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Characterization of Intermediates in Atmospherically Relevant Hydrocarbon Oxidation Processes

Craig A. Taatjes

Combustion Research Facility, Sandia National Laboratories, Livermore CA

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Sunday River, Newry ME

Sandia National Laboratories

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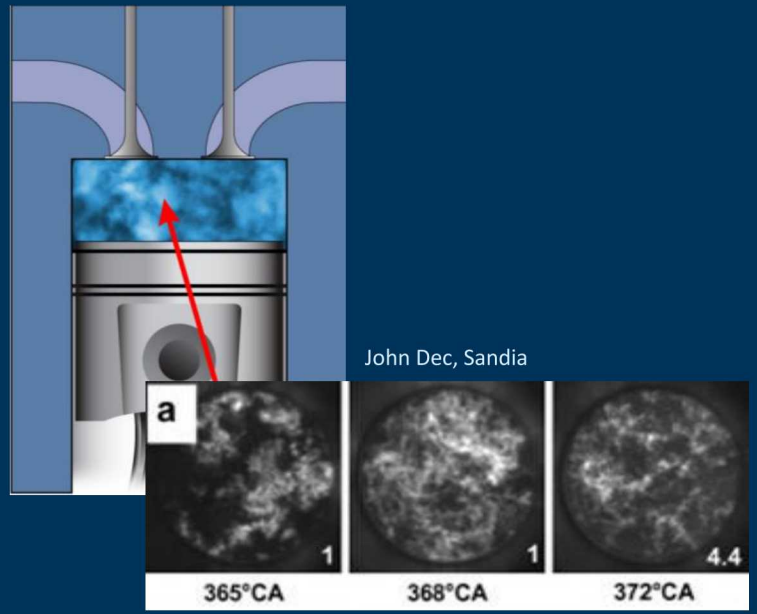
Comparing different (but related) chemical systems

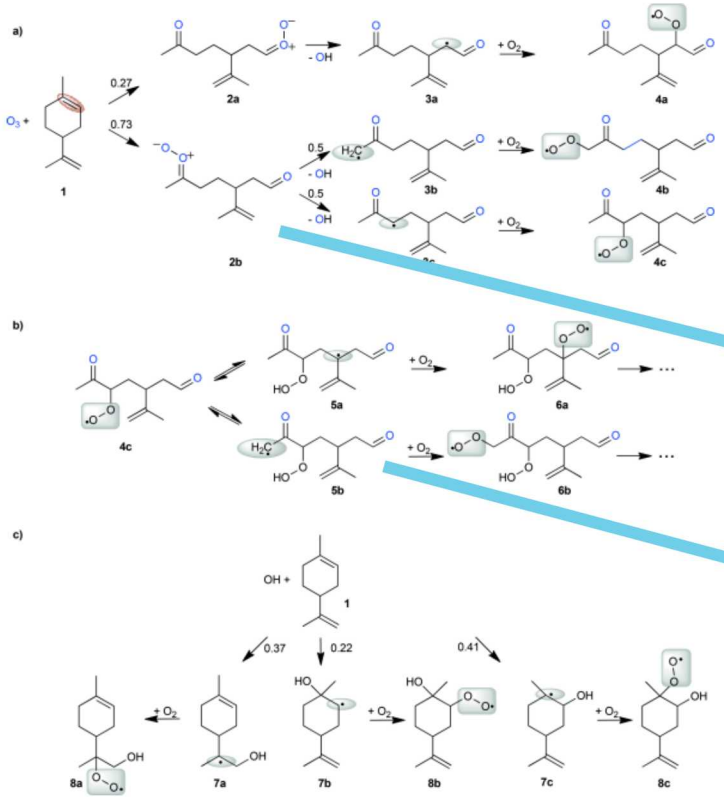
Autoignition chemistry



John Dec, Sandia

Tropospheric oxidation

William Putman, NASA/Goddard



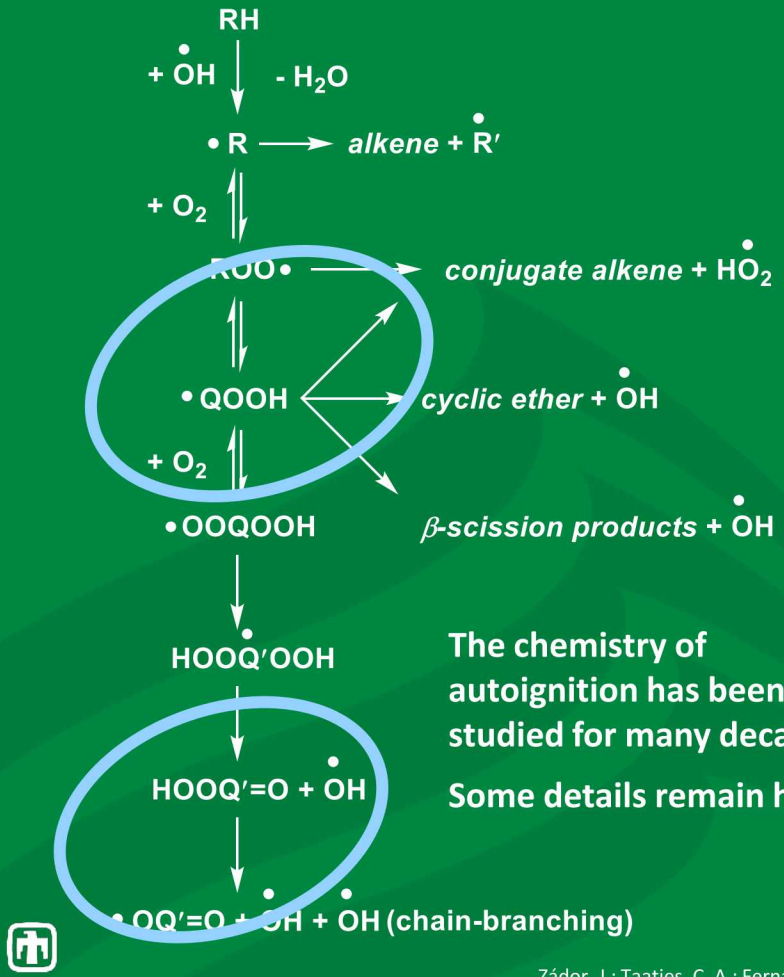
T. Jokinen et al., *Angew. Chem. Int. Ed.* **53,** 14596-14600 (2014)

Specific investigations target individual reaction types

Understanding mechanisms allows rigorous generalization

Ozonolysis – can we focus on individual carbonyl oxide channels?

Peroxy radical chemistry – can we isolate specific transformations?

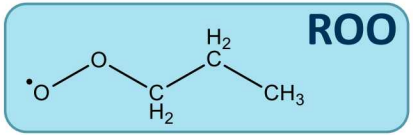


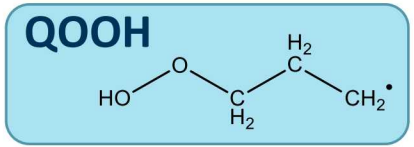
The chemistry of autoignition has been studied for many decades –

Some details remain hidden

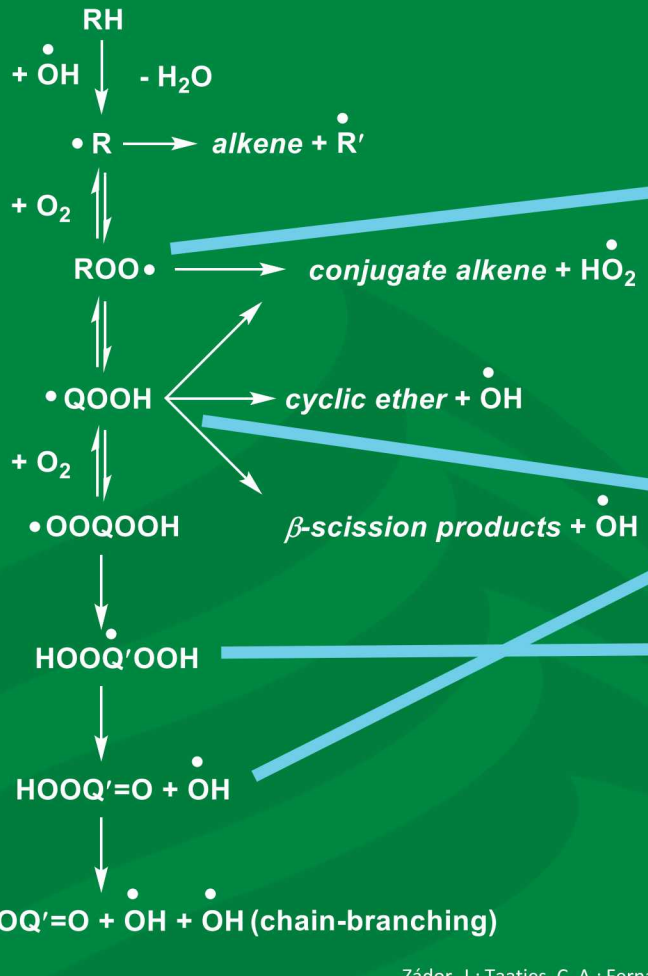
Zádor, J.; Taatjes, C. A.; Fernandes, R. X.
Prog. Energy Combust. Sci. **2011**, *37*, 341.

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



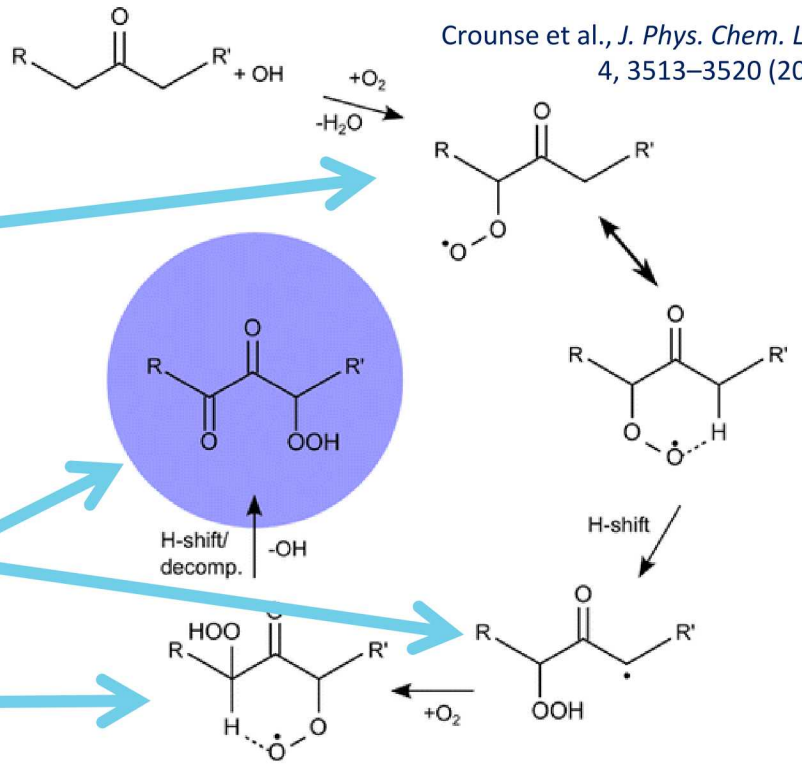


- QOOH + O_2 is responsible for chain branching
- Chain branching step goes through dissociation of a ketohydroperoxide
- Isomers make a difference

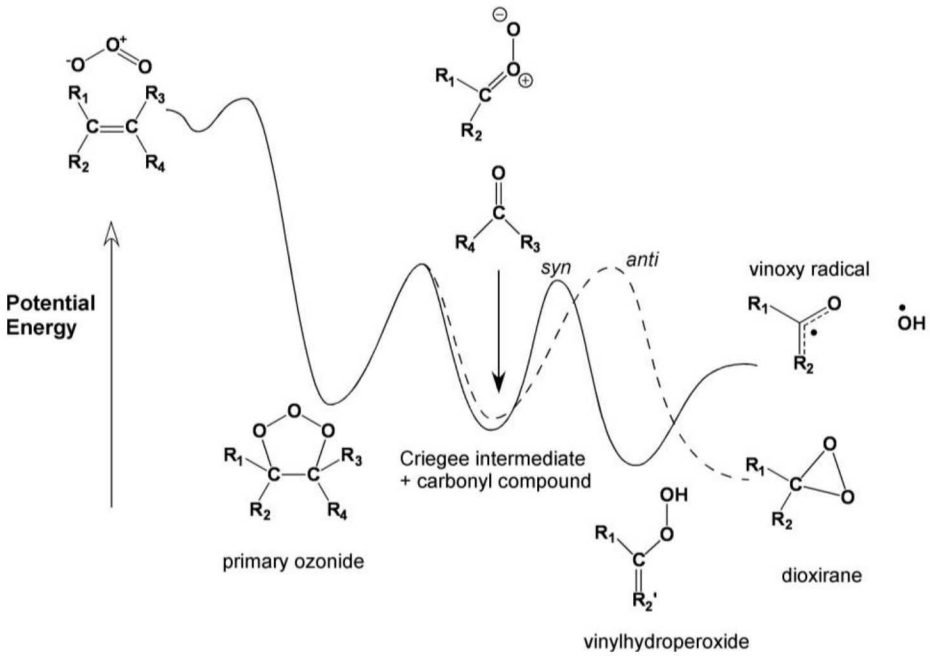


Zádor, J.; Taatjes, C. A.; Fernandes, R. X.
Prog. Energy Combust. Sci. **2011**, *37*, 341.

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



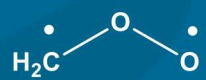
Tropospheric oxidation shares the same isomerizations and intermediates

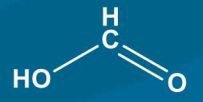


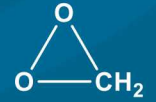
Kinetic models for tropospheric oxidation require knowing reactions of other intermediates

Carbonyl oxides ("Criegee intermediates") formed in ozonolysis are potential tropospheric reactants

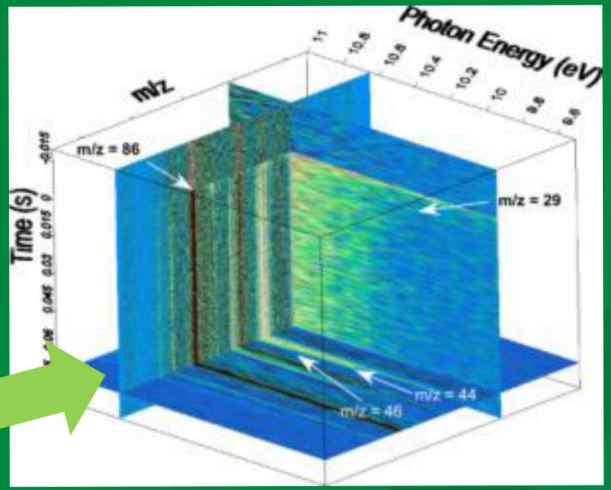
Intermediates are isomers of other stable or reactive species

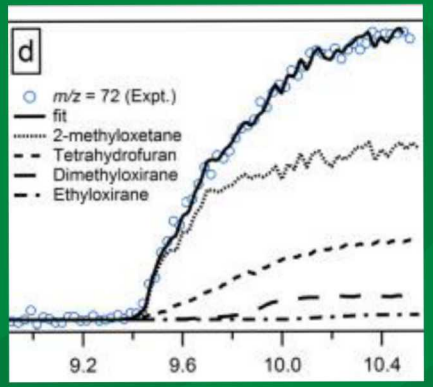






Synchrotron photoionization mass spectrometry can detect and characterize these intermediates

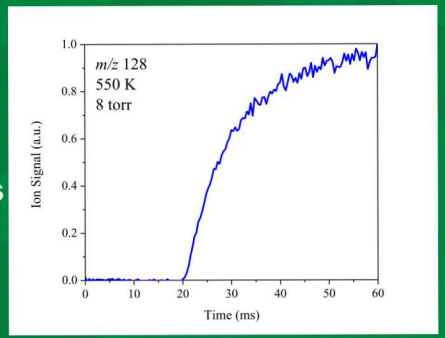


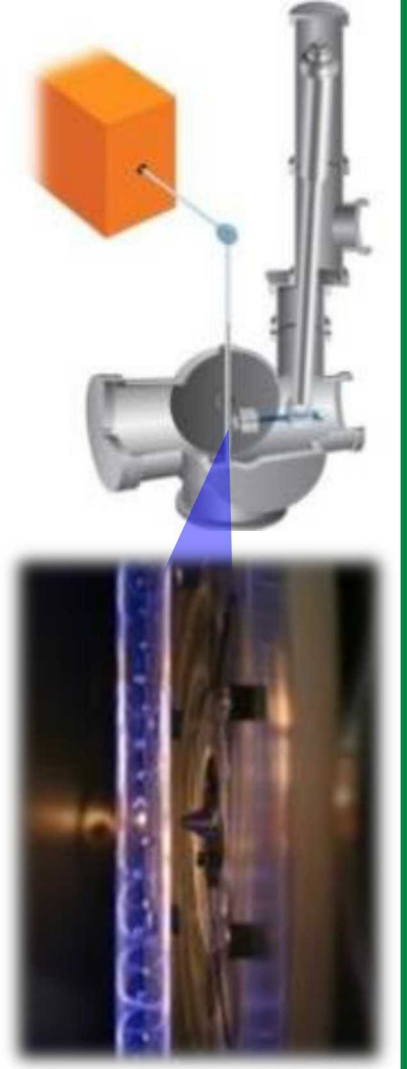


David Osborn

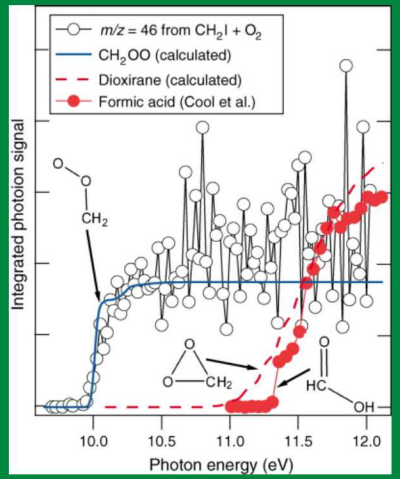
Isomer-Resolved Species Identification

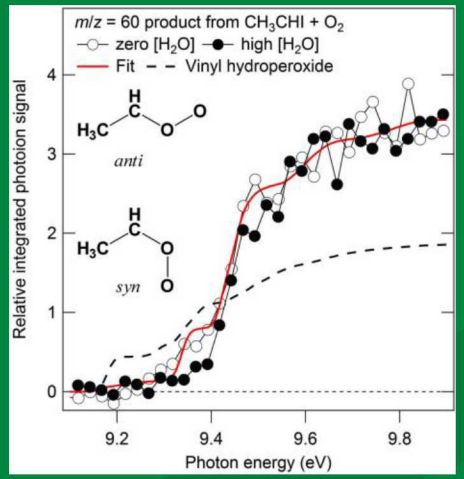
Time-Dependent Chemical Kinetics





Need to make the intermediates and then we can detect them

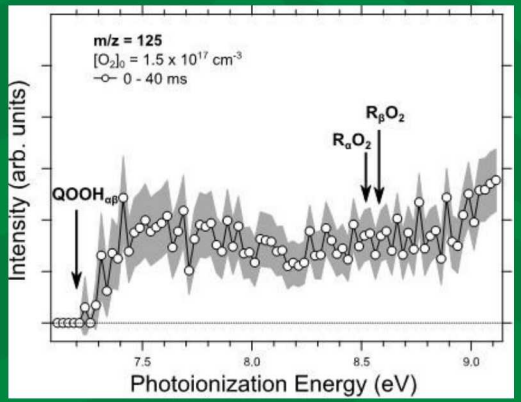


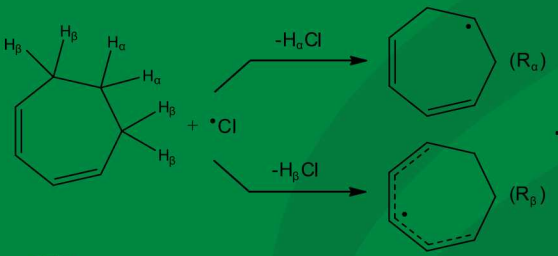


$CH_2I + O_2 \rightarrow CH_2OO + I$

gem-iodoalkyl + O_2 → carbonyl oxide + I

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

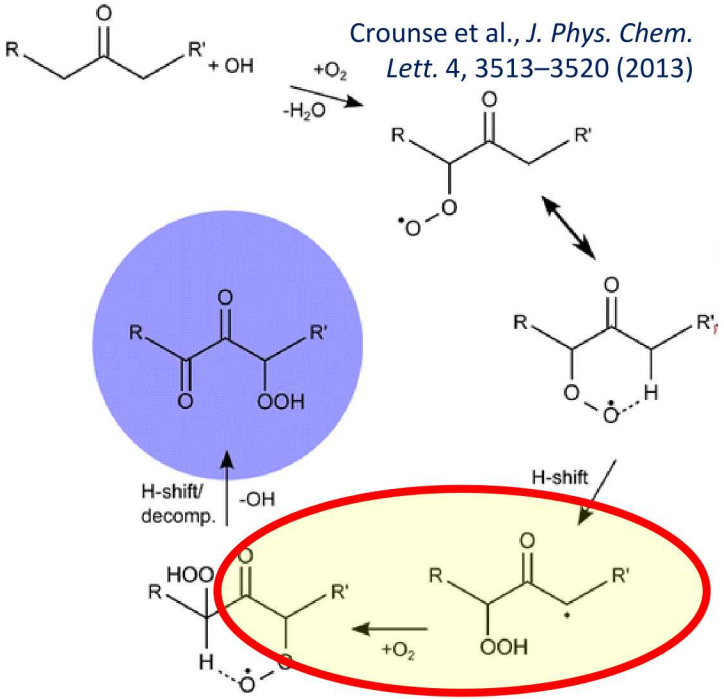




+ O_2

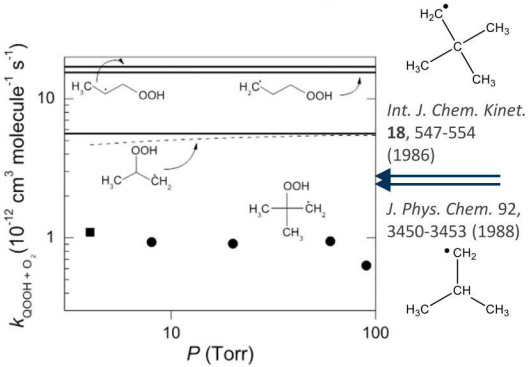
J.D. Savee, E. Papajak, B. Rotavera, H. Huang, A.J. Eskola, O. Welz, L. Sheps, C.A. Taatjes, J. Zádor, **D.L. Osborn**, *Science* **347**, 643-646 (2015).

Additions of QOOH to O_2 are important to complex oxidation submechanisms



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

- 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

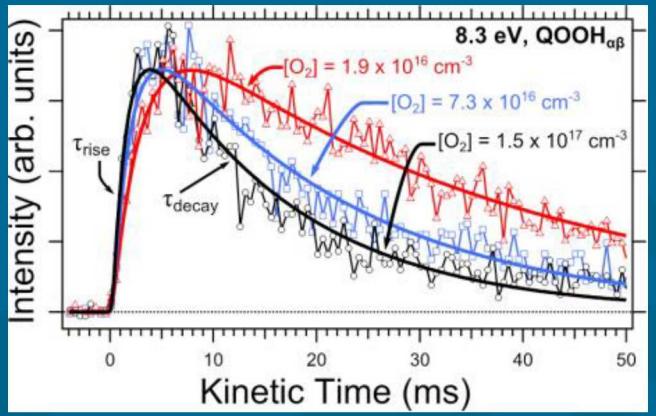


Int. J. Chem. Kinet. **18**, 547-554 (1986)

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

Double resonance stabilization allowed first direct detection of QOOH

Resonance stabilization greatly reduces reactivity with O_2



Both rise and decay of $C_7H_9O_2$ faster as $[O_2]$ increases

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

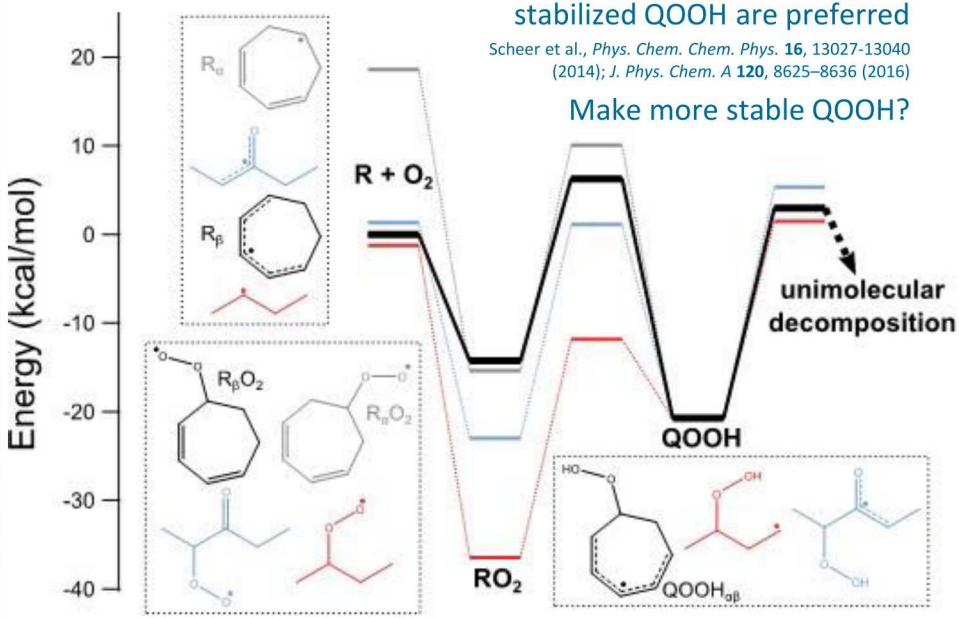
$k_{R+O2} = (3.2 \pm 0.5) \times 10^{-16}$ cm^3 s^{-1}

Extreme resonance stabilization

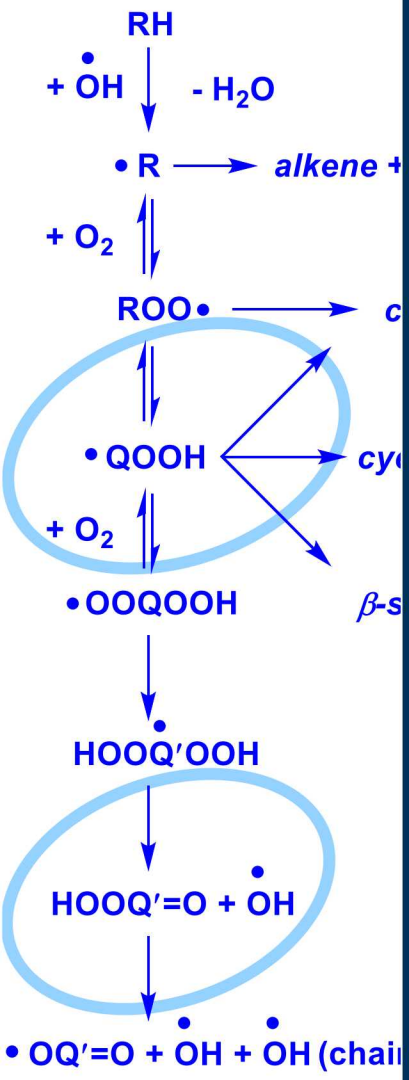
Ketone oxidation – resonance stabilized QOOH are preferred

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

Make more stable QOOH?

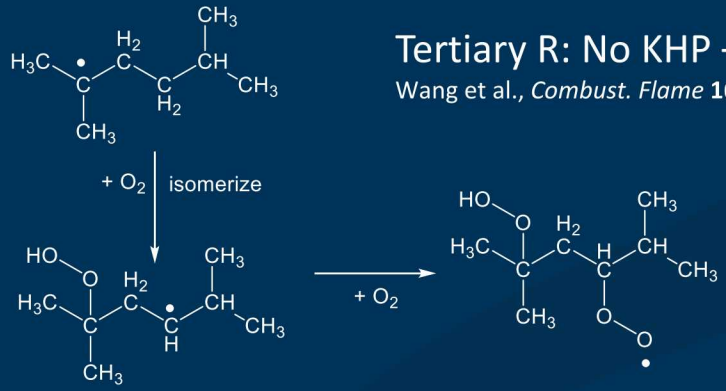


J.D. Savee, E. Papajak, et al., *Science* **347**, 643-646 (2015).



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?

Alkyl radicals can be removed more rapidly … with OH?

OH + CH_3OO rate coefficient is large: effect depends on products

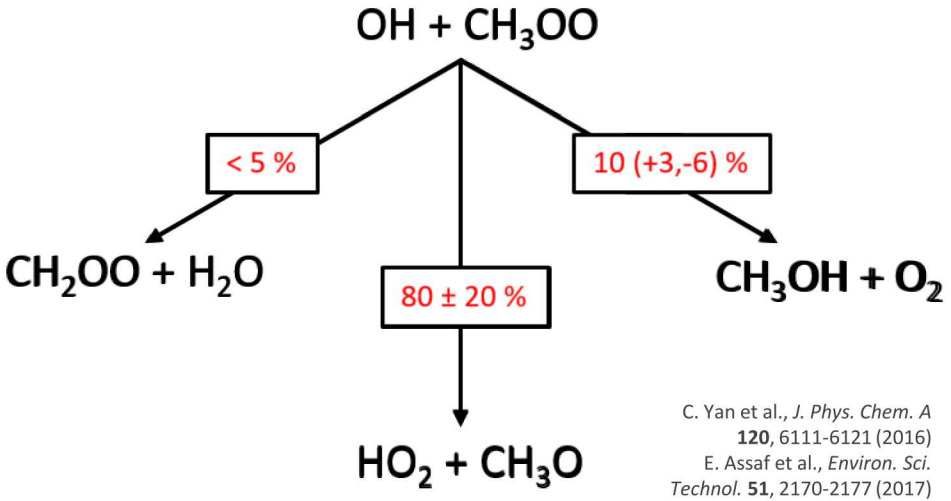
Calculated ~ 7% branching to methanol (Müller et al., *Nature Comm.***7**,13213 (2016))

At high side of uncertainty could solve "methanol problem" (Kim et al.)

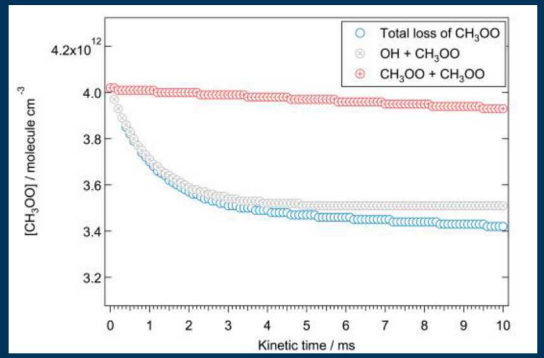
MPIMS shows all products at once

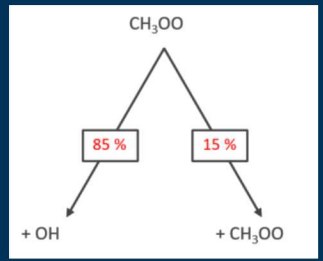
Can arrange kinetics so that most of CH_3OO is consumed by OH

Correct the observed methanol yield for other CH_3OH sources



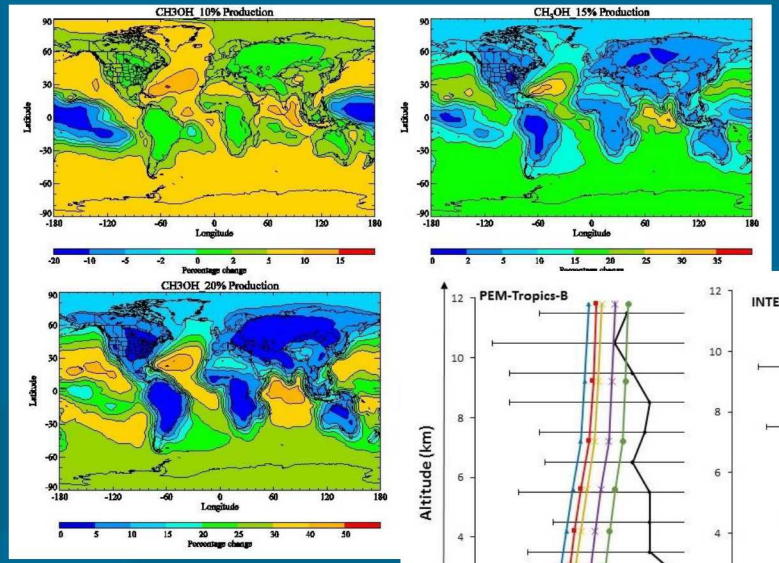
C. Yan et al., *J. Phys. Chem. A* **120**, 6111-6121 (2016)
E. Assaf et al., *Environ. Sci. Technol.* **51**, 2170-2177 (2017)



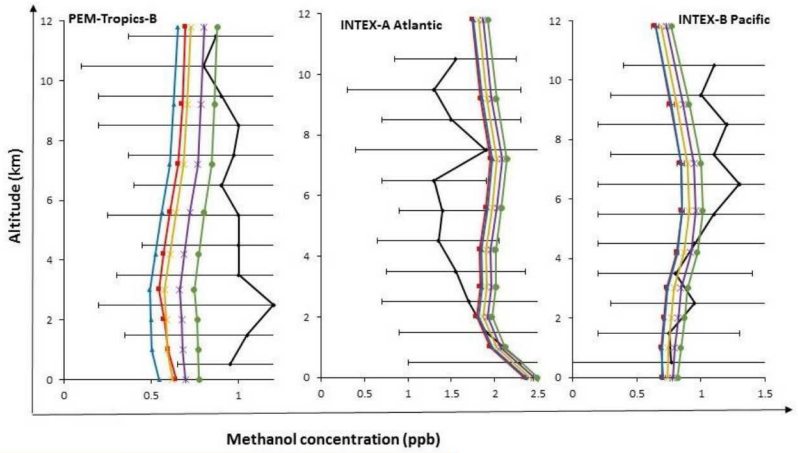


Caravan et al., unpublished

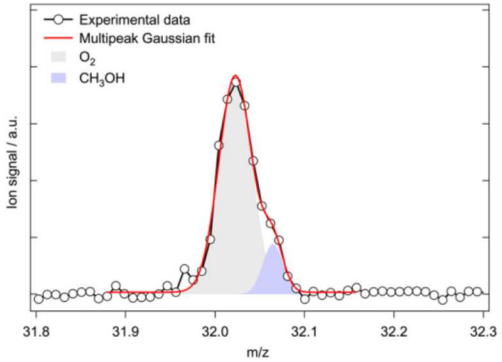
Branching may not be enough to solve the problem!

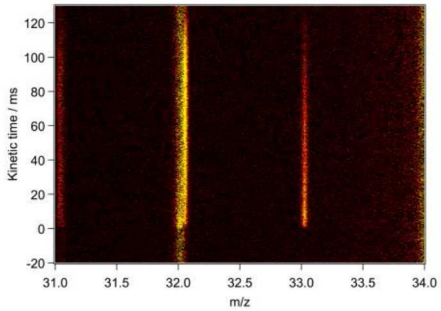


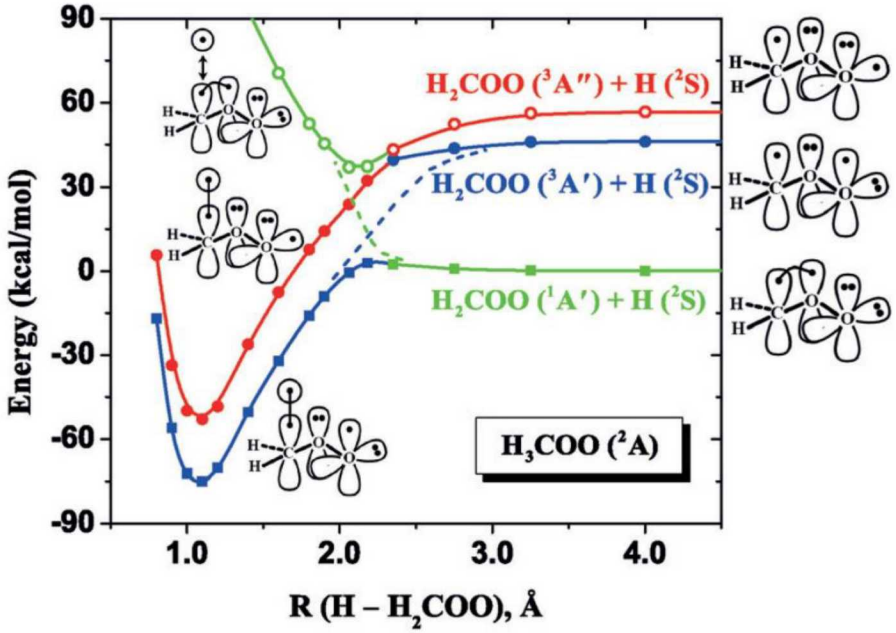
Khan et al., unpublished



Remaining experimental changes may improve accuracy



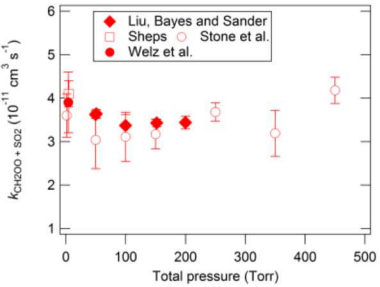


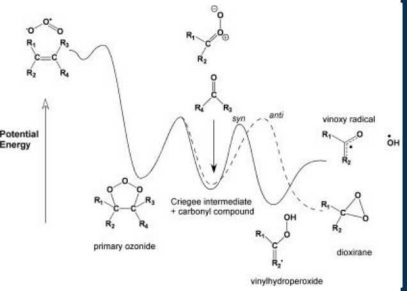


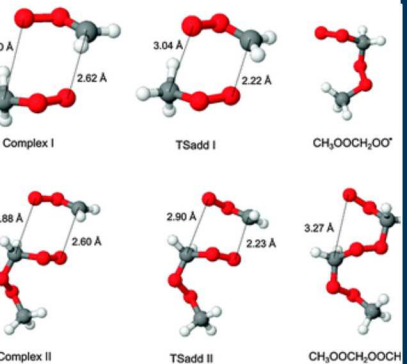
Miliordos and Xantheas, *Angew. Chem. Int. Ed.* **55**, 1015-1019, 2015

- 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)
  - $CH_2OO + NO$ $< 6 \times 10^{-14}$ cm^3 s^{-1}
    Welz et al., *Science* **335**, 204 – 207 (2012)
  - What about reactions with closed-shell species?





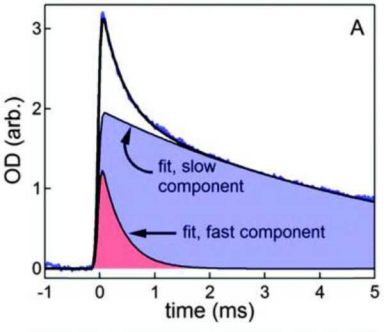


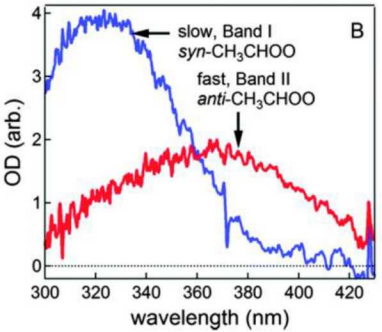
The chemistry of ozonolysis was largely worked out from solution phase – gas phase can be different!

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

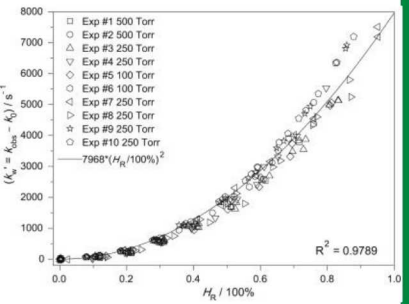
Generalization (CAT, *Annu. Rev. Phys. Chem.* 2017):

- 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)

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

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

Nature of products can make a difference in troposphere

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

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))

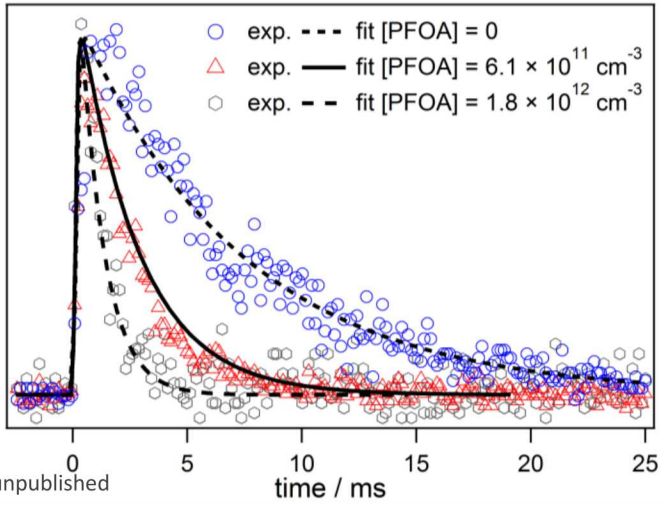
Carbonyl oxide reactions in solution: $ROH > H_2O > CH_3CO_2H$

In gas phase $RCO_2H >> ROH, H_2O$

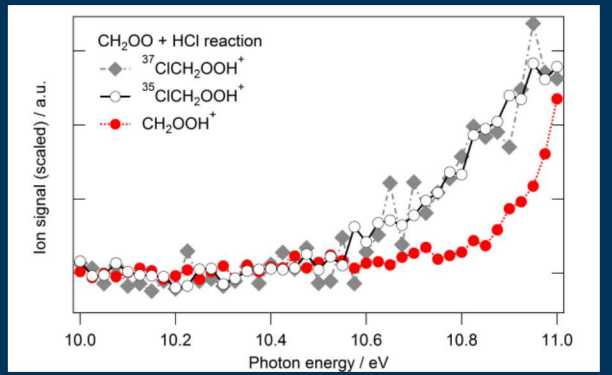
Fast reaction general for all acids

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

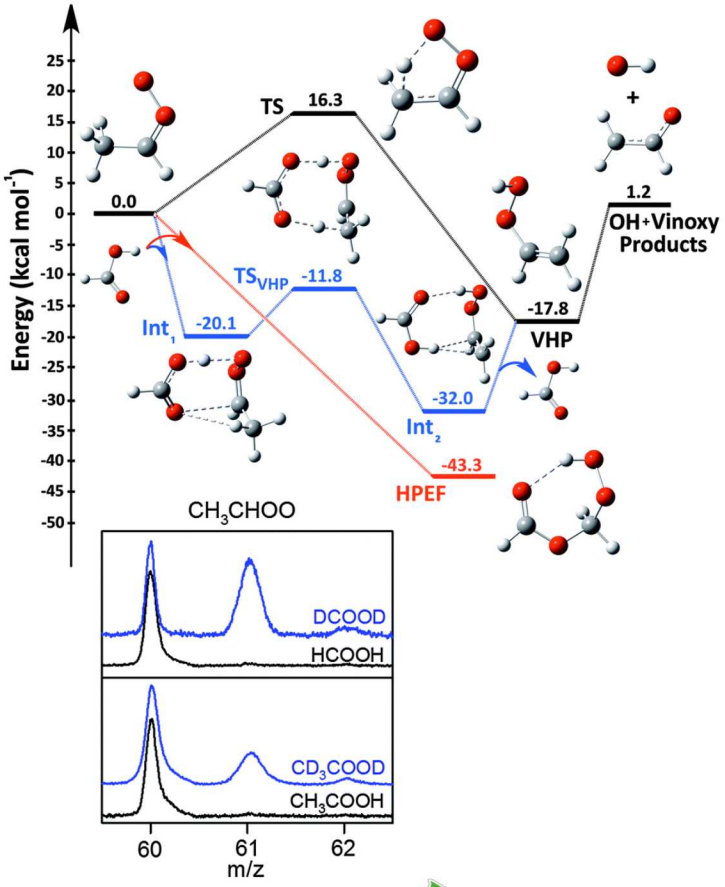
What are the products of reactions with acids?



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)

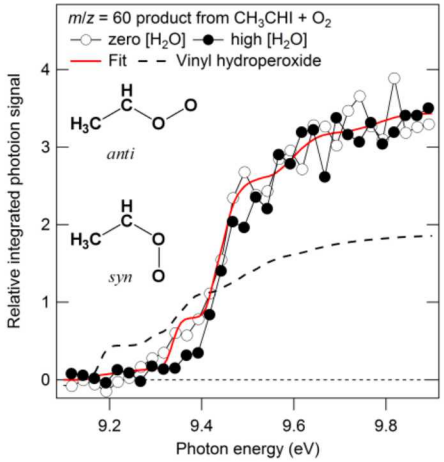
Most common proton active species – H_2O

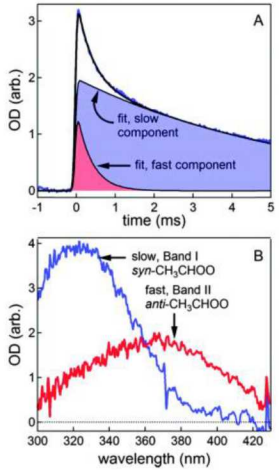
Differences in reactivity among carbonyl oxides:

- $(CH_3)_2COO < 1.5 \times 10^{-16}$ (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

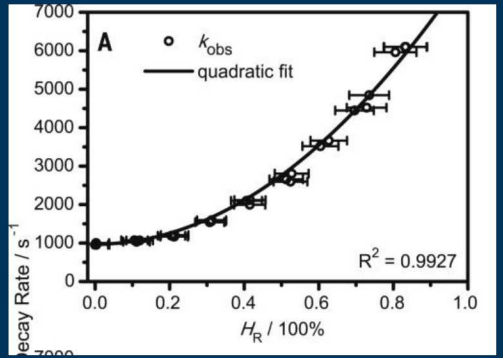
H_2O dimer reaction is the dominant removal mechanism for tropospheric CH_2OO





$CH_2OO + (H_2O)_2 \sim 5 \times 10^{-14}\ cm^3\ s^{-1}$

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?

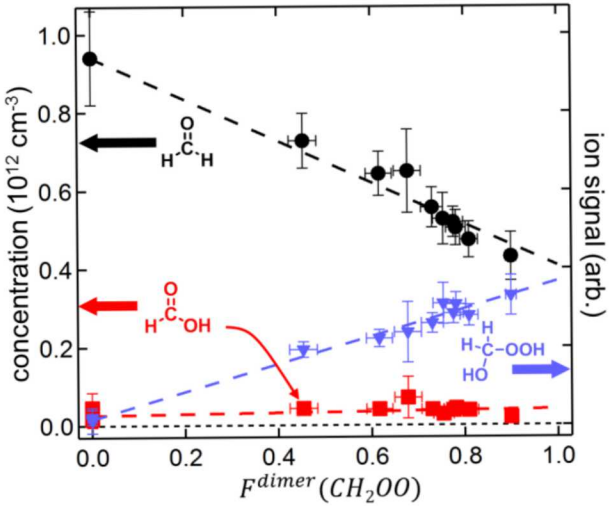
Water monomer reaction makes hydroperoxymethanol (hydroxymethyl hydroperoxide)

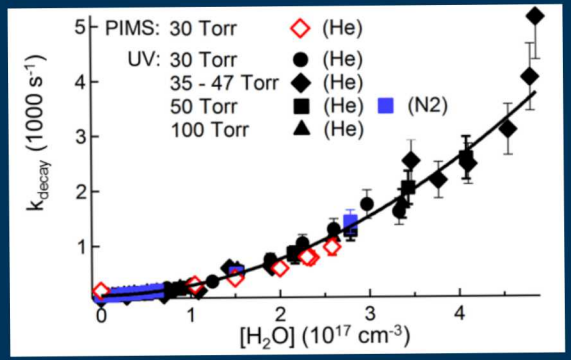
Suggestion that reaction with dimer makes ~ 50% HCOOH (Nguyen et al., *Phys. Chem. Chem. Phys.* **18**, 10241-10254 (2016))

Can confirm rate coefficient with UV absorption, photoionization

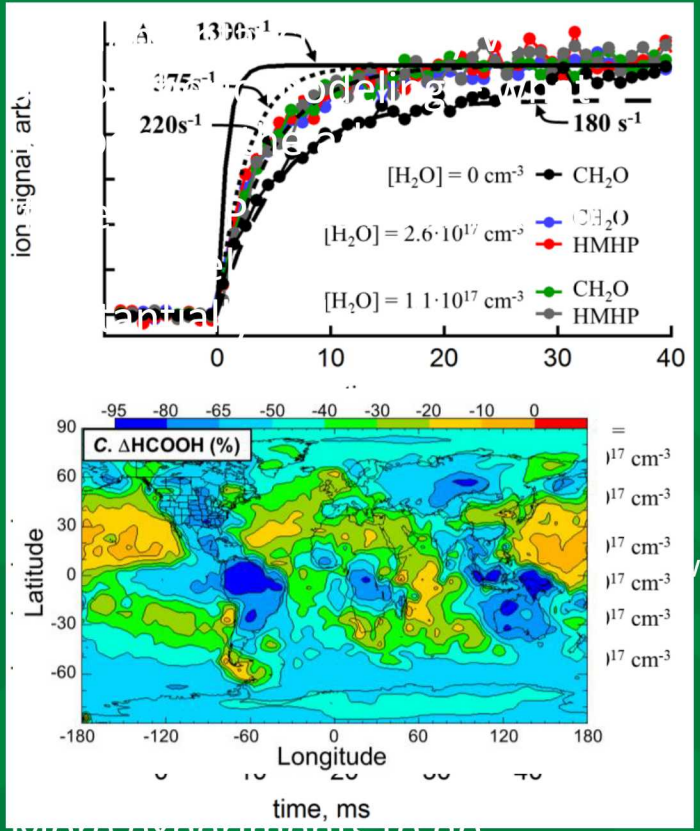
MPIMS measures all products

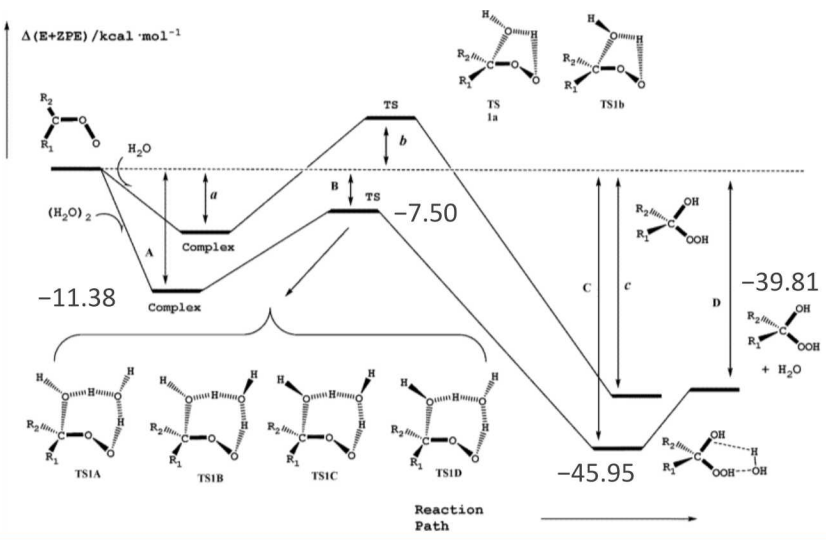
Lenny Sheps





Sheps et al., in review





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)

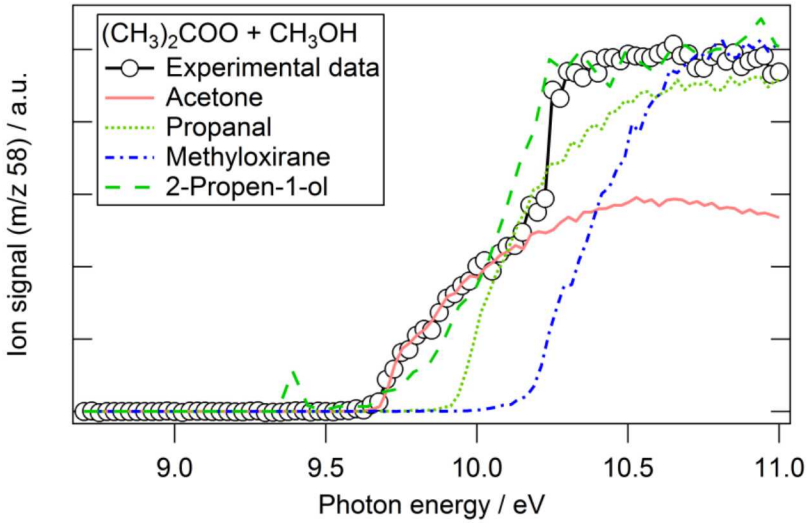
Do other proton-active species in the gas phase also insert?

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

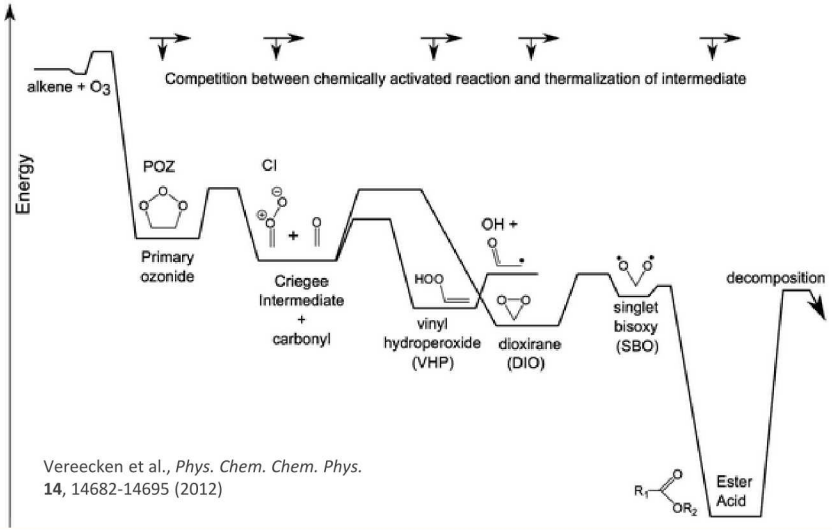
ROH? – reactions with CH_3OH insert in solution phase

Acetone oxide + methanol

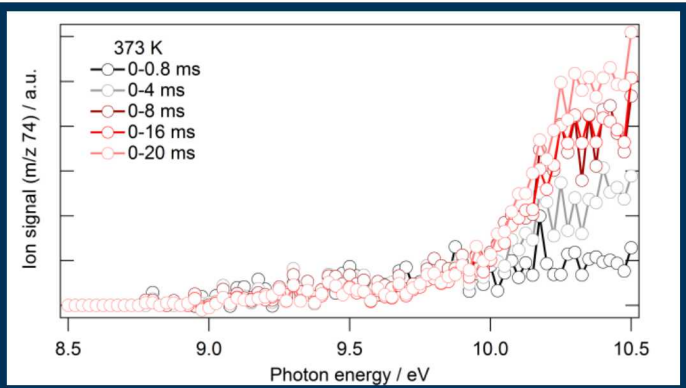
- No observed adduct mass
- Product at carbonyl mass?
- Product with CD_3OH is acetone



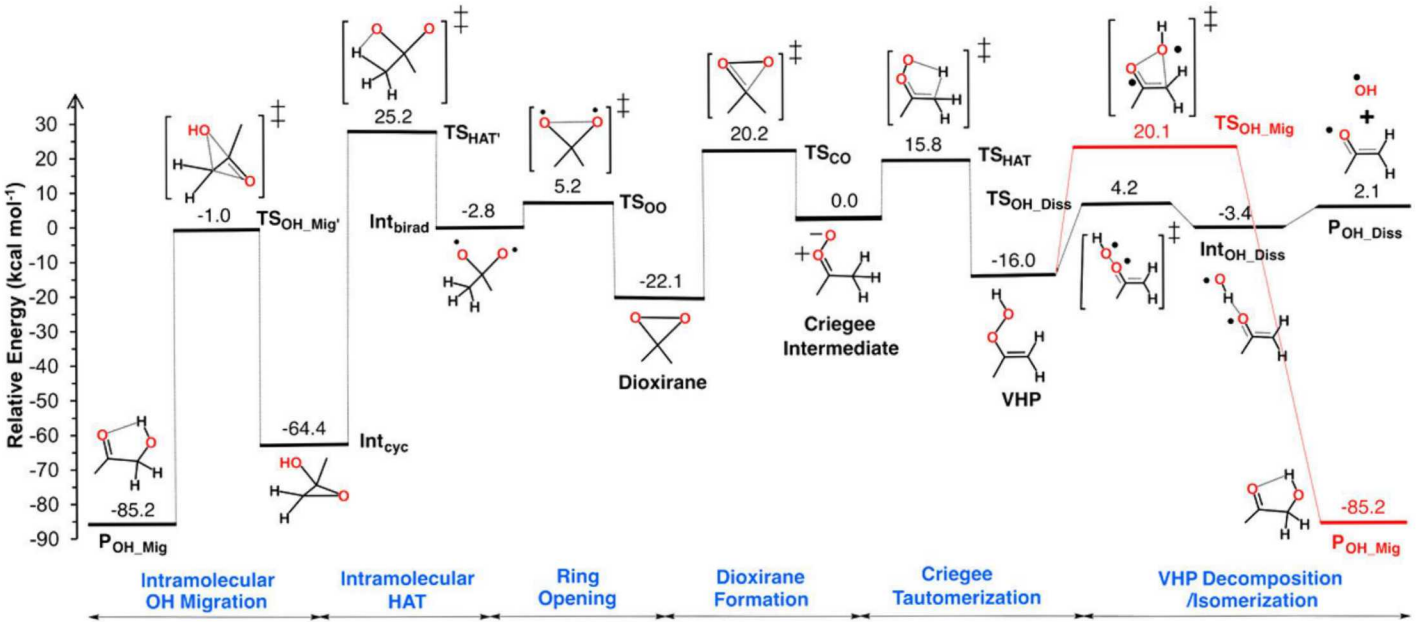
Caravan, Eskola et al., unpublished



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

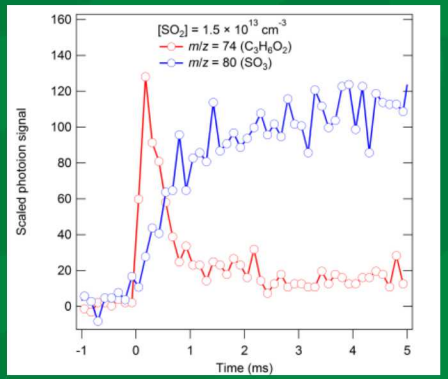


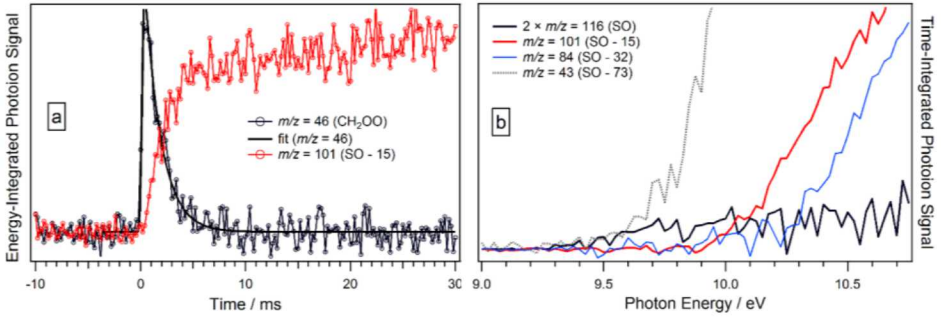
(Ward Thompson, in *J. Phys. Chem. A* **121** 16–23 (2017))

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

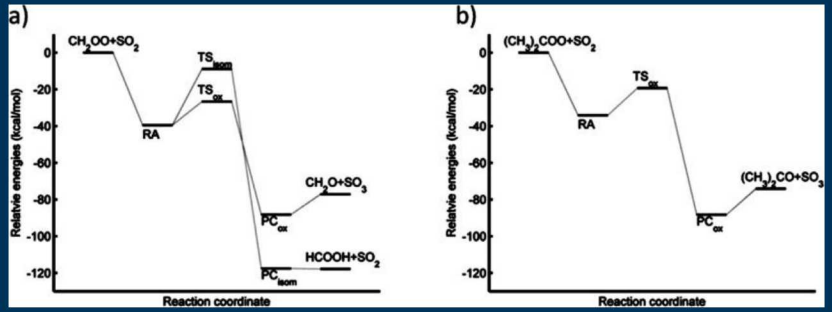
Detect secondary ozonides

Carbonyl oxides can transfer O atom – are these mediated by cycloaddition?





Eskola et al., unpublished

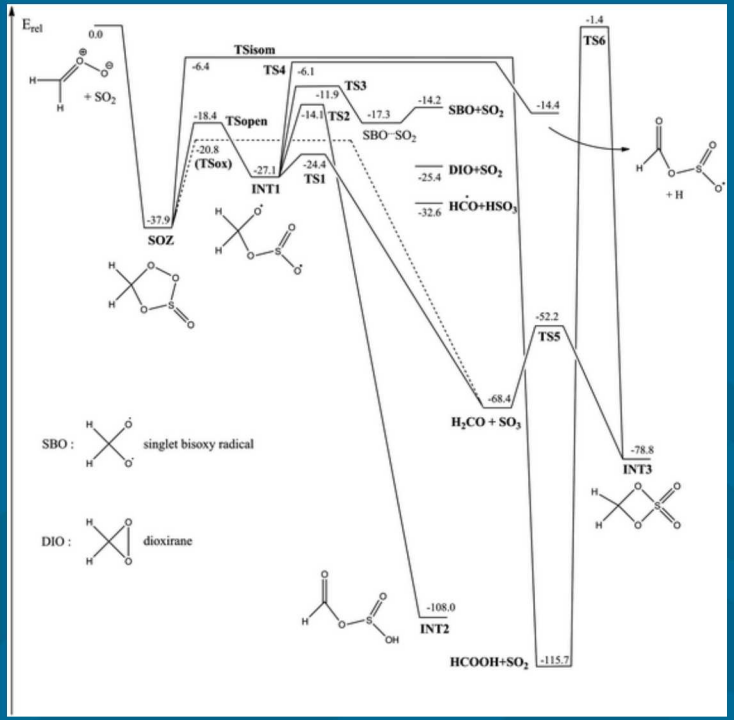


Kurtén et al., *J. Phys. Chem. A* **115**, 8669–8681 (2011)

SO_2 reactions make SO_3 but other pathways are possible

Pressure dependence 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



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

Reactions with radicals?

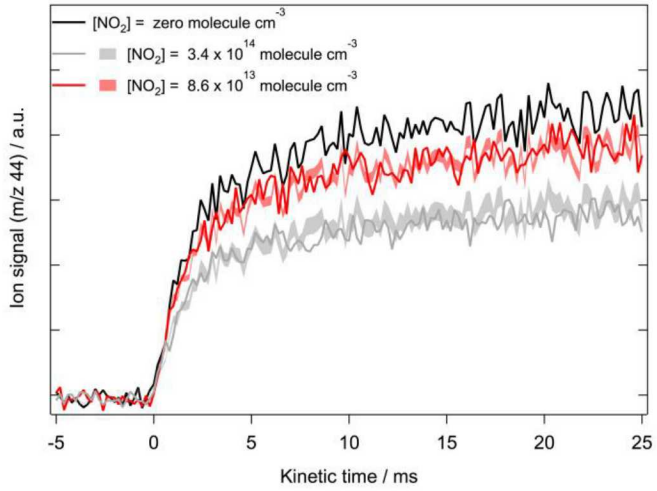
Look at NO_2 – how does this reaction proceed?

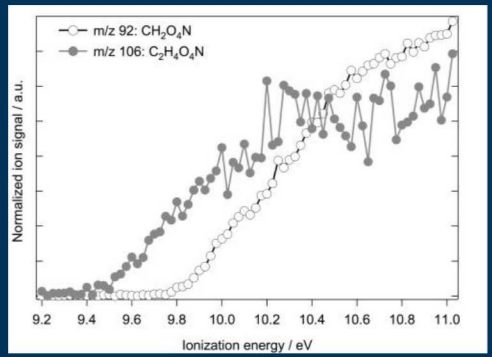
Could be source of NO_3?

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

Effect of carbonyl oxides on NO_3 may be even smaller than we thought

CH_3CHOO
+ NO_2





Caravan et al., *Faraday Discuss.* in press

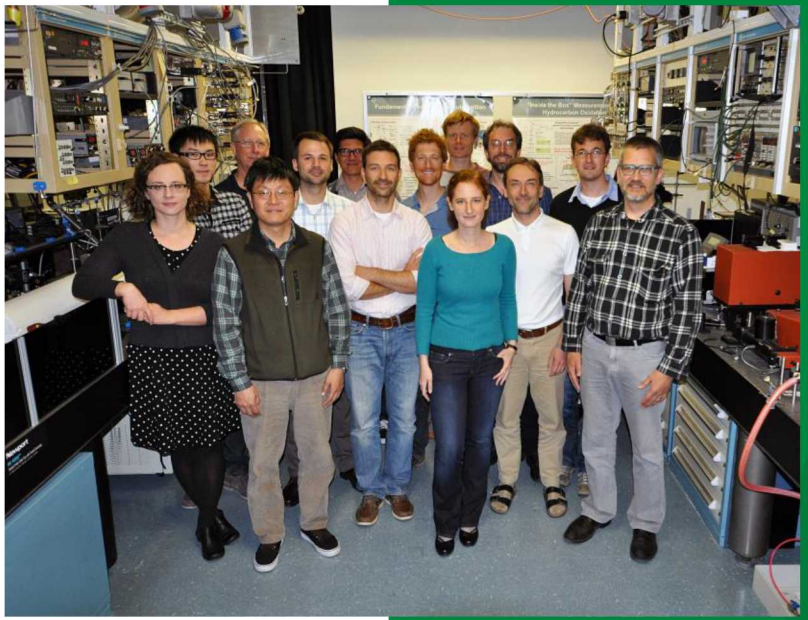
- Hydrocarbon structure and resonance stabilization can dramatically affect autoxidation processes

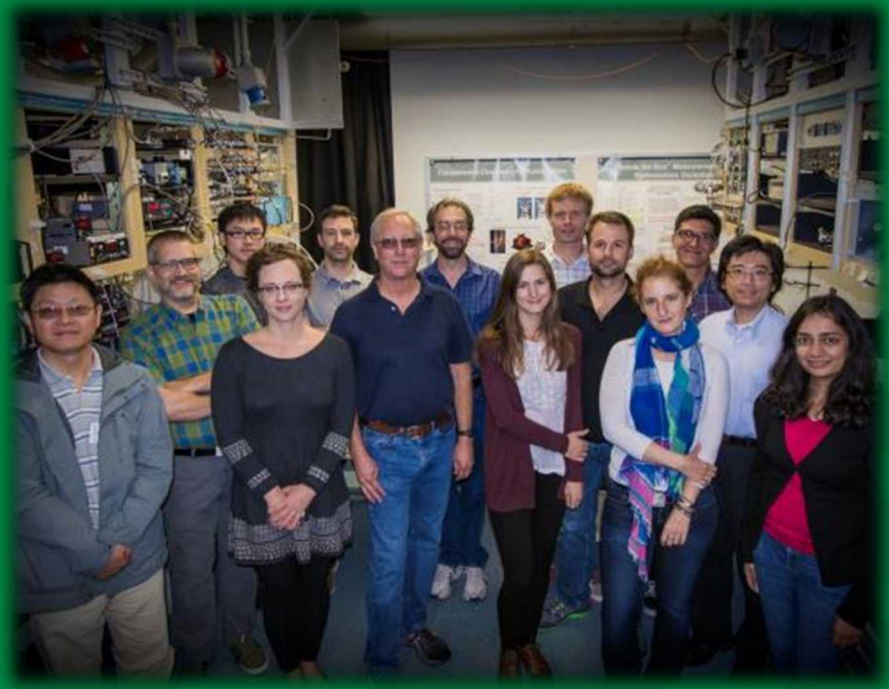
- Importance of carbonyl oxide reactions to the atmosphere depends on fate of adducts

Hydrocarbon oxidation research in the CRF Combustion Chemistry Department

Rebecca Caravan
Arkke Eskola
Brandon Rotavera
John Savee

David Osborn
Howard Johnsen
Lenny Sheps
Kendrew Au





Raybel Almeida
Ivan Antonov
Judit Zádor

Krupa Ramasesha
Ming-Wei Chen
Haifeng Huang

Adam Scheer
Oliver Welz

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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)