This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-10323C

Hydrocarbon oxidation and reactions on multiple potential energy surfaces

Craig A. Taatjes

Combustion Research Facility, Sandia National Laboratories, Livermore CA

Spectroscopy and Dynamics on Multiple Potential Energy Surfaces

Telluride Science Research Center Workshop

July 17-20 2018

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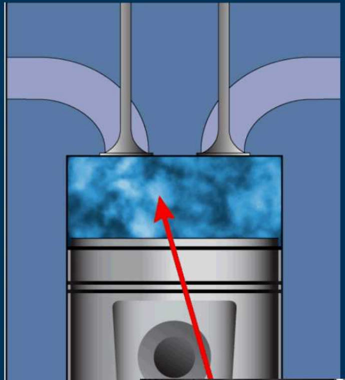
Hydrocarbon oxidation drives many complex chemical systems

Autoignition chemistry

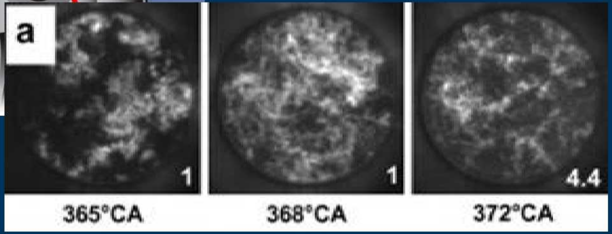


Complex networks of chemical reactions

Deliberate control of reaction conditions

Simple goal: clean/efficient

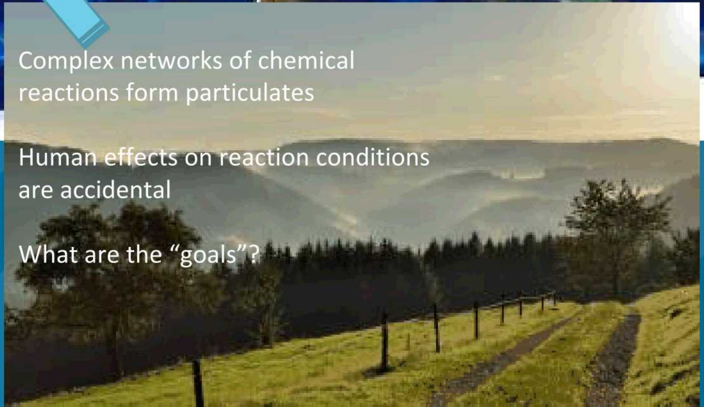
John Dec, Sandia



Tropospheric oxidation

William Putman, NASA/Goddard

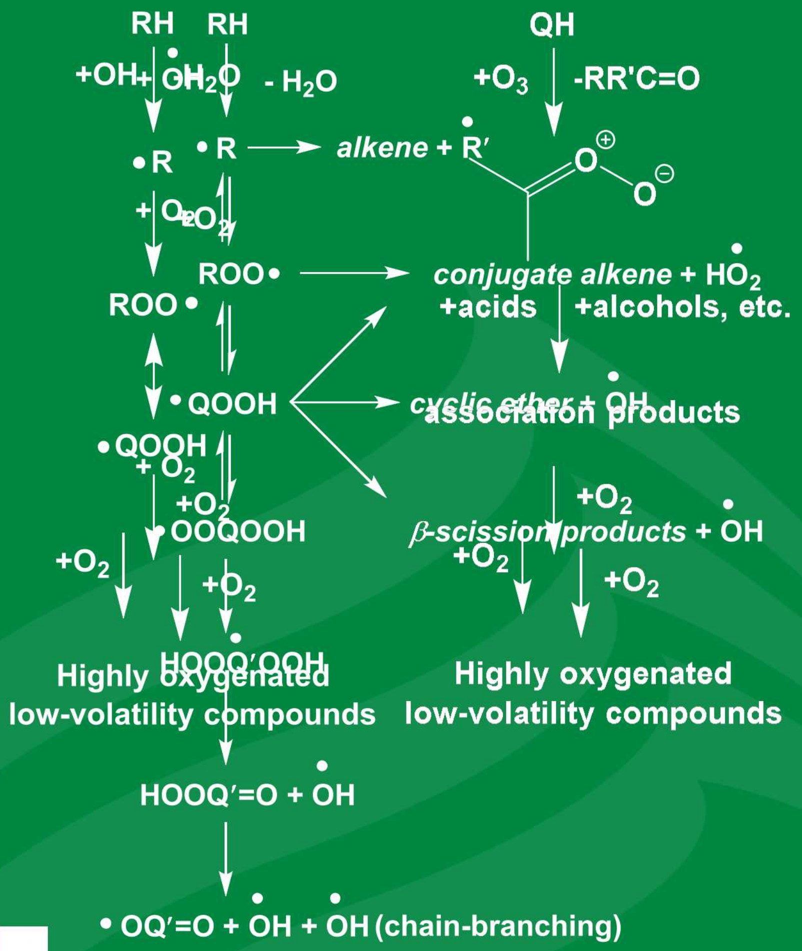
Complex but important!!
Look at what parts can be understood



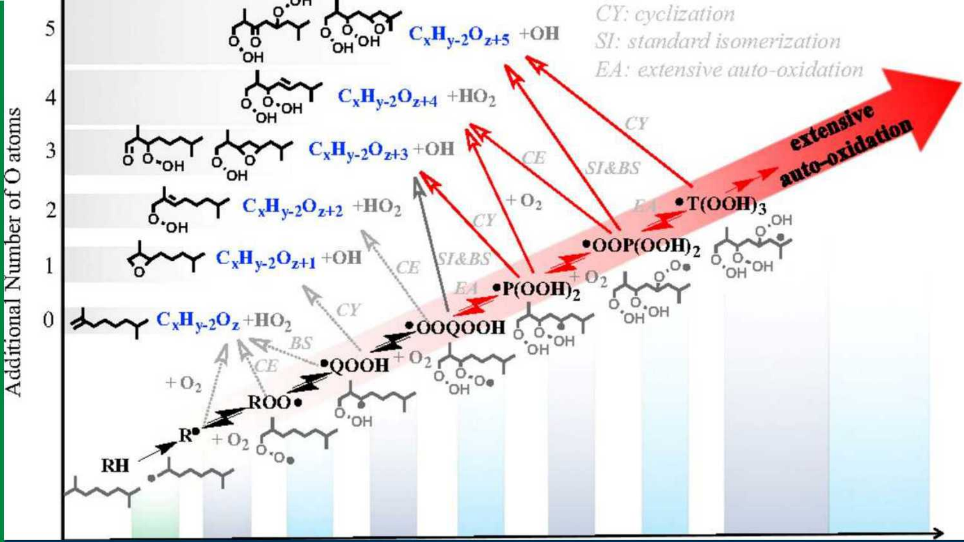
Complex networks of chemical reactions form particulates

Human effects on reaction conditions are accidental

What are the “goals”?



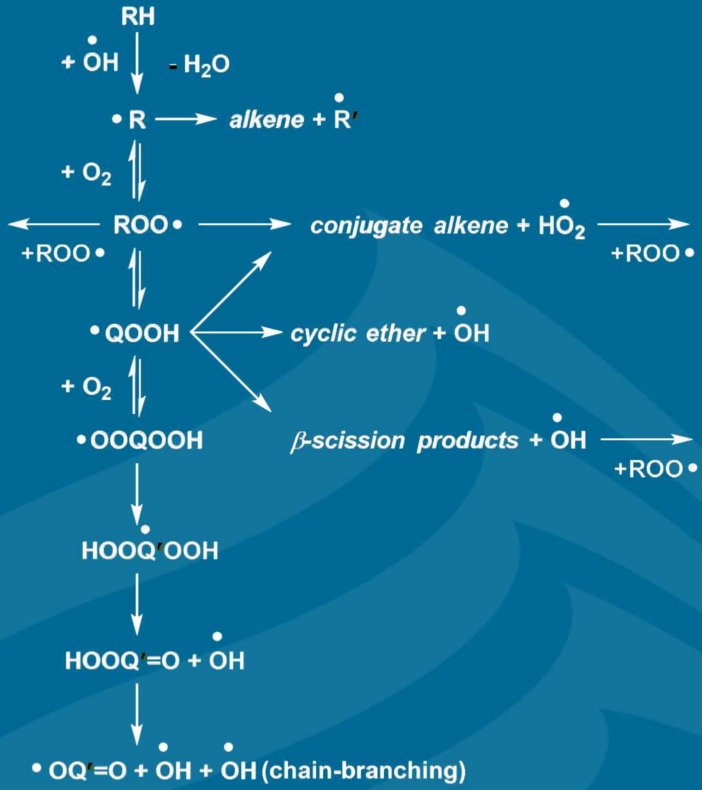
Zádor, J.; Taatjes, C. A.; Fernandes, R. X.
Prog. Energy Combust. Sci. **2011**, *37*, 341.



Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds
Wang et al., PNAS **114**, 13102-13107 (2017)

Tropospheric oxidation and autoignition share isomerizations and key intermediates

Other oxidants may involve other reactive intermediates



RH

+ $\dot{O}H$ ↓ − H_2O

$\cdot R$ → *alkene* + $\dot{R}'$

+ O_2 ⇅

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

+ROO•

⇅

•QOOH → *cyclic ether* + $\dot{O}H$

+ O_2 ⇅

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

↓

$HOO\dot{Q}'OOH$

↓

HOOQ′=O + $\dot{O}H$

↓

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

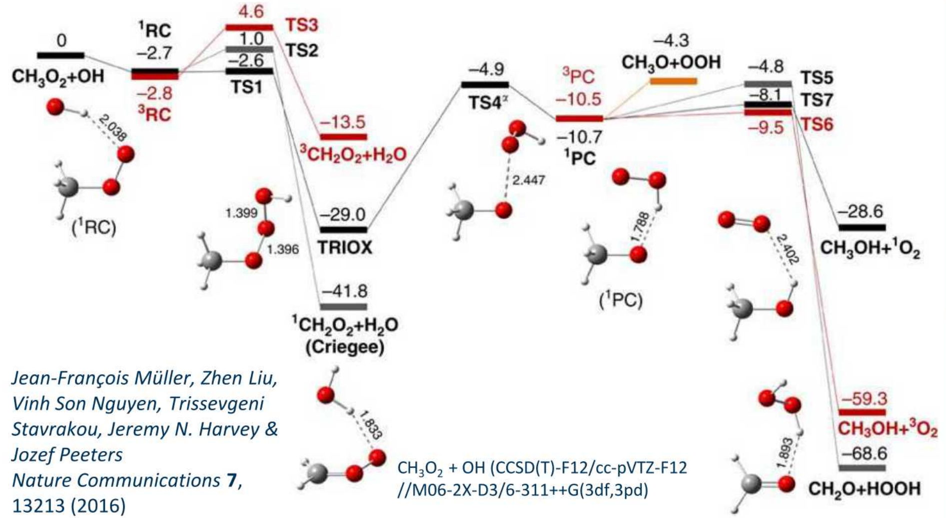
Zádor, J.; Taatjes, C. A.; Fernandes, R. X.
Prog. Energy Combust. Sci. **2011**, *37*, 341.

Other reactions can remove intermediate species and interrupt the chain

Radical-radical reactions can terminate chain chemistry

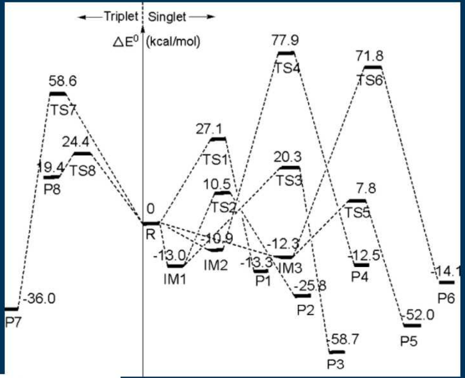
Some of these radical-radical reactions are important, e.g., in tropospheric chemistry

Radical-radical reactions involve more than one potential energy surface



Jean-François Müller, Zhen Liu, Vinh Son Nguyen, Trissevgeni Stavrakou, Jeremy N. Harvey & Jozef Peeters
Nature Communications **7**, 13213 (2016)

CH_3O_2 + OH (CCSD(T)-F12/cc-pVTZ-F12
//M06-2X-D3/6-311++G(3df,3pd)



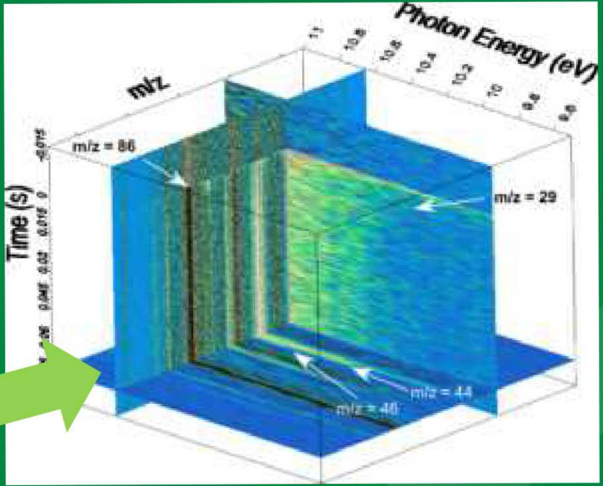
Yan-Ni Liang; Jun Li; Quan-De Wang; Fan Wang; Xiang-Yuan Li; *J. Phys. Chem. A* **2011,** 115, 13534-13541.

CH3O2• + CH3O2•

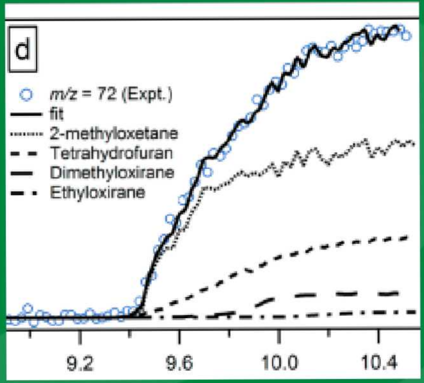
CCSD(T)/cc-pVTZ
//B3LYP/6-311++G(2df, 2p)

- Multireference transition states – e.g., radical-radical reactions with singlet and triplet product channels
    - Multireference electronic structure and effective two-transition state kinetics
    - Product branching can probe which state participates
- Even simple reactions start to appear pretty complicated
- Look at what parts can be understood

Synchrotron photoionization mass spectrometry can detect and characterize products and intermediates



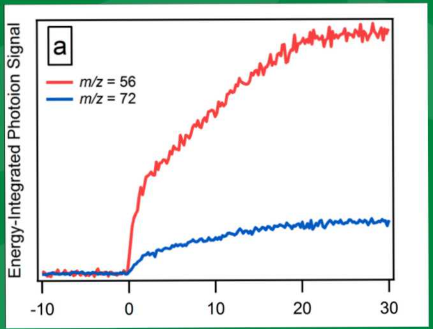
Form reactants in a controlled way by pulsed laser photolytic initiation



Isomer-Resolved Species Identification

David Osborn

Time-Dependent Chemical Kinetics



The reaction OH + CH_3OO has several product channels

The rate coefficient is f

enough to

trop

Heard

pp 770

Singl

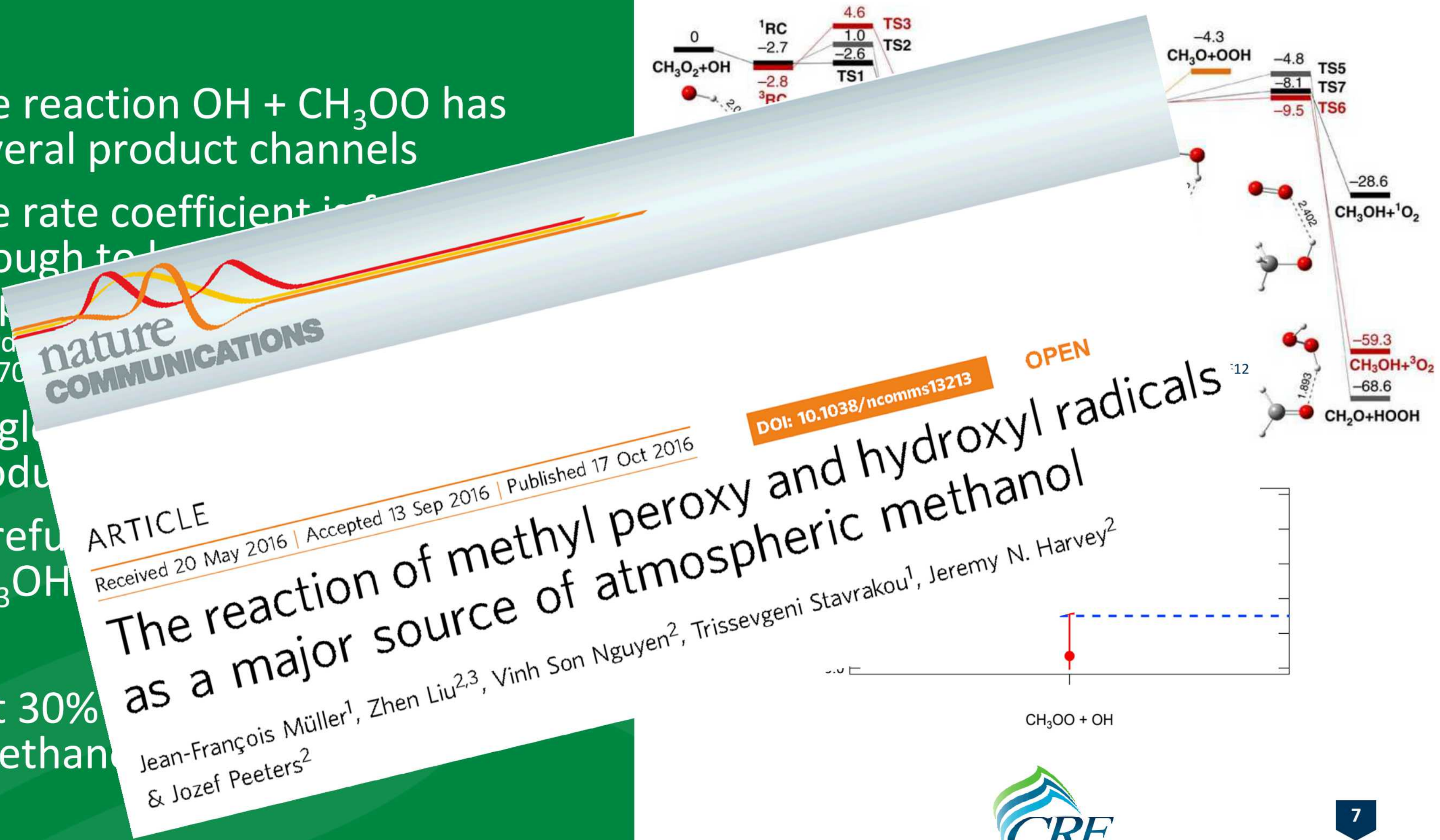
produ

Careful

CH_3OH

But 30%

“methan



nature COMMUNICATIONS

ARTICLE

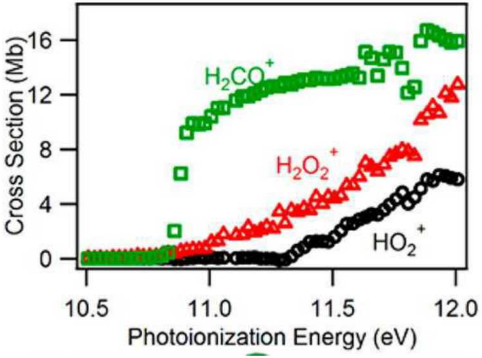
OPEN
DOI: 10.1038/ncomms13213
Received 20 May 2016 | Accepted 13 Sep 2016 | Published 17 Oct 2016

The reaction of methyl peroxy and hydroxyl radicals as a major source of atmospheric methanol

Jean-François Müller[1], Zhen Liu[2,3], Vinh Son Nguyen[2], Trissevgeni Stavrakou[1], Jeremy N. Harvey[2] & Jozef Peeters[2]

- That looks like a challenge to experiment!
- Make CH_3OO and OH photolytically (CH_3I / H_2O_2 / O_2 or F + CH_4 / H_2O / O_2)
- Isotopically label reactants to distinguish products we want
  - $^{13}CH_3OO$ + OH
  - CH_3OO + OD
- Have photoionization cross sections for quantifying H_2O_2, CH_2O, CH_3OH

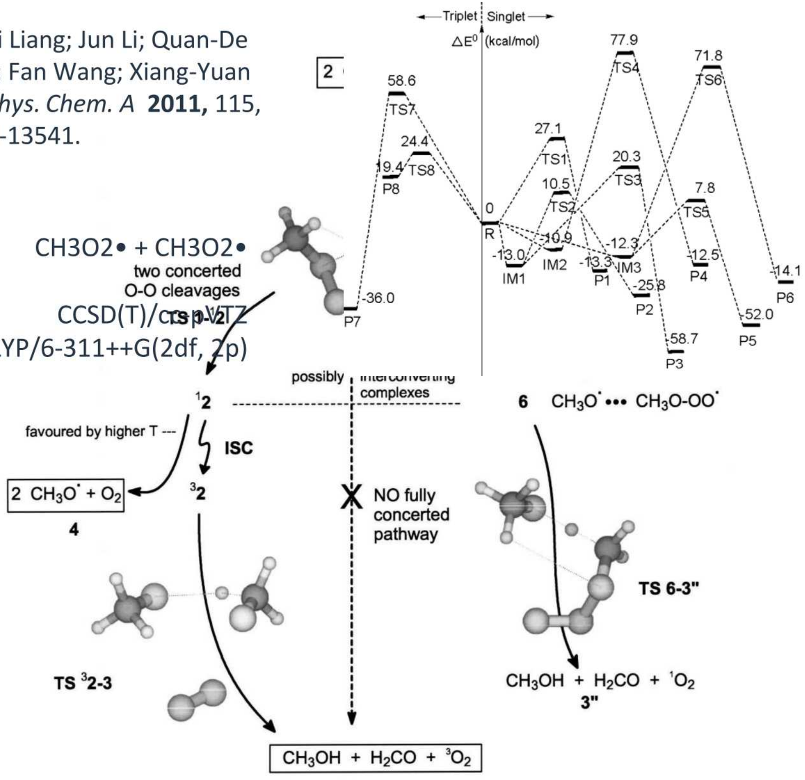
Ratios of cross sections to that of methanol measured precisely (Dodson et al., *J. Phys. Chem. A*, 2015, 119, 1279–1291)



Absolute scale by reference to propene

Consider competing reactions that make methanol – like CH_3OO self-reaction

Yan-Ni Liang; Jun Li; Quan-De Wang; Fan Wang; Xiang-Yuan Li; *J. Phys. Chem. A* **2011,** 115, 13534-13541.



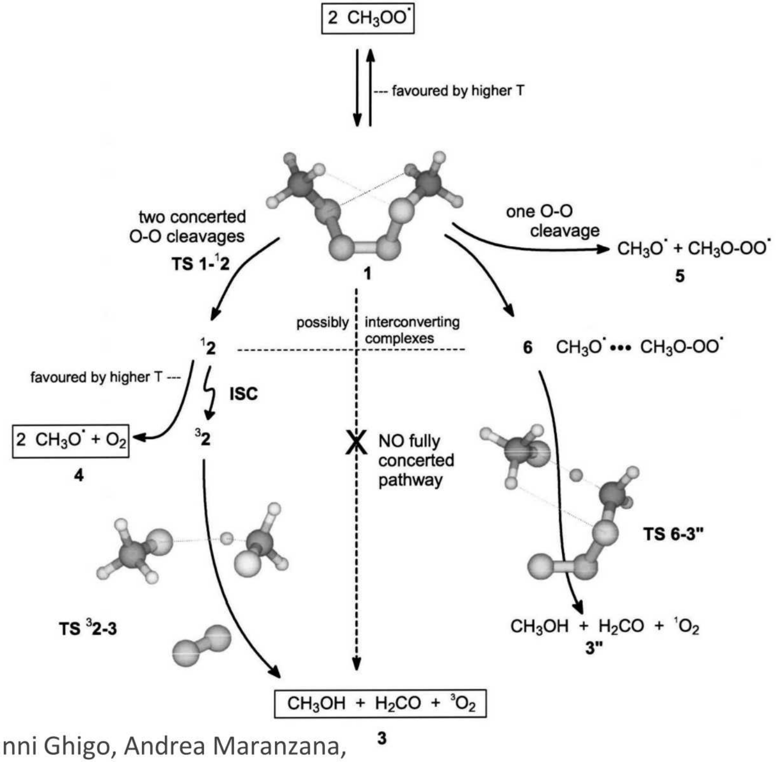
CH3O2• + CH3O2•

CCSD(T)/cc-pVTZ
//B3LYP/6-311++G(2df, 2p)

Giovanni Ghigo, Andrea Maranzana, and Glauco Tonachini
J. Chem. Phys. 118, 10575 (2003);

CAS(16,12)-PT2/6-311G(2*d f* ,*p*)

- CH_3OO self reaction makes 2 CH_3O or CH_2O and CH_3OH
  - CH_2O : CH_3OH ratio implies methoxy channel 41 ± 4% (Tyndall et al., *J. Phys. Chem. A*, 1998, 102, 2547–2554)
  - CH_3OOCH_3 < 6%
  - Same products as OH + CH_3OO!
- Theory on CH_3OO reaction is interesting
- Barriers seem too high!
- Suggested ISC to make triplet product channel?



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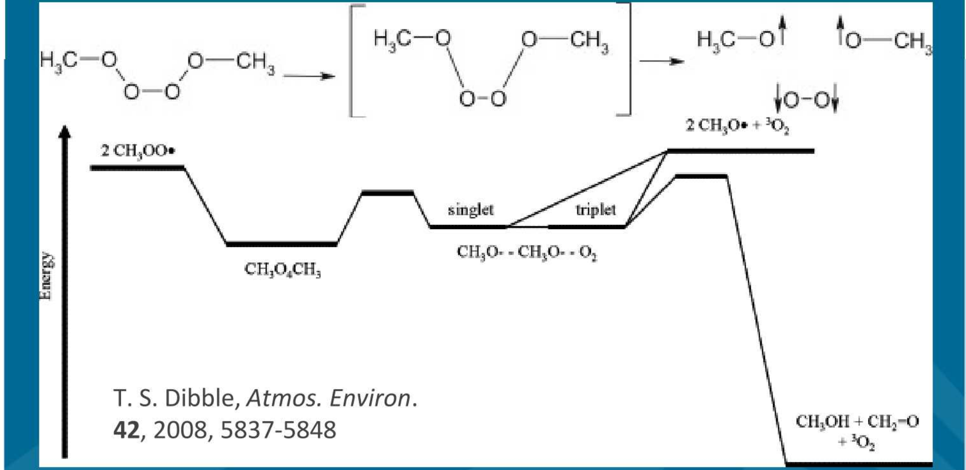
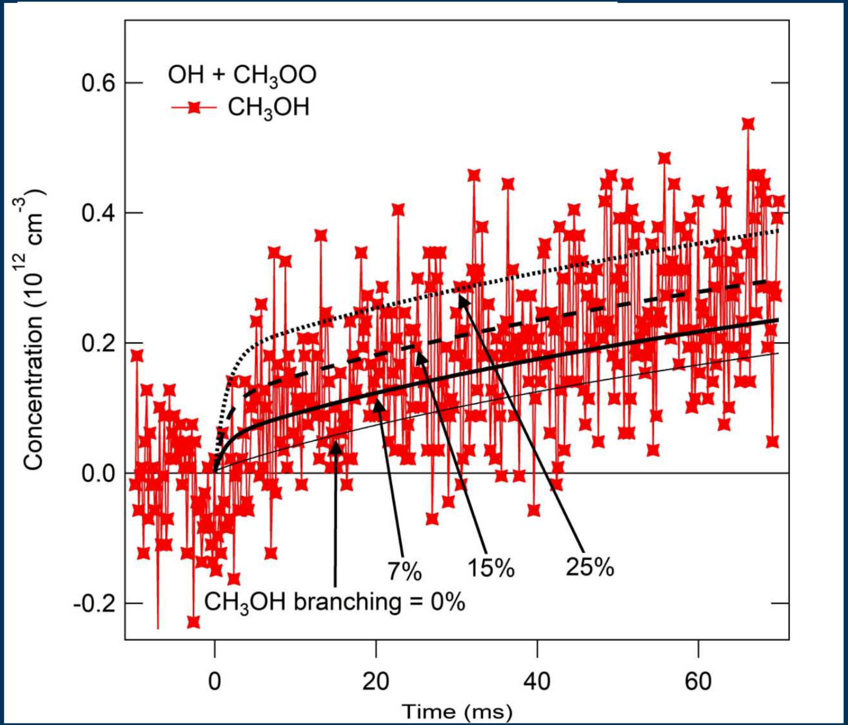


T. S. Dibble, *Atmos. Environ*. **42**, 2008, 5837-5848

Objection that 2 CH_3O would make CH_3OOCH_3 rather than disproportionate

But CH_3O self reaction is dominated by disproportionation (~ 9x addition, Shortridge & Heicklen, *Can. J. Chem.* **51** (1973))

- Getting branching fractions from absolute concentrations entails lots of uncertainties
- Initial radical concentration (depletion profile)
- Methoxy is converted rapidly to formaldehyde at high O_2
- But what about other products?
- CH_3OOCH_3 is "negligible"
  - But there it is! Use upper limit value for its branching



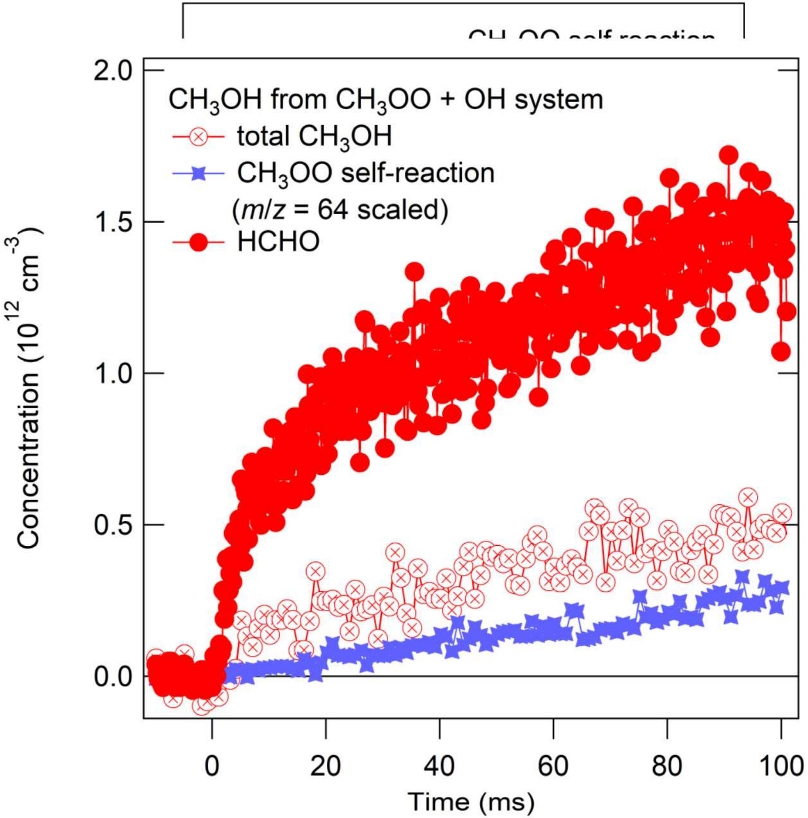
Propagating uncertainties gives discouraging picture – but there is a way out …

Calibration quantities are measured from ratios

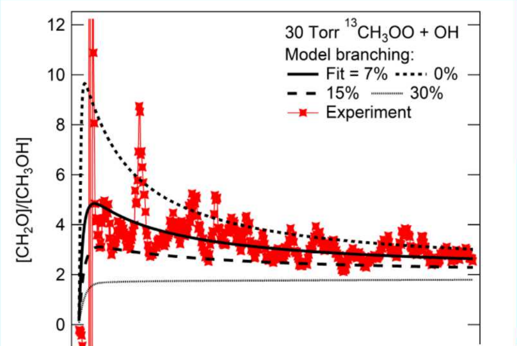
CH_2O and CH_3OH have similar dependence on many experimental factors

Ratio is much more robust to many kinetic parameters

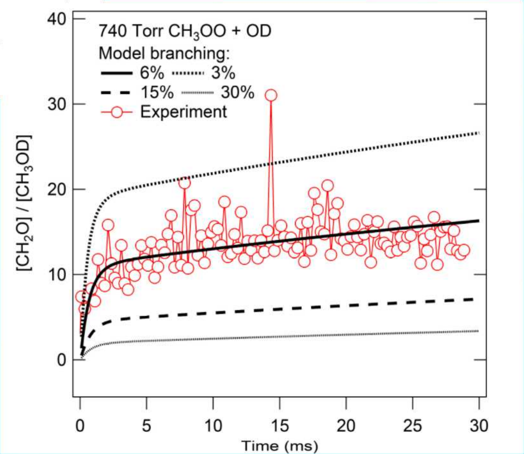
Can see clear added CH_3OH production when OH is added



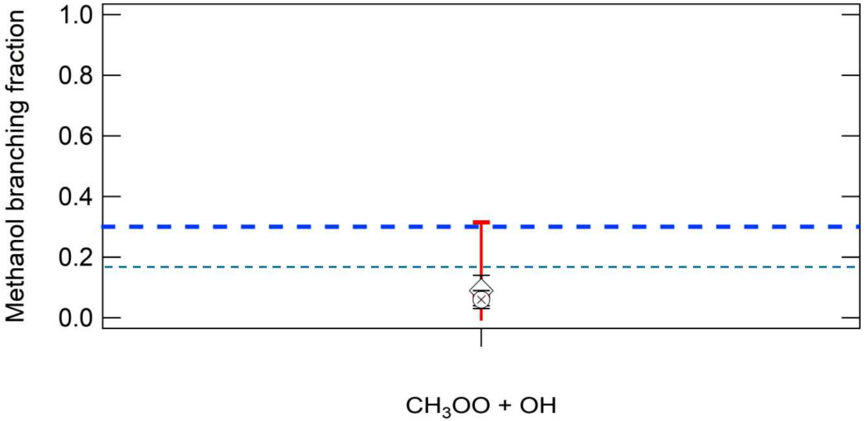
Fitting ratio of CH_2O to CH_3OH gives value for branching ratio



30 Torr CH_3OH branching fraction 9 ± 5 %



740 Torr CH_3OH branching fraction 6 ± 2 %



In fact, branching fraction of 15% is “break even” for the effect of the reaction on tropospheric methanol

Reaction may *reduce* CH_3OH levels

Caravan et al., in press

Measured branching *ratio* for reaction – what about other products?

Criegee intermediate negligible

Stabilization of trioxide calculated to be ~ 11% at 1 atm (Müller et al.)

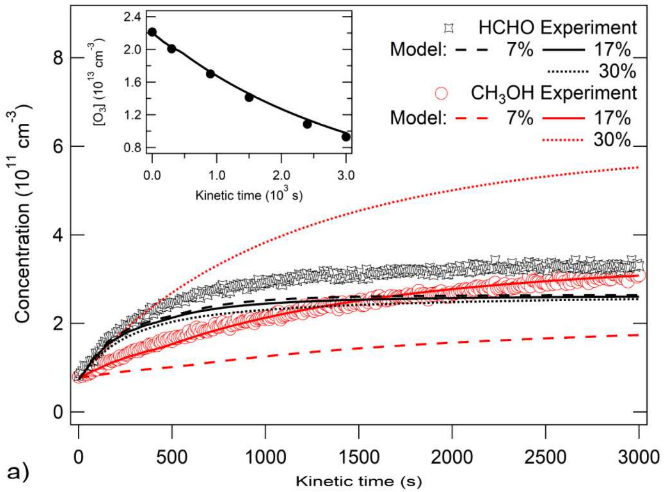
Chamber experiments with PTR-MS show apparently higher CH_3OH (17%)!

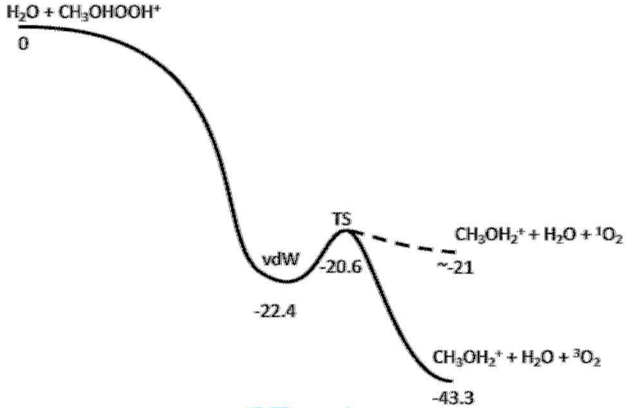
Chamber sampling might convert trioxide heterogeneously

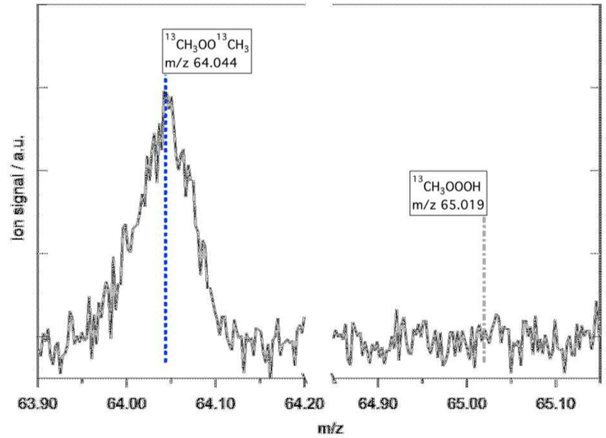
PTR-MS of trioxide may not give signal at parent mass

If that explanation is right, MPIMS should see trioxide product at high P

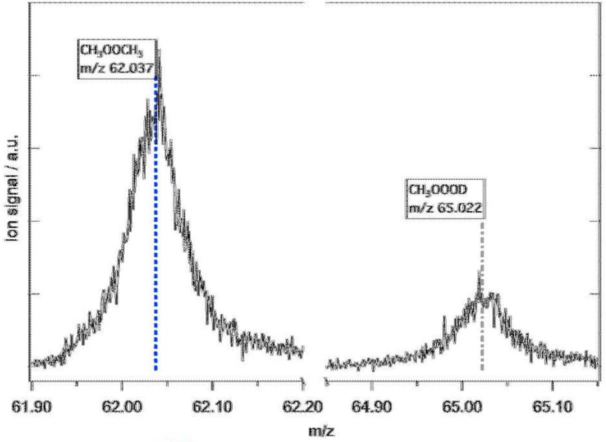
Caravan et al., in press







$^{13}CH_3OO + OH$
30 Torr

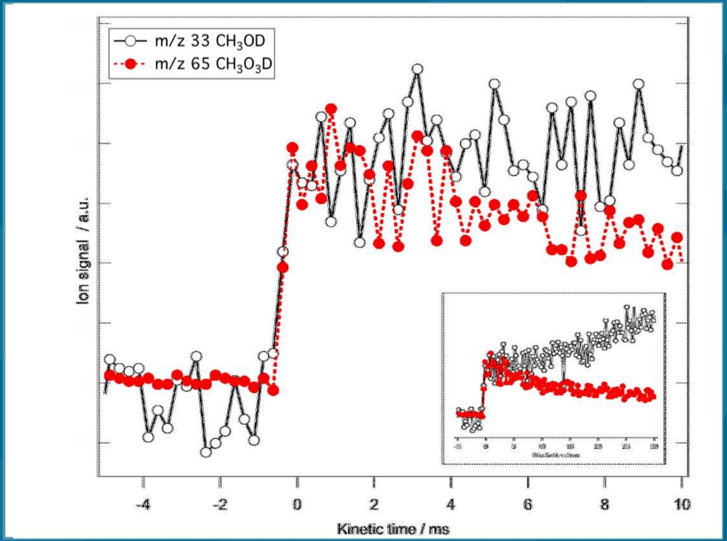


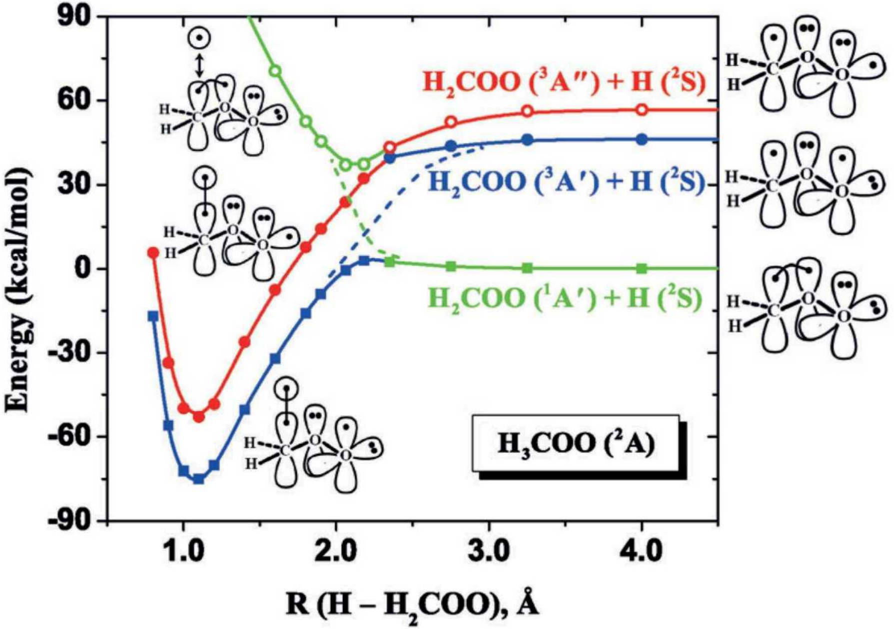
$CH_3OO + OD$
740 Torr

Caravan et al., in press

Trioxide should appear at high pressure (Müller et al. calculate 9.6% at 740 Torr) but not at low pressure (0.016% at 30 Torr)

Trioxide should rise rapidly, with no secondary formation





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

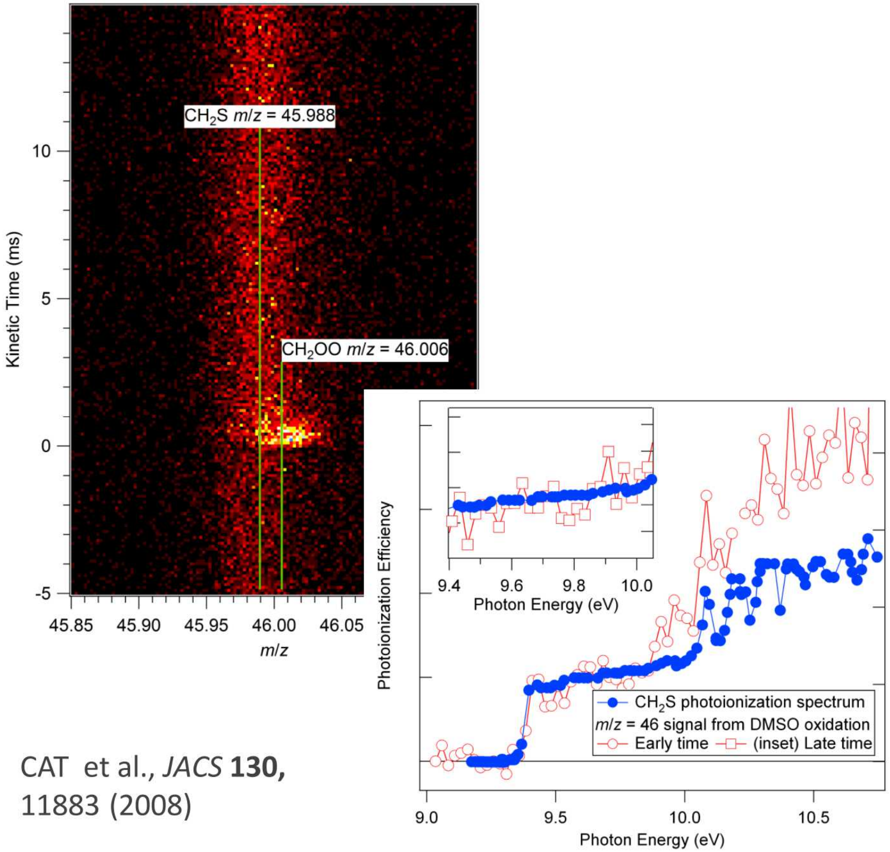
- Criegee intermediates have multireference electronic character
  - Ground state is dominantly the closed-shell singlet zwitterion

  - 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)
  - Many reactions with closed-shell species are much faster!

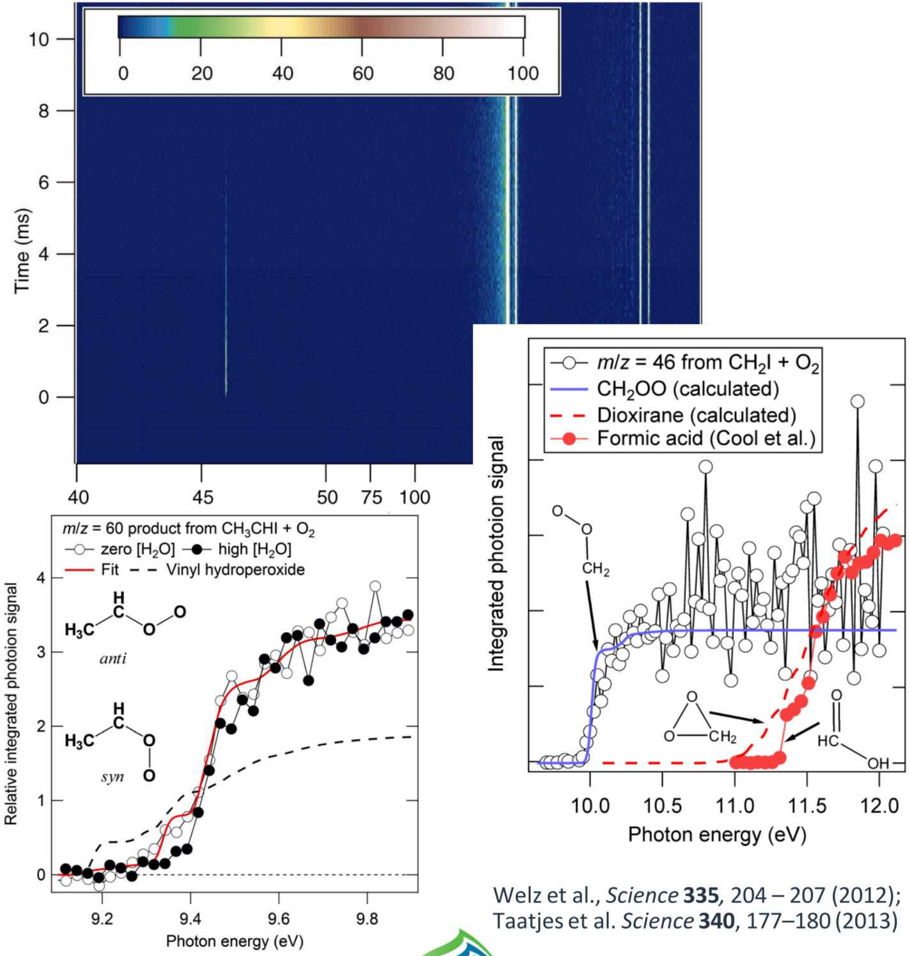
For Criegee intermediates have strategy for direct synthesis

Verified by mass, kinetics, and spectrum

Reaction of CH_3SOCH_2 with O_2 makes CH_2OO



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



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

For Criegee intermediates have strategy for direct synthesis

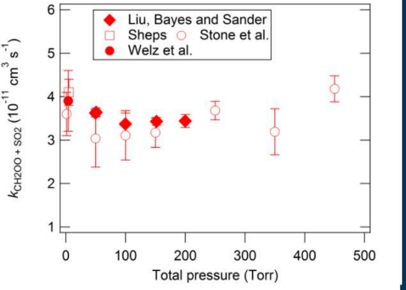
Verified by mass, kinetics, and spectrum

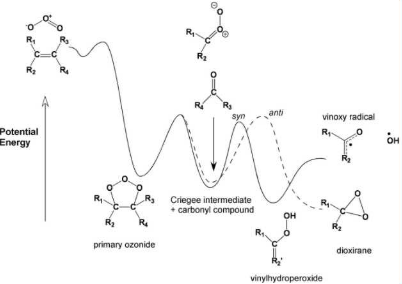
Reaction of CH_3SOCH_2 with O_2 makes CH_2OO

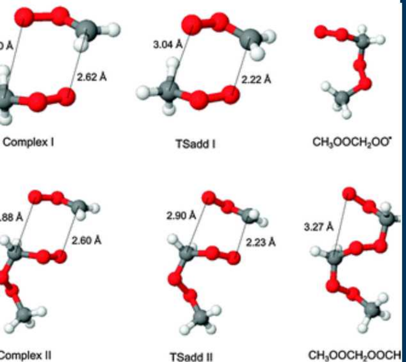
Reaction of gem-iodoalkyl radicals with O_2 makes lots of carbonyl oxides

Now can measure carbonyl oxide reaction kinetics directly

Craig Murray (Irvine); Marsha Lester (Penn); Jim Lin (IAMS); Andrew Orr-Ewing (Bristol); Bill Green (MIT); Paul Seakins, Dan Stone (Leeds), etc.







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

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))

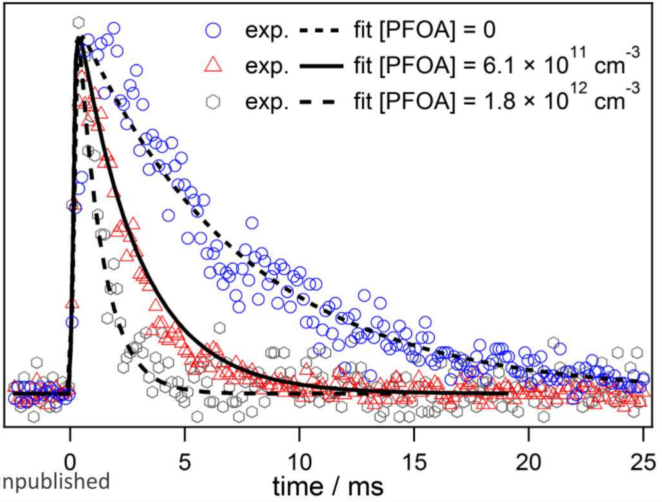
Carbonyl oxide reactions in solution: ROH>H_2O>CH_3CO_2H

In gas phase RCO_2H >> ROH, H_2O

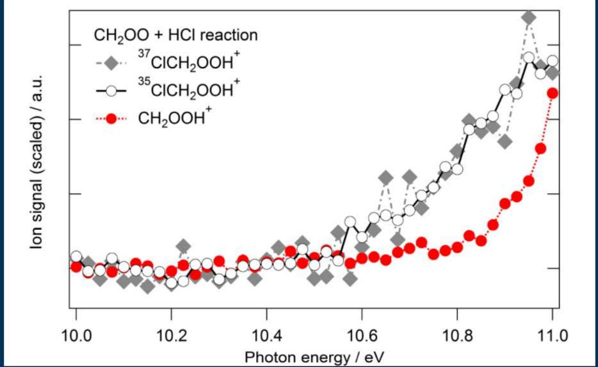
Fast reaction general for all acids

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

Products are hydroperoxyesters (c.f. Cabezas & Endo, *ChemPhysChem* **18**, 2017, 1860-1863)



Eskola et al., unpublished



Caravan, Rotavera et al., unpublished

Reactions with radicals?

Look at NO_2 – how does this reaction proceed?

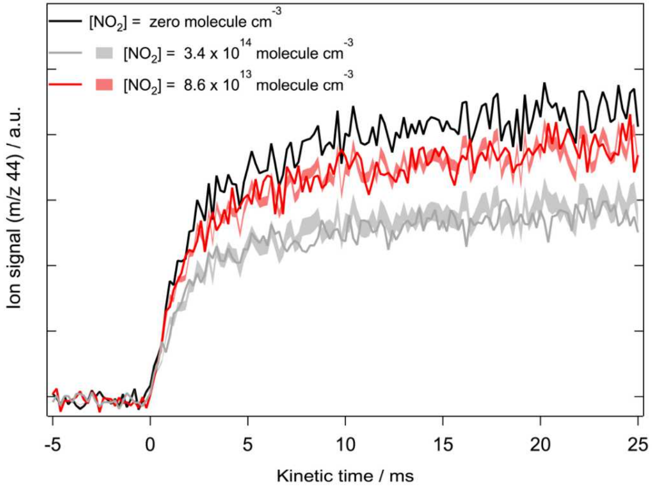
Could be source of NO_3?

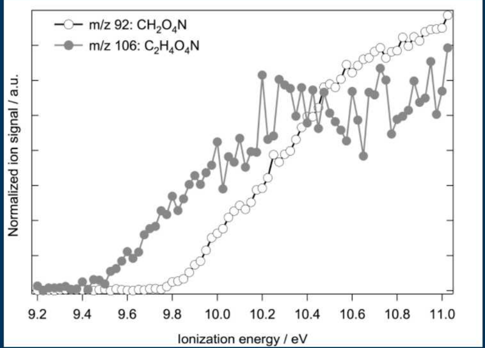
- No NO_3 observed
- See signal at mass of adduct
- See decrease in carbonyl
- Upper limit of 30% NO_3

May limit effect of carbonyl oxides on NO_3 concentrations

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

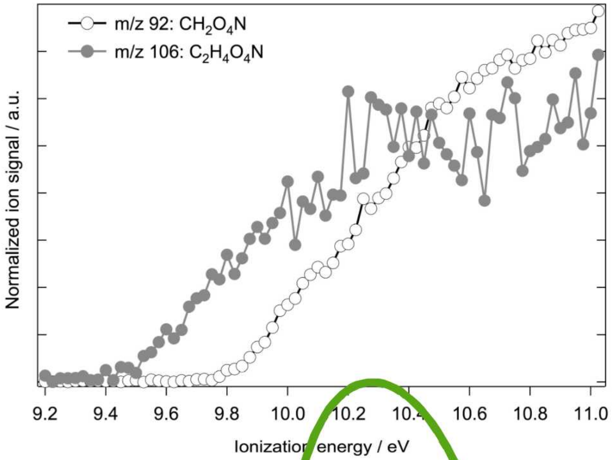
CH_3CHOO
$+ NO_2$

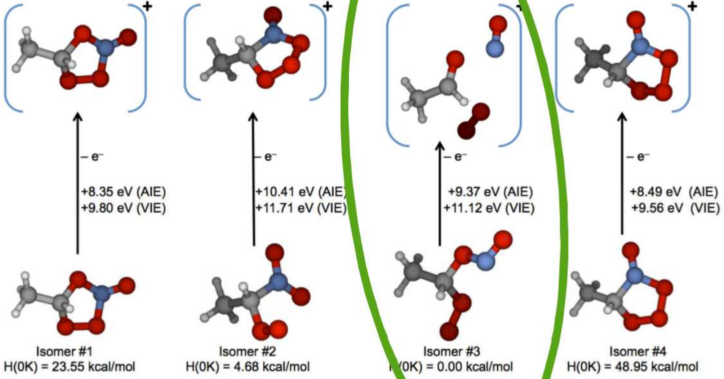




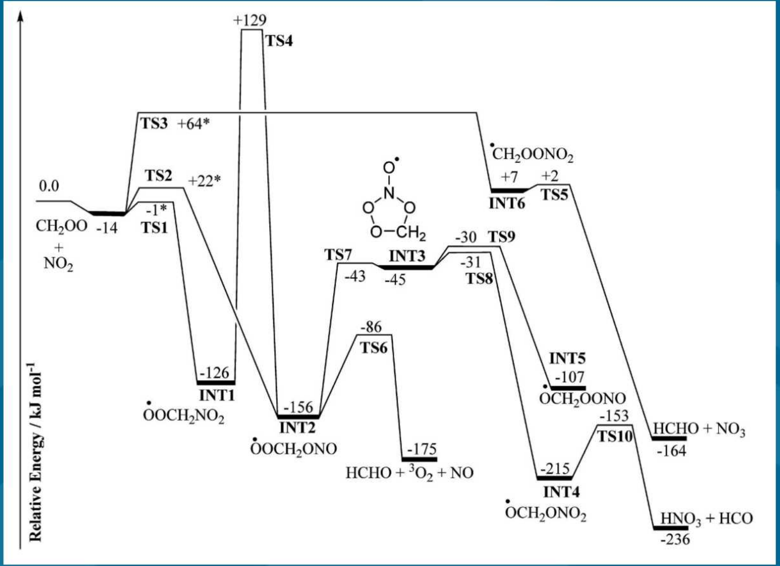
Photoionization spectrum suggests adduct identification

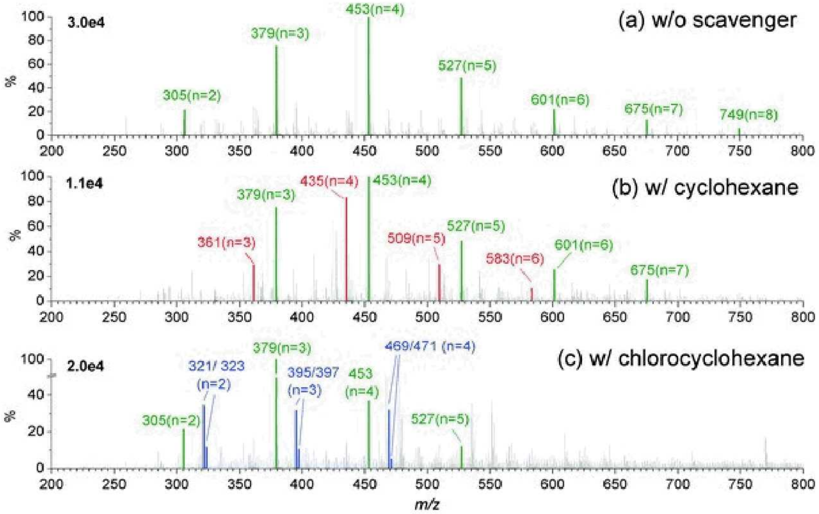
Adduct formation consistent with theory (Vereecken and Nguyen, *Int. J. Chem. Kinet.* **49**, 752-760 (2017))

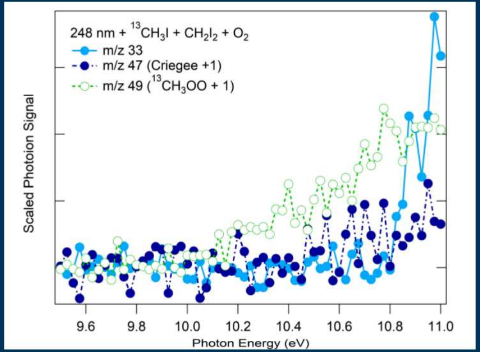




Caravan et al., *Faraday Discuss.* **200**, 313-330 (2017)







What about “real” radicals?

Suggestion that reactions of Criegee intermediates with alkylperoxy radicals can initiate oligomerization reactions (Zhao et al., *Physical Chemistry Chemical Physics* 17:12500-14)

Make CH_3OO and CH_2OO together

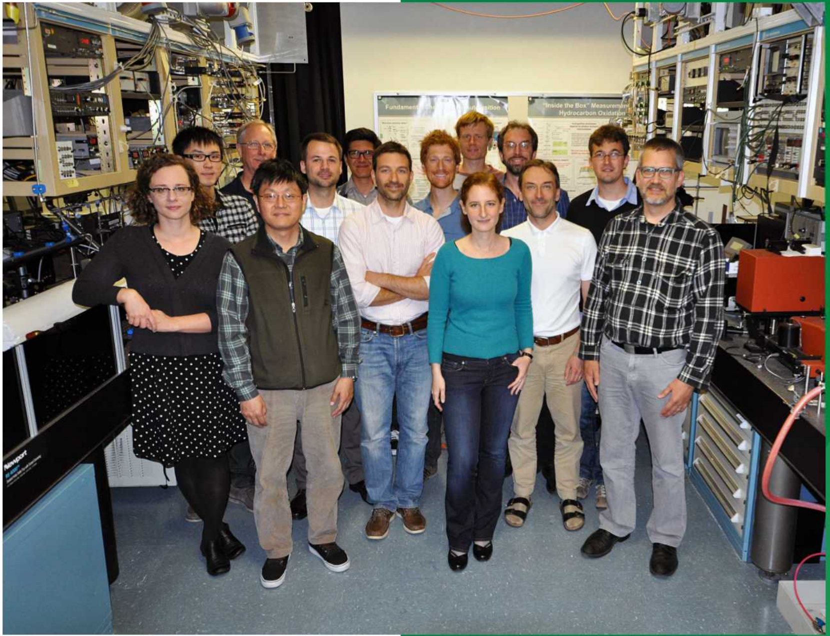
Observe possible products but only at dissociative ionization mass

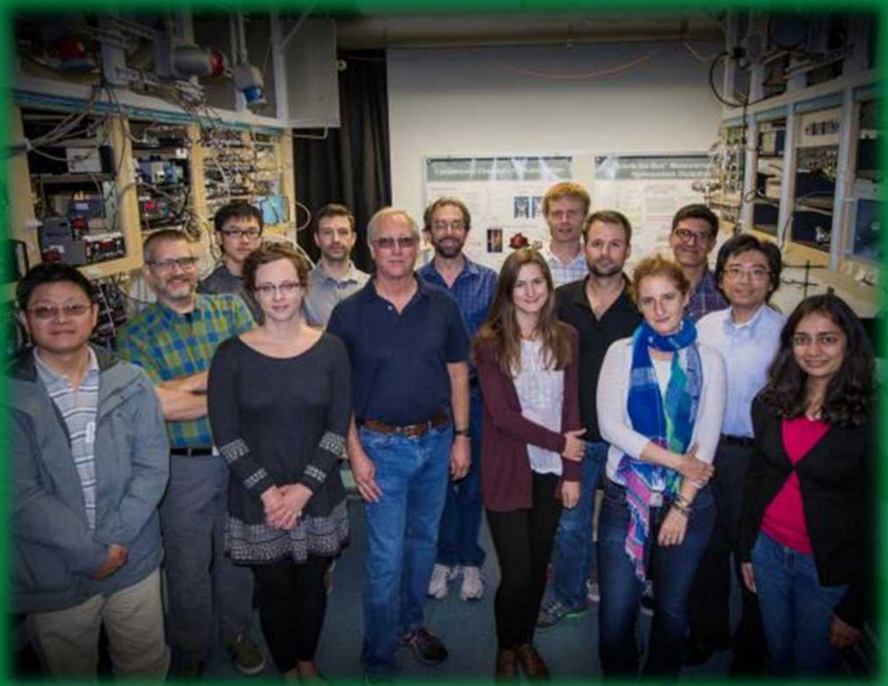
Needs more investigation!

Hydrocarbon oxidation research in the CRF Combustion Chemistry Department

Rebecca Caravan
Arkke Eskola
Brandon Rotavera
John Savee
Kai Moshammer

David Osborn
Howard Johnsen
Lenny Sheps
Kendrew Au
Nils Hansen





Raybel Almeida
Ivan Antonov
Judit Zádor

Krupa Ramasesha
Ming-Wei Chen
Haifeng Huang

Adam Scheer
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