COMBUSTION RESEARCH FACILITY

SAND2012-5242C

Low-temperature oxidation chemistry of 1-butanol: A combined photoionization mass spectrometry and quantum-chemical/master-equation study

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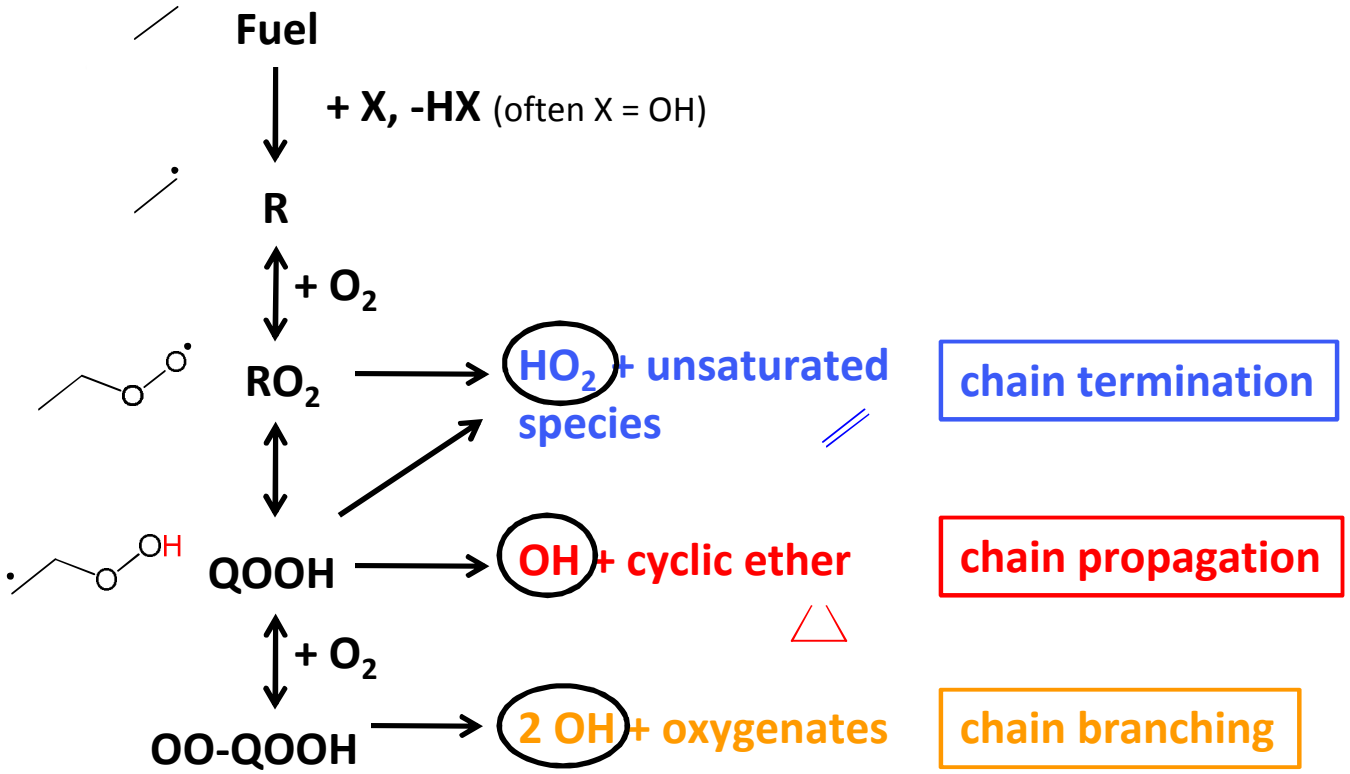
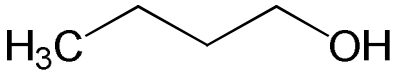
22nd International Symposium on Gas Kinetics
Boulder, CO

Modern internal combustion engine concepts rely on compression ignition

Peroxy radical chemistry governs low-temperature (T < 900 K) ignition.

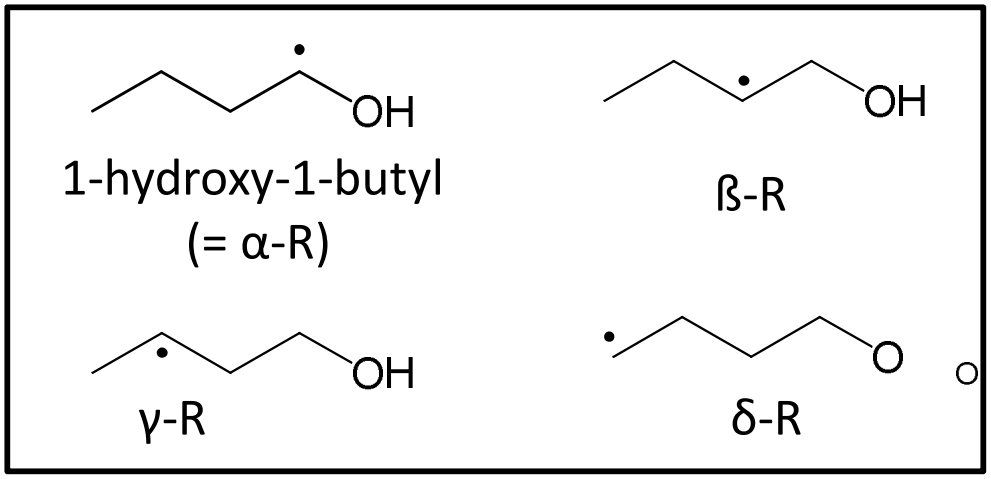


The low-temperature oxidation chemistry of 1-butanol is underexplored



1-butanol

H-abstraction



O_2

Products

550 K, 4 Torr

How does the OH group in 1-butanol influence reactivity, in particular the critical competition between HO_2 vs OH forming pathways?

Theoretical characterization of the hydroxybutyl + O_2 reactions

Quantum chemistry:

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

Time-dependent master-equation calculations (Variflex)

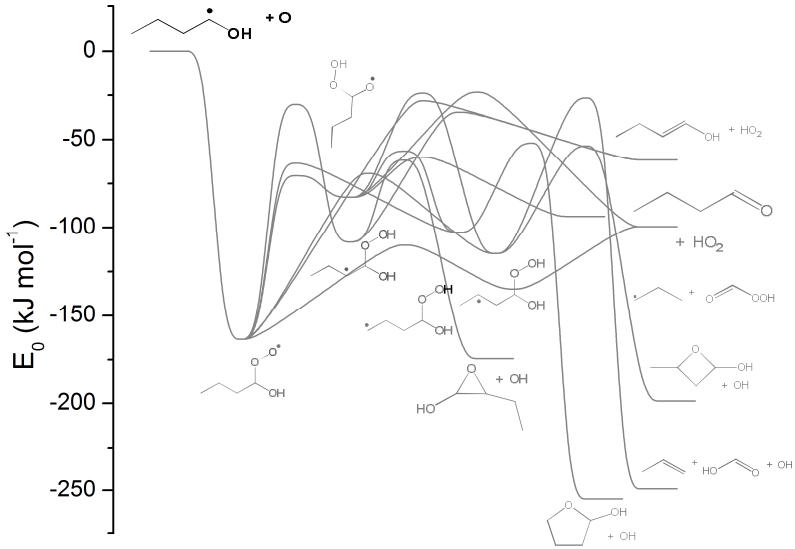
- VRC-TST for the barrierless R + O_2 entrance channel
- RRKM calculations for tight transition states
- Collisional energy transfer: Exponential-down model
- Torsional modes treated as 1-D hindered internal rotations
- Tunneling: Asymmetric Eckhart potential

H

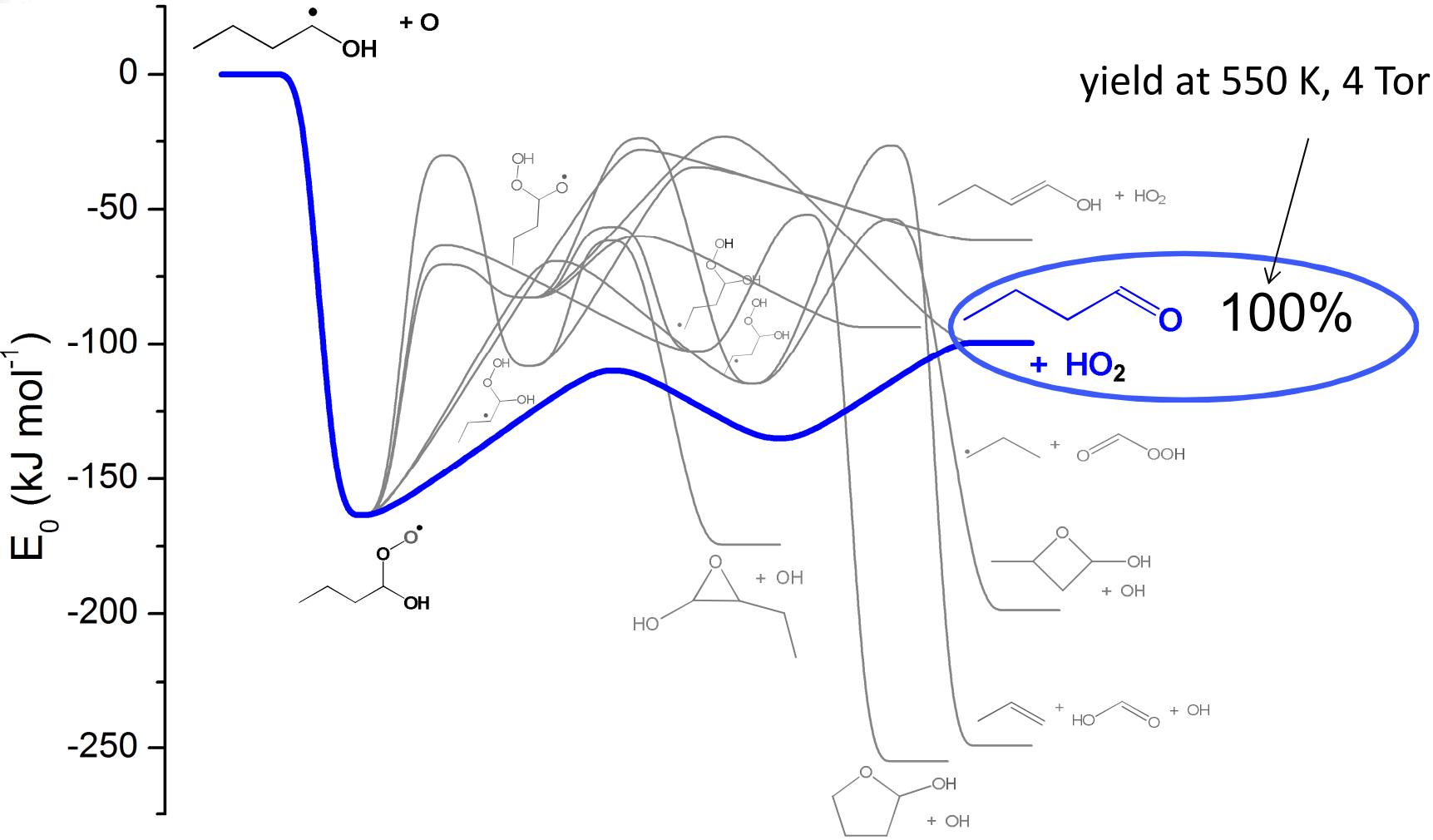
The solution of the time-dependent master equation

→ gives product branching ratios within each hydroxybutyl + O_2 reaction (here at 550 K, 4 Torr)

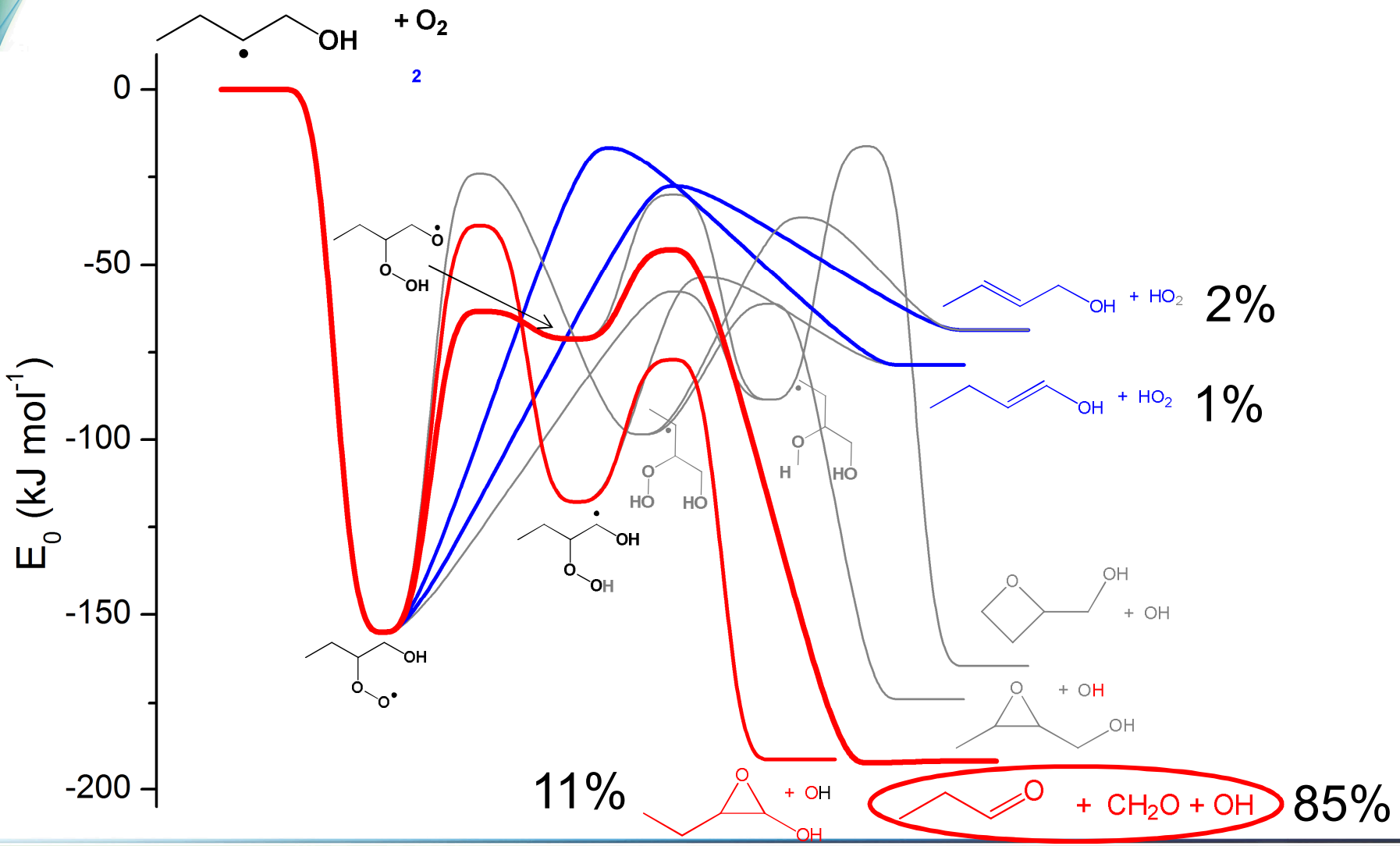
→ includes formally direct and sequential pathways



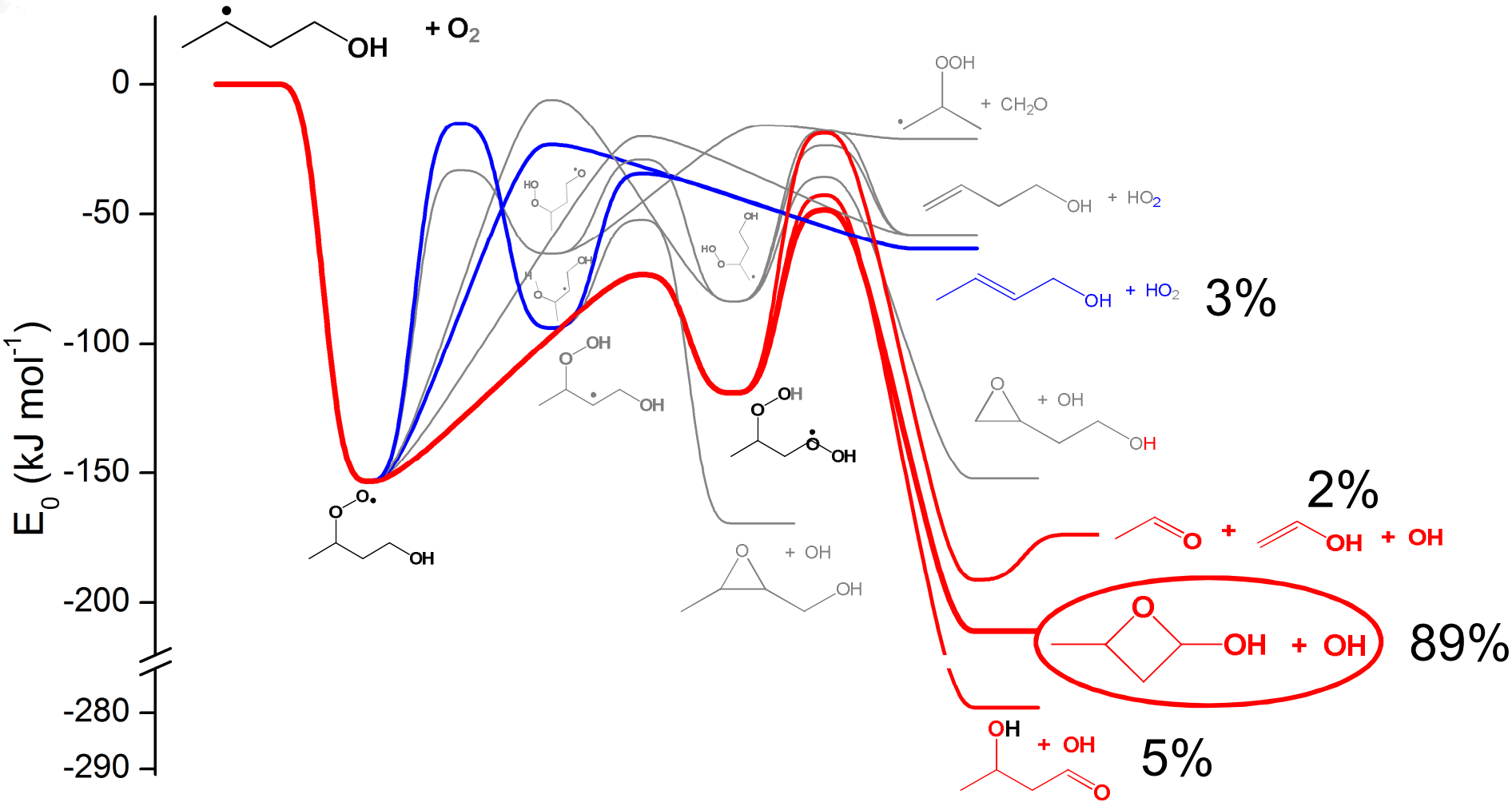
α-hydroxybutyl + O_2 leads to chain-terminating formation of butanal + HO_2



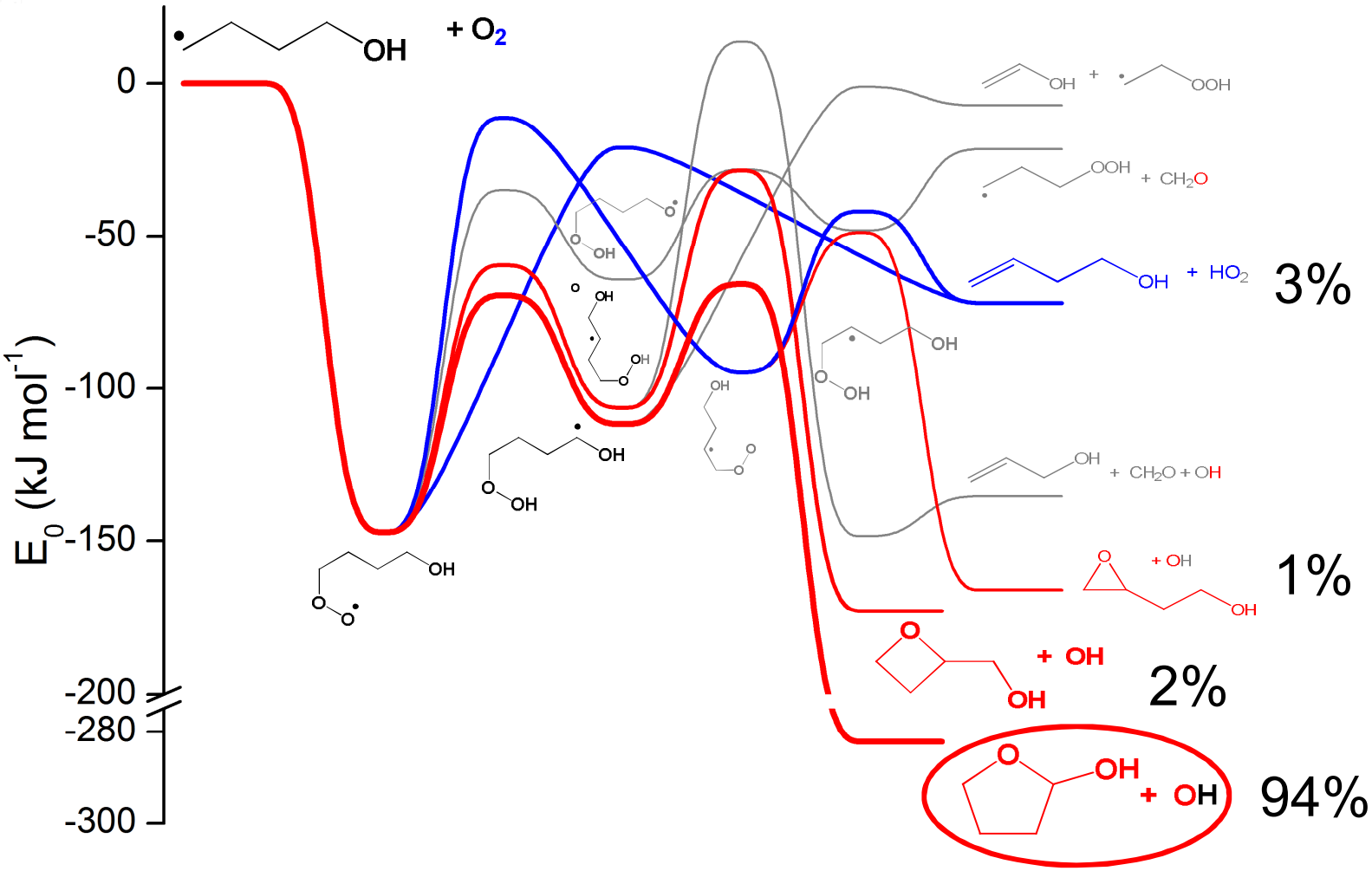
ß-hydroxybutyl + O_2 makes mainly OH via the "Waddington mechanism"



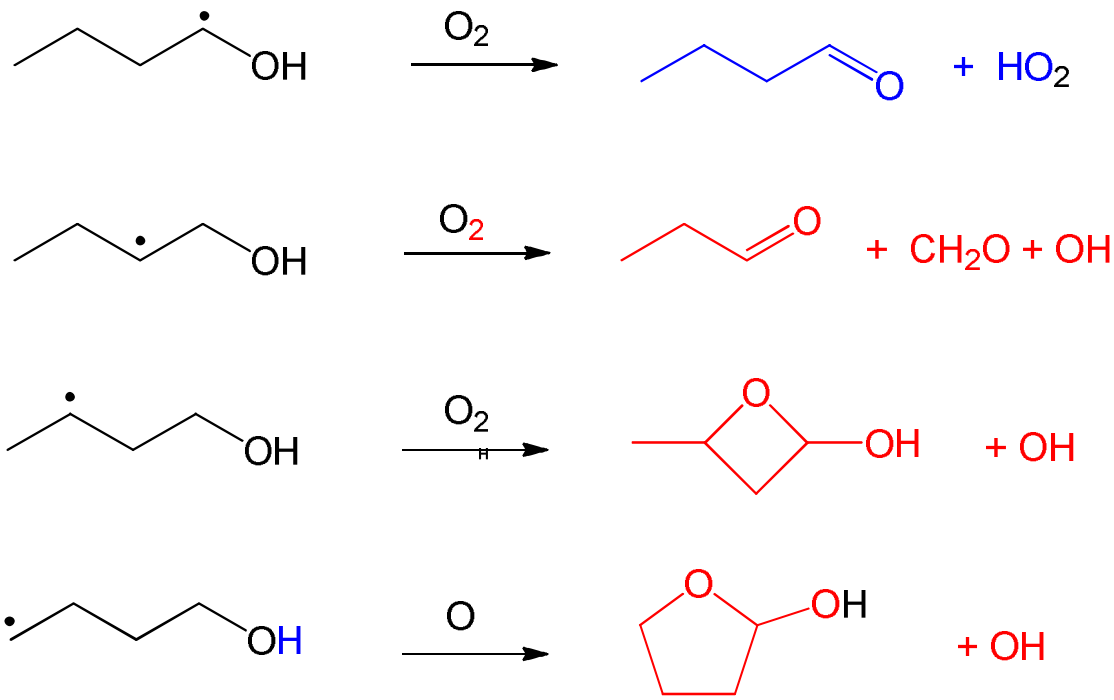
γ-hydroxybutyl + O_2 is dominated by OH-forming pathways as well



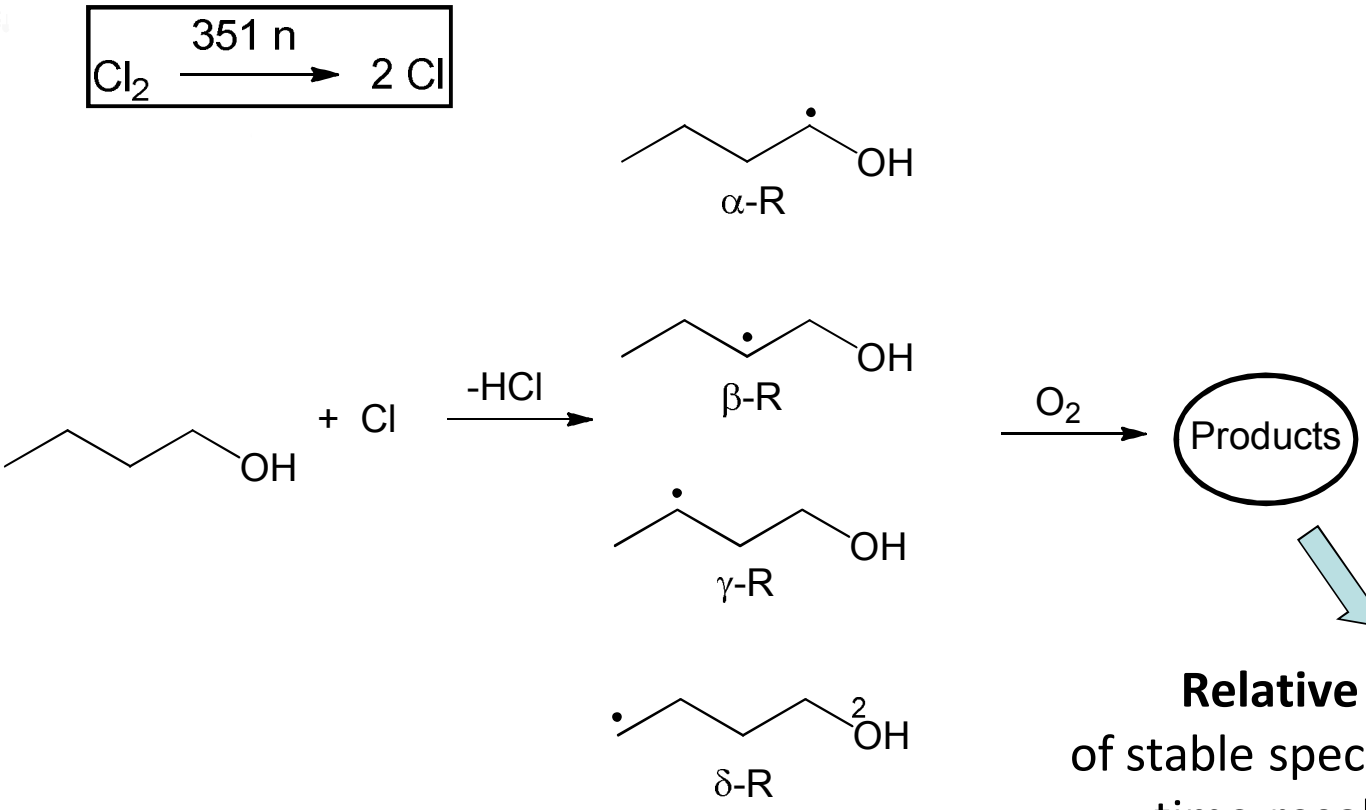
The OH group influences the reactivity even in δ-hydroxybutyl + O_2



Predicted main product channels for each hydroxybutyl + O_2 reaction

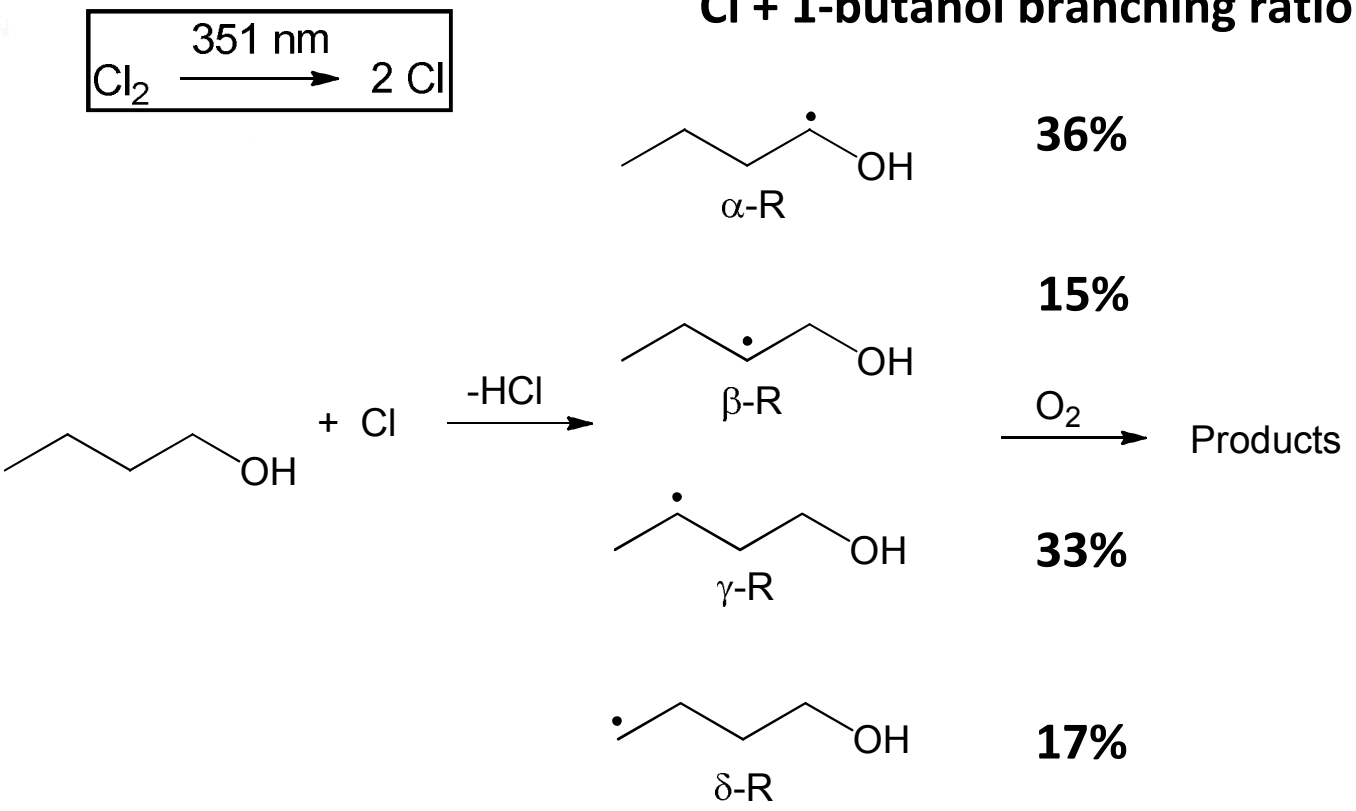


Experimentally we probe the chemistry of ALL four hydroxybutyl isomers simultaneously

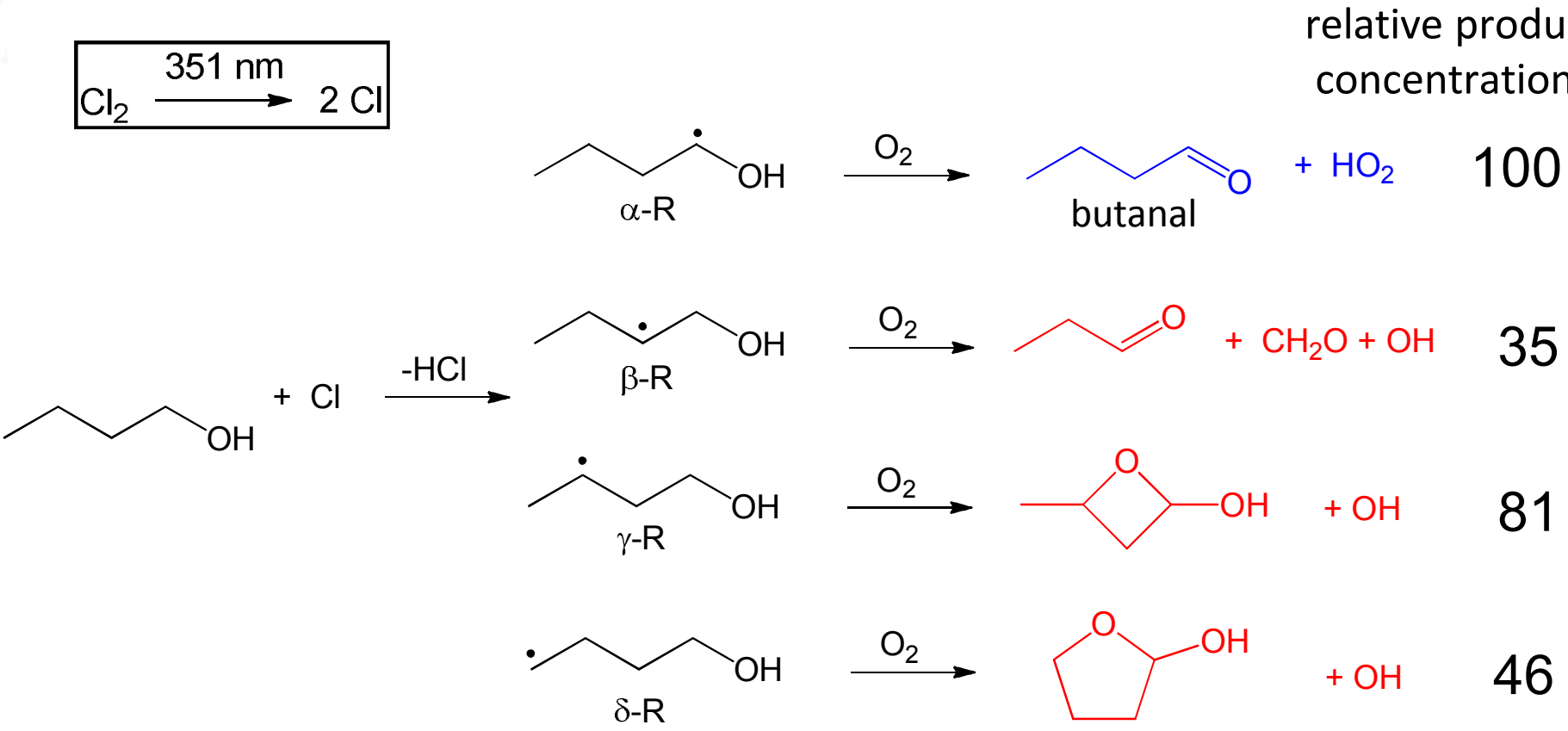


Relative concentrations of stable species from multiplexed time-resolved synchrotron photoionization mass spectrometry (MPIMS)

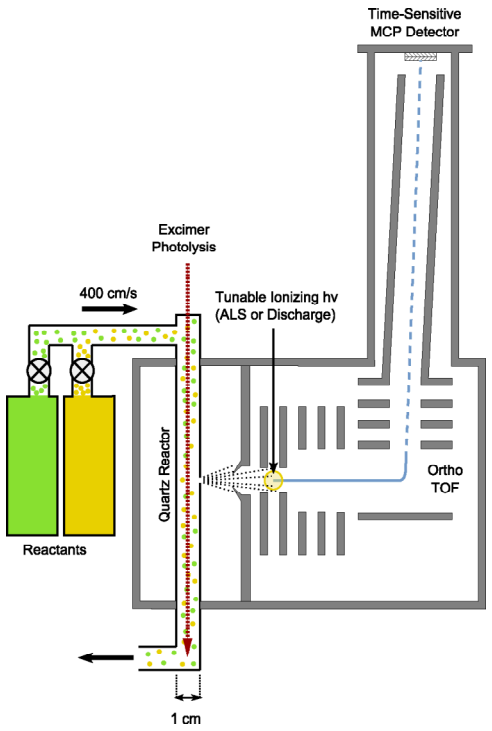
Experimentally we probe the chemistry of ALL four hydroxybutyl isomers simultaneously



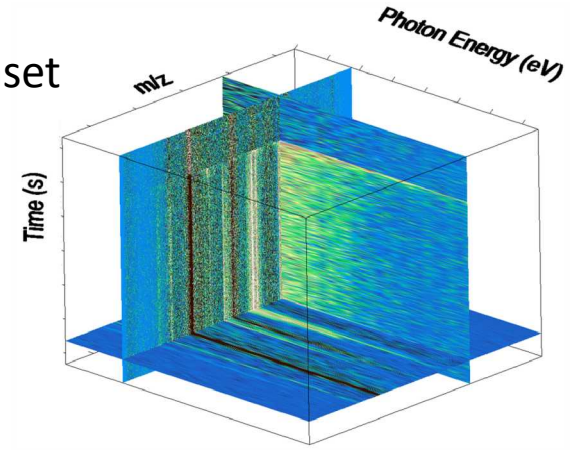
“Simulation” of the experiment



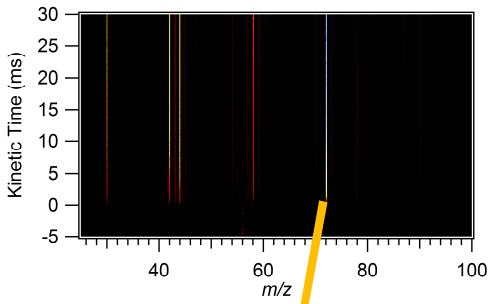
Probing oxidation chemistry using MPIMS



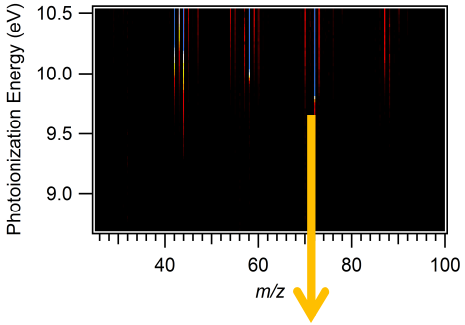
3-D dataset



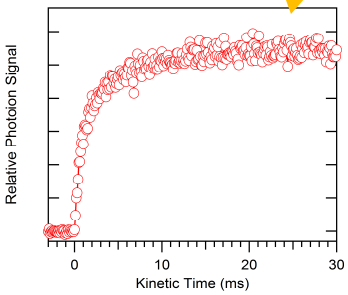
Time-resolved mass spectrum



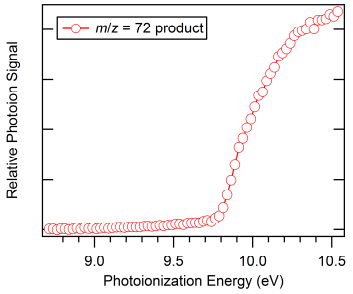
Photoionization spectrum



m/z = 72



m/z = 72



Concentrations (in molecules cm^{-3})

[1-butanol]: 4 x 10^{13}

[O_2]: 1 x 10^{16}

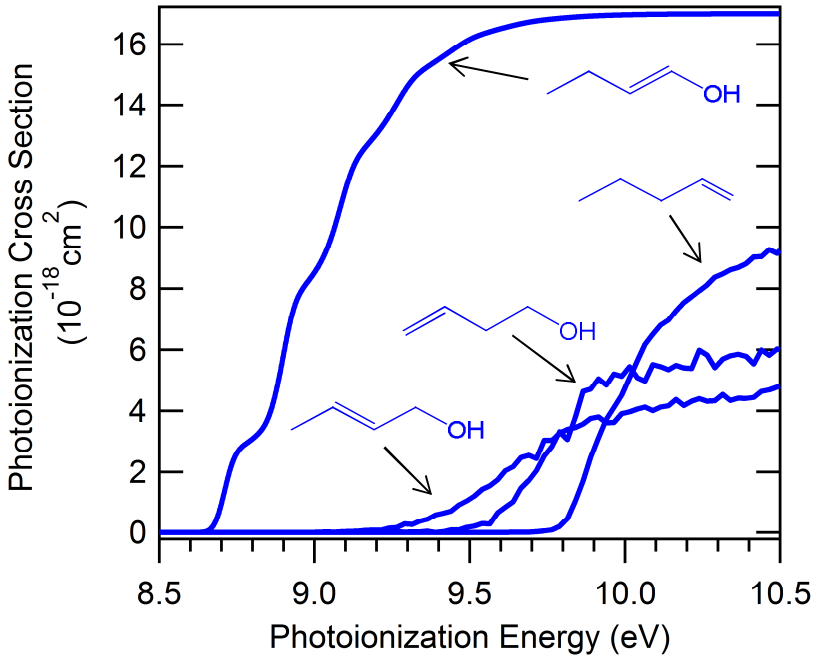
[Cl_2]: 2 x 10^{14}

[$Cl]_0$: 6 x 10^{12}

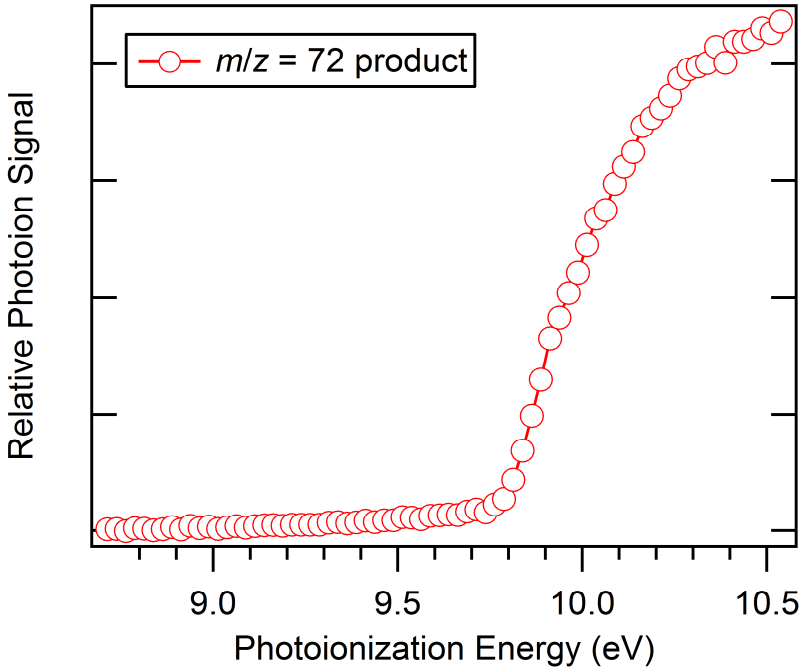
m/z = 72 corresponds to the HO_2 byproducts

Calibration spectra

m

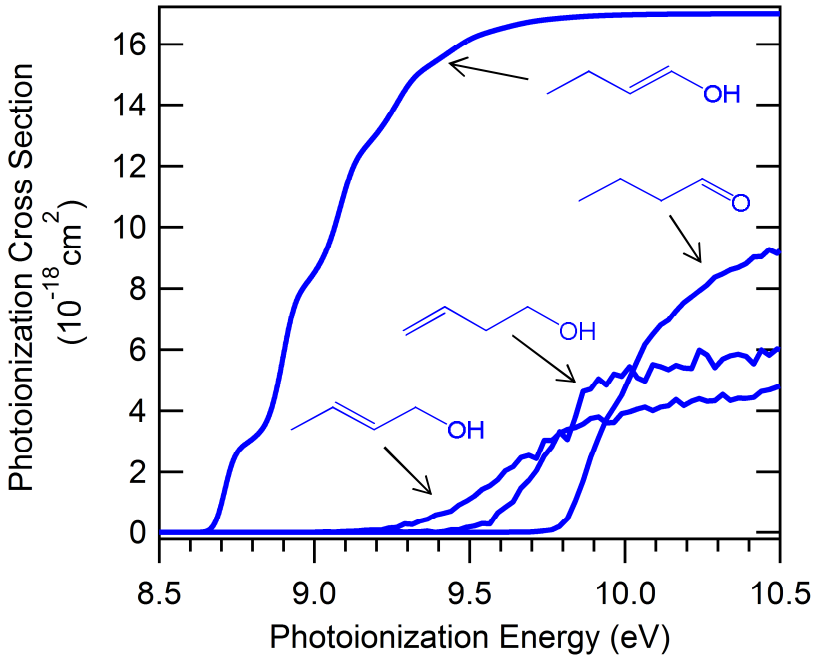


Product spectrum

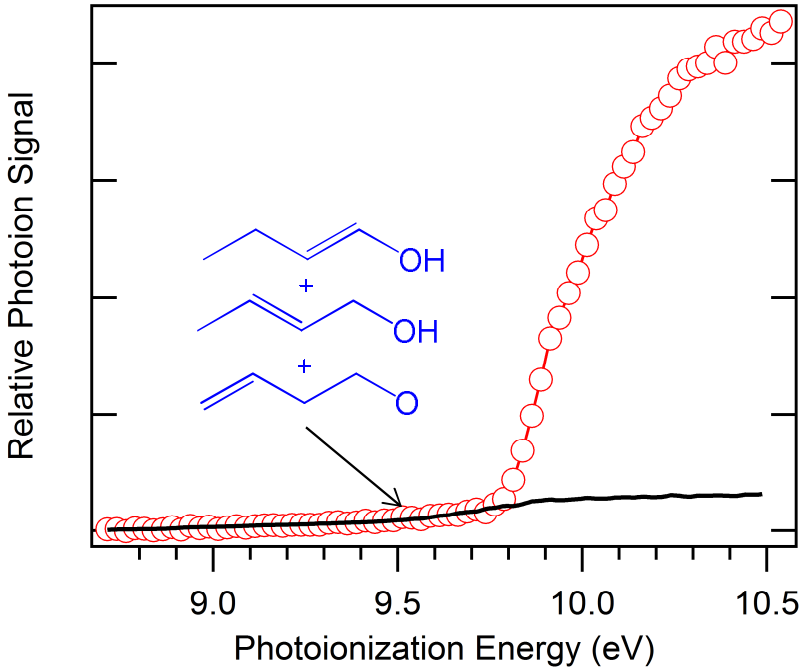


m/z = 72 corresponds to the HO_2 byproducts

Calibration spectra



Product spectrum



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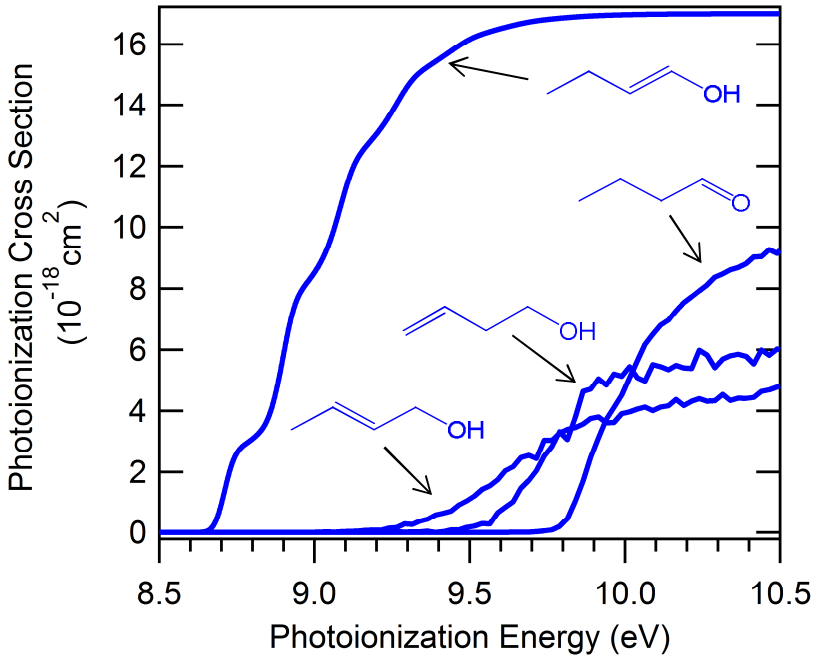
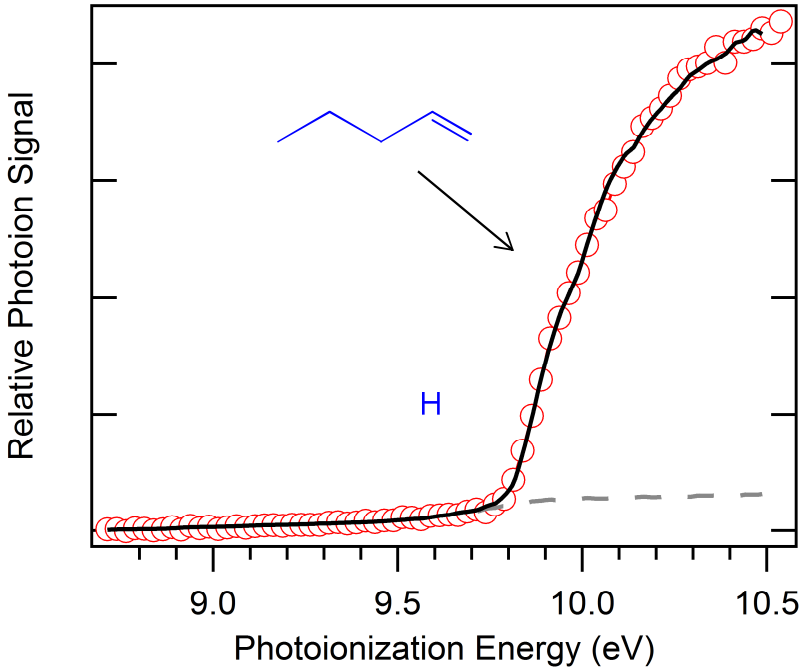
Calibration spectra



Product spectrum



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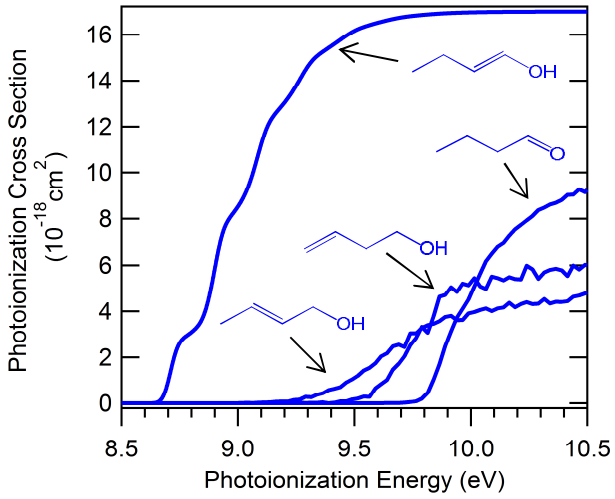
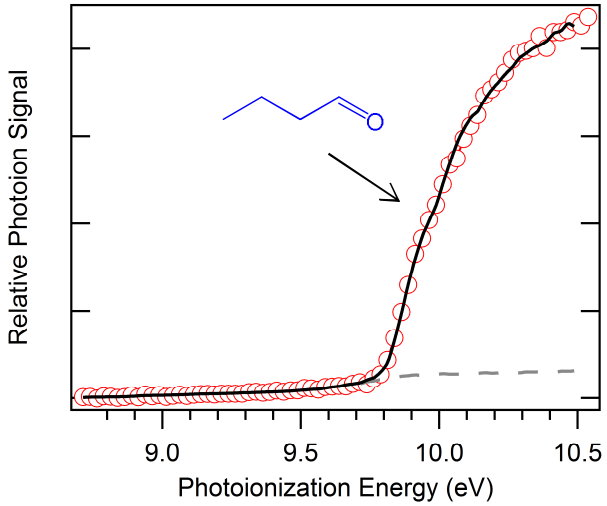
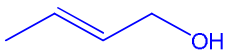
Calibration spectra

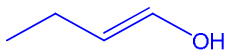


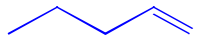
Product spectrum



Relative product concentrations

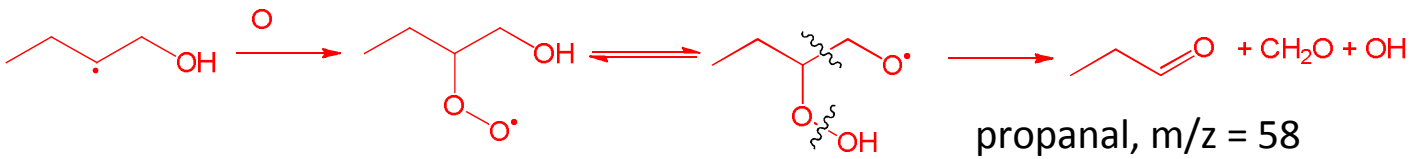






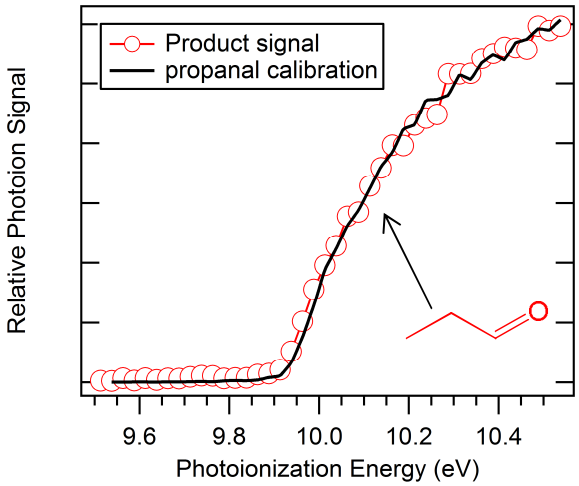
Theory:	2	:	4	:	<1	:	100
Experiment:	0 – 5	:	5 – 10	:	<1	:	100

We detect propanal – a product of the Waddington mechanism in ß-hydroxybutyl + O_2

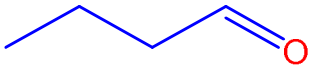


propanal, m/z = 58

The photoionization spectrum of *m/z* = 58 contains mainly propanal

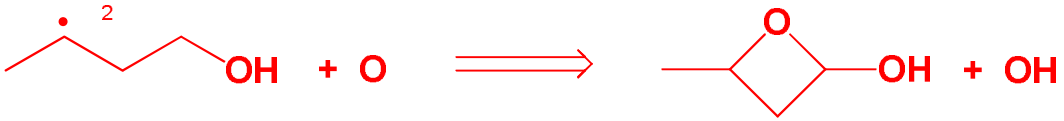


The observed concentration relative to butanal agrees well with theory



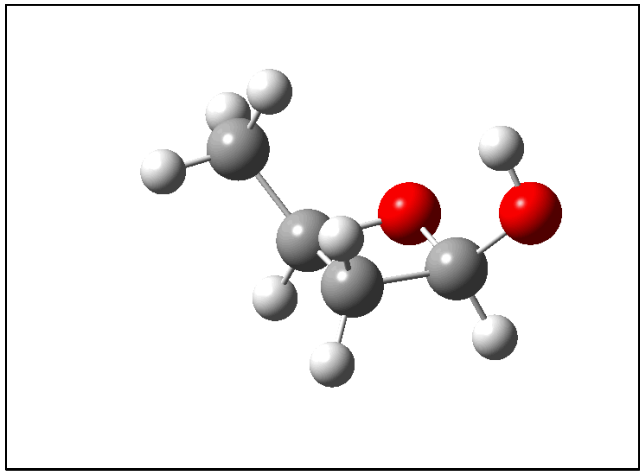
Theory:	35	:	100
Experiment:	37	:	100

The main product from γ-hydroxybutyl + O_2 has an unstable cation

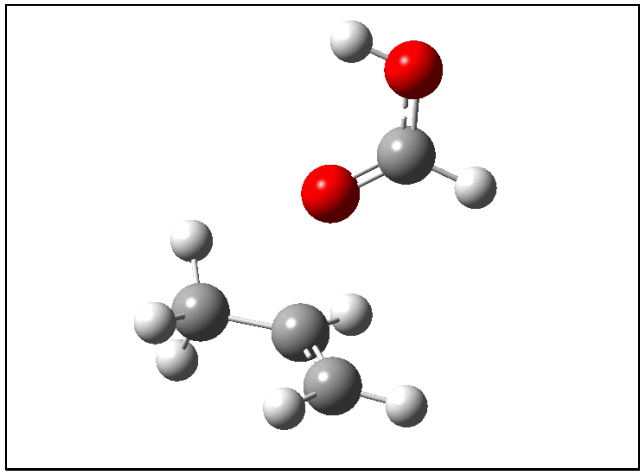


lactol

neutral



cation



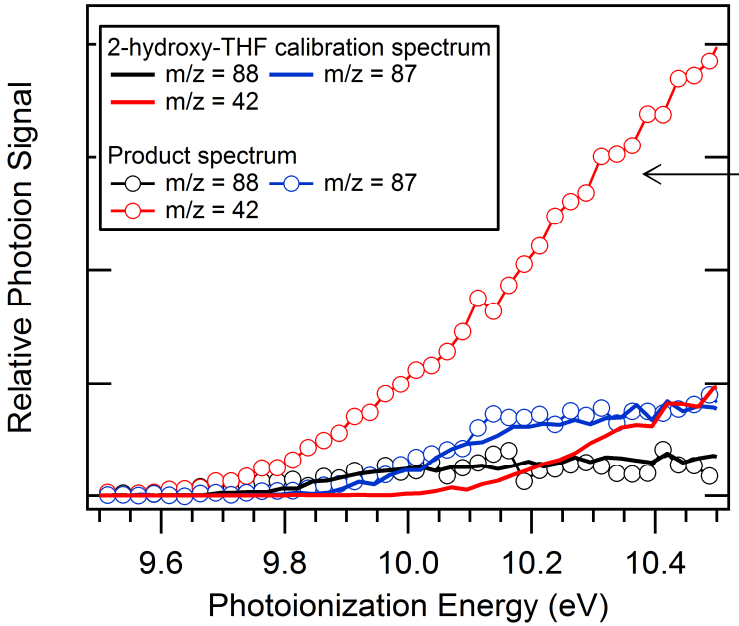
→ weak Franck-Condon overlap between neutral and cationic state

→ weak detection efficiency

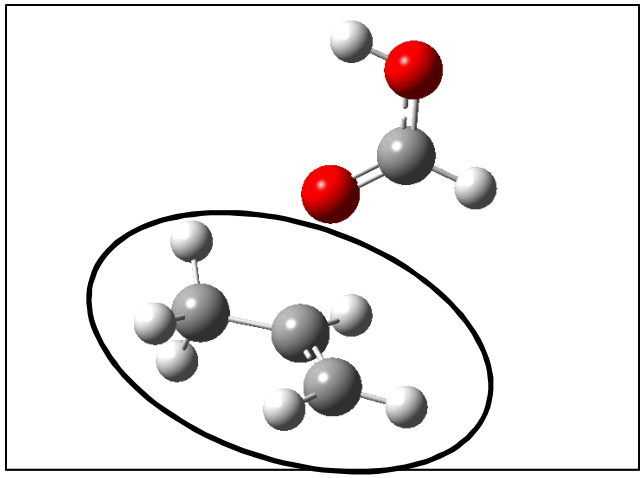
We are unable to experimentally identify and quantify this product

Our data is consistent with lactol formation from δ-hydroxybutyl + O_2

2-hydroxy-THF (m/z = 88)

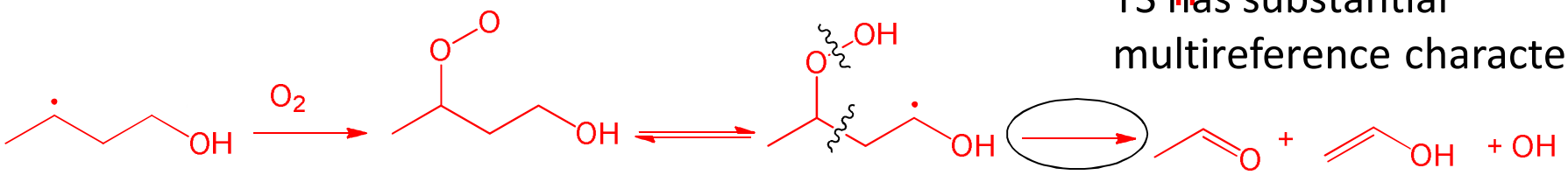


m/z = 42 does not come from propene photoionization. Is it from dissociative ionization of a lactol?



The experimental yield is a factor of 8 lower than predicted!

The experimental acetaldehyde yield is much larger than predicted

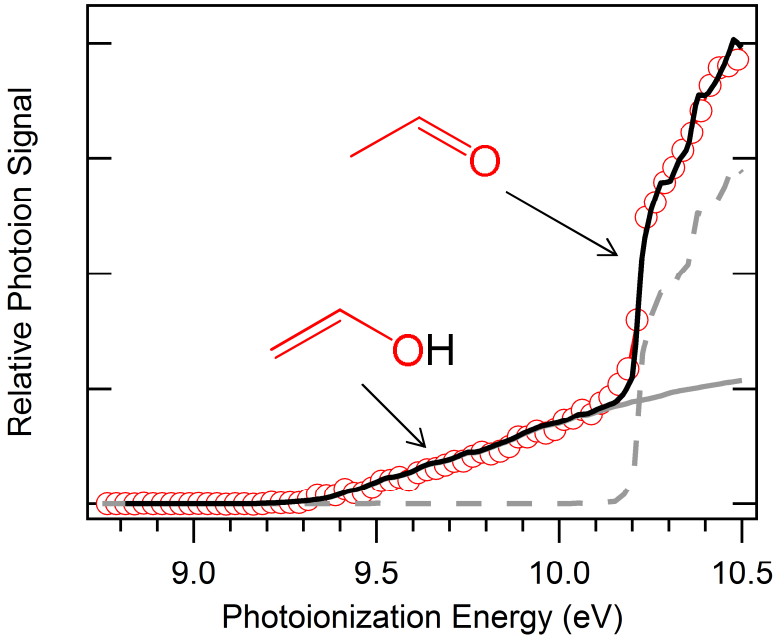


TS has substantial multireference character

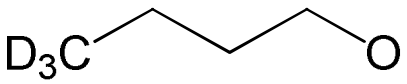
expected: 1 : 1

observed: 3 : 1

We see 57% acetaldehyde relative to butanal, theory predicts 2%

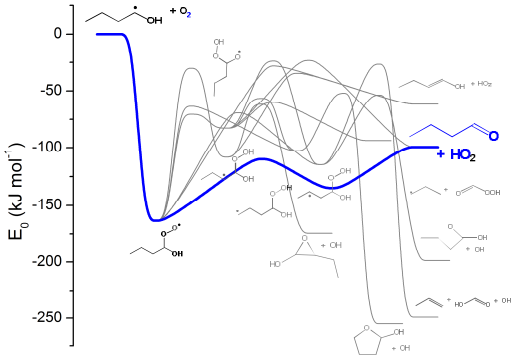


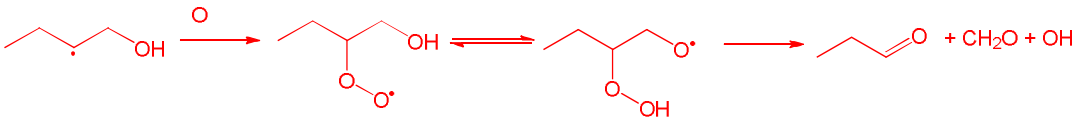
Acetaldehyde formation occurs also on the "wrong" side



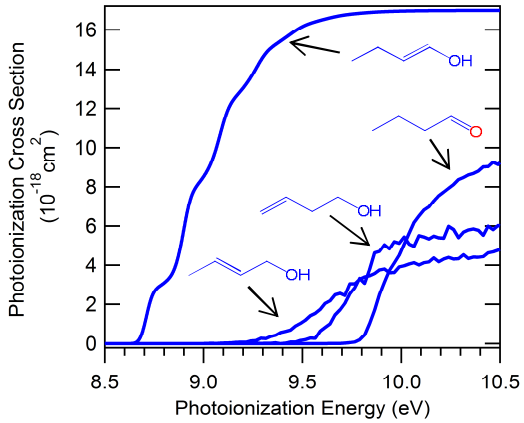
Summary

The reaction of the hydroxybutyl isomers with O_2 shows selectivity for either HO_2 (α) or OH formation (ß, γ, δ)





The OH group substantially influences the RO_2 chemistry



MPIMS experiments give relative product concentrations, which can be prepared to theoretical predictions.

H

Acknowledgements

- Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, and the U.S. Department of Energy, in part under the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry, (ANL FWP # 59044; SNL FWP # 014544).

- Chemical Dynamics Beamline at the Advanced Light Source