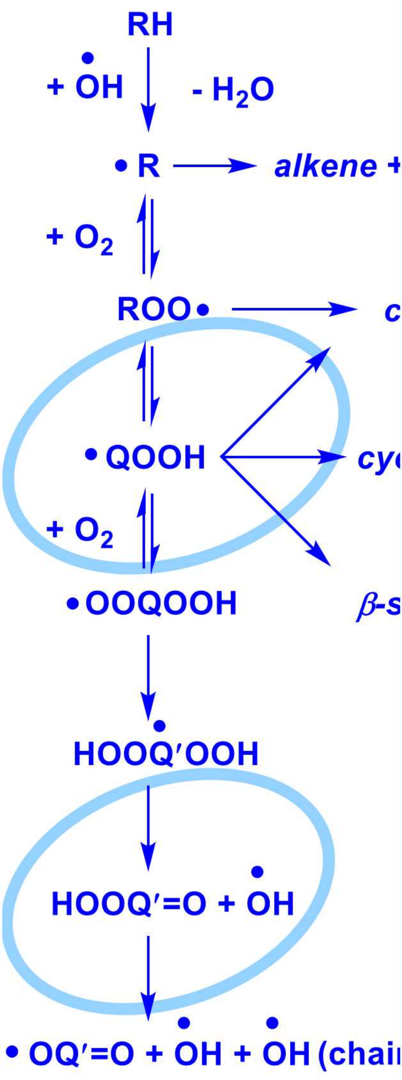
$$k_{QOOH+O2} = (2.9 \pm 1.0) \times 10^{-15}\ \mathrm{cm^3\ s^{-1}}$$
$$k_{R+O2} = (3.2 \pm 0.5) \times 10^{-16}\ \mathrm{cm^3\ s^{-1}}$$

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?





RH

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

$\bullet R \rightarrow$ *alkene +*

$+ O_2$

$ROO\bullet \rightarrow$ *c*

$\bullet QOOH \rightarrow$ *cy*

$+ O_2$

$\bullet OOQOOH$ *β-s*

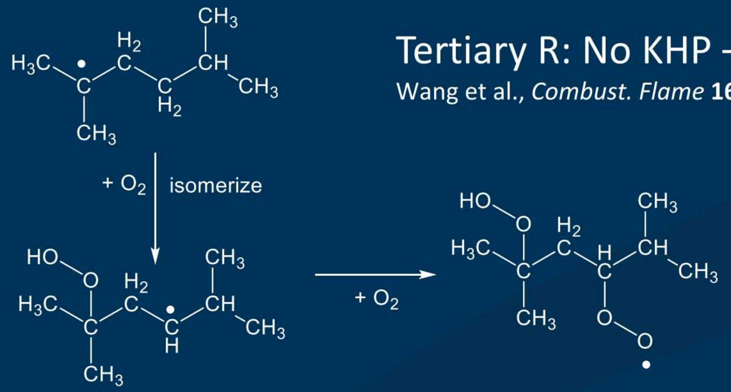
$HOO\dot{Q}'OOH$

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

$\bullet OQ'{=}O + \dot{O}H + \dot{O}H$ (chai

Compare the autoignition process to the autoxidation to highly oxygenated species in the troposphere

What stops the process towards chain branching?

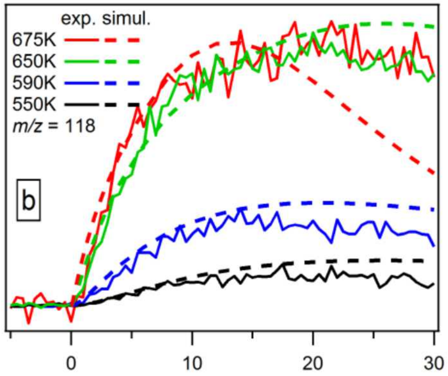


Tertiary R: No KHP – 3rd O_2 addition instead

Wang et al., *Combust. Flame* **164**, 386–396 (2016).

What else can intercept these molecules on the path?

Ketohydroperoxides have now been observed in many kinetic systems

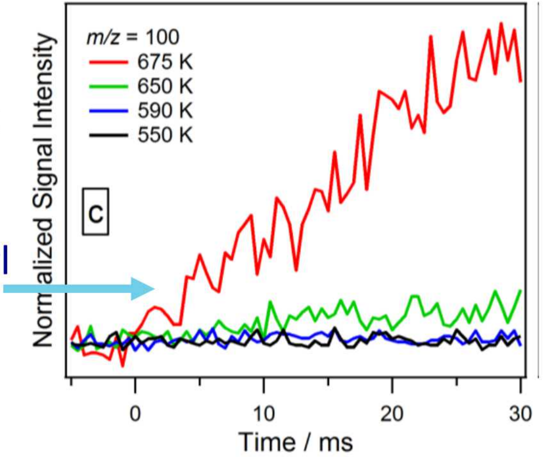


Pulsed photolytic neopentane oxidation shows KHP formation

Eskola et al., *Phys. Chem. Chem. Phys.* **19**, 13731-13745 (2017)

Time-resolved products suggest some KHP does not make OH + oxy radical

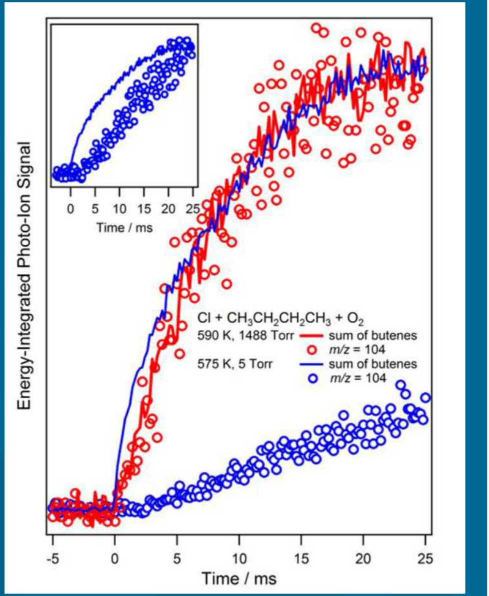
KHP → 2,2-dimethyl propanedial + H_2O

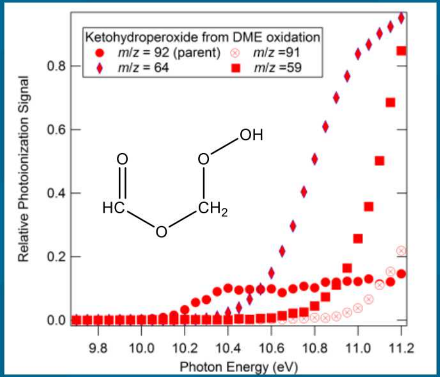


Pulsed photolytic oxidation of butane shows KHP formation

Identified as 3-hydroperoxybutanal

Eskola et al., *Proc. Combust. Inst.* **35**, 291-298 (2015)



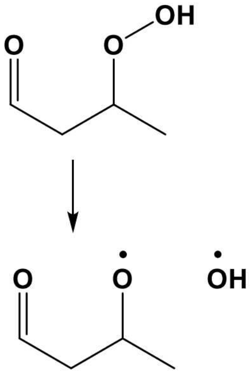


Hydroperoxymethyl formate measured in dimethyl ether oxidation in jet-stirred reactor

Moshammer et al. *J. Phys. Chem. A* **119**, 7361–7374 (2015)

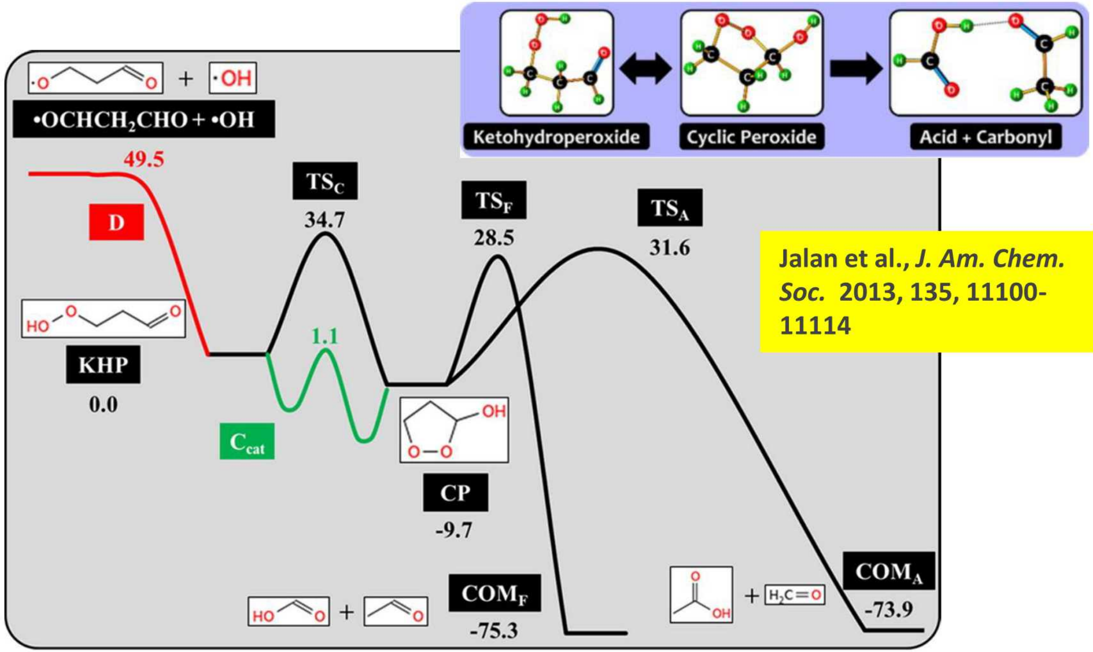
What if ketohydroperoxides don't fall apart to two radicals? Look at γ-ketohydroperoxides

So far observed species are all gamma-ketohydroperoxides



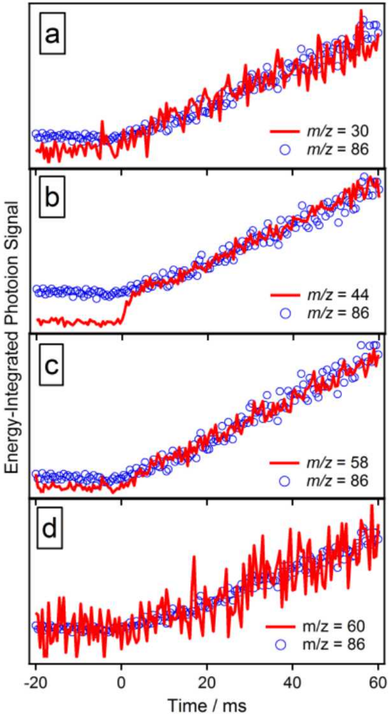
O-O bond fission leads to chain branching

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

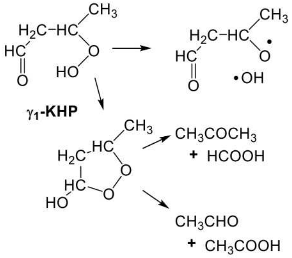


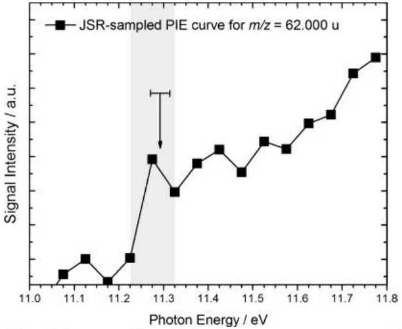
Jalan et al., *J. Am. Chem. Soc.* 2013, 135, 11100-11114

Does this happen? Organic acid products may be a signature of Korcek dissociation

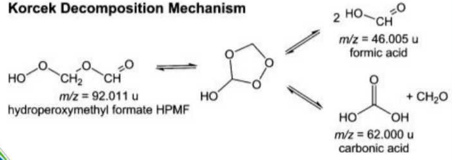


Eskola, Popolan-Vaida et al.



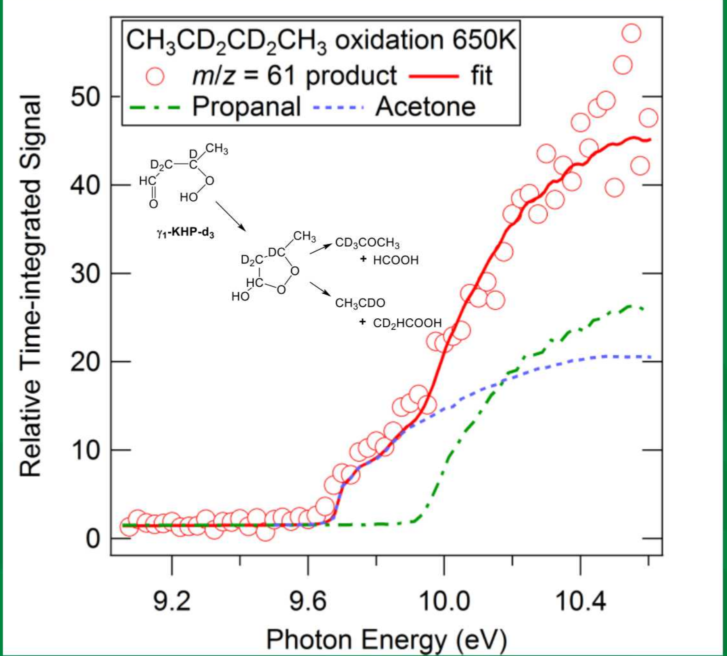


Korcek Decomposition Mechanism



Moshammer et al., *J. Phys. Chem. A* **119**, 7361–7374 (2015)

Modeling acid formation may constrain Korcek rate coefficient

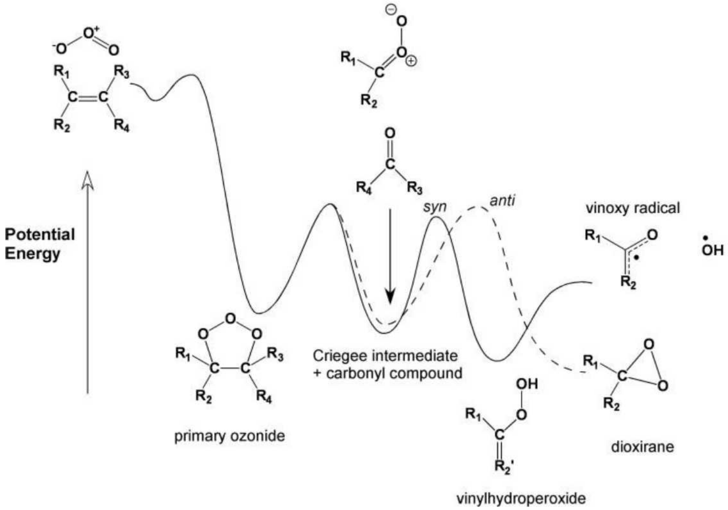


Eskola, Popolan-Vaida et al.

In butane-d_4 oxidation, observe acetone-d_3 isotopolog

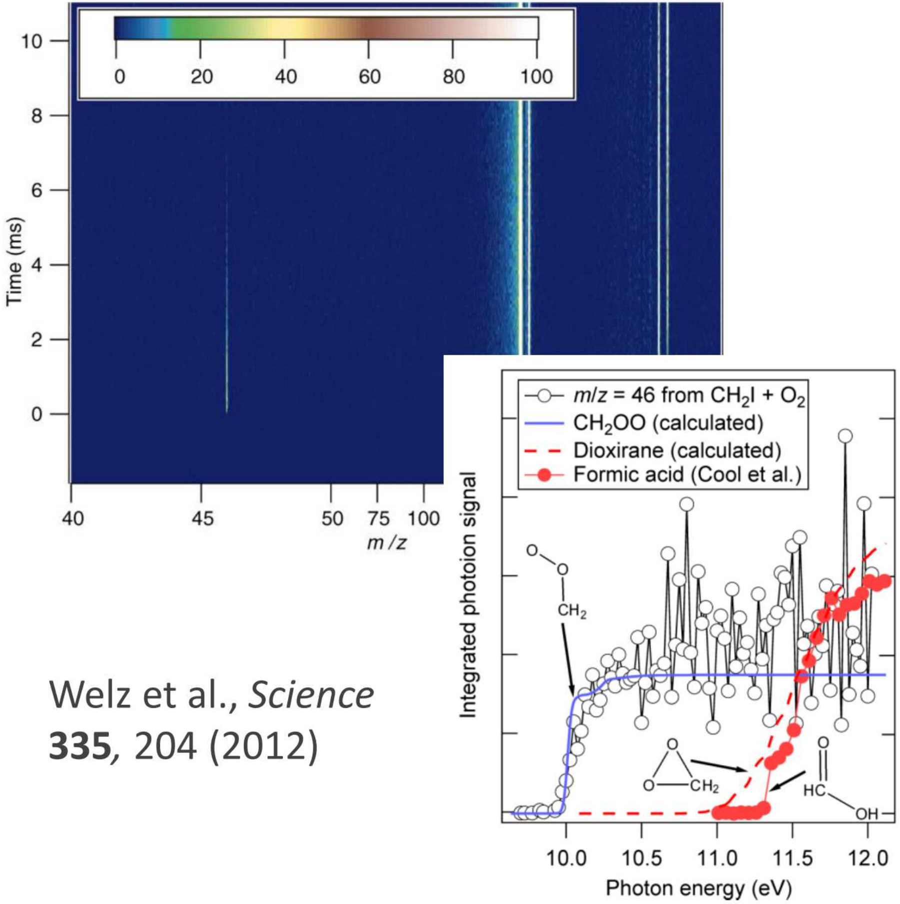
For Criegee intermediates the strategy is direct synthesis

Verified by mass, kinetics, and spectrum



Ozonolysis is too slow and too energetic

For Criegee intermediates the strategy is direct synthesis



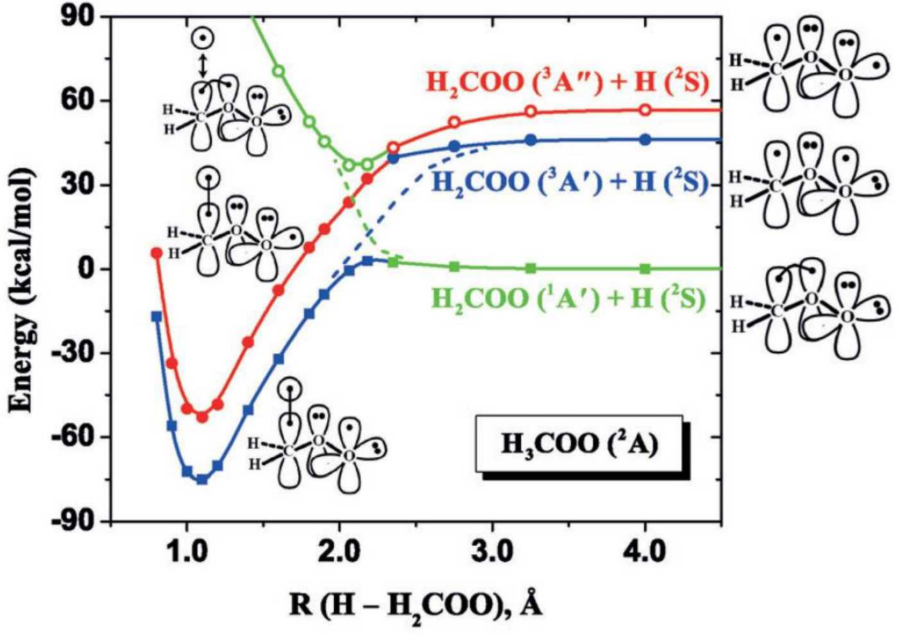
Welz et al., *Science* **335**, 204 (2012)

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

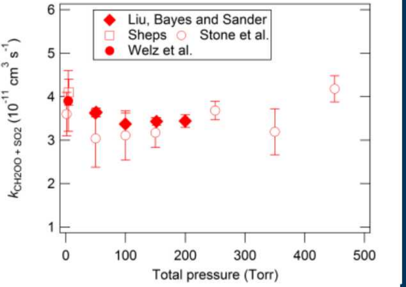
Now can measure carbonyl oxide reaction kinetics directly

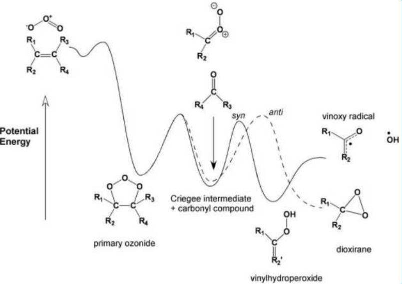


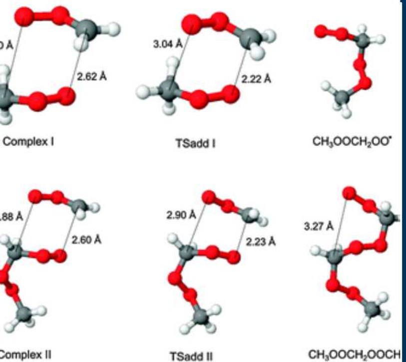
Miliordos and Xantheas, *Angew. Chem. Int. Ed.* **55**, 1015-1019, 2015

- 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?





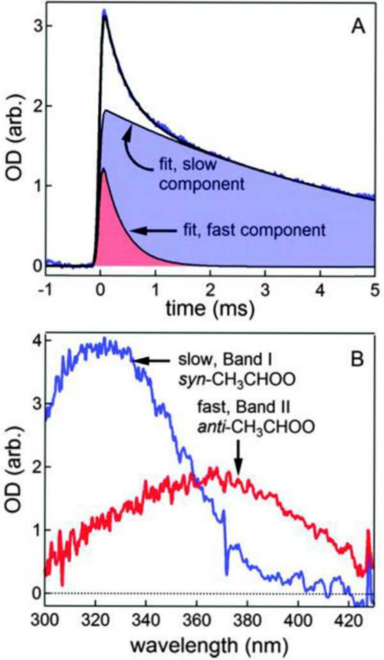


The chemistry of ozonolysis was largely worked out from solution phase – gas phase can be different!

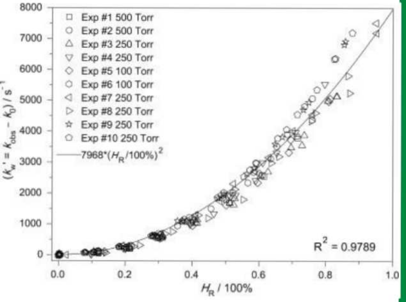
Criegee (1975) outlined four types of reactions that carbonyl oxides undergo: dimerization, reaction with carbonyls, isomerization, and reactions with “proton active substances”

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

- ***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))

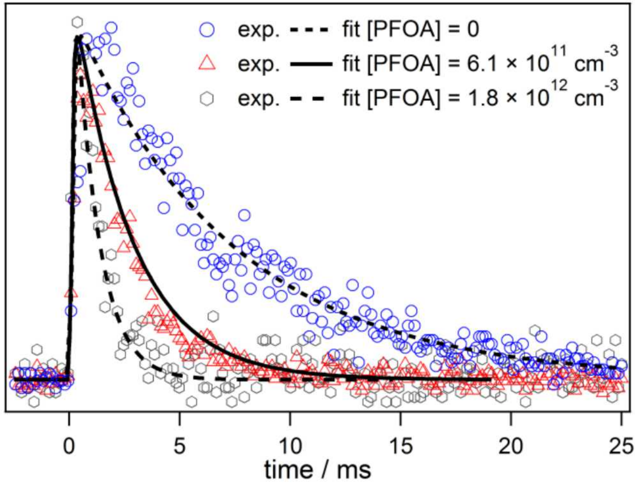
Carbonyl oxide reactions in solution: ROH>H_2O>CH_3CO_2H

In gas phase RCO_2H >> ROH, H_2O

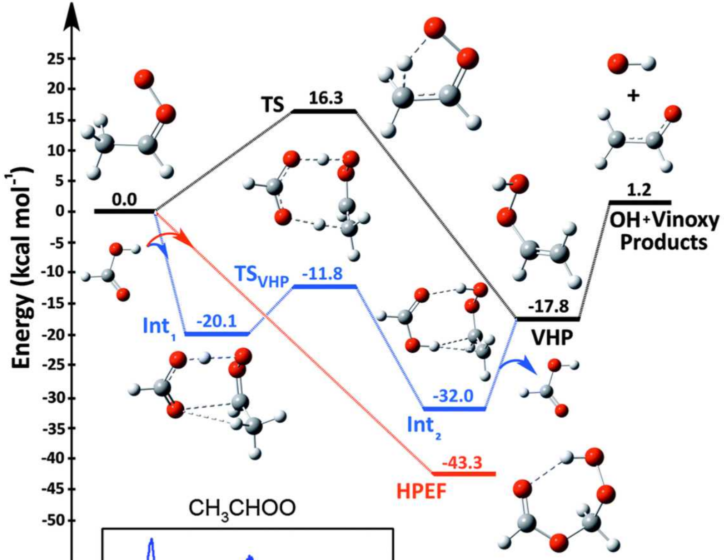
Fast reaction general for all acids

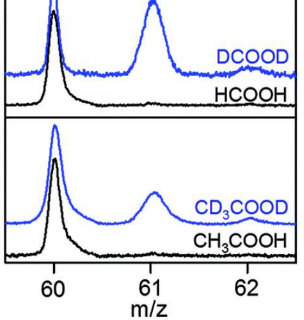
- PFOA reacts slowly with OH
- Reaction with CH_2OO is fast:
  - $(4.7 \pm 0.7) \times 10^{-10}$ cm^3 s^{-1}

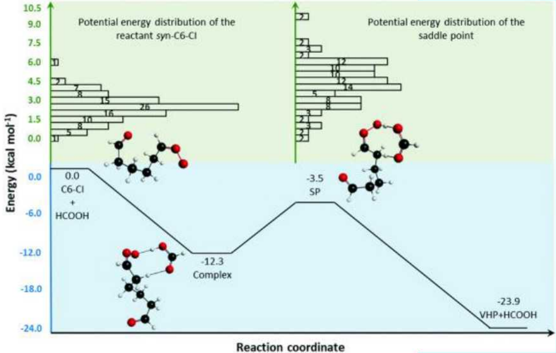
Eskola et al., unpublished



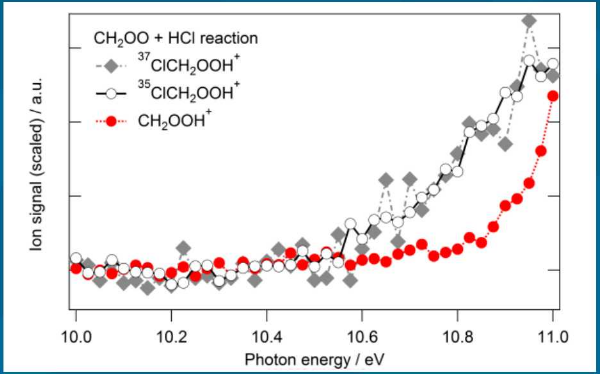
What are the products of reactions with acids?





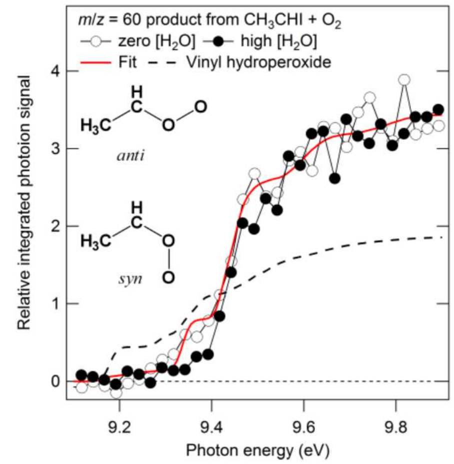


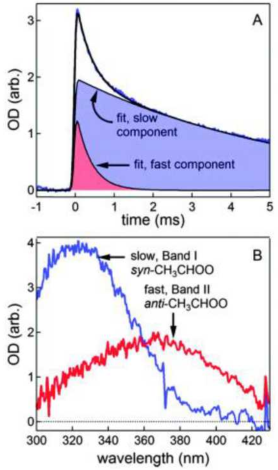
- Reactions with acids appear to form hydroperoxyesters
  - Adduct mass observed
  - Dissociative ionization to protonated carbonyl oxides
- Another possibility is acid-assisted tautomerization (Kumar et al., Phys. Chem. Chem. Phys. 16, 22968-22973 (2014); Liu et al., Phys. Chem. Chem. Phys. 17, 20490-20494 (2015), Monge-Palacios et al. Phys. Chem. Chem. Phys. doi:10.1039/C7CP08538A (2018))



Caravan, Rotavera et al., unpublished

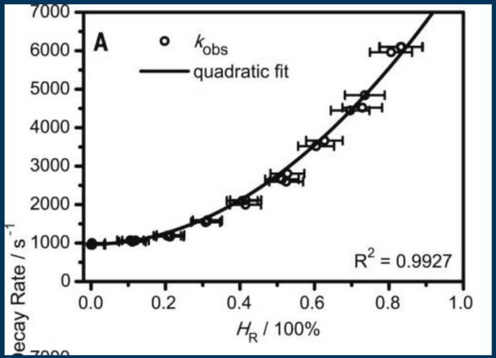
- Most common proton active species – H_2O
- Differences in reactivity among carbonyl oxides:
  - $(CH_3)_2COO < 1.5 \times 10^{-16}$ (Huang et al., *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10857–10862 (2015))
  - $CH_2OO\ (3.2 \pm 1.2) \times 10^{-16}$ (Berndt et al., *Phys. Chem. Chem. Phys.* **17**, 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





$CH_2OO + (H_2O)_2 \sim$
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)

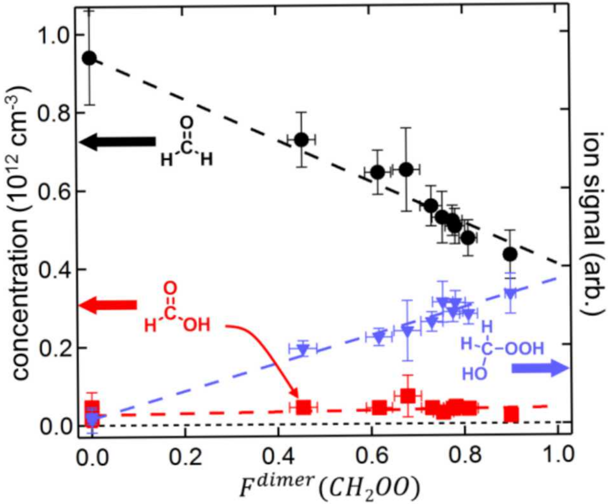
Suggestion that reaction with dimer makes ~ 50% HCOOH (Nguyen et al., *Phys. Chem. Chem. Phys.* **18**, 10241-10254 (2016))

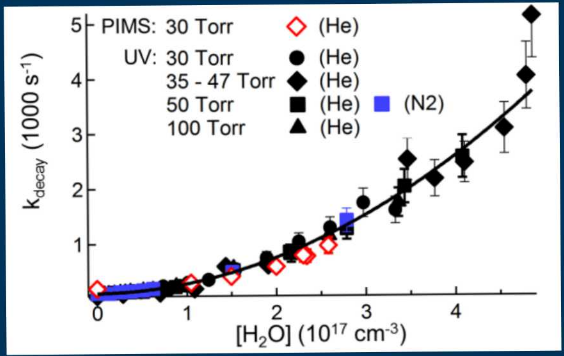
Can confirm rate coefficient with UV absorption, photoionization

MPIMS measures all products

Lenny Sheps

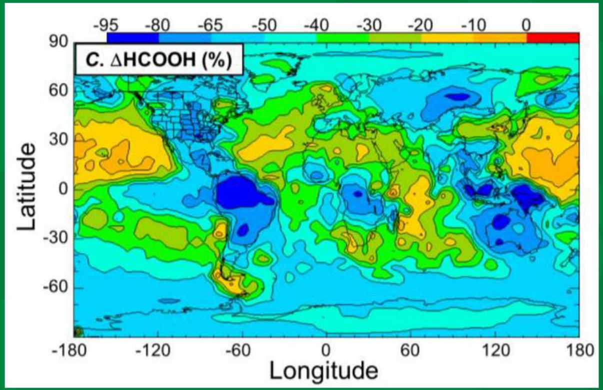
Sheps et al., *Phys. Chem. Chem. Phys.*, **19**, 21970-21979 (2017)





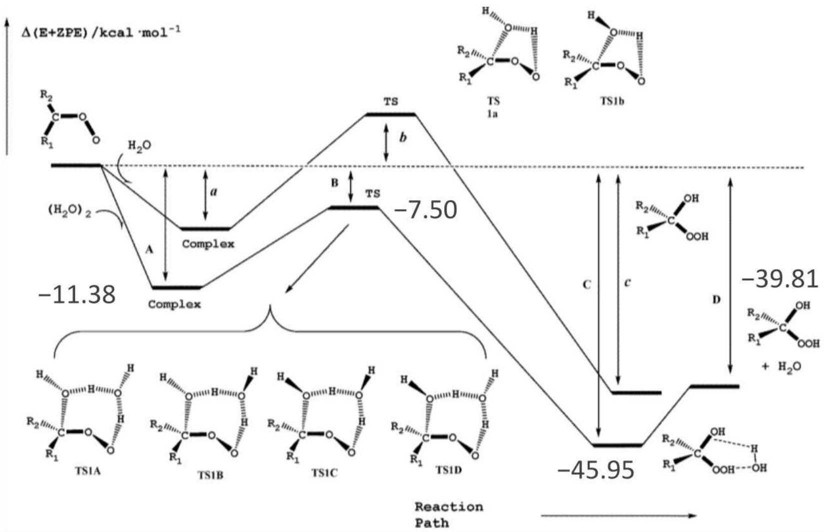
Fundamental chemistry vs atmospheric modeling – what happens to the adduct??

If the HMHP does not make formic acid, modeled HCOOH is substantially reduced



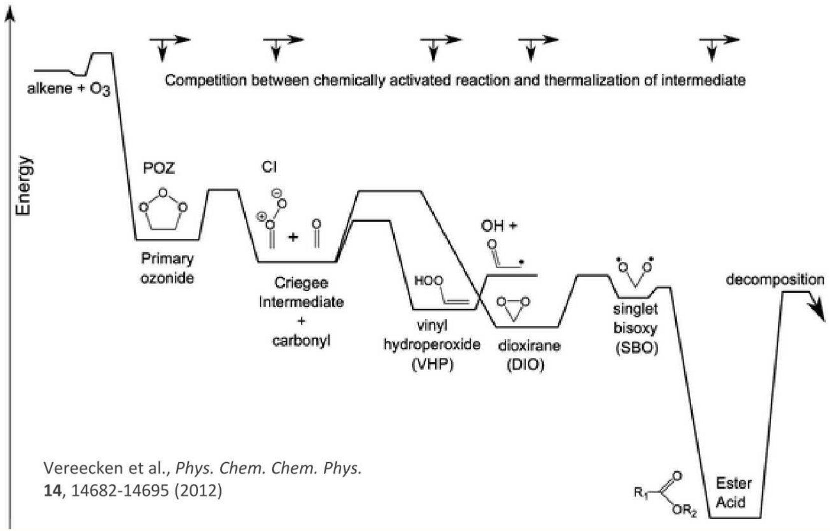
Anwar Khan

More experiments to do

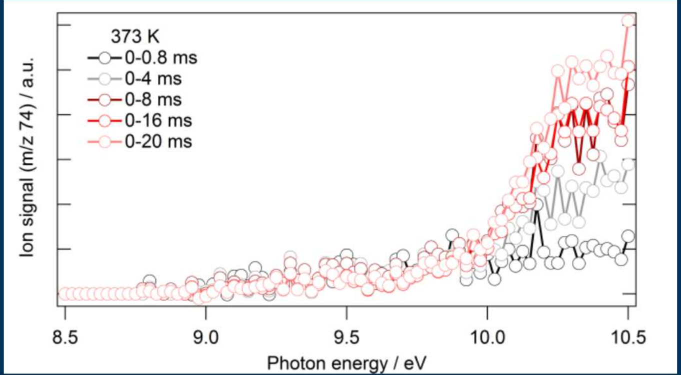


Calculation of $CH_2OO + (H_2O)_2$ reaction suggests entrance complex that dissociates to HMHP and H_2O

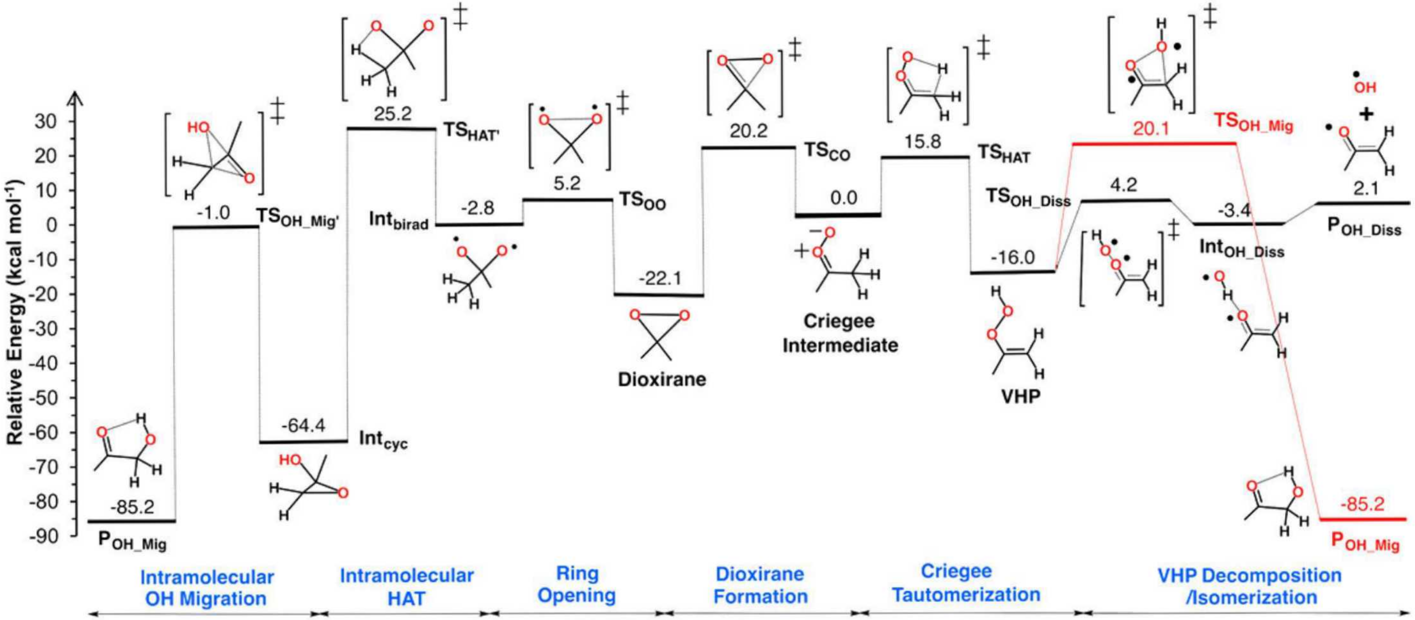
Anglada and Solé *Phys. Chem. Chem. Phys.* **18**, 17698-17712 (2016)



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



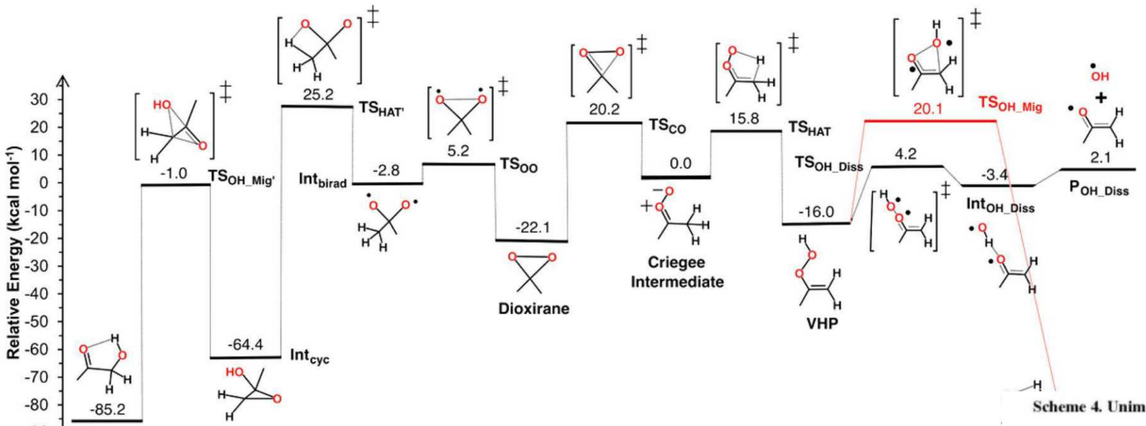
- Isomerization has two basic pathways – dioxirane and vinyl hydroperoxide
- Is it that simple?
- $(CH_3)_2COO$ isomerizes to hydroxyacetone (CAT et al, J. Phys. Chem. A **121** 16–23 (2017))
- Temperature dependence confirms first-order gas phase reaction (Caravan et al., unpublished)
- Observed in 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

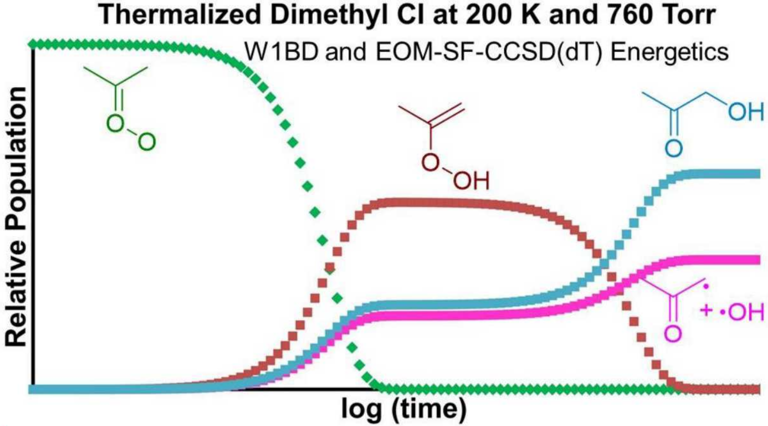


(Ward Thompson, in *J. Phys. Chem. A* **121** 16–23 (2017))

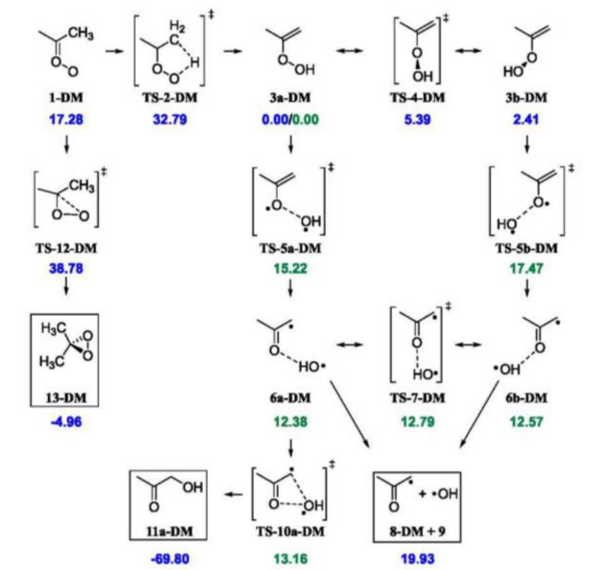
Kuwata et al. recently calculated a roaming style pathway through the vinyl hydroperoxide (*J. Phys. Chem. A* **just accepted DOI:** 10.1021/acs.jpca.8b00287 (2018)) that obviates the high transition state

They also predicted product branching for the acetone oxide decomposition.





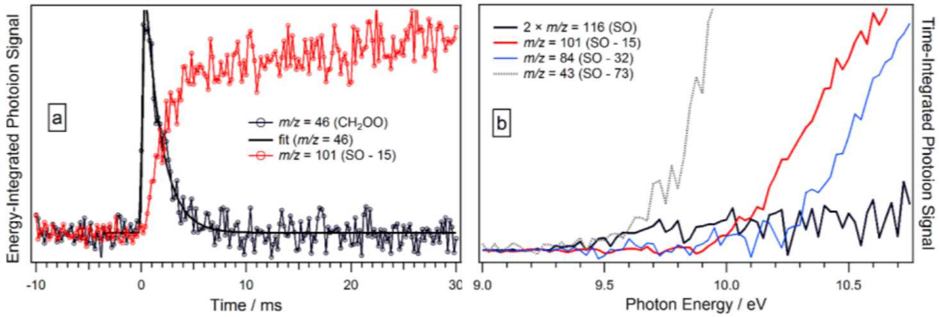
Scheme 4. Unimolecular Reactivity of the Dimethyl Criegee Intermediate[a]



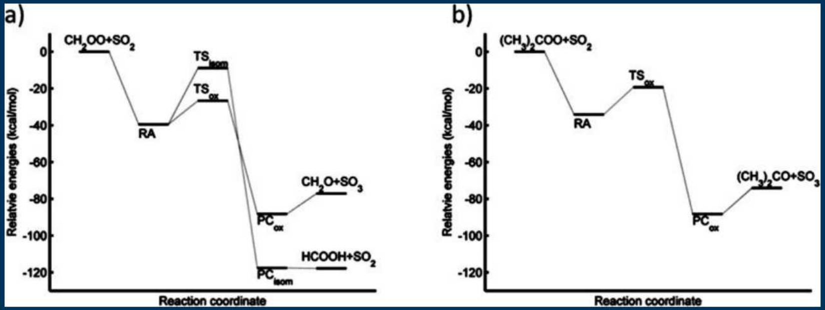
Cycloaddition – reaction with carbonyls is one of the three steps in the Criegee mechanism

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



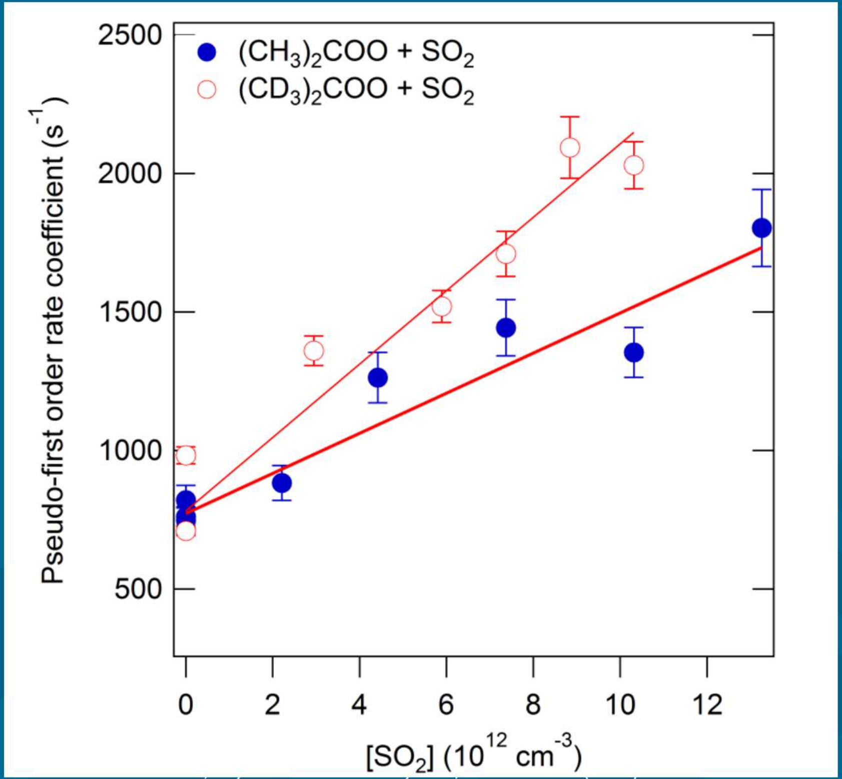
Kurtén et al., *J. Phys. Chem. A* **115**, 8669–8681 (2011)

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

Y. P. Lee group identified adduct in CH_2OO reaction with SO_2 Wang et al., *J. Chem. Phys.* **148**, 064301 (2018)

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?

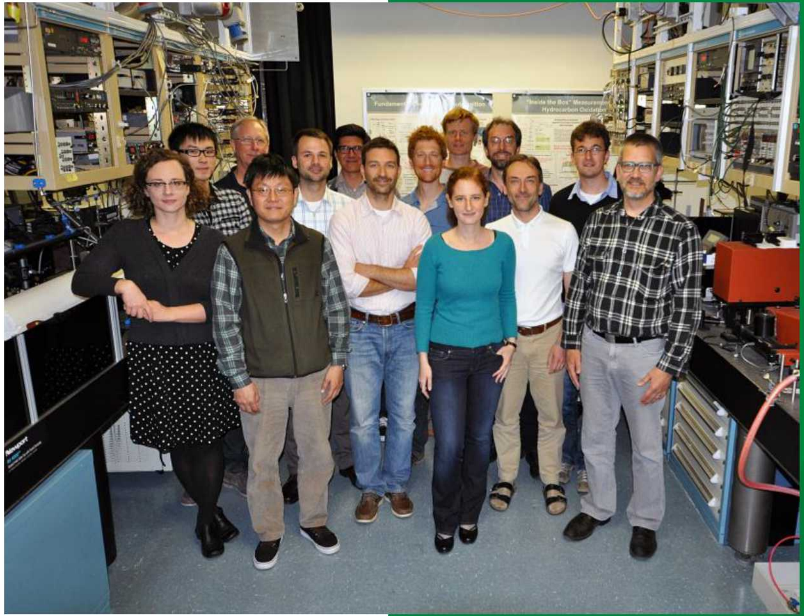
What does it mean to make a difference?

  - 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



Raybel Almeida
Ivan Antonov
Judit Zádor

Krupa Ramasesha
Ming-Wei Chen
Haifeng Huang

Adam Scheer
Oliver Welz

- 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)