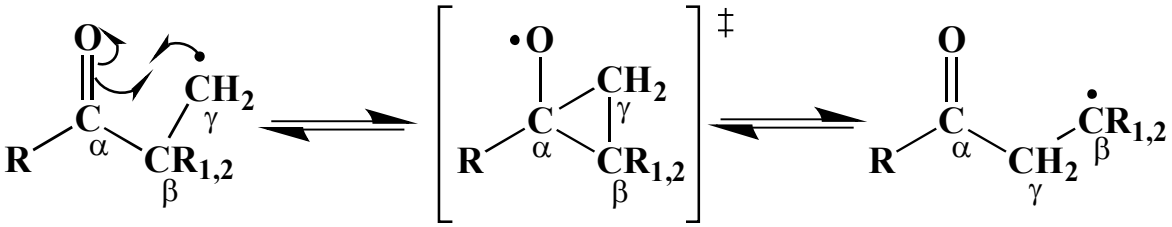
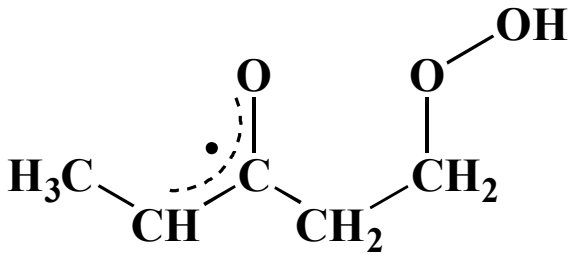
SAND2013-5551C

Rapid Radical Rearrangement of Ketones and selective chain-propagating channels via resonantly-stabilized QOOH





Adam Scheer, Oliver Welz, David Osborn and Craig Taatjes

7/12/2013

Liquid Fuels in The United States

- 140 billion gallons of gasoline a year

Energy Independence and Security Act of 2007:

Cellulosic Biofuel Requirements:

- 500 million gallons of cellulosic biofuels for 2012
- 1 billion gallons for 2013
- 16 billion gallons by 2022

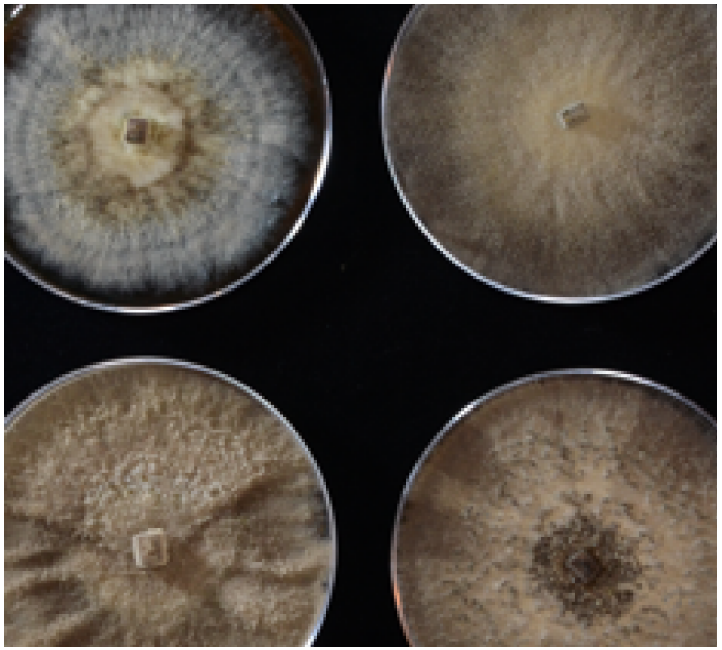
*corn ethanol production = 13 billion gallons (2012)

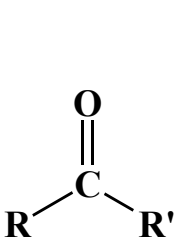
20,000 gallons of cellulosic biofuels actually produced in 2012.

500,000,000 – 20,000 = 499,980,000.

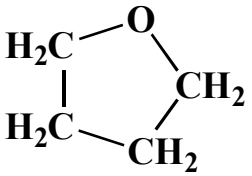
Breaking Down Cellulose: Fungal Endophytes are Tunable Platforms

- Certain fungi can convert cellulose directly into a variety of volatile organic compounds (VOCs).
- Unfortunately these VOCs do not include octane.
- These "fuels" need to be characterized.

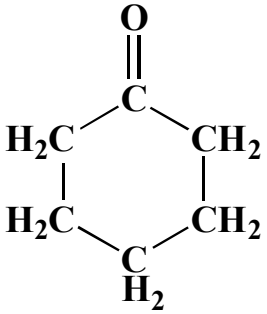




Open-Chain Ketones

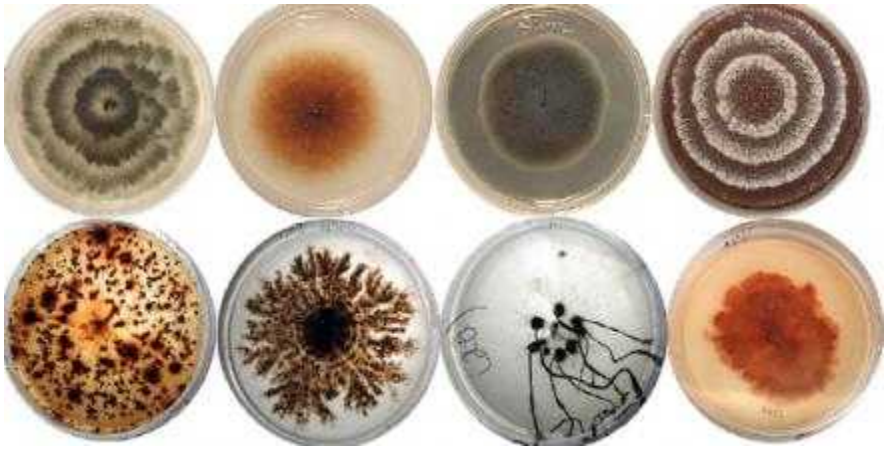


Cyclic Ethers



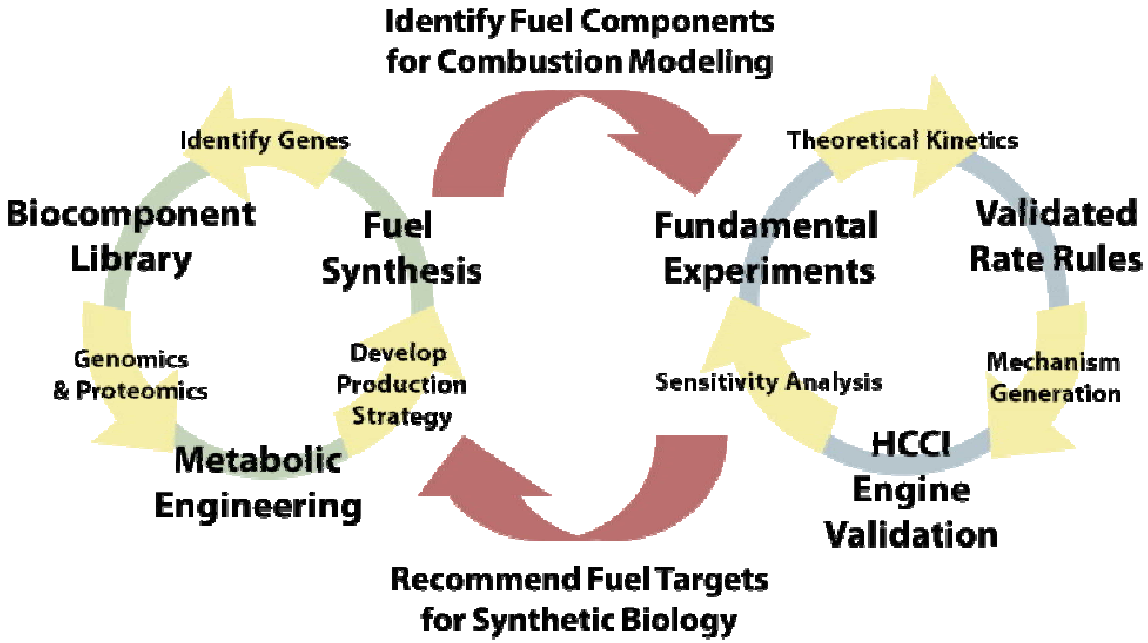
Cyclic Ketones

Families of molecules from fungal metabolism of cellulose



G. A. Strobel, et al. *J. Microbiology-(UK)* **2008**, *154* (3319).

Investigating Fungal Conversion of Cellulose for Liquid Fuels: Collaboration!



MONTANA STATE UNIVERSITY | College of AGRICULTURE

COMBUSTION RESEARCH FACILITY

ALS ADVANCED LIGHT SOURCE

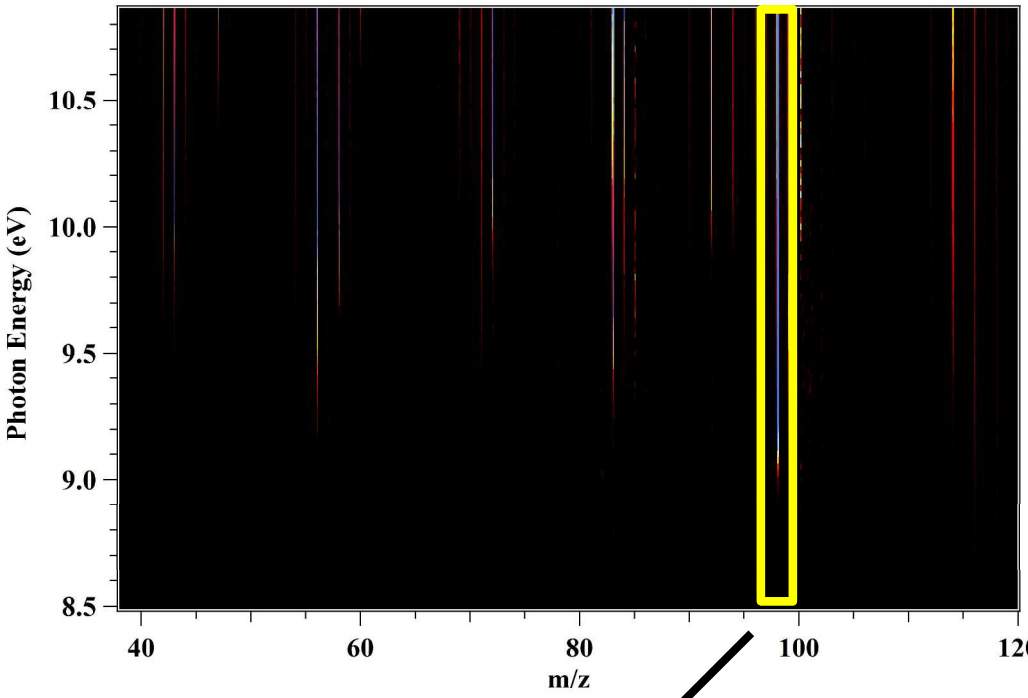
MIT

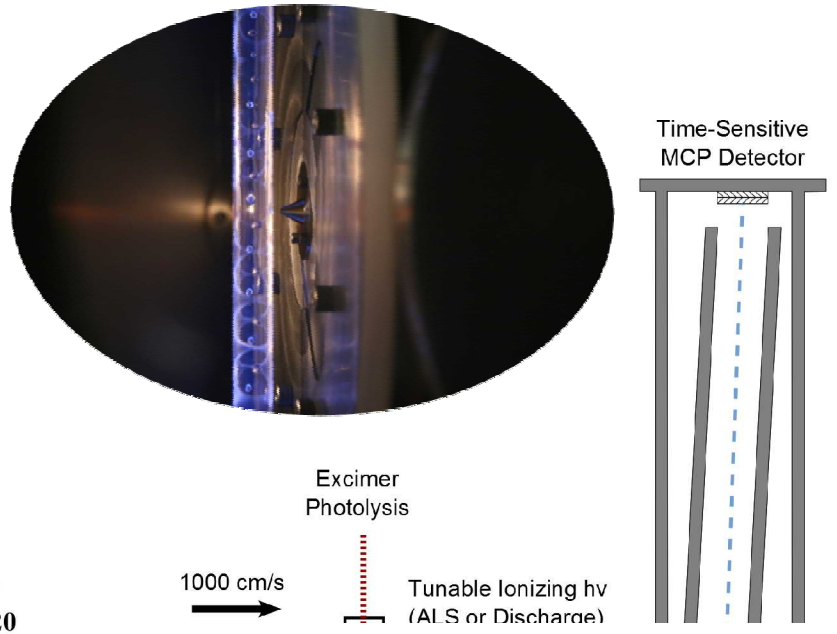
RWTH AACHEN UNIVERSITY

jbei Joint BioEnergy Institute

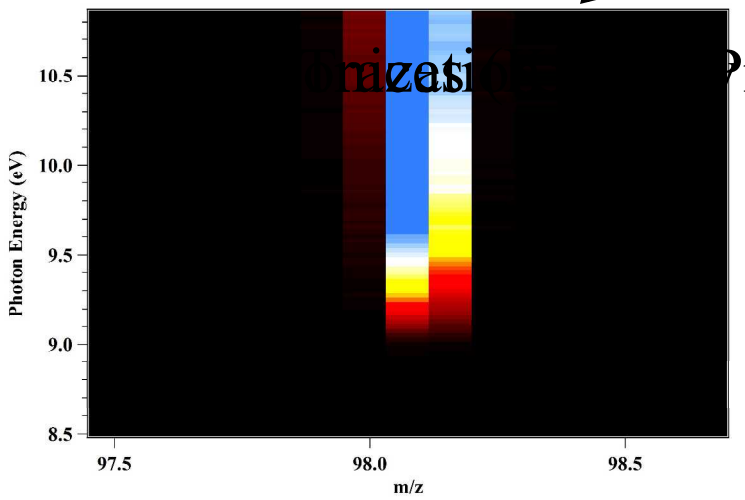
USTC NSRL

Experiment: Chlorine-Initiated Oxidation using MPIMS

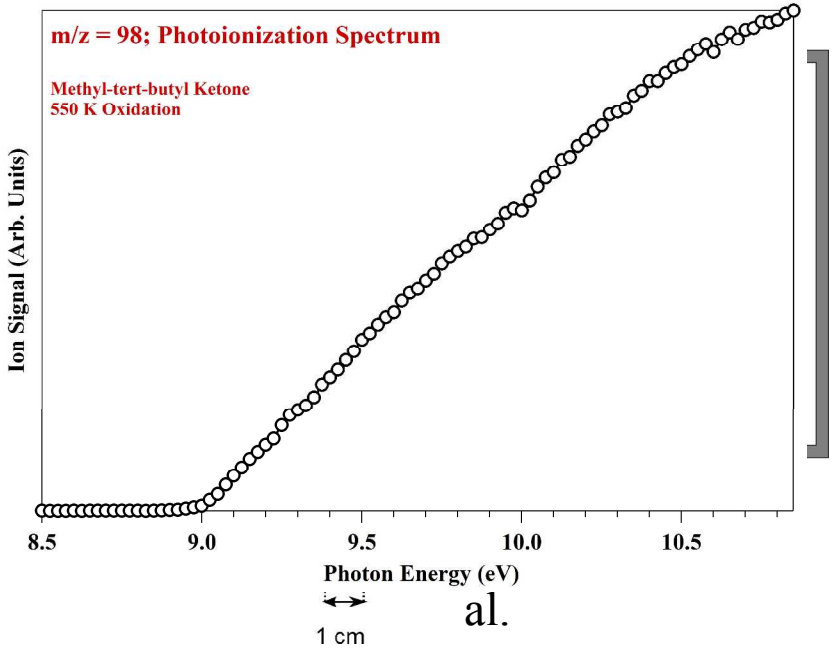




hν (351 nm)

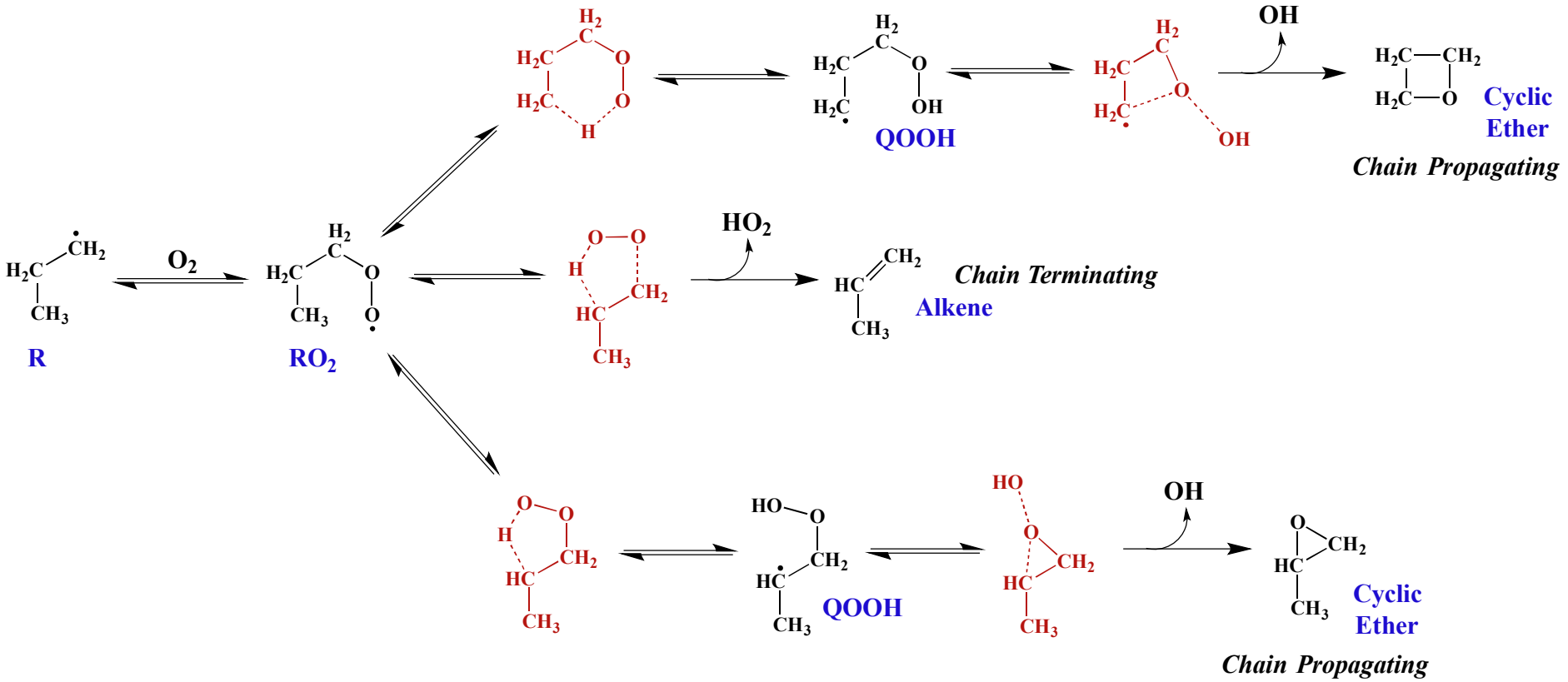


+ HCl



al.

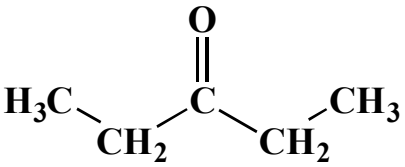
Background: Oxidation of n-propyl Radical



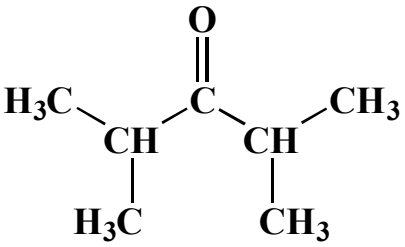
J. D. DeSain et al. *J. Phys. Chem. A* **2003**, *107*, (4415).

- Do not typically detect OH and HO_2 directly in MPIMS.
- Instead observe coproducts at Parent – 2 (unsaturated hydrocarbon) and Parent + 14 (cyclic ether)
- QOOH never observed but vital intermediate in chain-propagating and chain-branching channels

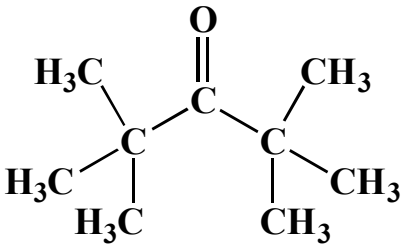
Fuels From Fungus: Investigating Branched Ketones



Diethyl Ketone

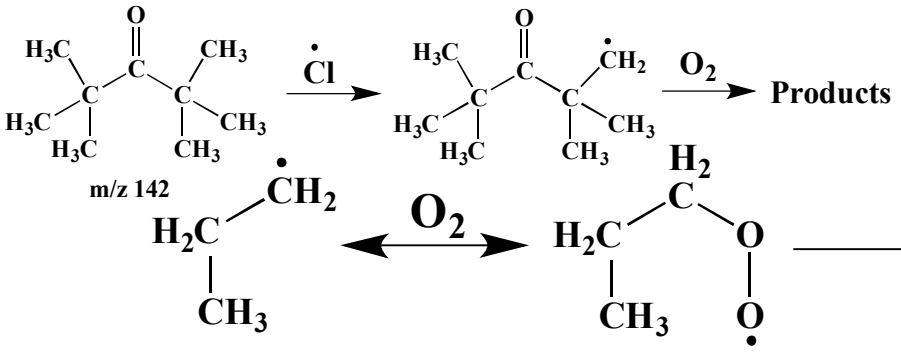


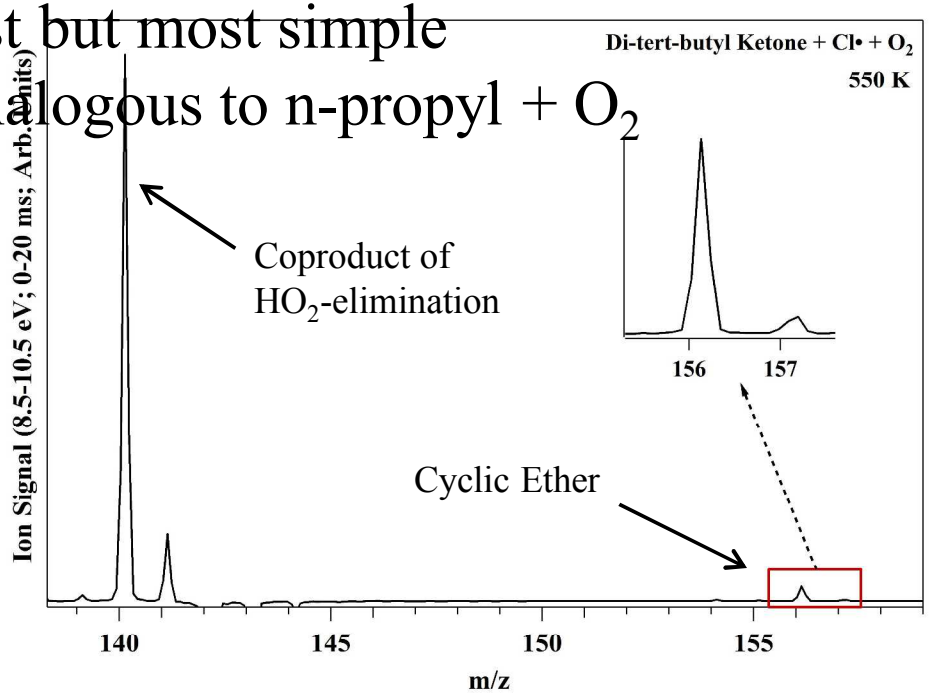
Diisopropyl Ketone



Di-tert-butyl Ketone

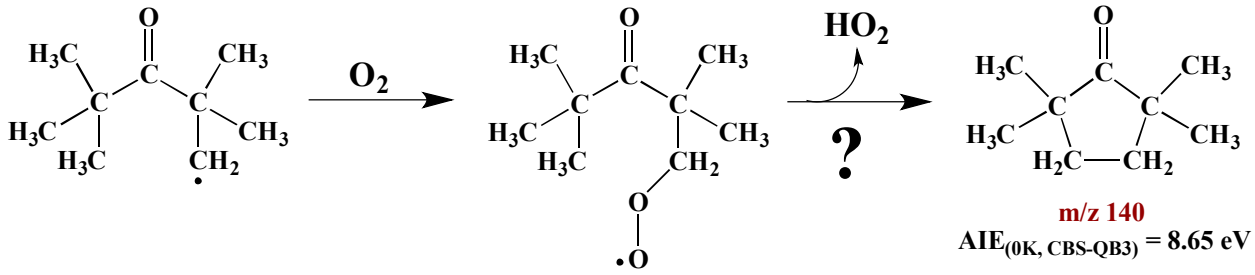
- Di-tert-butyl ketone is the largest but most simple
- No HO_2-elimination pathway analogous to n-propyl + O_2



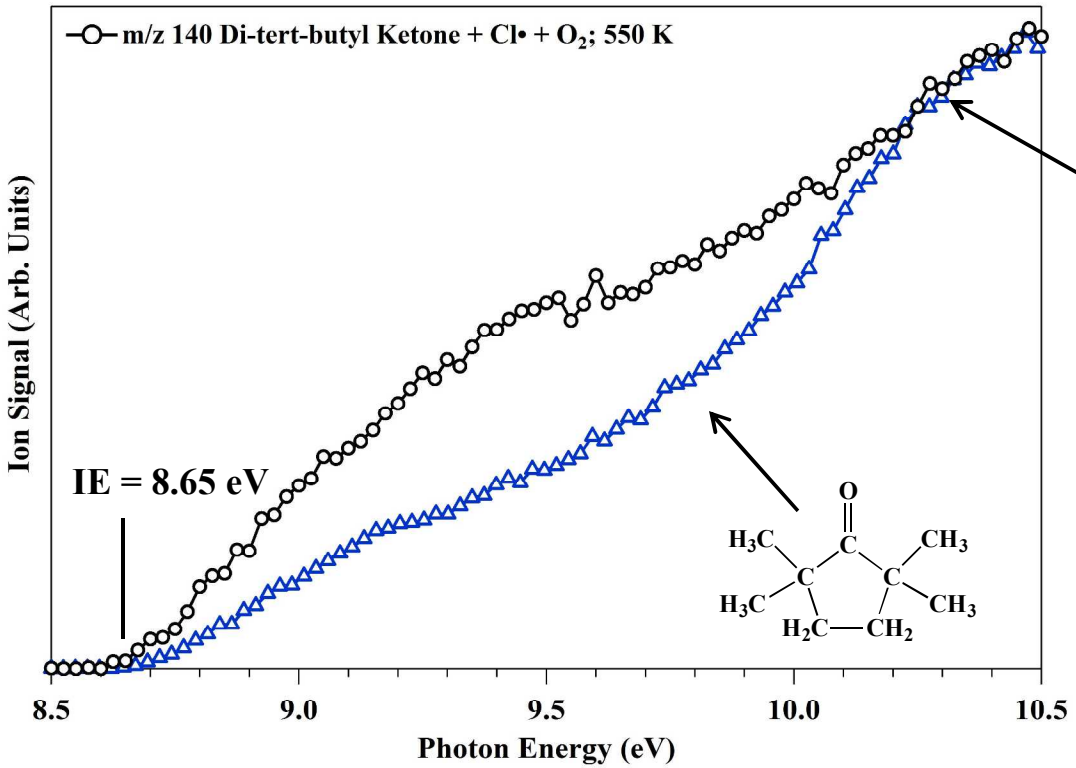


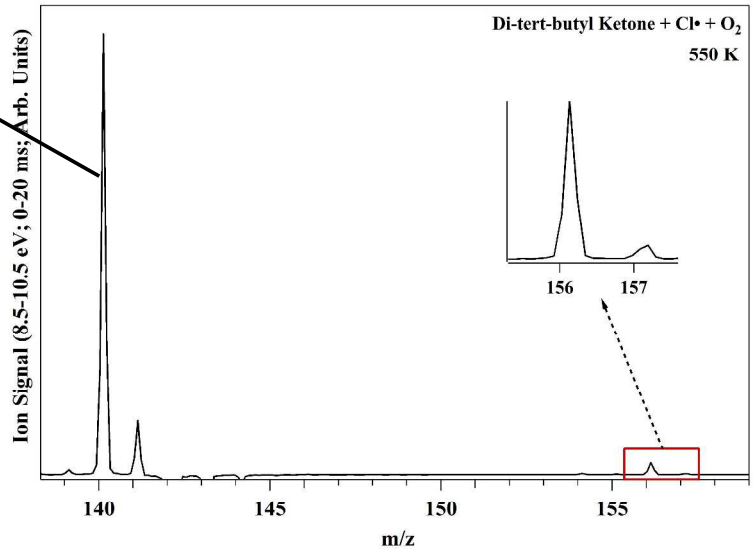
Fuels From Fungus: Investigating Branched Ketones

Ring Closure Yielding HO_2-Elimination?

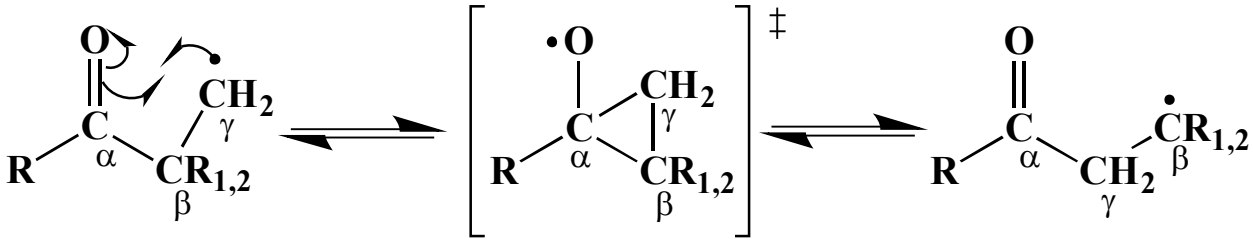


Calculated ionization energy matches experimental onset.



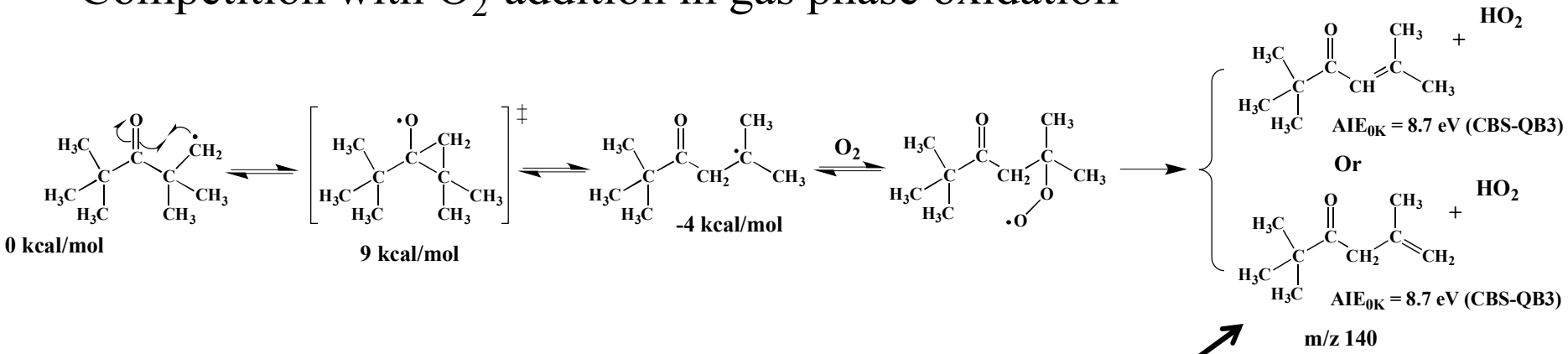


Open-Chain Ketones: **Rapid Radial Rearrangement Reactions?**



Karl et al. *J. Org. Chem.* **37**, 2834 (1972)

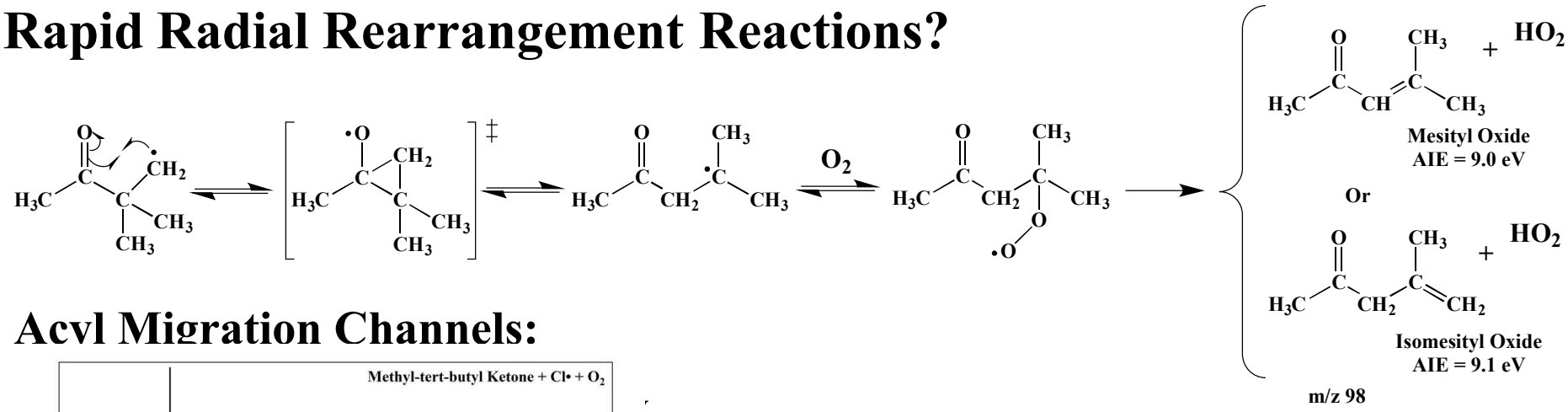
- Thermodynamic driving force depending on substituents
- Competition with O_2-addition in gas phase oxidation



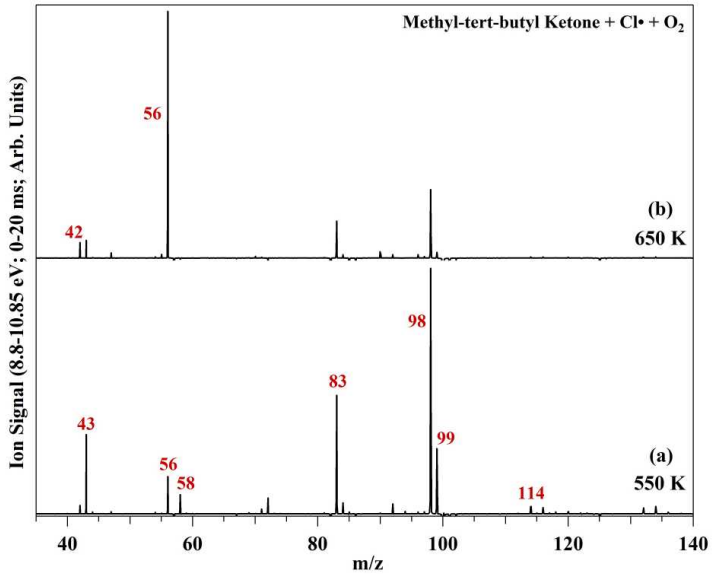
- Neither product available for comparison.

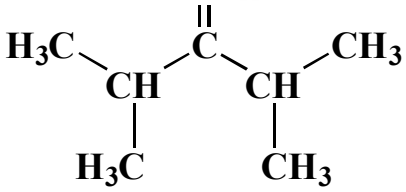
Fuels From Fungus: Methyl-tert-butyl Ketone

Rapid Radial Rearrangement Reactions?

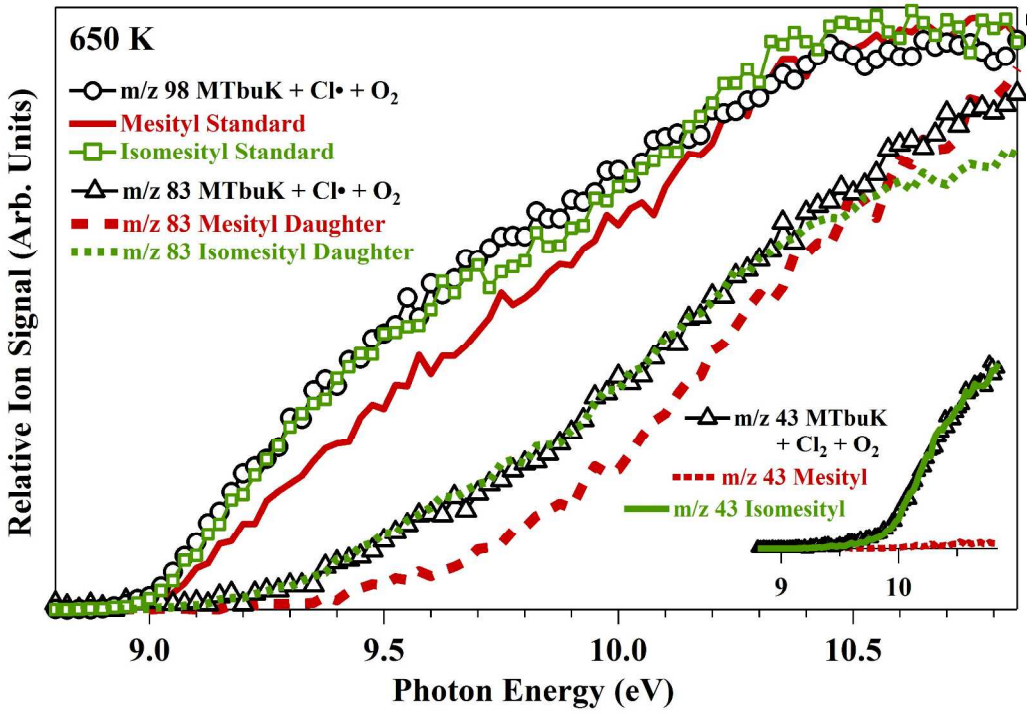


Acyl Migration Channels:



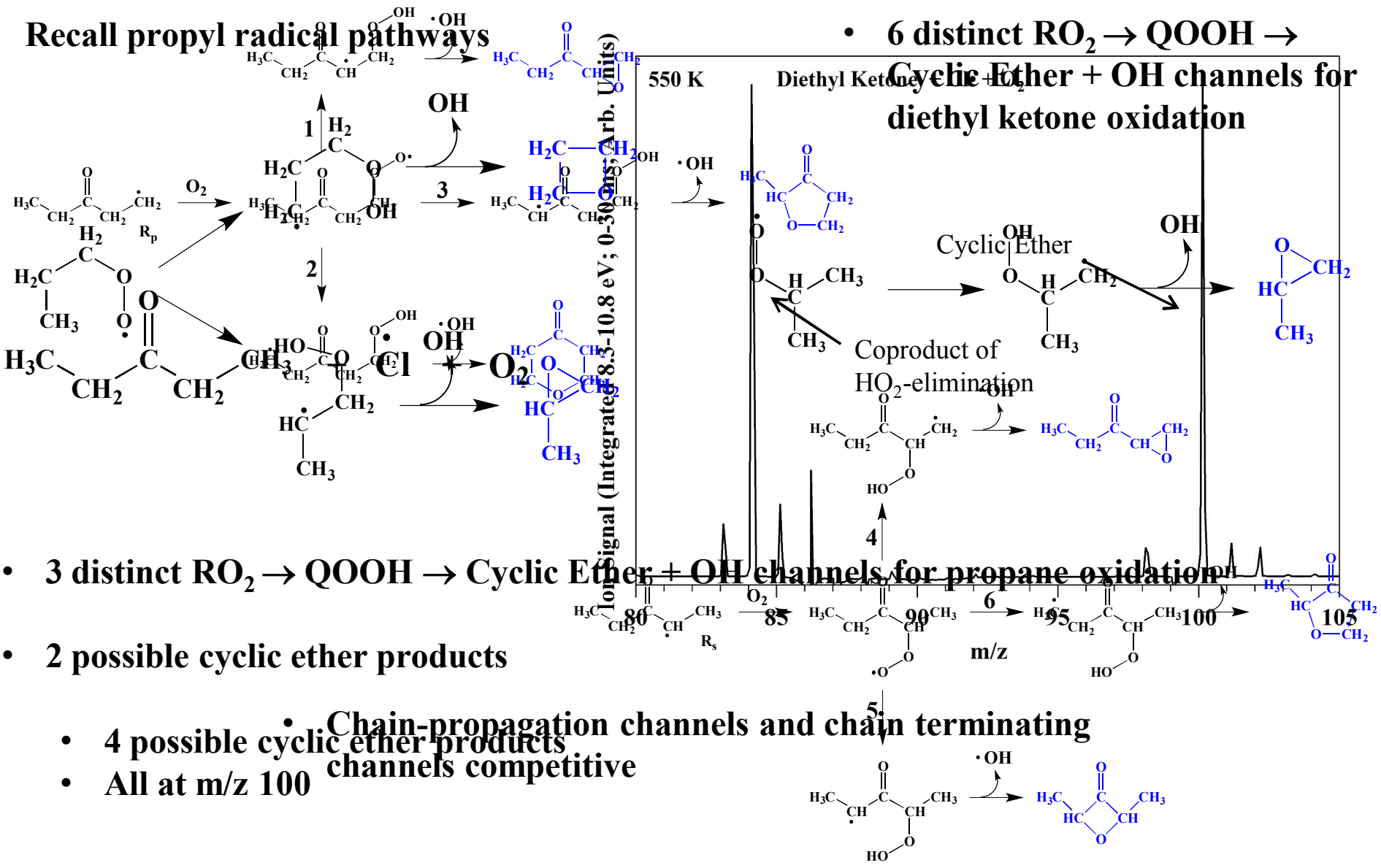


Diisopropyl Ketone



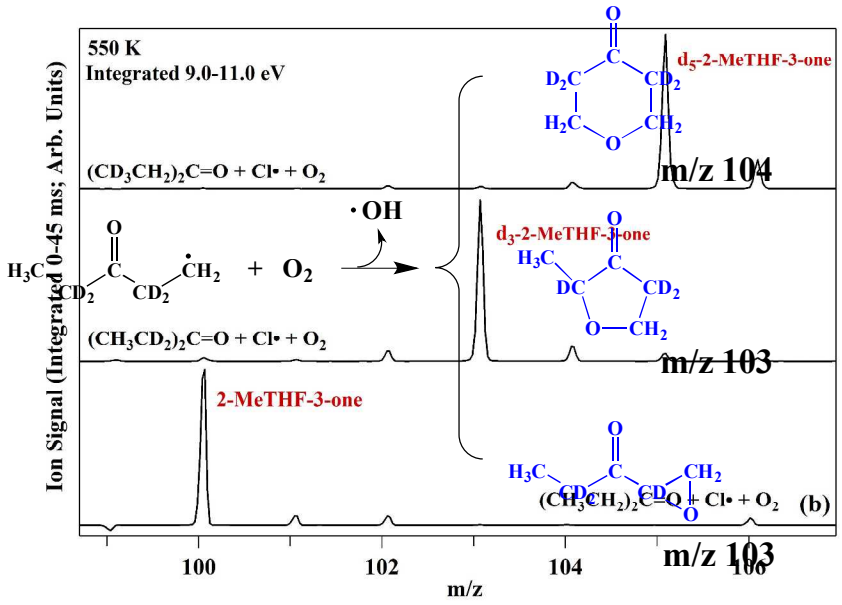
Switching Gears: Cyclic Ether Formation Possibilities in Diethyl Ketone Oxidation

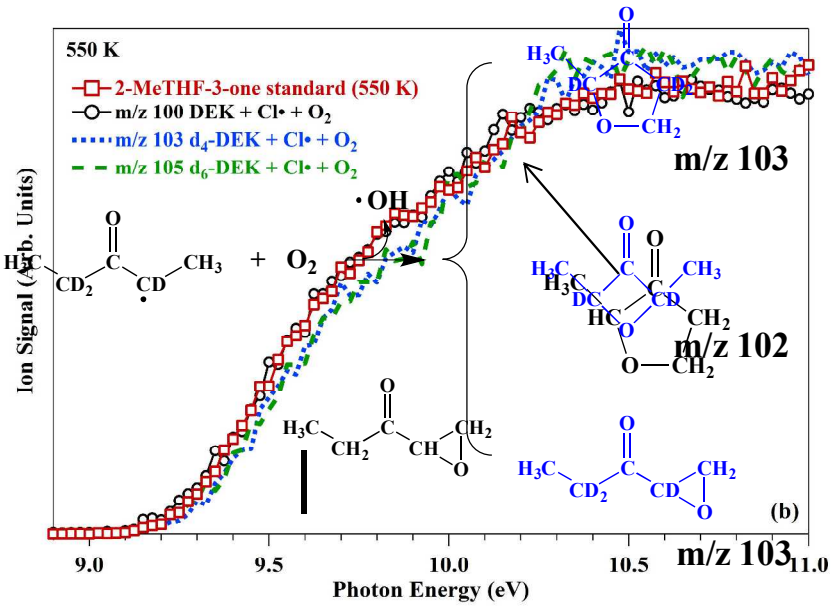
Recall propyl radical pathways

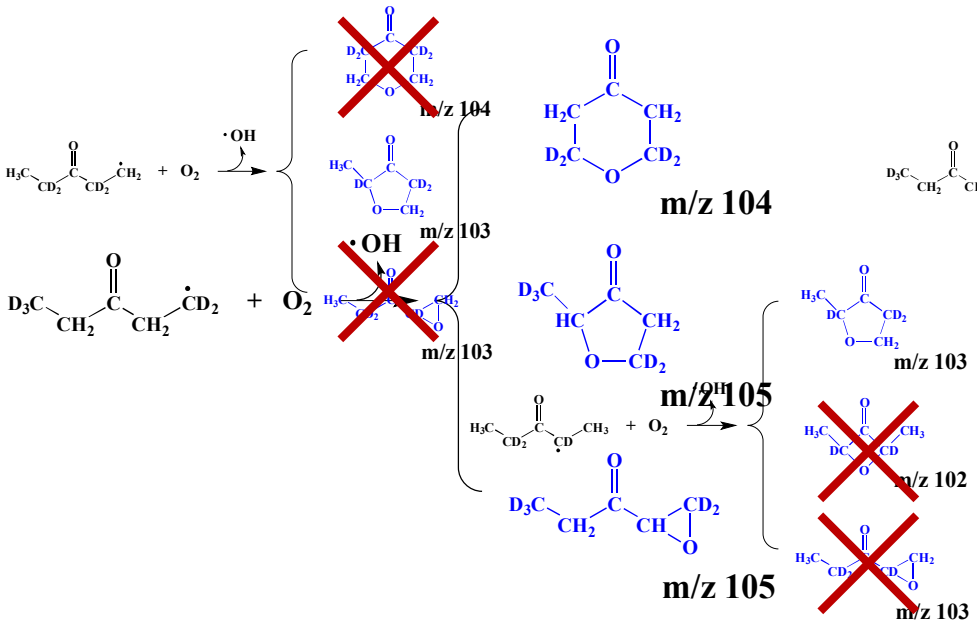


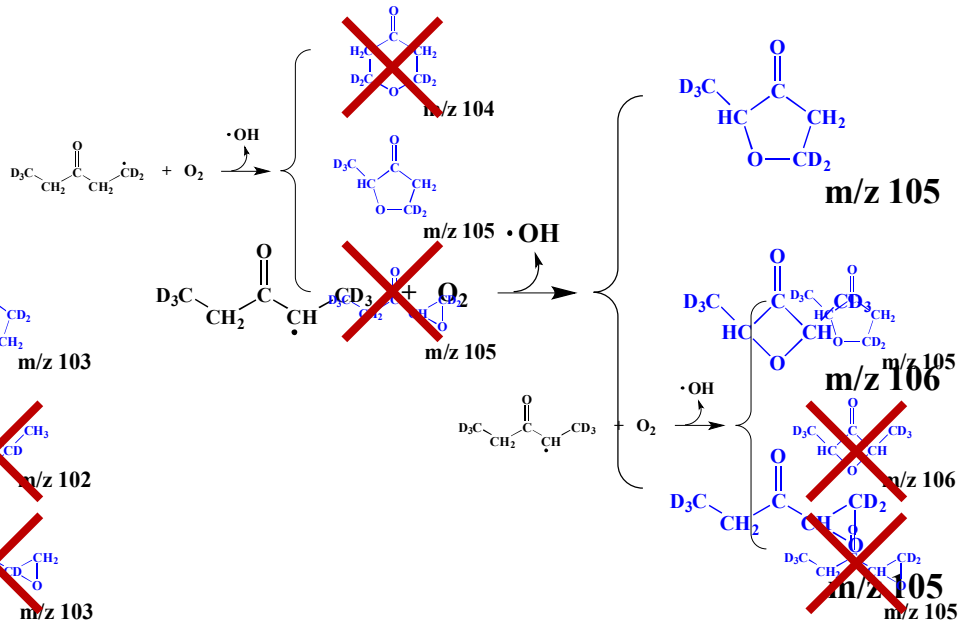
- **6 distinct $RO_2 \rightarrow QOOH \rightarrow$ Cyclic Ether + OH channels for diethyl ketone oxidation**
- **3 distinct $RO_2 \rightarrow QOOH \rightarrow$ Cyclic Ether + OH channels for propane oxidation**
- **2 possible cyclic ether products**
  - **4 possible cyclic ether products**
  - **All at m/z 100**
- **Chain-propagation channels and chain terminating channels competitive**

Isolation of Cyclic Ether Channels: Deuterated Diethyl Ketones

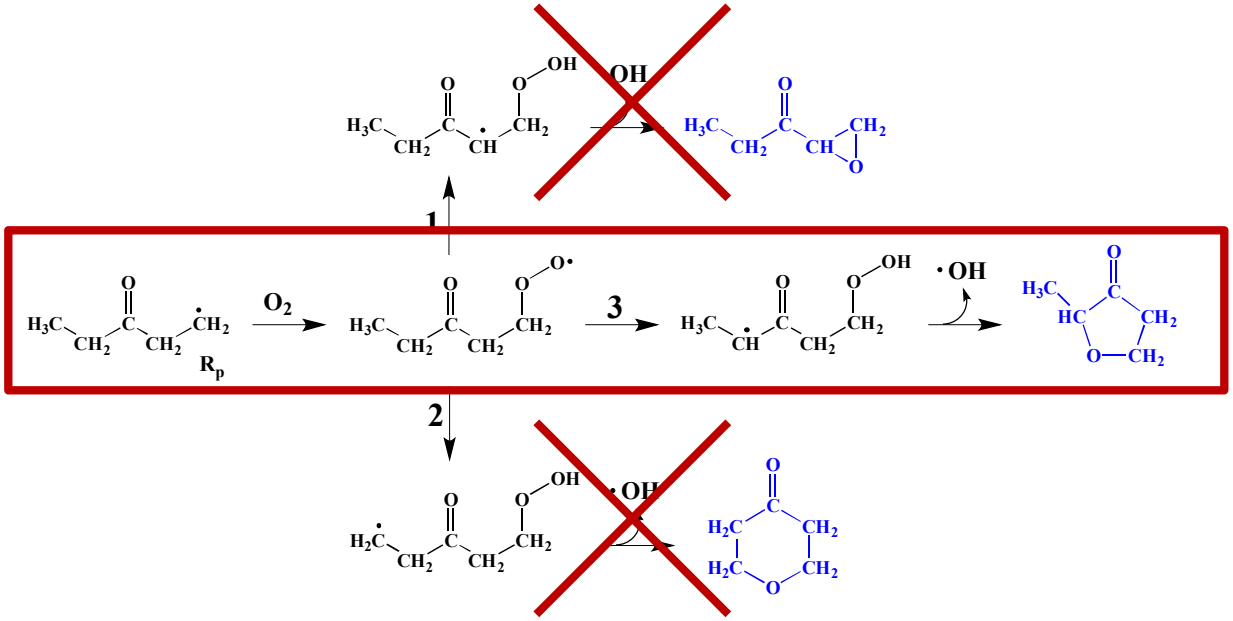




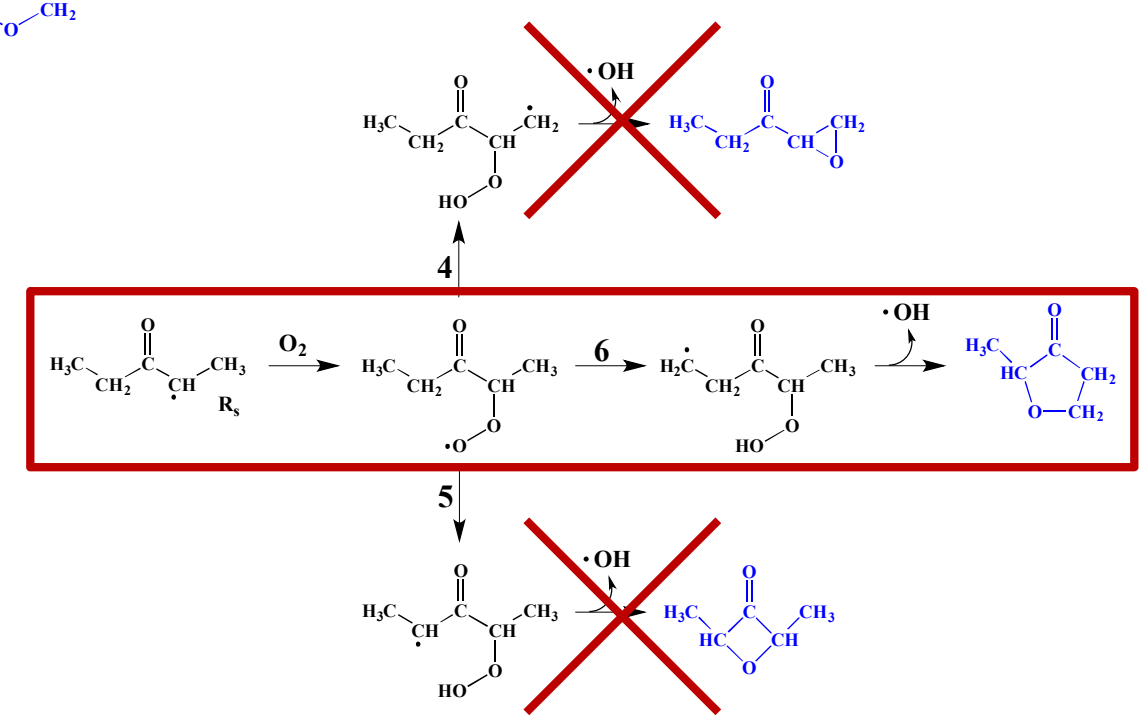




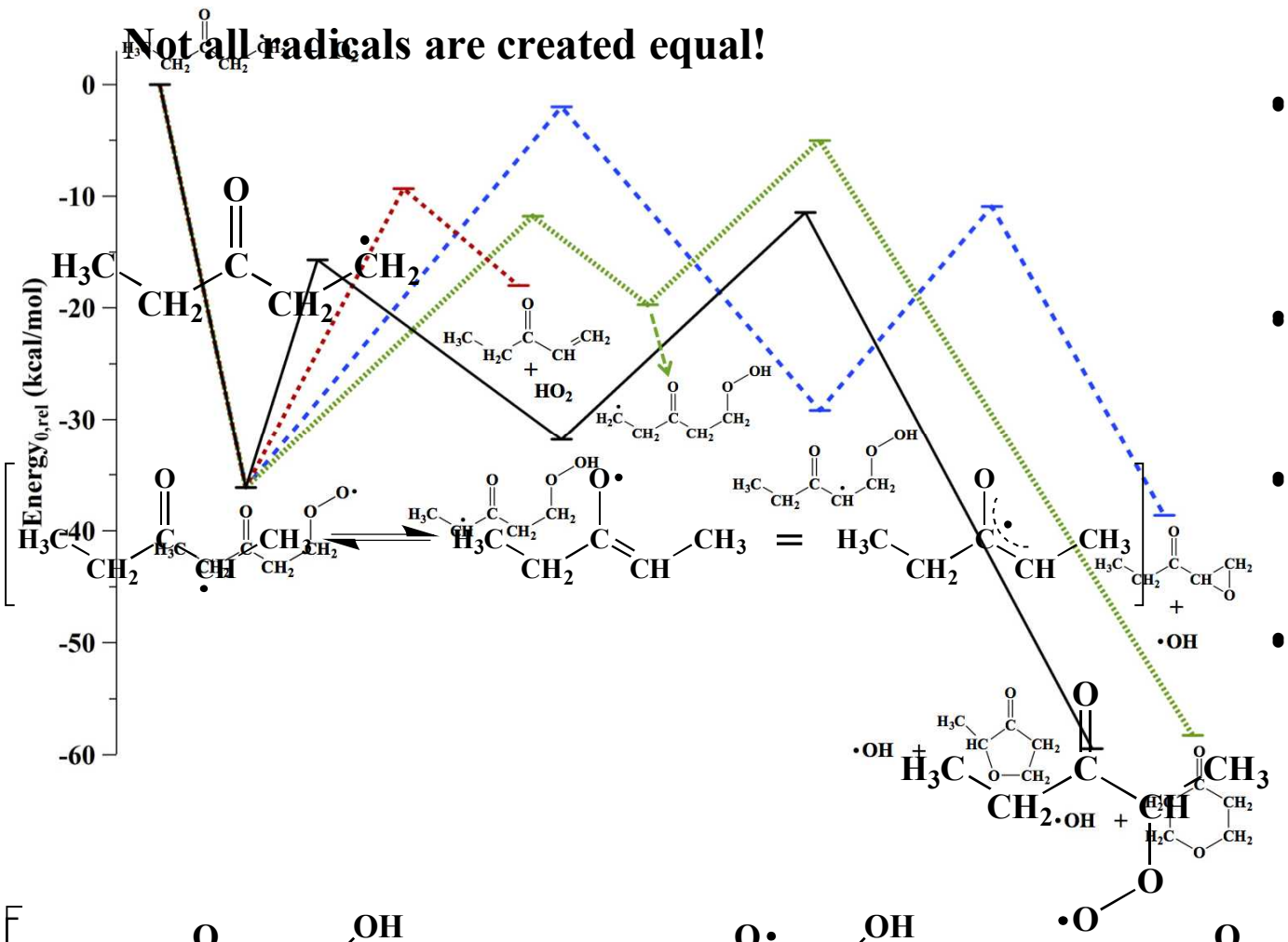
Isolation of Cyclic Ether Channels: Deuterated Diethyl Ketones



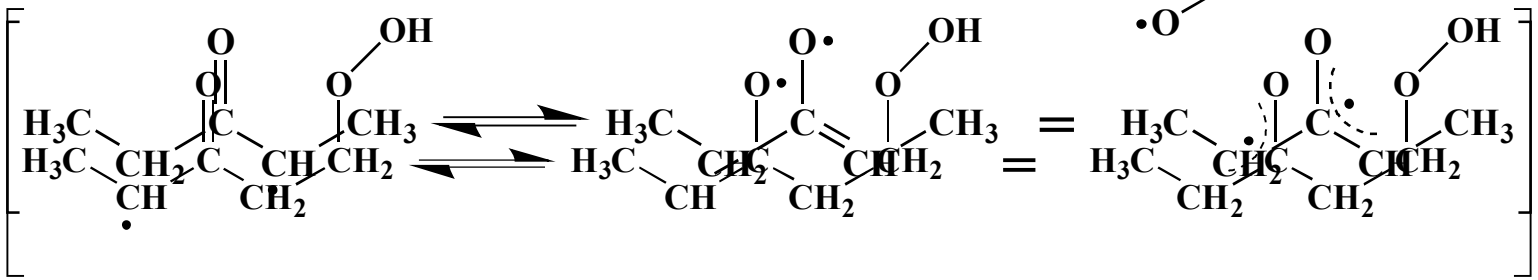
2 channels available for 5-membered ring cyclic ether + OH



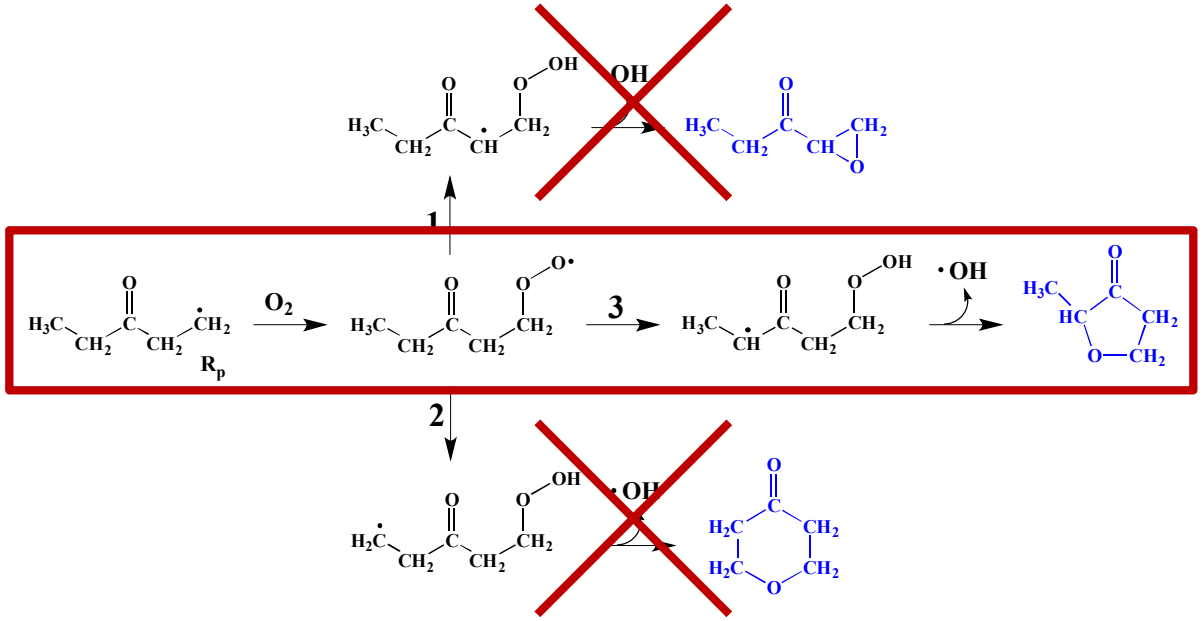
Why Cyclic Ether Selectivity in Diethyl Ketone Oxidation?



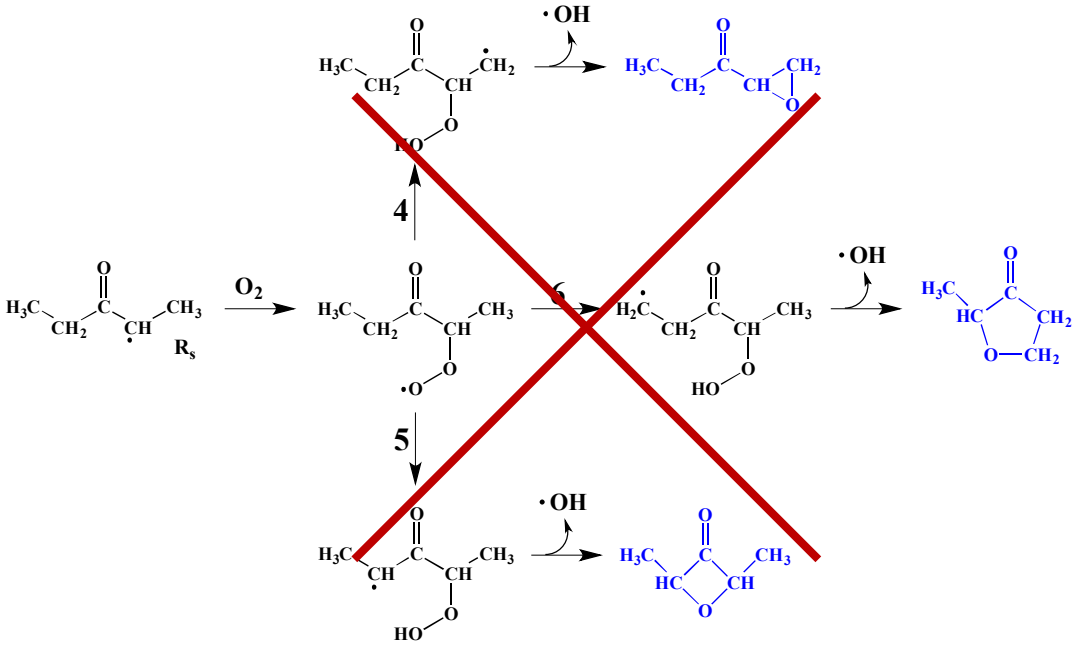
- Resonance stabilization of secondary radical
- RO_2-well ≈ 34 kcal/mol – shallow!
- $R + O_2\rightleftharpoons RO_2$ shifted to reactants
- 5-membered ring HO_2-elimination pathway lowest energy and benefits from resonantly stabilized QOOH



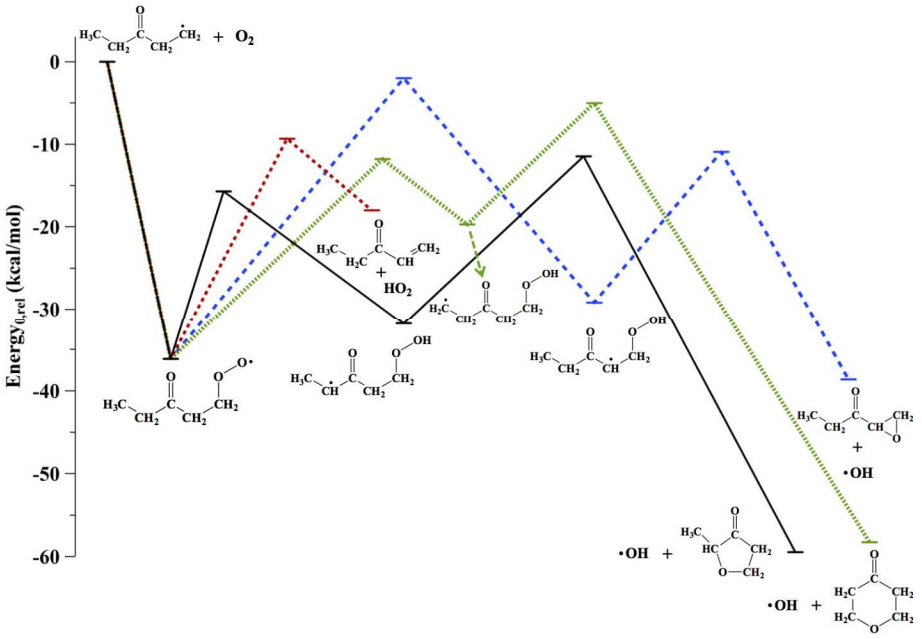
Isolation of Cyclic Ether Channels: Deuterated Diethyl Ketones



Combination of experiment and theory allows assignment of predominant channel

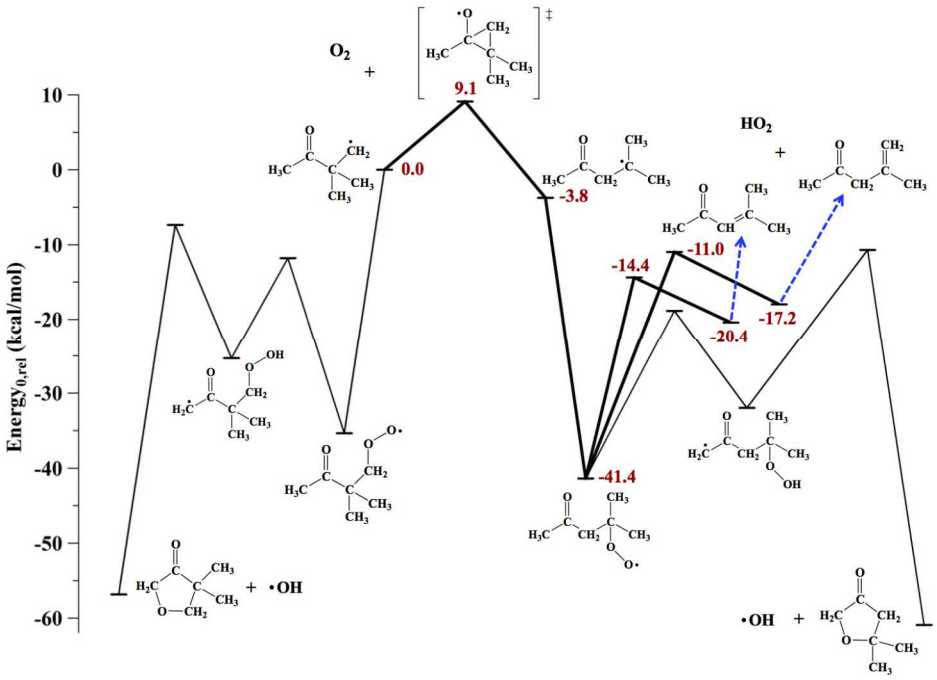


Why is Very Little Cyclic Ether produced in Methyl-tert-butyl Ketone Oxidation Compared to Diethyl Ketone?



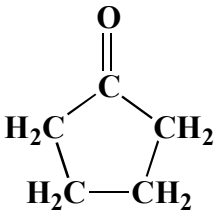
- **Lowest energy oxidation pathway for diethyl ketone is formation of 5-membered ring Cyclic Ether + OH**
- **HO_2-elimination competes as well**

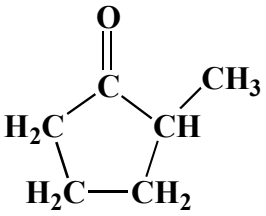
- **Radical rearrangement of methyl-tert-butyl ketone radical is fast relative to O_2 addition**
- **Lowest energy pathway of rearranged tertiary radical is HO_2-elimination**
- **Ignition delay experiments consistent (Chang, Fernandes et al.)**

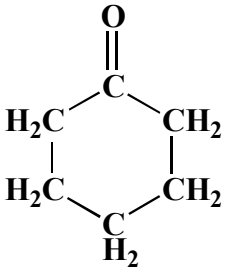


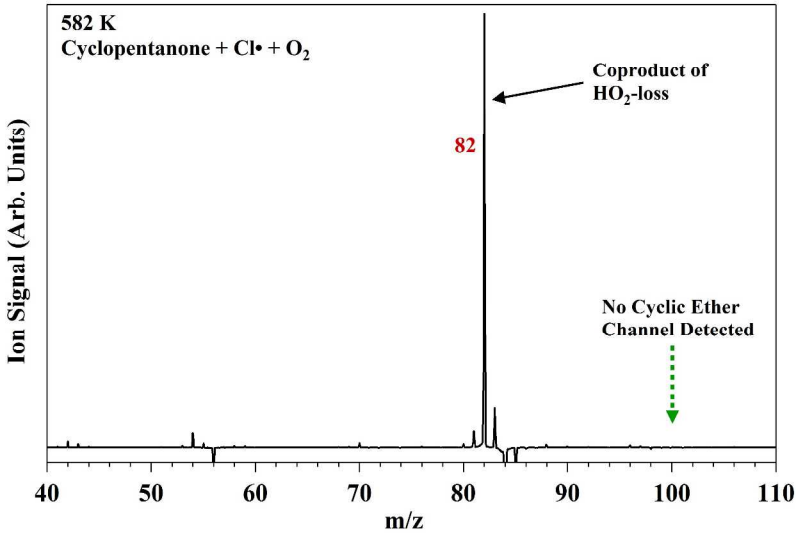
Investigating fundamental ignition chemistry of promising biofuels: Cyclic ketones

- **Cyclic ketones** almost exclusively undergo HO_2-elimination. No cyclic ether product observed.

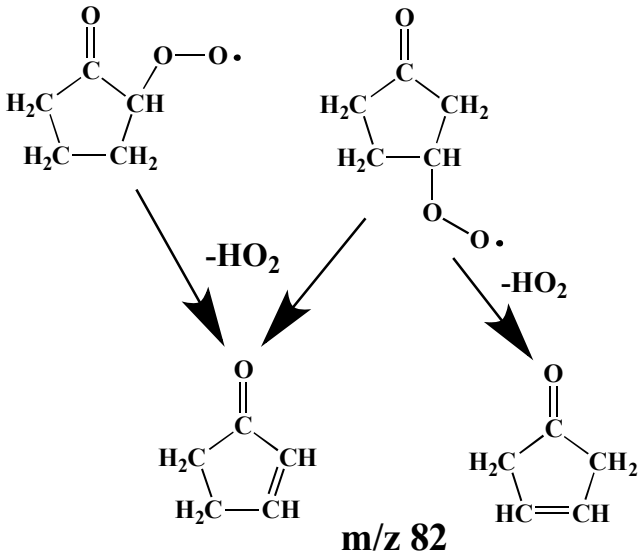


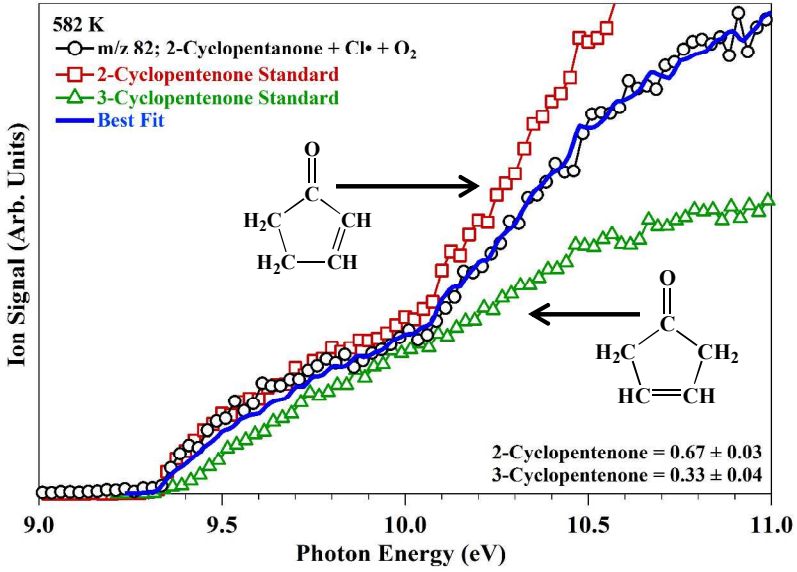






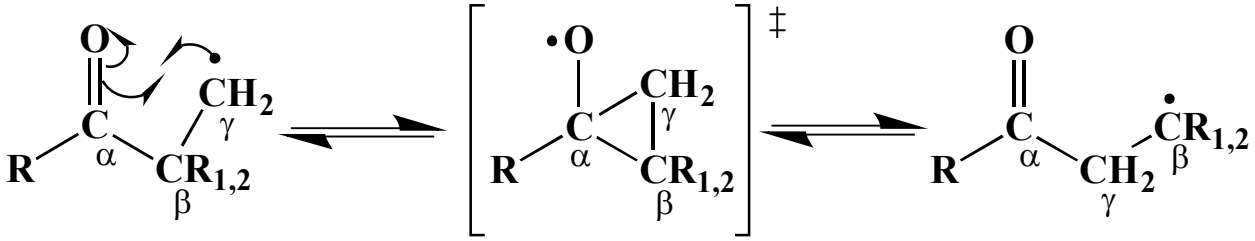
- **Very stable** oxidation products can slow or prevent ignition



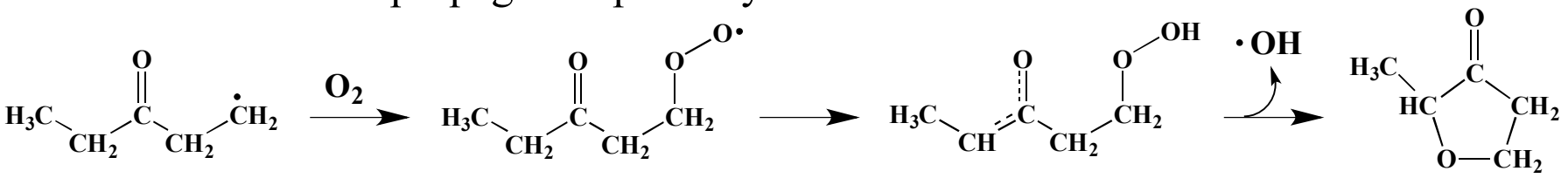


Oxidation of ketones: What have we learned?

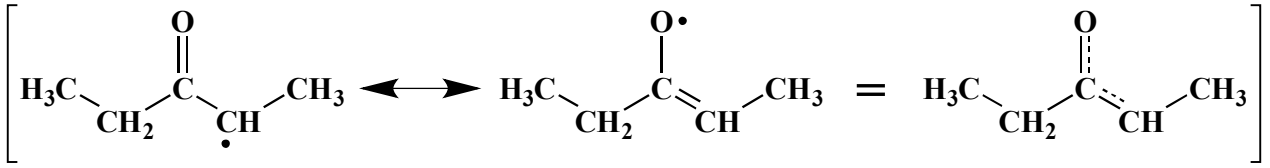
- Thermodynamic driving force leads to rapid radical rearrangement of γ-radicals



- These internal isomerizations lead to new chain-terminating HO_2-elimination channels.
- 5-membered ring cyclic ether formation via resonantly-stabilized QOOH dominates chain-propagation pathways.



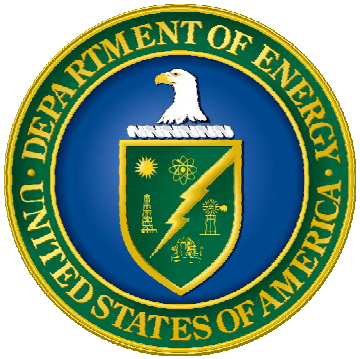
- Resonance stabilization of initial vinoxylic radicals results in very low reactivity.



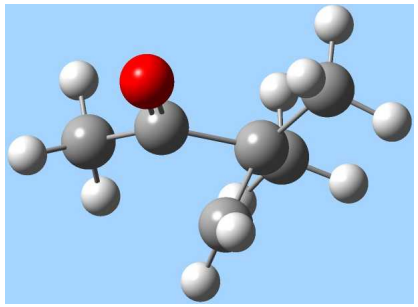
- Cyclic ketones react almost exclusively by chain-terminating HO_2-elimination.

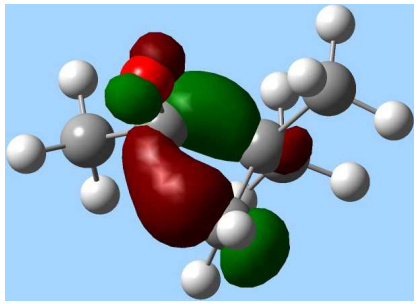
Thanks to:

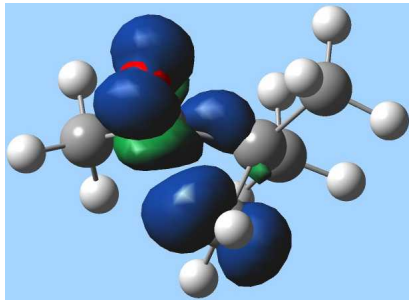
- Dr. Craig Taatjes, Dr. David Osborn et al.
- Prof. Barry Carpenter
- Dr. Darryl Sasaki
- Howard Johnson
- Collaborators at MIT, jbei, Aachen, NSRL, MSU

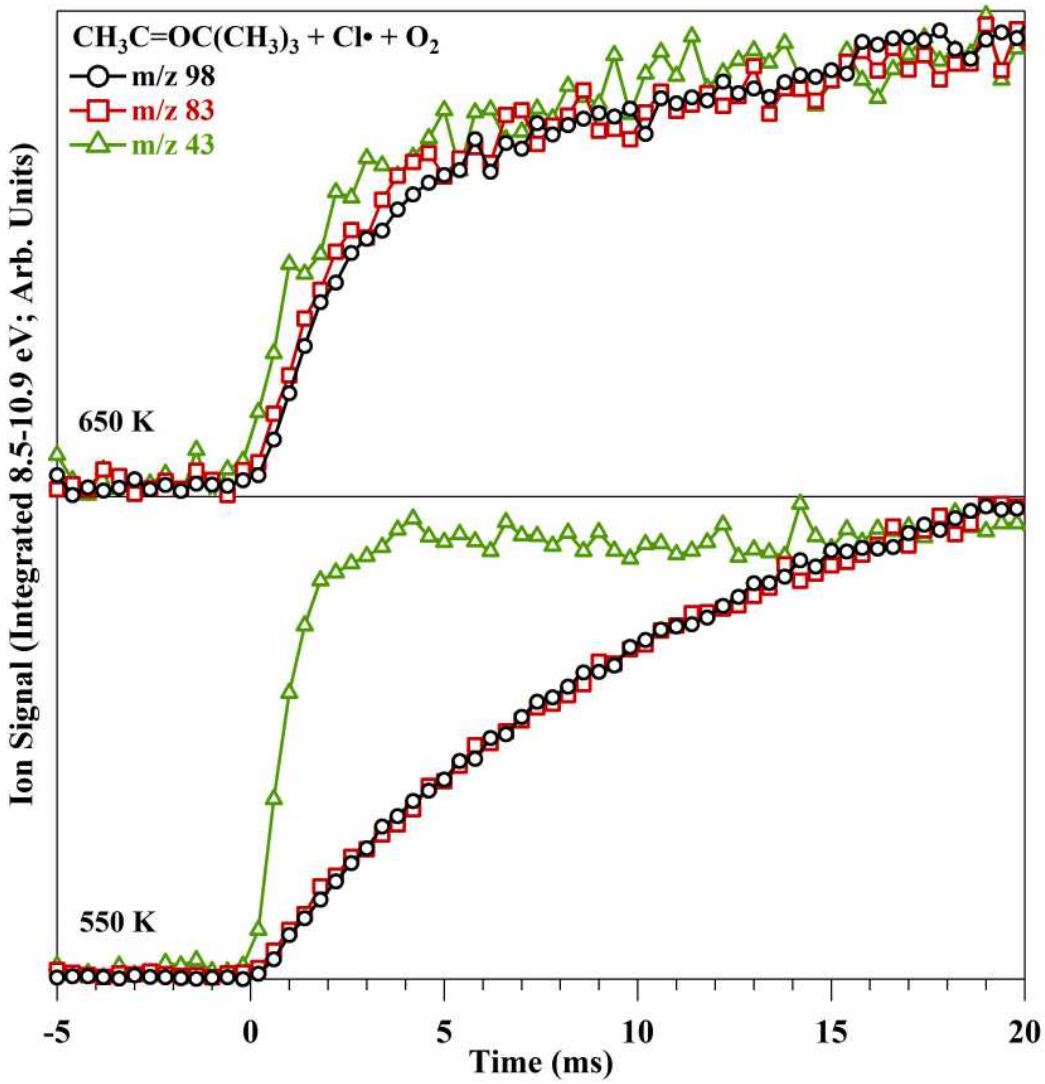


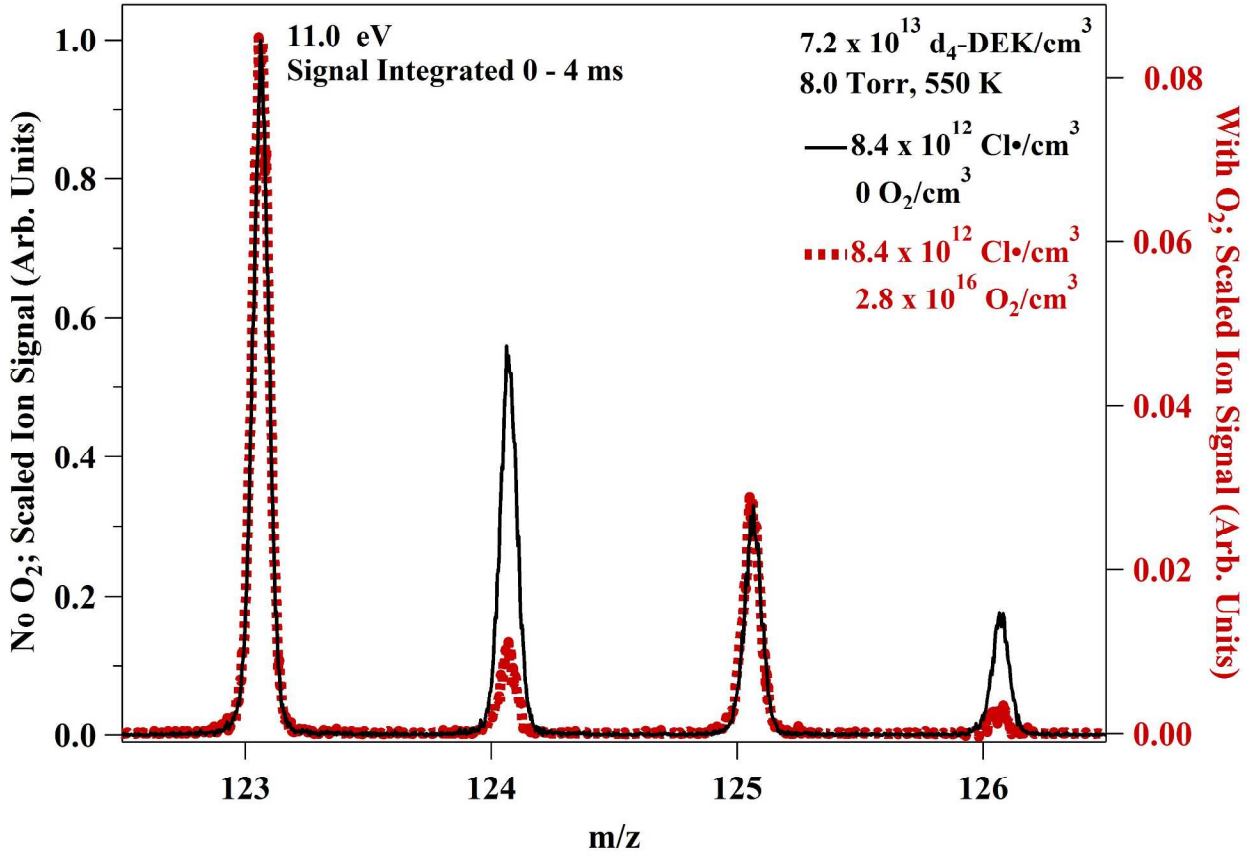
This work is funded by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy, under contract DE-AC04-94AL85000.








CH3C=OC(CH3)3 + Cl• + O2
m/z 98
m/z 83
m/z 43
650 K
550 K
Ion Signal (Integrated 8.5-10.9 eV; Arb. Units)
-5
0
5
10
15
20
Time (ms)


11.0 eV
Signal Integrated 0 - 4 ms
7.2 x 10^13 d4-DEK/cm^3
8.0 Torr, 550 K
8.4 x 10^12 Cl•/cm^3
0 O2/cm^3
8.4 x 10^12 Cl•/cm^3
2.8 x 10^16 O2/cm^3
No O2; Scaled Ion Signal (Arb. Units)
With O2; Scaled Ion Signal (Arb. Units)
m/z
1.0
0.8
0.6
0.4
0.2
0.0
0.08
0.06
0.04
0.02
0.00
123
124
125
126