SAND2019-10328C

Reactions of 'Elusive' Intermediates & Trying to Understand Complicated Chemistry Step by Step

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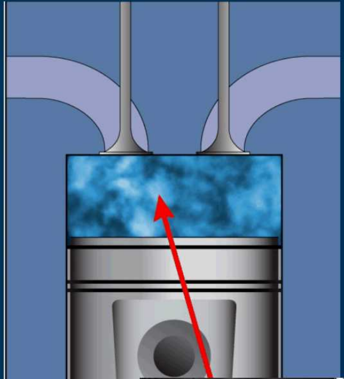
2018 Gordon Conference on Molecular Interactions & Dynamics

Stonehill College, Easton MA

Comparing different (but related) chemical systems

Autoignition chemistry

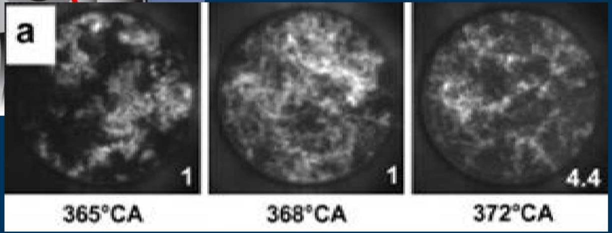


Complex networks of chemical reactions

Deliberate control of reaction conditions

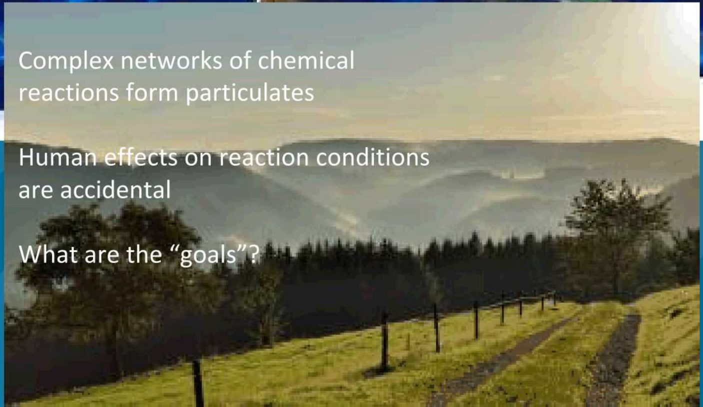
Simple goal: clean/efficient

John Dec, Sandia



Tropospheric oxidation

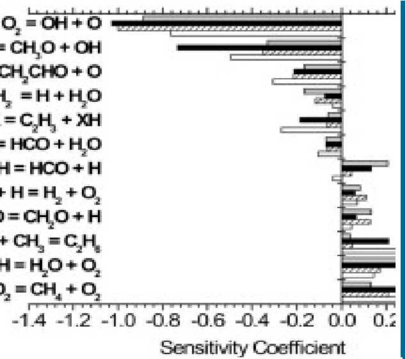
William Putman, NASA/Goddard

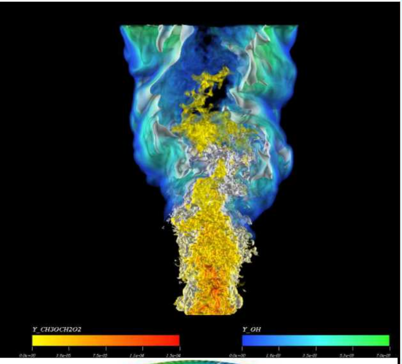


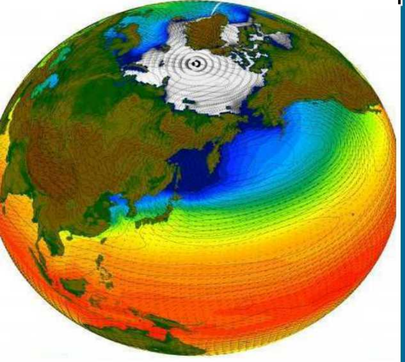
Complex networks of chemical reactions form particulates

Human effects on reaction conditions are accidental

What are the “goals”?







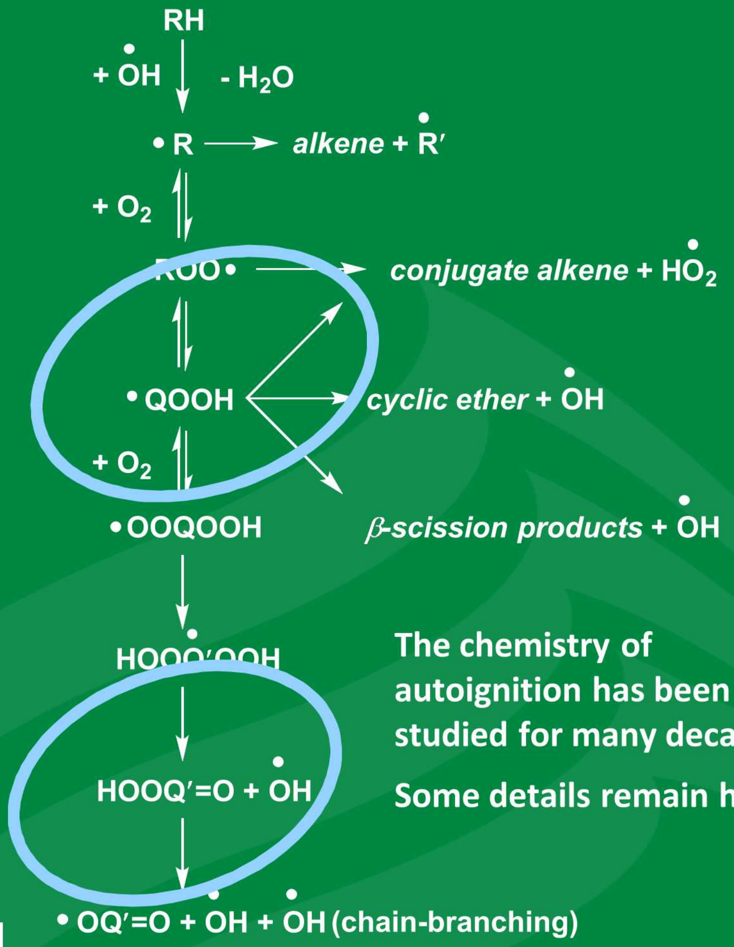
Even for complex systems, chemistry often depends on reactions of a few key intermediates

- ROO• ↔ •QOOH —(+O_2)→ ketohydroperoxides
- Criegee intermediates

Reactions often have multiple possible channels that have different impacts on the complex system behavior

Characterizing individual crucial intermediate steps is often difficult if one looks only at the global system

Kinetic Models for Ignition Chemistry Require Knowing Reactions of “Intermediates”

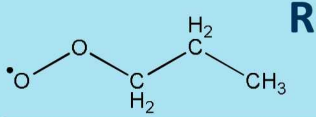

RH
$+ \dot{O}H$ $- H_2O$
$\bullet R \longrightarrow$ *alkene* $+ \dot{R}'$
$+ O_2$
$ROO\bullet \longrightarrow$ *conjugate alkene* $+ H\dot{O}_2$
$\bullet QOOH \longrightarrow$ *cyclic ether* $+ \dot{O}H$
$+ O_2$
$\bullet OOQOOH$ *β-scission products* $+ \dot{O}H$
$HOO\dot{Q}'OOH$
$HOOQ'{=}O + \dot{O}H$
$\bullet OQ'{=}O + \dot{O}H + \dot{O}H$ (chain-branching)

The chemistry of autoignition has been studied for many decades –

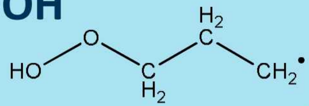
Some details remain hidden

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

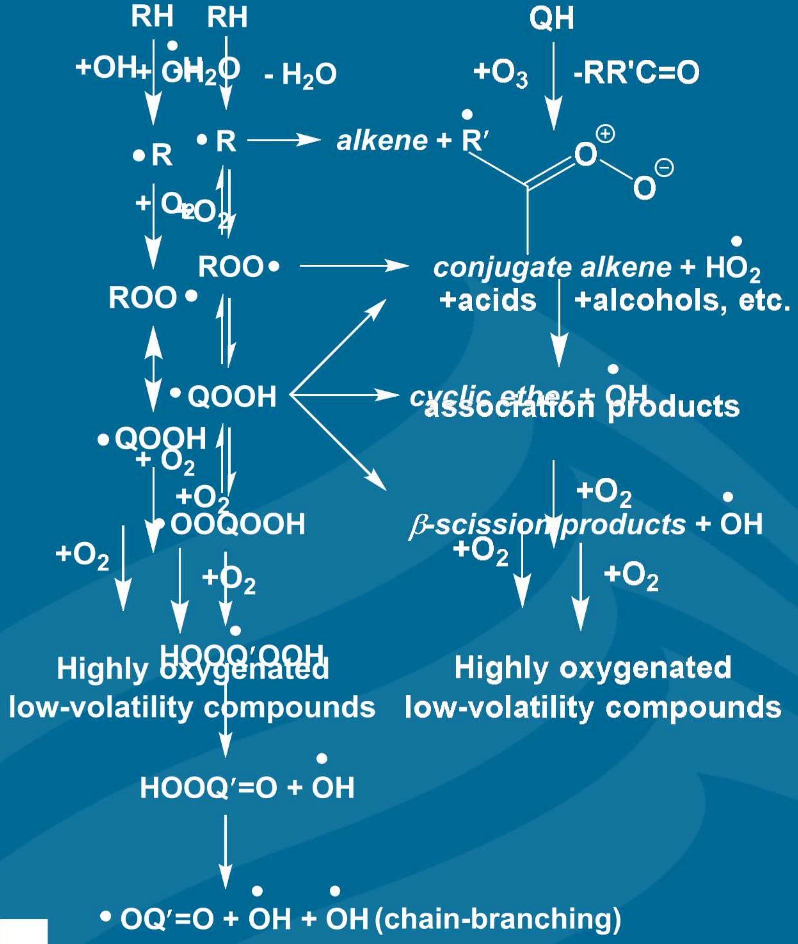
ROO



QOOH



- QOOH + O_2 is responsible for chain branching
- Chain branching step goes through dissociation of a ketohydroperoxide
- Different isomers behave differently



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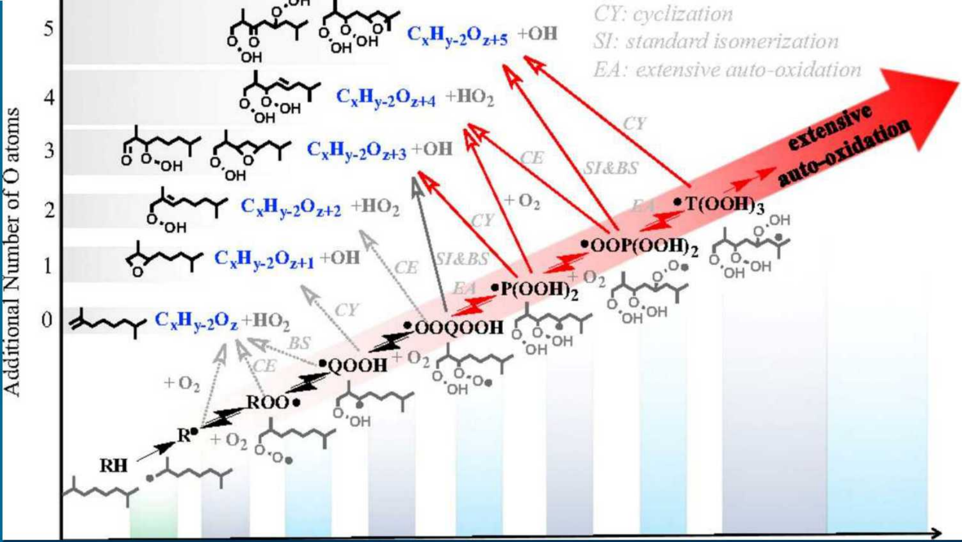
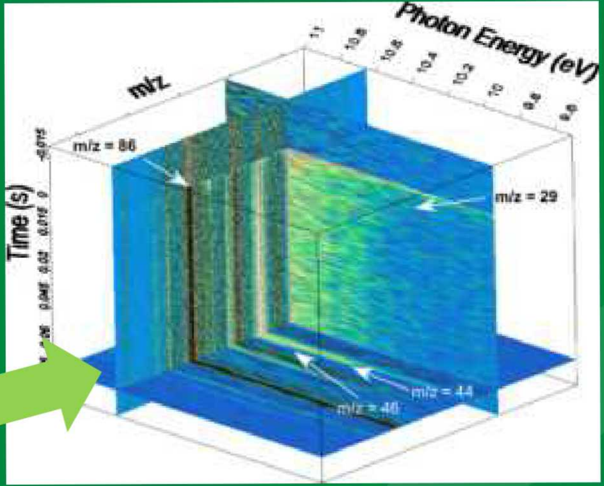


Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds
Wang et al., PNAS **114**, 13102-13107 (2017)

Tropospheric oxidation and autoignition share some isomerizations and intermediates

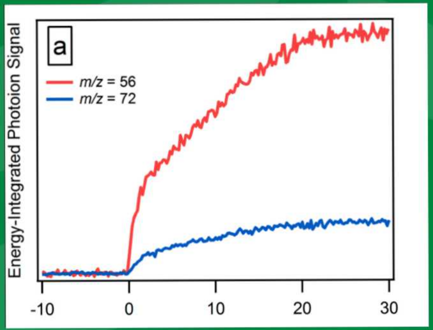
Other oxidants may entail new intermediates

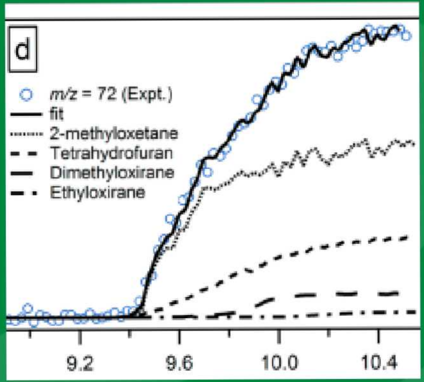
Synchrotron photoionization mass spectrometry can detect and characterize these intermediates



Form intermediates in a controlled way by pulsed laser photolytic initiation of oxidation

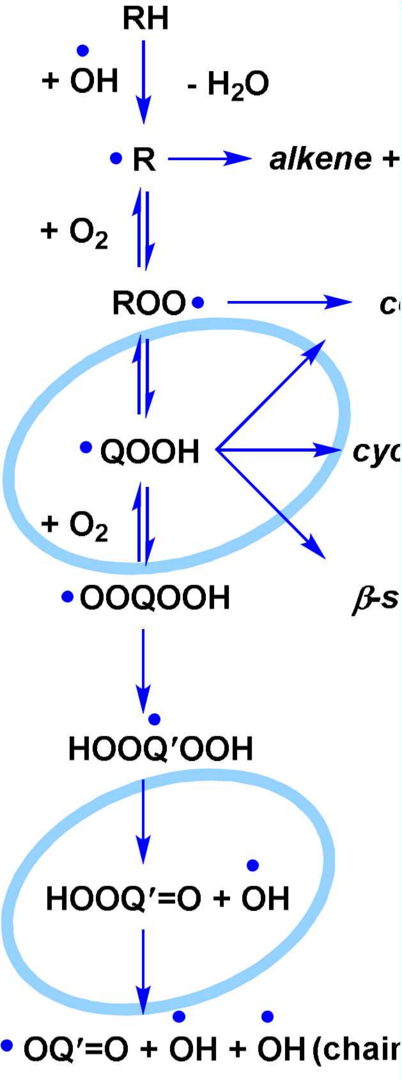
Time-Dependent Chemical Kinetics





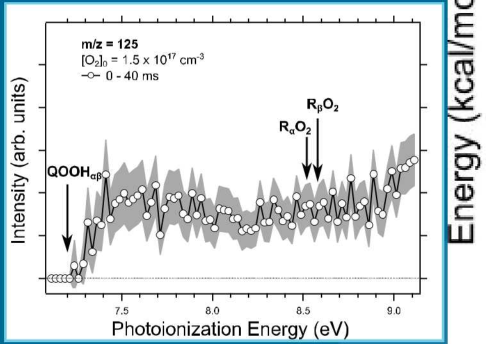
Isomer-Resolved Species Identification

David Osborn

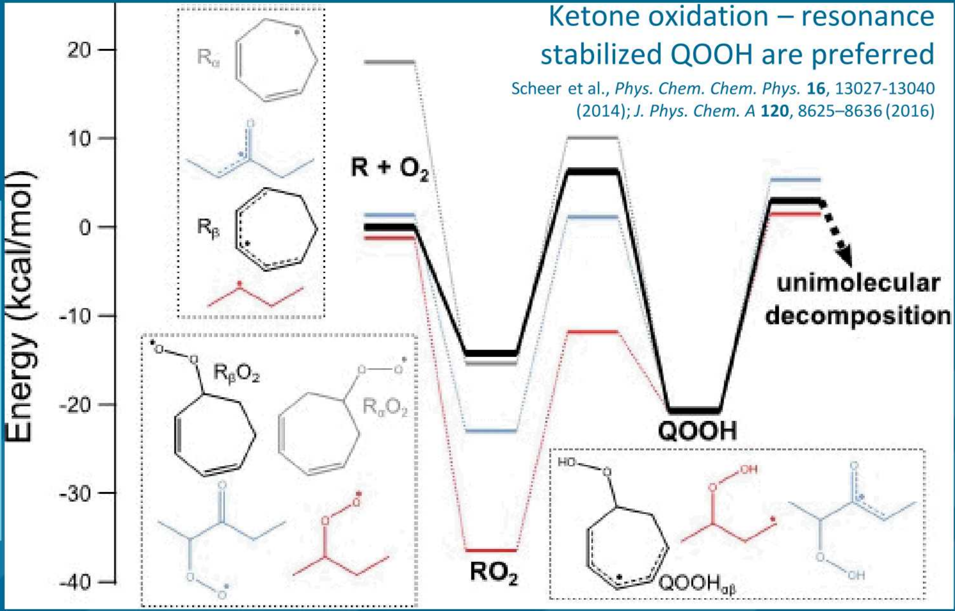


The autoignition or autoxidation process can be dramatically affected by resonance stabilization

Double resonance stabilization allowed first direct detection of QOOH



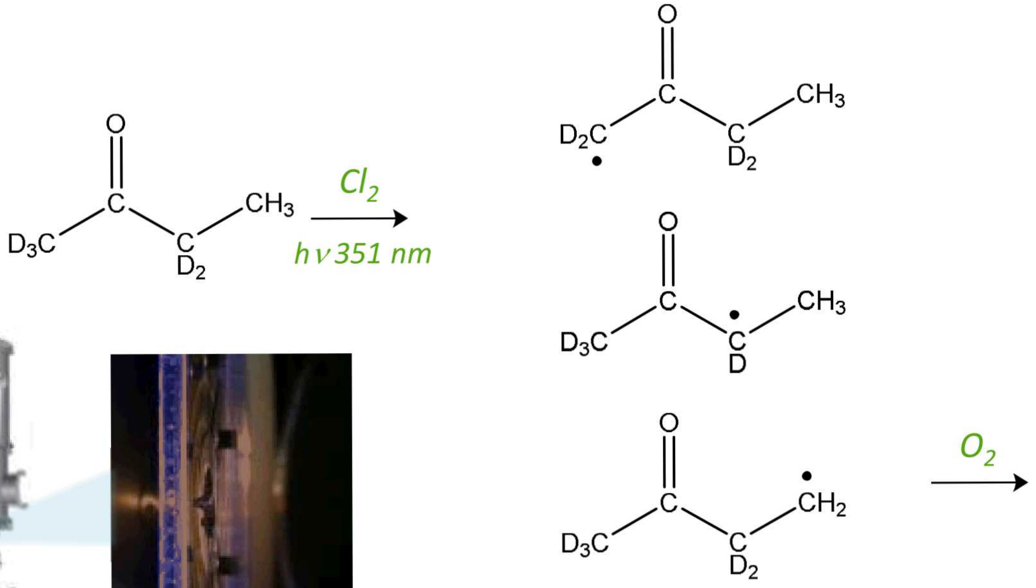
J.D. Savee, E. Papajak, et al., *Science* **347**, 643-646 (2015).



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)

Butanone is a prototype for ketone oxidation



Cl_2

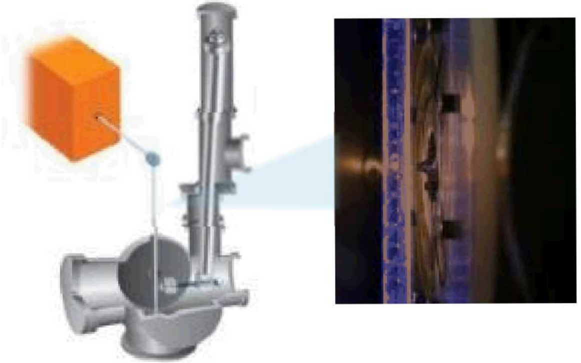
$h\nu$ 351 nm

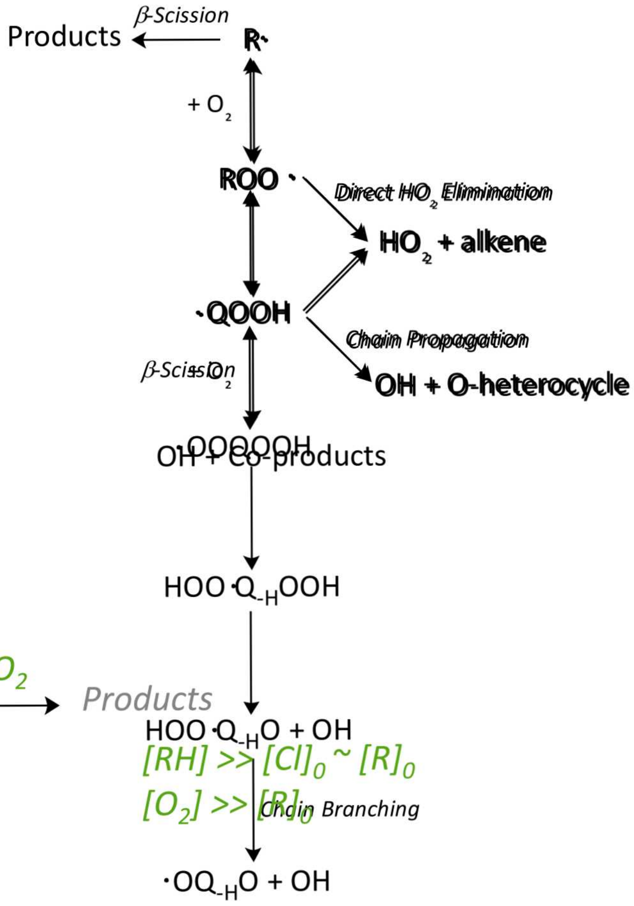
O_2

Products

$[RH] >> [Cl]_0 \sim [R]_0$

$[O_2] >> [R]_0$





Products ← β-Scission R·

$+ O_2$

ROO·

Direct HO_2 Elimination

HO_2 + alkene

·QOOH

Chain Propagation

OH + O-heterocycle

β-Scission

$+ O_2$

·OOQOOH

OH + Co-products

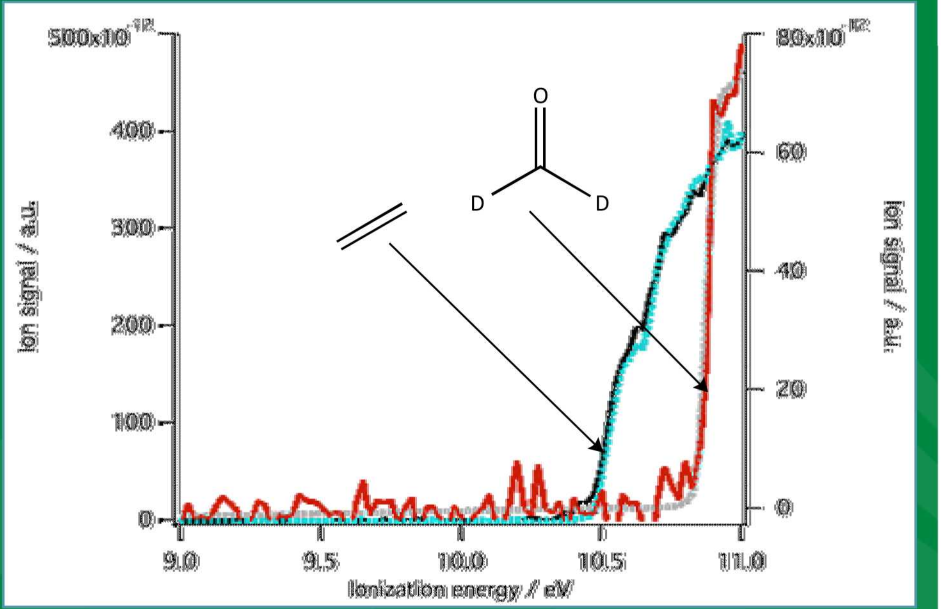
$HOO{\cdot}Q_{-H}OOH$

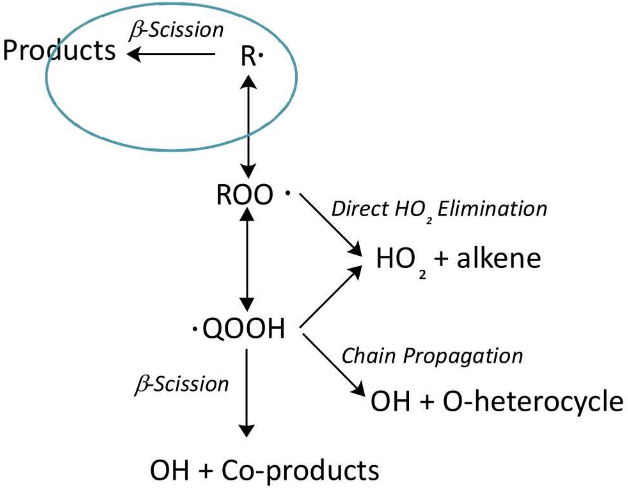
$HOO{\cdot}Q_{-H}O + OH$

Chain Branching

$\cdot OQ_{-H}O + OH$

Resonance stabilized radical shows less β-scission





Products ← *β-Scission* R·

ROO ·

Direct HO_2 Elimination

HO_2 + alkene

·QOOH

Chain Propagation

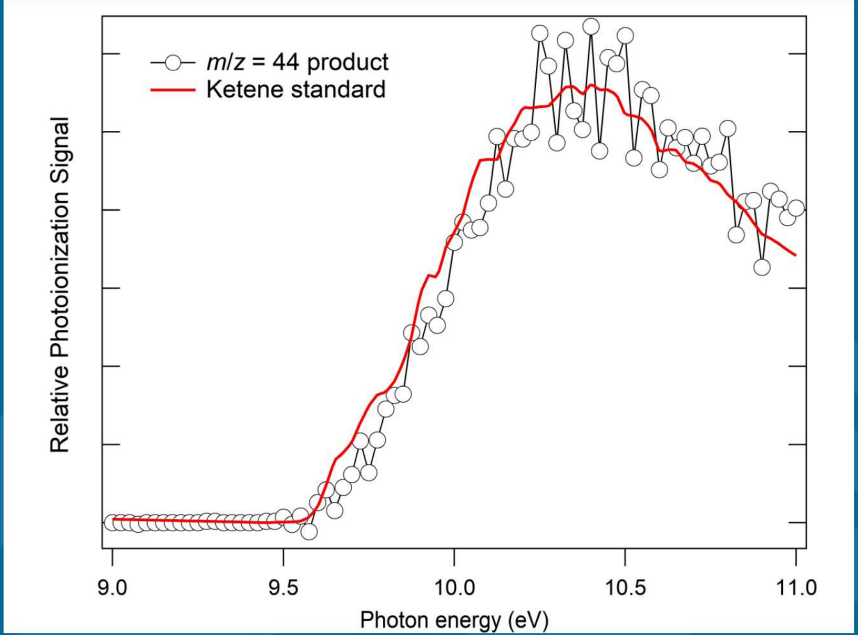
OH + O-heterocycle

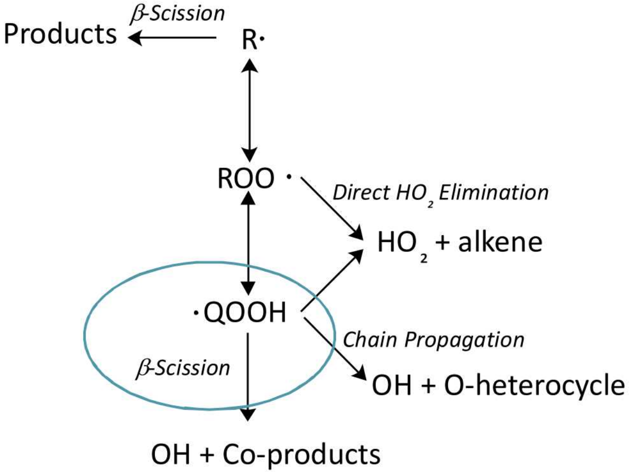
β-Scission

OH + Co-products

Decomposition (e.g., β-scission) of initial R or of QOOH can divert course of oxidation

Resonance stabilized QOOH shows less reactivity with O_2





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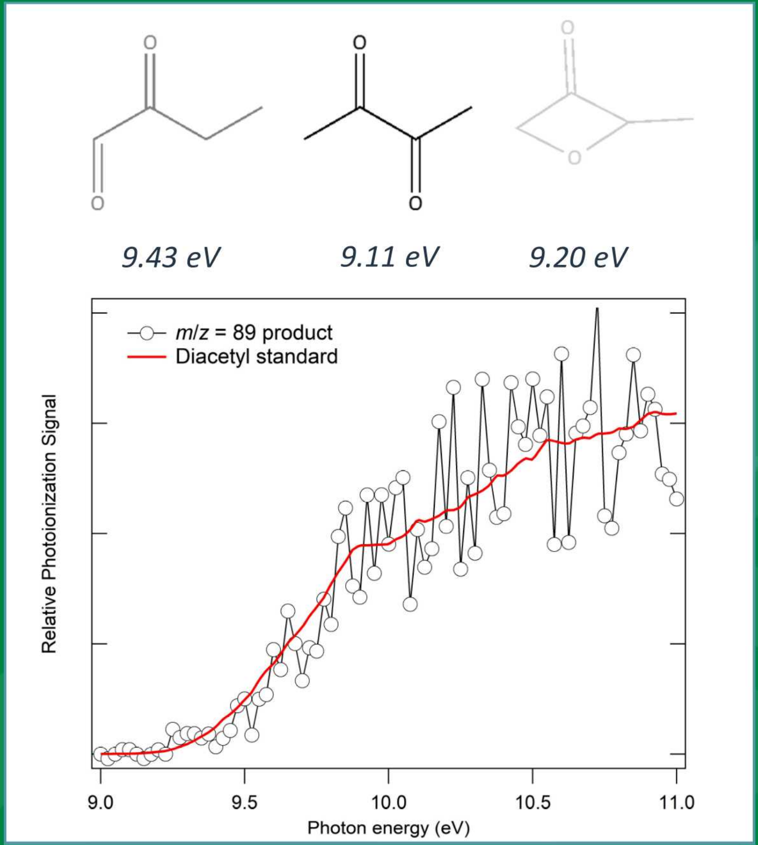
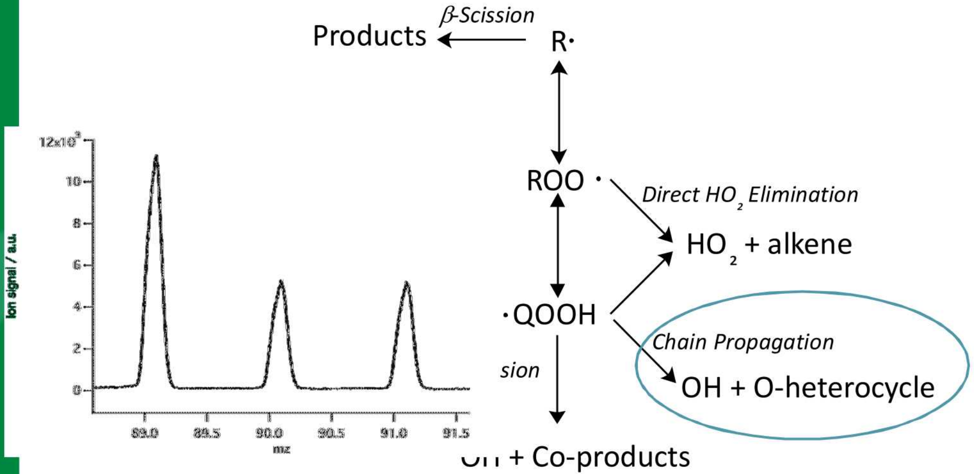
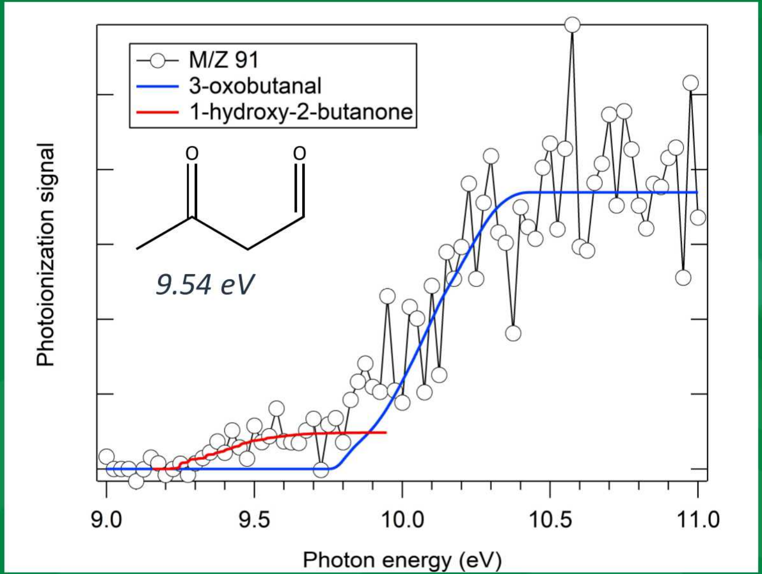


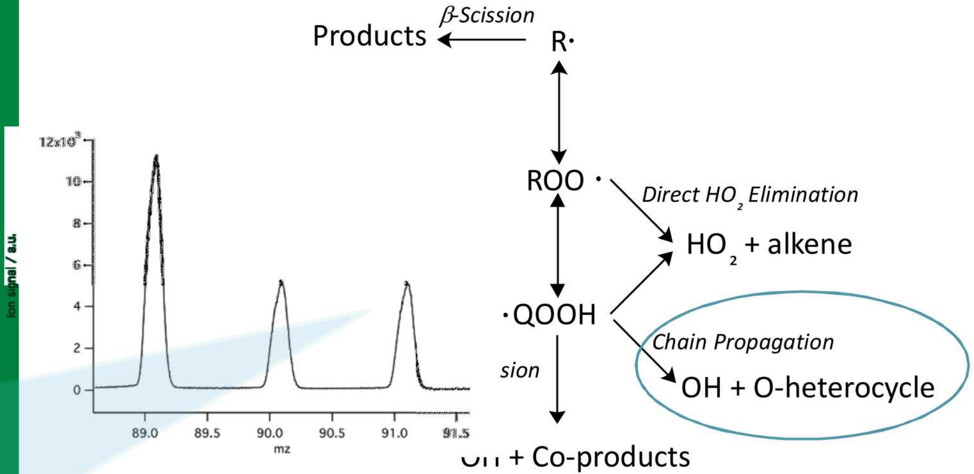


Chain-propagation produces carbonyls as well as cyclic ethers

Products are isotopically distinguished



500 K, 10 Torr, D5-butanone oxidation



Products ← *β-Scission* R·

ROO·

Direct HO_2 Elimination

HO_2 + alkene

·QOOH

Chain Propagation

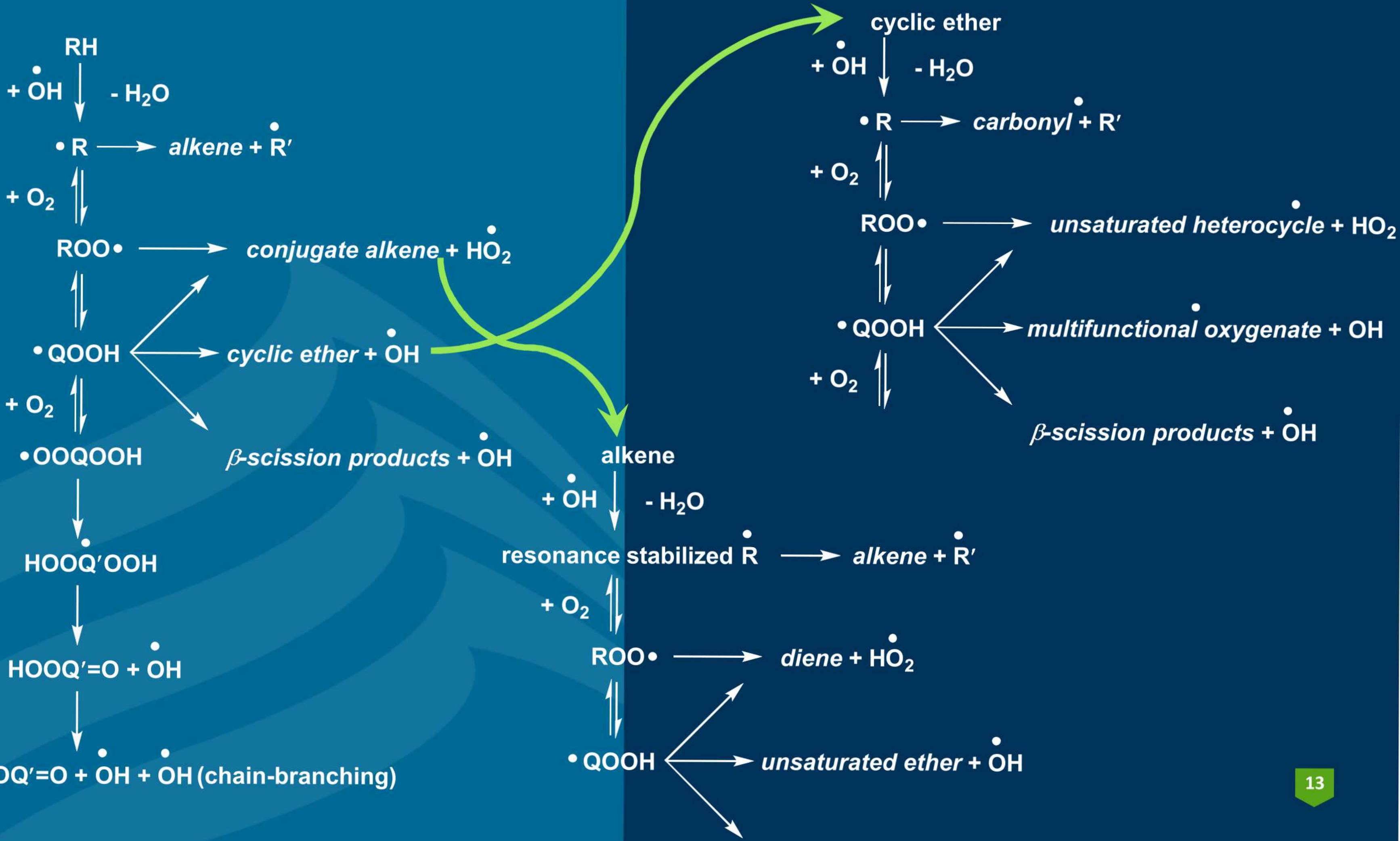
OH + O-heterocycle

sion

OH + Co-products

Chain-propagation produces carbonyls as well as cyclic ethers

Products are isotopically distinguished



RH

+ $\dot{O}H$ - H_2O

•R → *alkene* + $\dot{R}'$

+ O_2

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

•QOOH → *cyclic ether* + $\dot{O}H$

β-scission products + $\dot{O}H$

+ O_2

•OOQOOH

$HOO\dot{Q}'OOH$

HOOQ′=O + $\dot{O}H$

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

alkene

+ $\dot{O}H$ - H_2O

resonance stabilized $\dot{R}$ → *alkene* + $\dot{R}'$

+ O_2

ROO• → *diene* + $H\dot{O}_2$

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

cyclic ether

+ $\dot{O}H$ - H_2O

•R → *carbonyl* + $\dot{R}'$

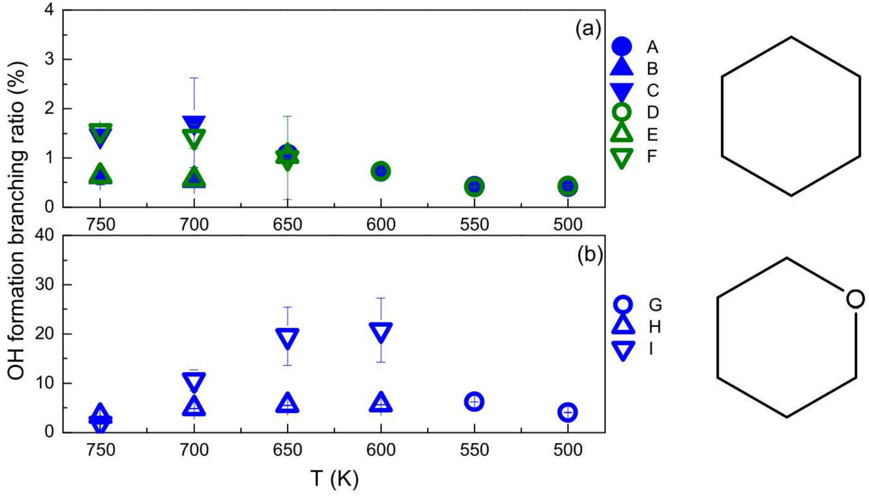
+ O_2

ROO• → *unsaturated heterocycle* + $H\dot{O}_2$

•QOOH → *multifunctional oxygenate* + $\dot{O}H$

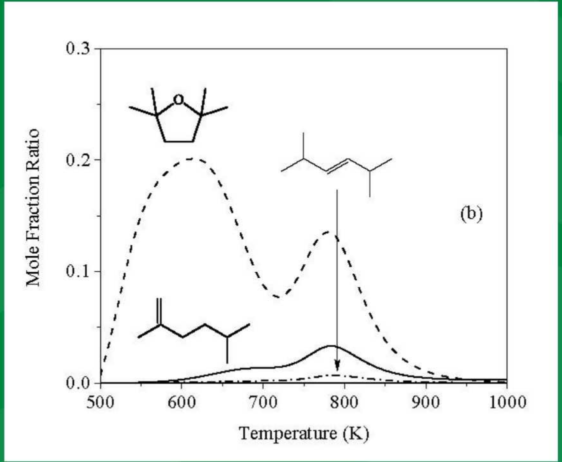
β-scission products + $\dot{O}H$

+ O_2

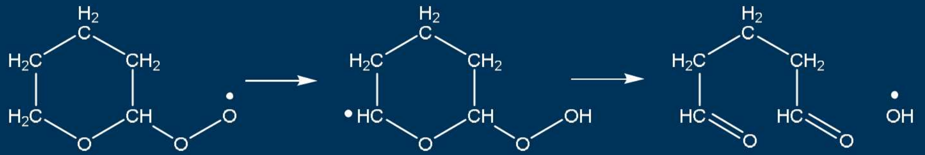


Oxidation products may undergo substantially different oxidation chemistry than the initial reactants

Alkane oxidations create substantial fractions of functionalized products



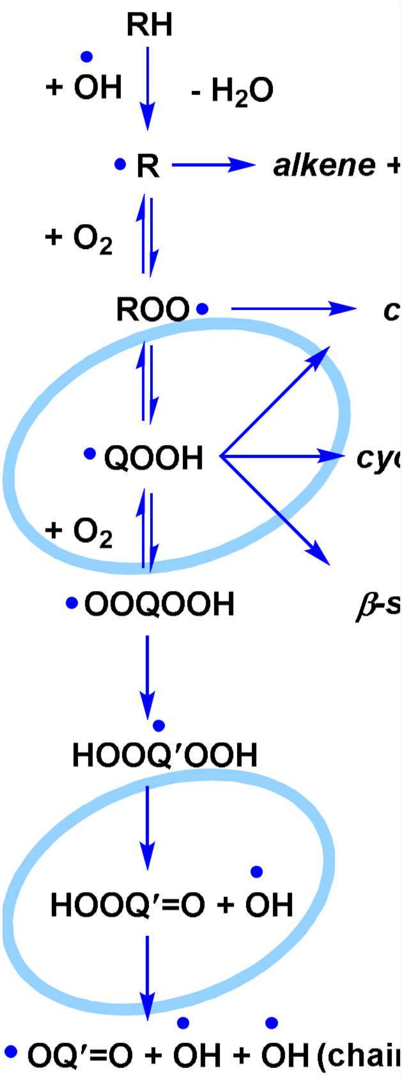
Comparing cyclohexane and tetrahydropyran shows effect of ether group



6-hydroperoxytetrahydro-2H-pyran-2-yl

Ming-Wei Chen et al., *Phys. Chem. Chem. Phys.* **20**, 10815 – 10825 (2018)

B. Rotavera, R. L. Caravan and CAT, *“Subsequent R + O_2 Chemistry of Intermediates Formed in Low-Temperature R + O_2 Reactions: Potential Importance in Modeling Autoignition Behavior,”* **SANDIA REPORT** SAND2017-9099



RH

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

$\dot{R}$ → *alkene +*

$+ O_2$

$ROO\dot{}$ → *c*

$\dot{Q}OOH$ → *cy*

$+ O_2$

$\dot{O}OQOOH$ *β-s*

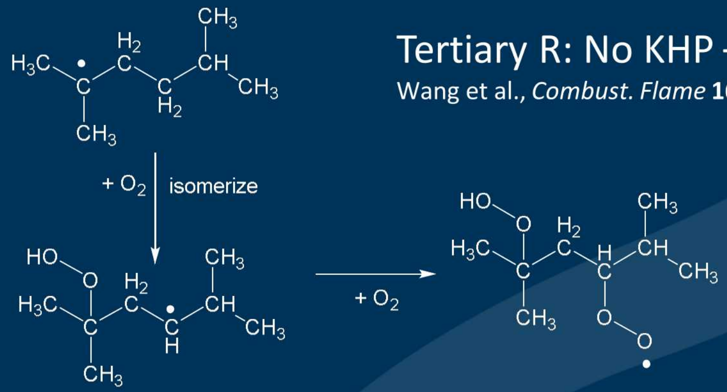
$HOO\dot{Q}'OOH$

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

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

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

What stops the process towards chain branching?



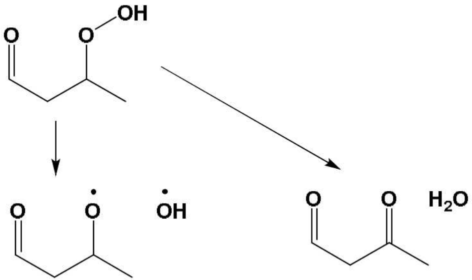
Tertiary R: No KHP – 3rd O_2 addition instead

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

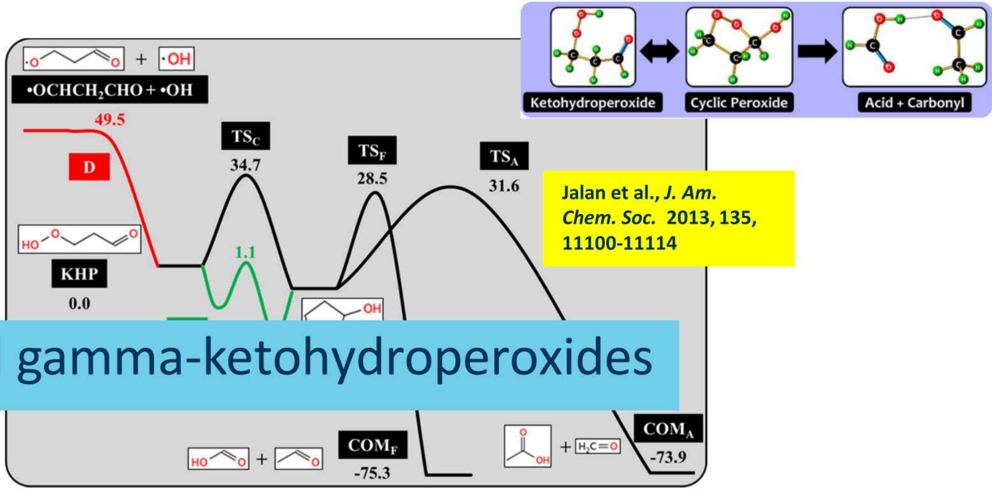
What else can intercept these molecules on the path?

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

O-O bond fission leads to chain branching



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

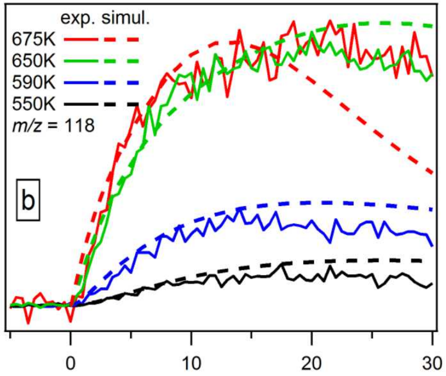


Jalan et al., *J. Am. Chem. Soc.* 2013, 135, 11100-11114

So far observed KHP species are all gamma-ketohydroperoxides

Chem. Soc. **140**, 1035–1048 (2018)) show even more pathways, including water elimination to form dicarbonyl

Ketohydroperoxides have now been observed in many kinetic systems

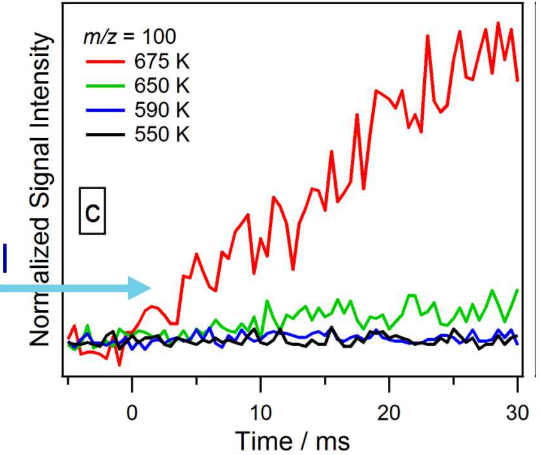


Pulsed photolytic neopentane oxidation shows KHP formation

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

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

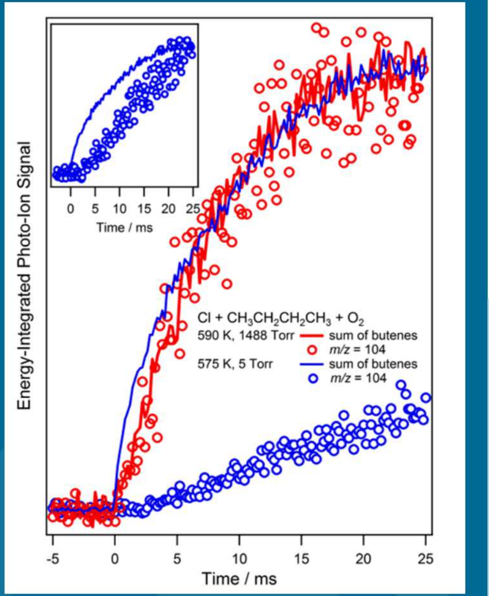
KHP → 2,2-dimethyl propanedial + H_2O

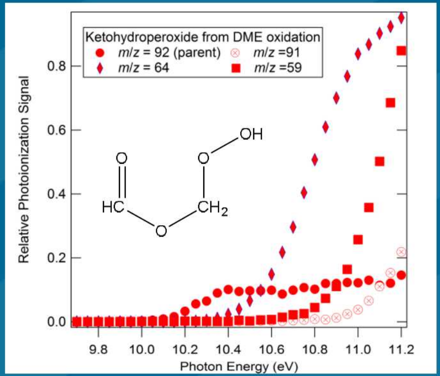


Pulsed photolytic oxidation of butane shows KHP formation

Identified as 3-hydroperoxybutanal

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

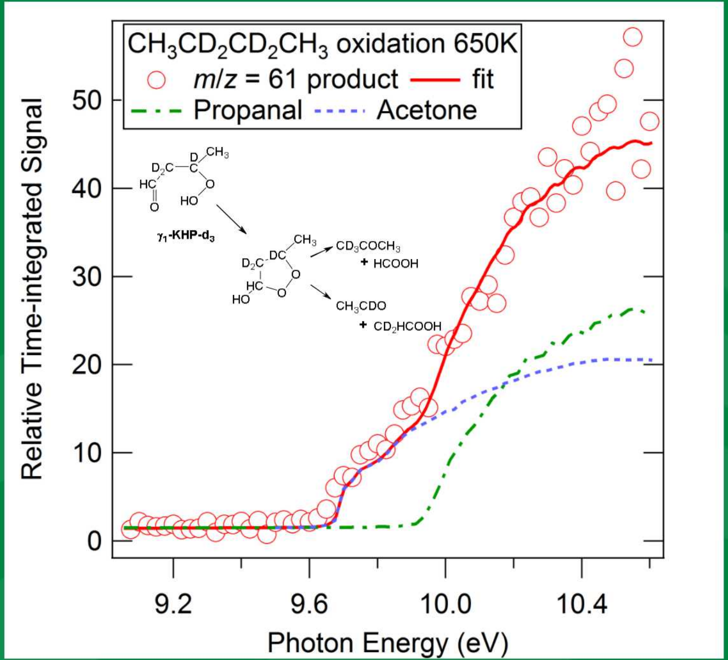




Hydroperoxymethyl formate measured in dimethyl ether oxidation in jet-stirred reactor

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

In butane-d_4 oxidation, acetone-d_3 may be a marker for Korcek decomposition



Eskola, Popolan-Vaida et al.

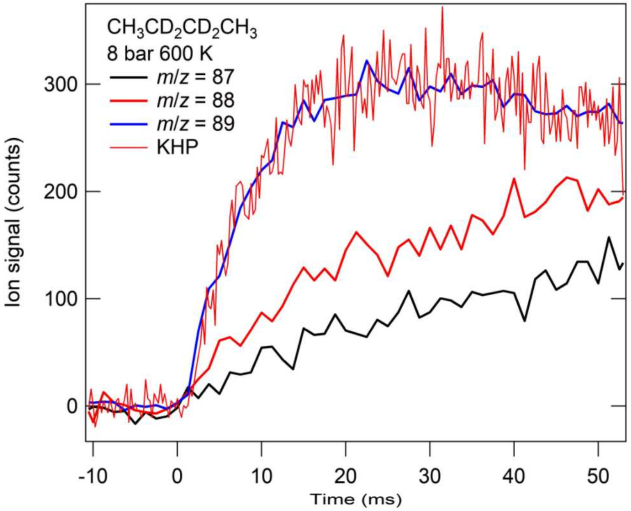
Butane oxidation is a test system for KHP chemistry

KHP observed by photoionization mass spectrometry in jet-stirred reactor and photolysis experiments

Korcek pathways make formic acid + acetone or acetic acid + acetaldehyde

Other non-chain branching pathways for KHP may occur

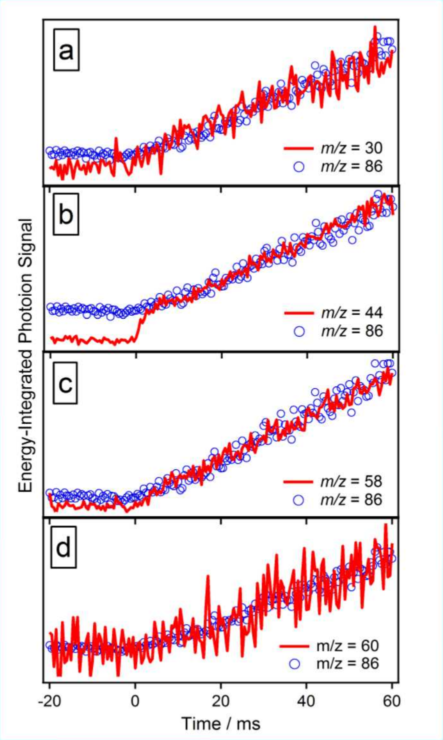
Identification of non-chain branching KHP products



But in butane-d_4 oxidation time profiles for adjacent masses differ

(KHP-18) is dissociative ionization

(KHP-19) and (KHP-20) look like non-chain-branching products – loss of HDO or D_2O

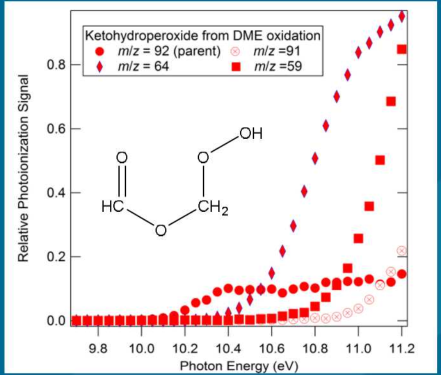


Photolytic oxidation of C_4H_{10} shows several possible non-chain branching products with the same time profile as *m/z* = 86 (KHP-18)

Acetaldehyde
Acetic acid
Acetone

Eskola, Popolan-Vaida et al.

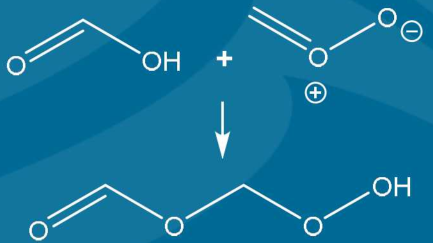
Next steps -- make KHP directly and follow reactions?



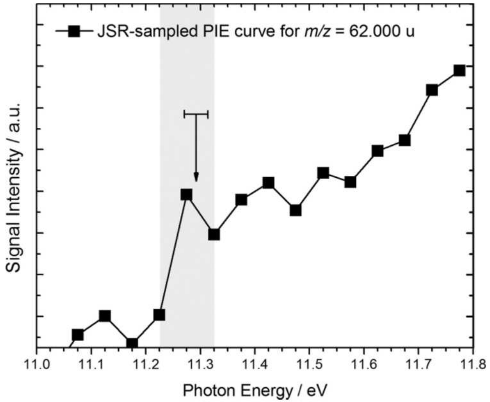
Hydroperoxymethyl formate is the KHP in dimethyl ether oxidation

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

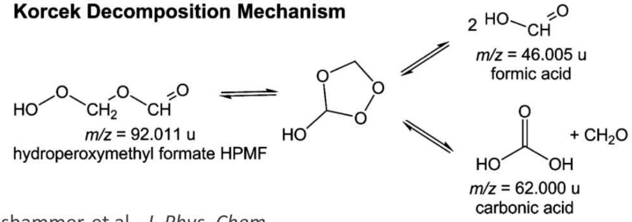
Reaction of Criegee intermediate CH_2OO with formic acid makes same KHP



Specific organic acid products may be a signature of Korcek dissociation



Modeling acid formation may constrain Korcek rate coefficient


Korcek Decomposition Mechanism

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

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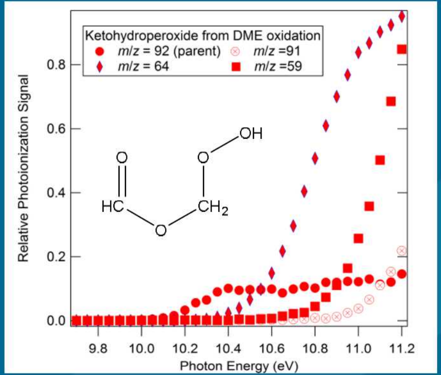

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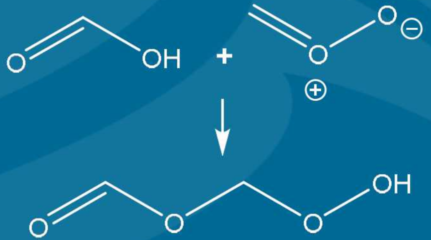
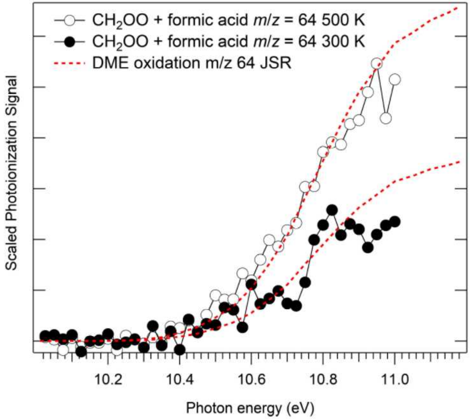
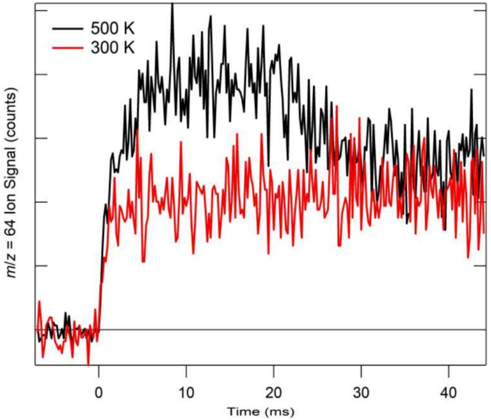
Reaction of Criegee intermediate CH_2OO with formic acid makes same KHP





Successfully produce KHP, identify by spectrum of fragment ion

Initial experiments suggest temperature dependence but no products yet observed



Complex Chemical Systems One Step at a Time

Analysis of controlled oxidation reactions – photolysis, isotopic labelling – by isomer specific detection

Products of one reaction are the reactants of the next

Functionalization can bring resonance stabilization, change pathways

Start on the intermediate steps

Hydrocarbon oxidation research in the CRF Combustion Chemistry Department

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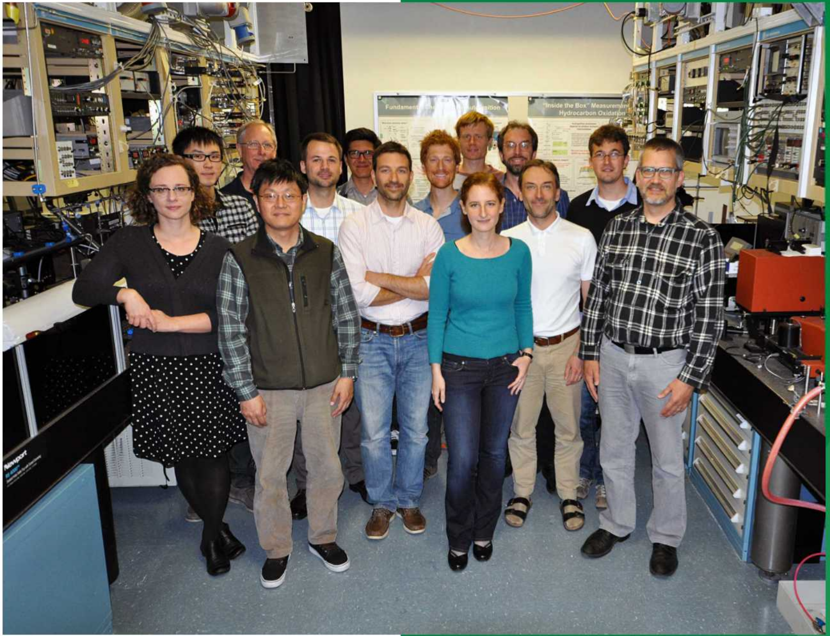

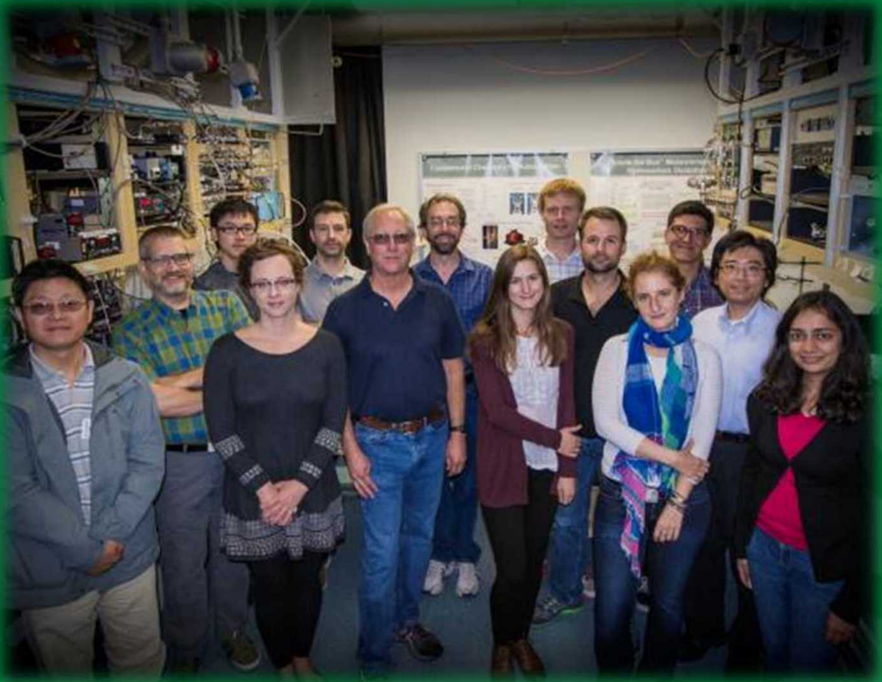

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