COMBUSTION RESEARCH FACILITY

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Component-Centered Approach Towards Oxidation Studies of Complex Biofuels

Brandon Rotavera[1], Mohamad A. Ali[4], Oliver Welz[1], Leonid Sheps[1], Adam M. Scheer[1], John D. Savee[1], David L. Osborn[1], Taek Soon Lee[3], Angela Violi[4], Blake A. Simmons[1,3], and Craig A. Taatjes[1]

[1] Combustion Research Facility, Sandia National Laboratories
[2] Biofuels & BioMaterial Science and Technology, Sandia National Laboratories
[3] Joint BioEnergy Institute (JBEI)
[4] Department of Mechanical Engineering, University of Michigan

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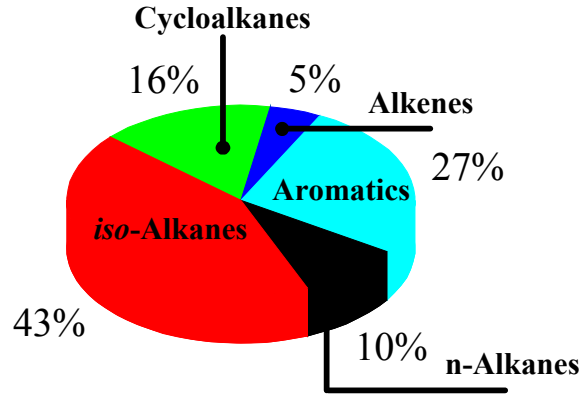
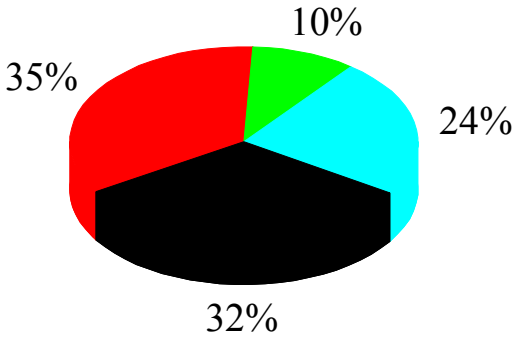
Sandia National Laboratories UNIVERSITY OF MICHIGAN jbei Joint BioEnergy Institute

Conventional Transportation Fuels Contain Wide Distributions of Hydrocarbon Classes, Species

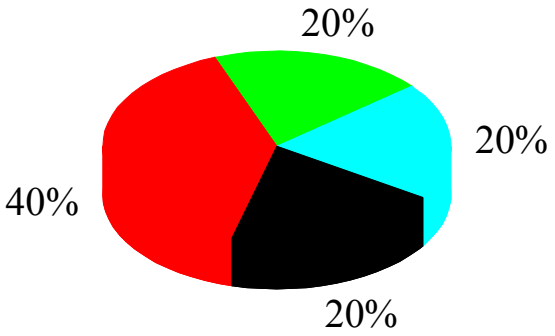
Gasoline Fuel
- Appropriate (high) octane number
- Short-chain alkanes
- Highly branched species
- Some aromatics



Diesel Fuel
- Appropriate cetane number
- Long-chain alkanes
- Limited branched species
- Some aromatics



Jet Fuel
- Long-chain alkanes
- Limited branched species
- Some aromatics



EtOH, Methyl Esters Impose Blending Limits for Practical Engines, Fuel-Transport Infrastructure

Gasoline Fuel

- Appropriate (high) octane number
- Short-chain alkanes
- Highly branched species
- Some aromatics

Diesel Fuel

- Appropriate cetane number
- Long-chain alkanes
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Jet Fuel

- Long-chain alkanes
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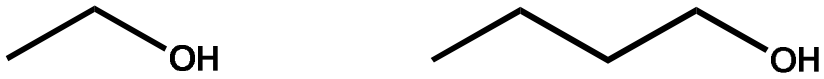
- Some aromatics

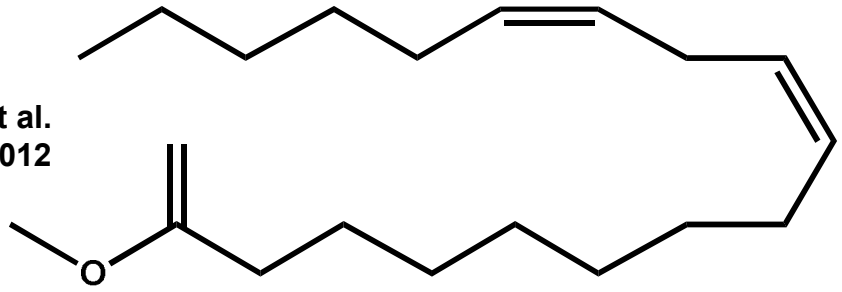
Comparison of Alcohol Properties to Gasoline

Fuel	Energy Content ($MJ \cdot L^{-1}$)	Octane Number (MON)	Viscosity (15 °C) ($mPa \cdot s$)
Gasoline	32.0	84 – 93	0.700
Ethanol	19.6	102	1.337
1–Butanol	29.2	78	3.515



Comparison of Biodiesel Properties to Diesel

Fuel	Density ($g \cdot mL^{-1}$)	Cetane Number	Viscosity ($mPa \cdot s$)
Diesel	0.85	40 – 55	1.3 – 4.1
Biodiesel	0.88	48 – 65	4.0 – 6.0



Peralta-Yahya et al.
Nature, 2012

"Ideal" Biofuels Share Similar Fuel Properties with Conventional Hydrocarbons

Gasoline Fuel
- Appropriate (high) octane number
- Short-chain alkanes
- Highly branched species
- Some aromatics

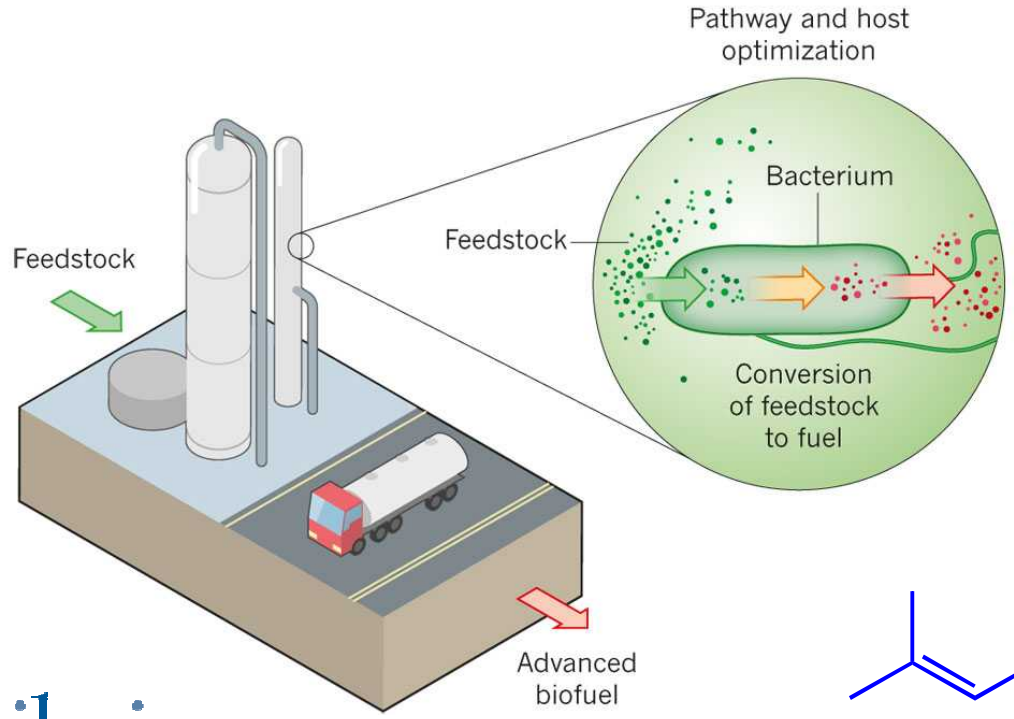
Diesel Fuel
- Appropriate cetane number
- Long-chain alkanes
- Limited branched species
- Some aromatics

Jet Fuel
- Long-chain alkanes
- Limited branched species
- Some aromatics

Ideal Biofuel Target:

Biofuels with **properties similar to petroleum-based fuels** for all engines types

Targeted Biofuel Production using Microbial Synthesis



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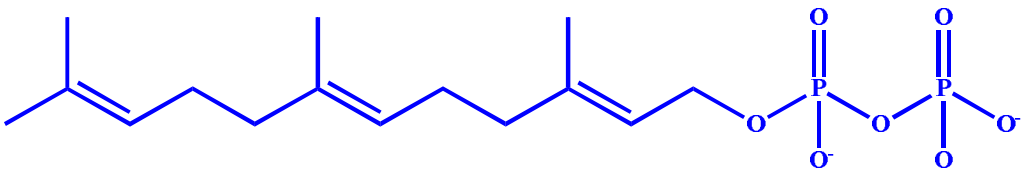
Simple Sugars

Acetyl CoA (Enzyme)

Mevalonate Pathway



Farnesyl Pyrophosphate

(Precursor for Biofuel Production)

Peralta-Yahya, Zhang, del Cardayre, and Keasling, (2012).
Microbial engineering for the production of advanced biofuels. *Nature*, 488, 320.

Microbial Production of Biofuel Provides Some Control Over Fuel Structure

Sesquiterpenes	Production using *S. cerevisiae*	Production using *E. coli*
Farnesene	2 µg/L	240 mg/L
Bisabolene	150 µg/L	517 mg/L
Curcumene	Not detected	130 µg/L
Vetispiradiene	300 µg/L	73 mg/L
Cadinene	3.6 mg/L	10.3 µg/L
Aristolochene	190 µg/L	33 mg/L
Amorphadiene	120mg/L	20 g/L

Peralta-Yahya et al.
Nature Communications, 2011

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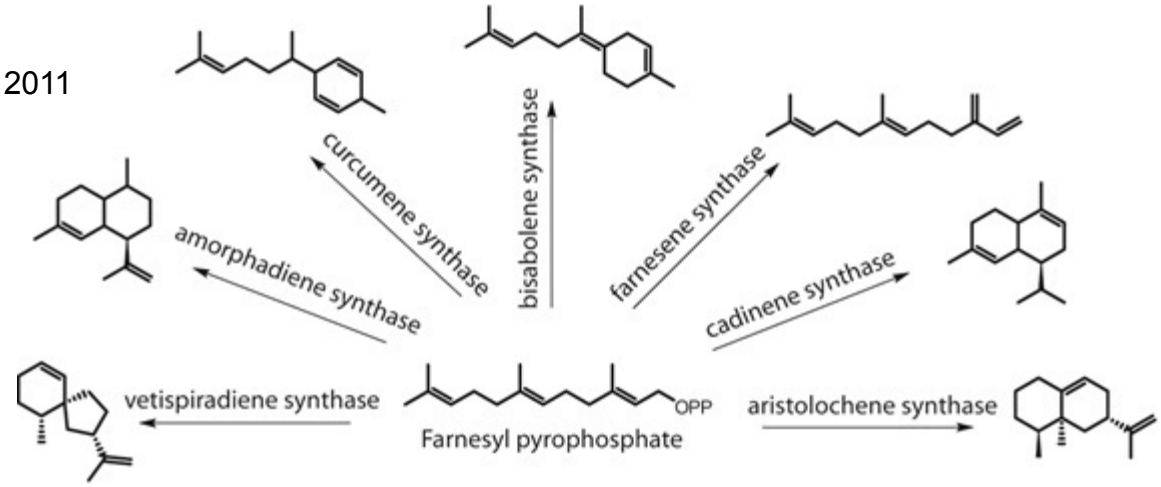

Selected Biosynthetic Pathway Leads to Diesel-like Fuel Molecule

Sesquiterpenes	Production using *S. cerevisiae*	Production using *E. coli*
Farnesene	2 µg/l	240 mg/l
Bisabolene	**150 µg/L**	**517 mg/L**
Curcumene	Not detected	130 µg/L
Vetispiradiene	300 µg/L	73 mg/L
Cadinene	3.6 mg/L	10.3 µg/L
Aristolochene	190 µg/L	33 mg/L
Amorphadiene	120mg/L	20 g/L

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Nature Communications, 2011

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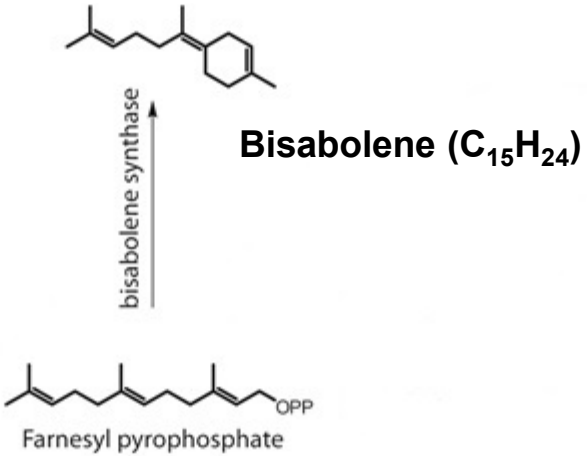
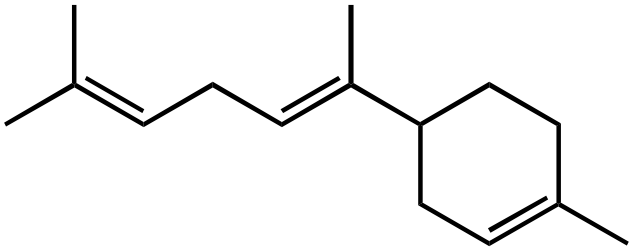


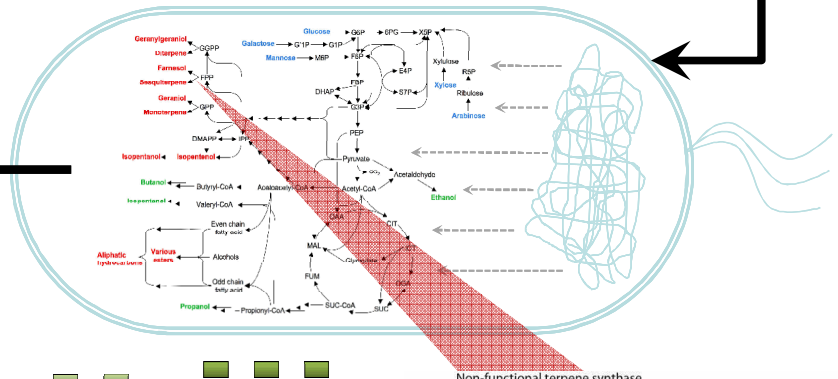
Bisabolene ($C_{15}H_{24}$)

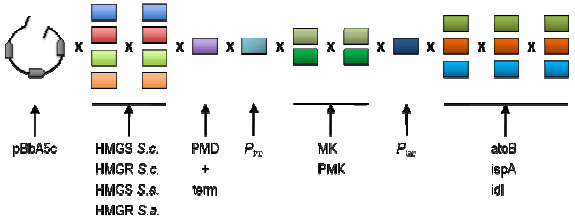
Microbially-Derived Sesquiterpenoid Biofuel Produced with Structural Characteristics of Diesel

Bisabolene ($C_{15}H_{24}$)



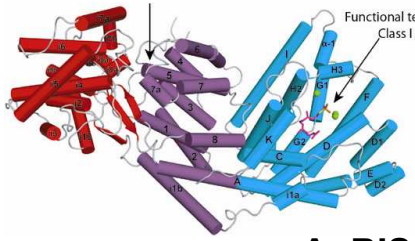
Micro-organism





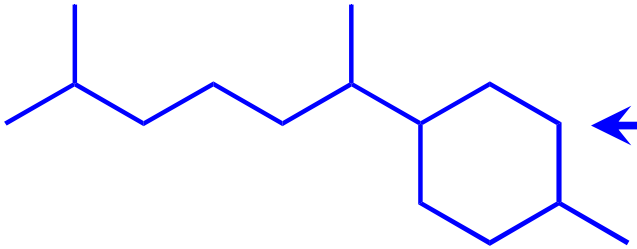
Non-functional terpene synthase
Class II active site

Functional terpene synthase
Class I active site



AgBIS
(Bisabolene Synthase)

Chemical Hydrogenation



Bisabolane ($C_{15}H_{30}$)

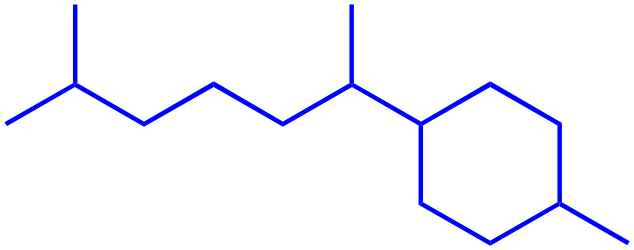
Biosynthetic Alternative to D2 Diesel Fuel

Peralta-Yahya, Zhang, del Cardayre, and Keasling, (2012).
Microbial engineering for the production of advanced biofuels. *Nature*, 488, 320.

Physical Properties of Bisabolane Compatible with Conventional Diesel Fuel

Properties	*D2 Diesel*	*Biodiesel*	*Hydrogenated bisabolene*
Density (g/ml)	0.85	0.88	0.82
API Gravity	35	29.3	41.1
Flash point (°C)	60–80	100–170	111
Viscosity (mm^2/s)	1.3–4.1	4.0–6.0	2.91
Boiling point (°C)	180–340	315–350	267
Cloud point (°C)	−35 to 5	−3 to 15	<−78
Cetane number	40–55	48–65	41.9

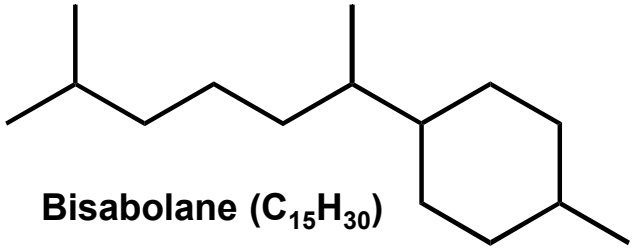
Peralta-Yahya et al.
Nature Communications, 2011



Bisabolane ($C_{15}H_{30}$)

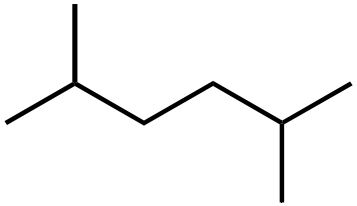
Component-Centered Approach Towards Oxidation Studies on Microbially-Derived Bisabolane

Target Molecule

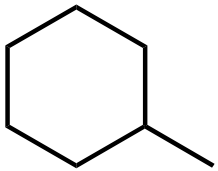


Bisabolane ($C_{15}H_{30}$)

Component System 1

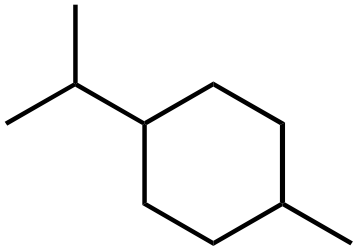


2,5-dimethylhexane



MCH

Component System 2



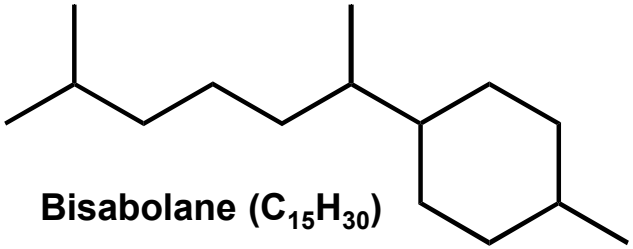
Limonane

General Objectives

1. Characterize low-temperature RO_2-related oxidation mechanisms of sub-systems
2. Quantum chemical, *ab initio* calculations (PES, rate coefficients)

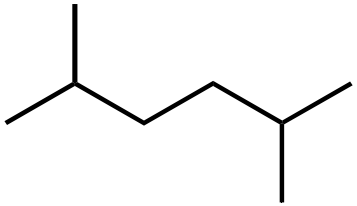
Component-Centered Approach Towards Oxidation Studies on Microbially-Derived Bisabolane

Target Molecule



Bisabolane ($C_{15}H_{30}$)

Component System 1



2,5-dimethylhexane

MCH

Component System 2

Limonane

General Objectives

1. Characterize low-temperature RO_2-related oxidation mechanisms of sub-systems
2. Quantum chemical, *ab initio* calculations (PES, rate coefficients)

Knowledge of Initial Low-Temperature Oxidation Steps of Biofuels Critical to Advanced-Engine Development

Temperature

RH

R → Olefin + R′

O_2

ROO·

·QOOH

O_2

·OOQOOH

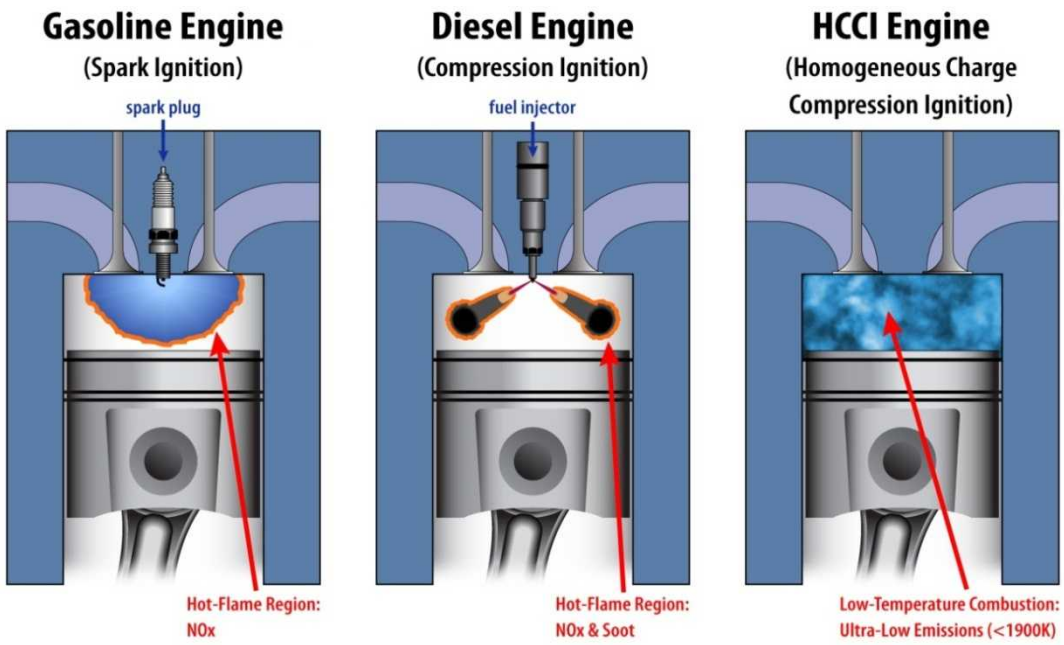
Ketohydroperoxide + OH

Low-Temperature Branching

Olefin + HO_2

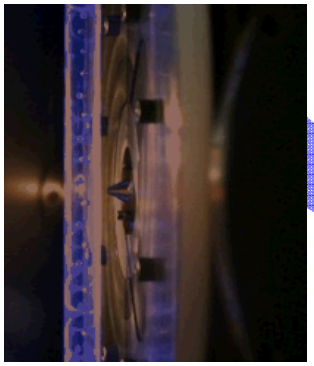
Cyclic Ether + OH

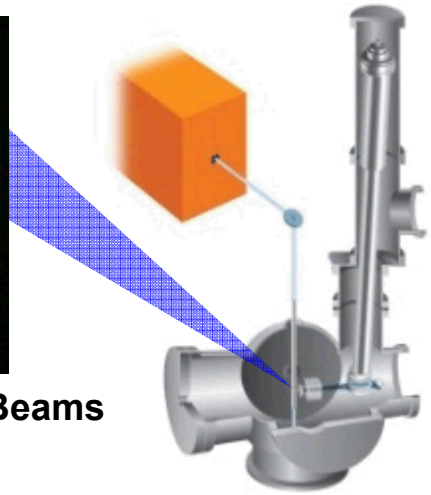
β-Scission Products + OH



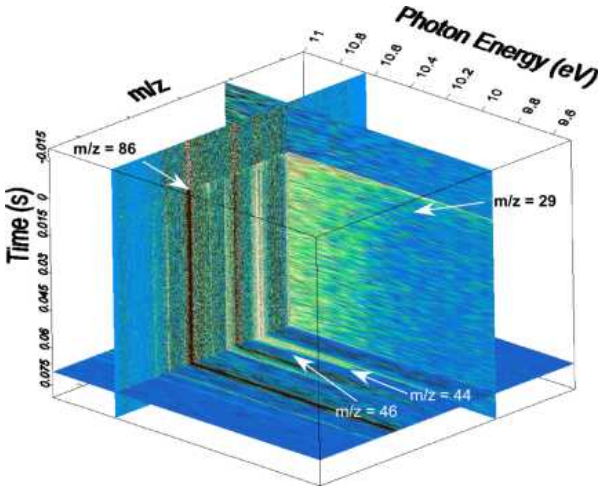
Direct probing of intermediates related to R + O_2

VUV Photoionization of Molecular Beams Produced during Low-Temperature Hydrocarbon Oxidation

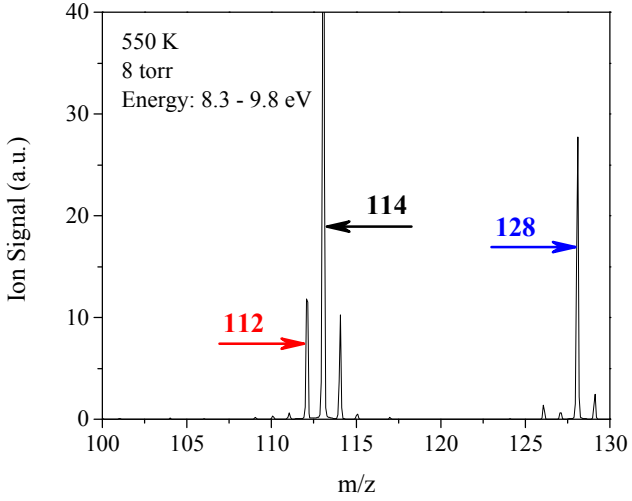




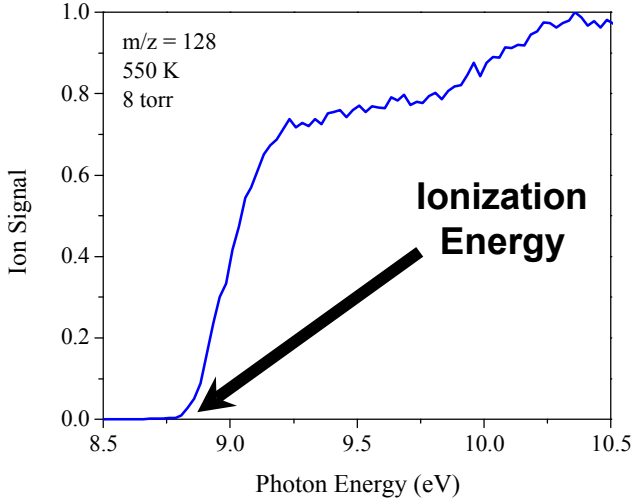
Probing of Molecular Beams



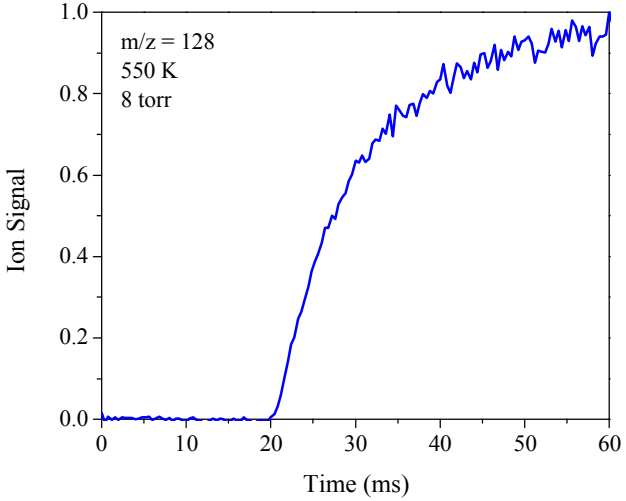
High-Resolution Mass Spectra



Isomer-Resolved Species Identification

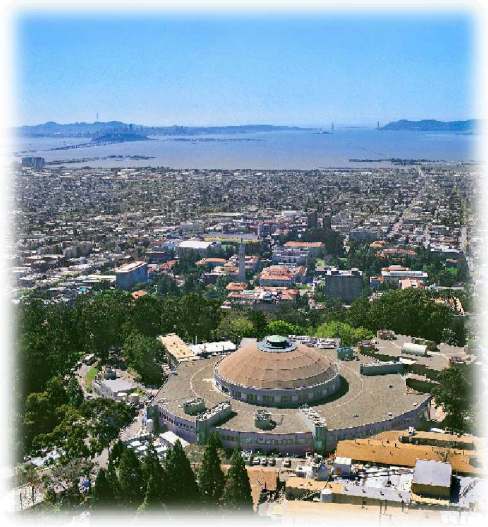


Time-Dependent Chemical Kinetics

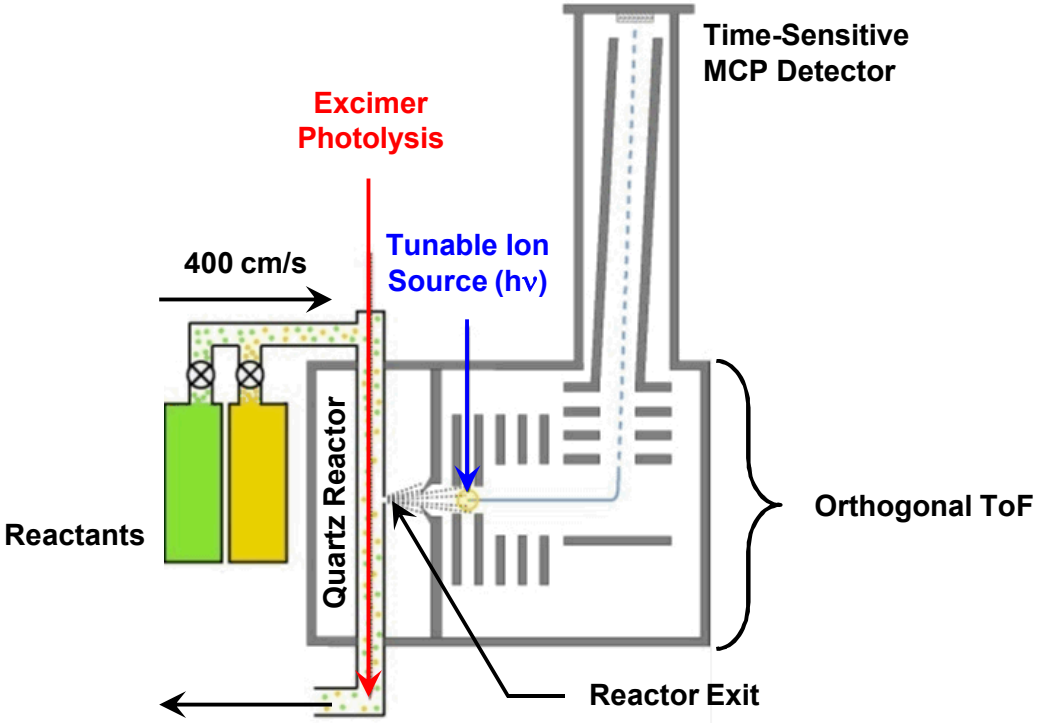


Experimental and Computational Methods

Experimental Setup/Conditions: Cl-Initiated Oxidation, MBMS Detection

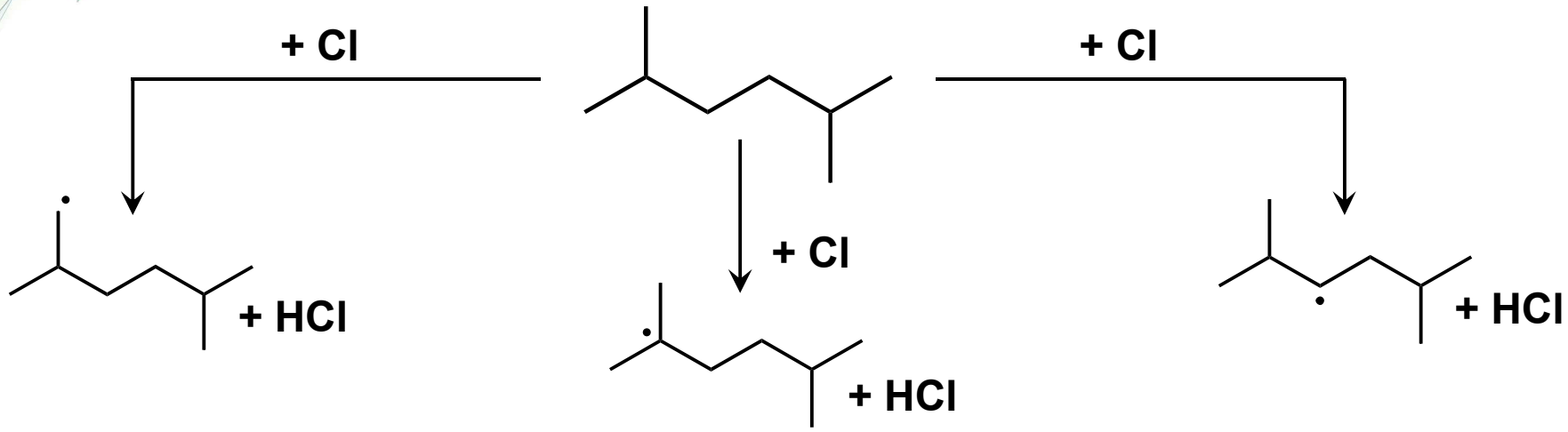


Advanced Light Source Synchrotron

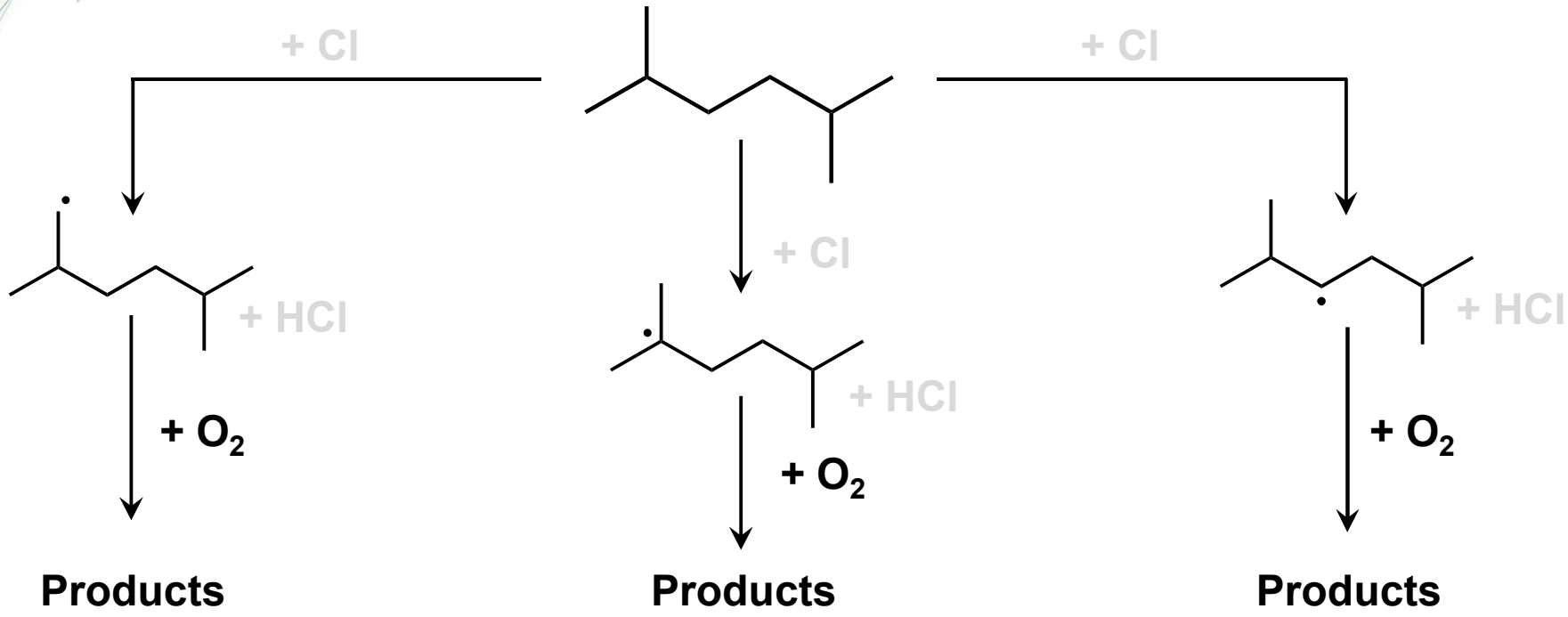


Species	Number Density (molecules/cm^3)	Mole Fraction
2,5-dimethylhexane	$1.3 \cdot 10^{14}$	0.001
O_2	$2.8 \cdot 10^{16}$	0.219
Cl_2	$1.4 \cdot 10^{14}$	0.001
Cl (Photolyzed Cl_2)	$2.1 \cdot 10^{12}$	–
He	$1.1 \cdot 10^{17}$ (550 K) /$8.5 \cdot 10^{16}$ (650 K)	0.779

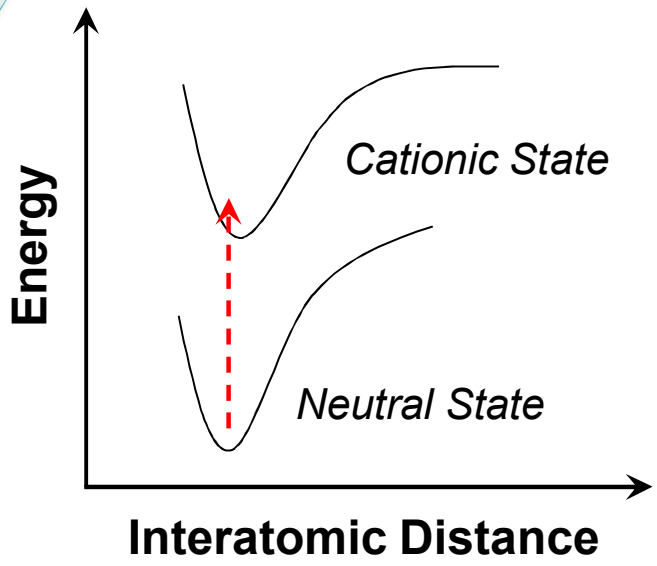
Initial Alkyl Radicals Generated using Photolyzed Cl_2

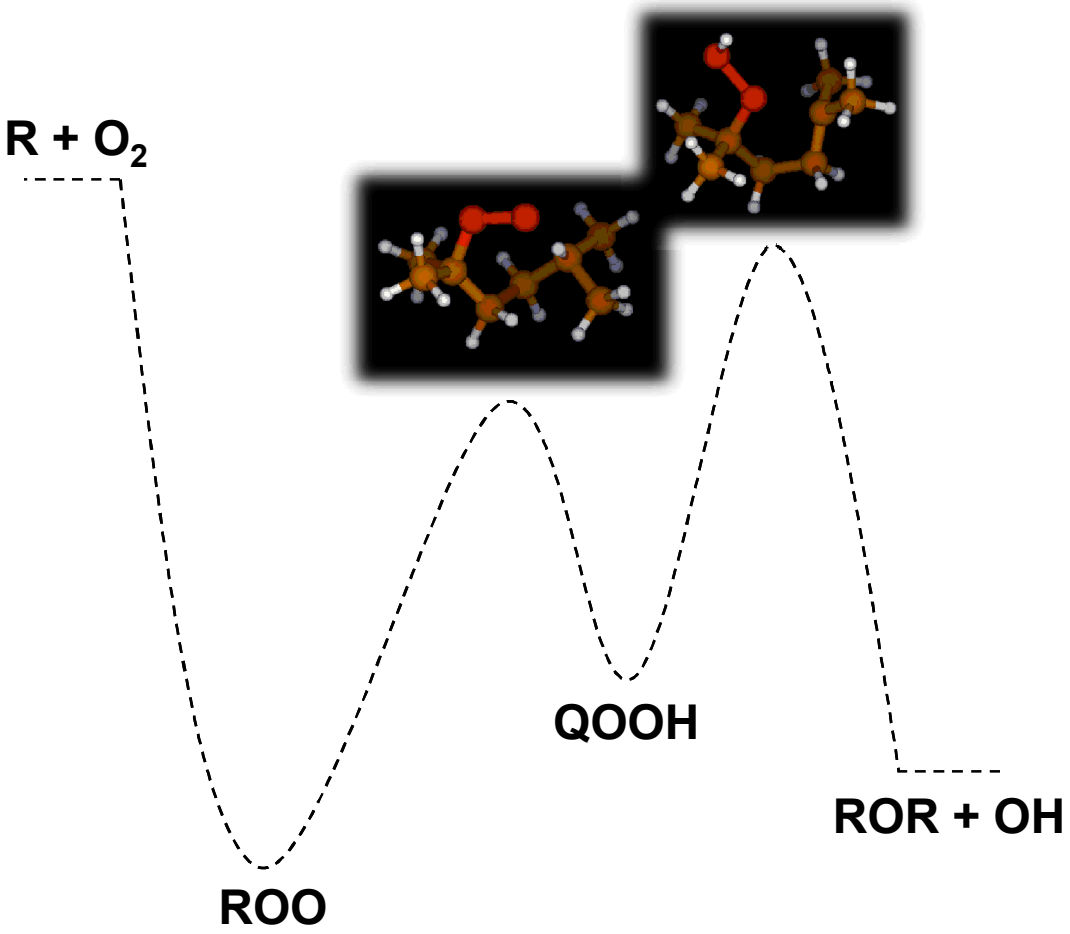


Experimental Conditions Favor R + O_2



Computational Methods





Computational Objectives –

1. Electronic transition intensities
2. PES (stationary points)
   - 2,5-dimethyl-1-hexyl + O_2
   - 2,5-dimethyl-2-hexyl + O_2
   - 2,5-dimethyl-3-hexyl + O_2

16 cyclic ether channels, 11 products

Organization of Results

(1) HO_2-elimination channel, species fractional yield quantification

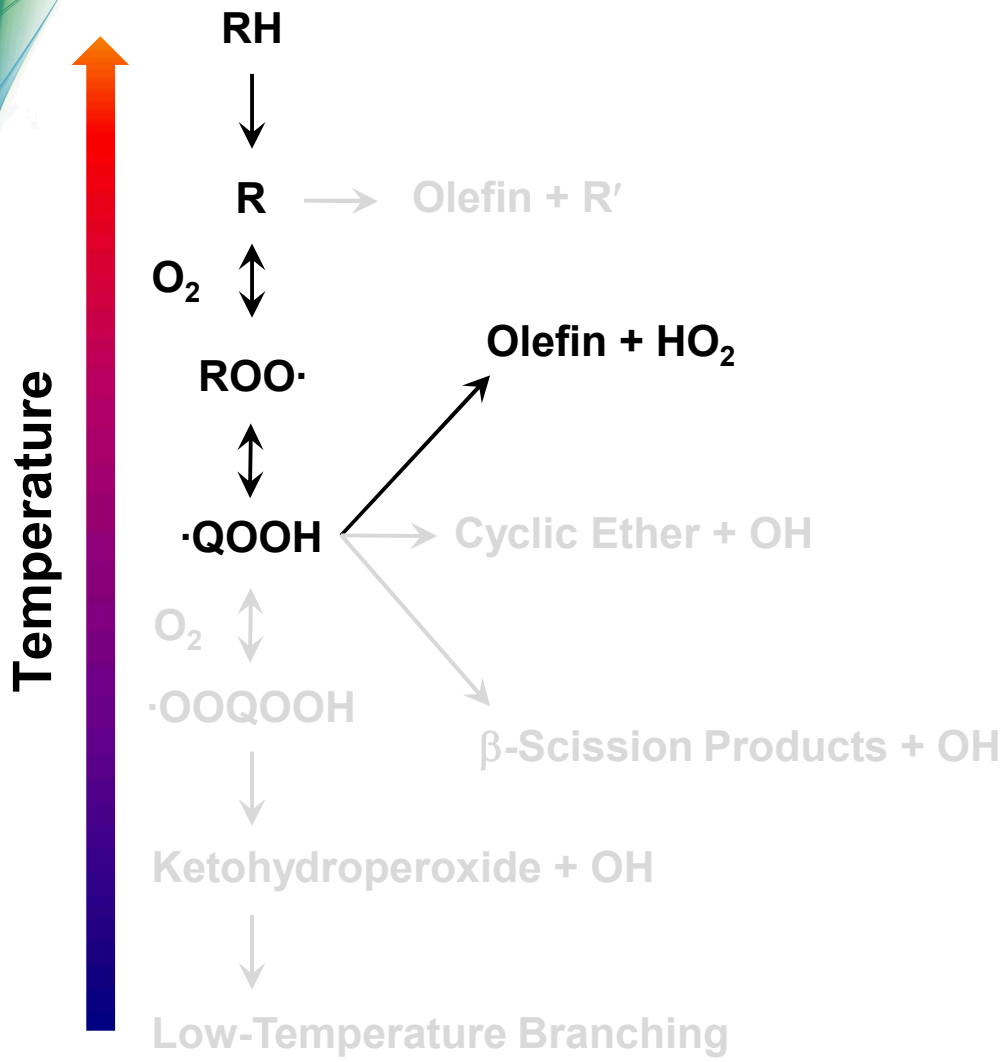
(2) Analysis of cyclic ether formation channels

(3) Evidence of 'other' channels (unimolecular QOOH decomposition)

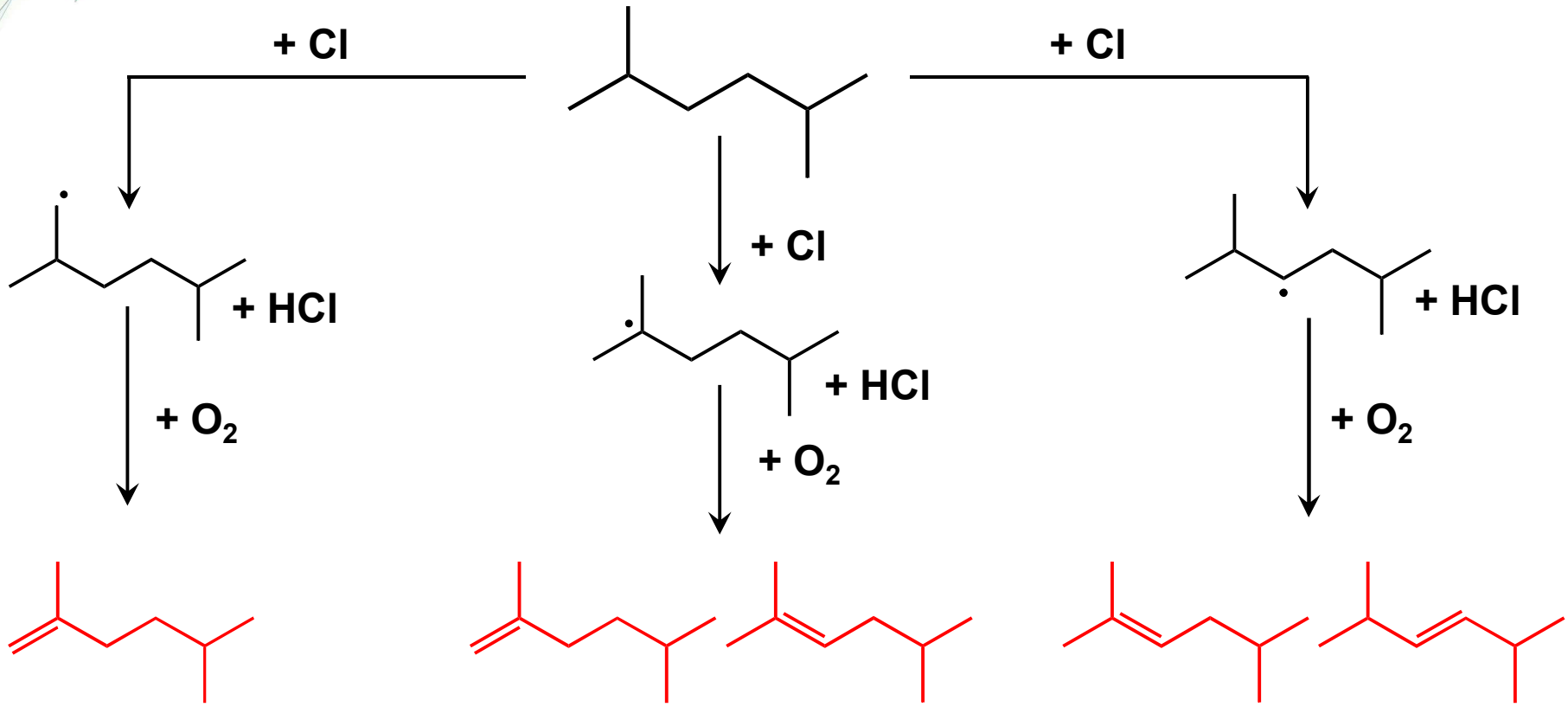
(4) Role of primary radicals in cyclic ether formation

Results (1): HO_2-Elimination Channel, Species Fractional Yield Quantification

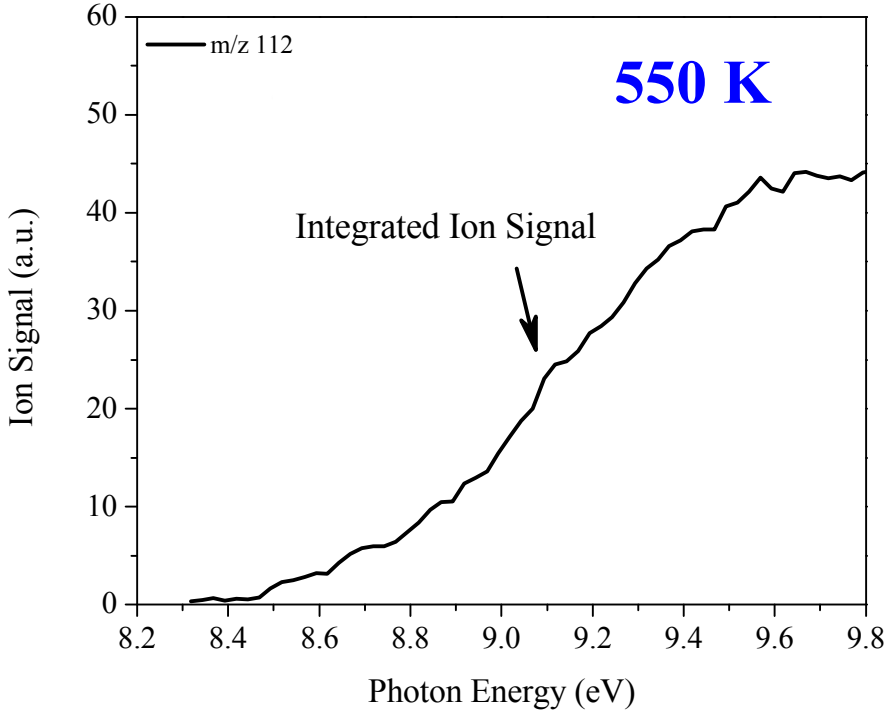
Direct Measurement of HO_2-Elimination Channel



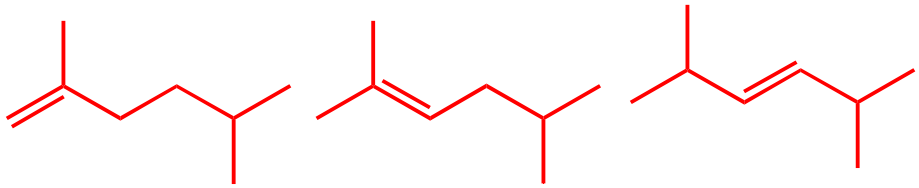
HO_2-Elimination Co-Products of R + O_2



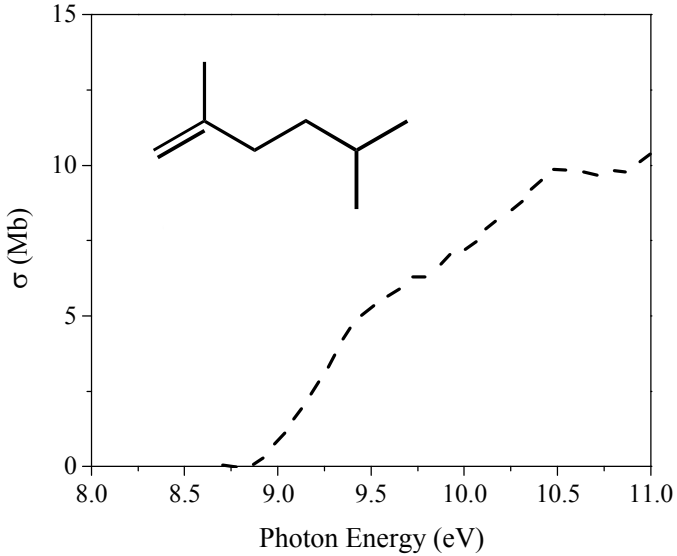
Separate Experiments Conducted to Determine Branching Ratios

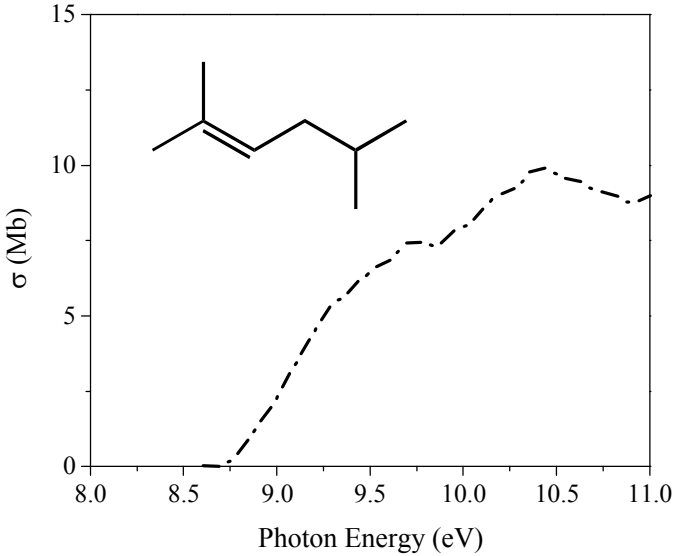


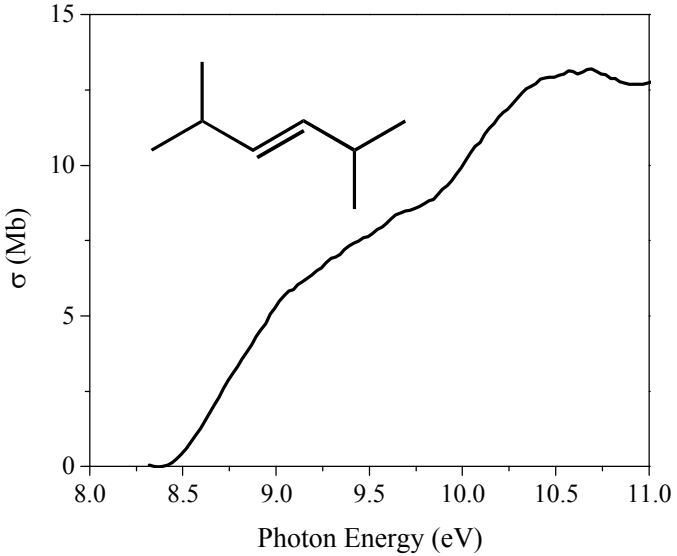
Unknown, temperature-dependent contributions to integrated ion signal



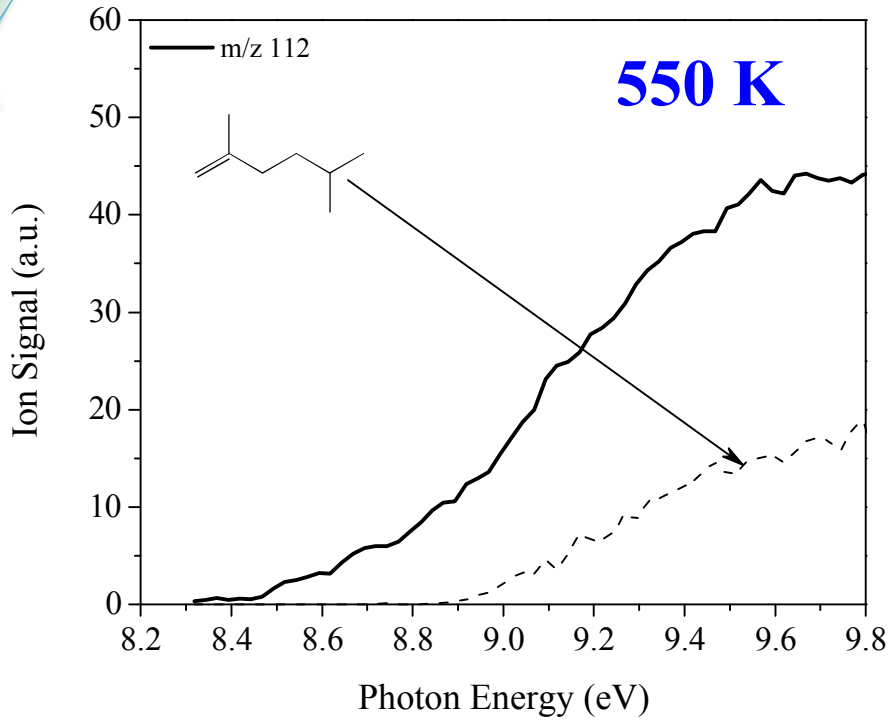
Isomeric Contributions Quantified using Absolute Photoionization Cross-Sections

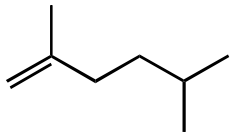




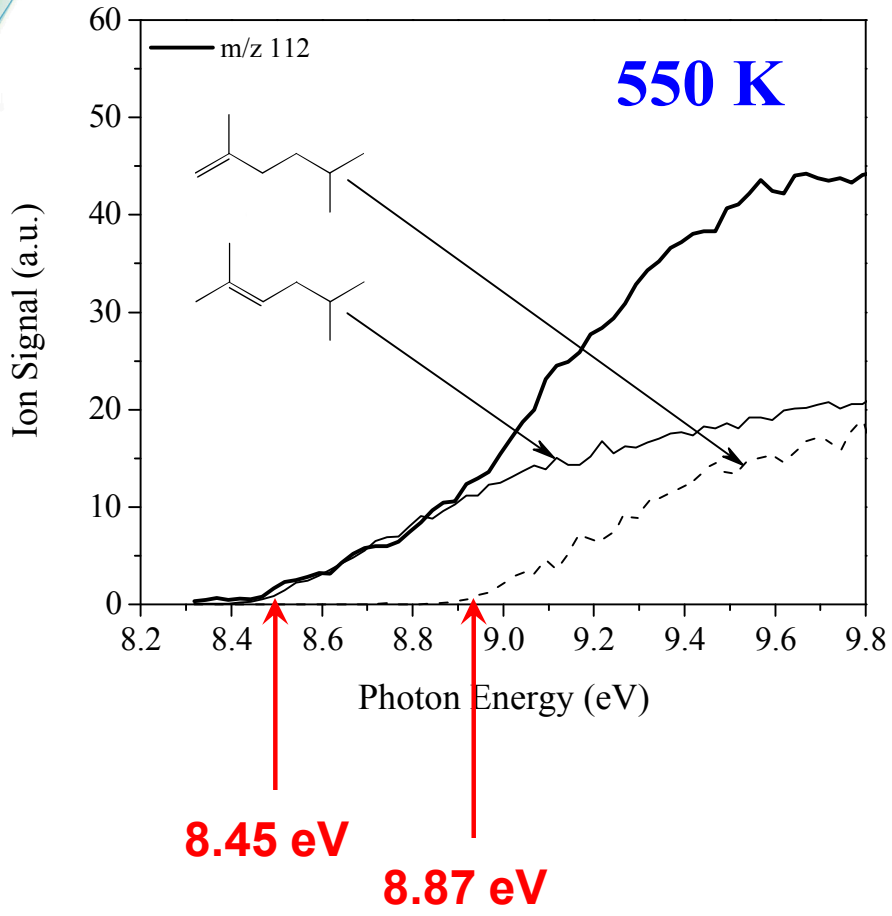


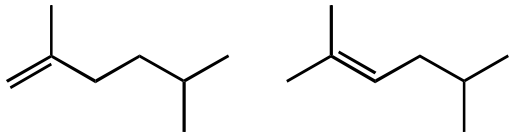
Temperature-Dependent Branching Ratios of HO_2-Elimination Yields



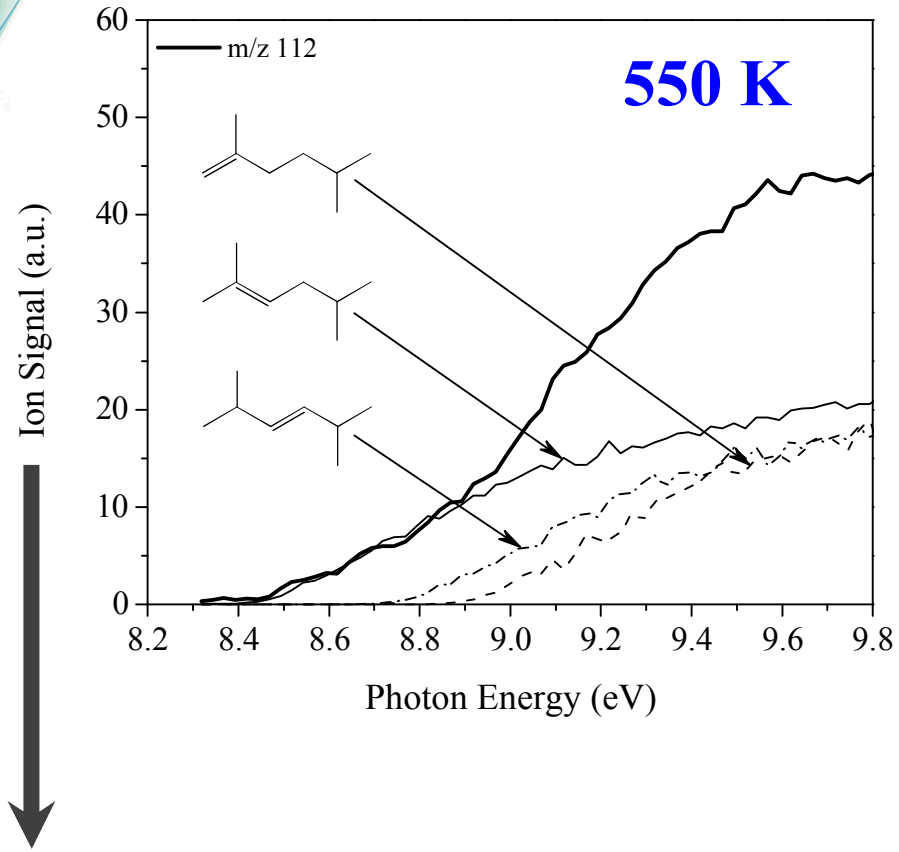


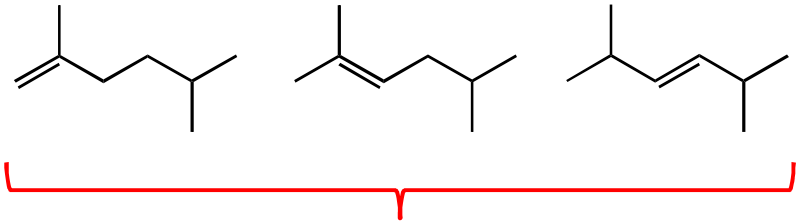
Temperature-Dependent Branching Ratios of HO_2-Elimination Yields





Temperature-Dependent Branching Ratios of HO_2-Elimination Yields





Isomers of m/z 112

Isomer-specific contributions quantified using results from separate measurements of absolute photoionization cross-sections $\sigma_i(E)$ for each species and application of fitting routine:

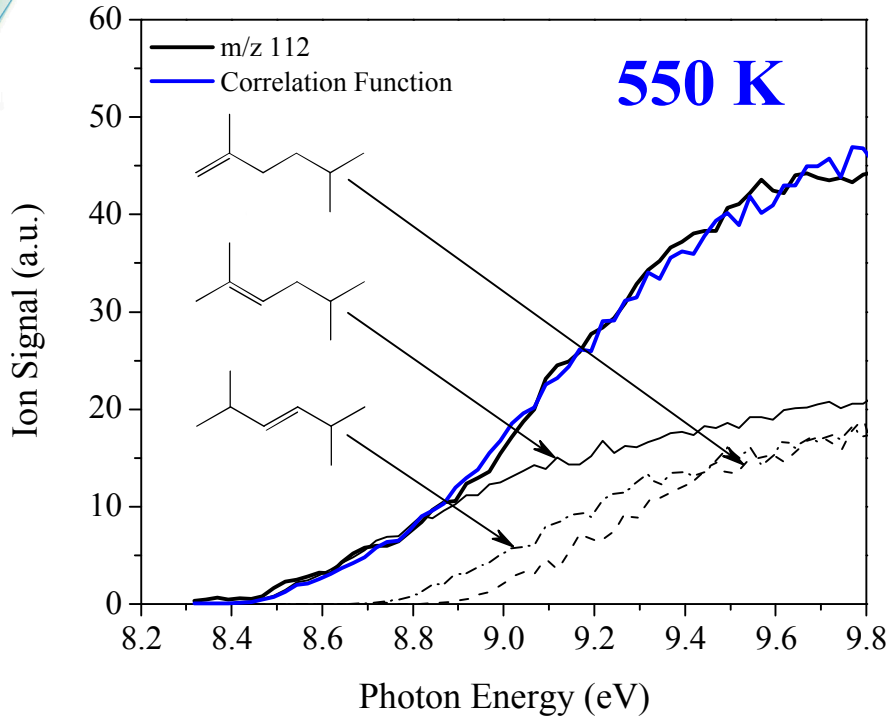
$$S_{m/z}(E) = \sum_i^N A_i \sigma_i(E)$$

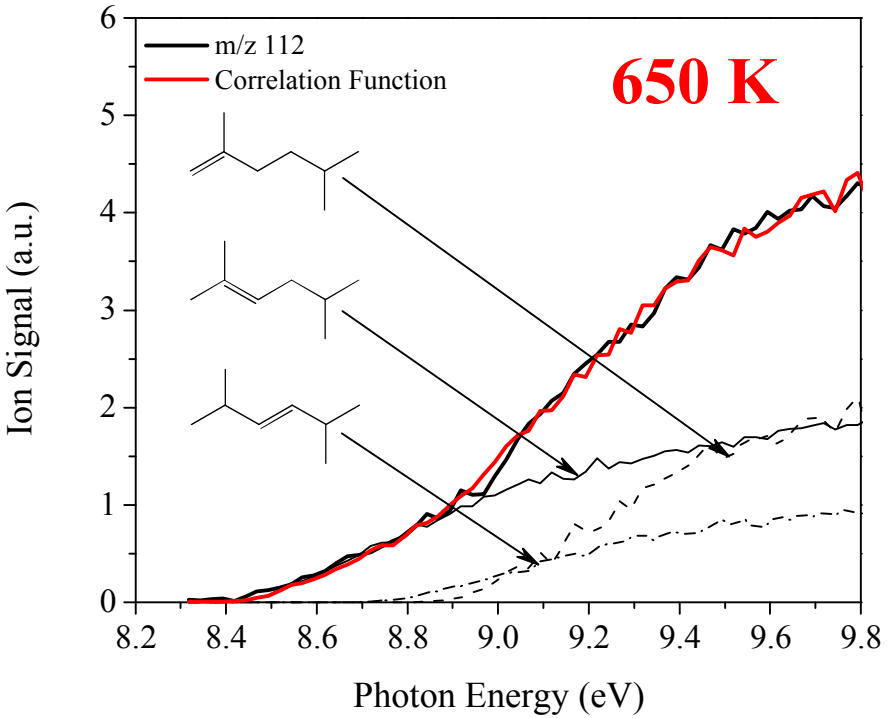
Ion Signal Definition:

$$S_i(E) = \Lambda \sigma_i(E) c_i \alpha_i$$

For known $\sigma_i(E)$, ion signals $\propto$ concentration c_i

Temperature-Dependent Branching Ratios of Alkenes from HO_2-Elimination





Alkene	550 K	650 K
2,5-dimethyl-1-hexene	30%	47%
2,5-dimethyl-2-hexene	32%	33%
2,5-dimethyl-3-hexene	38%	19%

Quantification of Fractional Yields of Products

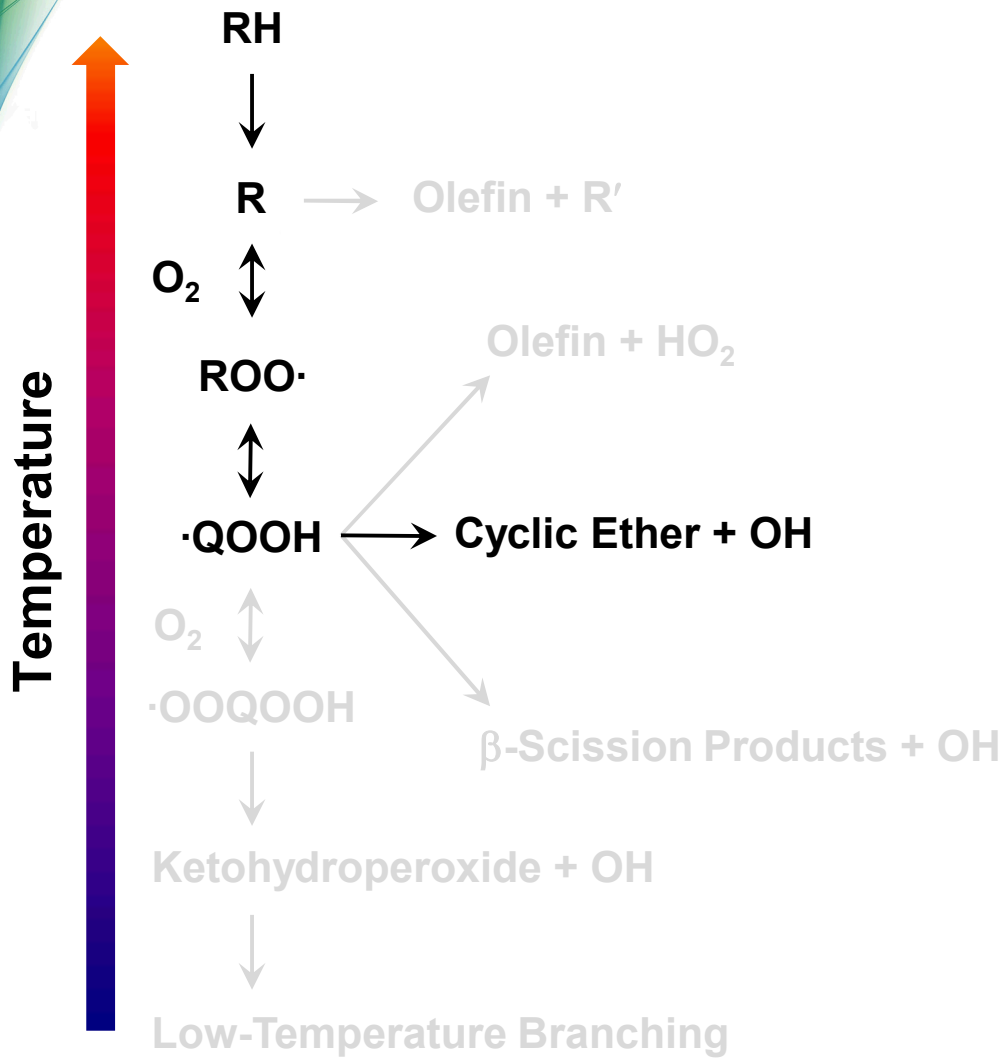
m/z	Species	Fractional Yield	
		550 K	650 K
42	propene	0.10	0.38
44	acetaldehyde	0.04	0.02
	vinyl alcohol	0.02	0.01
56	*iso*-butene	1.05	0.88
58	acetone	0.49	0.21
	methyloxirane	0.21	0.00
68	isoprene	0.01	0.01
72	methyl-propanal	1.46	0.58
98	5-methyl-2-hexene	0.00	0.07
112	***2,5-dimethyl-1-hexene***	***1.00***	***1.00***
	2,5-dimethyl-2-hexene	1.13	0.71
	2,5-dimethyl-3-hexene	1.16	0.41
128	2,2,5,5-tetramethyl-THF	73.69	12.91

Fractional yields defined relative to formation of HO_2-elimination co-product 2,5-dimethyl-1-hexene:

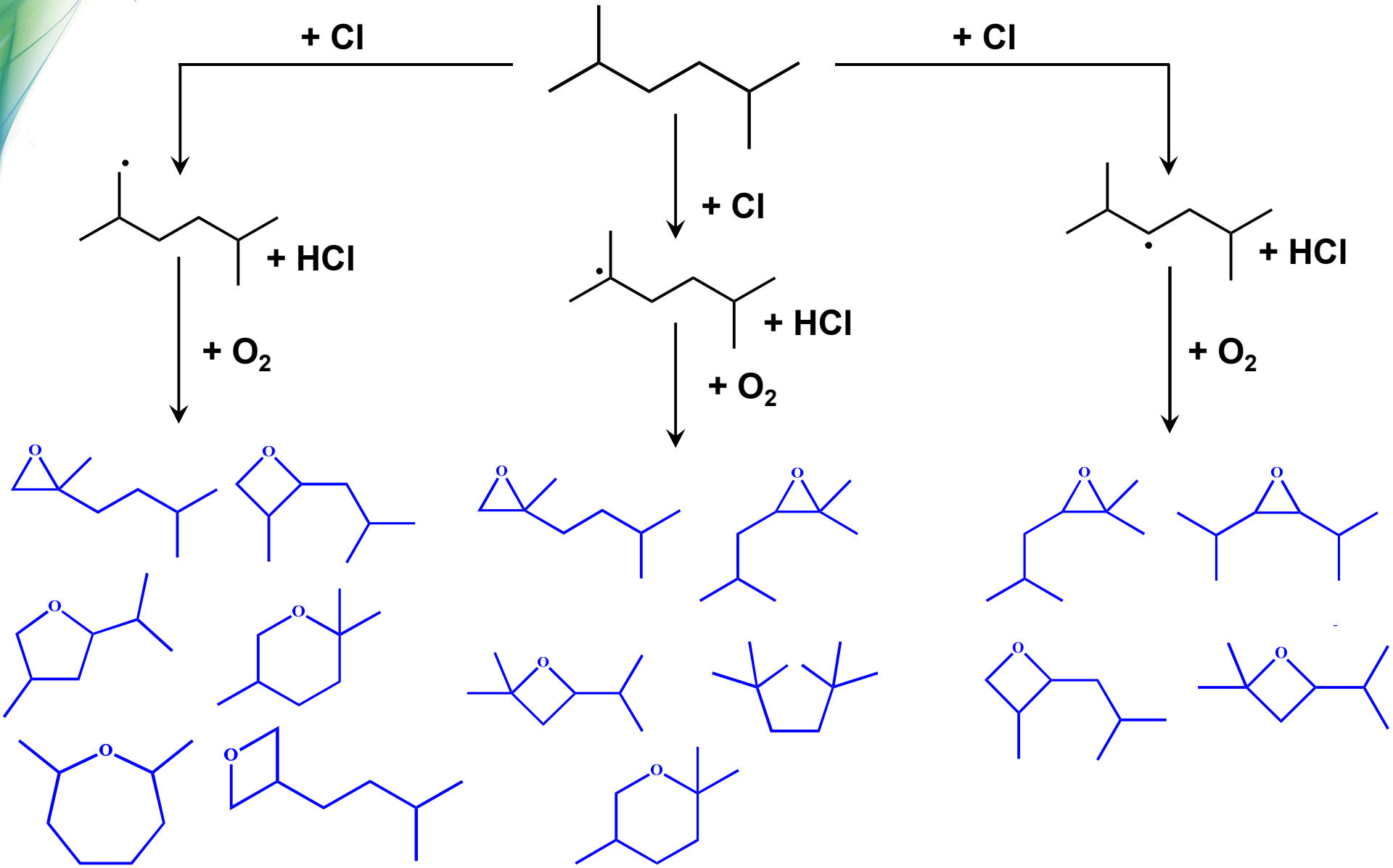
$$Fractional\ Yield = \frac{[Species\ i]}{[2,5-dimethyl-1-hexene]}$$

Results (2): Cyclic Ether Formation

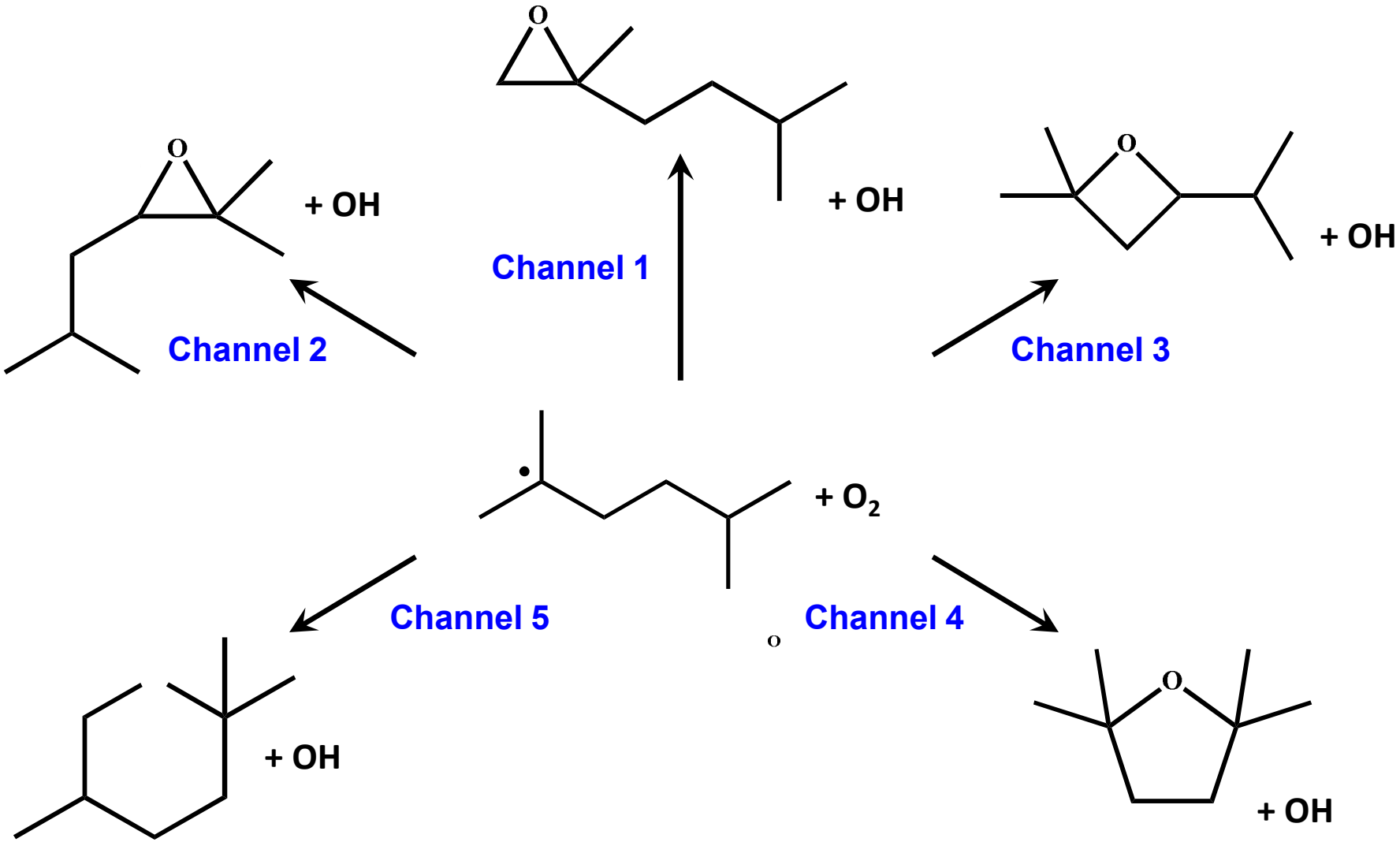
Direct Measurement of OH-Loss Channel



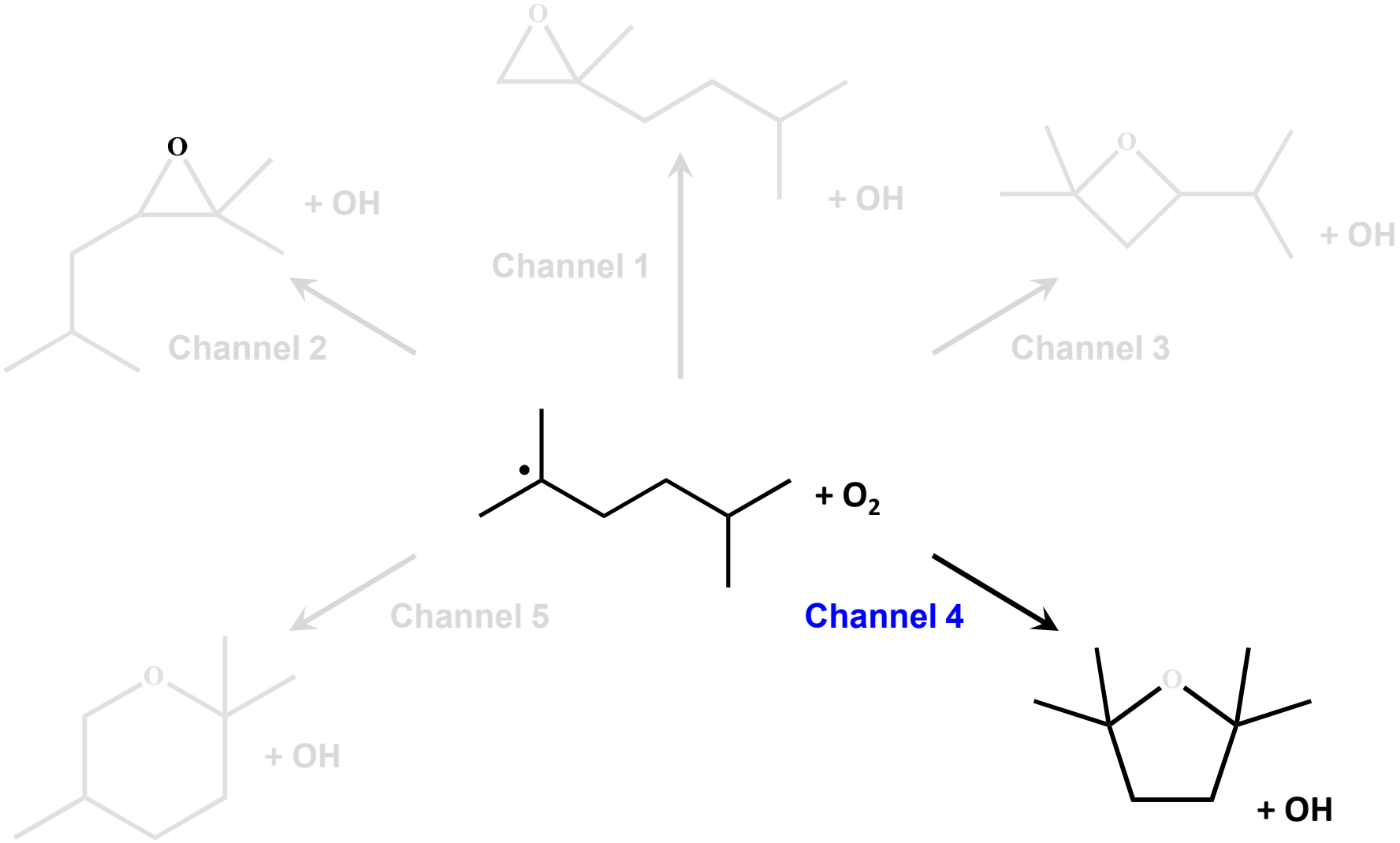
OH-Loss Co-Products from QOOH Species



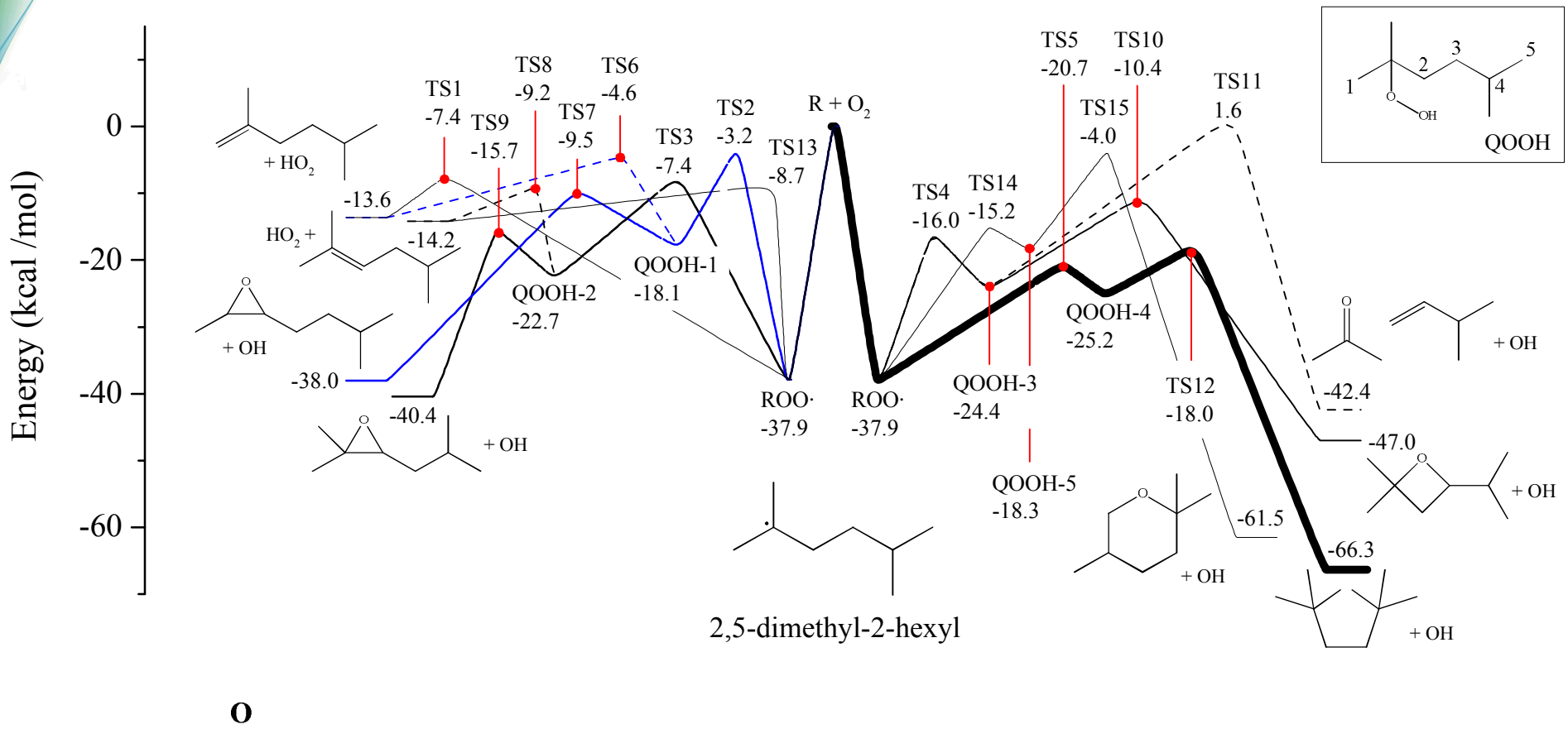
Cyclic Ether Formation from O_2-Addition to Tertiary R



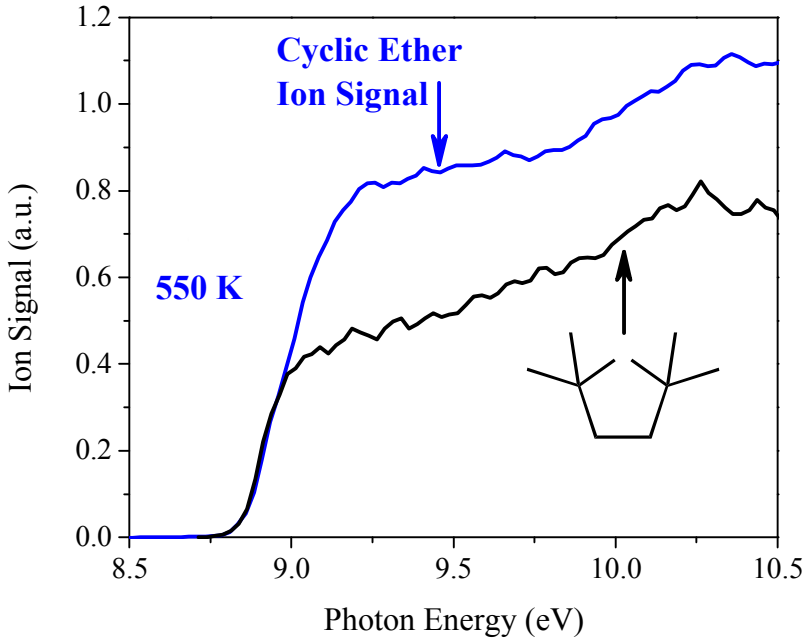
Cyclic Ether Formation: 2,2,5,5-tetramethyl-THF

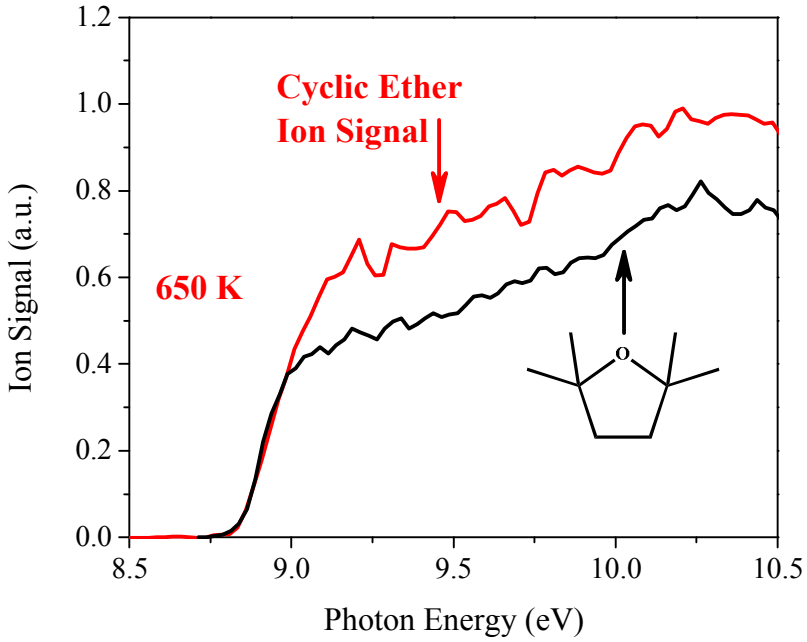


Stationary Points: 2,5-dimethyl-2-hexyl + O_2 Calculated at CBS-QB3 Level



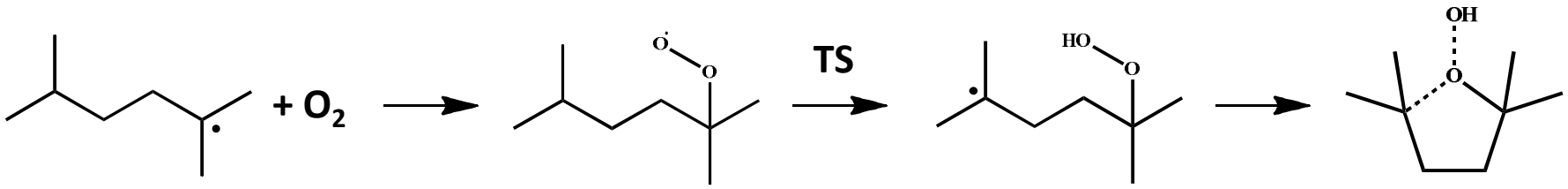
Significance of 2,2,5,5-tetramethyl-THF to Cyclic Ether Channel



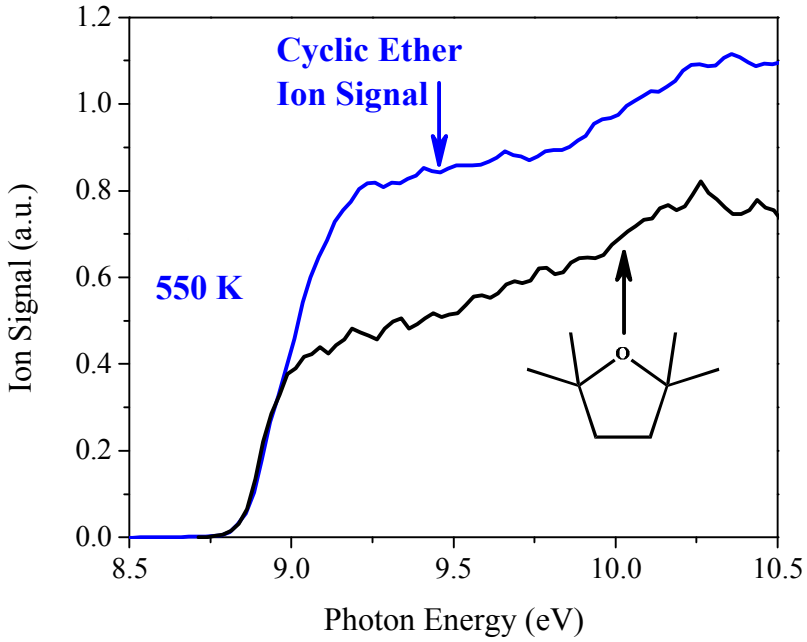


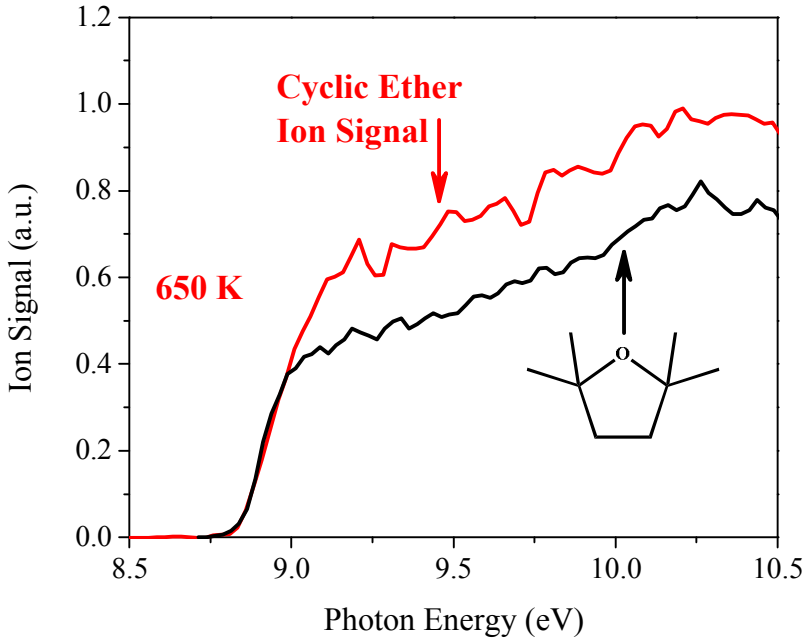
$$Fractional\ Yield\ (550\ K) = 73.69$$

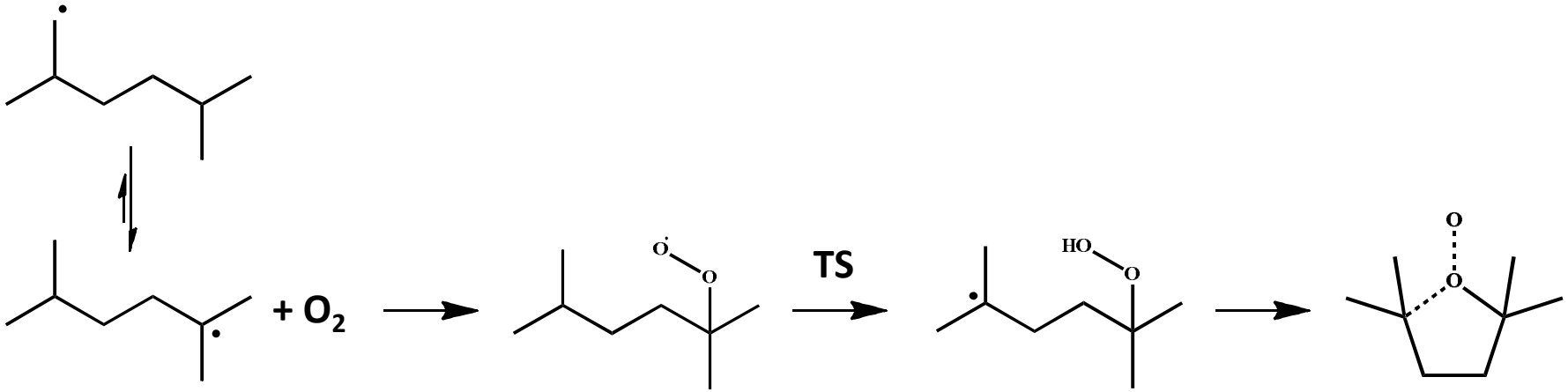
$$Fractional\ Yield\ (650\ K) = 12.61$$



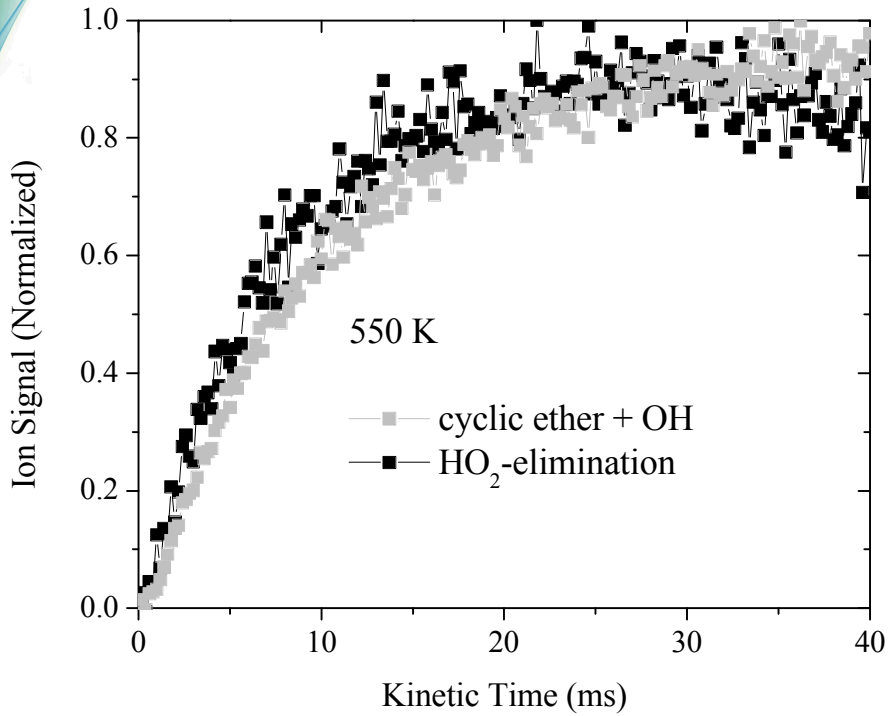
Significance of 2,2,5,5-tetramethyl-THF to Cyclic Ether Channel

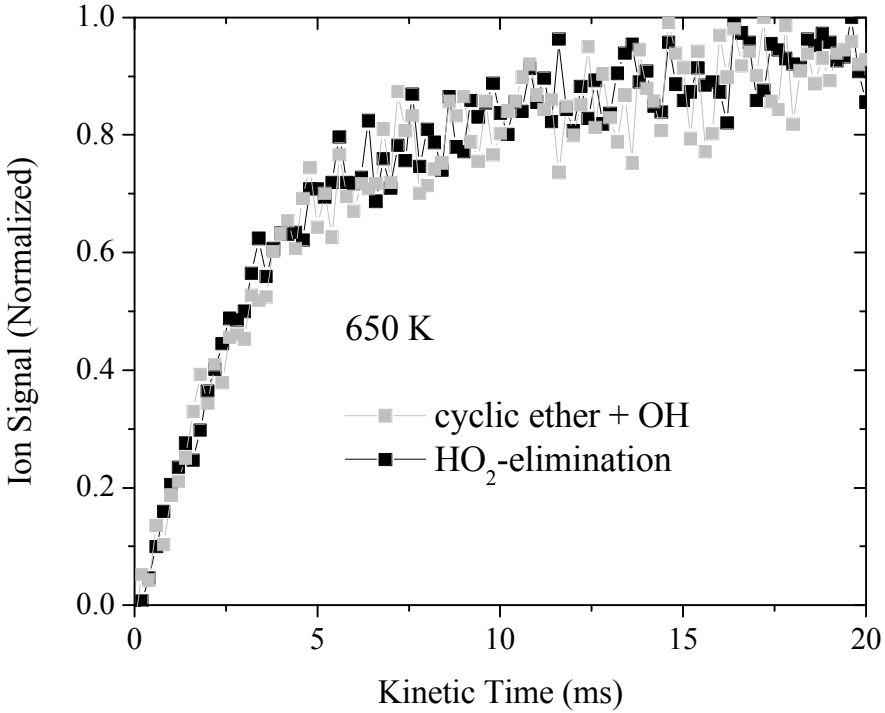






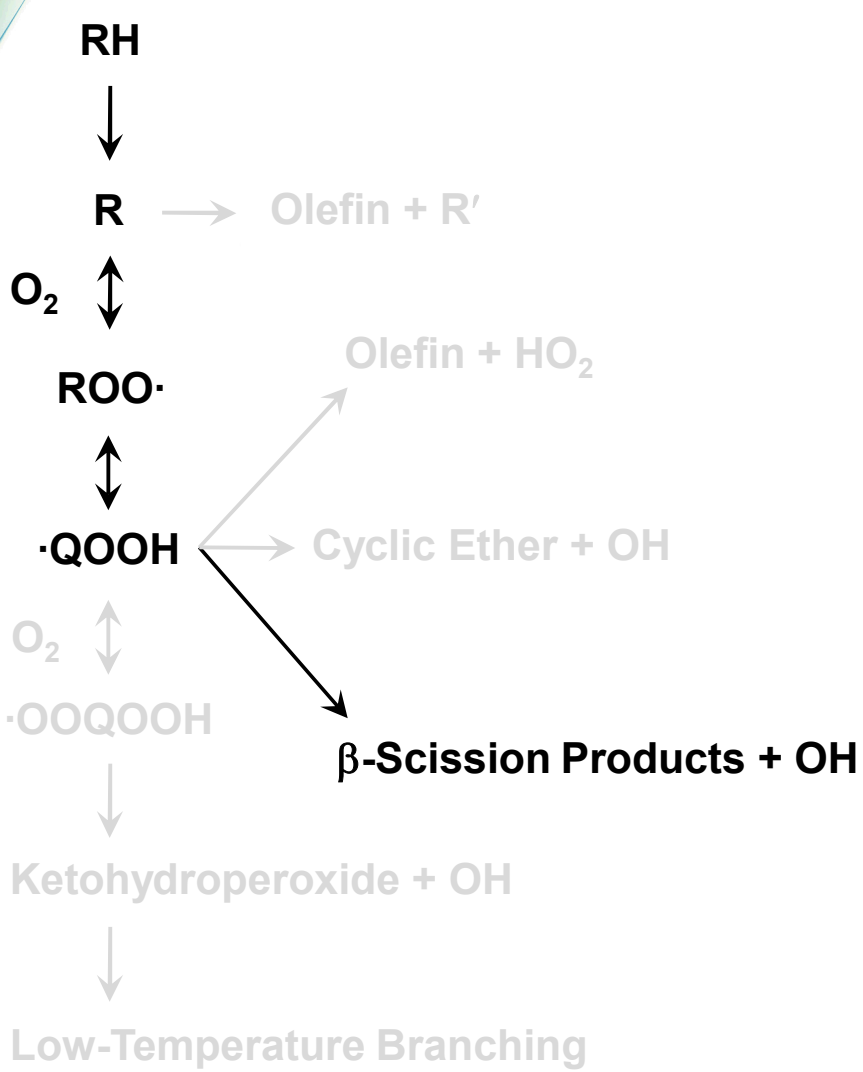
Comparison of Cyclic Ether, HO_2-Elimination Channels



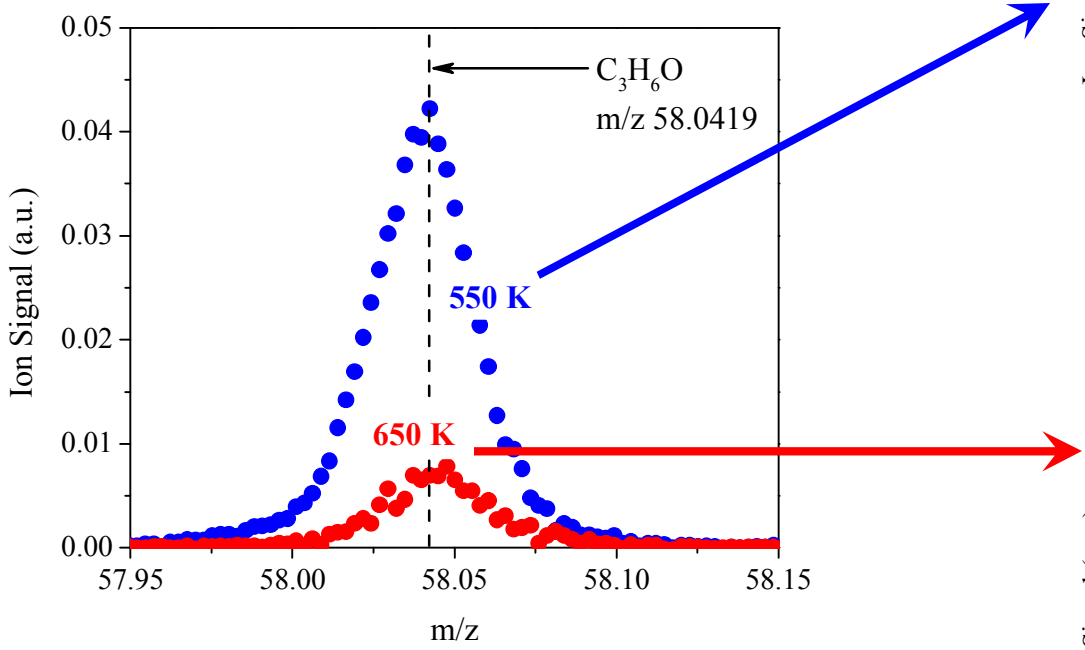


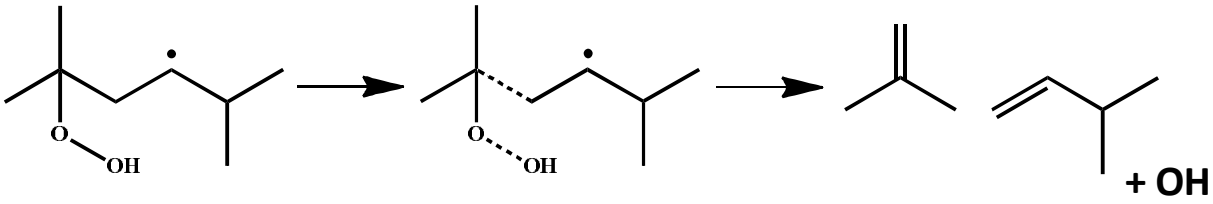
Results (3): Other Channels

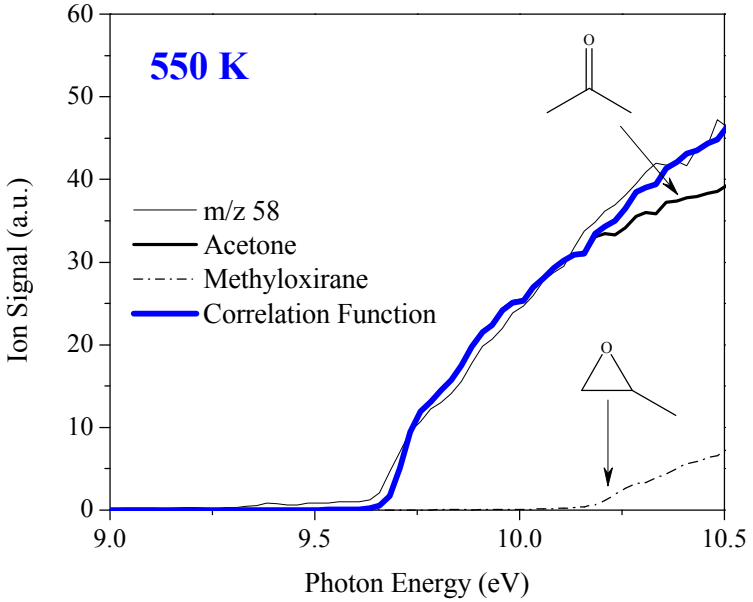
β-Scission Products of QOOH Species

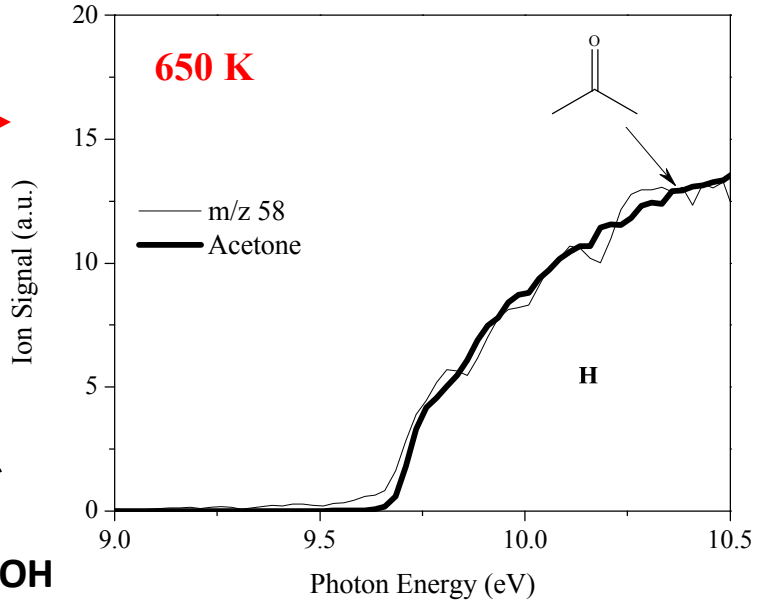


Ion Signal (m/z 58): Acetone

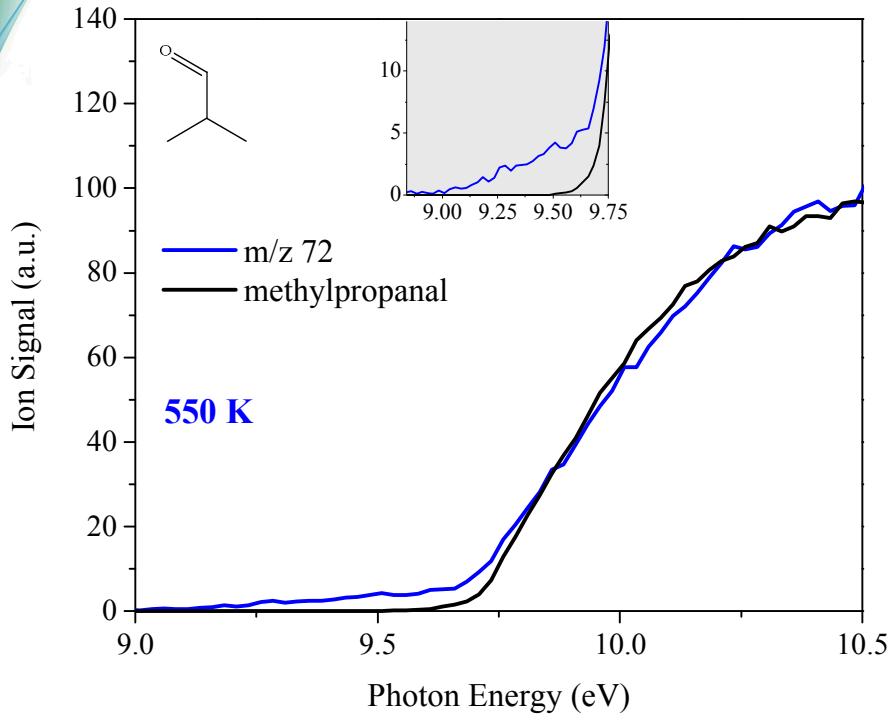


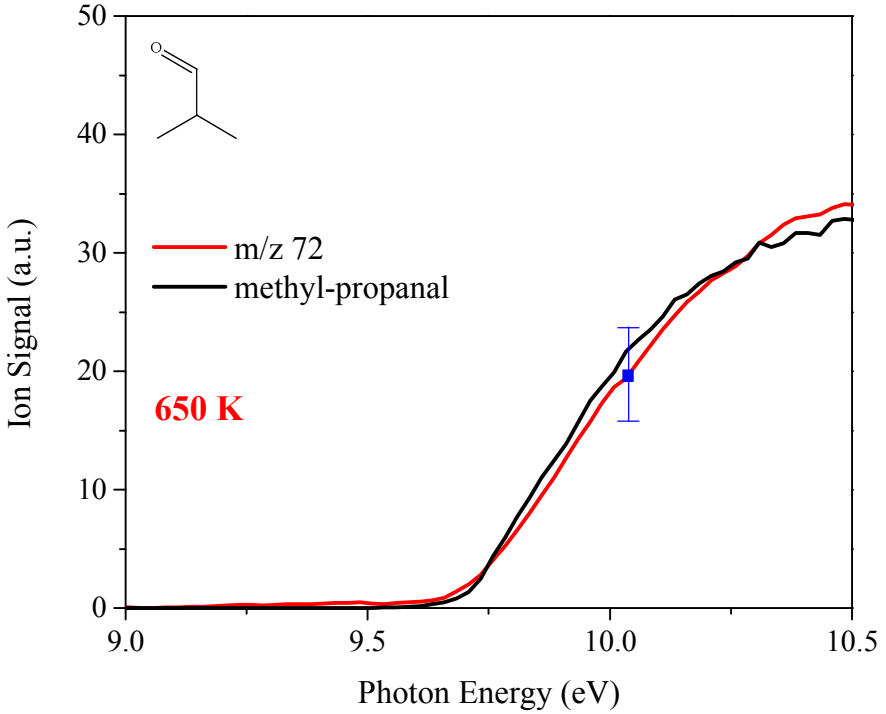






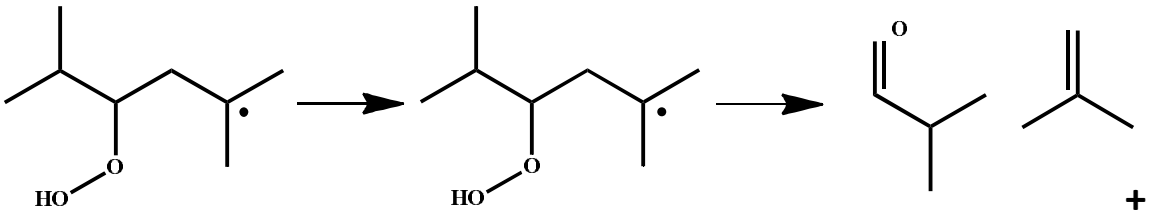
Ion Signal (m/z 72): Methyl-Propanal



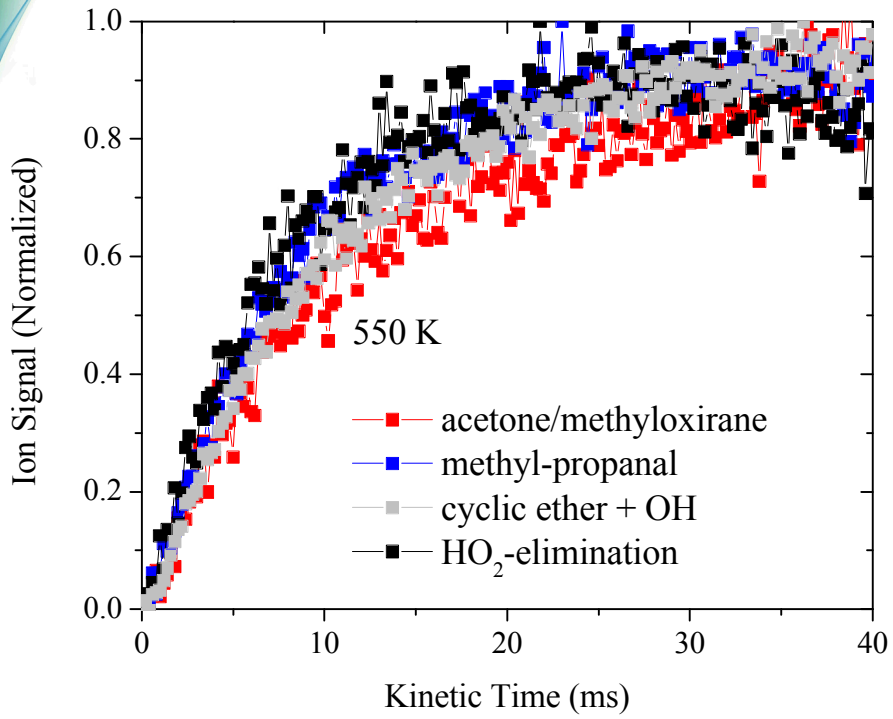


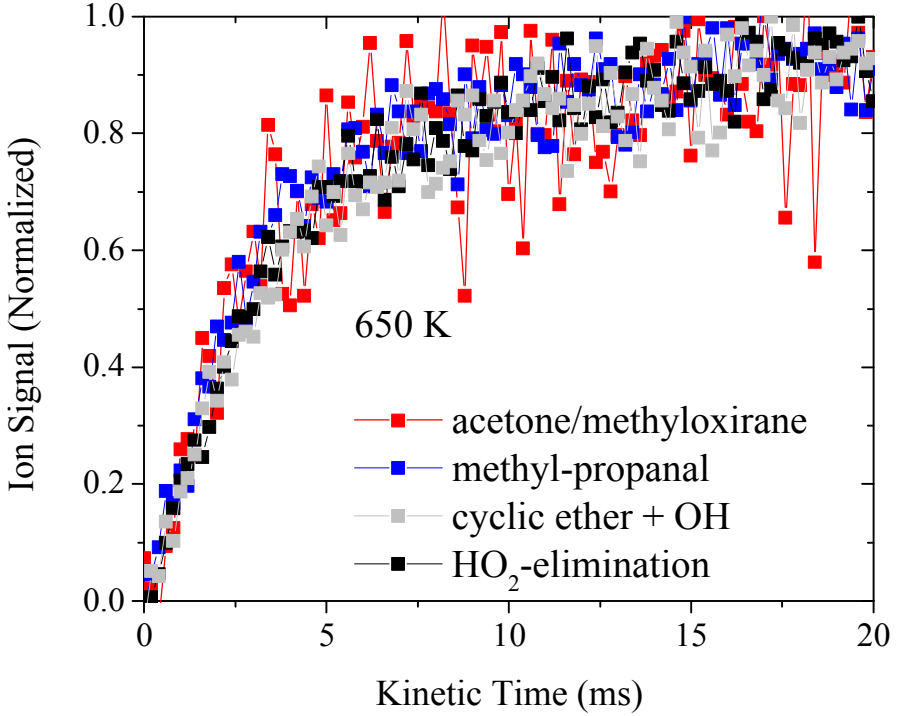
$$Fractional\ Yield\ (550\ K) = 1.46$$

$$Fractional\ Yield\ (650\ K) = 0.58$$

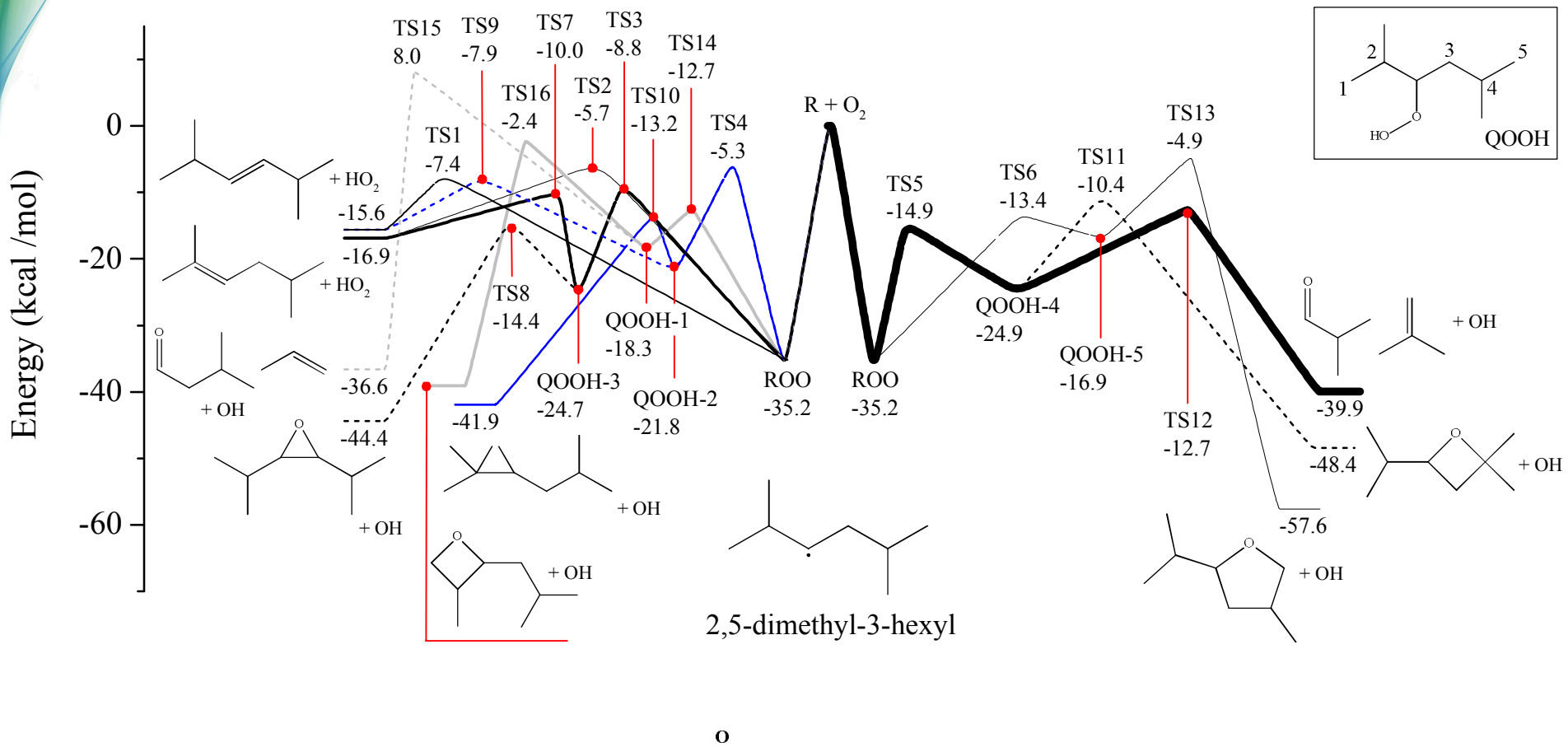


Comparison of m/z 58, 72 Time Histories to Cyclic Ether and HO_2-Elimination





Stationary Points: 2,5-dimethyl-3-hexyl + O_2



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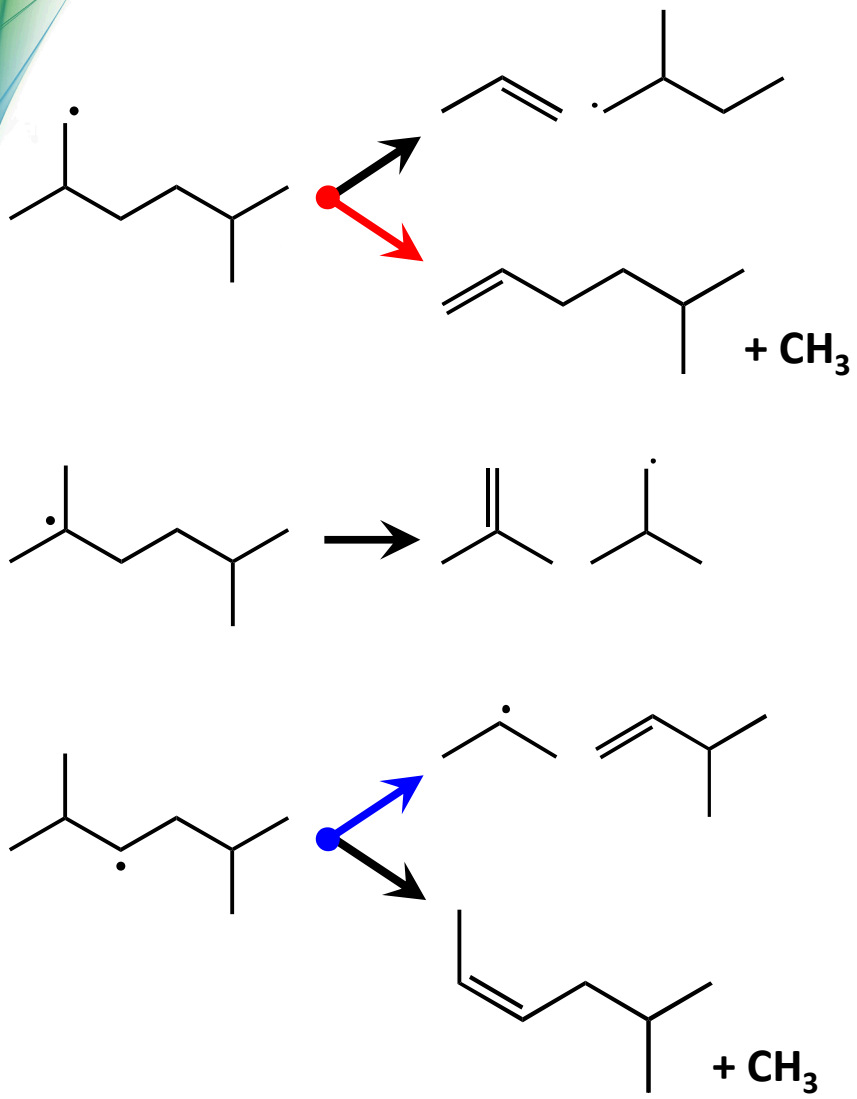
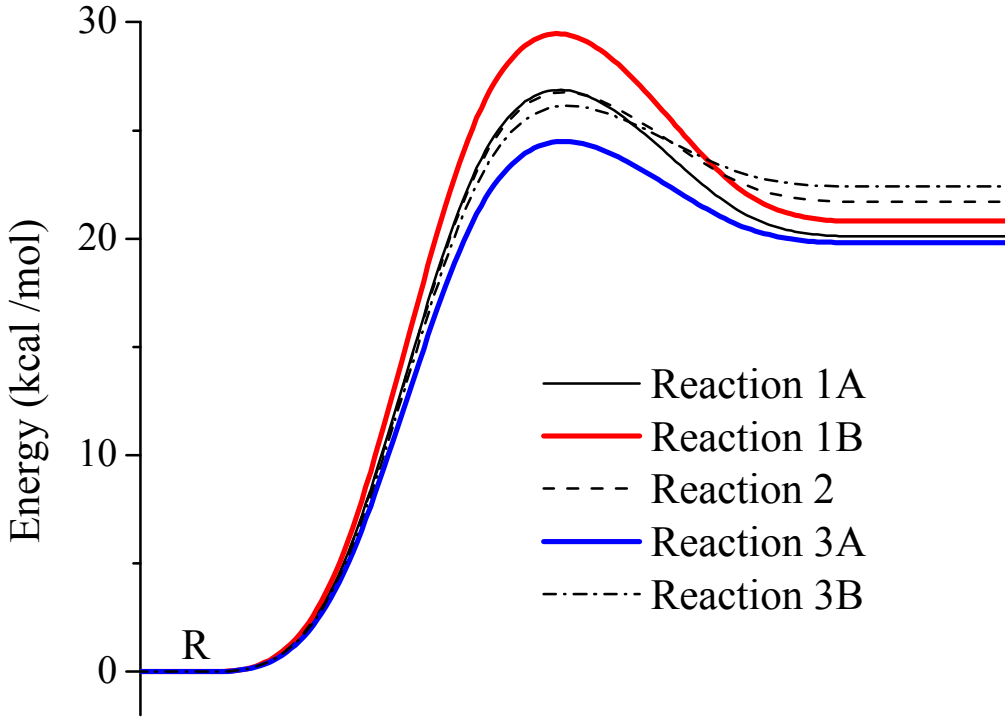
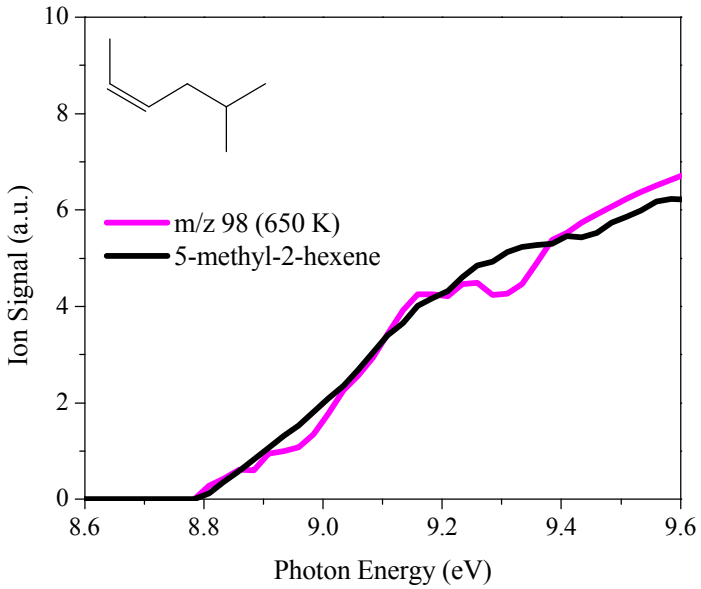
Results (4): Role of Primary Radicals in Cyclic Ether Formation

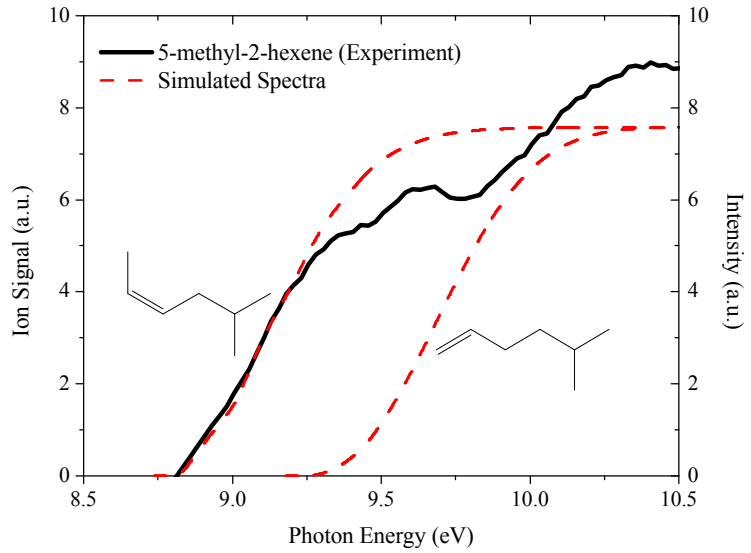
β-Scission Pathways in 2,5-dimethylhexane

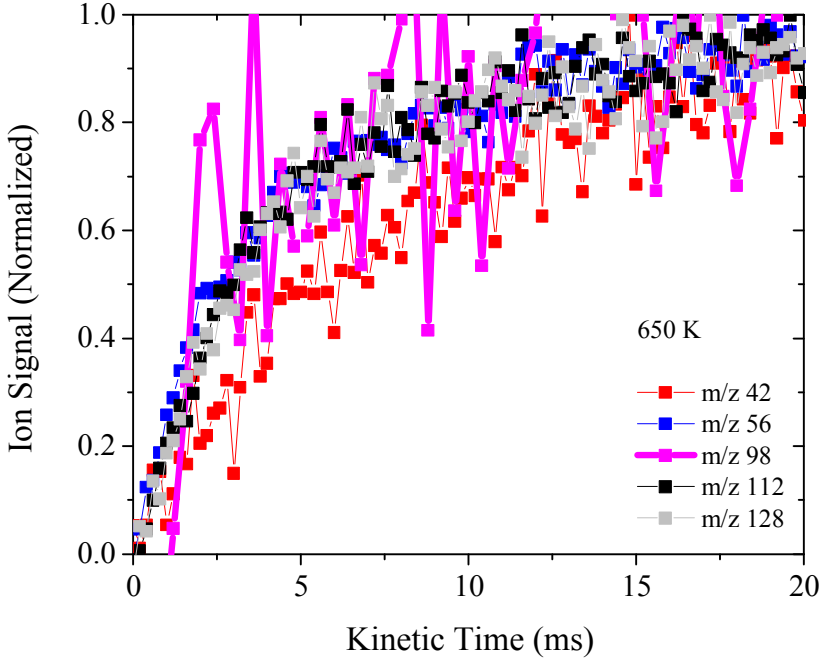




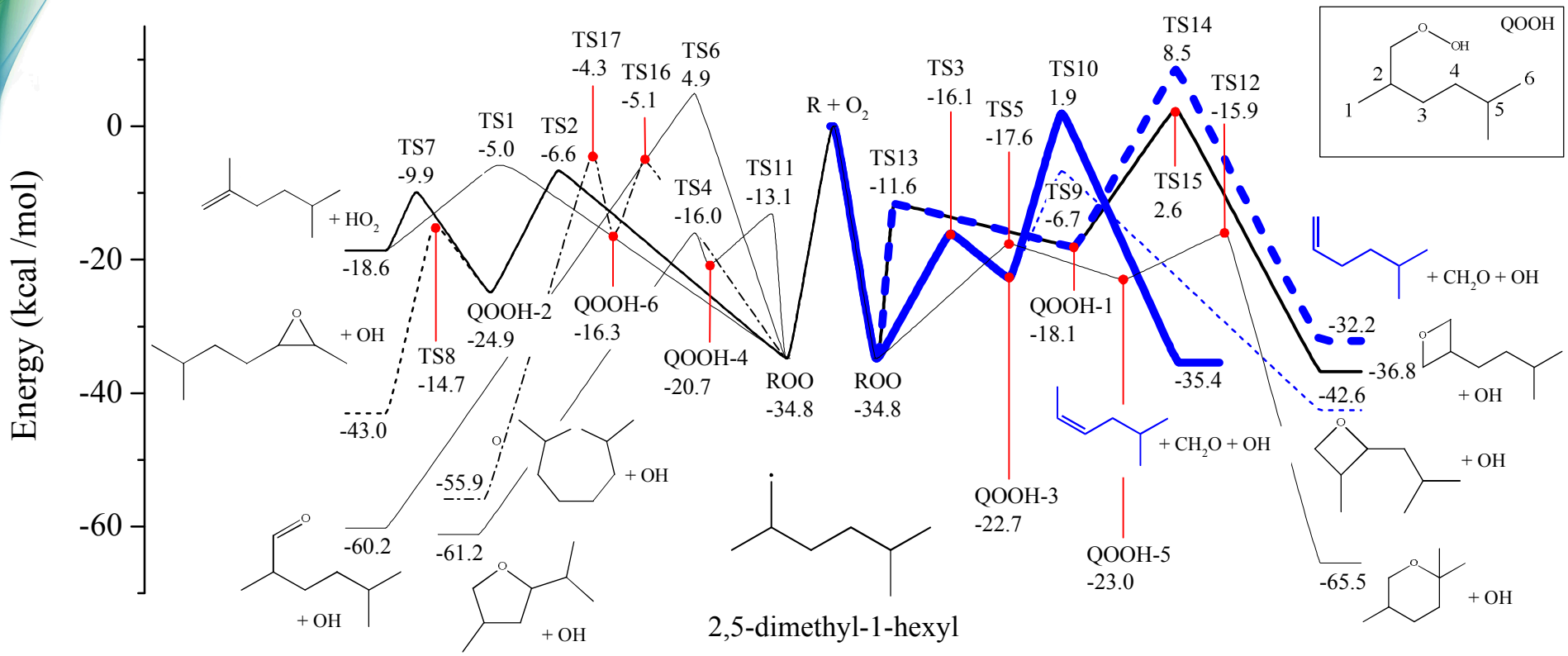
Evidence of β-Scission: m/z 98





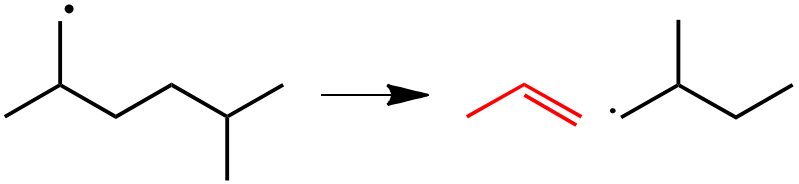


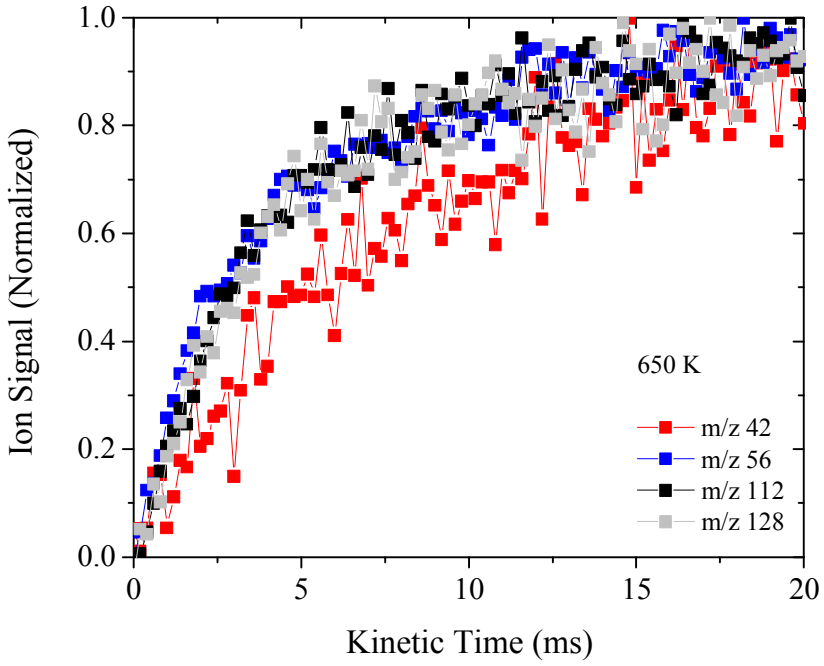
Stationary Points: 2,5-dimethyl-1-hexyl + O_2

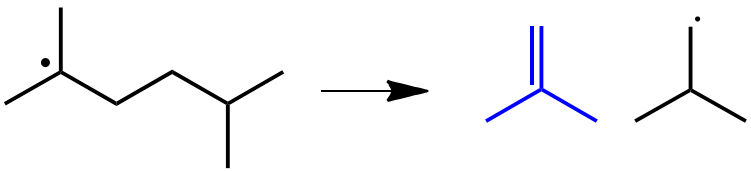


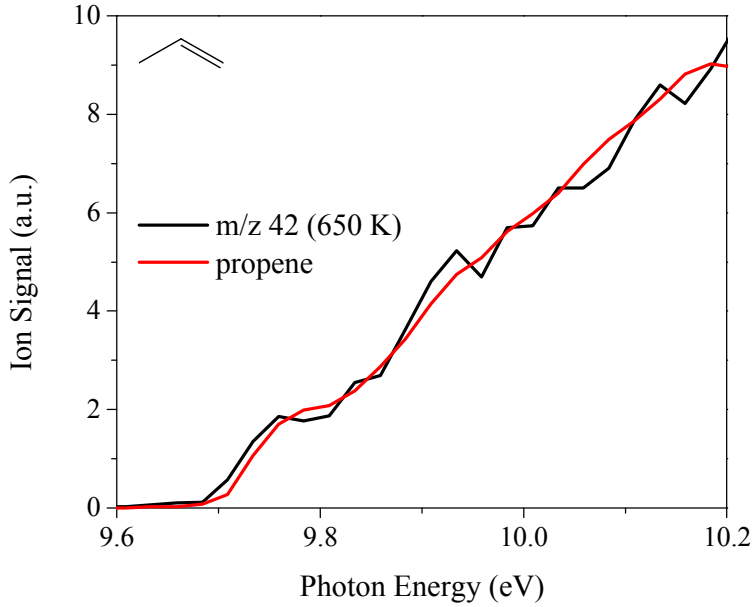
Energy barriers to m/z 98 alkene formation from QOOH lie above entrance channel for R + O_2

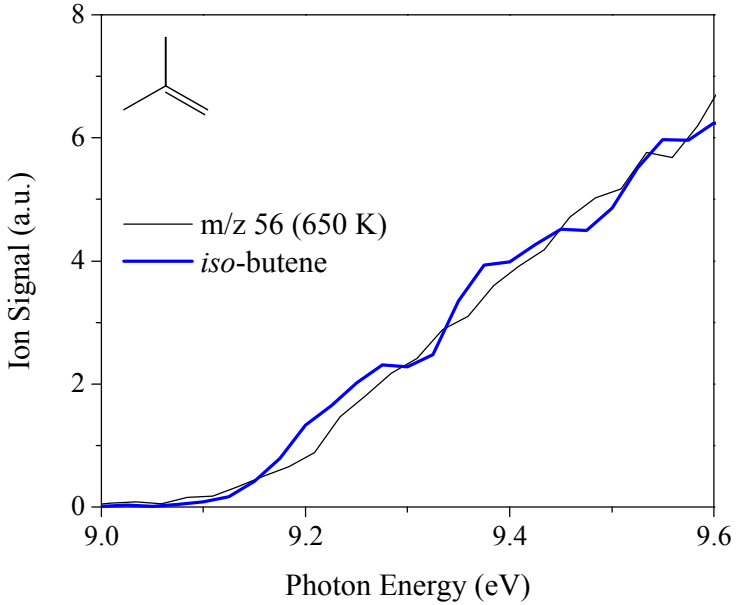
β-Scission Species Identified



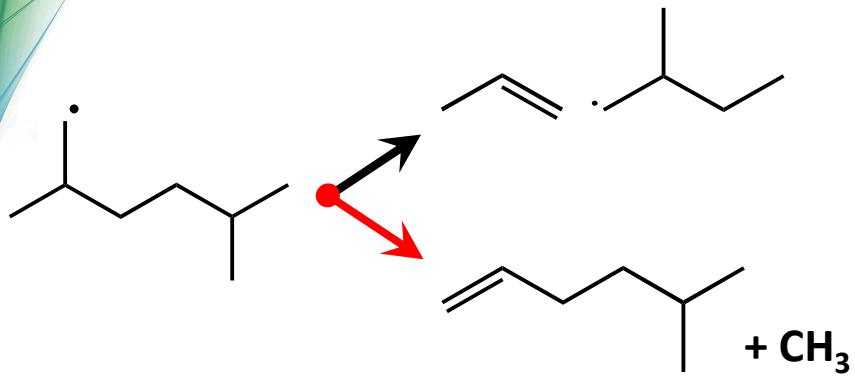


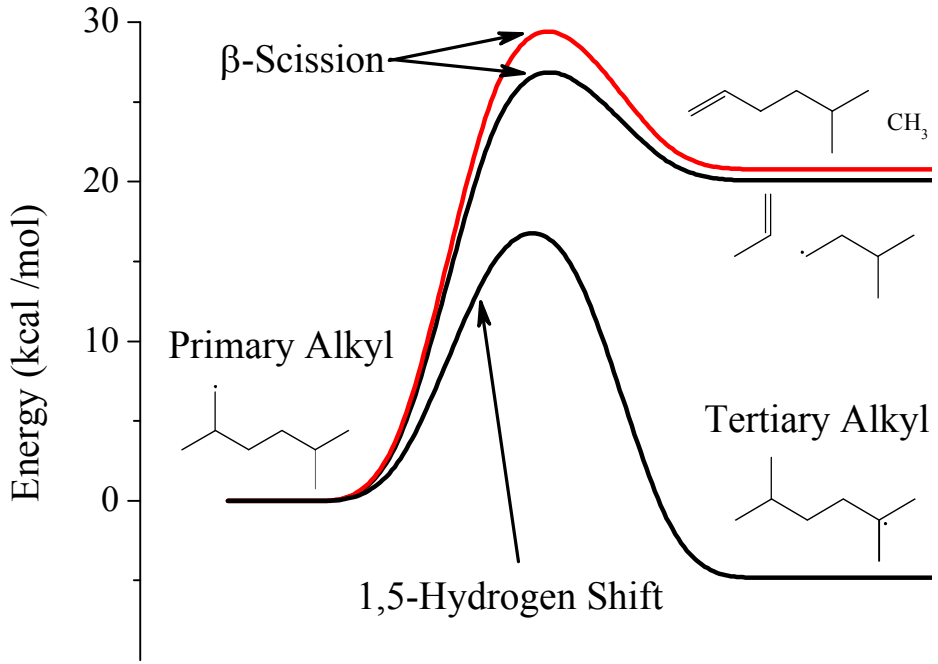


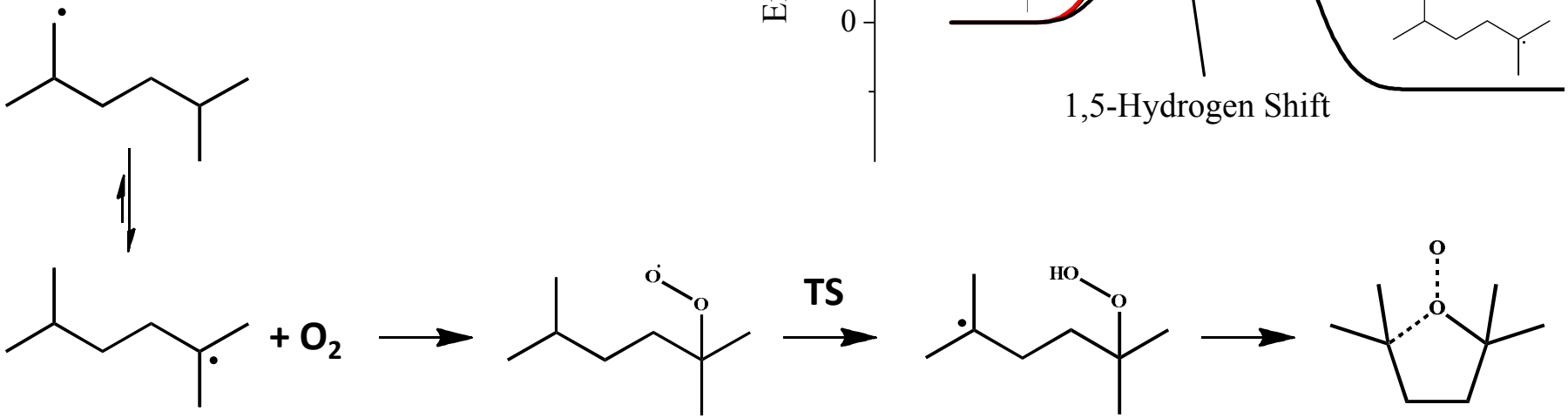




Role of Primary Alkyl Radicals in Forming 2,2,5,5-tetramethyl-THF



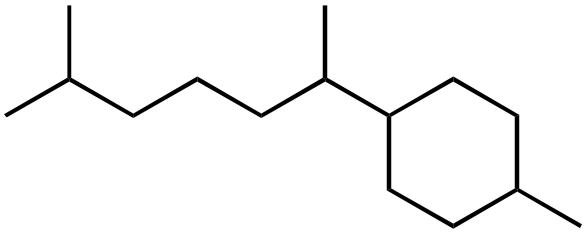




Concluding Remarks

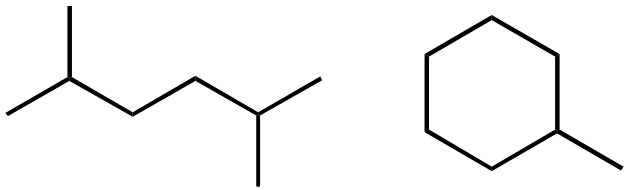
Concluding Remarks

Bisabolane ($C_{15}H_{30}$)



Target Fuel

2,5-dimethylhexane **MCH**



Component Analogs

- RO_2-related oxidation of 2,5-dimethylhexane studied at 550 K, 650 K
  - Branching ratios of HO2-elimination pathways determined
  - Formation of 2,2,5,5-tetramethyl-THF potentially vital to low-temperature oxidation modeling of 2,5-dimethylhexane
  - Isomerization of primary alkyl to tertiary alkyl *energetically* favored over unimolecular decomposition
  - Relevance of concerted QOOH decomposition
  - Potential energy surfaces calculated for R + O_2 reactions
- Ongoing work
  - (1) time-dependent OH- and HO_2-yield measurements of 2,5-dimethylhexane + O_2
  - (2) characterization of MCH oxidation

Sandia National Laboratories

University of Michigan

jbei
Joint BioEnergy Institute

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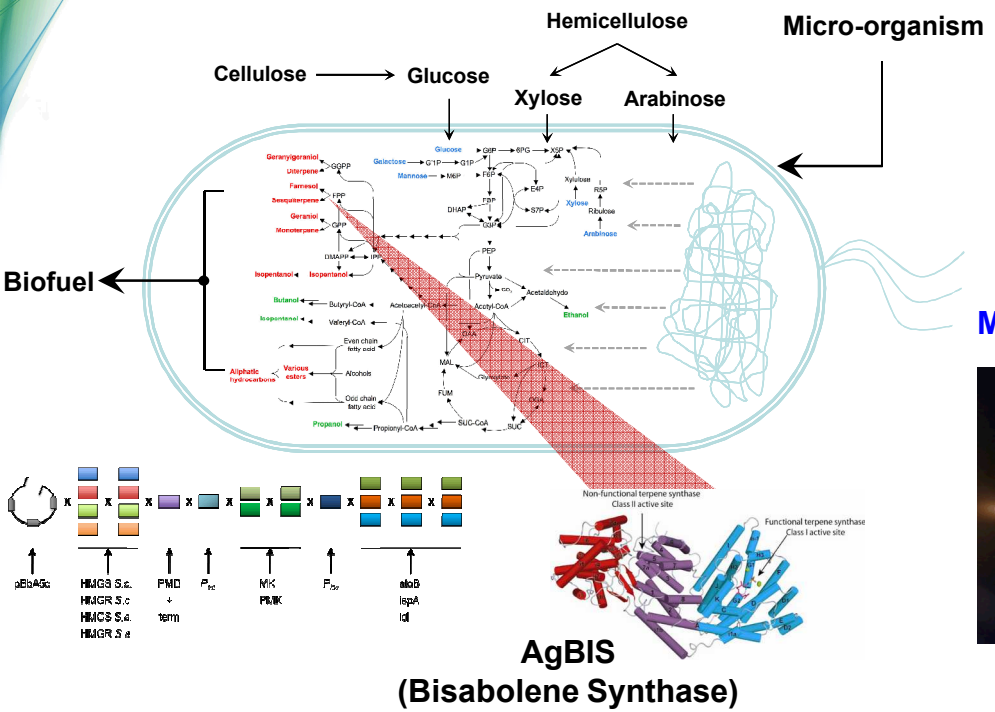
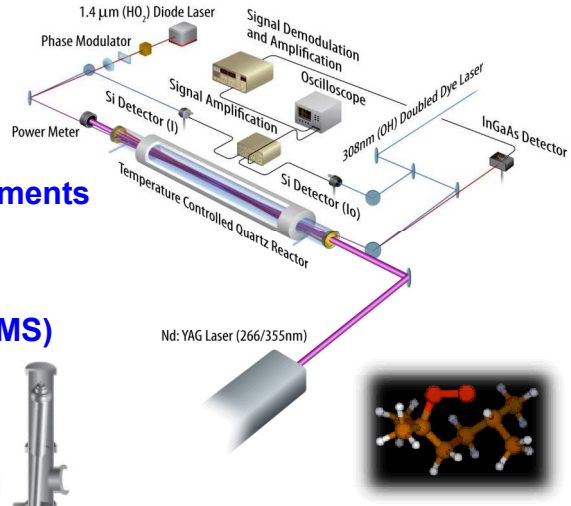
Funded by U.S.-China Clean Energy Research Center for Clean Vehicles

Joint Synthesis-Experimental-Computational Effort Towards Complex-Biofuel Oxidation Studies

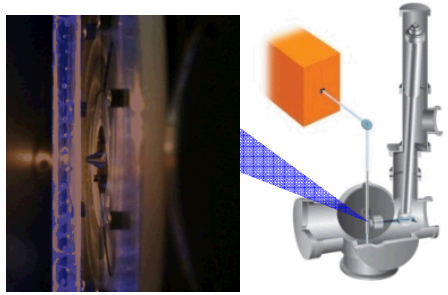


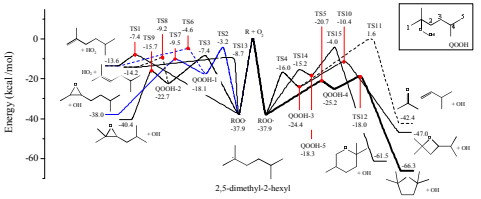
AgBIS
(Bisabolene Synthase)



OH, HO_2 Measurements

Molecular Beam Mass Spectrometry (MBMS)





Joint BioEnergy Institute (JBEI):
Synthesis of Advanced Biofuels

→

Sandia National Laboratories, University of Michigan:
Fundamental Oxidation Measurements, *ab initio* Calculations

Direct Feedback **of Experimental Results Supports Further Development of Advanced Biofuels**

Overview of Species Detected in Mass Spectra

m/z	Linear Formula	550 K	650 K	
128	$C_8H_{16}O$	2,2,5,5-tetramethyl-tetrahydrofuran	2,2,5,5-tetramethyl-tetrahydrofuran	**Cyclic Ether**
126	$C_8H_{14}O$	(unidentified)	(unidentified)	
112	C_8H_{16}	2,5-dimethyl-1-hexene	2,5-dimethyl-1-hexene	**Alkene (HO_2-Elimination)**
		2,5-dimethyl-2-hexene	2,5-dimethyl-2-hexene	
		2,5-dimethyl-3-hexene	2,5-dimethyl-3-hexene	
104	$C_4H_8O_3$ (minor)	(unidentified)	(unidentified)	
98	C_7H_{14}	–	5-methyl-2-hexene	**Alkene**
90	$C_3H_6O_3$ (minor)	(unidentified)	(unidentified)	
86	$C_5H_{10}O$	(unidentified)	(unidentified)	
84	C_5H_8O	(unidentified)	(unidentified)	
72	C_4H_8O	methyl-propanal	methyl-propanal	**Aldehyde**
70	C_5H_{10}	(unidentified)	(unidentified)	
68	C_5H_8	isoprene	isoprene	**Diene**
58	C_3H_6O	acetone	acetone	**Ketone**
		methyloxirane	–	
56	C_4H_8	*iso*-butene	*iso*-butene	**Alkene**
44	C_2H_4O	acetaldehyde	acetaldehyde	**Aldehyde**
		vinyl alcohol	vinyl alcohol	**Alcohol**
42	C_3H_6	propene	propene	**Alkene**

Quantification of Fractional Yields of Products

m/z	Species	Fractional Yield	
		550 K	650 K
42	propene	0.10	0.38
44	acetaldehyde	0.04	0.02
	vinyl alcohol	0.02	0.01
56	*iso*-butene	1.05	0.88
58	acetone	0.49	0.21
	methyloxirane	0.21	0.00
68	isoprene	0.01	0.01
72	methyl-propanal	1.46	0.58
98	5-methyl-2-hexene	0.00	0.07
112	***2,5-dimethyl-1-hexene***	***1.00***	***1.00***
	2,5-dimethyl-2-hexene	1.13	0.71
	2,5-dimethyl-3-hexene	1.16	0.41
128	2,2,5,5-tetramethyl-THF	73.69	12.91

Ion Signal:

$$S_i(E) = \Lambda \sigma_i(E) c_i \alpha_i$$

Absolute Photoionization Cross-Section:

$$\sigma_i(E) = \sigma_{ref.}(E) \left(\frac{S_i(E)}{S_{ref.}(E)}\right) \left(\frac{c_i}{c_{ref.}}\right) \left(\frac{m_i}{m_{ref.}}\right)^{\beta(P,T)}$$

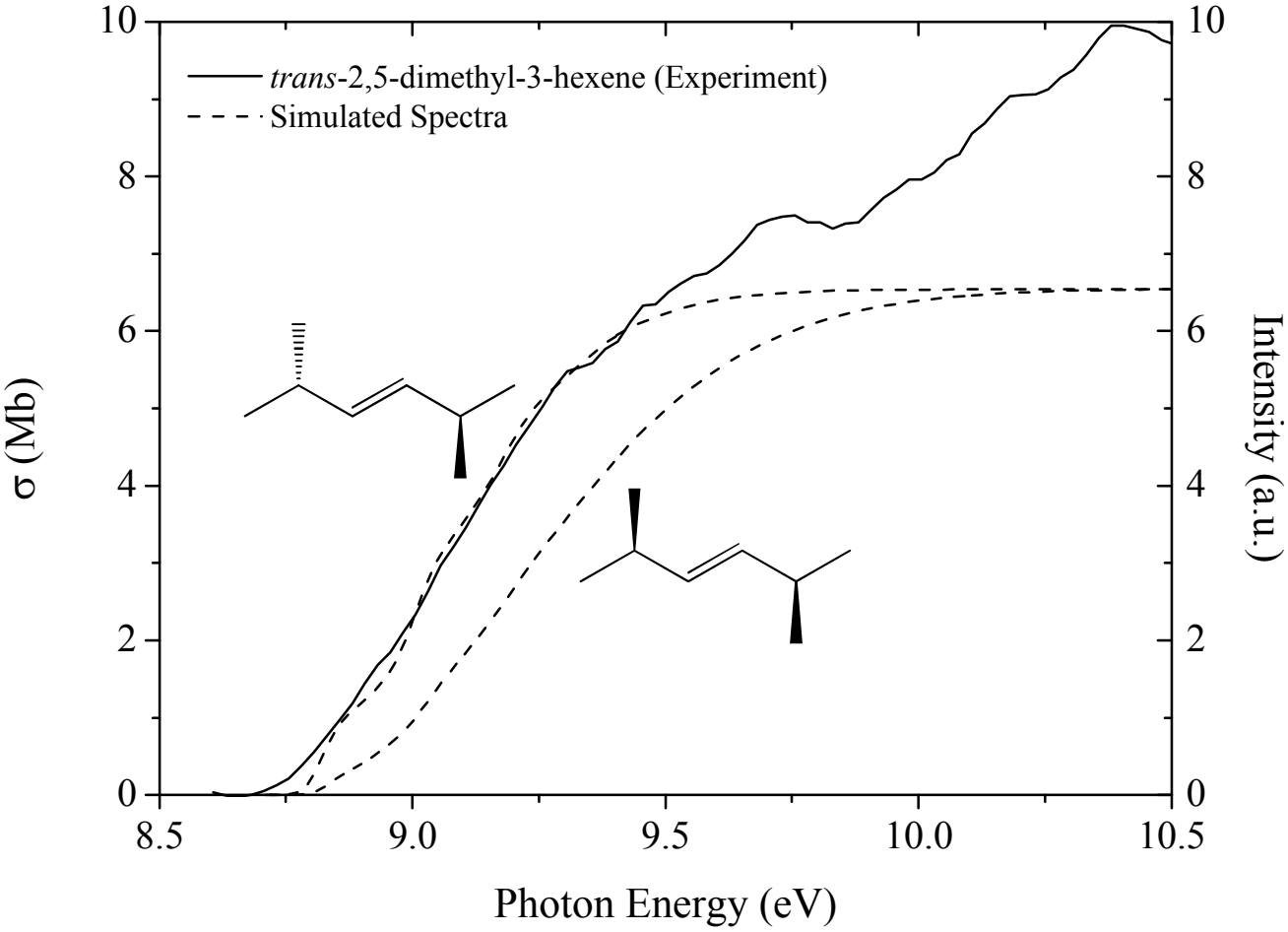
$$\sigma_i(E) = S_i(E) \left(\frac{\gamma(P,T)}{c_i m_i^{\beta(P,T)}}\right)$$

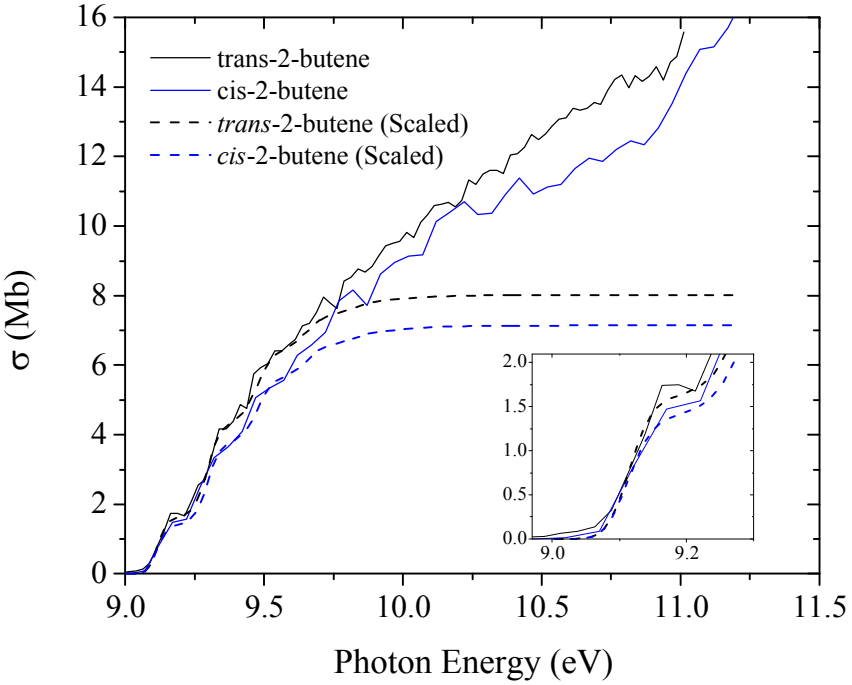
Fitting Coefficients:

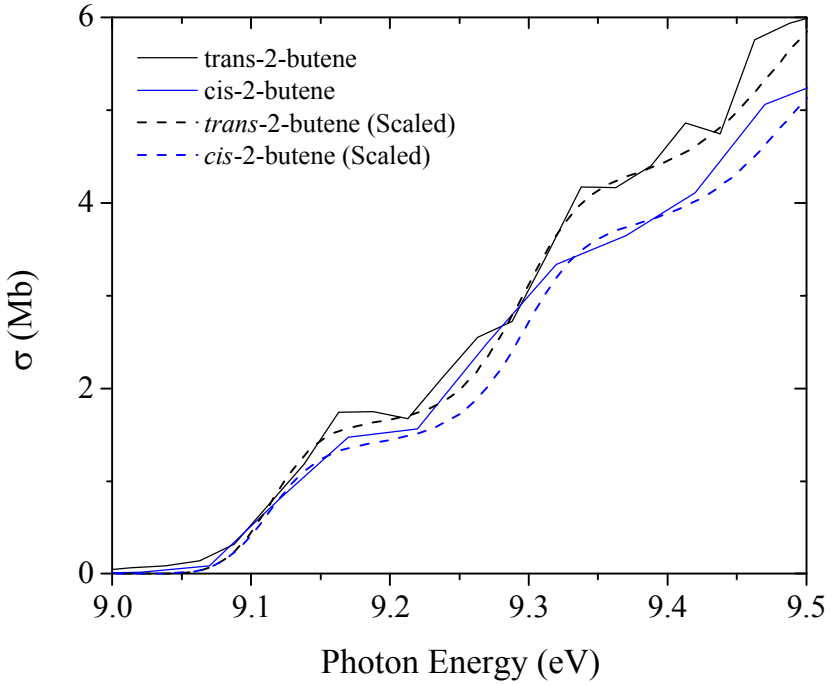
$$S(E) = \sum_i^N A_i \sigma_i(E)$$

Fractional Yield:

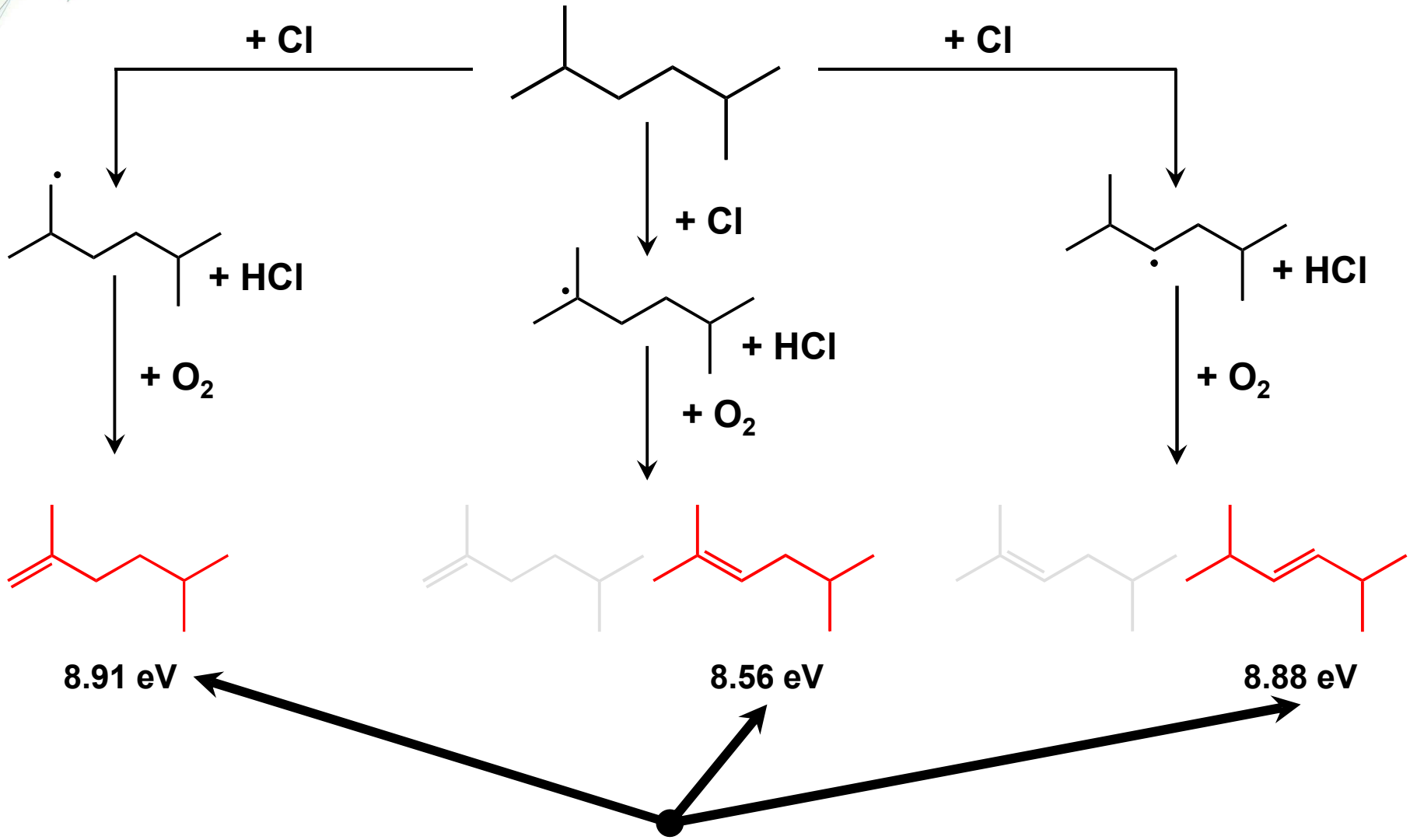
$$\rho = \left(\frac{A_i}{A_{2,5-dimethyl-1-hexene}}\right) \left(\frac{m_i}{112.125}\right)^{\beta(P,T)}$$


trans-2,5-dimethyl-3-hexene (Experiment)
Simulated Spectra
σ (Mb)
Intensity (a.u.)
Photon Energy (eV)
0
2
4
6
8
10
8.5
9.0
9.5
10.0
10.5


trans-2-butene
cis-2-butene
trans-2-butene (Scaled)
cis-2-butene (Scaled)
σ (Mb)
Photon Energy (eV)
0
2
4
6
8
10
12
14
16
9.0
9.5
10.0
10.5
11.0
11.5
0.0
0.5
1.0
1.5
2.0
9.0
9.2

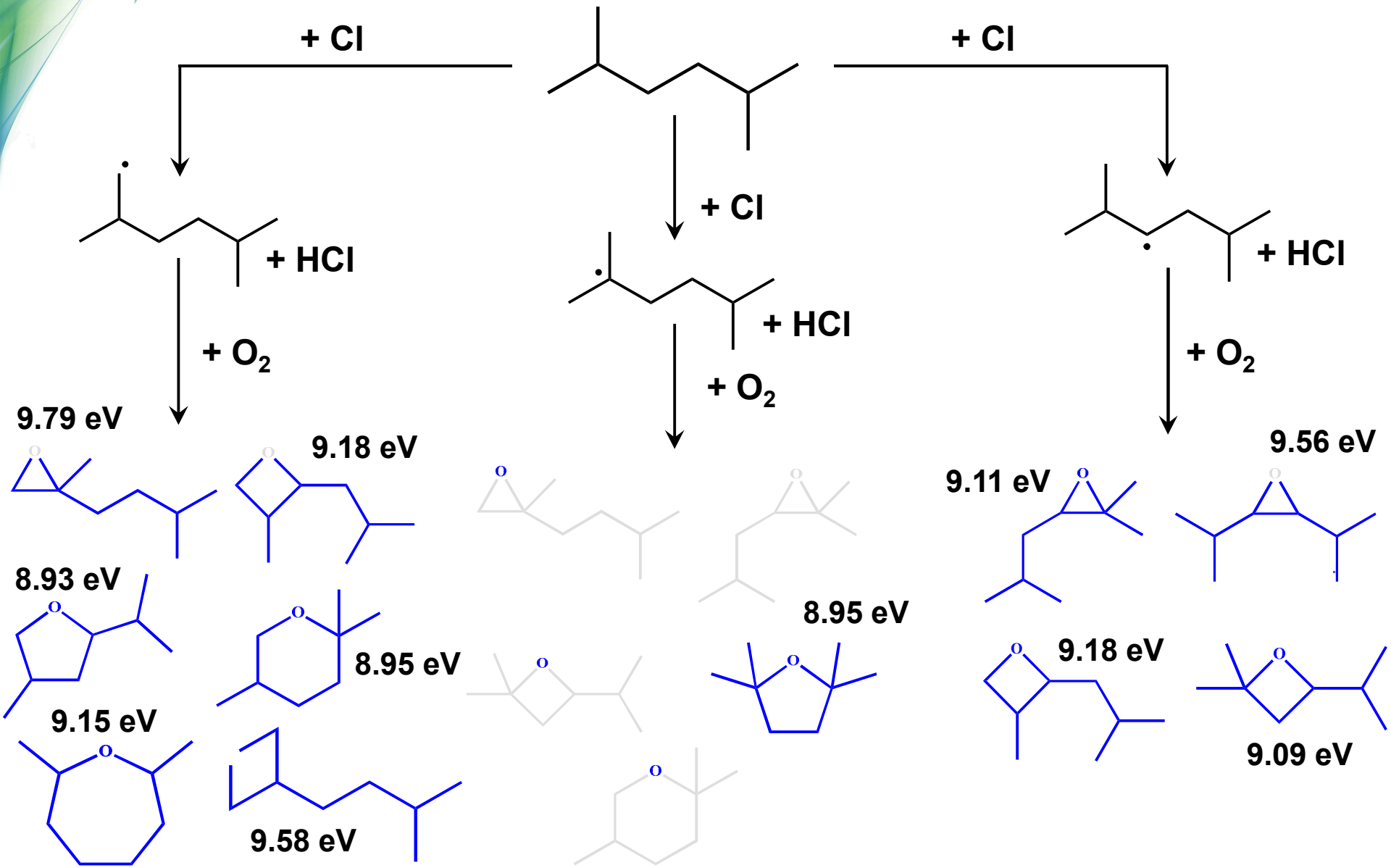

trans-2-butene
cis-2-butene
trans-2-butene (Scaled)
cis-2-butene (Scaled)
σ (Mb)
Photon Energy (eV)
0
2
4
6
9.0
9.1
9.2
9.3
9.4
9.5

HO_2-Elimination Co-Products of R + O_2

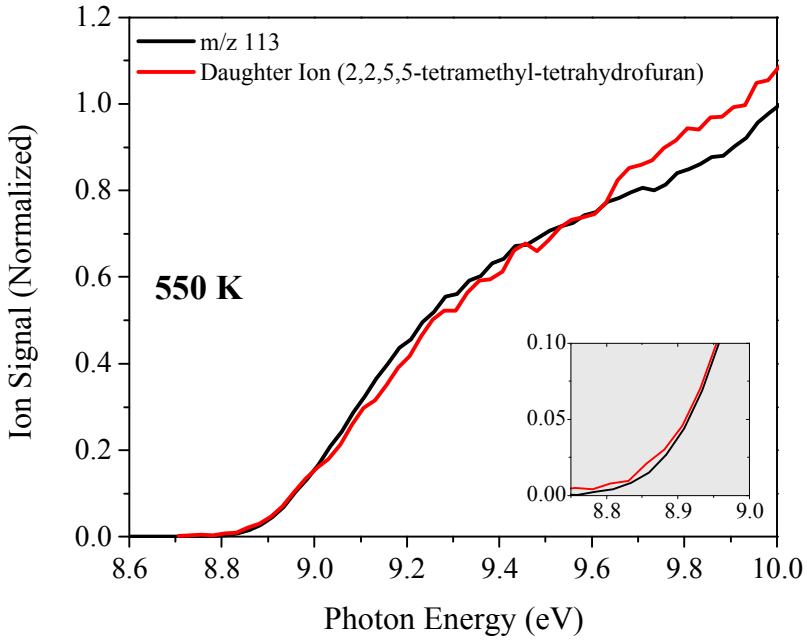


CBS-QB3-Calculated Adiabatic Ionization Energies

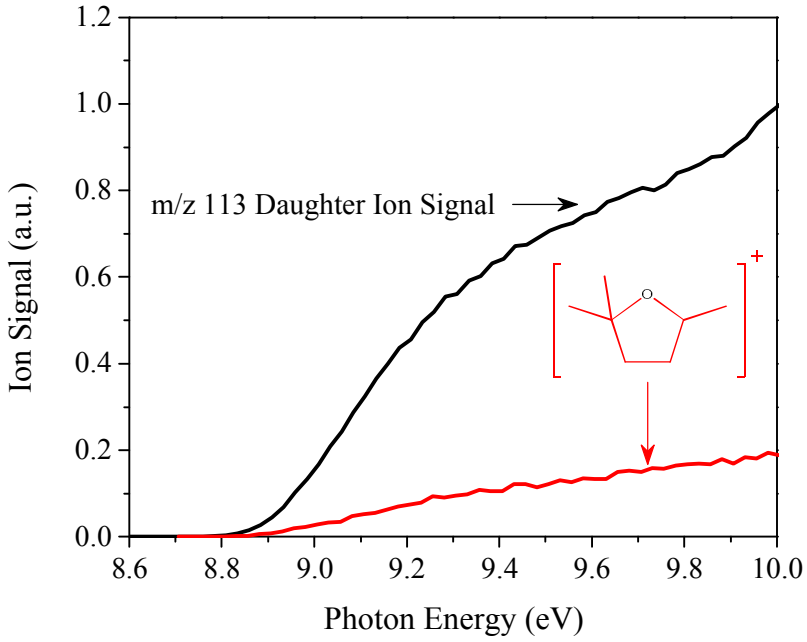
OH-Loss Co-Products from QOOH Species



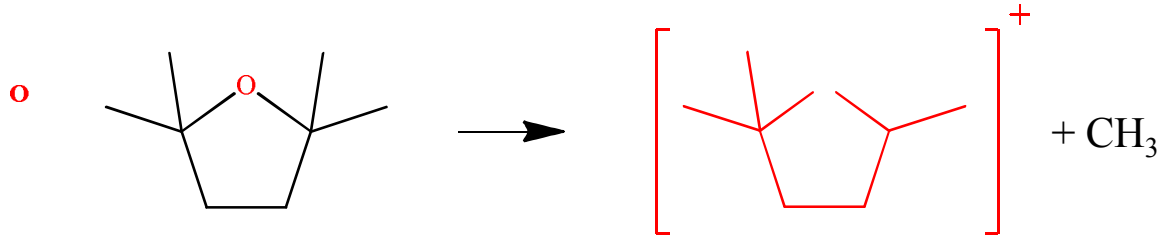
Daughter Ion Measurements Support Quantification of Upper Limit to 2,2,5,5-tetramethyl-THF



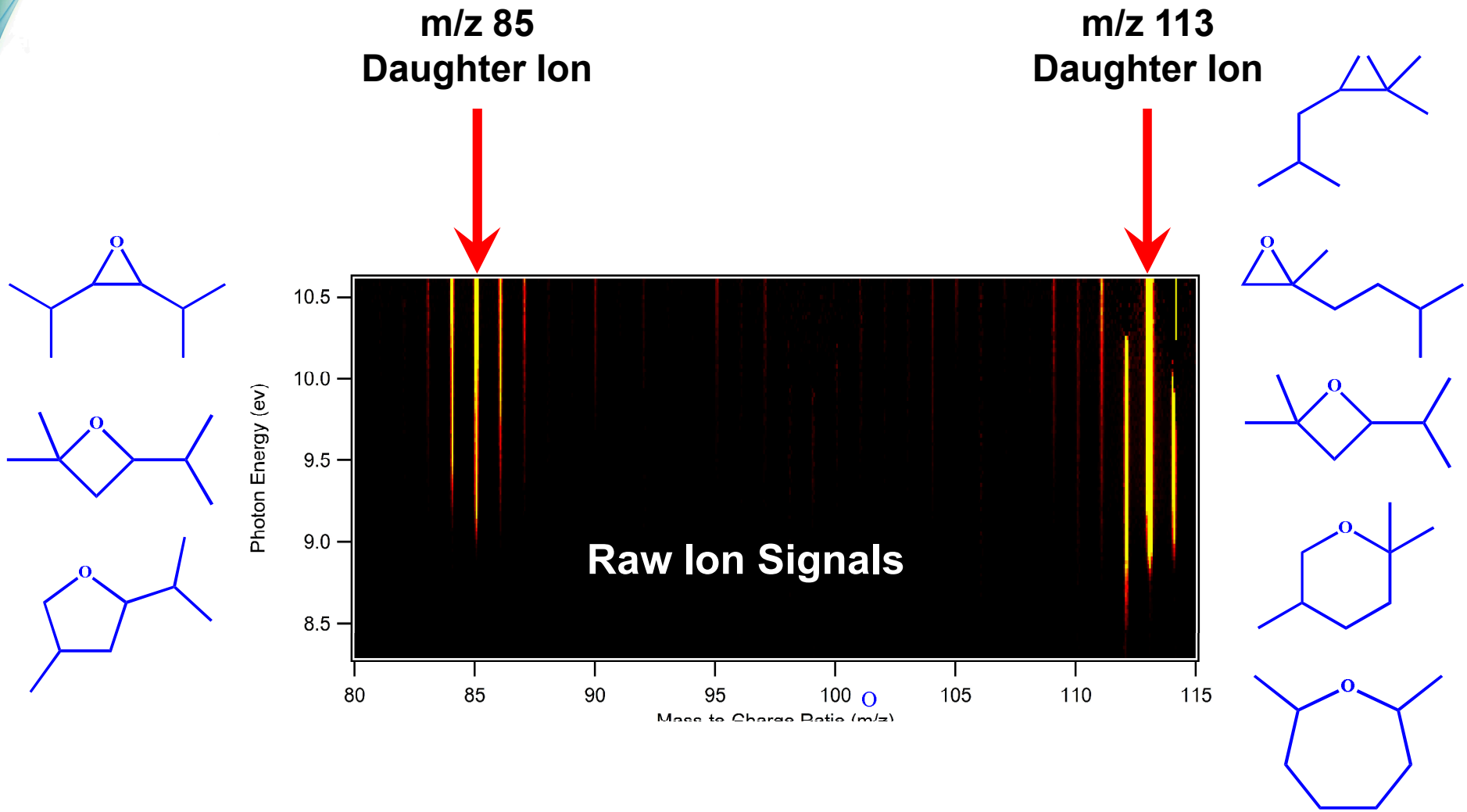
Normalized m/z 113 daughter ion signals



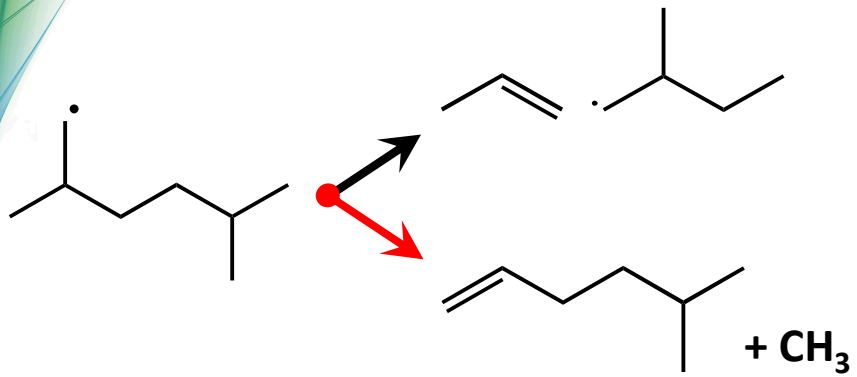
Scaled m/z 113 daughter ion signals

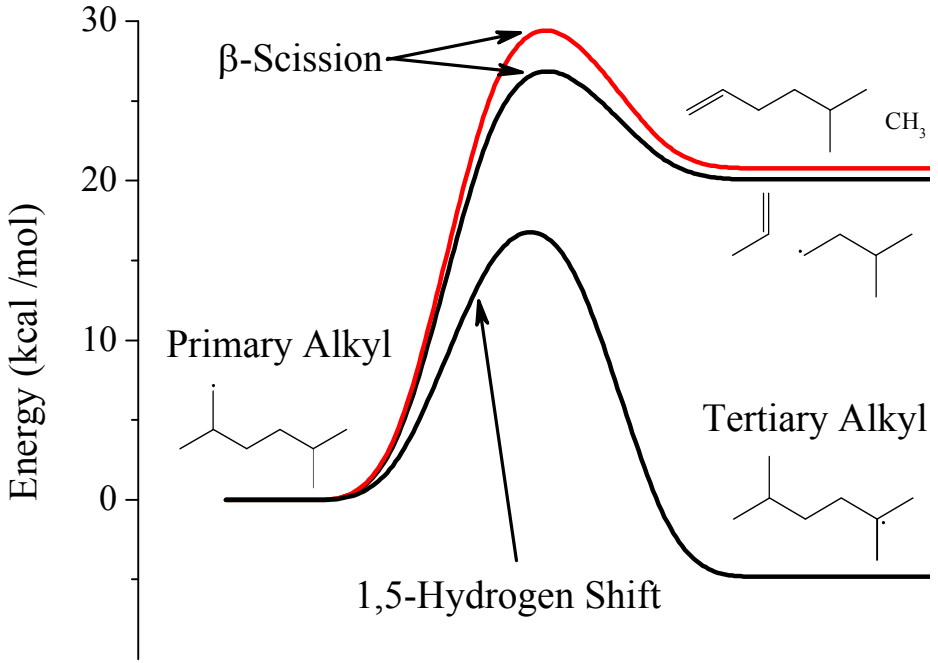


Daughter Ion Signals Indicate Potential for Other Cyclic Ethers Formed by QOOH Decomposition



Role of Primary Alkyl Radicals in Forming 2,2,5,5-tetramethyl-THF





OH-, HO_2-Loss Channels of Methylcyclohexane