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Uncovering Details of Combustion Chemistry by Using Synchrotron Photoionization Mass Spectrometry

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Measurements Confirm Enol Production from OH-Initiated Alkene Oxidation

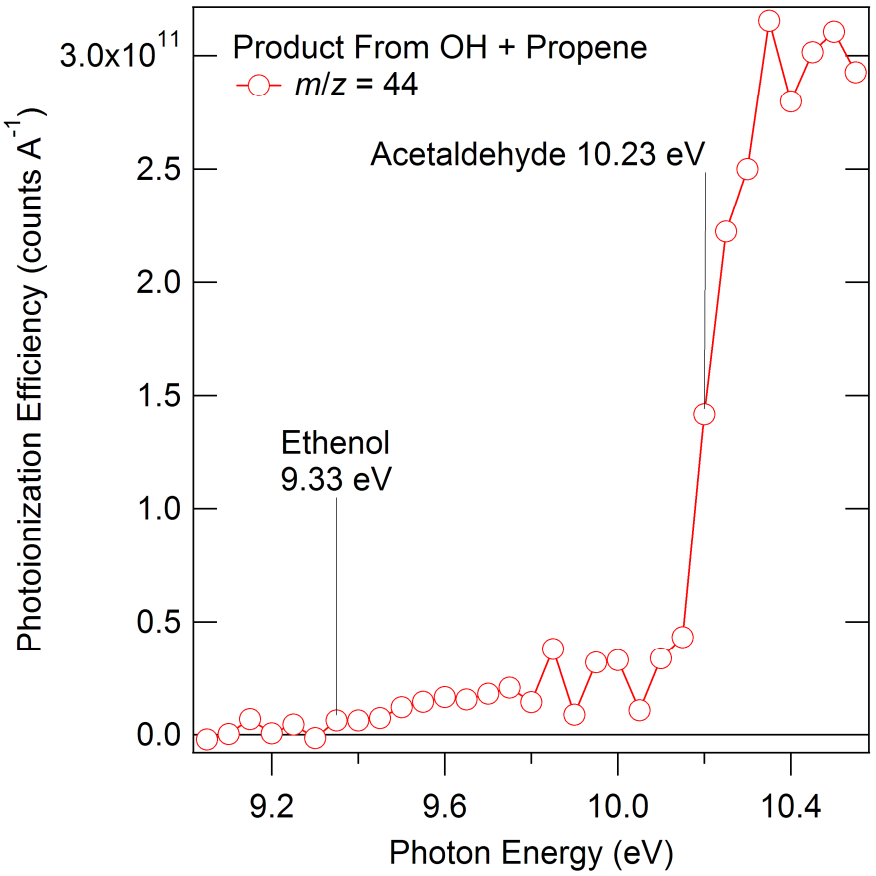
- OH is formed by 248 nm photolysis of H_2O_2 or HNO_3
- Alkene is in great excess
- At 500 K, substantial ethenol is observed from OH + ethene

- OH + propene reaction has been shown to produce C_2H_4O and C_3H_6O products (Hoyermann, K.; Sievert, R. *Ber. Bunsen-Ges. Phys. Chem.* 1979, *83*, 933)

Are these products the enols??

***m/z* = 58 is propenol**

But *m/z* = 44 is mostly acetaldehyde



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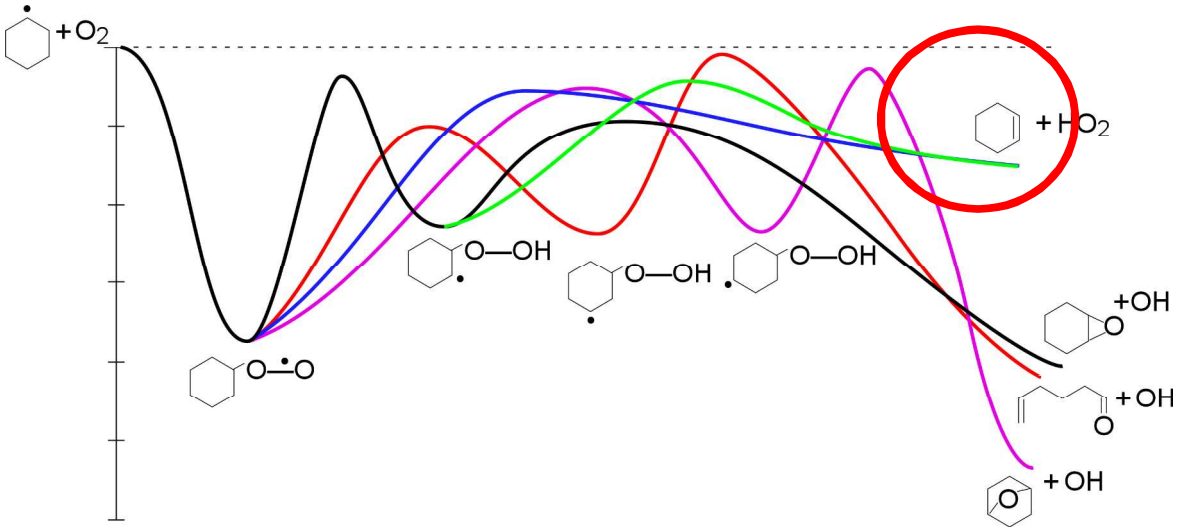
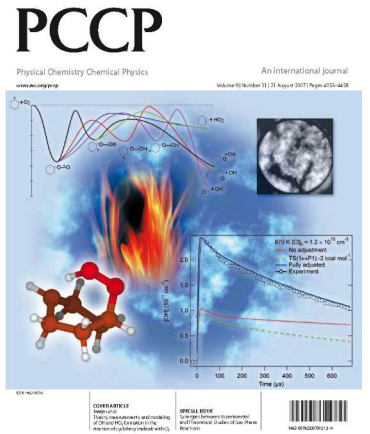
Ignition Chemistry of Cycloalkanes is of Increasing Technological Importance





- Fuels from non-traditional hydrocarbon sources (e.g., oil sands) have more cyclic alkanes (napthenes)
- Measurements and master equation modeling of OH and HO_2 from prototype cyclohexyl + O_2 system (Knepp et al., PCCP 9, 4315 (2007))
- Cycloalkene oxidation is important subsequent step – chemistry remains poorly understood

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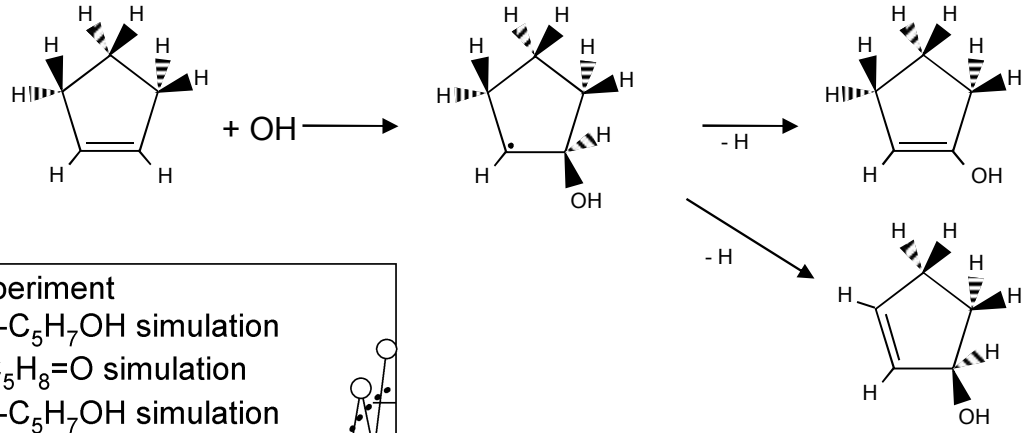
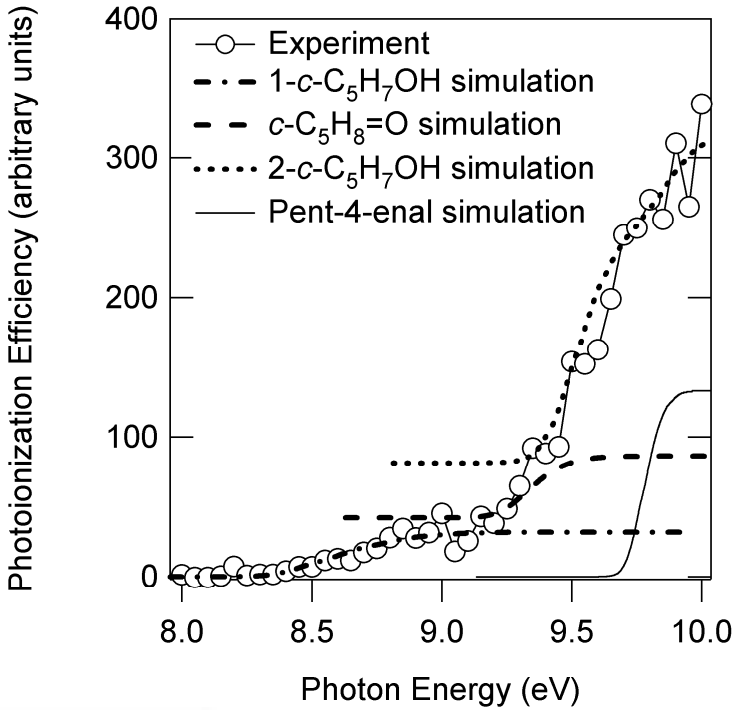
OH-initiated Oxidation of Cycloalkenes Shows Two Mechanistic Pathways





- OH-initiated oxidation of cyclopentene shows product of OH addition and (possibly O_2 mediated) H-atom loss
  - Like ethene and propene
- Only cyclic C_5H_8O isomers are observed

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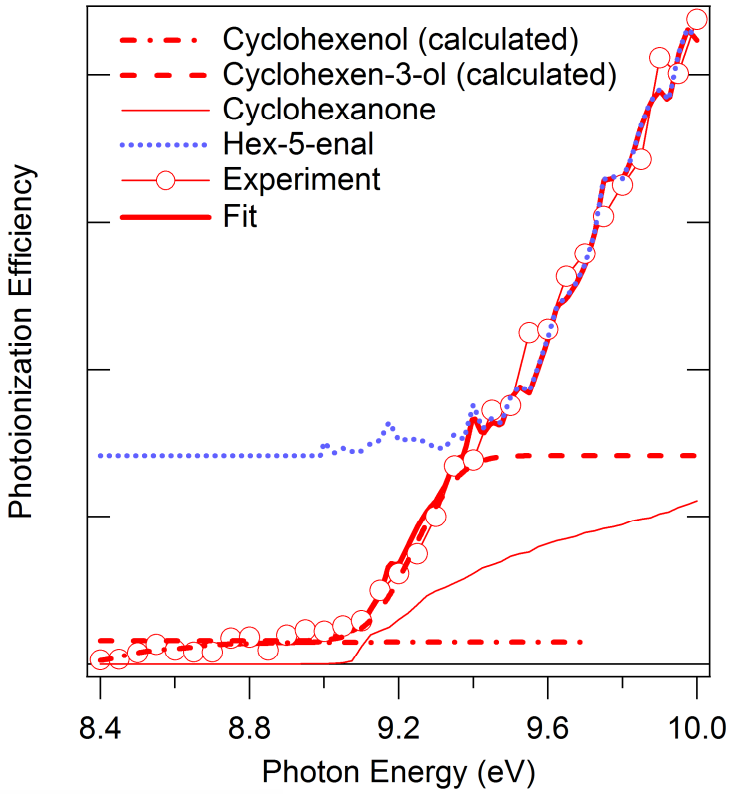
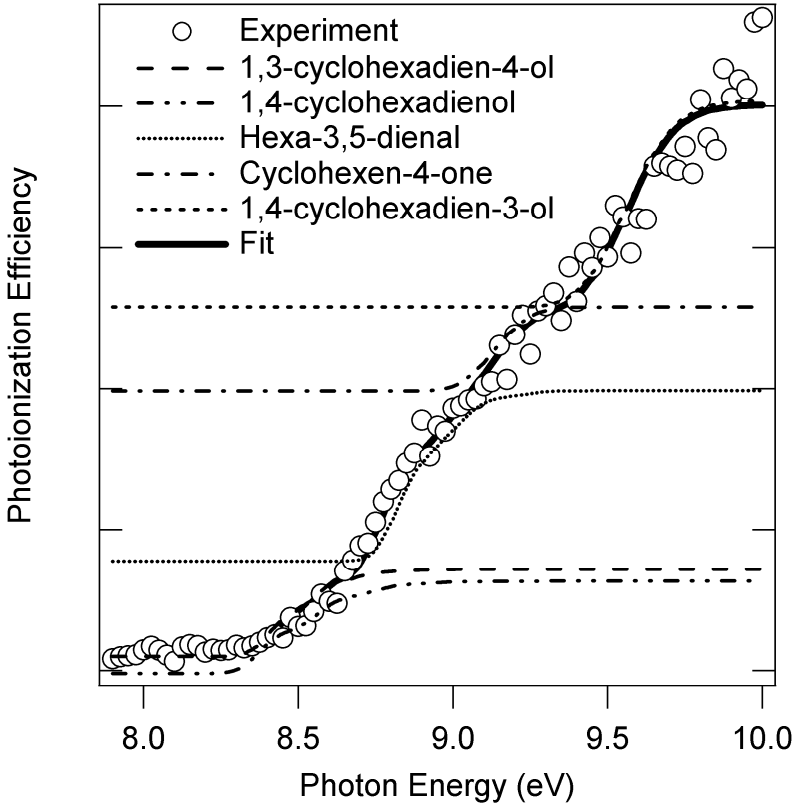
Six-Carbon Cycloalkenes Show Ring-Opening in OH-Initiated Oxidation





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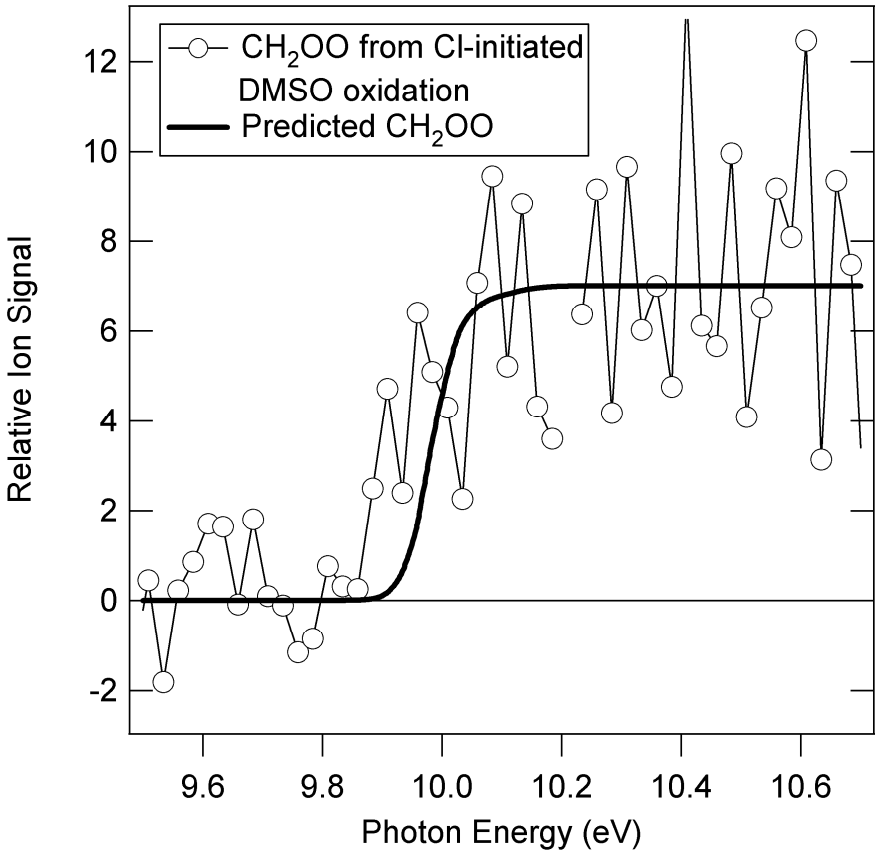
Tunable Synchrotron Photoionization Can Identify Isomeric Products

- The ozonolysis of alkenes is now generally accepted to go via a carbonyl oxide intermediate ("Criegee intermediate")
- These species are predicted to be important tropospheric reactants, affecting HO_x and organic peroxides
- Dimethyl Sulfoxide oxidation may form CH_2OO (Asatryan and Bozzelli, PCCP **10**, 1769 (2008))



had
^
No one ~~has~~ ever seen a gas phase Criegee intermediate

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