SAND2013-5794C

Low-Temperature Oxidation Chemistry of Biofuels – Insights from Experiment and Theory

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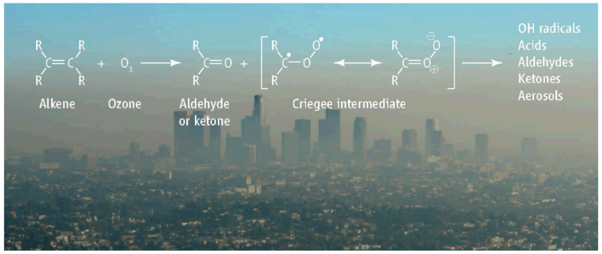
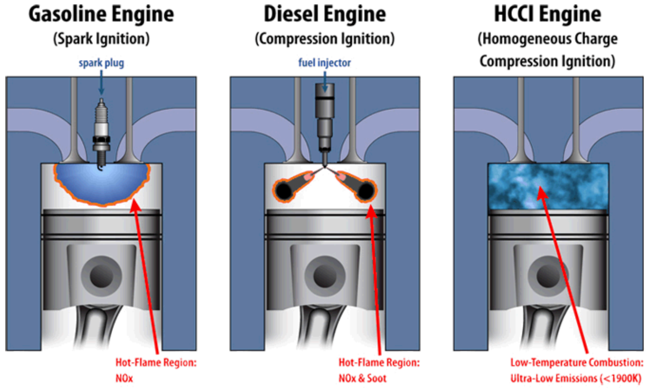
Understanding the fundamental chemistry of hydrocarbon oxidation

→ Atmosphere



G. Marston, *Science* **335**, 178 (2012)

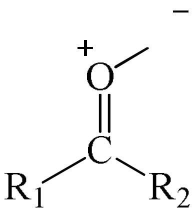
→ Combustion



Manley, McIlroy, Taatjes, Physics Today, Nov. 2008

Directly probing key reactive intermediates:

- Criegee intermediates
- QOOH



Welz, Savee, Osborn, Vasu, Percival, Shallcross, Taatjes, Science 2012, 335, 204-207.

Taatjes, Welz, Eskola, Savee, Scheer, Shallcross, Rotavera, Lee, Dyke, Mok, Osborn, Percival, Science 2013, 340, 177-180

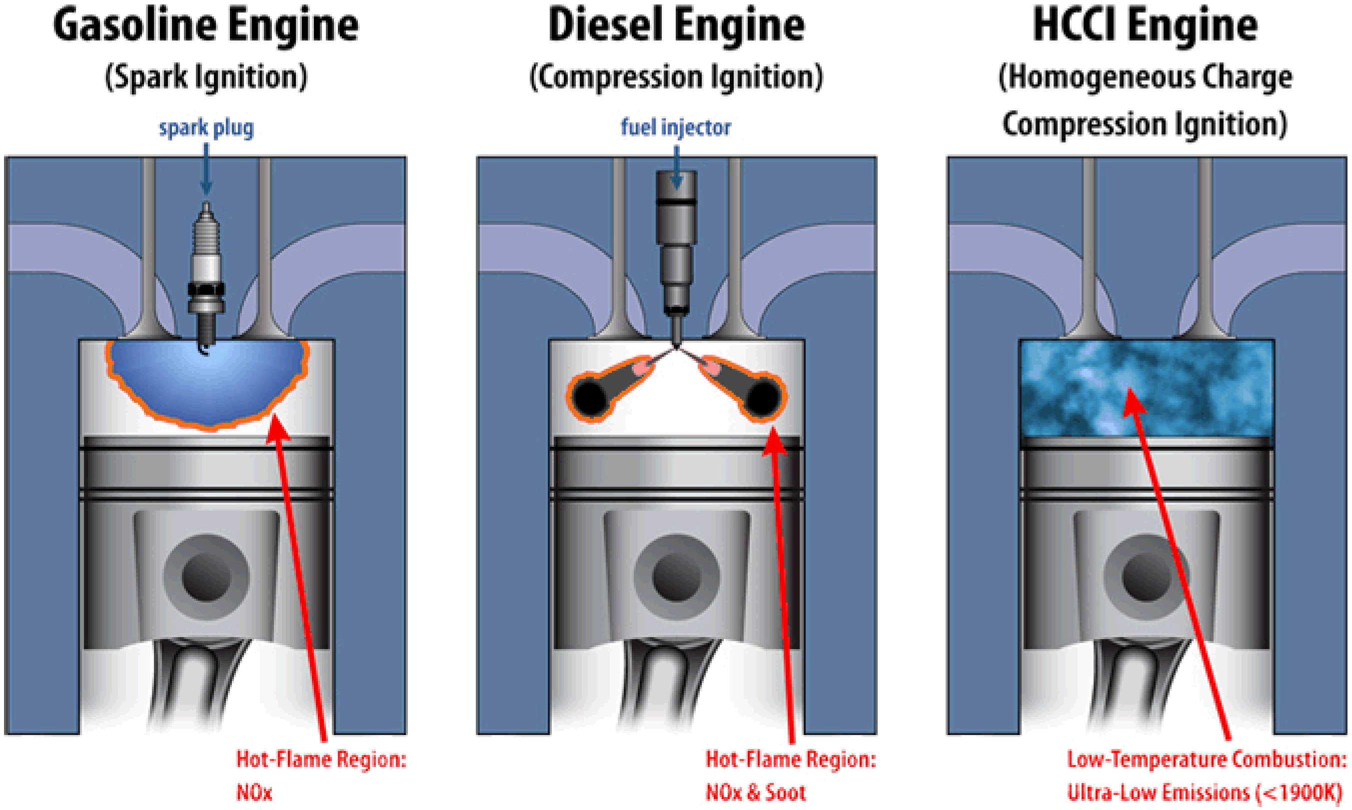
Experiment
+
Theory

Reactions of O(^{3}P) with unsaturated hydrocarbons, nonadiabatic effects

Low-temperature oxidation of alkanes and novel biofuels:

- Mechanism
- pressure- and temperature dependence
- effects of fuel structure

Advanced internal combustion engine concepts rely on low-temperature autoignition



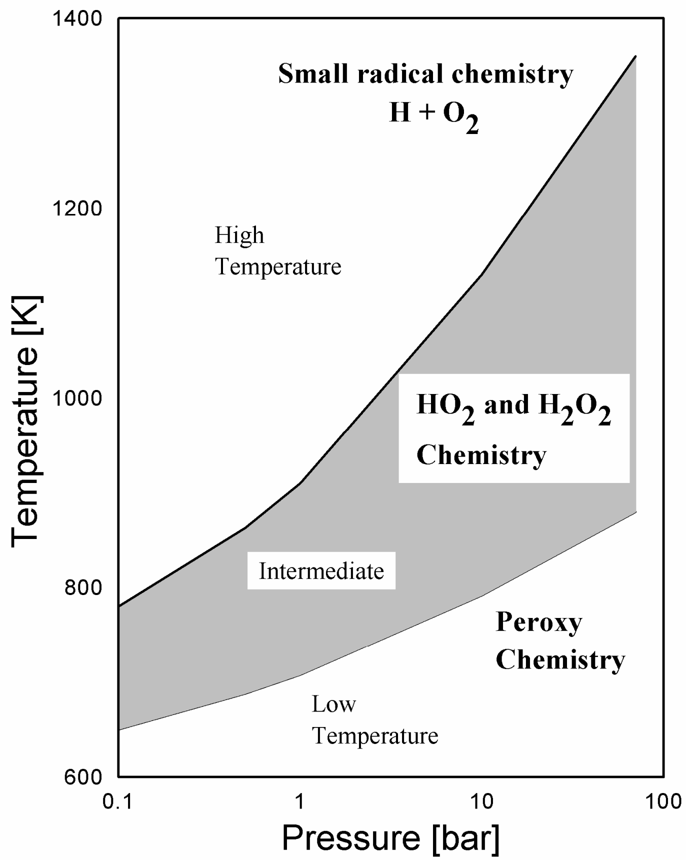
Manley, McIlroy, Taatjes, Physics Today, Nov. 2008

Ignition in an HCCI engine happens at low temperature (T < 1000 K) and is controlled by fuel-specific chemistry in the gas phase

→ Detailed knowledge of the underlying fundamental chemistry is important to predict autoignition behaviour!

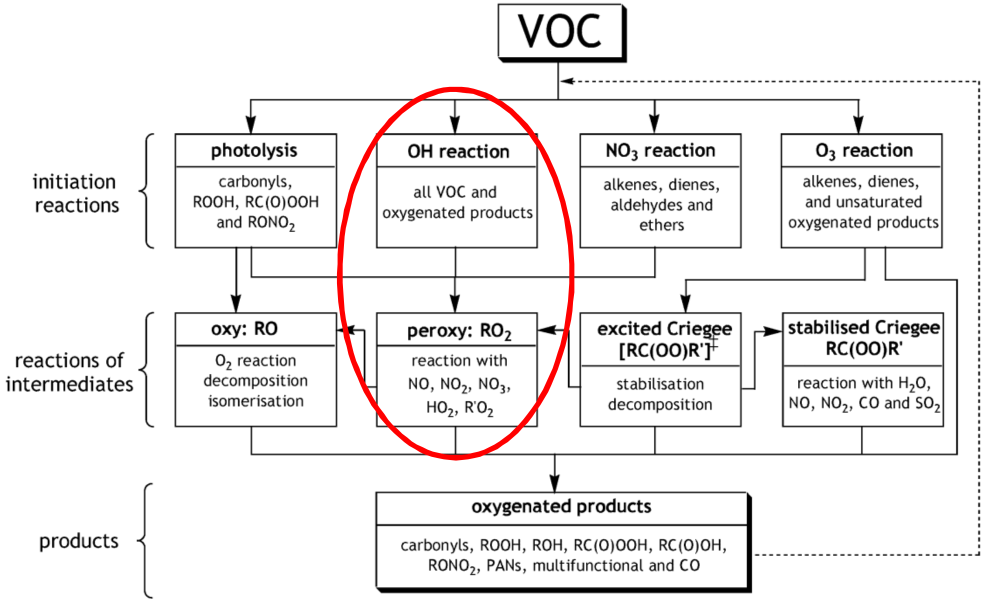
Peroxy radical (RO_2) chemistry is central to low-temperature autoignition

Regimes of hydrocarbon oxidation



Miller, Pilling, Troe, Proc. Combust. Inst. 30 (2005) 43

… and to atmospheric chemistry!

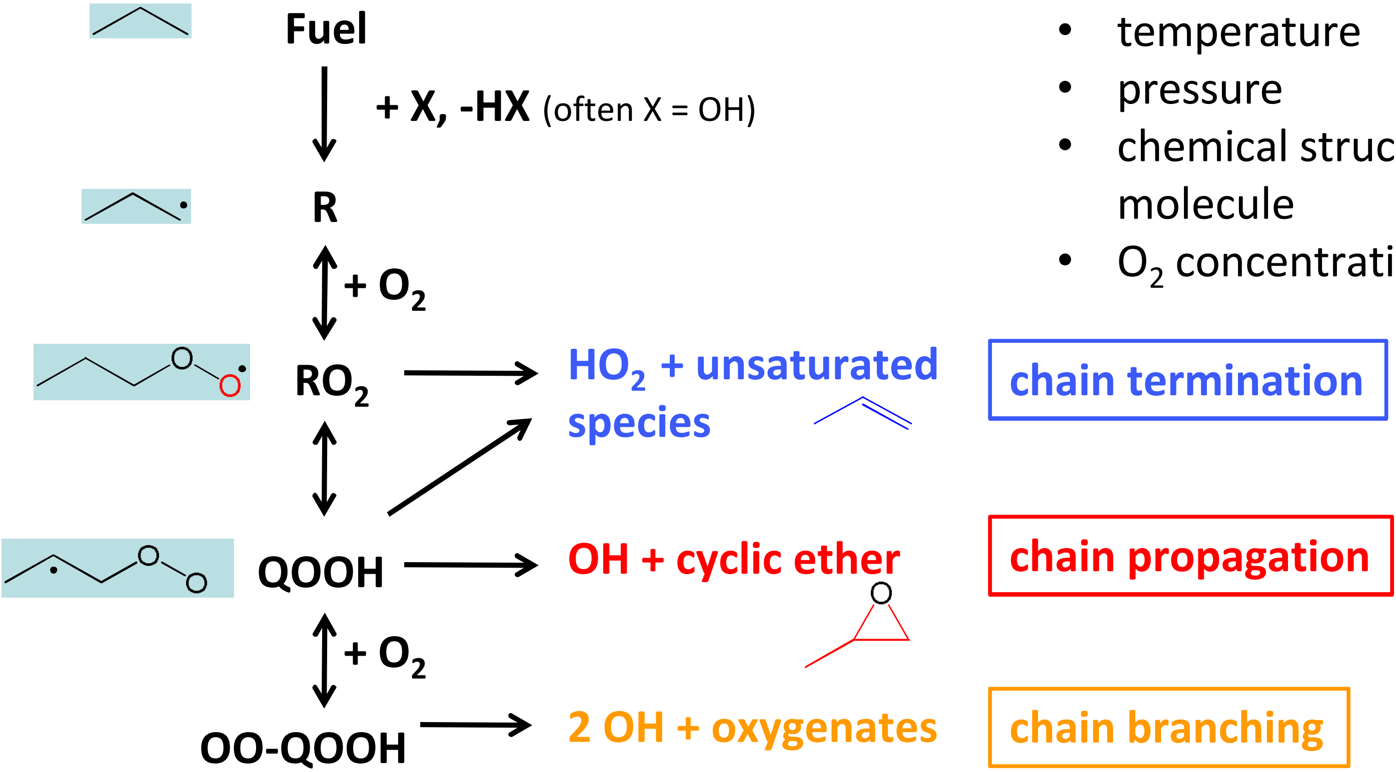


Atmos. Chem. Phys., 3, 161–180, 2003

Peroxy radical (RO_2) chemistry forms a radical chain sequence

The branching into the different channels depends on

- temperature
- pressure
- chemical structure of the fuel molecule
- O_2 concentration



Fuel

+ X, -HX (often X = OH)

R

+ O_2

RO_2

HO_2 + unsaturated species

chain termination

QOOH

OH + cyclic ether

chain propagation

+ O_2

OO-QOOH

2 OH + oxygenates

chain branching

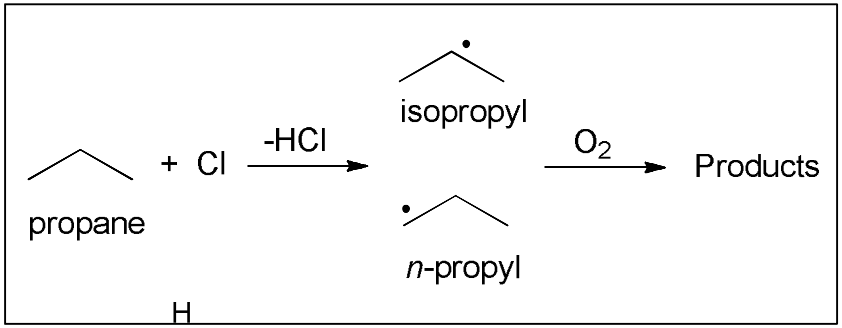
How do we learn about this chemistry?

Pulsed-photolytic Cl initiation

$$Cl_2 \xrightarrow{351\ \text{nm}} 2\ Cl$$

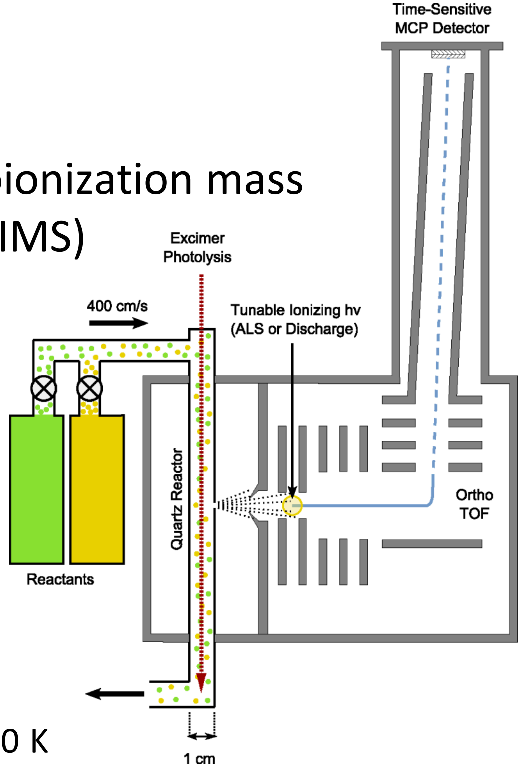
or

$$(COCl)_2 \xrightarrow{248\ \text{n}} 2\ Cl + 2\ CO$$



$[Cl]_0 << [O_2]$, [propane]

Experiment:
Multiplexed photoionization mass spectrometry (MPIMS)



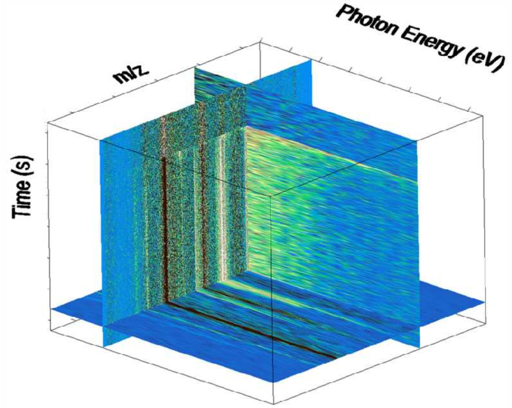
- *T* range: 300 – 1000 K
- *P* range: 1 - 10 Torr (low-pressure reactor) or up to 100 bar (high-pressure reactor)
- Mass spectra are taken in intervals of 20 µs
  → **Time resolution**
- **Tunable VUV radiation from the Advanced Light Source: Photoionization energy can be varied**

  → **Isomeric resolution**

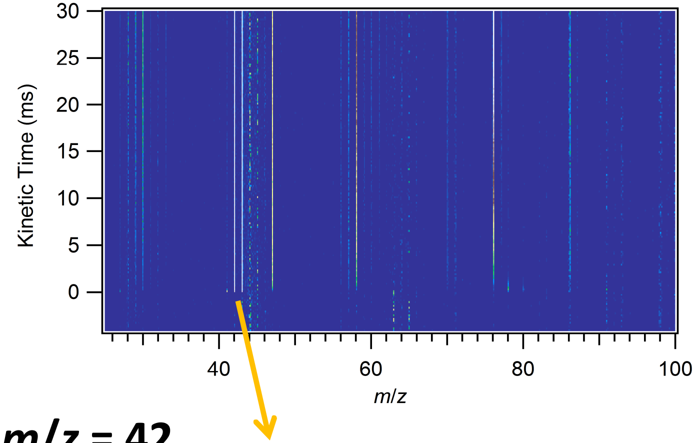
How do we learn about this chemistry?

3-D dataset

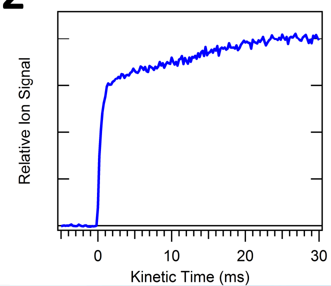
- *m/z*
- kinetic time
- photoionization energy



Time-resolved mass spectrum



***m/z* = 42**

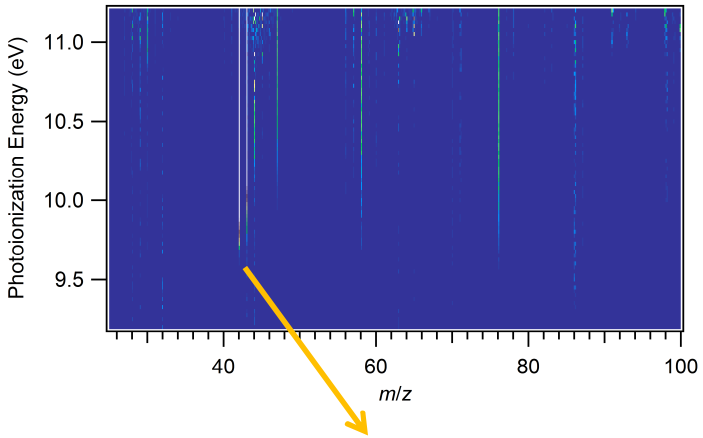


Good mass resolution:

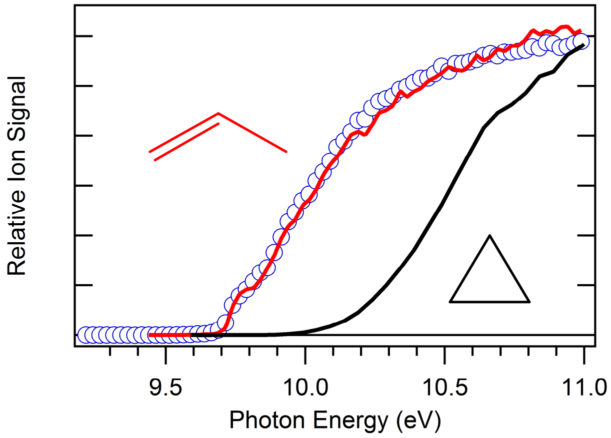
m/Δ*m* ~ 1500

→m/z = 42 is C_3H_6,
not C_2H_2O

Photoionization spectrum (PIE)



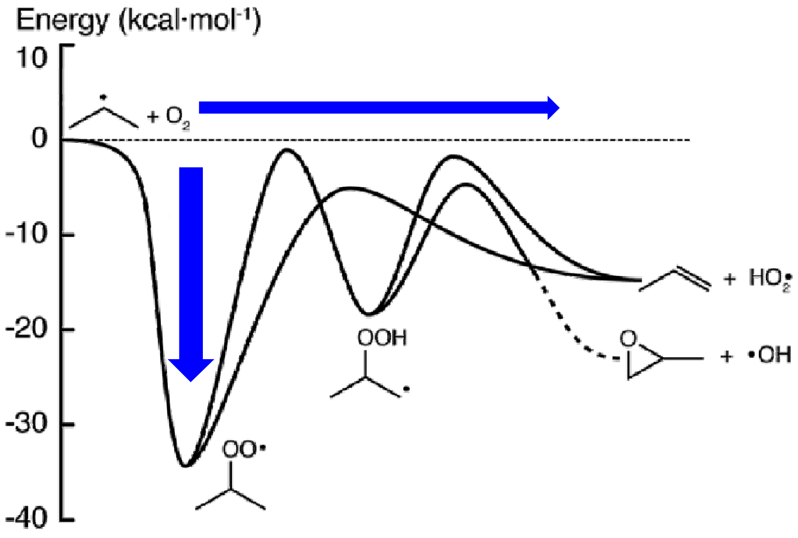
PIE of C_3H_6 (*m/z* = 42)



Isomer resolution!

Propane oxidation at 4 Torr

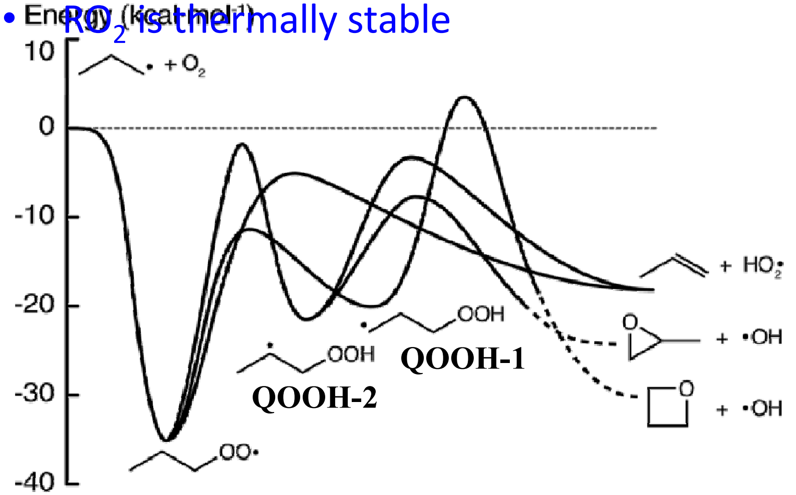
isopropyl + O_2



530 K:

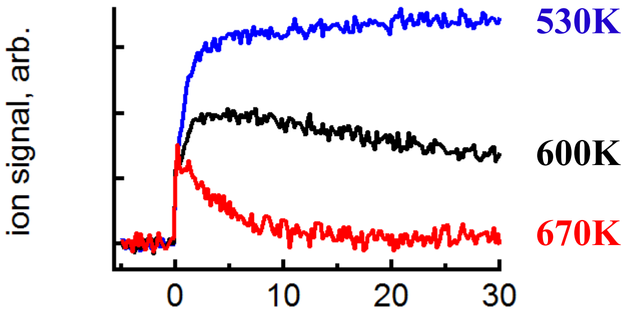
- Propene is formed ***formally direct***
- RO_2 is thermally stable

n-propyl + O_2

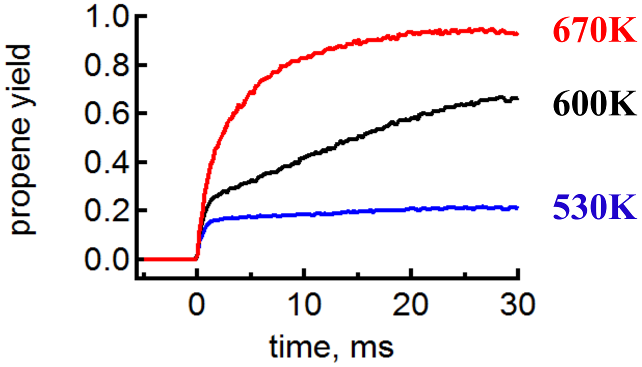


Huang et al, Proc. Combust. Inst. 2009, 33, 293

Propyl peroxy (RO_2) (sum of iso- and $_n$-)

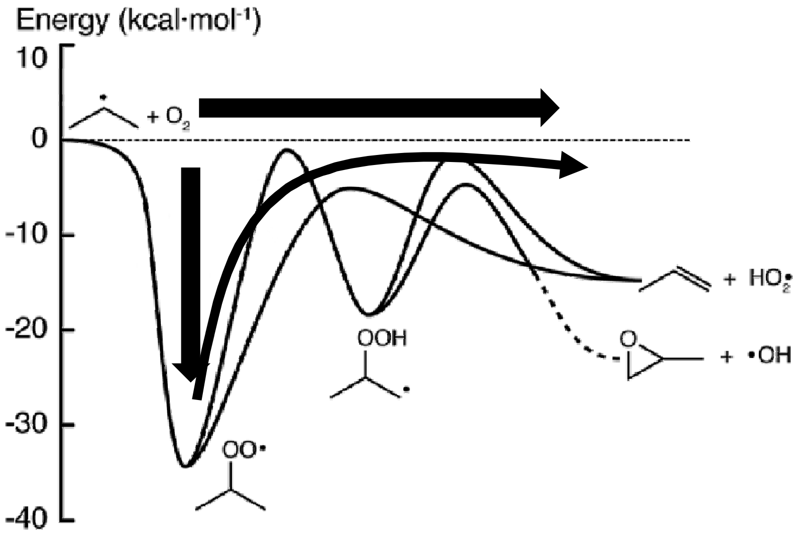


Propene (main stable product)



Propane oxidation at 4 Torr

isopropyl + O_2



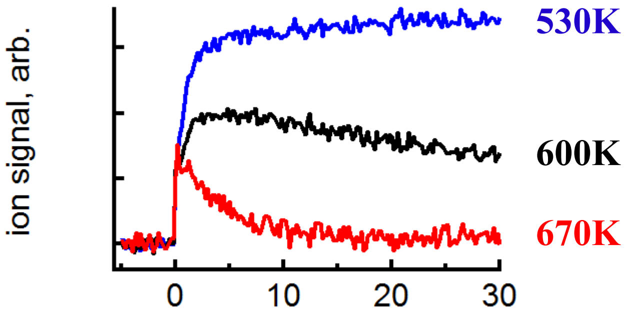
530 K:

- Propene is formed ***formally direct***
- RO_2 is thermally stable

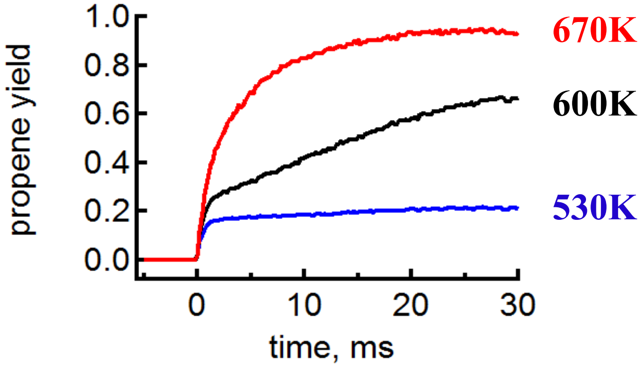
600 K:

- More propene is formed ***formally direct***
- RO_2 becomes thermally unstable and forms propene delayed (***sequential pathway***)

Propyl peroxy (RO_2)

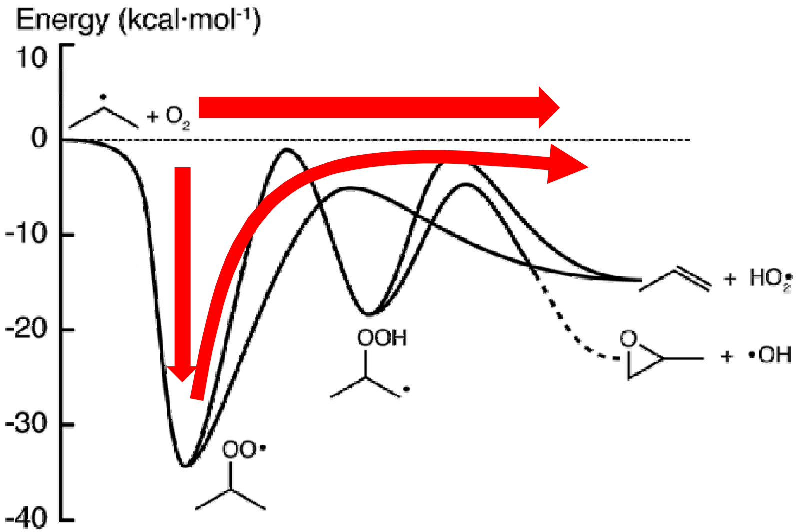


Propene (main stable product)



Propane oxidation at 4 Torr

isopropyl + O_2

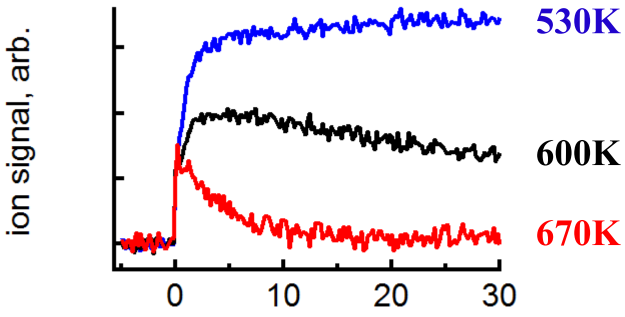


530 K:
- Propene is formed ***formally direct***
- RO_2 is thermally stable

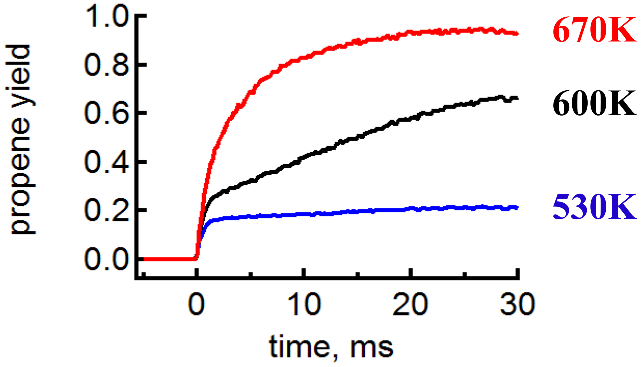
600 K:
- More propene is formed ***formally direct***
- RO_2 becomes thermally unstable and forms propene delayed (***sequential pathway***)

670 K:
- RO_2 decomposes faster
- Timescales for ***formally direct*** and ***sequential*** propene formation merge

Propyl peroxy (RO_2)

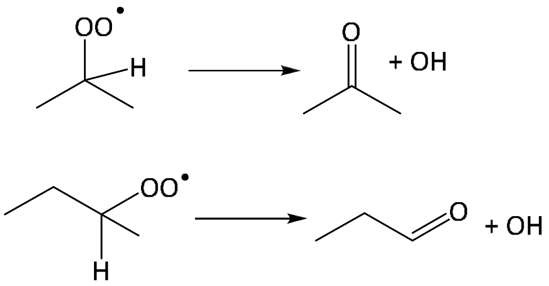


Propene (main stable product)

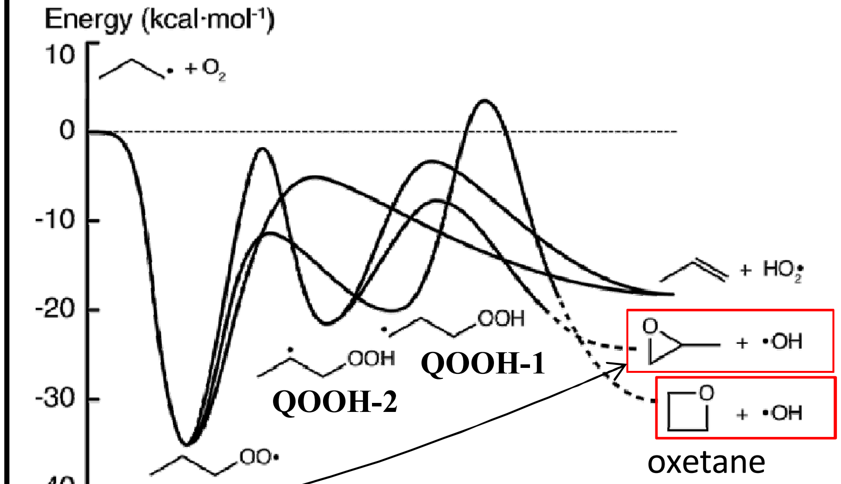


Propane oxidation at 4 Torr – Cyclic ether formation

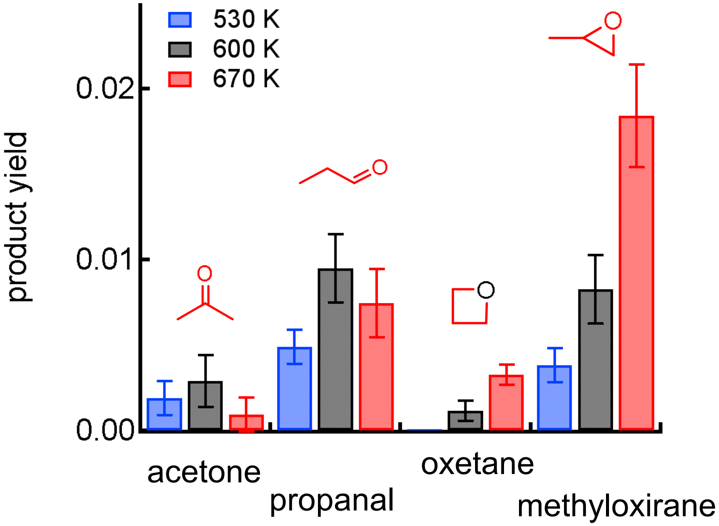
- Oxetane formation needs to be included in models
- Propanal and acetone are formed in comparable amounts to methyloxirane.
  - Experimental evidence: They are primary products, and ***not*** formed in secondary reactions (e.g., RO$_2$ + RO$_2$)
  - They were not included in previous propane combustion models.
  - Their formation pathways are still under investigation → *collaboration Sandia - Argonne (Mike Burke, Stephen Klippenstein)*
  - Calculated barrier for formation from RO$_2$ is too high



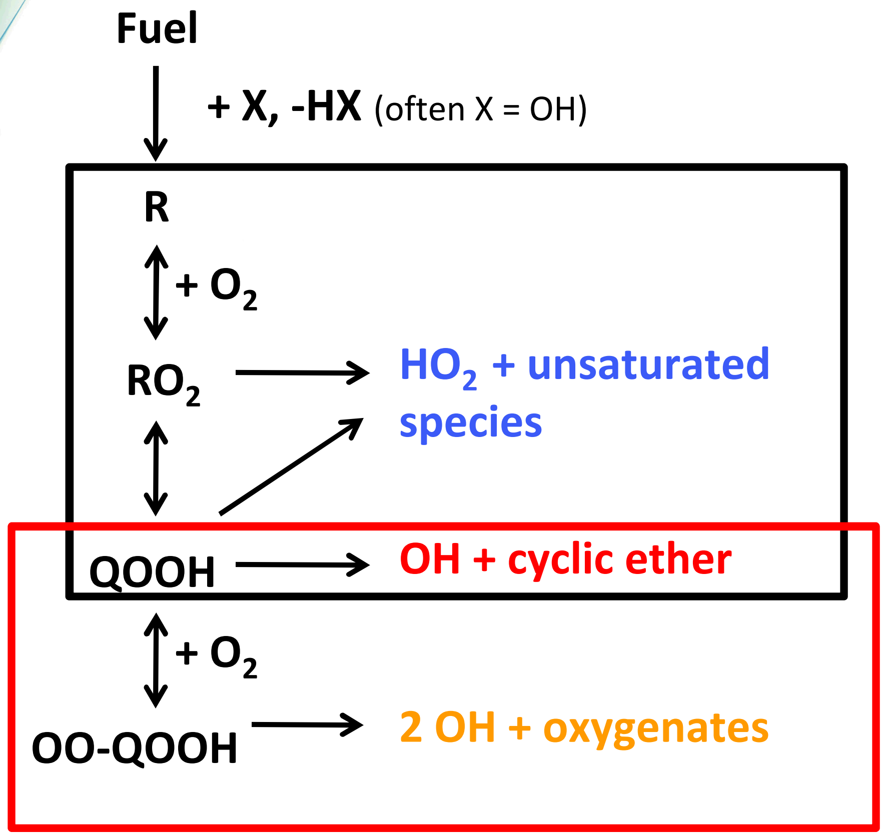
n-propyl + O$_2$



→ not included in previous models!



Status of the current understanding of low-temperature alkane oxidation



Fuel

+ X, -HX (often X = OH)

R

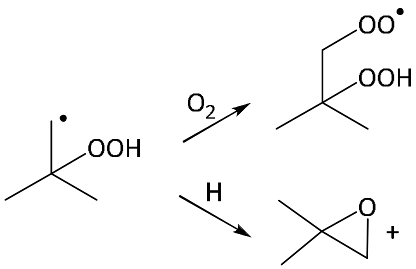
+ O_2

RO_2 → **HO_2 + unsaturated species**

QOOH → **OH + cyclic ether**

+ O_2

OO-QOOH → **2 OH + oxygenates**



R + O_2 chemistry

- Has been extensively studied
- Main pathways are established
- Advanced experiments reveal gaps in our understanding

Chain-branching QOOH + O_2 chemistry

- Much less well studied and understood
- No QOOH has even been detected!
- Until recently no direct study of QOOH + O_2 kinetics existed!

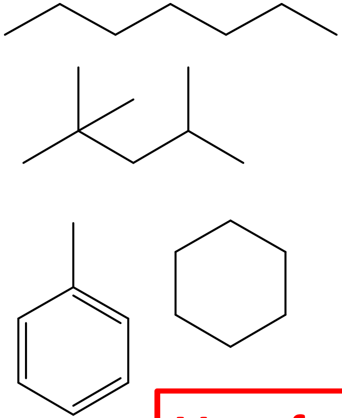
→ *Zador, Huang, Welz, Zetterberg, Osborn, Taatjes, PCCP, 2013, 15, 10753*

Biofuels are explored as alternatives to fossil fuels

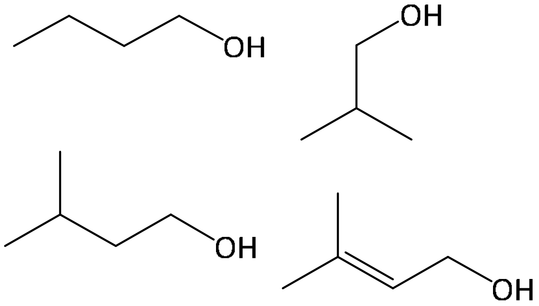
→ Reduce dependence on fossil oil
→ Cut CO_2 emissions

→ Unique opportunity: Design biofuels that meet requirements of advanced clean and efficient engines: Engine/Biofuel co-development

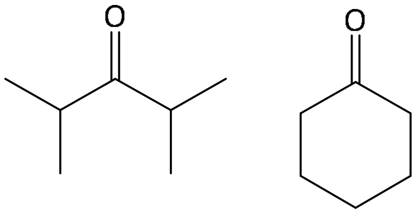
Structural motifs of fossil fuels



Medium-chain alcohols



Ketones



Very few fundamental studies on the R + O_2 chemistry of biofuels
→ Fundamental studies needed!
→ Novel and major(!) pathways keep being revealed!

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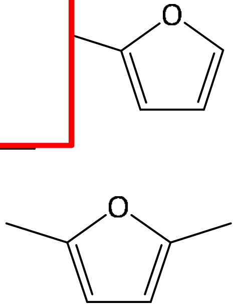
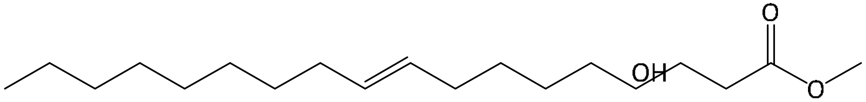
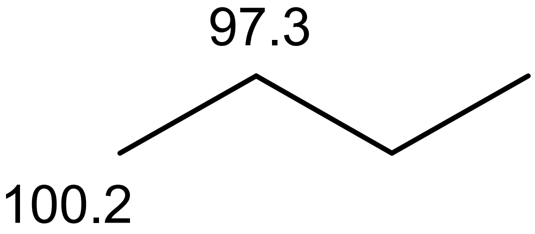


Methylester (Biodiesel)

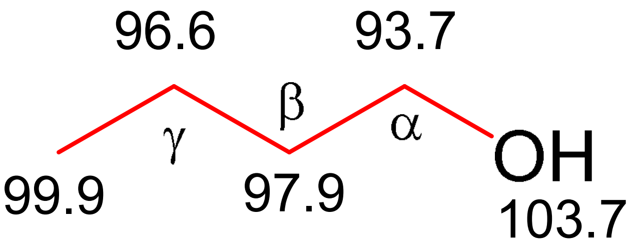


The alcoholic –OH group influences the C-H bond energies

n-Butane



n-Butanol



values are in kcal mol^{-1} at 0 K (CBS-QB3)

Weak α C-H bond
→ α site may play an important role in the RO_2 chemistry of alcohols

–OH group itself might be involved in RO_2 chemistry

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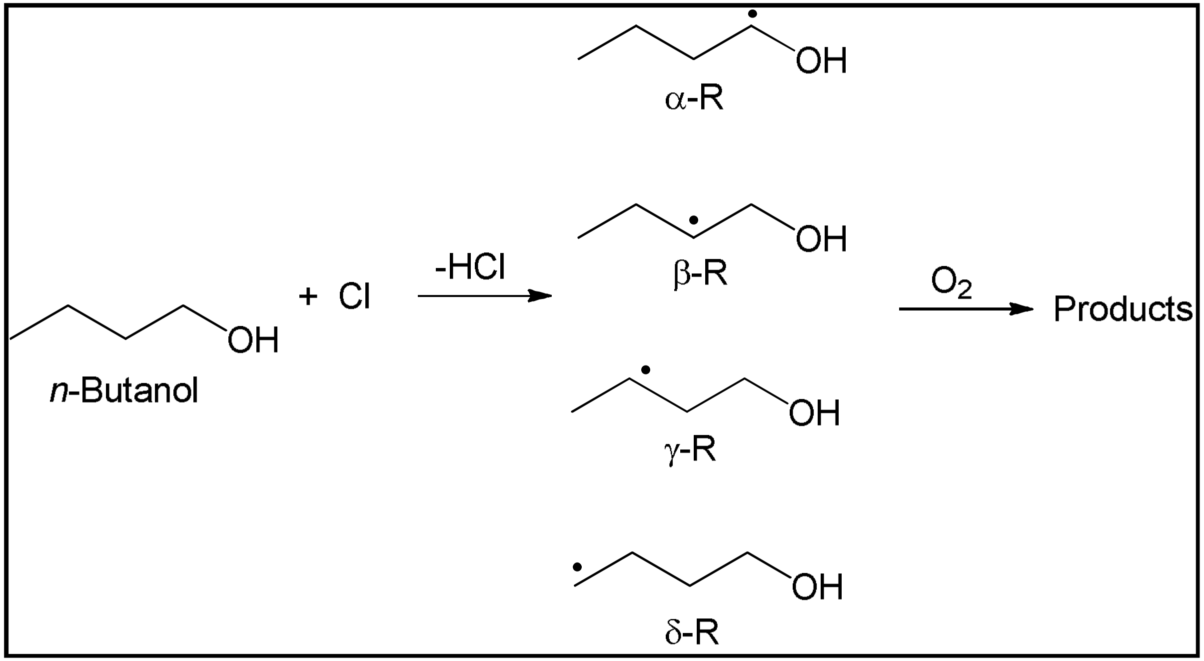
Probing the low-temperature oxidation chemistry of alcohols

Pulsed-photolytic Cl initiation

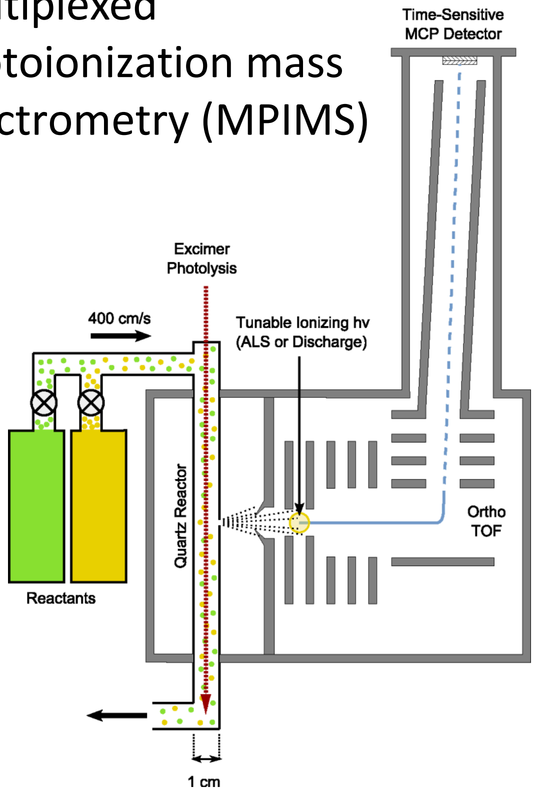
$$Cl_2 \xrightarrow{351\ n} 2\ Cl$$

δ



Experiment:

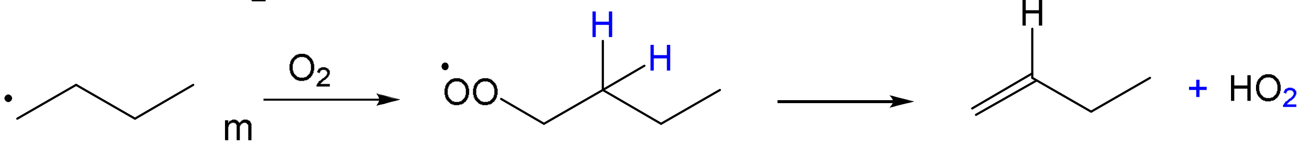
Multiplexed photoionization mass spectrometry (MPIMS)



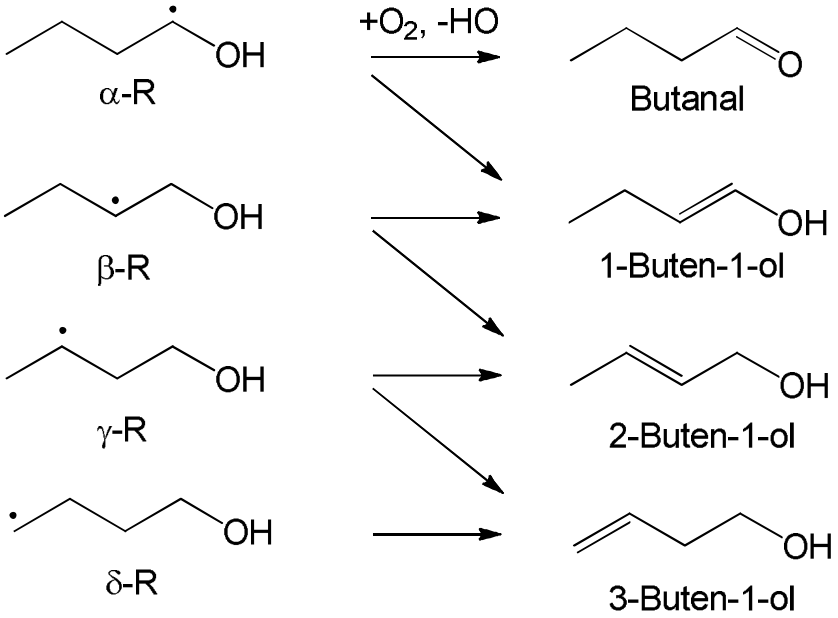
Welz, Zador, Savee, Sheps, Osborn, Taatjes., JPC A, 2013, accepted

Alkane oxidation: HO_2 elimination is typically a major product channel

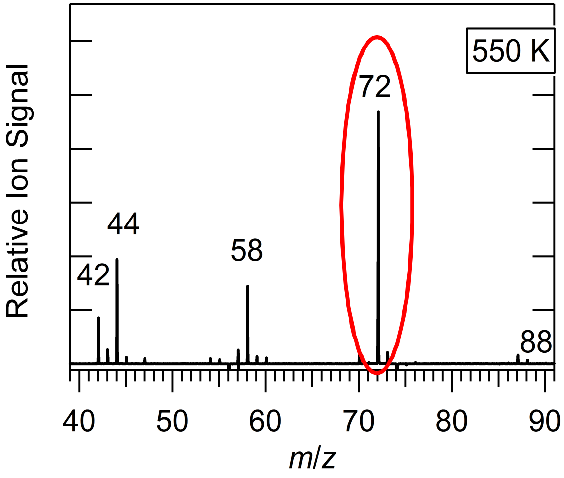
n-butyl + O_2



n-butanol oxidation:
4 different stable C_4H_8O co-products ($m/z = 72$) for HO_2 elimination

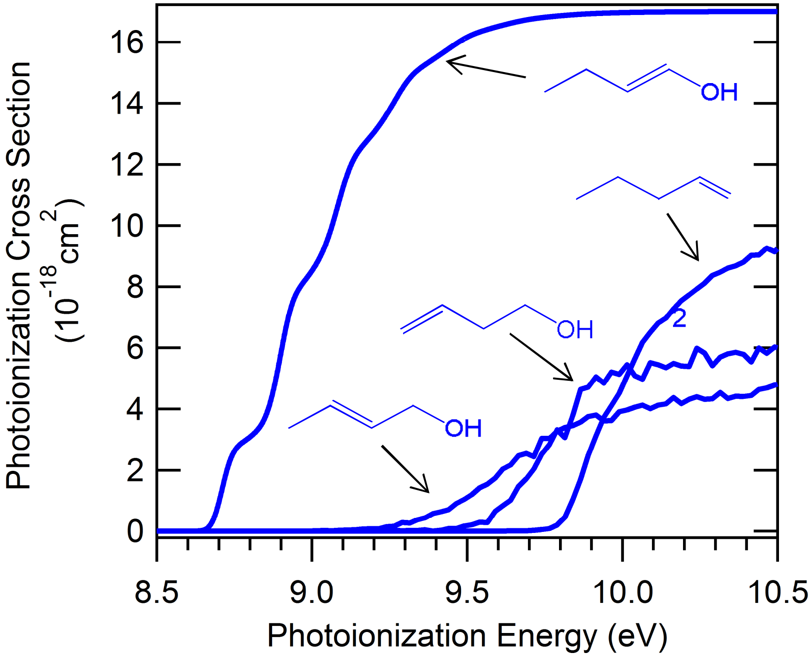


Product mass spectrum
(up to 10.5 eV)

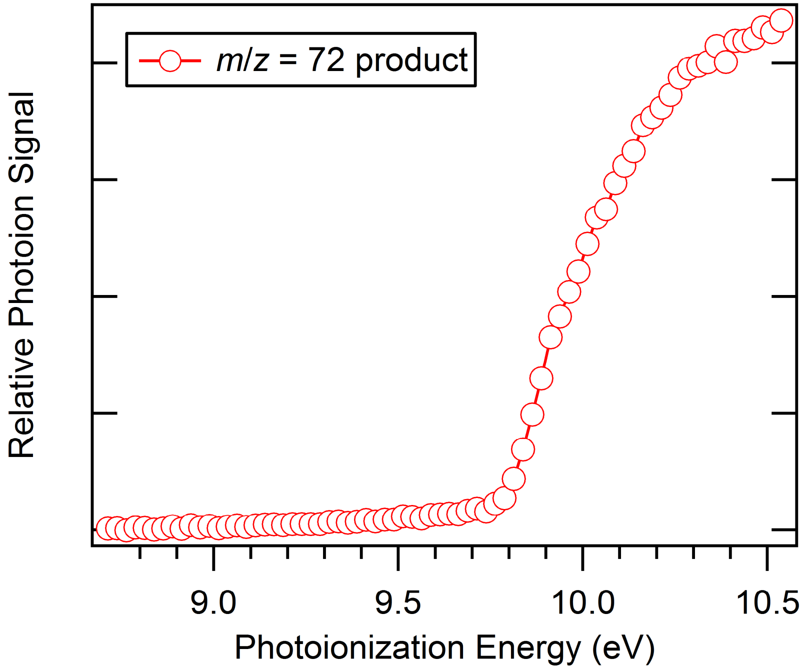


n-Butanol:
The co-products from HO_2 elimination can be distinguished

C_4H_8O calibration spectra

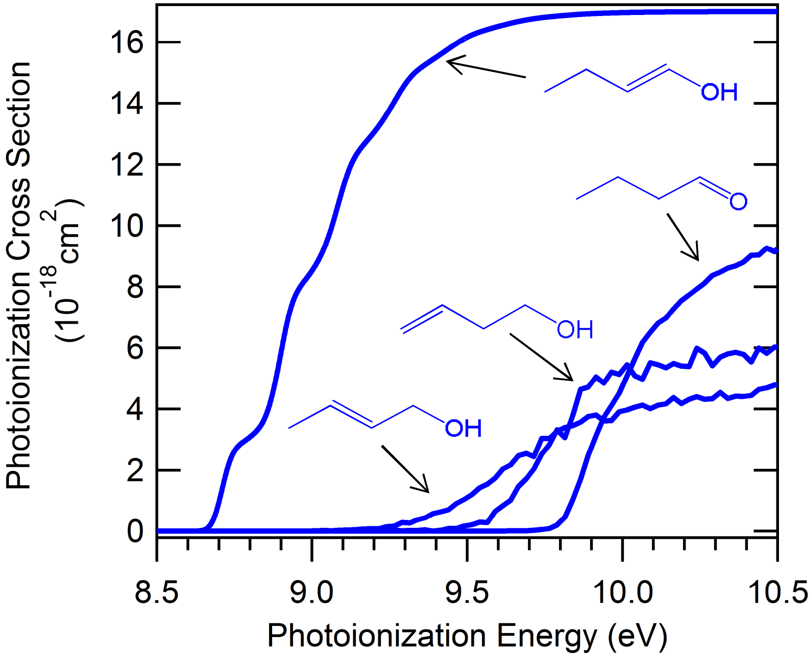


C_4H_8O photoionization product spectrum from *n*-butanol oxidation

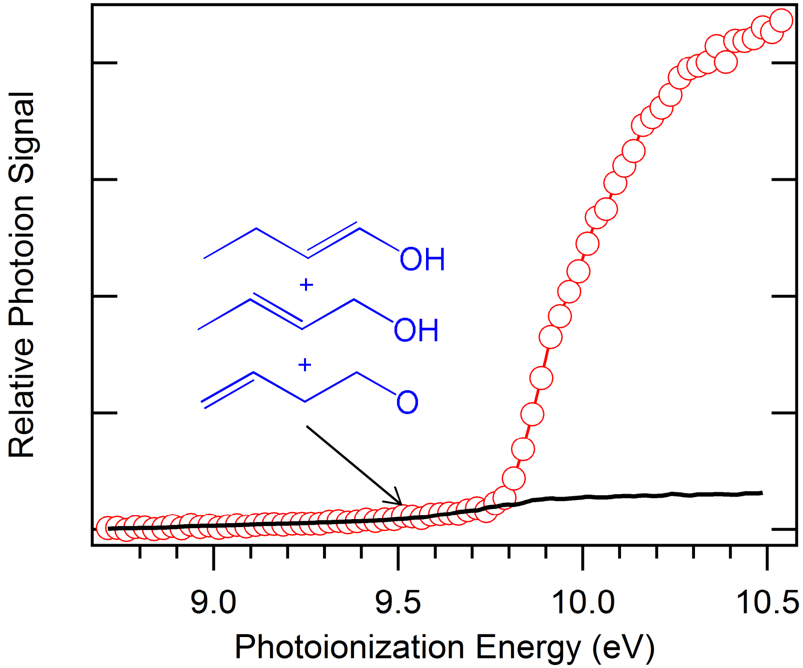


n-Butanol: The co-products from HO_2 elimination can be distinguished

C_4H_8O calibration spectra

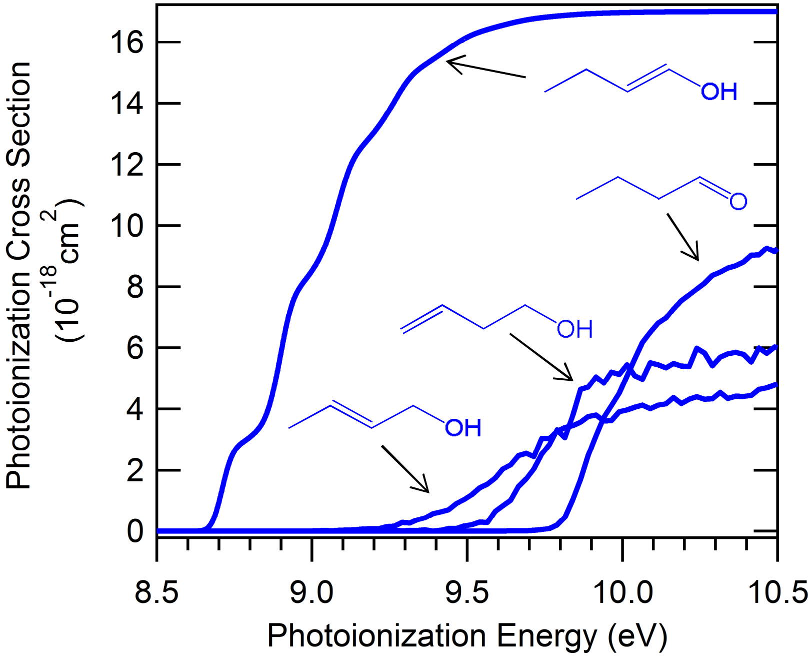


C_4H_8O photoionization product spectrum from *n*-butanol oxidation

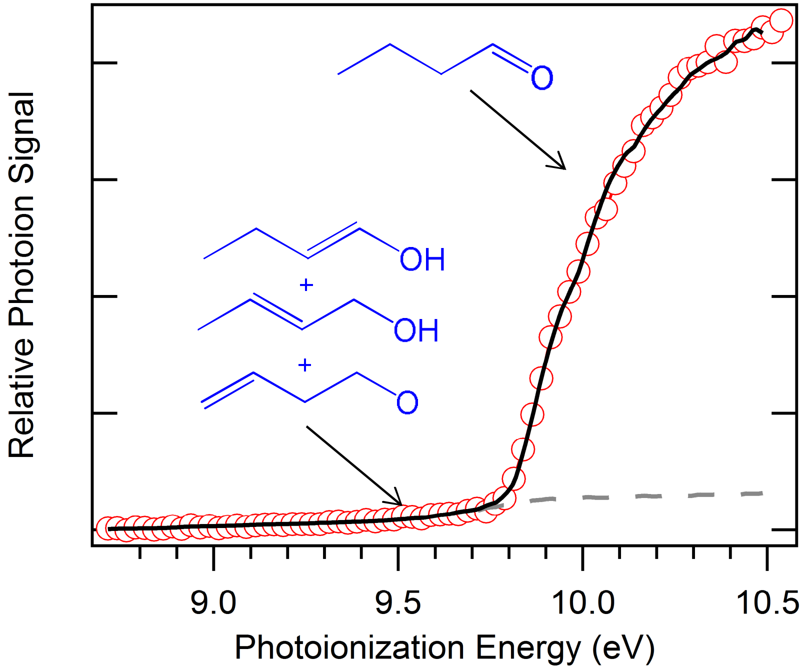


n-Butanol: The co-products from HO_2 elimination can be distinguished

C_4H_8O calibration spectra



C_4H_8O photoionization product spectrum from *n*-butanol oxidation

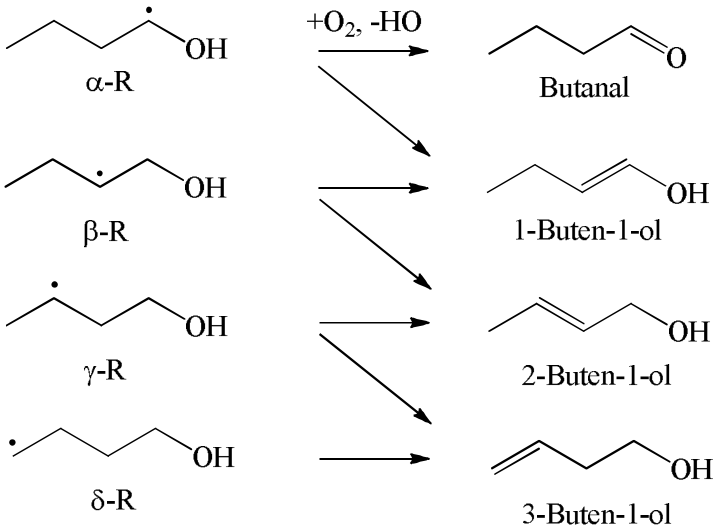


$$S(E) \propto \sum_i [i]\sigma_i(E)$$

→ isomer-resolved branching ratios

HO_2 elimination shows high selectivity
(550 K, 4 Torr)

Branching fraction (%) from Cl + *n*-butanol	Product yield (%) ([Product]/[*n*-butanol$_{consumed}$])
36	44 ± 12
20	0.4 ± 0.2
27	3.8 ± 1.5
27	0.4 ± 0.2



- HO_2 + butanal formation from α-R + O_2 has essentially unity yield
  → Alcohol-specific channel, α-R + O_2 is chain-terminating
- HO_2 elimination from β-, γ-, and δ-R + O_2 is disfavored
- Mass balance for detected stable products is unity (within the uncertainty)
  → Other product must exist for β-, γ-, and δ-R + O_2 . The RO_2 radicals are unstable at the time scale of the experiment (20 ms)

Theoretical characterization of the hydroxybutyl + O_2 reactions

Quantum chemistry:

- Geometries and harmonic frequencies: B3LYP/6-311G(d,p)
- Energies: CBS-QB3

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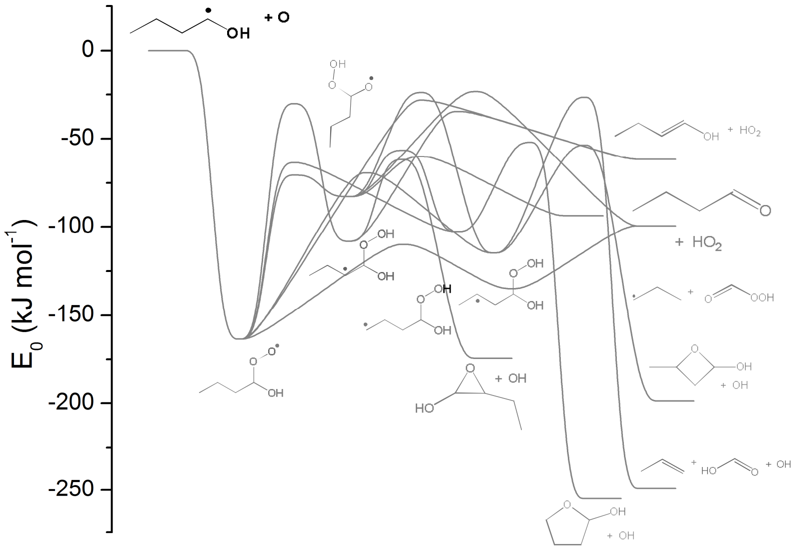
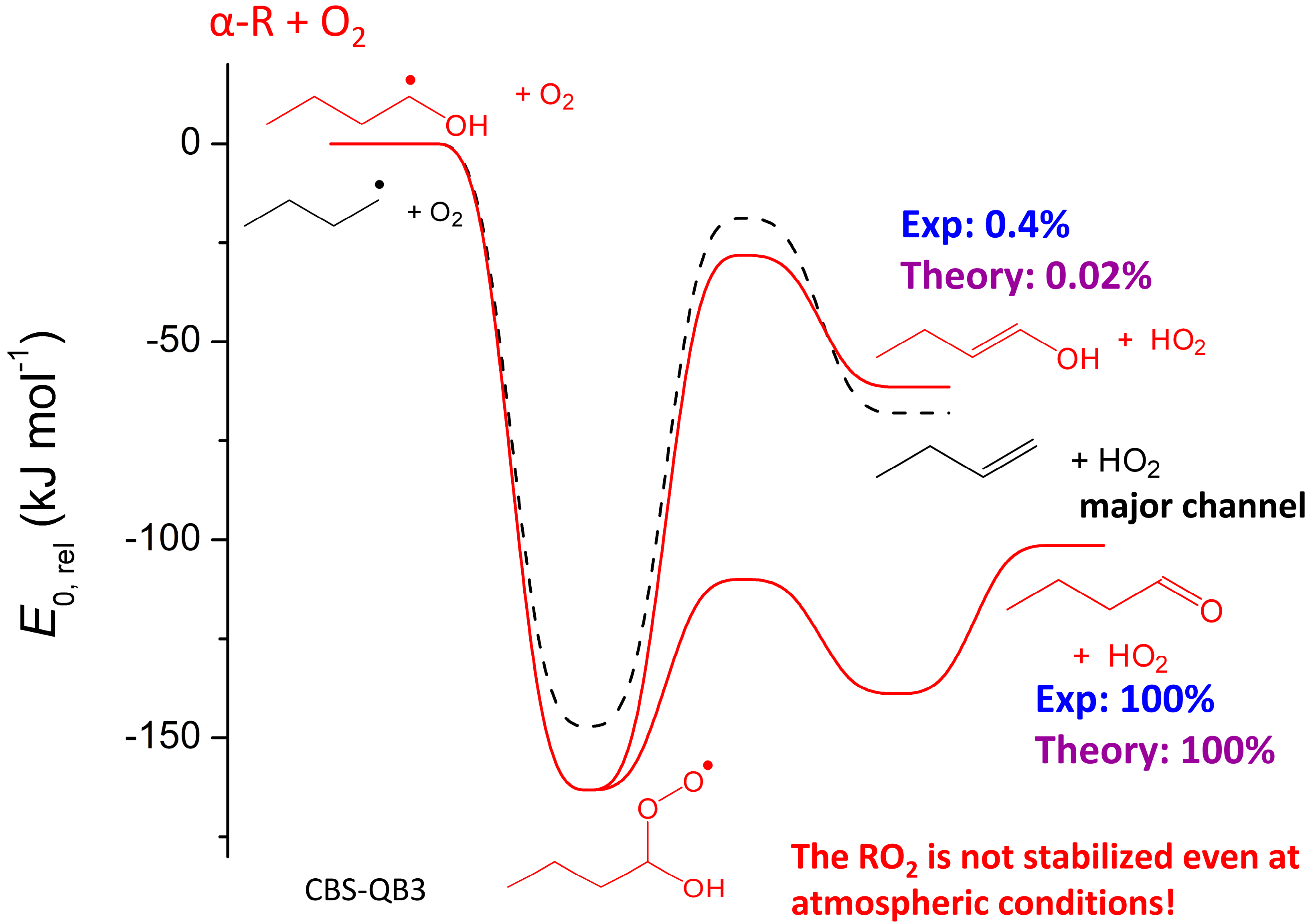


Time-dependent master-equation calculations (Variflex):

- VRC-TST for the barrierless R + O_2 entrance channel
- RRKM calculations for tight transition states
- Exponential-down model for collisional energy transfer
- Torsional modes treated as 1-D hindered internal rotations
- Tunneling: Asymmetric Eckart potential

- The solution of the master equation gives concentration-time profiles for reactants, intermediates and products → “simulation” of the experiment.
- Both formally direct and sequential pathways are accounted for.

α-R + O_2 *vs* *n*-butyl + O_2



Exp: 0.4%

Theory: 0.02%

major channel

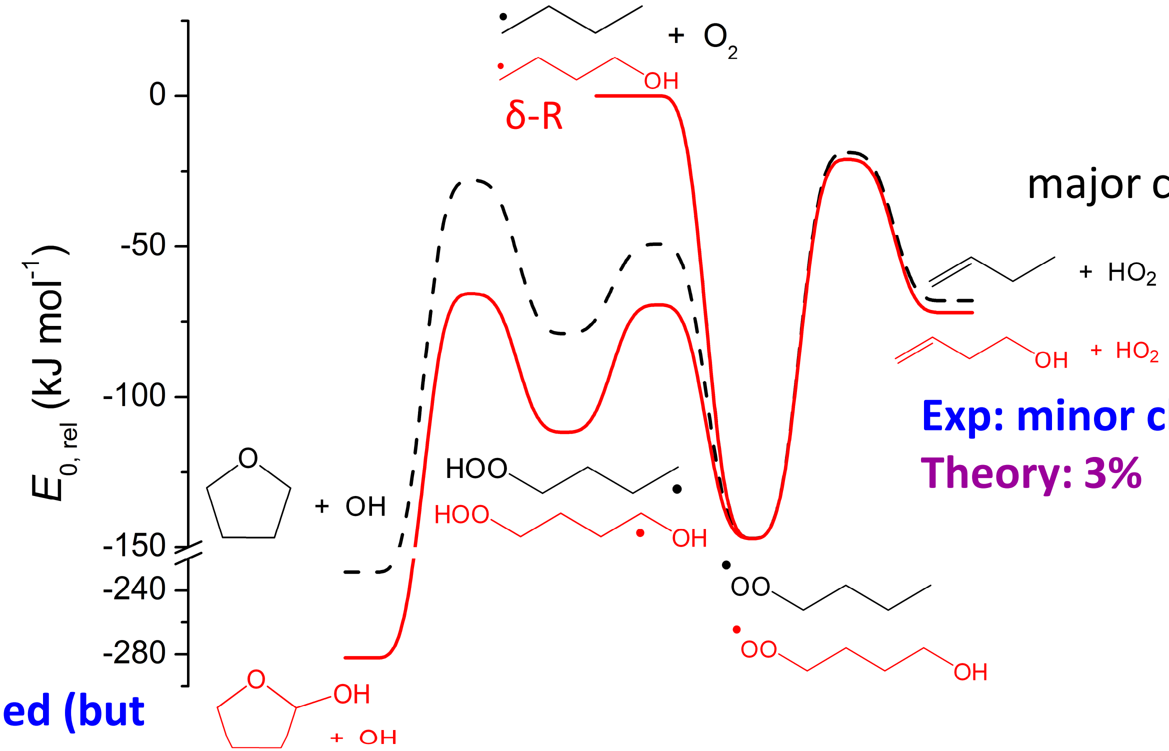
Exp: 100%

Theory: 100%

The RO_2 is not stabilized even at atmospheric conditions!

The δ-R + O_2 reaction is still influenced by the alcoholic OH-group

Compare *n*-butyl + O_2 with 4-hydroxy-1-butyl (δ-R) + O_2



major channel

Exp: minor channel (< 10%)

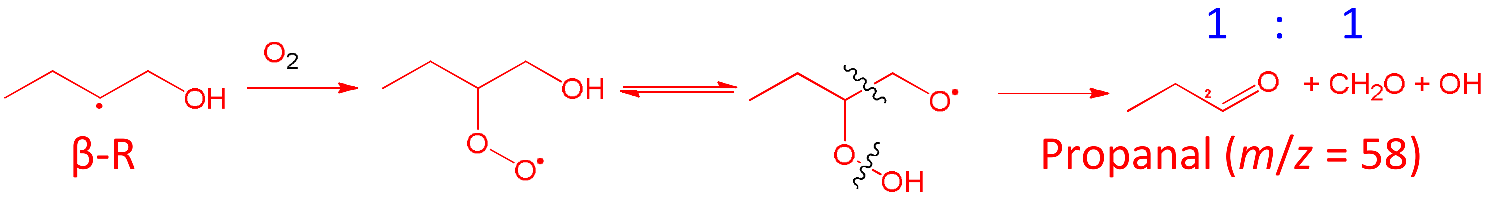
Theory: 3%

Exp: not quantified (but strong qualitative evidence)

Theory: 90%

What separation of alkyl radical center and –OH group is necessary to reduce the influence of the –OH group?

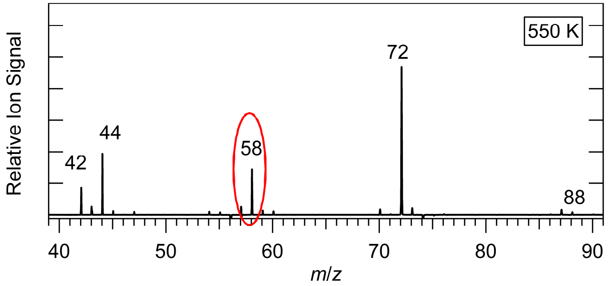
The "Waddington mechanism" is the major product channel in the β-R + O_2 reaction



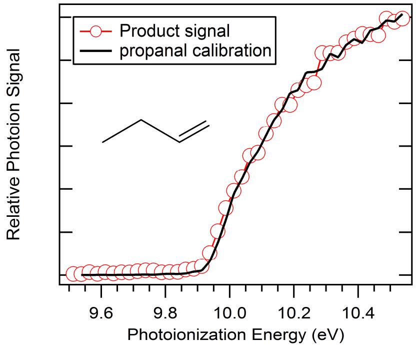
Exp: 100% (550 K, 4 Torr)

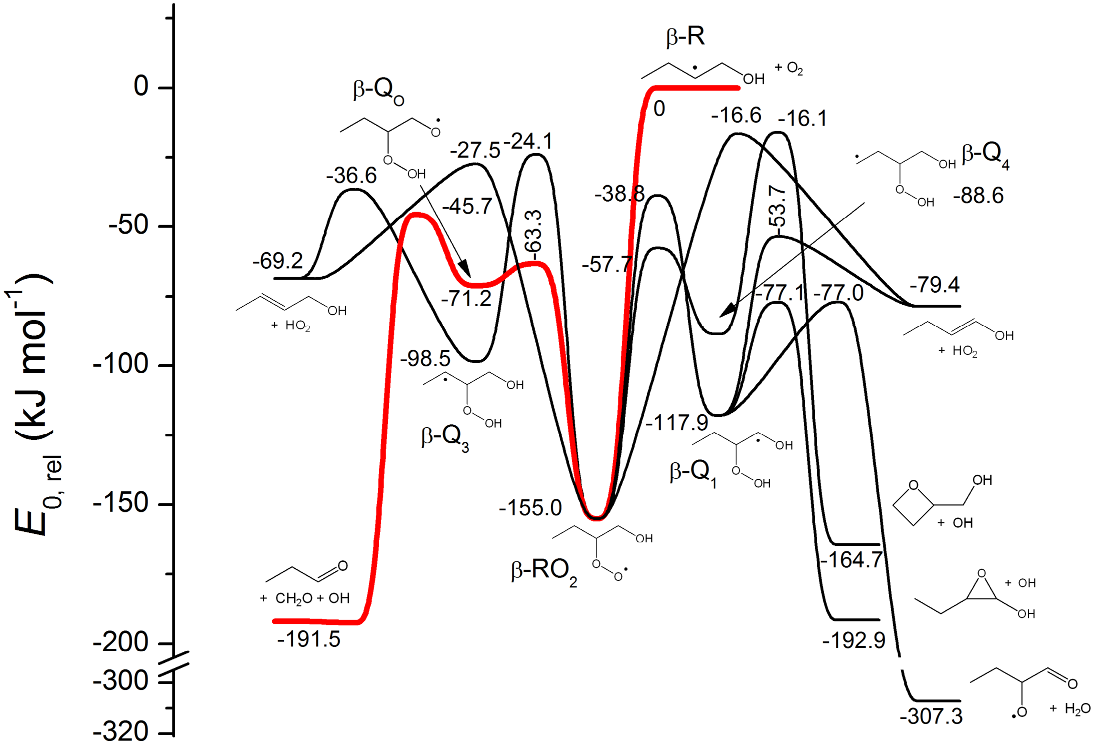
Theory: 85%

Product mass spectrum



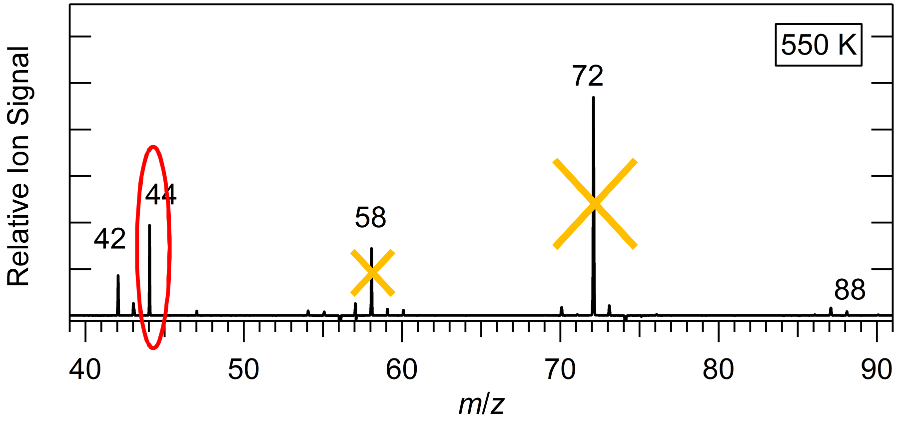
$m/z = 58$ (C_3H_6O) photoionization spectrum



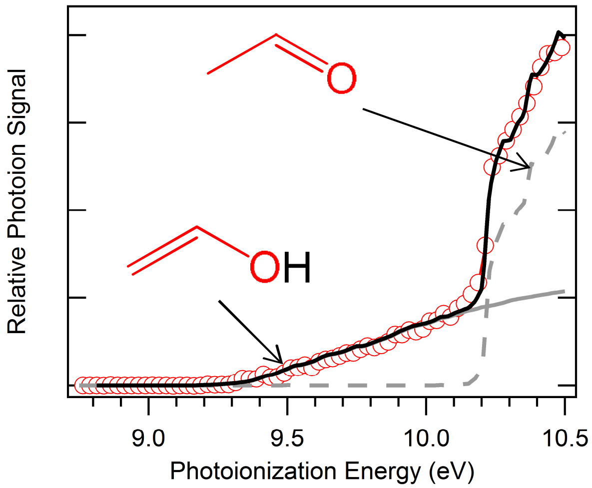


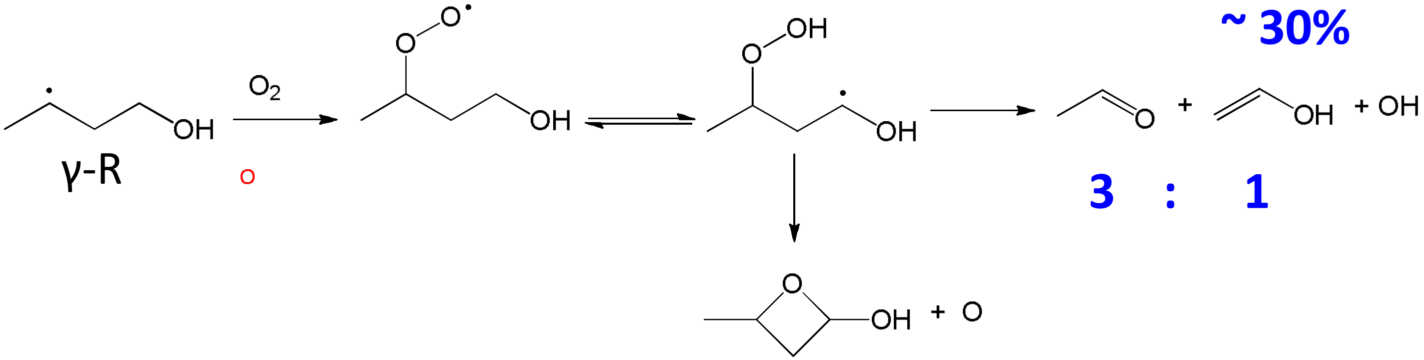
γ-R + O_2: Conventional RO_2 chemistry cannot account for the amount of acetaldehyde observed

Product mass spectrum



***m/z* = 44 (C_2H_4O) photoionization spectrum**





~ 30%

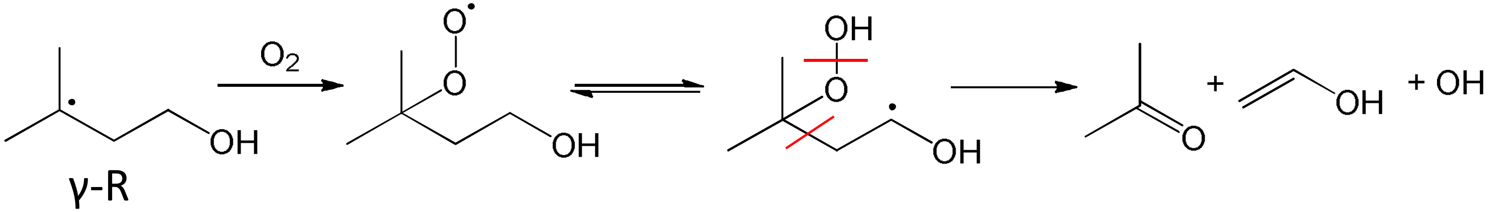
3 : 1

upper yield of 20%

Isopentanol: Excess of acetone over ethenol cannot be explained as well

isopentanol

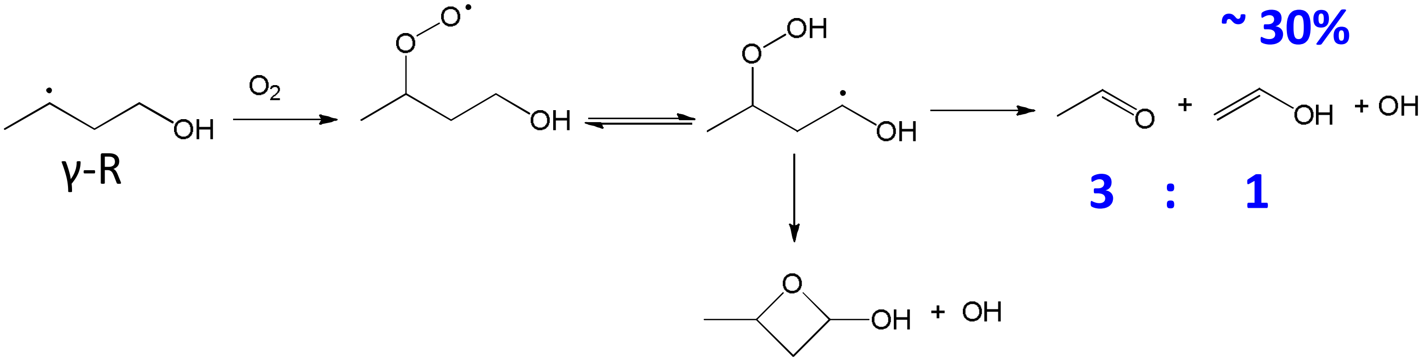
3 : 1



Welz et al, PCCP 2012, 14, 3112

Clear evidence of missing pathways!

n-butanol

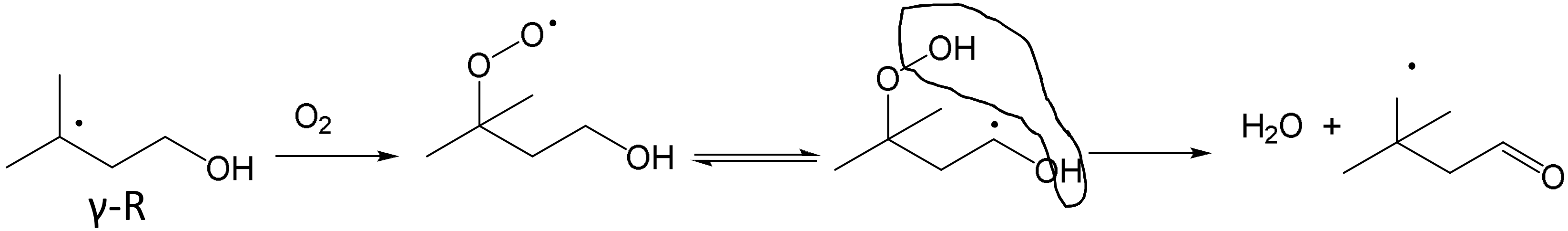


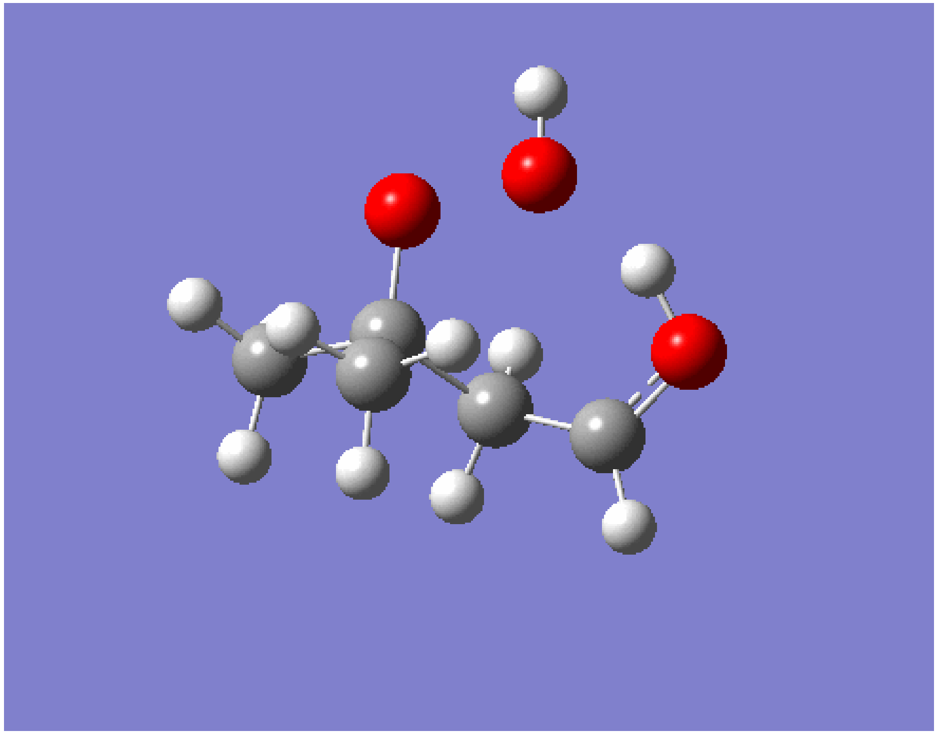
~ 30%

3 : 1

upper yield of 20%

Water elimination – Unconventional peroxy radical chemistry





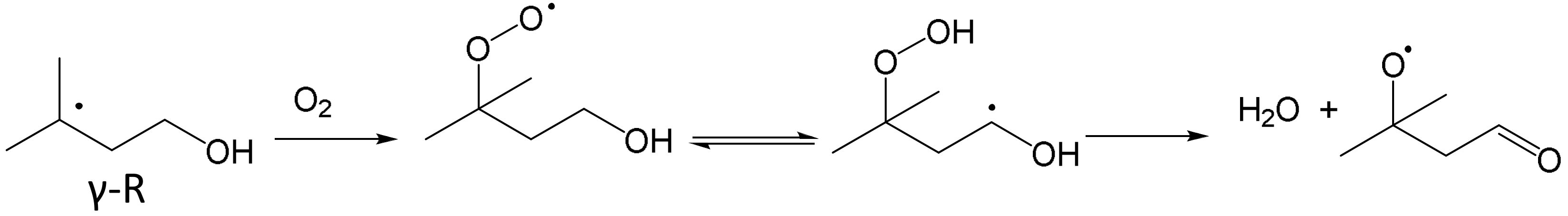
- happens via a single saddle point from QOOH
- concerted breaking of 2 bonds and making of 2
- product is a weakly bound alkoxyaldehyde

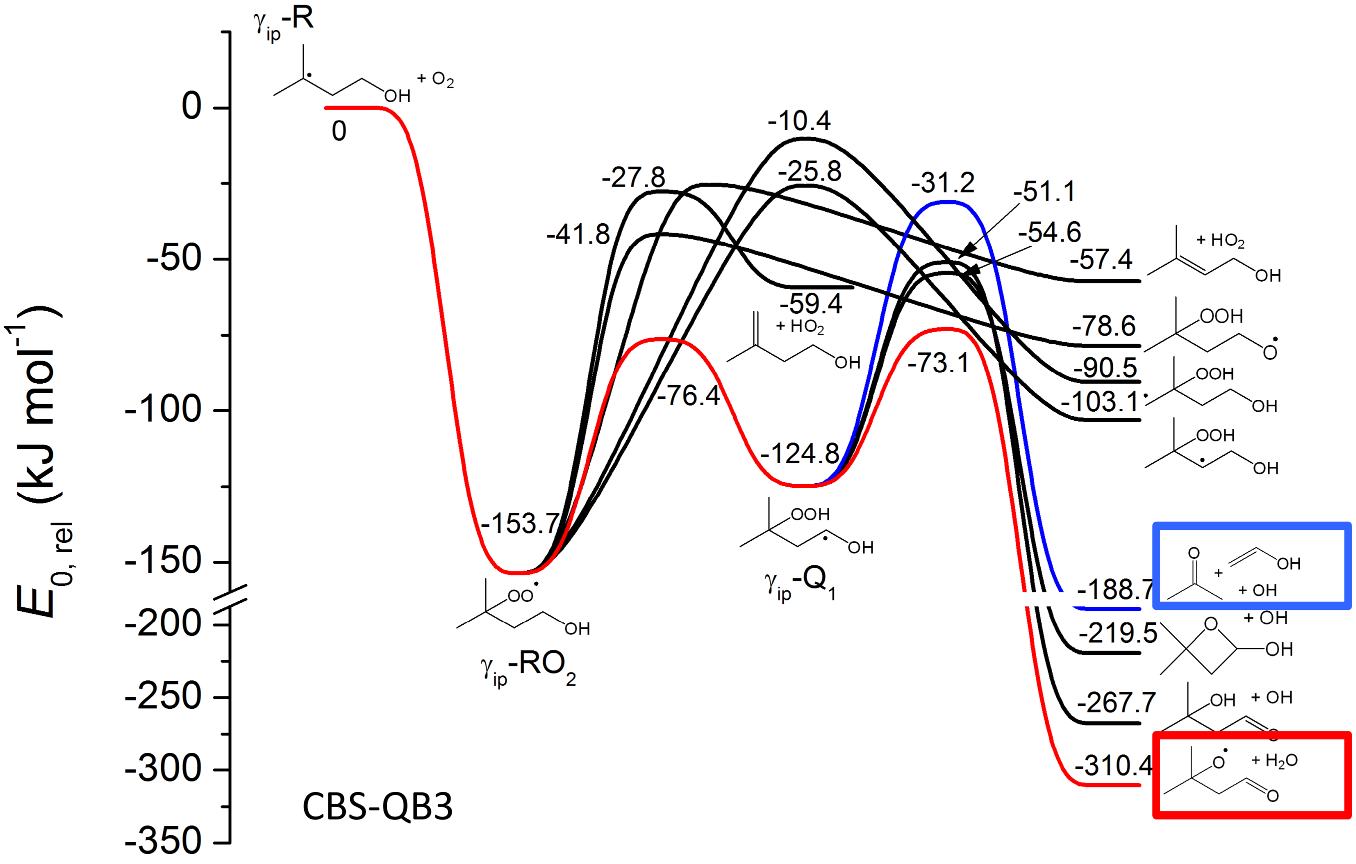
H

B3LYP/6-311G(d,p)

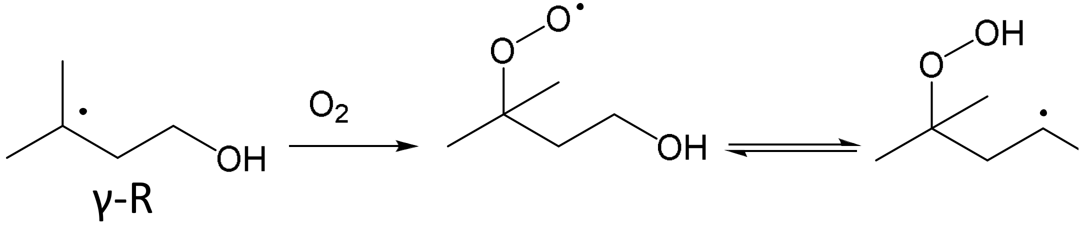
Welz, Klippenstein, Harding, Taatjes, Zádor, J. Phys. Chem. Lett. 2013, 4, 350

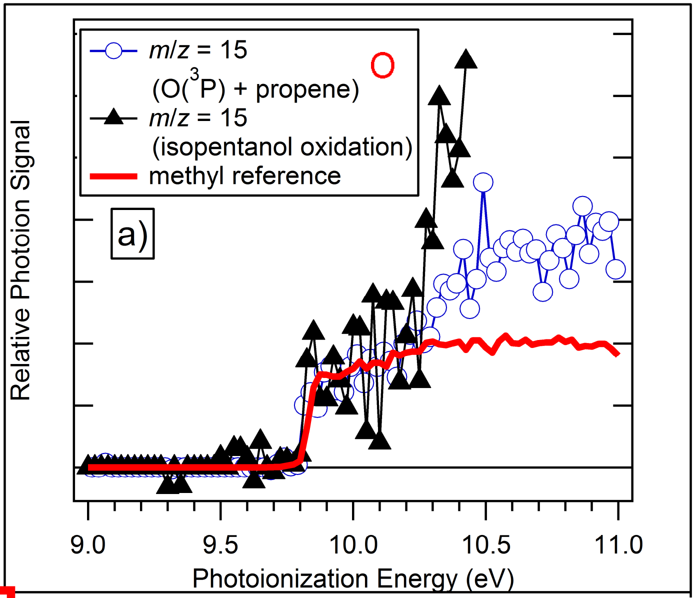
The water elimination channel is the overall lowest-lying pathway in the γ-R + O_2 reaction

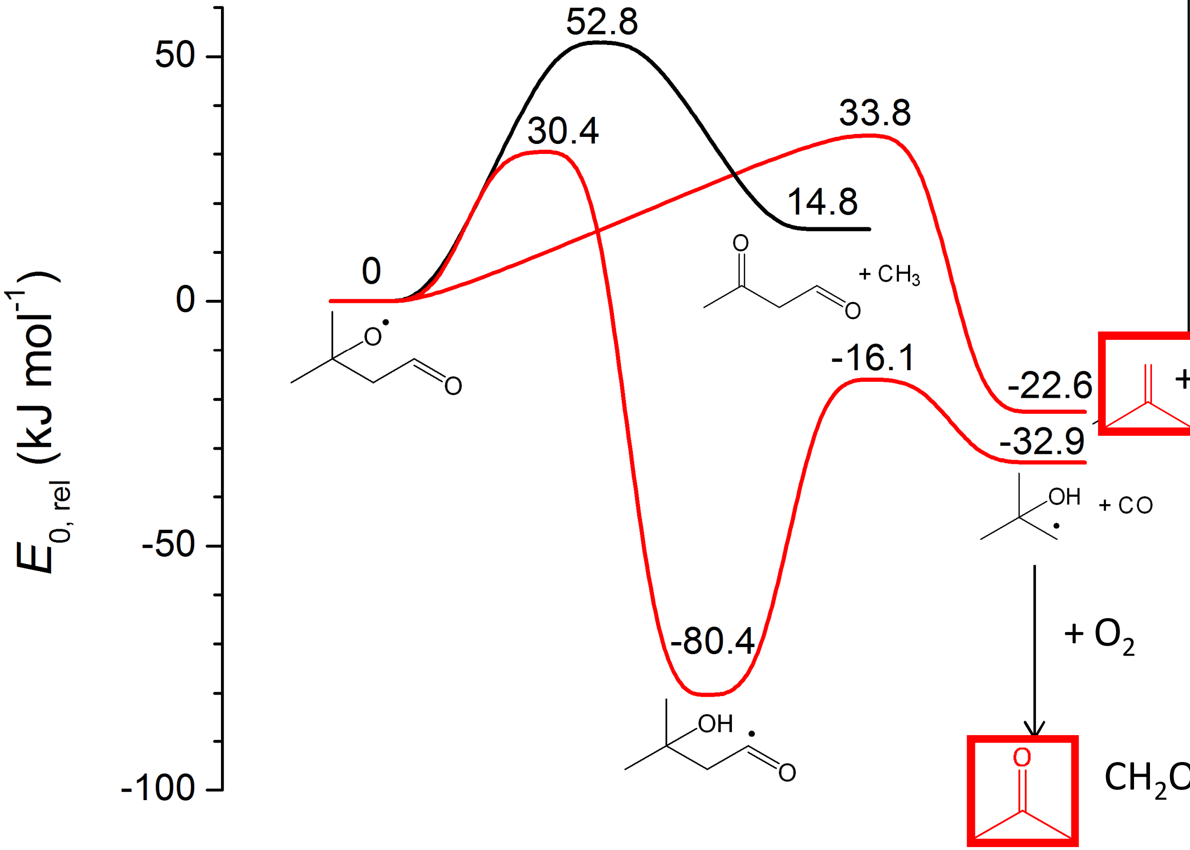


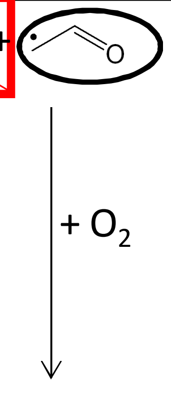


Decomposition of the alkoxyaldehyde produces acetone, but no ethenol









$CH_2O + OH + CO$

vinoxy radical fragments to m/z = 15

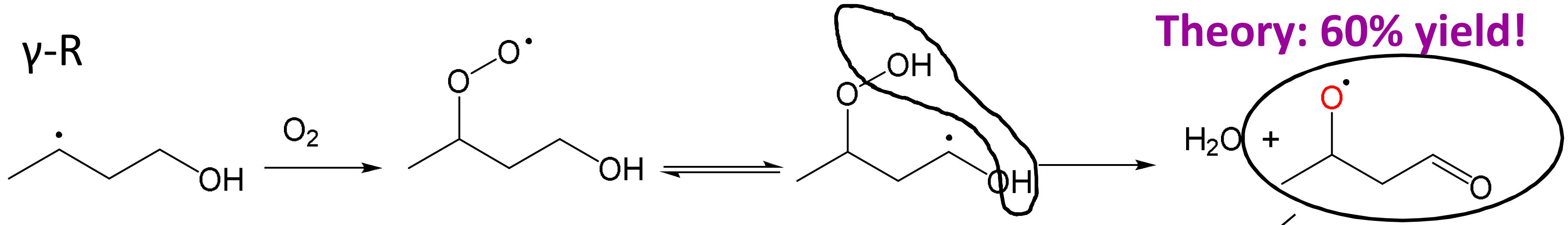
Savee et al., 2012, PCCP

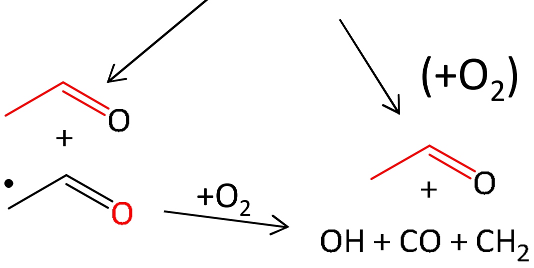
photoionization spectrum proves the presence of vinoxy

n-butanol: Water elimination is the dominant product channel in the γ-R + O_2 reaction and forms acetaldehyde !

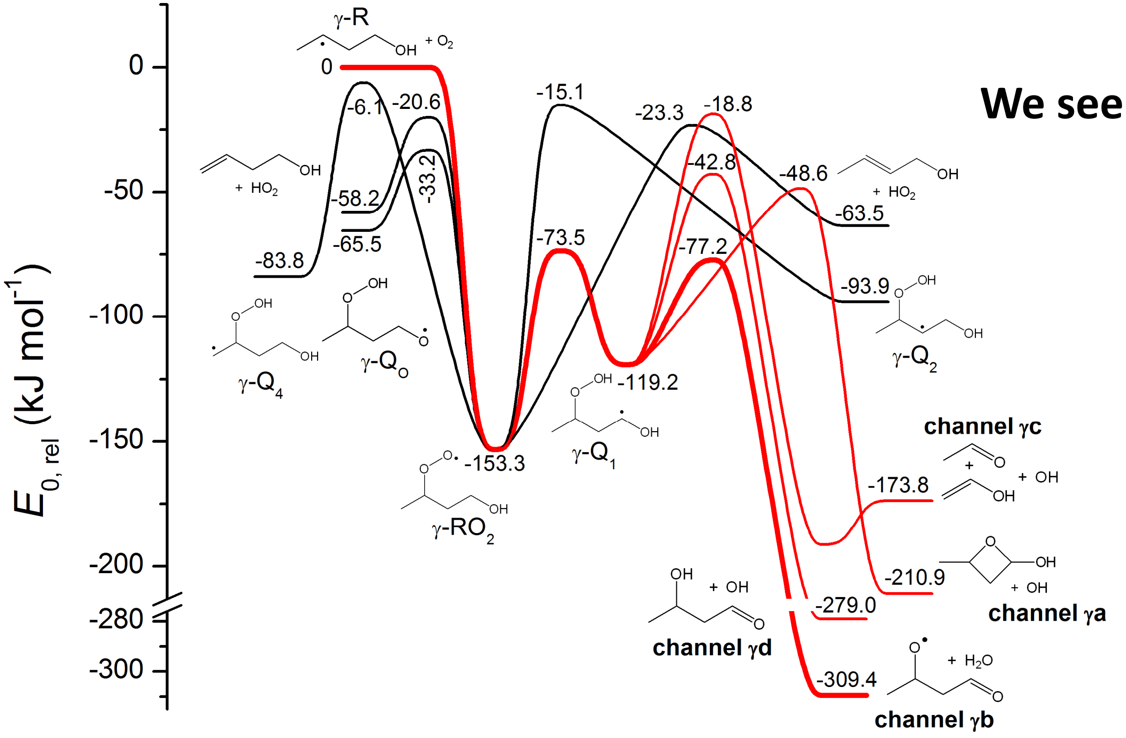
Exp: 50% yield!

Theory: 60% yield!





We see vinoxy



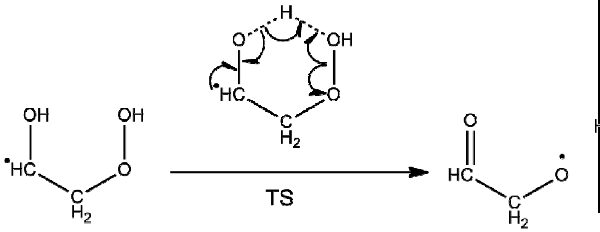
Exothermicity of 310 kJ/mol
→ substantial heat release;

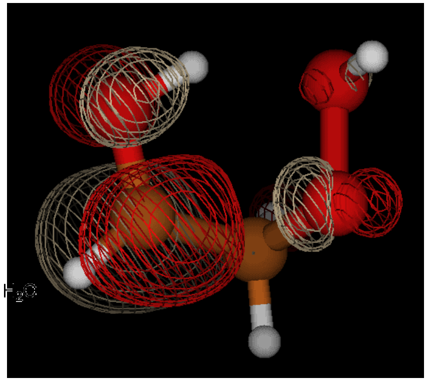
Associated with OH formation

Higher pressure further favors water elimination

Implications and general relevance of the water elimination channel

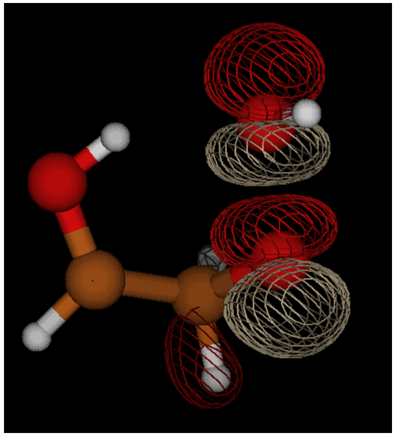
- Water elimination is very relevant in γ-R + O_2 reactions, but no alcohol combustion model contains this pathway yet!
- It can also happen in β-R + O_2 and δ-R + O_2 systems, but is less important there
- In the vicinity of the saddle point: weak interaction of radical and zwitterionic states





reactant side HOMO
C-centered radical

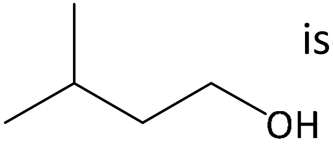
B3LYP/6-311++G*



product side HOMO
O-O σ^*

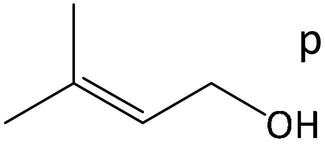
- Can water elimination happen in other QOOH systems? Alkanes? Other oxygenates?

Effect of unsaturation:
Cl-initiated oxidation of isopentanol vs prenol



isopentanol

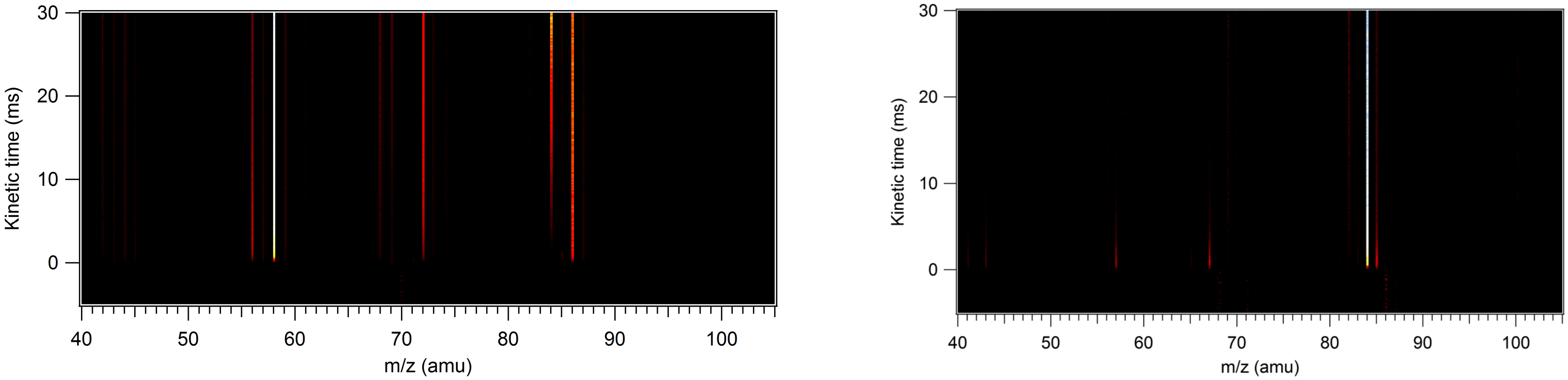
m/*z* = 88



prenol

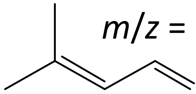
m/*z* = 86

Time-resolved product mass spectra at 550 K



O

m/*z* = 84

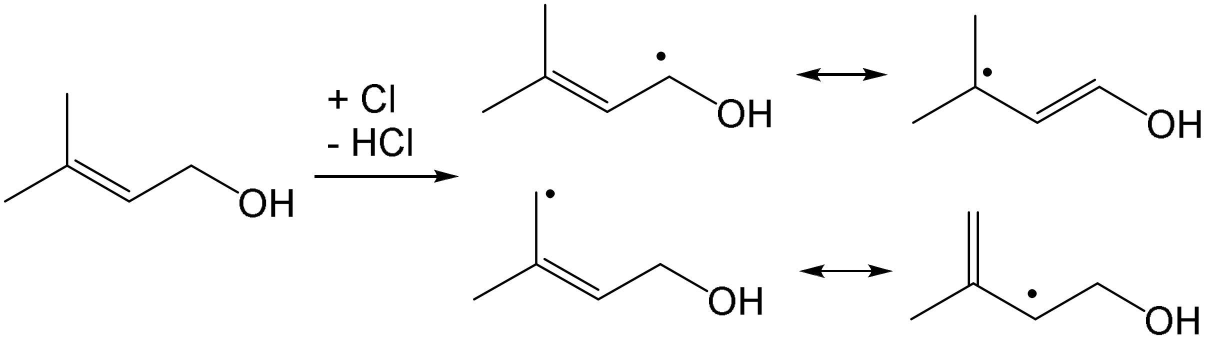


- Rich oxidation chemistry: multiple product channels
- similar to *n*-butanol

- Gives essentially only prenal + HO_2
- QOOH chemistry is absent

Allylic radicals inhibit low-temperature chemistry

Cl + Prenol forms allylic radicals!

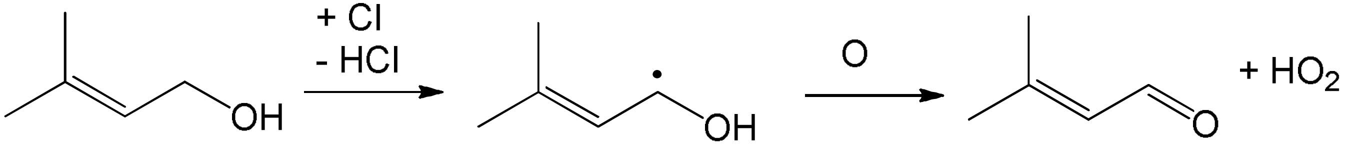


Resonance stabilization gets lost after O_2 addition

- → Allylperoxy radicals have shallower wells which favor backdissociation
- → Many barriers are above energy of the reactants

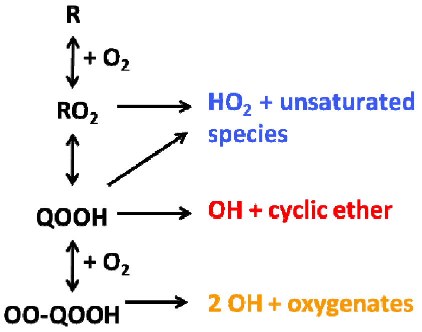
But: Barrier for HO_2 elimination of the α-OH radical is still below the energy of the reactants

o



Summary

Understanding the competition between channels in RO_2 chemistry is important to predict low-T autoignition behavior



R

$+ O_2$

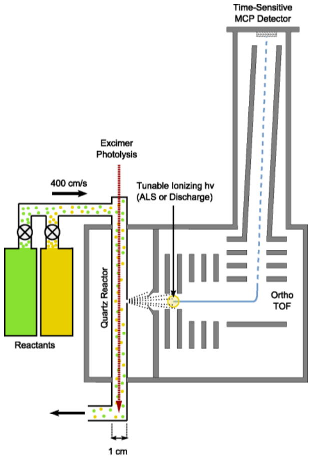
RO_2 → HO_2 + unsaturated species

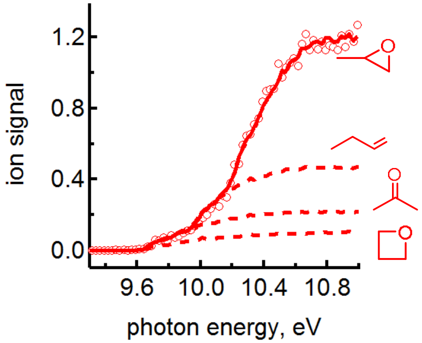
QOOH → OH + cyclic ether

$+ O_2$

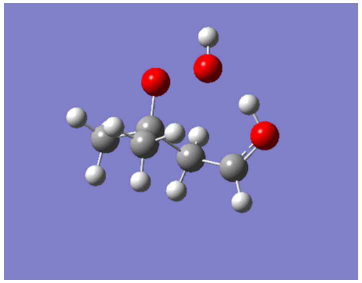
OO-QOOH → 2 OH + oxygenates

MPIMS in combination with quantum chemistry and theoretical kinetics is a powerful tool to investigate low-T oxidation chemistry.



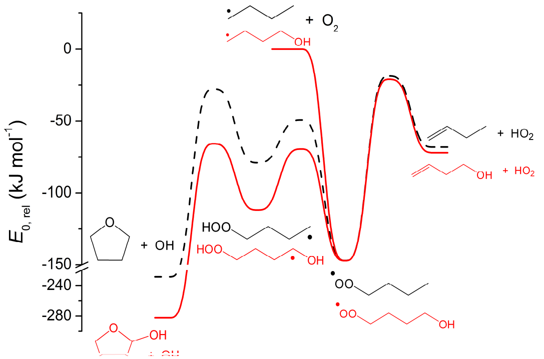


We found that water elimination is an important pathway in alcohol oxidation



The fuel structure has a substantial influence on the oxidation pathways

2



Acknowledgements

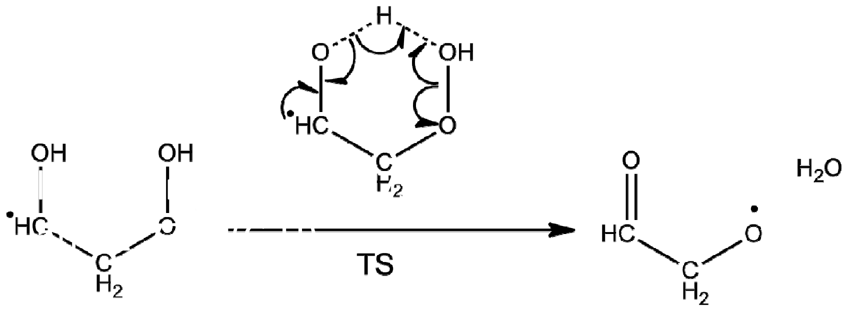
- Craig A. Taatjes, David L. Osborn, Judit Zádor, Leonid Sheps, John D. Savee, Arkke J. Eskola (Sandia)
- Stephen J. Klippenstein, Lawrence B. Harding , Michael P. Burke (Argonne)
- Howard Johnsen (Sandia) and the staff of the Chemical Dynamics Beamline at the Advanced Light Source for technical support

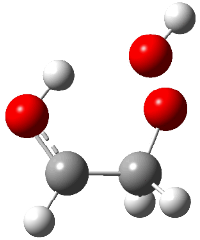
This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the United States Department of Energy (DOE); in part under the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry (ANL FWP # 59044; SNL FWP # 014544), and in part under the by the Laboratory Directed Research and Development program at Sandia National Laboratories.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the DOE under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.

Thank you!

Simplest system: Ethanol

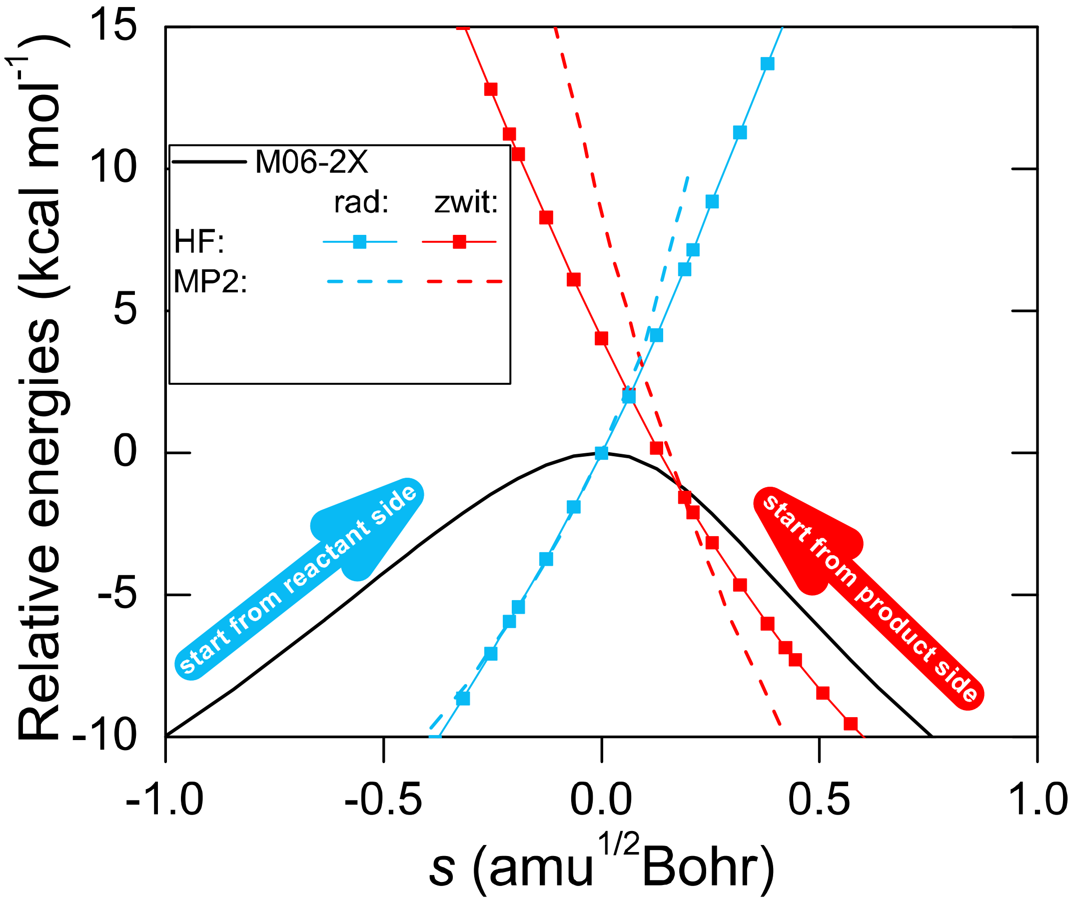




TS TS’

B3LYP/6-311++G*

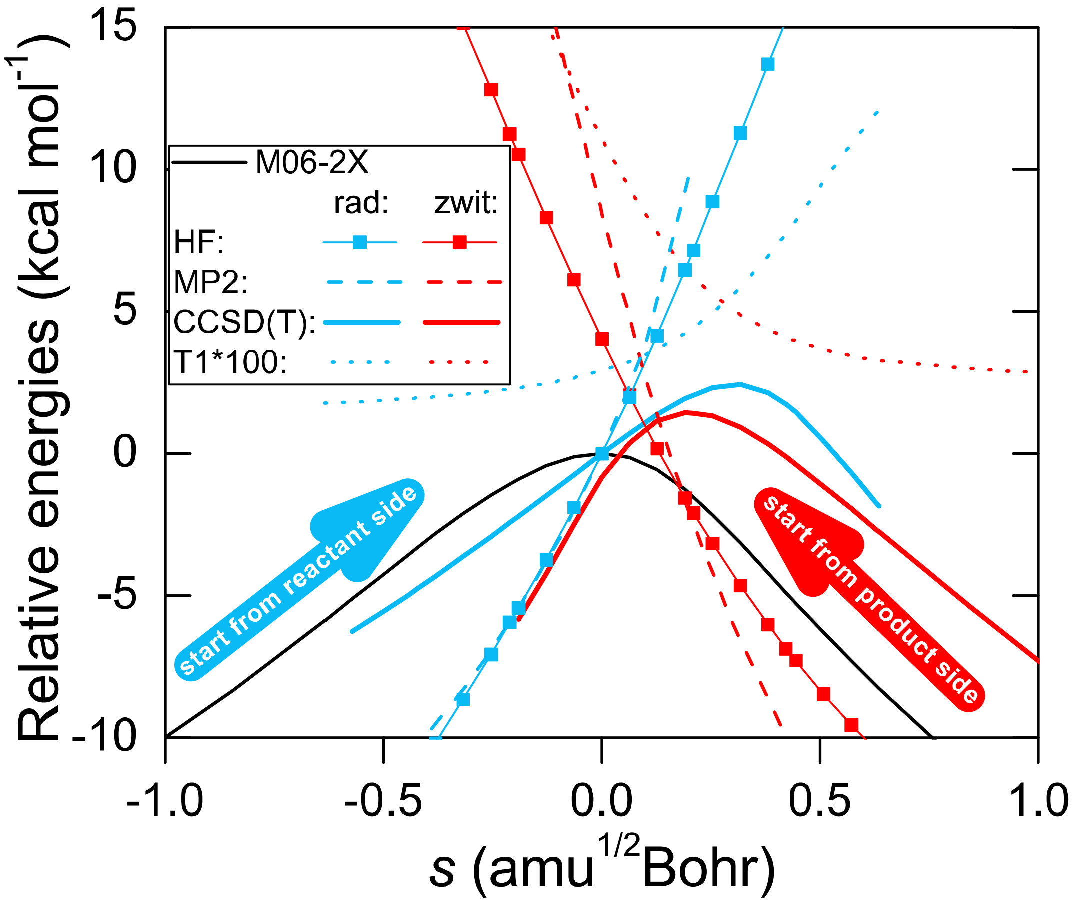
In the single reference framework two weakly interacting states can be found



reactant side: **radical** character, small dipole moment
porduct side: **zwitterion** character, larger dipole moment

Orbital character depends on where the calculation is started
HF solutions do not mix

In the single reference framework two weakly interacting states can be found



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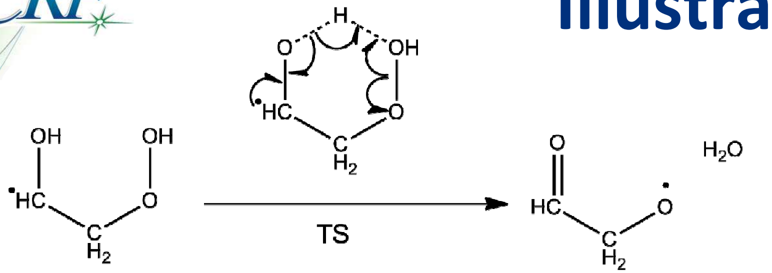
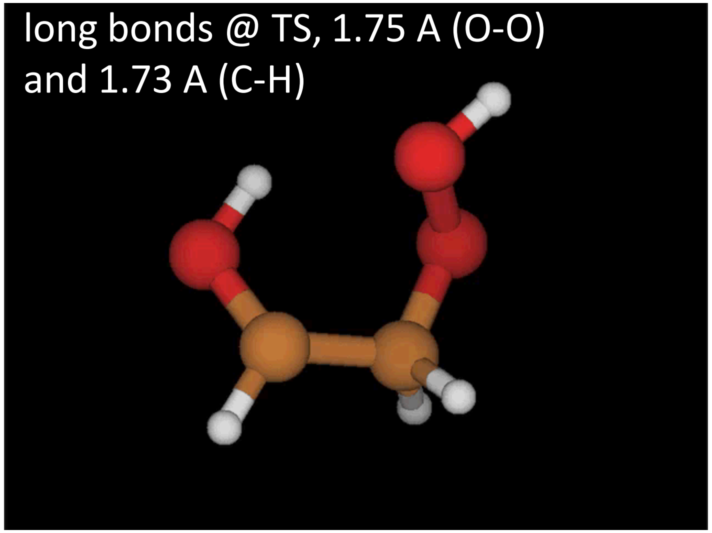
dipole moments (D)

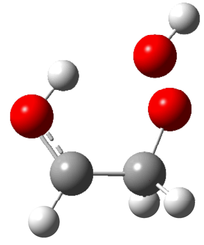
	radical	**zwitterion**
ROHF:	2.1	4.9
RMP2:	1.3	4.9
UCCSD:	1.1	2.9
UCCSD(T):	1.4	1.6

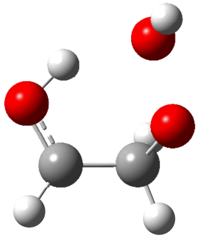
UCCSD(T) energies become less dependent on initial orbital guesses
barriers for ethanol case: 18.2 and 17.2 kcal mol^{-1}
M06-2X barrier: 16.9 kcal mol^{-1} ➔ close (within uncertainty) to the UCCSD(T) barriers.

The water elimination pathway – Illustrated on ethanol



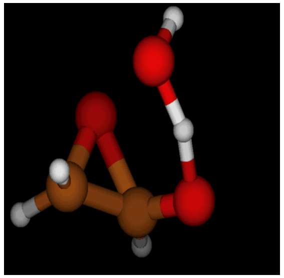

long bonds @ TS, 1.75 A (O-O) and 1.73 A (C-H)


TS


TS’

B3LYP/6-311++G*

- happens via a single saddle point barrier
- concerted breaking of 2 bonds and making of 2
- product is weakly bound alkoxy carbonyl
- at the saddle point interatomic distances are larger than typical tight transition states, but smaller than roaming
- the alternative 2-step cyclic ether + roaming pathway is similar in energy, but has small probability



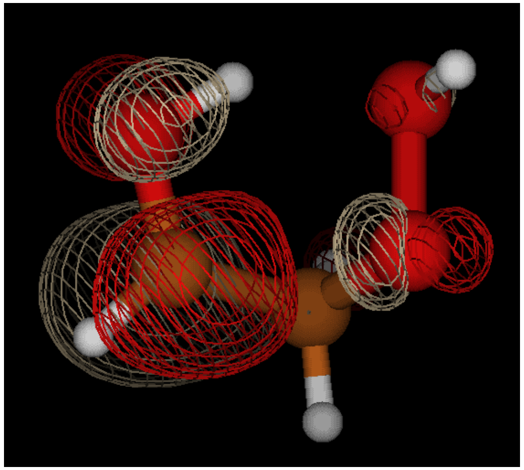
- the ordinary, two-step version of the above process does not play a role in the experiments because of the small radical and large precursor concentrations

Slide 39

A5 See my next comment -- I'd probably introdice the water elimination pathway for the gamma-QOOH. That connects better to the isopentanol and isobutanol systems.

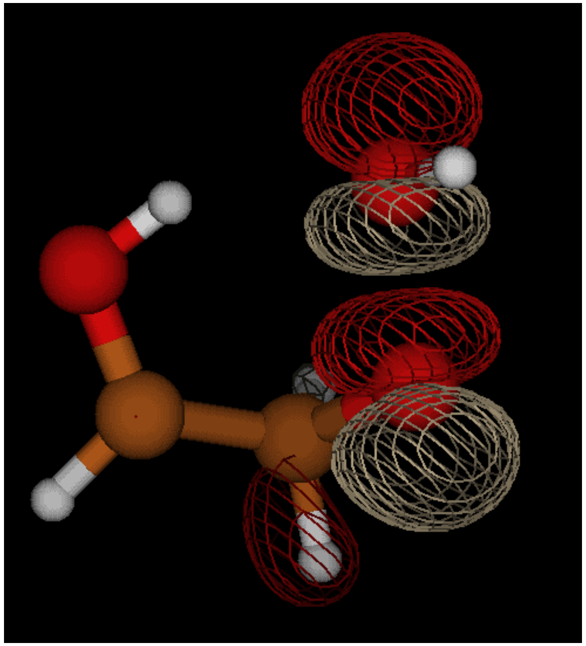
Administrator, 7/5/2013

HOMOs
on the two sides of the saddle point



reactant side HOMO

C-centered radical



product side HOMO

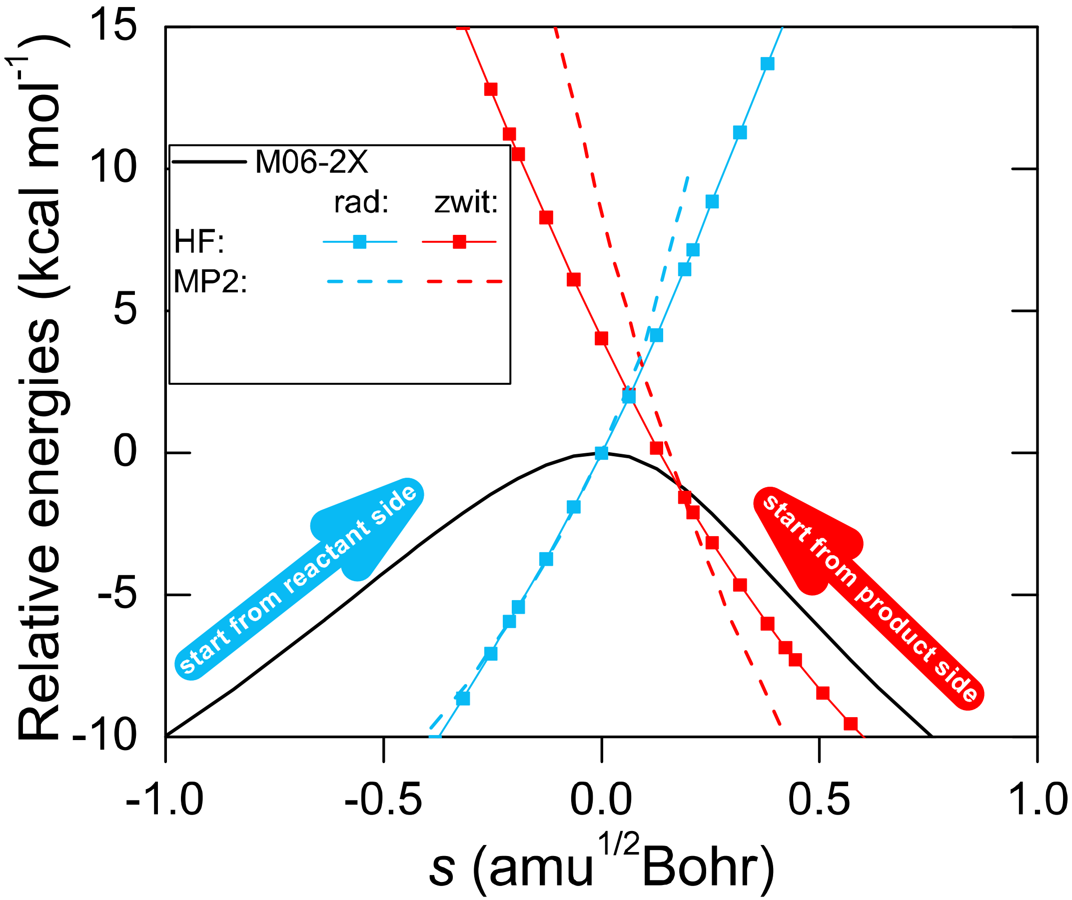
O–O σ*

The consecutive process (breaking O–O bond and then abstracting the H atom) involves a doublet triradical, which is energetically unfavored.

The simultaneous pathway involves the mixing of weakly interacting, spatially orthogonal orbitals.

Antibonding orbital being the HOMO ➔ this is an electronic state with **zwitterionic character**

In the single reference framework two weakly interacting states can be found



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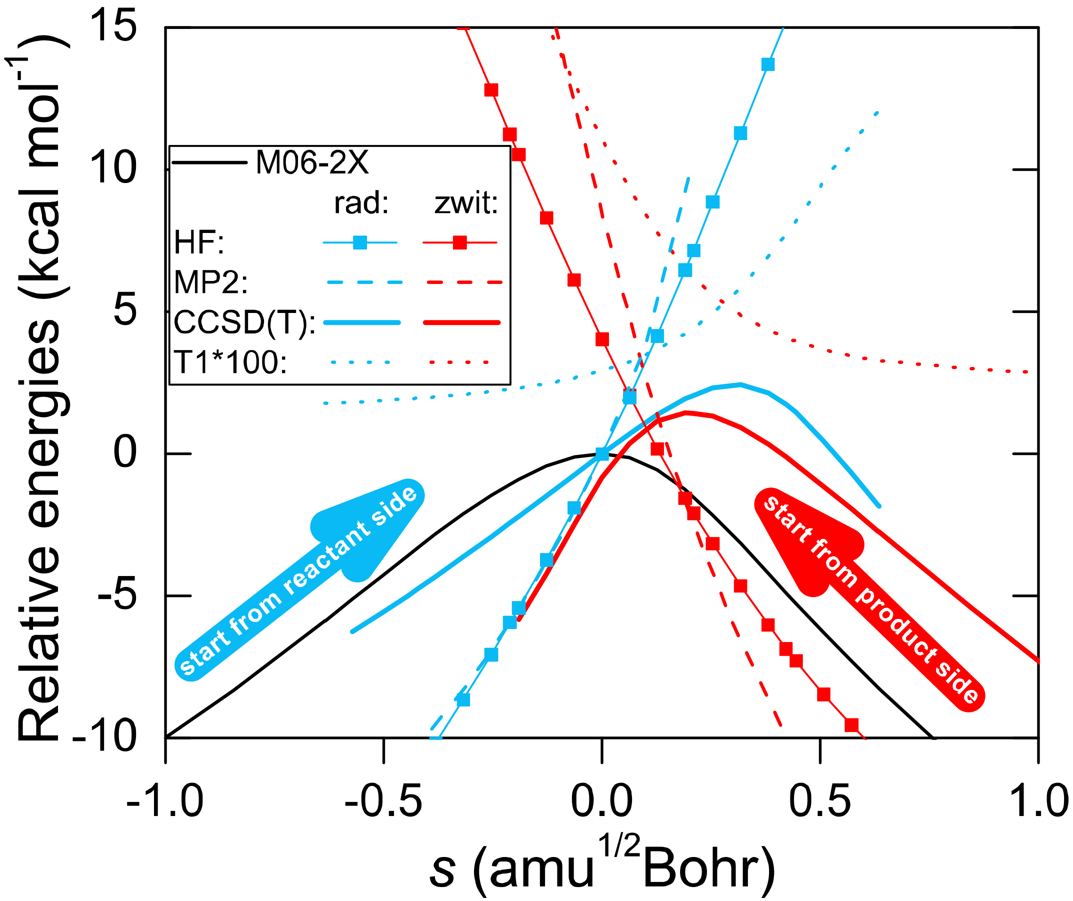

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