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Influence of Temperature and Resonance-Stabilization on the *ortho*- Effect in Cymene Oxidation

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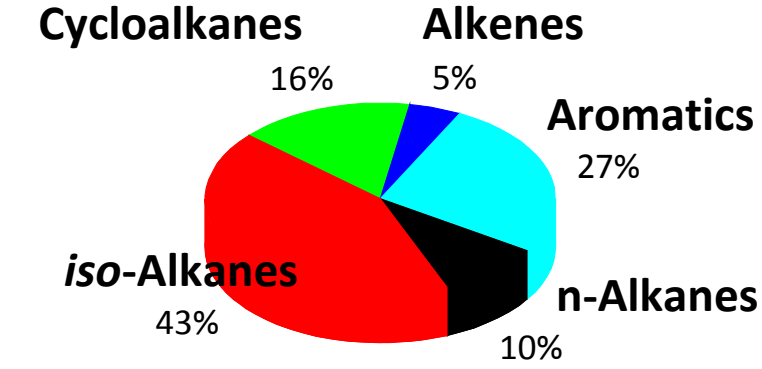
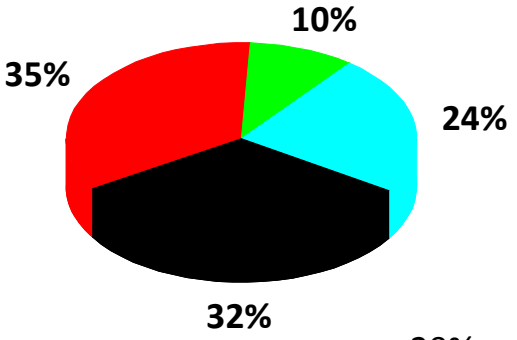
Conventional Transportation Fuels Contain Different Distributions of Hydrocarbon Classes, Species

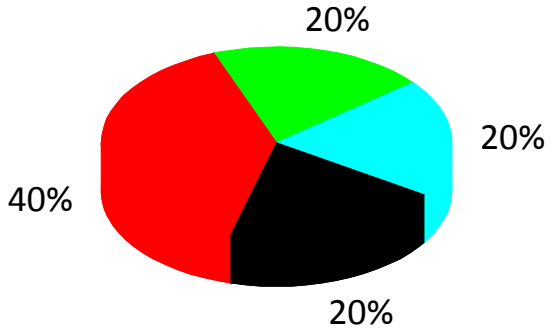
Gasoline
- High octane number
- Short-chain alkanes
- Highly branched species
- Aromatics



Diesel
- High cetane number
- Long-chain alkanes
- Limited branched species
- Aromatics



Jet Fuel
- Long-chain alkanes
- Limited branched species
- Aromatics



"Ideal" Biofuels Share Similar Fuel Properties with Conventional Hydrocarbons

Gasoline
- High octane number
- Short-chain alkanes
- Highly branched species
- Aromatics

Diesel
- High cetane number
- Long-chain alkanes
- Limited branched species
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Jet Fuel
- Long-chain alkanes
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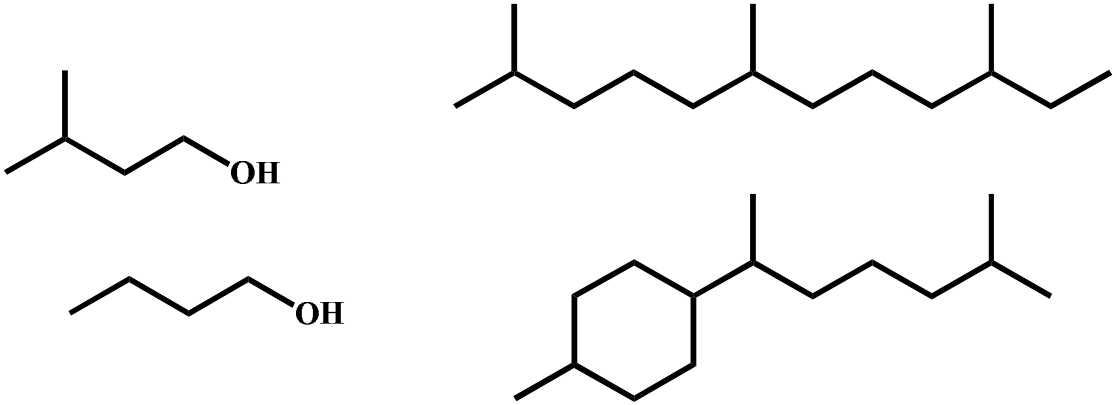
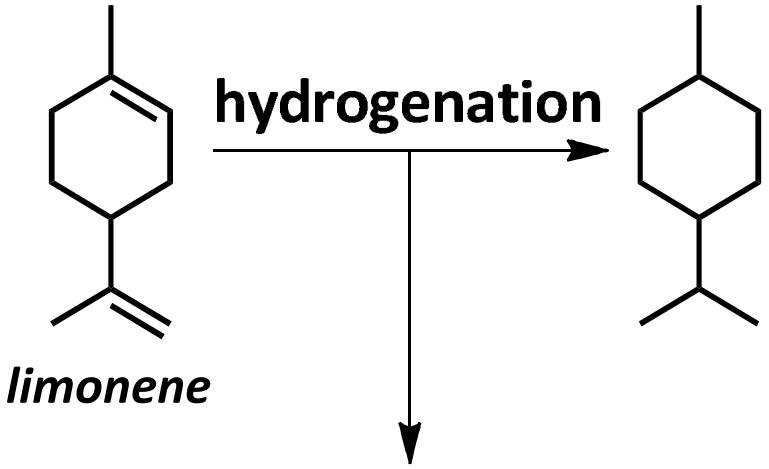
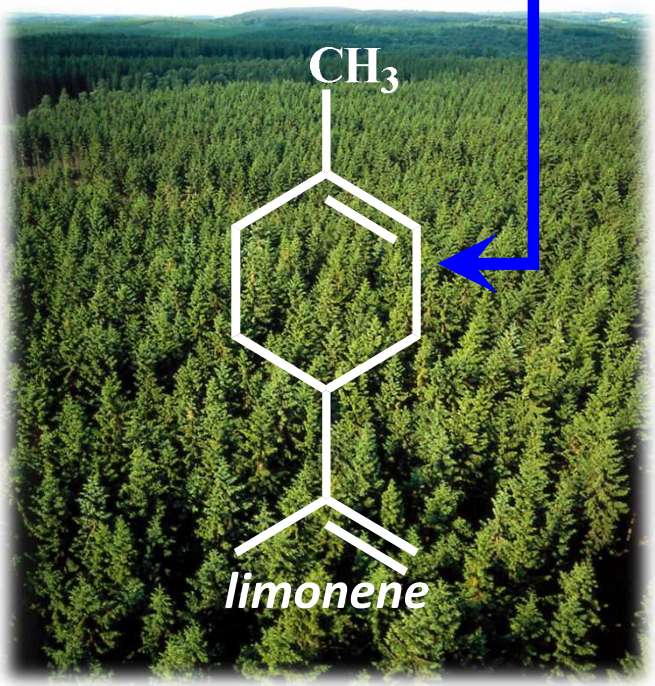


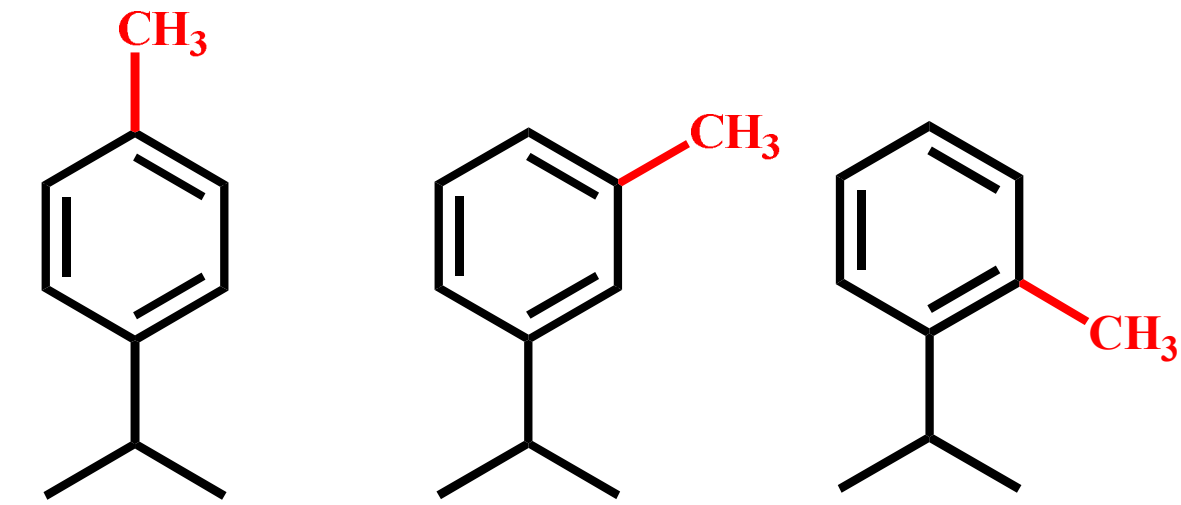


Peralta-Yahya et al., *Nature*, 488, 2012.

Aromatic Biofuel: Cymene (*iso*-propyltoluene)

Biofuel precursor





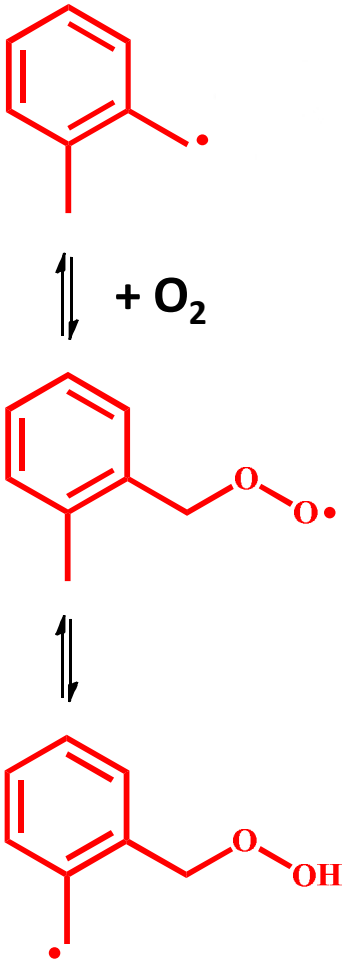
p-cymene *m*-cymene *o*-cymene

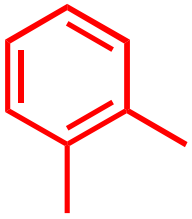
Byproducts of limonene hydrogenation

jbei Joint BioEnergy Institute

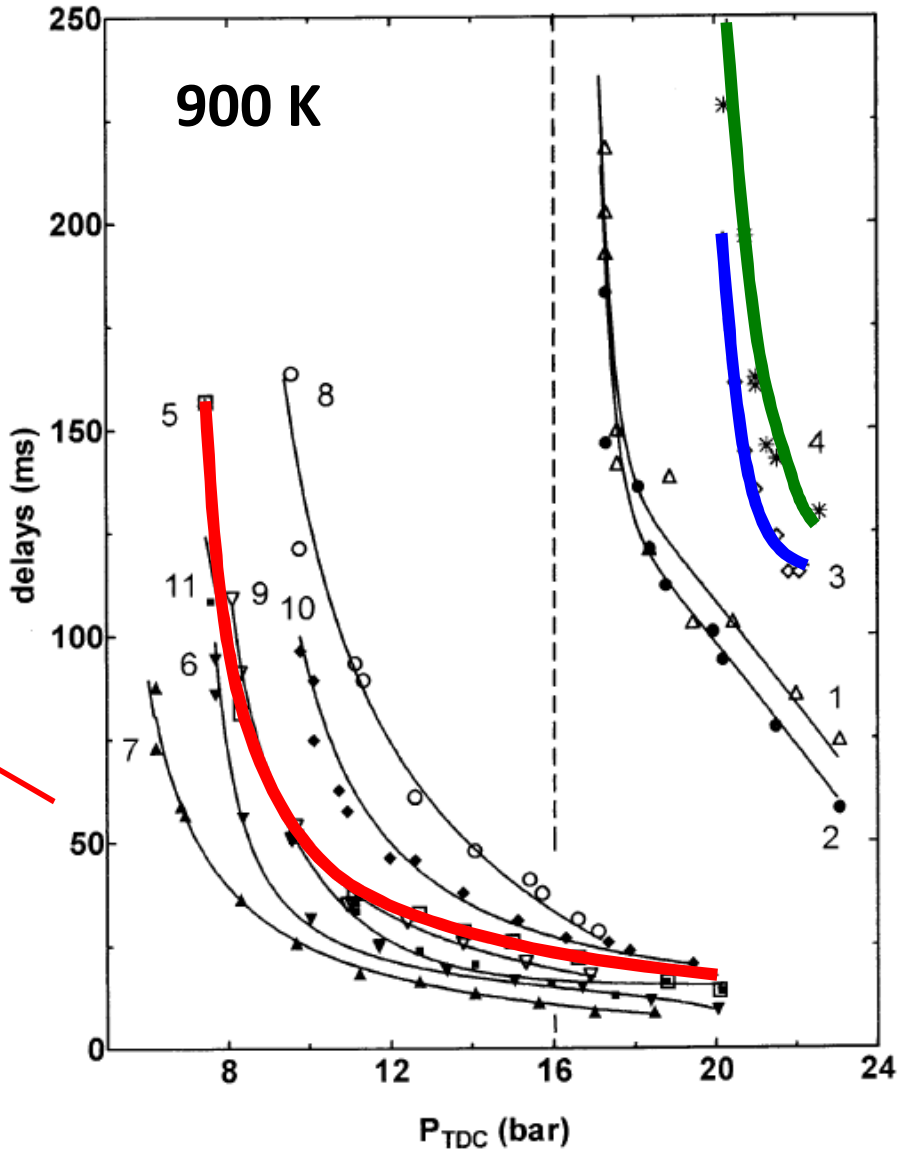
ortho-Effect Implications on Autoignition

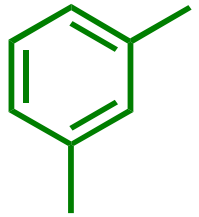
Minetti et al.
Comb. Flame, 121 (2000)



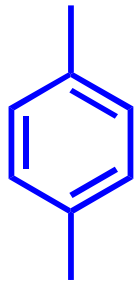


ortho-





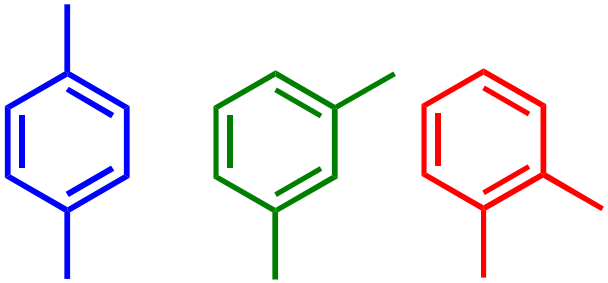
meta-



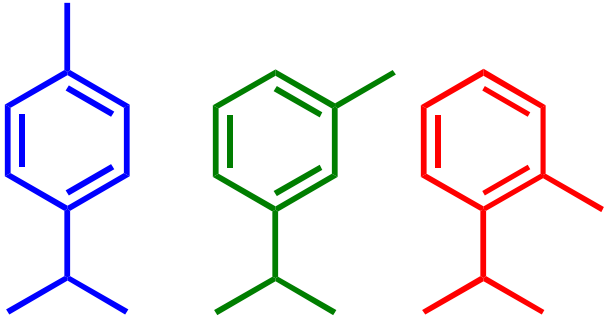
para-

Resonance Structures and Implications on the *ortho*- Effect

Xylene Isomers

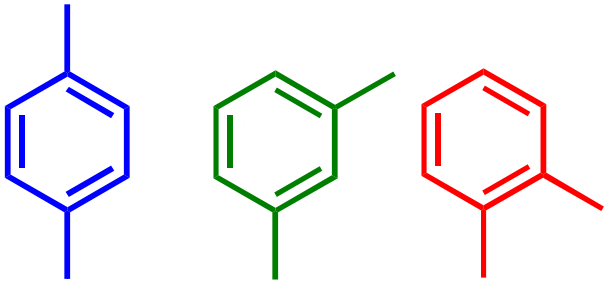


Cymene Isomers

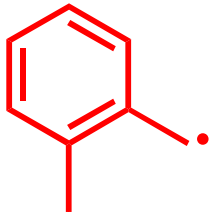


Resonance Structures and Implications on the *ortho*- Effect

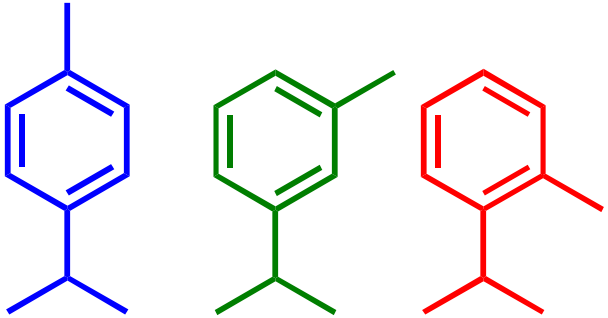
ortho-Xylene isomers



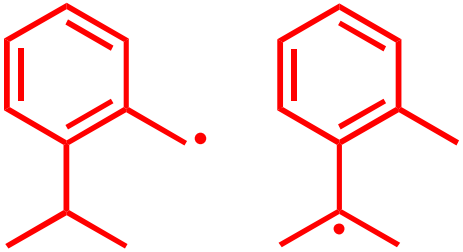
Resonance-Stabilized R



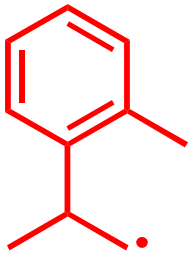
ortho-Cymene isomers



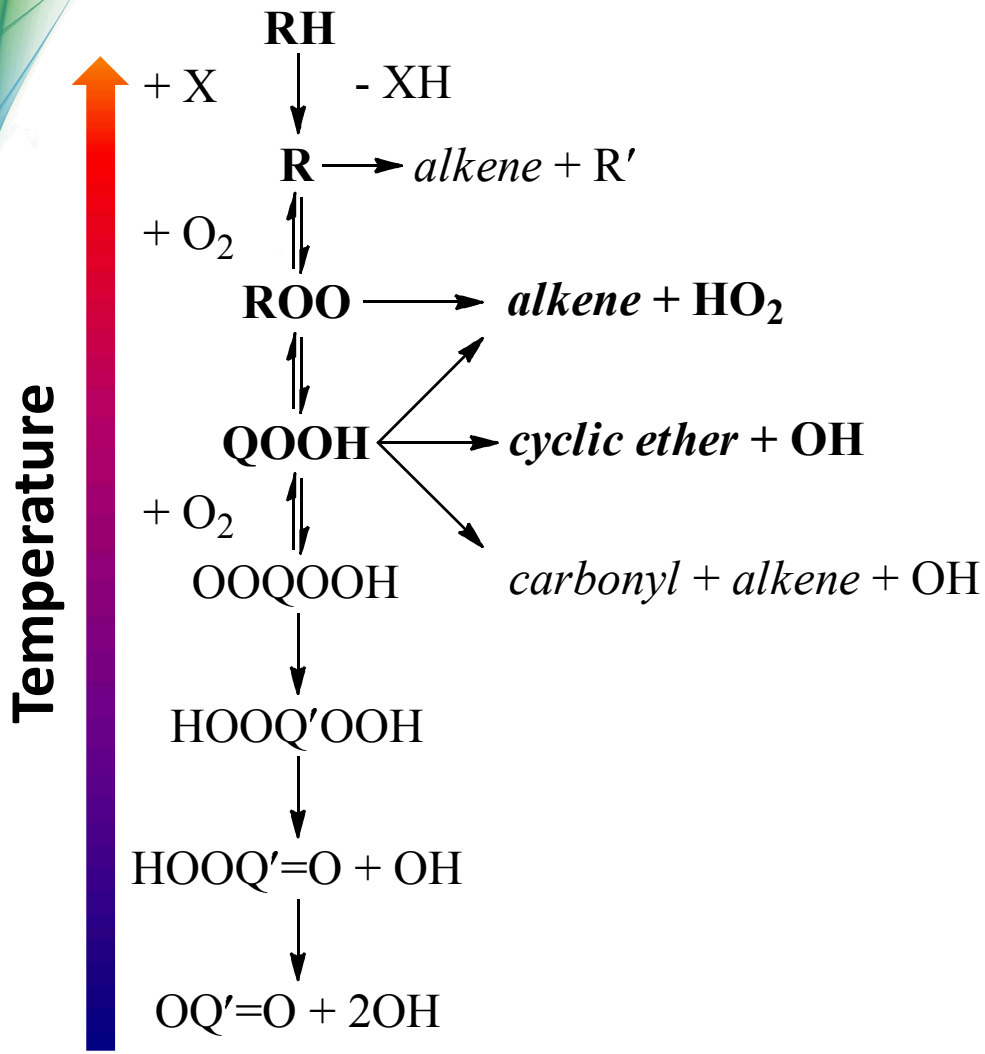
Resonance-Stabilized R

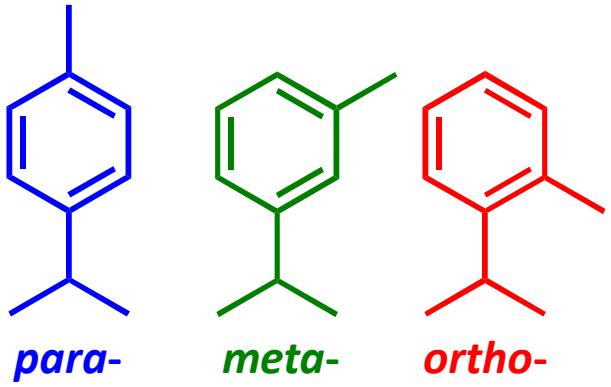


Non-Resonance-Stabilized R

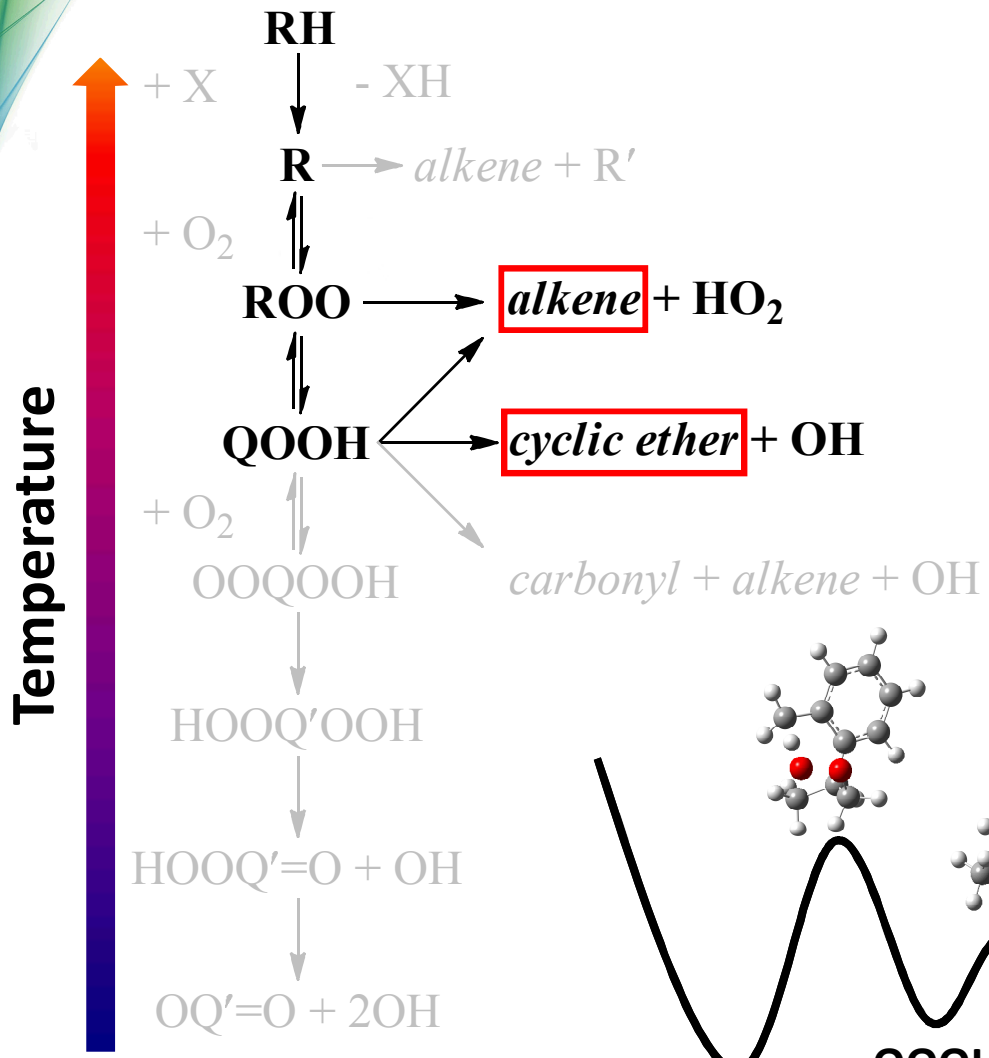


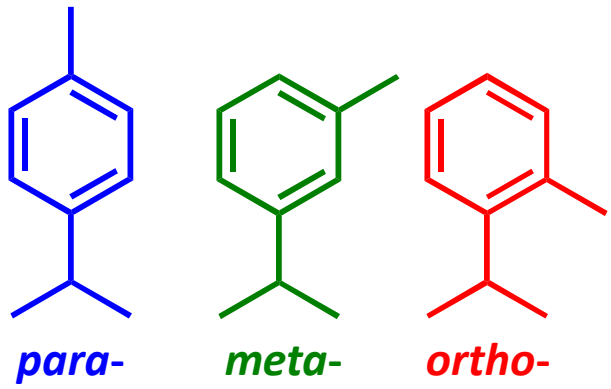
Experimental/Computational Approach

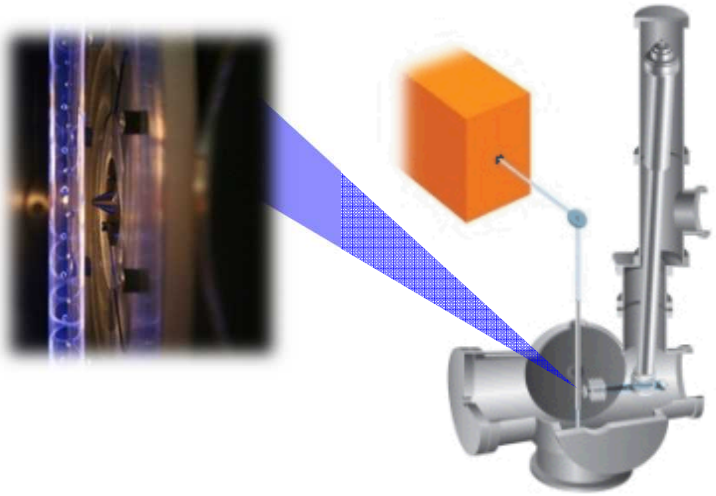


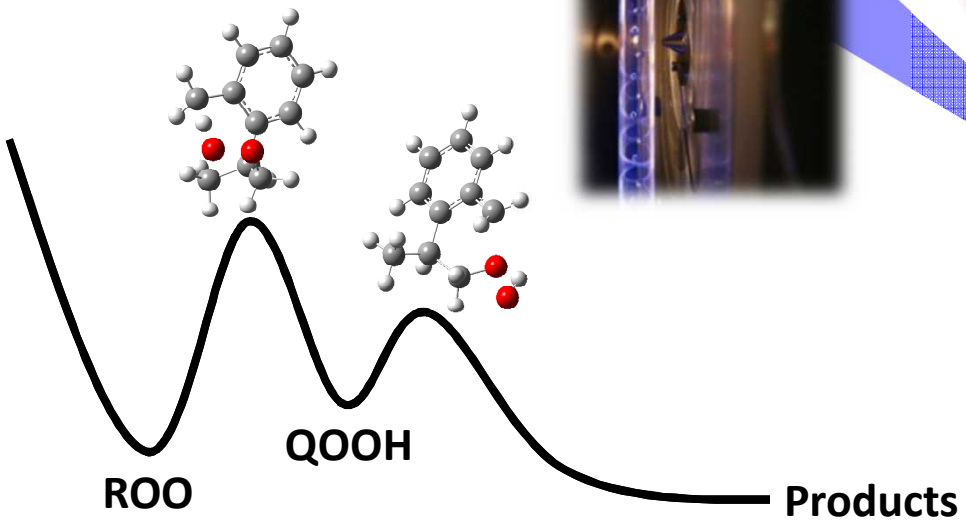


Experimental/Computational Approach

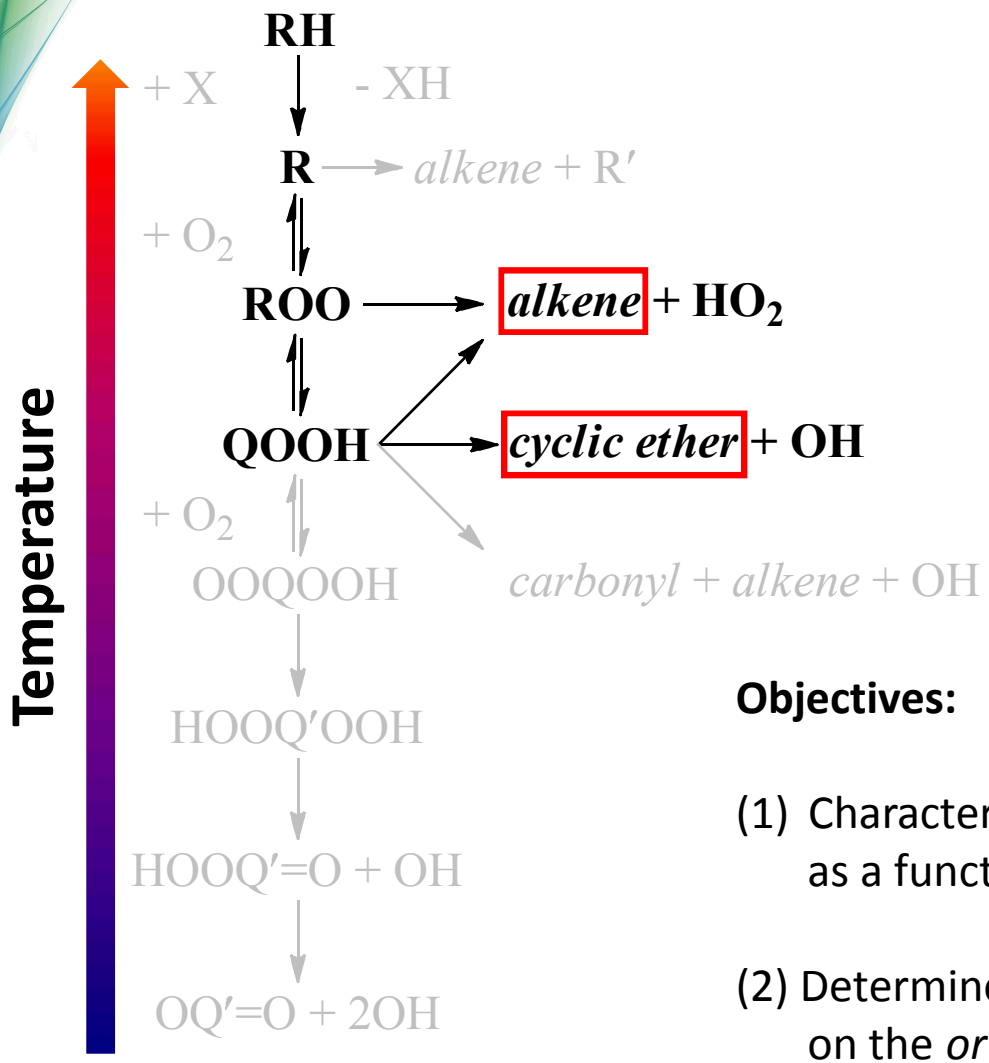


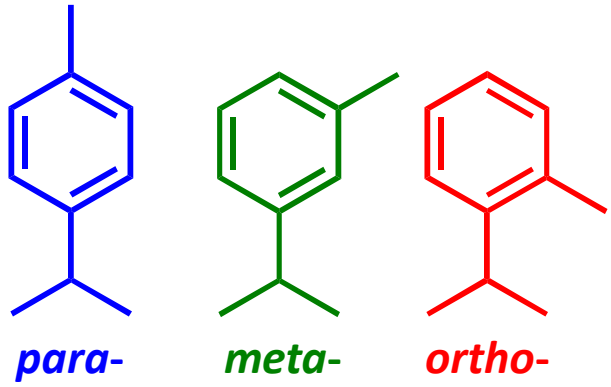






Experimental/Computational Approach





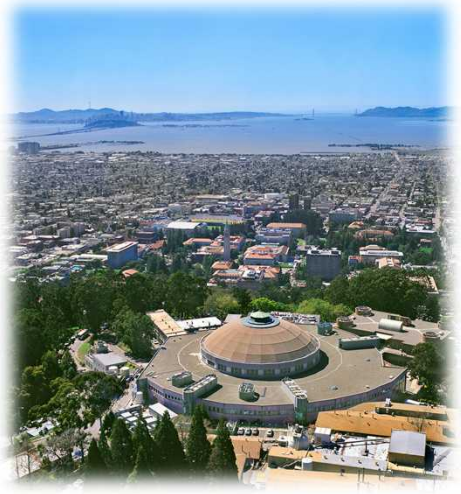
Objectives:

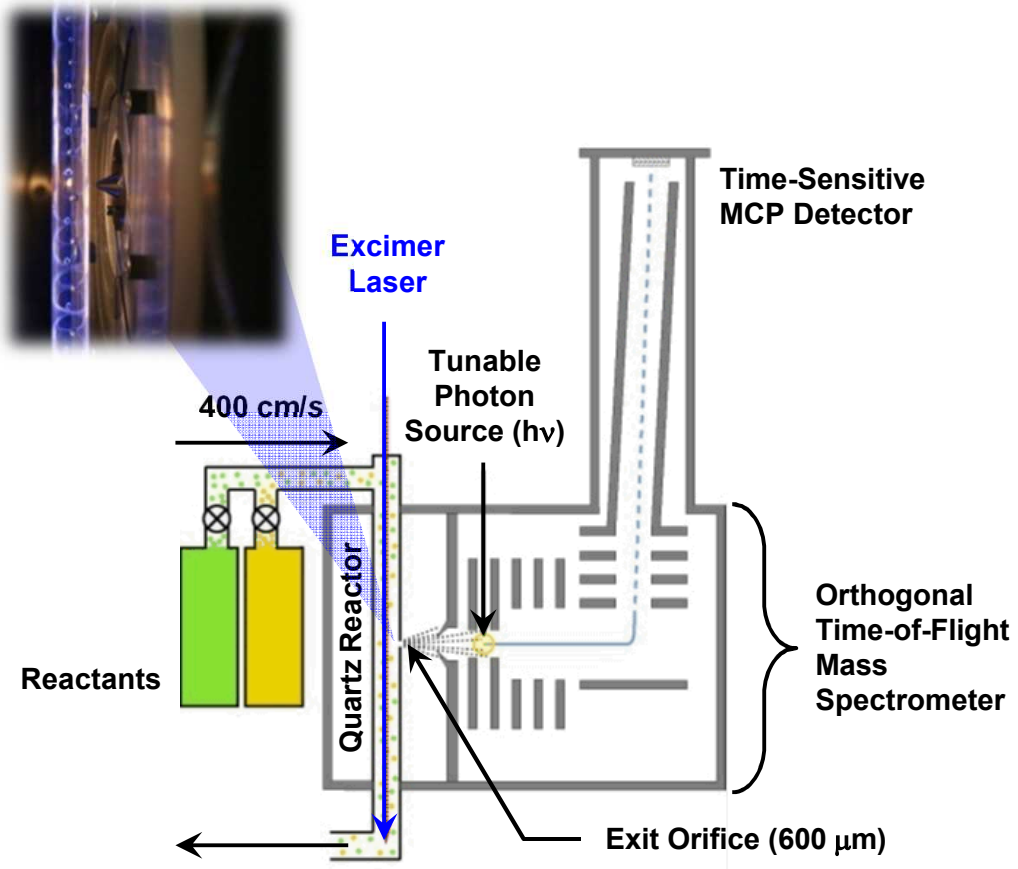
(1) Characterize the *ortho*- effect in cymene oxidation as a function of temperature

(2) Determine influence from resonance of initial R radical on the *ortho*- effect in cymene oxidation

Experimental and Computational Approach

Experimental Approach – Studying R + O_2 Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)





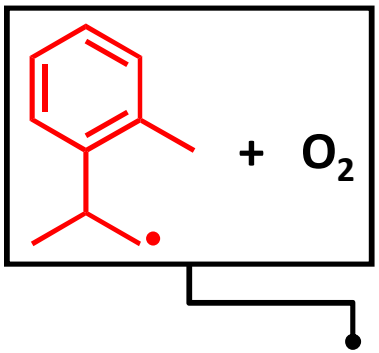
Multiplexed Photoionization Mass Spectrometer

Osborn et al., *Rev. Sci. Inst.* (2008)

Experimental Approach – Studying R + O_2 Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)

+ He

Photolysis



+ O_2 + Cl_2 + He

System of Interest (R + O_2)

Multiplexed Photoionization Mass Spectrometer

Osborn et al., *Rev. Sci. Inst.* (2008)

Experimental Approach – Studying R + O_2 Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)

450 – 700 K
8 Torr

Multiplexed Photoionization Mass Spectrometer

Number Densities (molecules/cm^3):

RH: $1.0\ 10^{13}$ O_2: $2.1\ 10^{16}$

Cl_2: $2.6\ 10^{13}$ He: $1.2\ 10^{17}$

Initial Conditions:

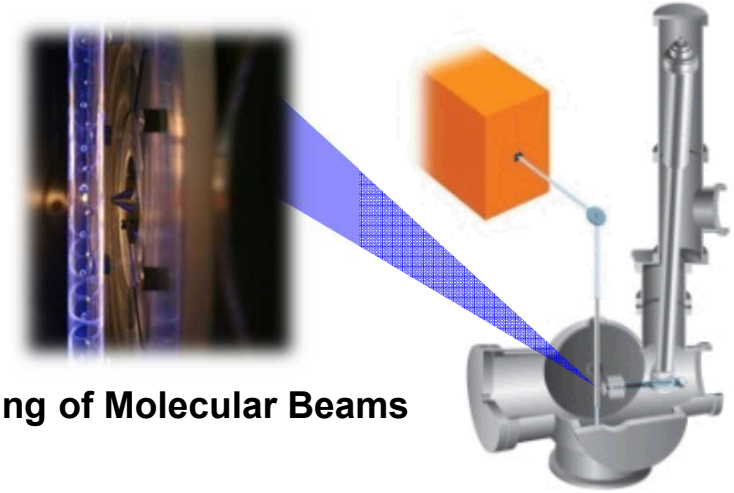
O_2/RH ~ 2000

O_2/Cl_2 ~ 1000

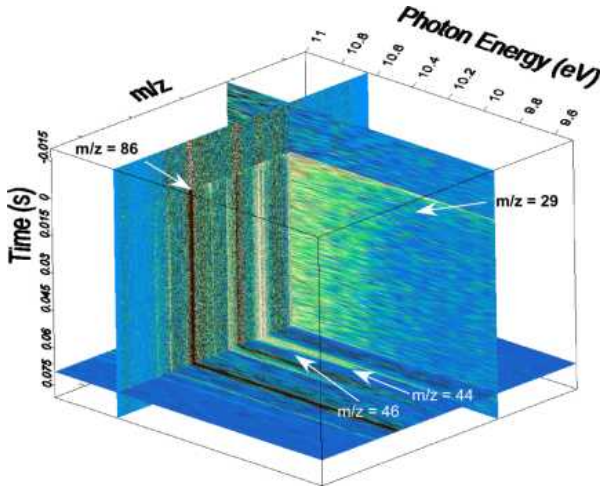
RH/Cl ~ 26

Osborn et al., *Rev. Sci. Inst.* (2008)

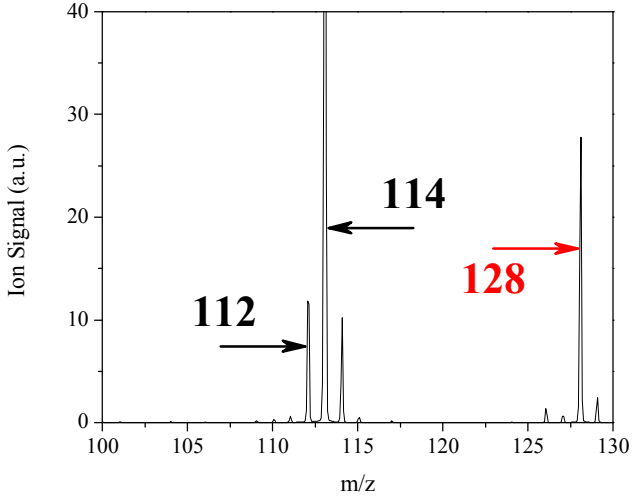
Experimental Approach – Studying R + O_2 Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)



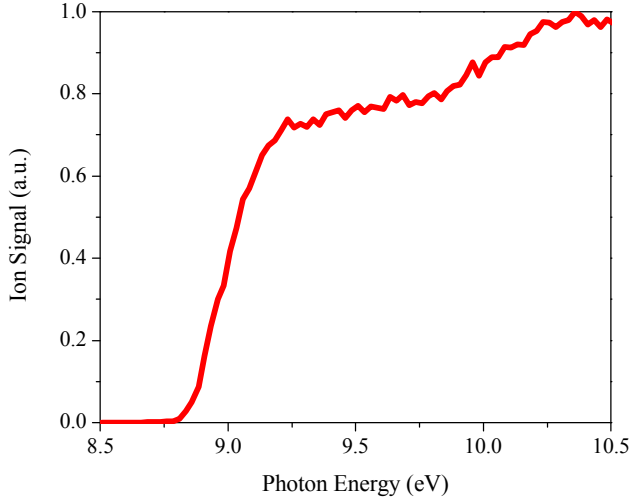
Probing of Molecular Beams



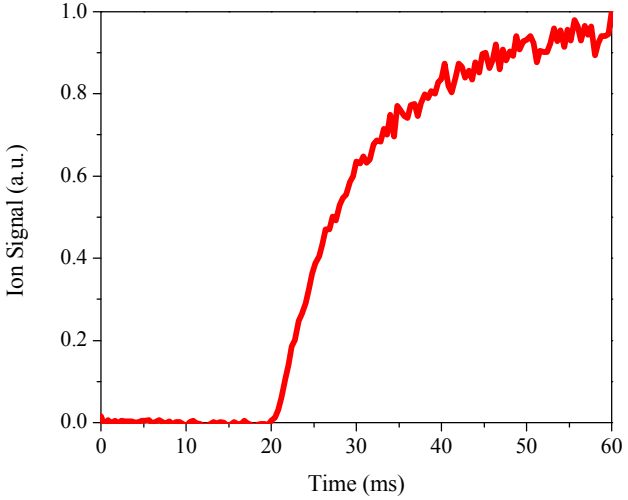
High-Resolution Mass Spectra



Isomer-Resolved Species Identification



Time-Dependent Chemical Kinetics



Organization of Results

(1) Comparison of mass spectra (*p*-, *m*-, *o*-cymene)

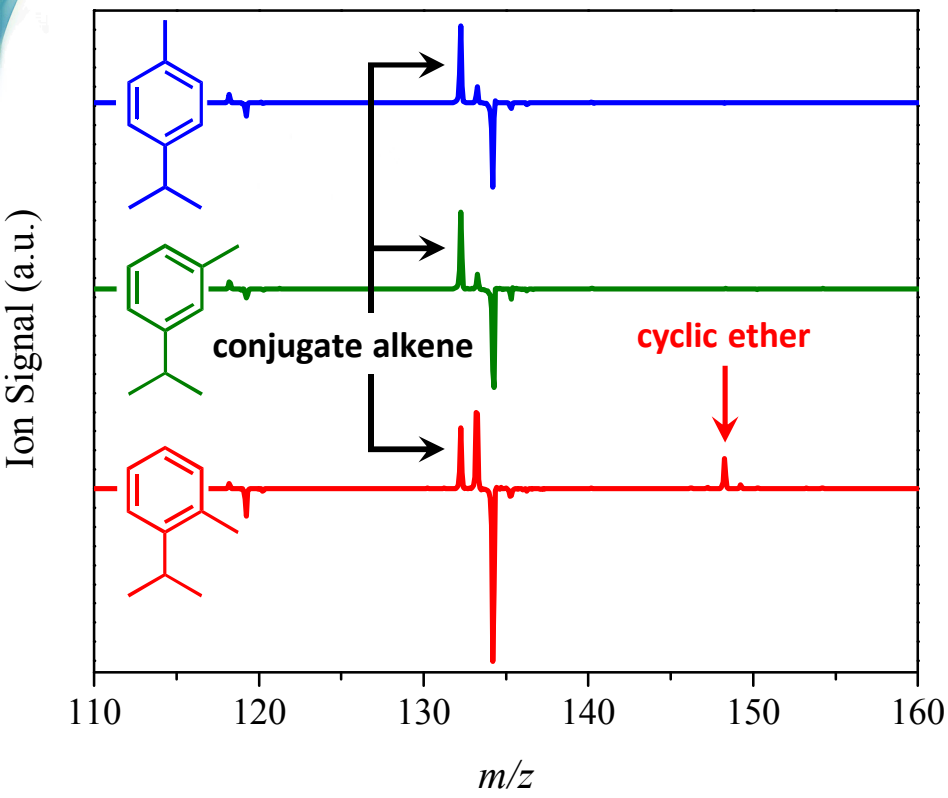
(2) Temperature-dependence of *ortho*- effect in cymene oxidation

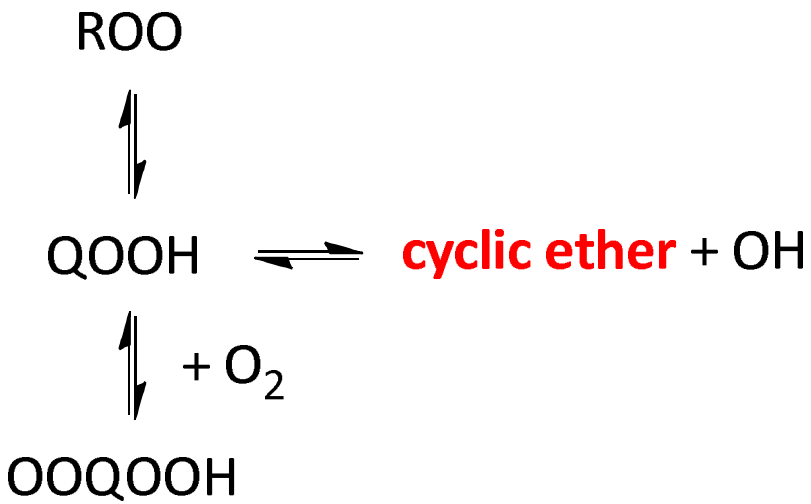
(3) Comparisons of PIE spectra (*o*-cymene)

(4) PES calculations (CBS-QB3): *o*-cymenyl + O_2

Results – *ortho*- Effect in Cymene Oxidation

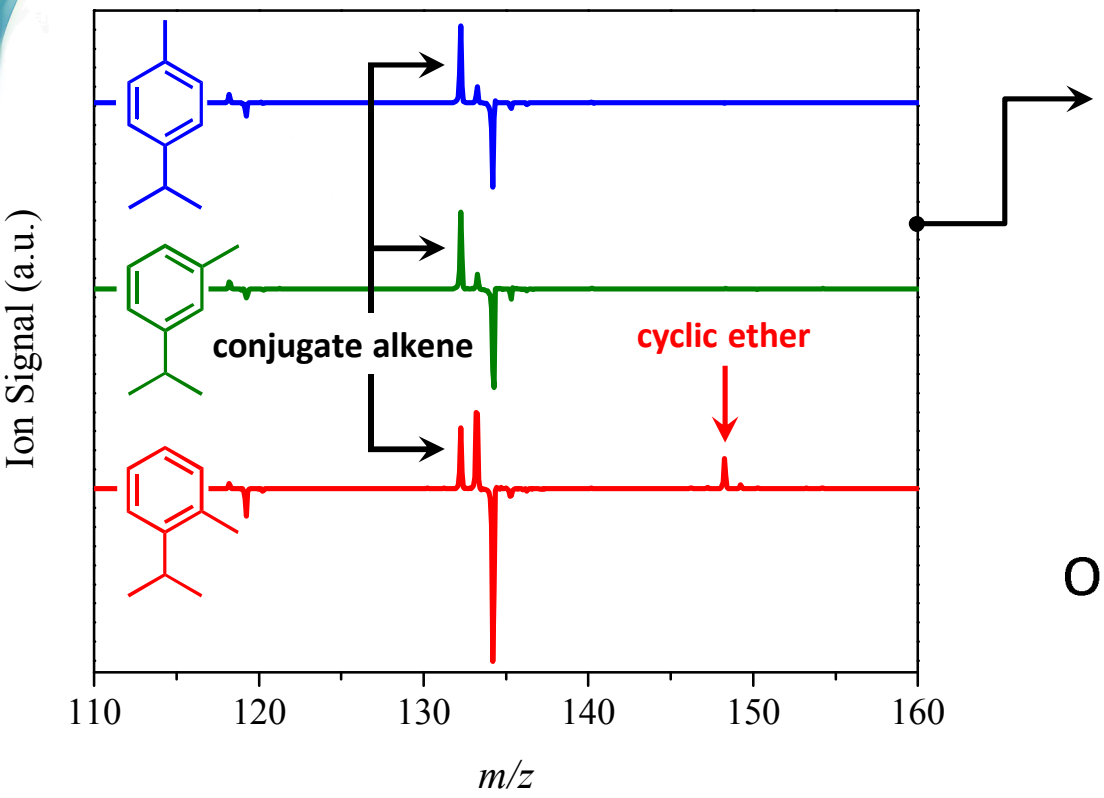
Results – Cyclic Ether Formation from Cymene *ortho*- Effect

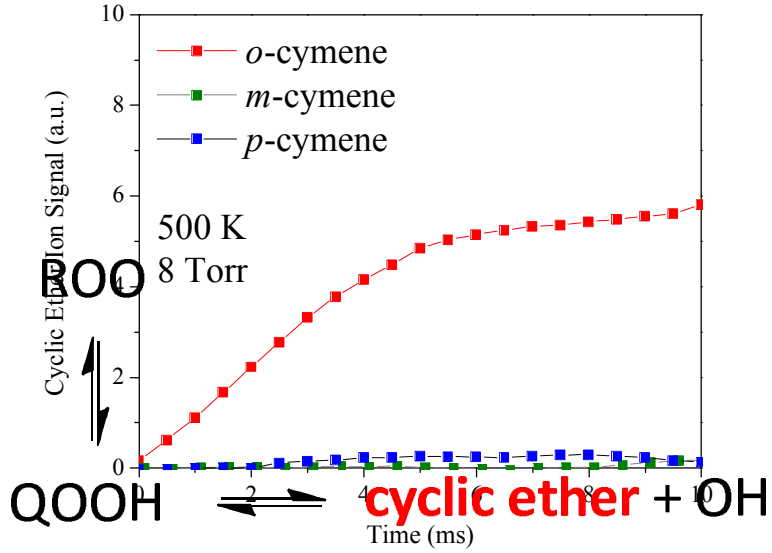


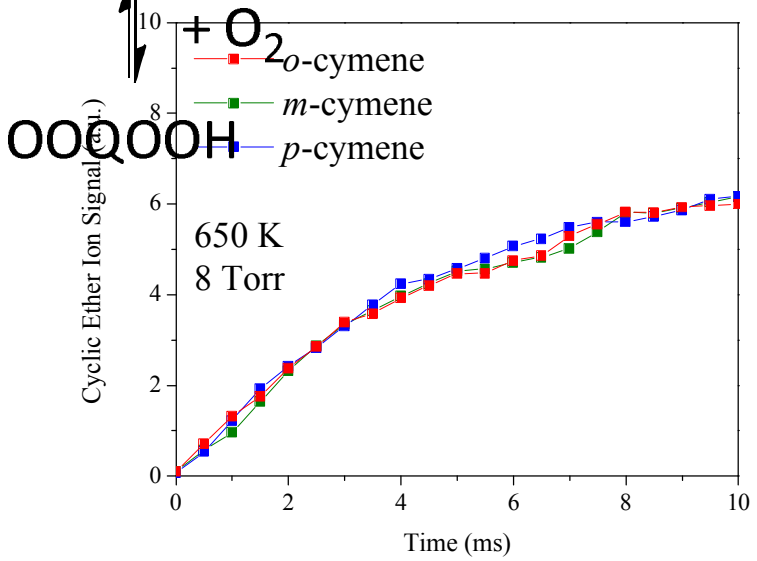


Mass Spectra from Cl-Initiated Oxidation of *p*-, *m*-, *o*-cymene; 500 K, 8 Torr

Results – Cyclic Ether Formation from Cymene *ortho*- Effect

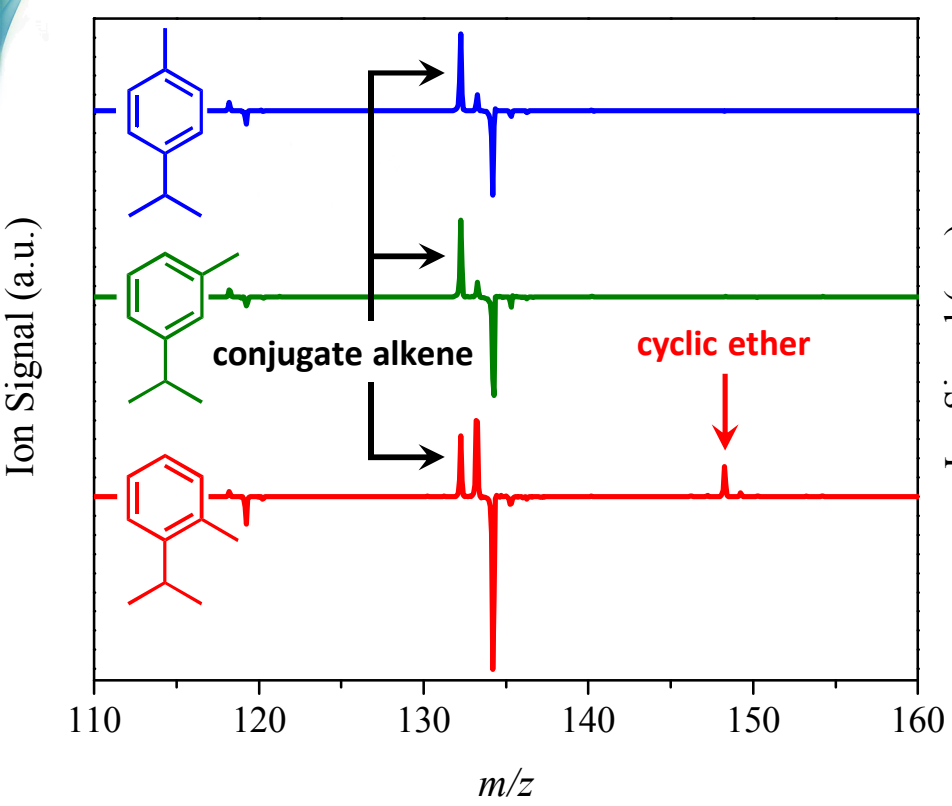


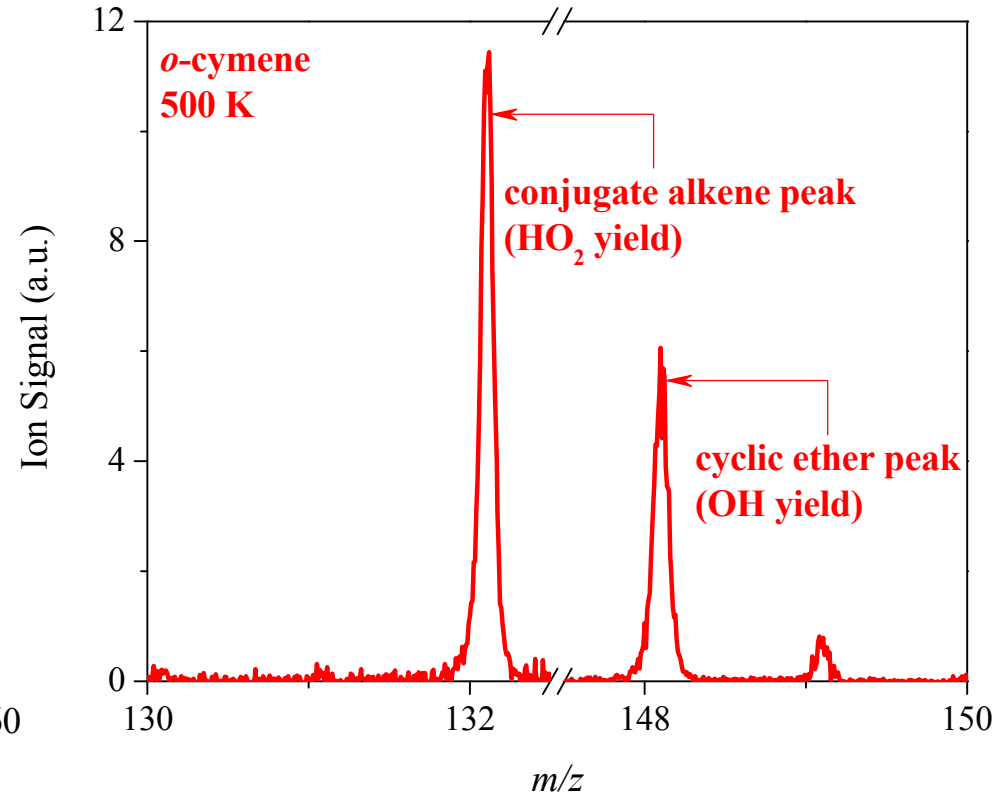




Mass Spectra from Cl-Initiated Oxidation of *p*-, *m*-, *o*-cymene; 500 K, 8 Torr

Results – Cyclic Ether Formation from Cymene *ortho*- Effect

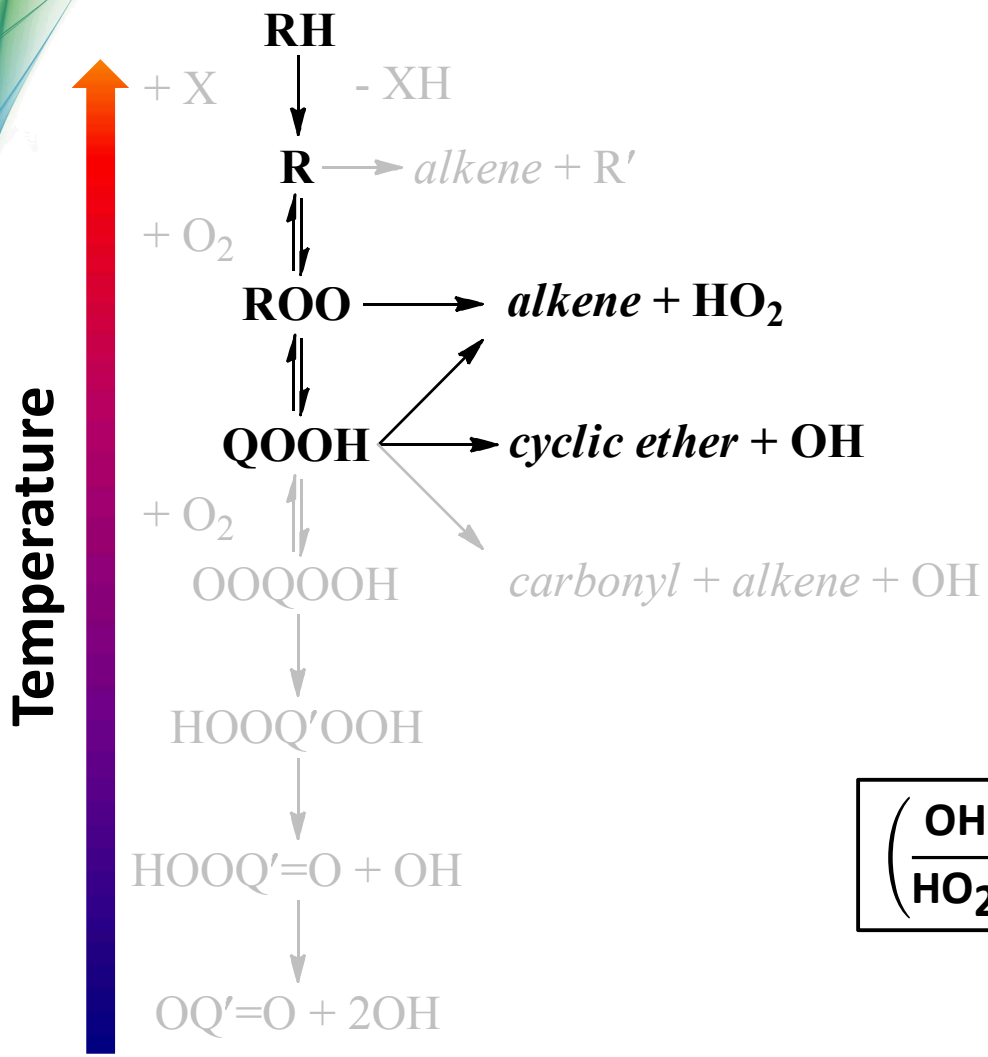




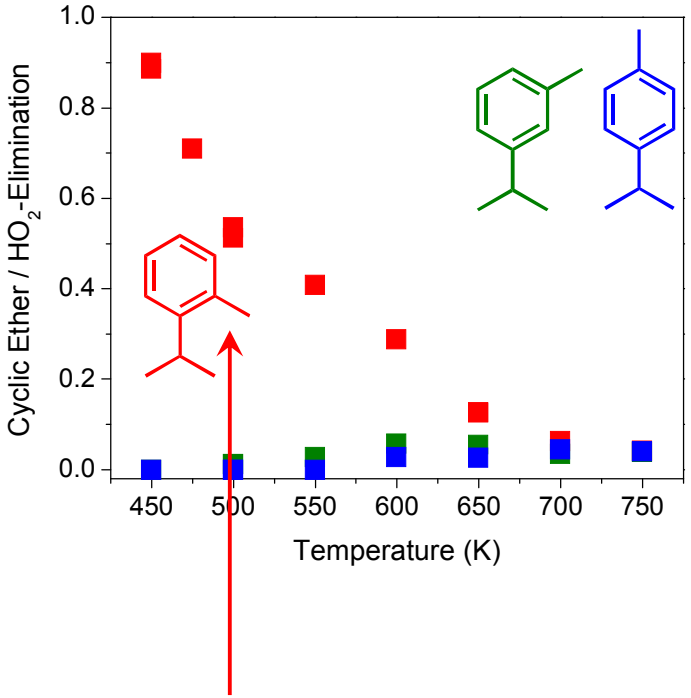
Mass Spectra from Cl-Initiated Oxidation of *p*-, *m*-, *o*-cymene; 500 K, 8 Torr

Results – Influence of Temperature on Cymene *ortho*- Effect

Results – Influence of Temperature on Cymene *ortho*- Effect

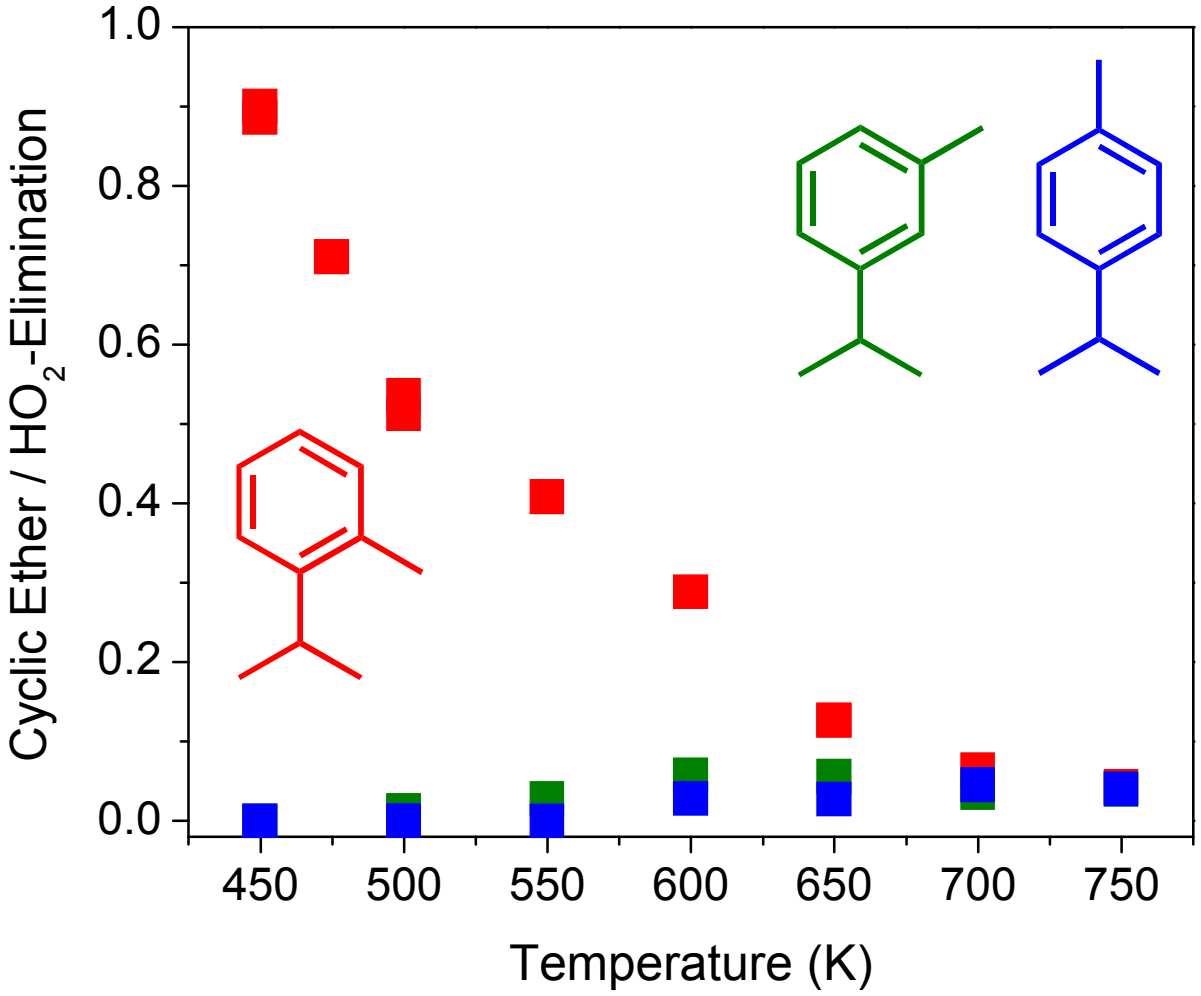


$\left(\frac{OH}{HO_2}\right)$ ratio



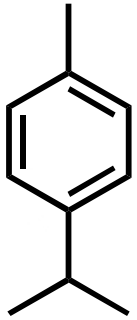
***ortho*- configuration of substituents enables chain-propagation over 200-K temperature range**

Results – Influence of Temperature on Cymene *ortho*- Effect

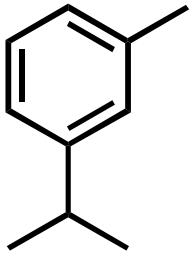


Results – Influence of Temperature on Cymene *ortho*- Effect

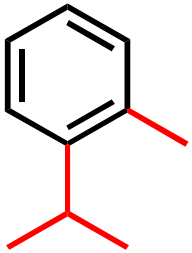
p-cymene

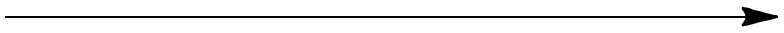


m-cymene

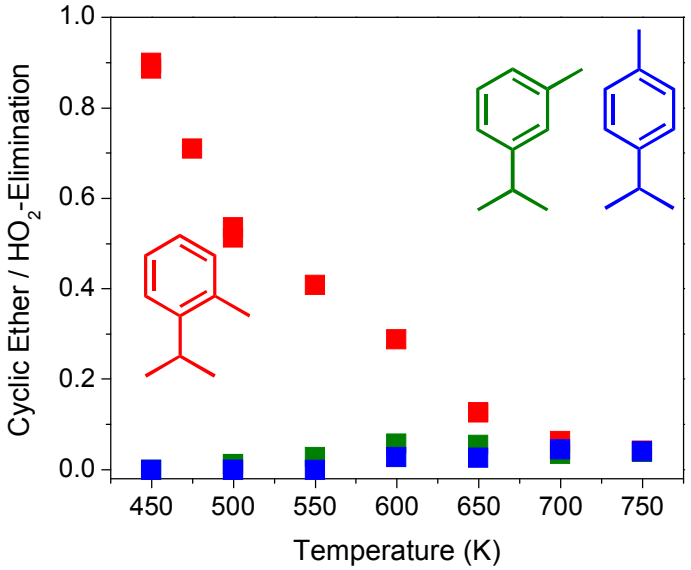


o-cymene



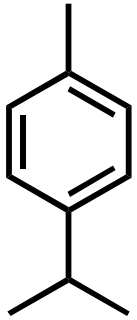


Temperature

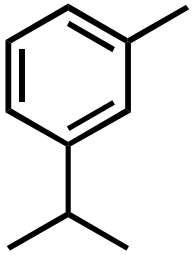


Results – Influence of Temperature on Cymene *ortho*- Effect

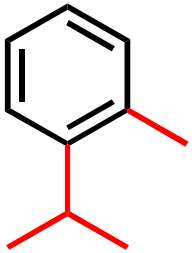
p-cymene

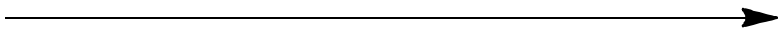


m-cymene

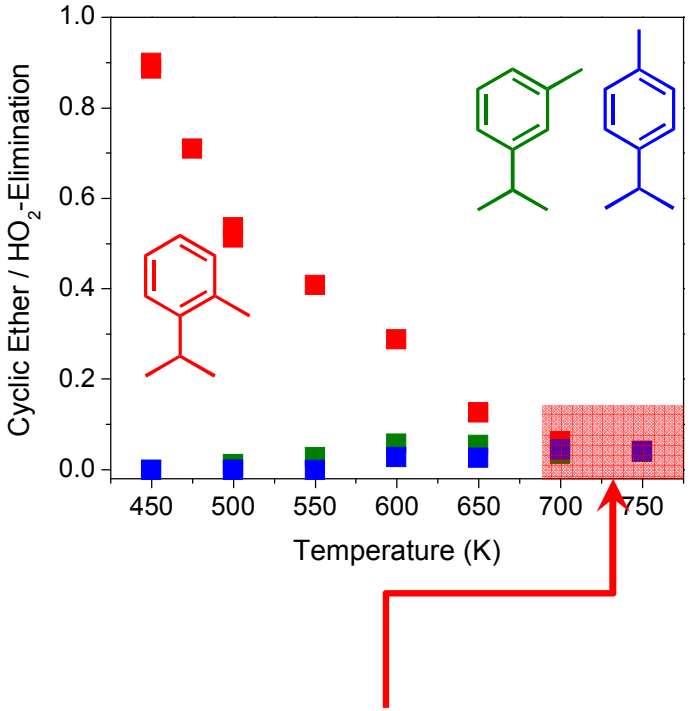


o-cymene





Temperature

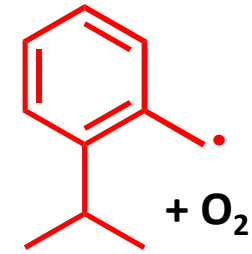


***ortho*- effect in cymenes diminishes above 700 K**

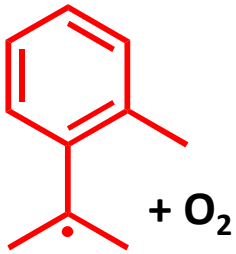
Results – R + O_2 Potential Energy Surfaces

Computational Approach

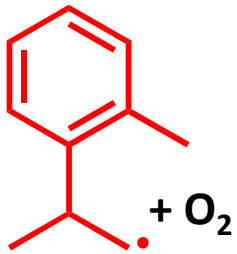
Calculations of saddle points on R + O_2 surfaces (CBS-QB3 level of theory)



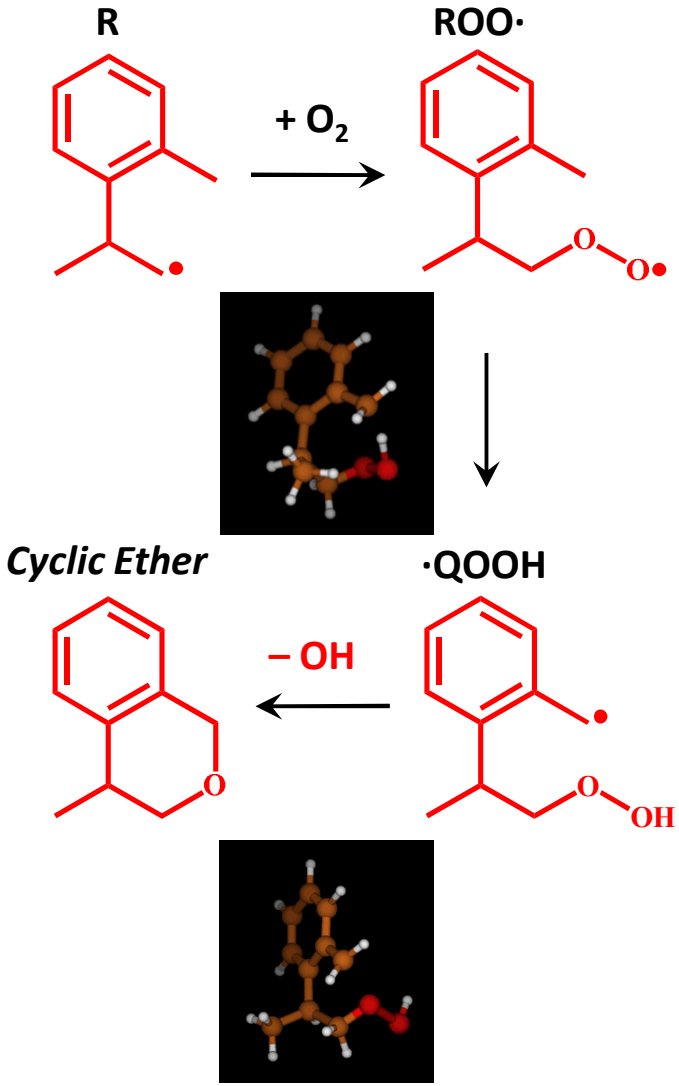
primary benzylic



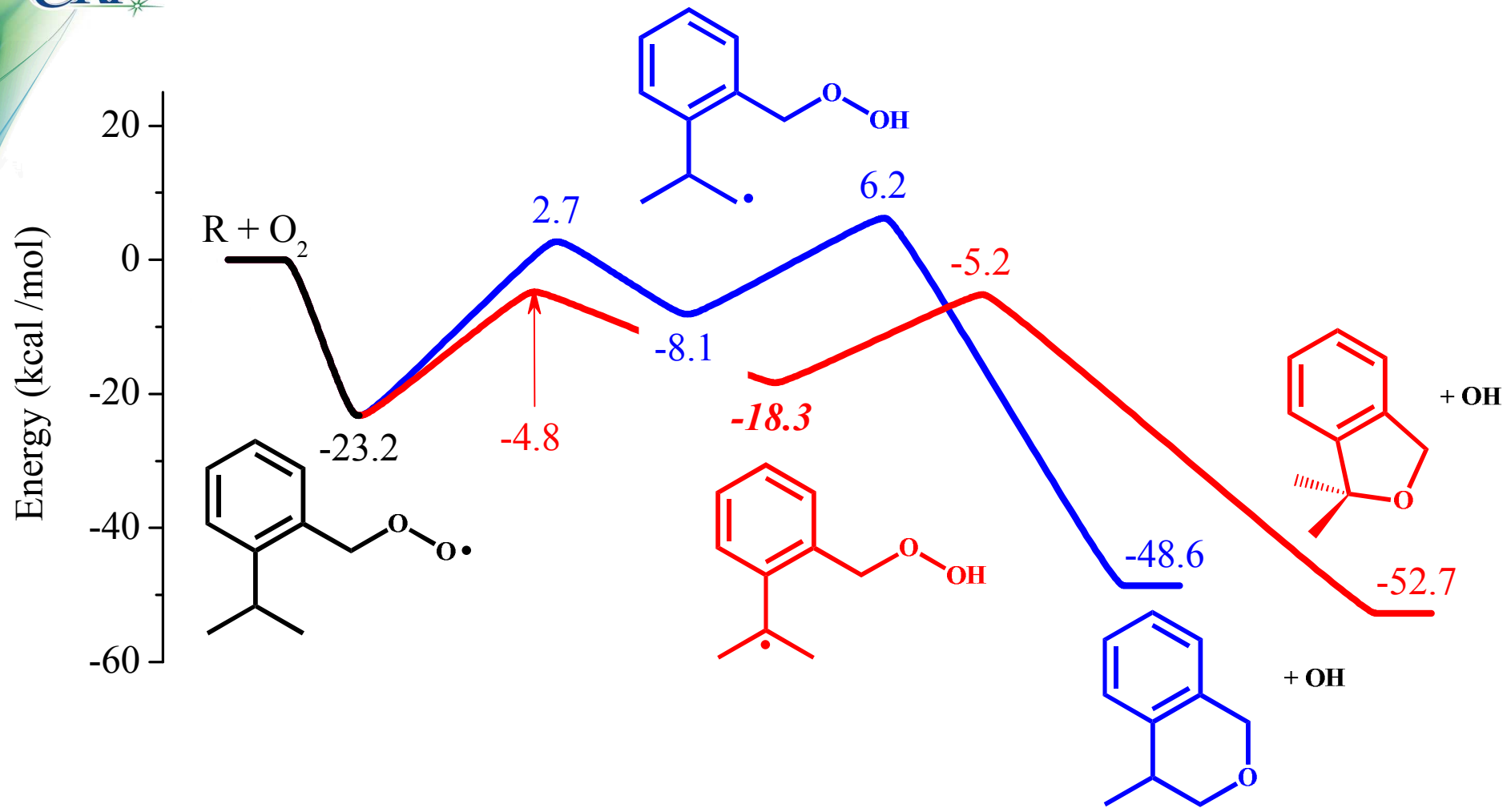
tertiary benzylic



primary alkyl

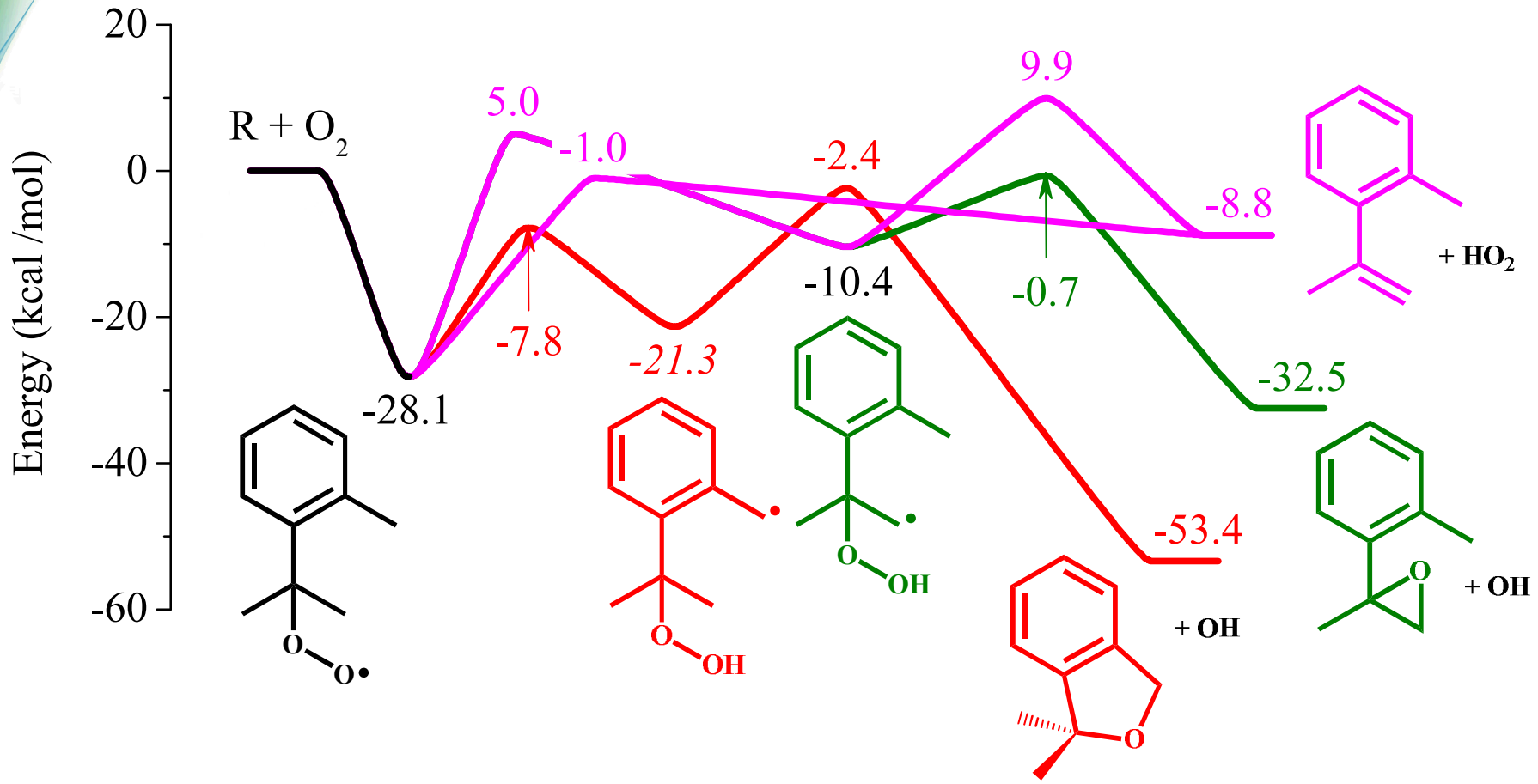


Potential Energy Surface – primary benzylic-cymenylperoxy



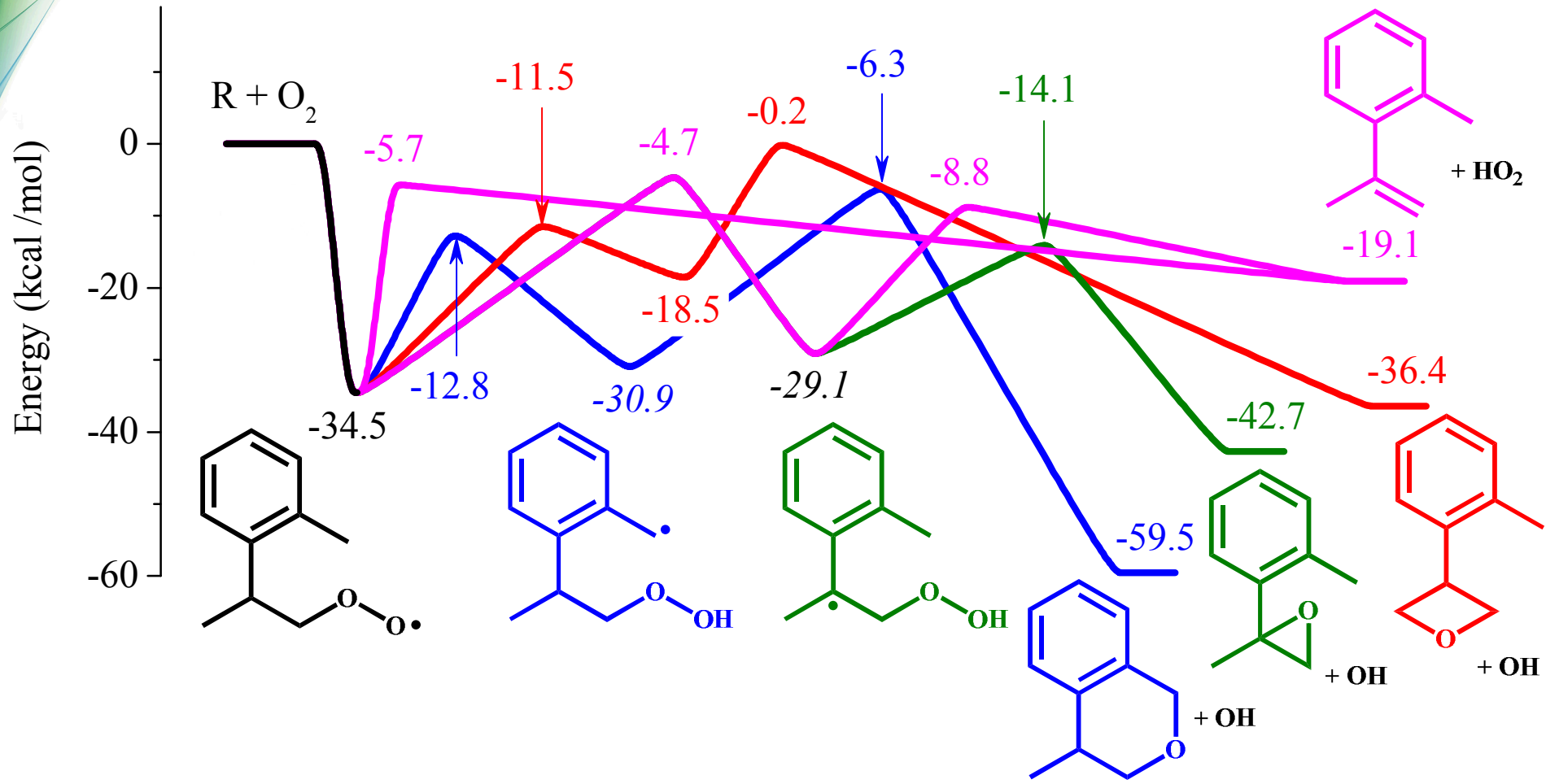
- *Resonance-stabilized R preferentially form resonance-stabilized QOOH*

Potential Energy Surface – tertiary benzylic-cymenylperoxy



- *Resonance-stabilized R preferentially form resonance-stabilized QOOH*

Potential Energy Surface – alkylic cymenylperoxy



- *High barrier to decomposition of non-resonance-stabilized QOOH into cyclic ether*
- *Competition between resonance-stabilized QOOH pathways*

Results – Influence of Temperature, Resonance-Stabilization on Cymene *ortho*- Effect

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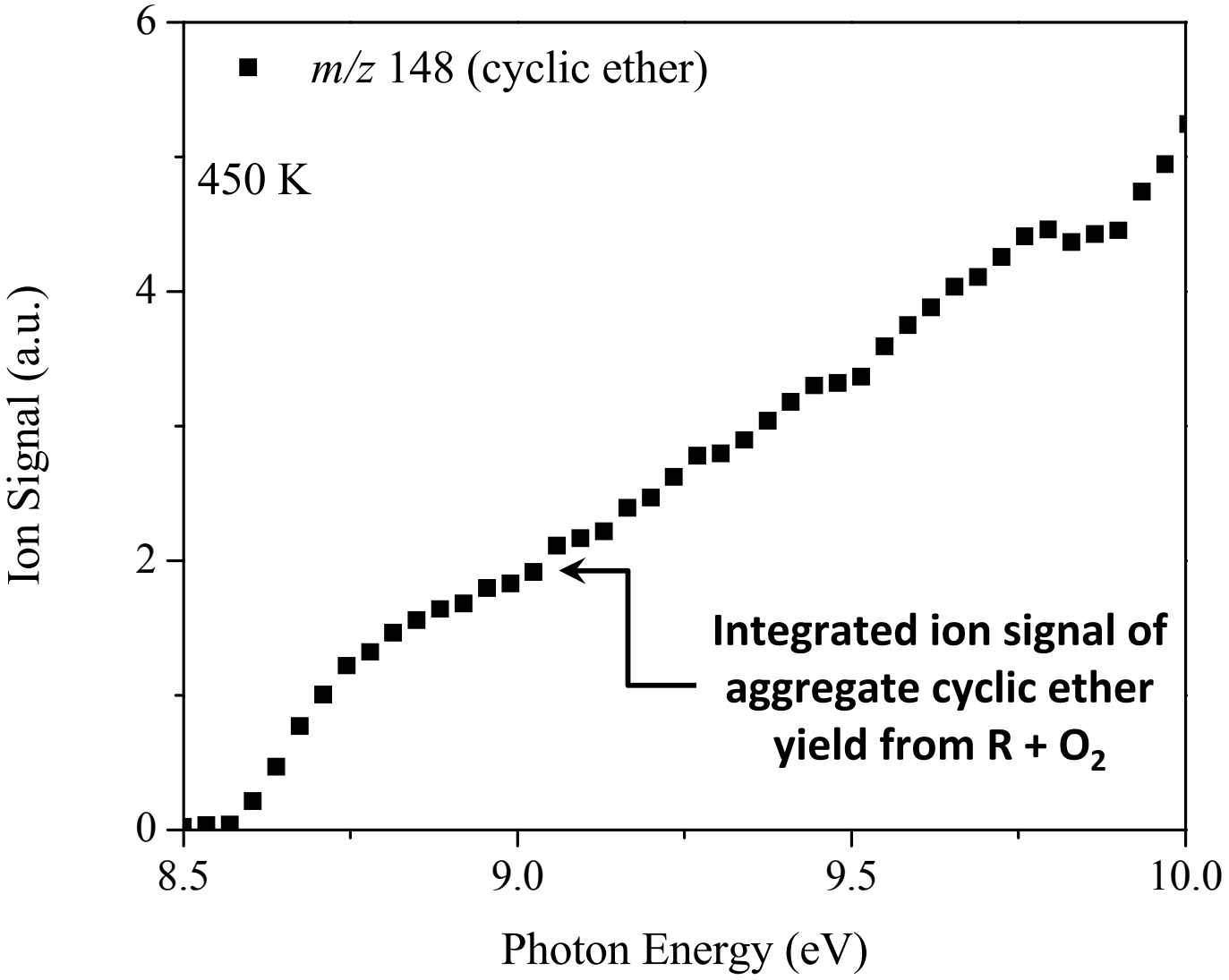
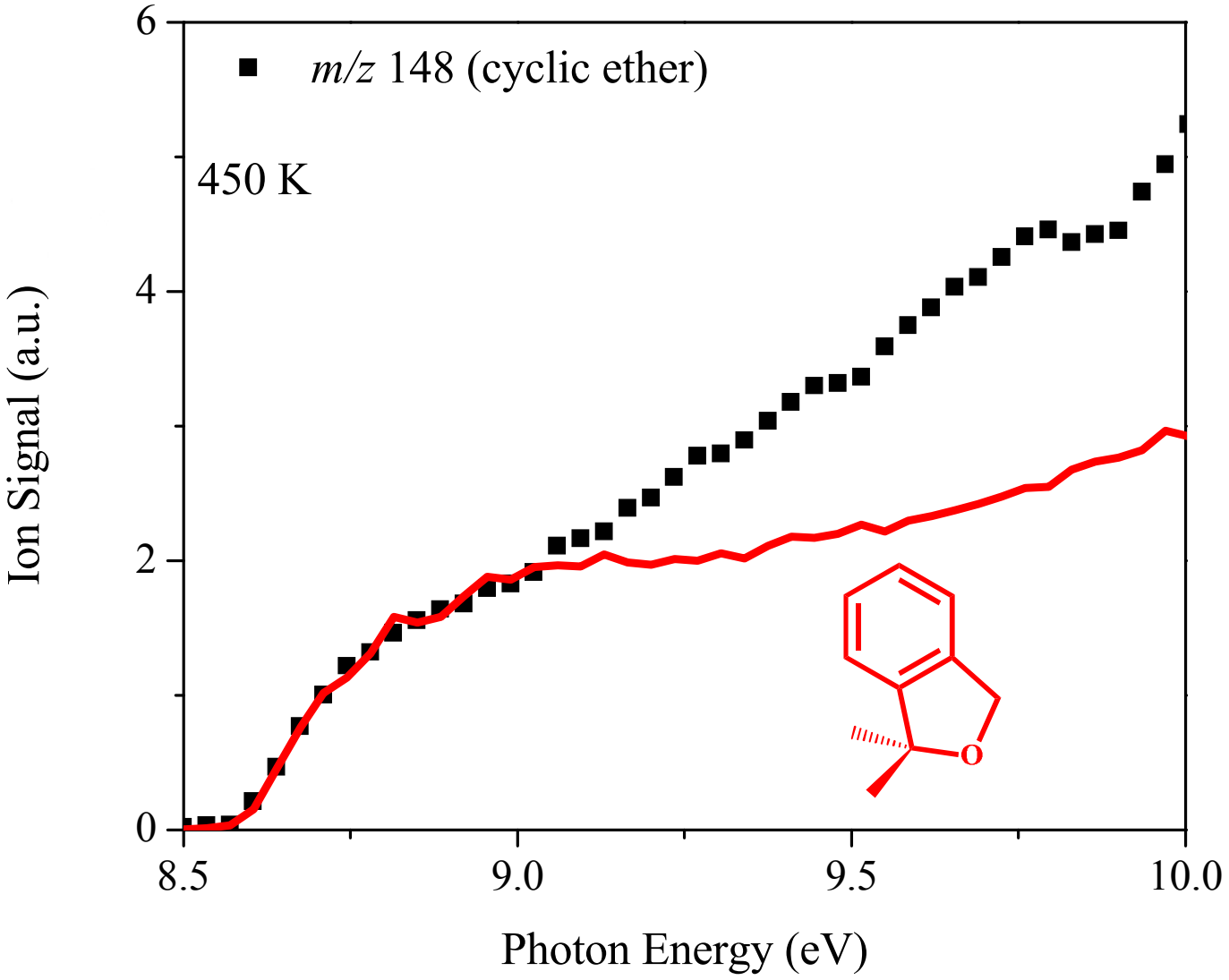
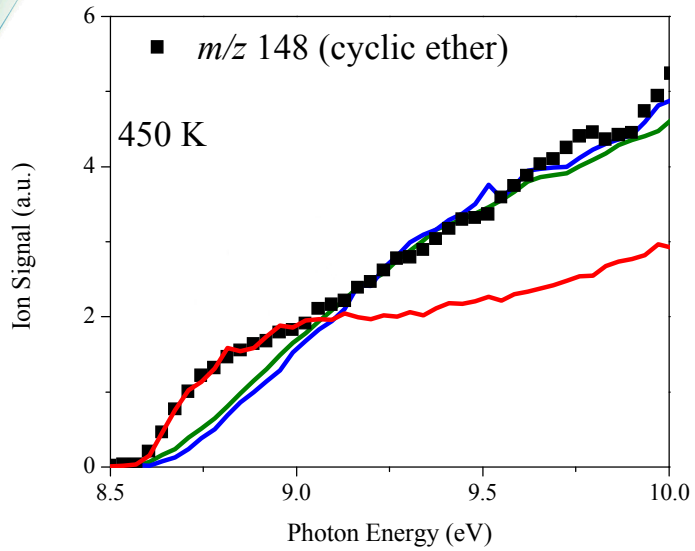
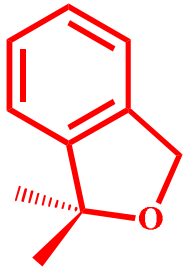


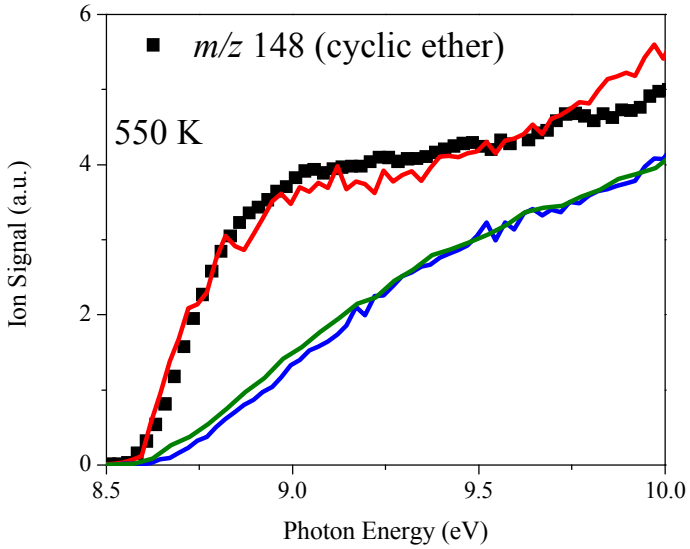
Results – Influence of Temperature, Resonance-Stabilization on Cymene *ortho*- Effect

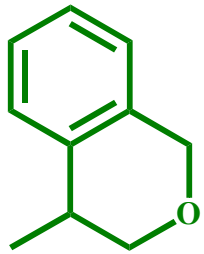


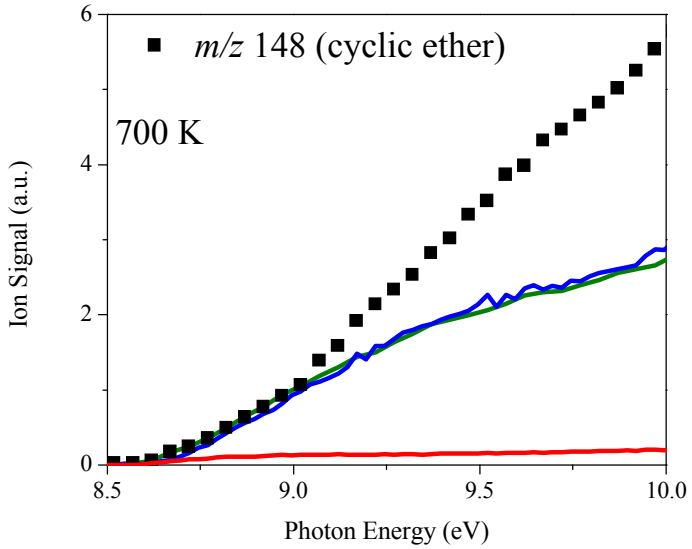
Results – Influence of Temperature, Resonance-Stabilization on Cymene *ortho*- Effect

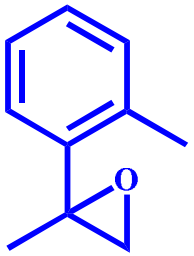




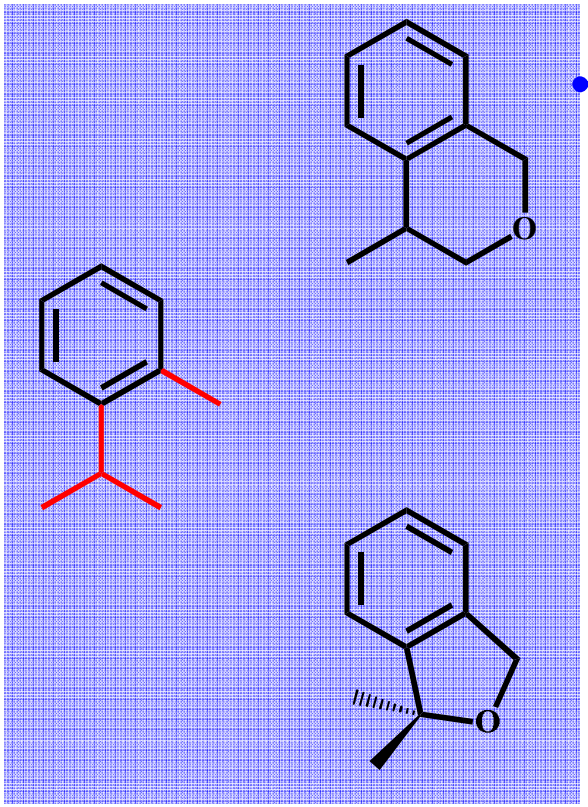






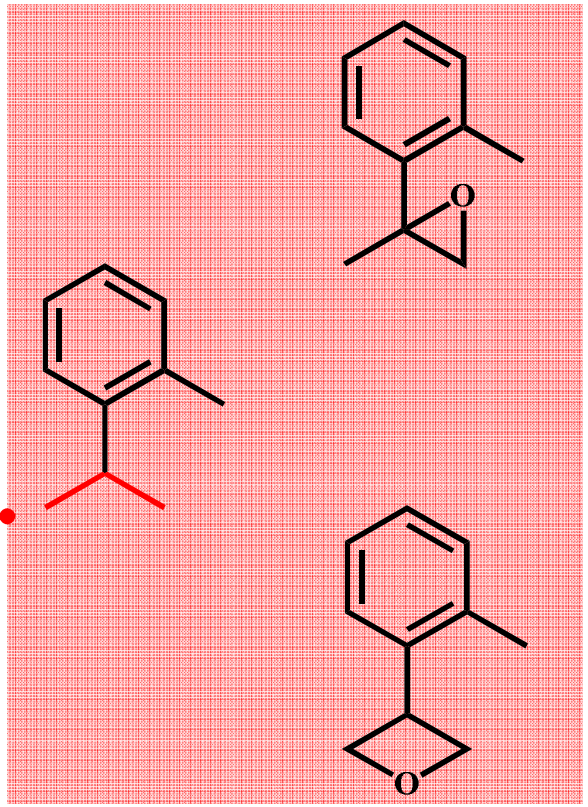


Results – Influence of Temperature, Resonance-Stabilization on Cymene *ortho*- Effect



cyclic ether pathways involving resonance-stabilized R, QOOH favored below 650 K

cyclic ether pathways involving non-resonance-stabilized R favored above 650 K



450 – 650 K

> 650 K

Concluding Remarks

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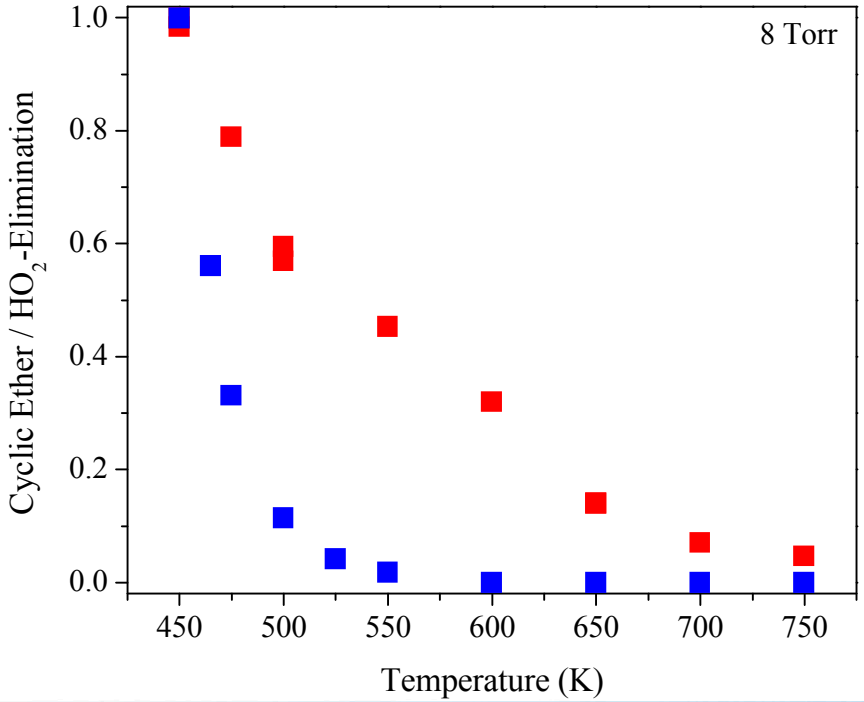
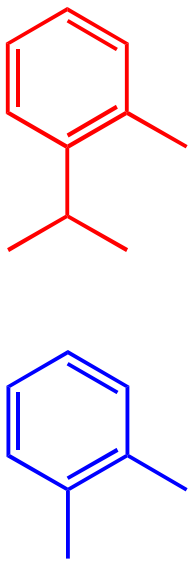
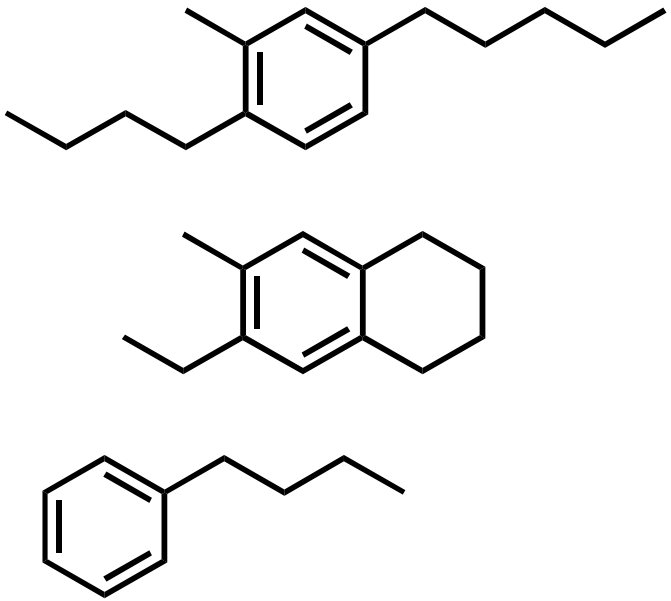
- *orhto*- effects are influenced by temperature and resonance-stabilization
  - $R + O_2 \rightleftharpoons ROO$ equilibria
  - $ROO \longrightarrow QOOH$ barriers
  - resonance-stabilized QOOH

Concluding Remarks

- *orhto*- effects are influenced by temperature and resonance-stabilization
  - R + O_2 ⇌ ROO equilibria
  - ROO ⟶ QOOH barriers
  - resonance-stabilized QOOH
- Fuel structure of polysubstituted aromatics controls the degree of influence of resonance and temperature (e.g. *o*-xylene)







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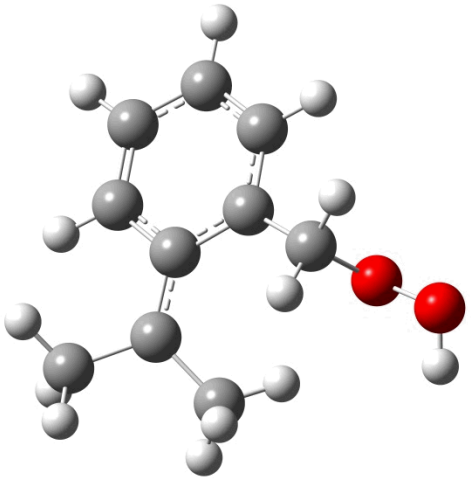
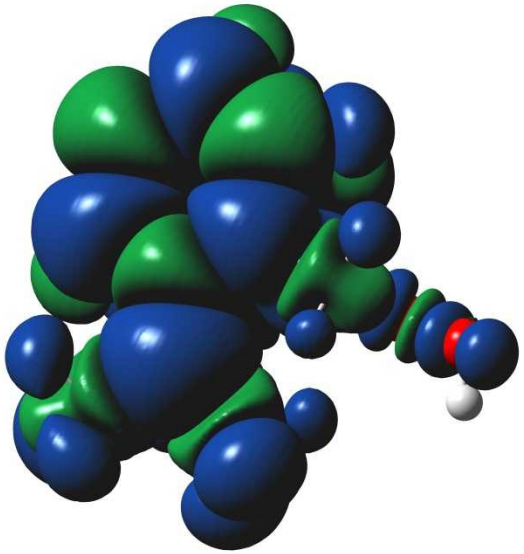
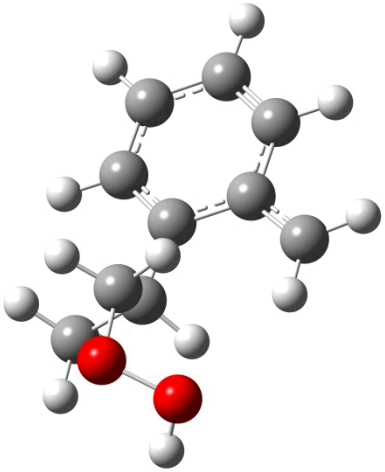
Funded by U.S.-China Clean Energy Research Center (CERC) for Clean Vehicles
Award Number DE-PI0000012

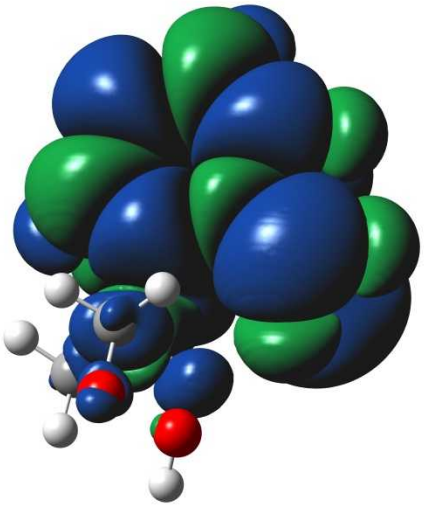
Spin Densities – Tertiary QOOH / Primary Benzylic R

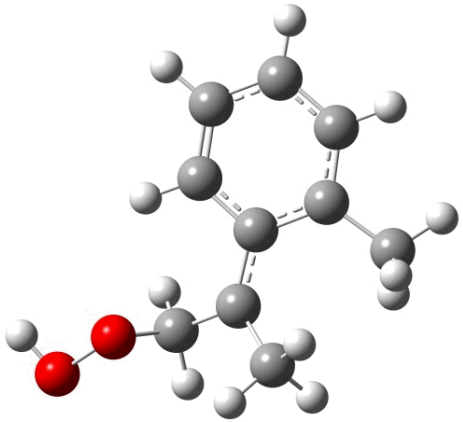


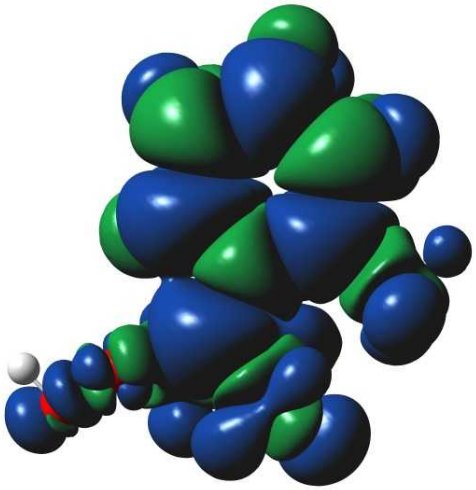


Spin Densities – Primary Benzylic QOOH / Alkyl R

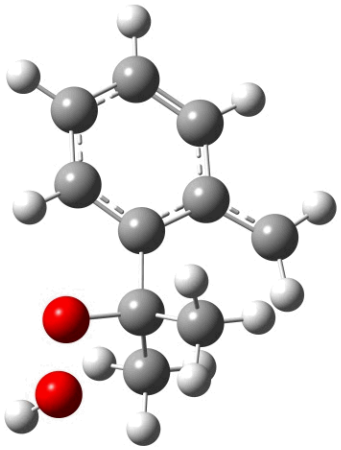


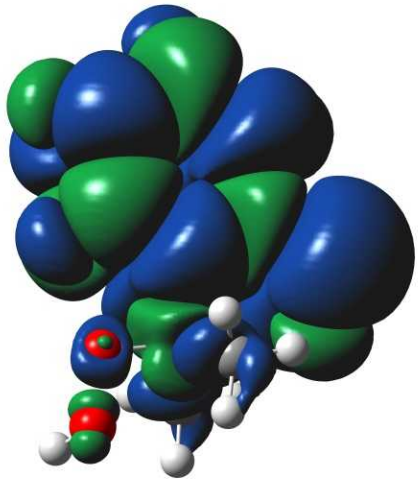


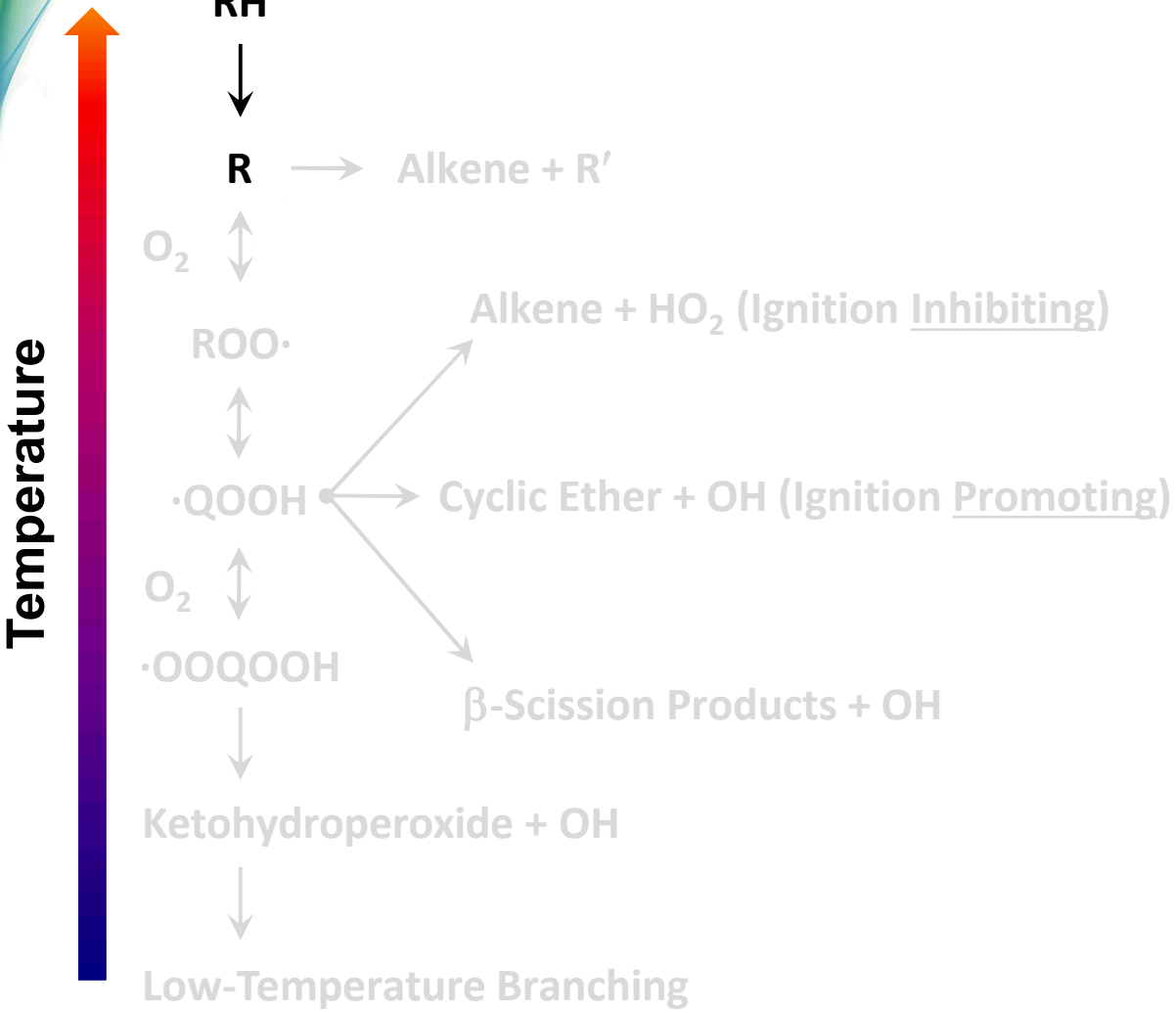


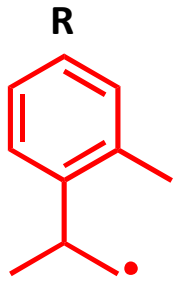


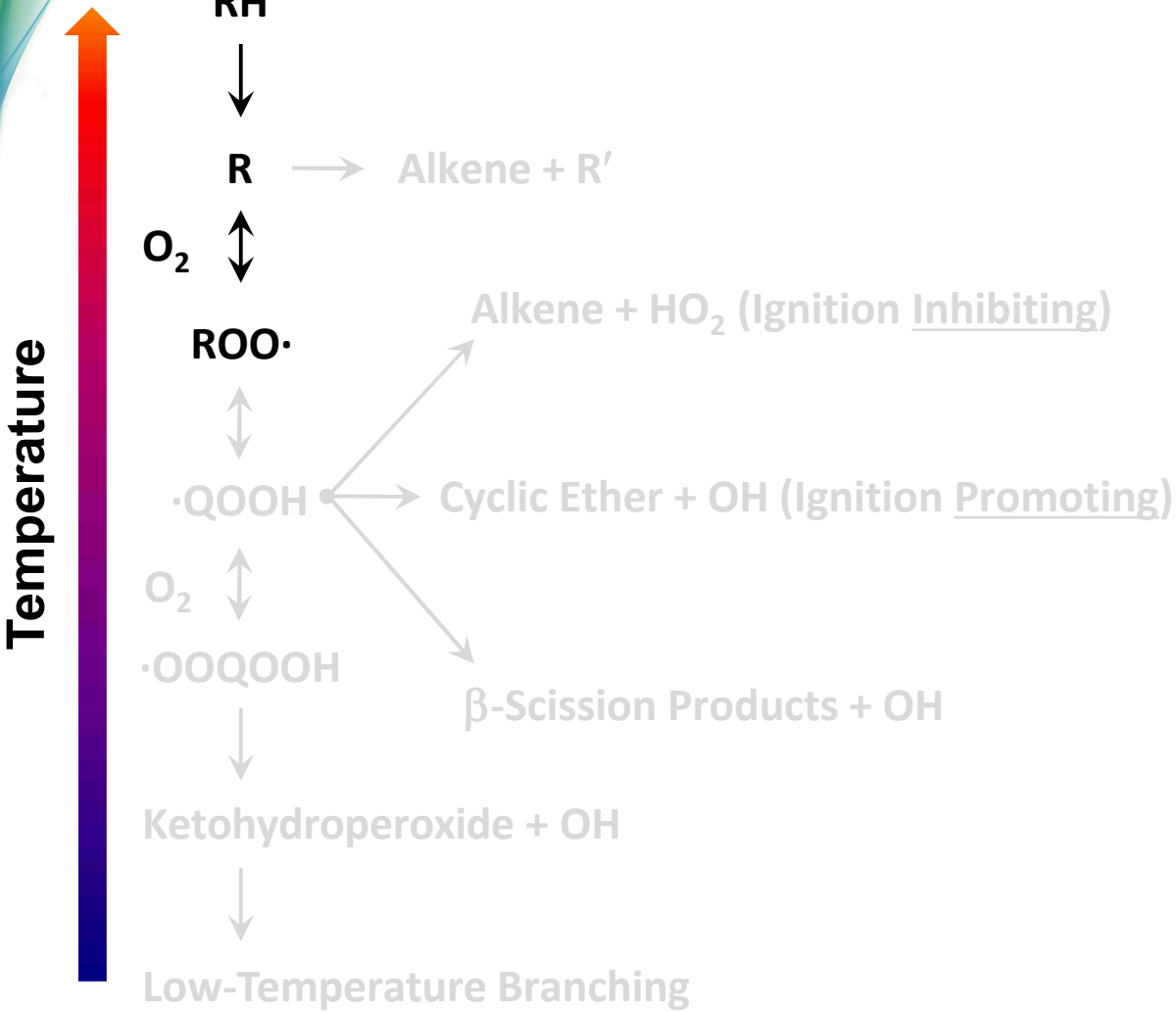
Spin Densities – Primary Benzylic QOOH / Tertiary Benzylic R






RH
R
Alkene + R′
O2
ROO·
Alkene + HO2 (Ignition Inhibiting)
·QOOH
Cyclic Ether + OH (Ignition Promoting)
O2
·OOQOOH
β-Scission Products + OH
Ketohydroperoxide + OH
Low-Temperature Branching
Temperature


R


RH
R
Alkene + R′
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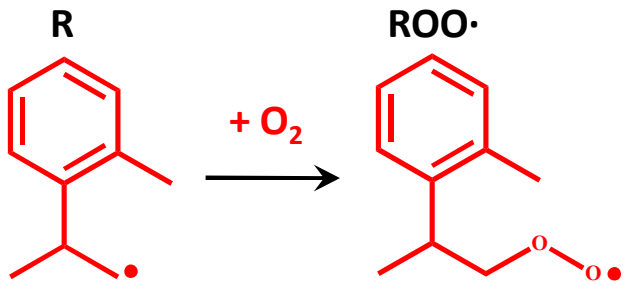
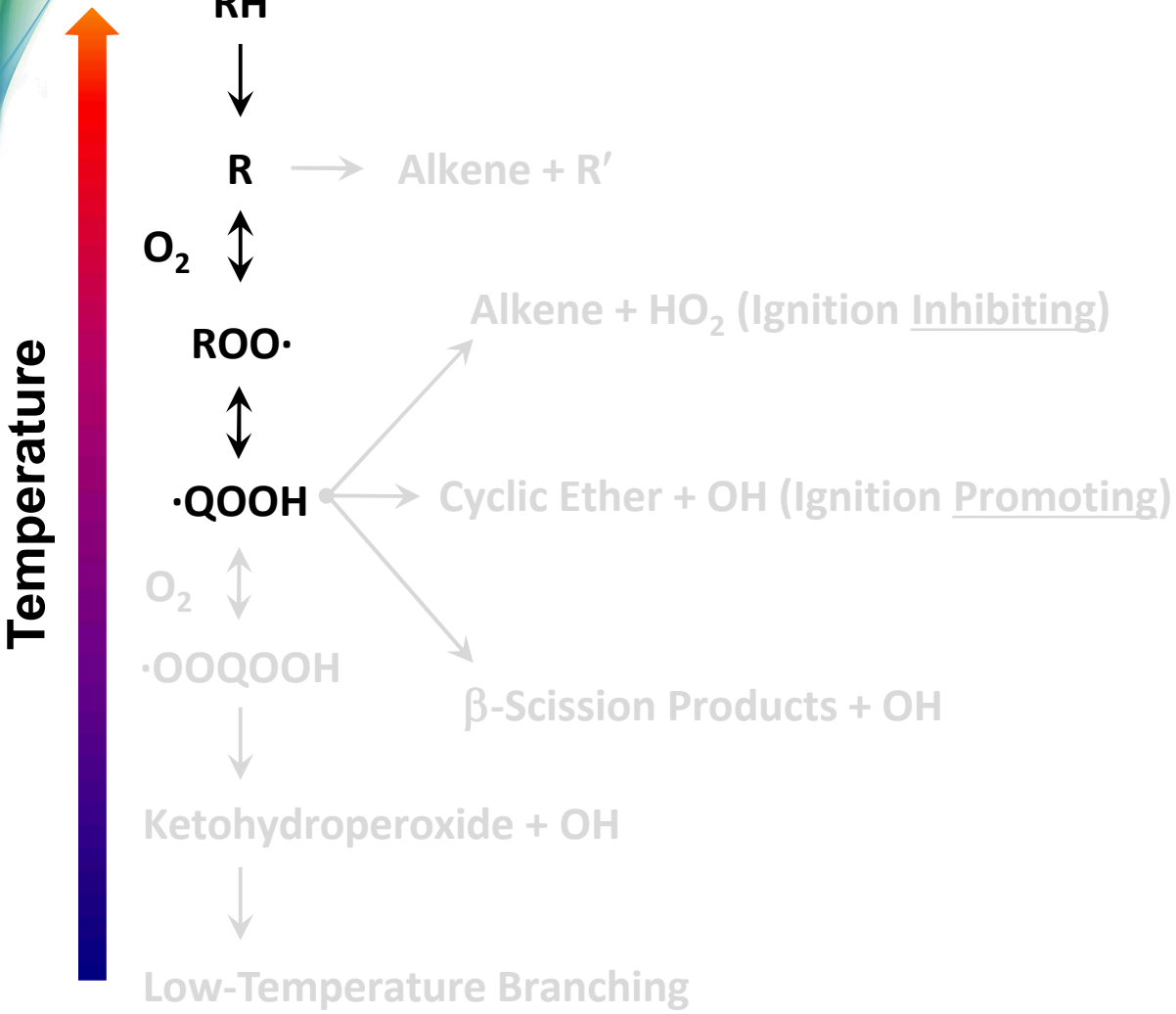

R
+ O2
ROO·


Temperature
RH
R
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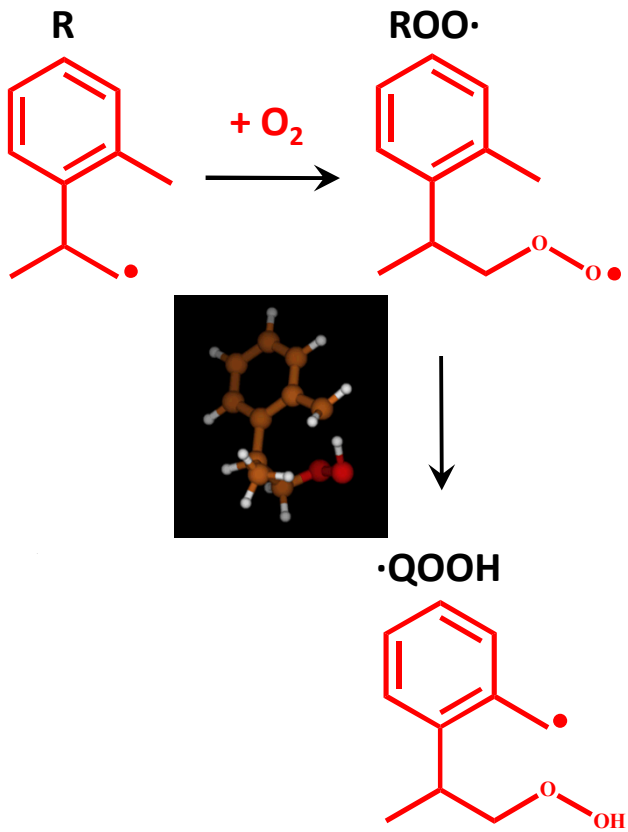
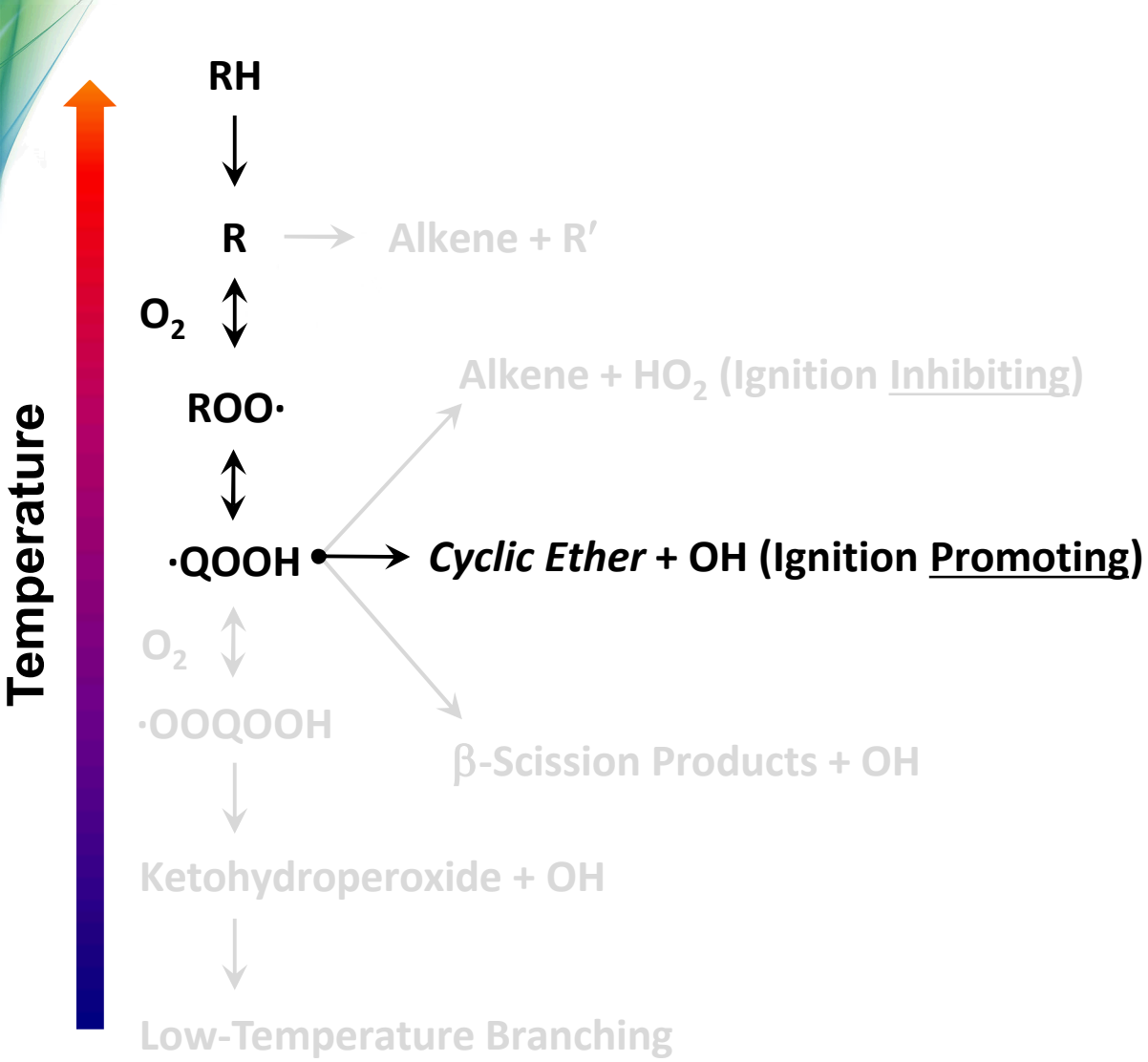

R
ROO·
+ O2
·QOOH
O
O
O
OH


Temperature
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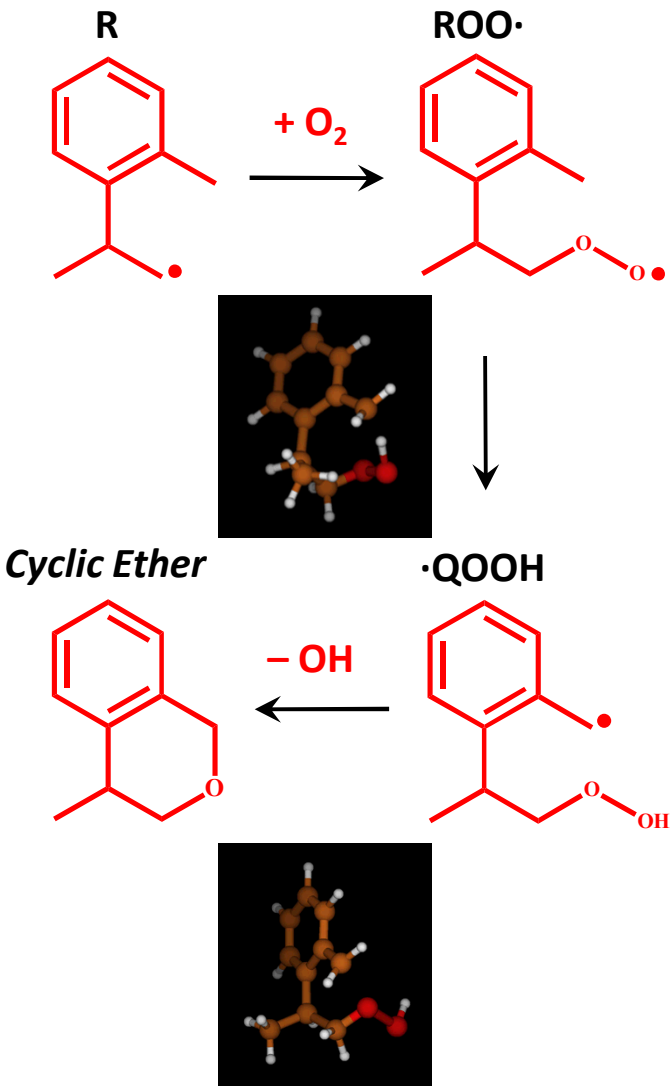
R
ROO·
+ O2
O
O
Cyclic Ether
·QOOH
– OH
O
O
OH