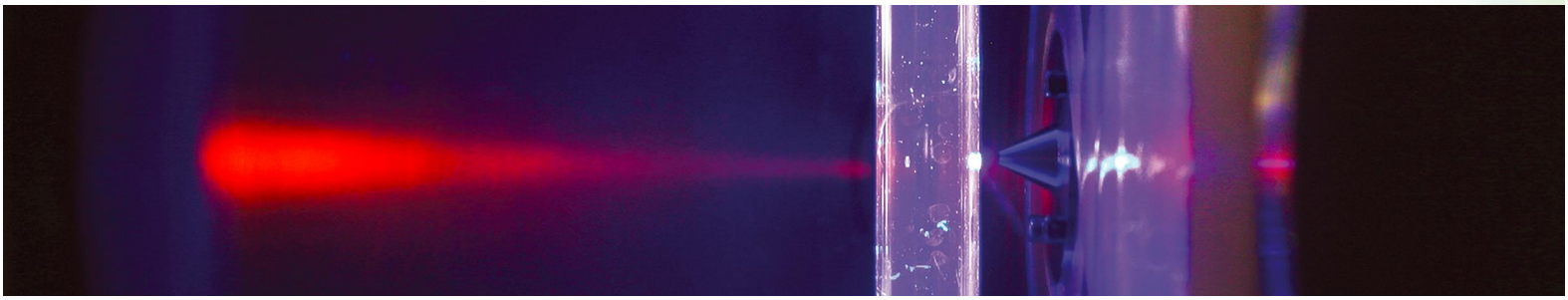
SAND2015-5017C

COMBUSTION RESEARCH FACILITY

The Multichannel Reaction of O(^{3}P) with Cyclopentene

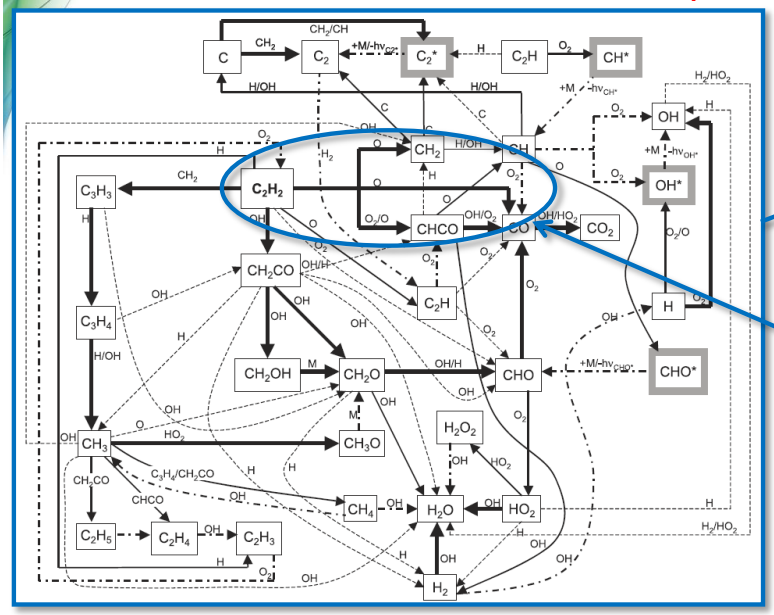


John D. Savee, Judit Zádor, Xiaohu Li, Ahren Jasper, Craig A. Taatjes, and David L. Osborn
Combustion Research Facility, Sandia National Labs

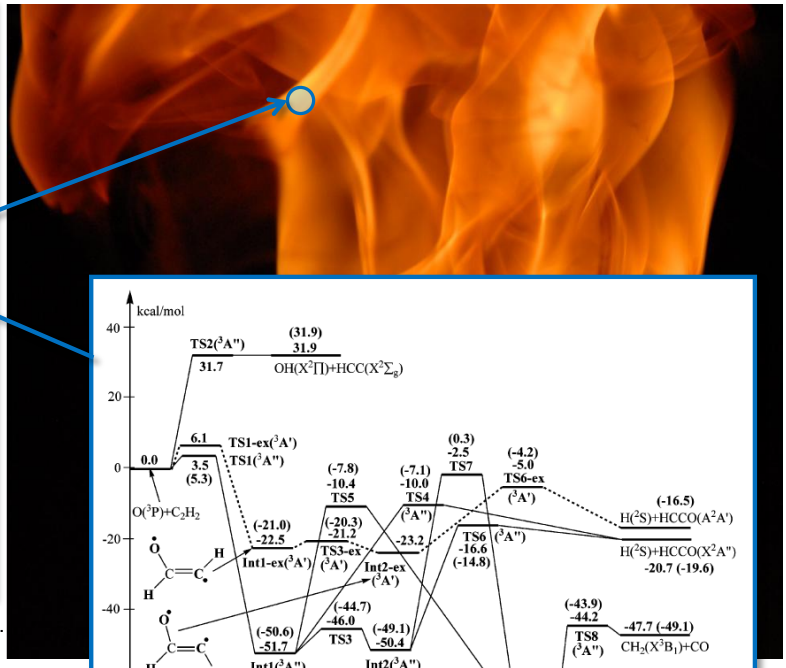
9th International Conference on Chemical Kinetics
Ghent, Belgium
June XX, 2015

Combustion is Complex!

Multiphase, turbulent flow driven by chemical reactions



C.S.T. Marques *et al.*, J. Braz. Chem. Soc. **17**, 302 (2006).



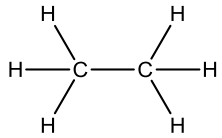
T.L. Nguyen et al., J. Phys. Chem. A 110, 6696 (2006).

Chemical mechanisms identify important reactions, heat release, etc.

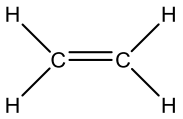
Mechanisms rely on accurate rate constants and branching fractions for individual reactions

O(^{3}P) + unsaturated hydrocarbons

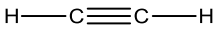
- H-atom abstraction is likely mechanism for O(^{3}P) + alkanes; what about O(^{3}P) + alkenes/alkynes?



ethane (C_2H_6)

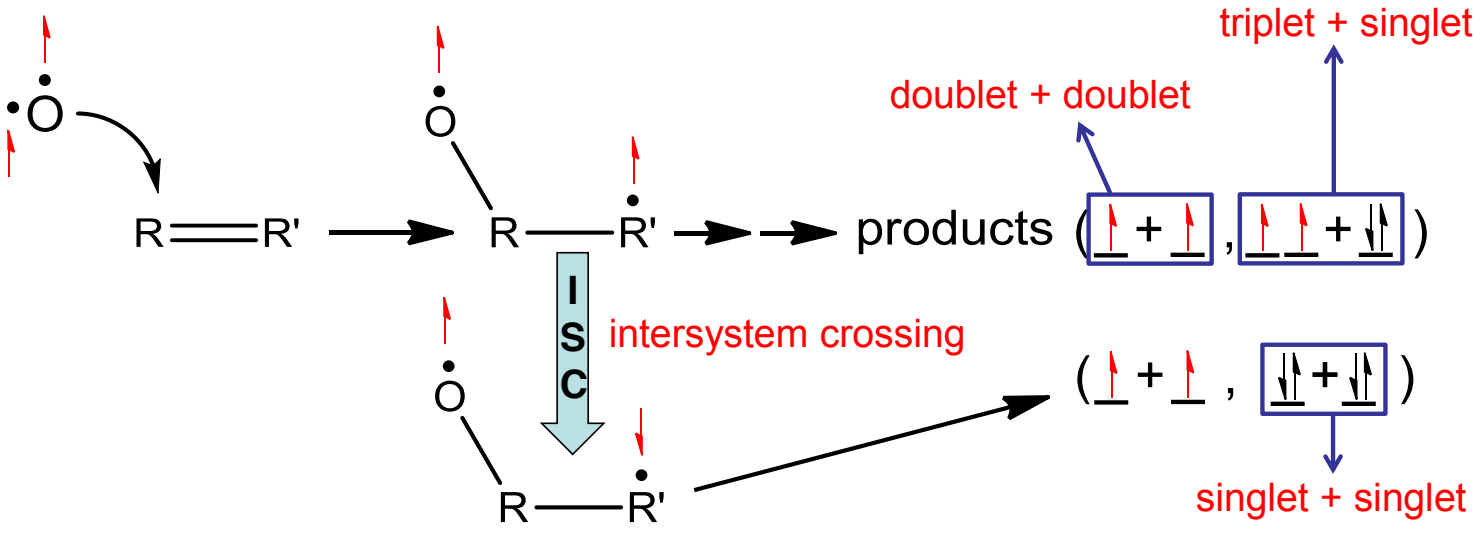
?? 

ethene (C_2H_4)

 ??

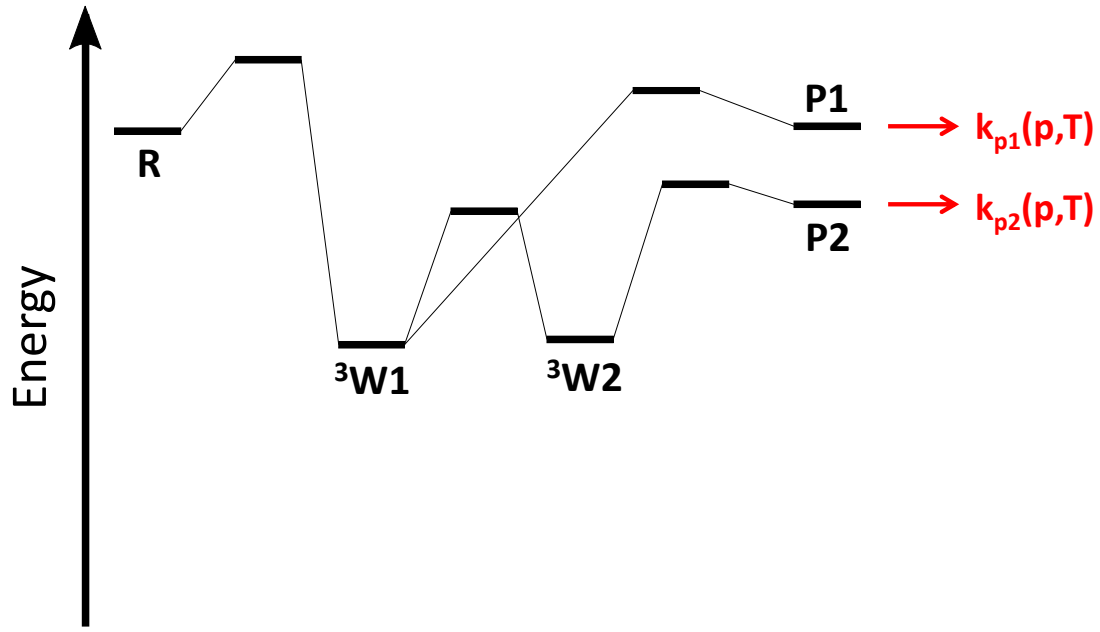
acetylene (C_2H_2)

- Abstraction is possible, but so are complex addition pathways:



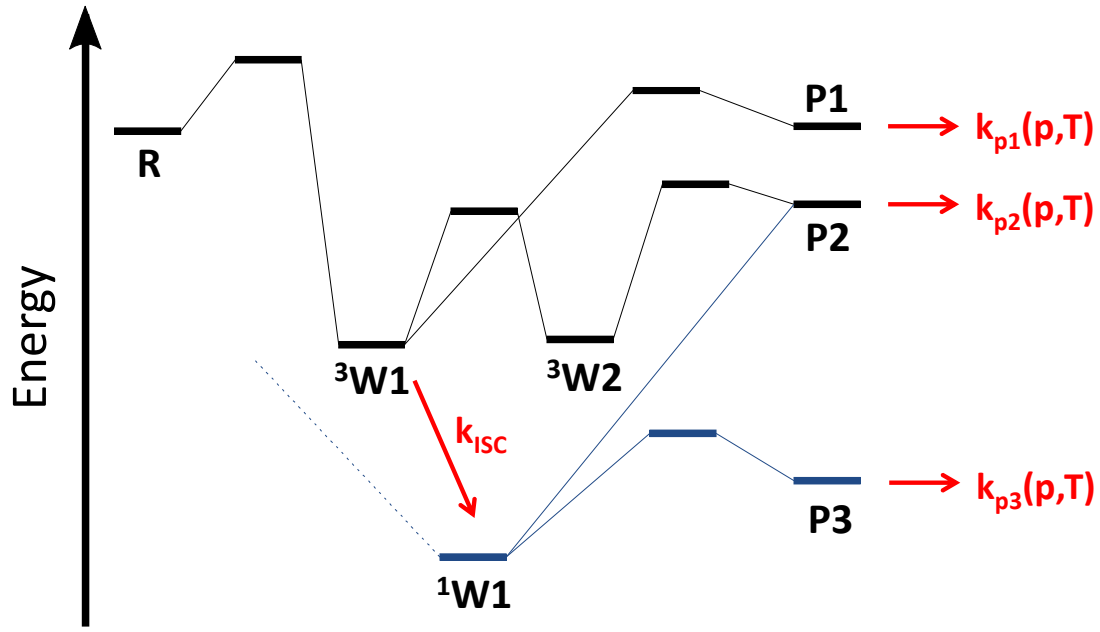
Rate Predictions

- For single potential energy surface, RRKM and master equation calculations allow prediction of k(p,T) from calculated stationary points



Rate Predictions

- Non-adiabatic couplings need to be known if multiple surfaces are involved



- Experiments play a key role in developing predictive models!

Experimental Approaches

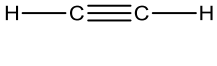
- Traditional approaches:
  - End product analysis (e.g., gas chromatography)
    - Can identify multiple stable products – hard to identify transient species
    - No time resolution; difficult to distinguish primary vs. secondary products
  - Optical methods
    - Offers time resolved product signals (transient + stable)
    - Typically limited to only a few species
- Need time-resolved method for quantifying yields of multiple transient/stable products

Universal Product Detection

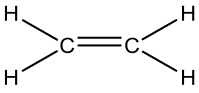
- Mass spectrometry with soft ionization is key – all molecules can be ionized!

- Crossed molecular beams (Casavecchia *et al.*/U. Perugia):
  - 5 - 40 kcal/mol collision energy, single collision environment
  - Tunable low-energy electron impact ionization and quadrupole mass spec.

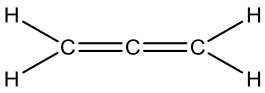
- Multiplexed Photoionization Mass Spectrometry (Osborn/Sandia):
  - Photolytic initiation inside flow reactor – 2 to 10 Torr, 300 to 1000 K
  - Tunable vacuum ultraviolet synchrotron radiation and time-of-flight mass spec.



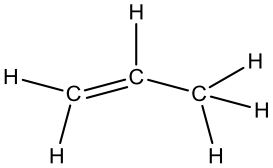
acetylene
ISC < 10 %



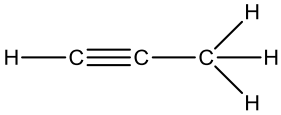
ethene
50%



allene
> 90%



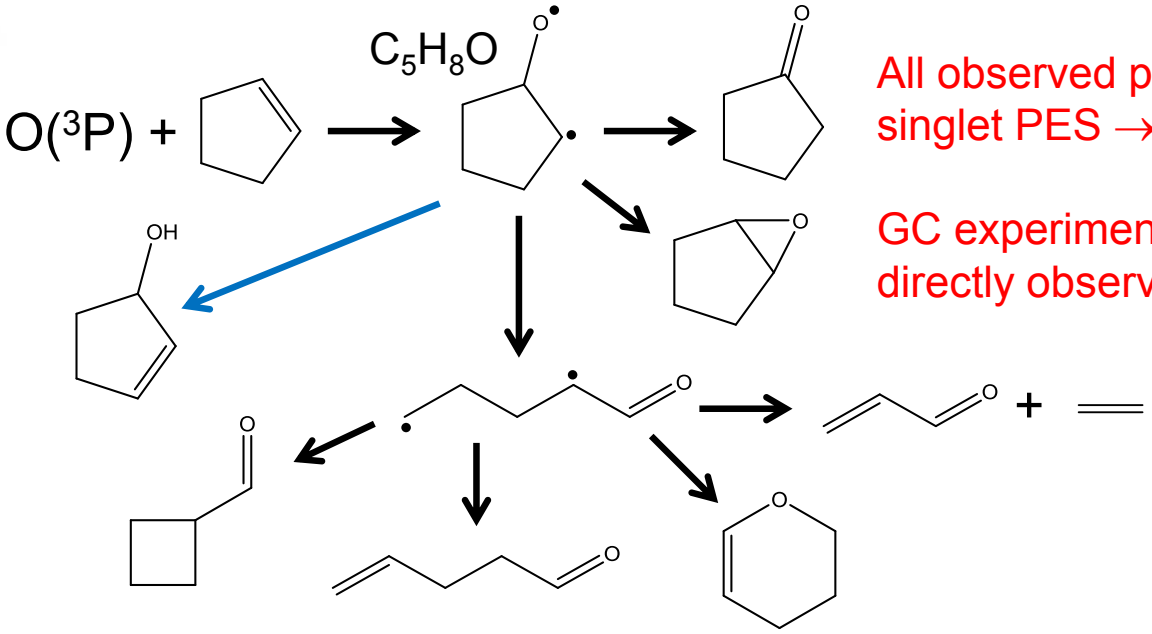
propene
40%



propyne
85%

O(^{3}P) + Cyclopentene

- Gas chromatography (200 Torr, 300 – 450 K):

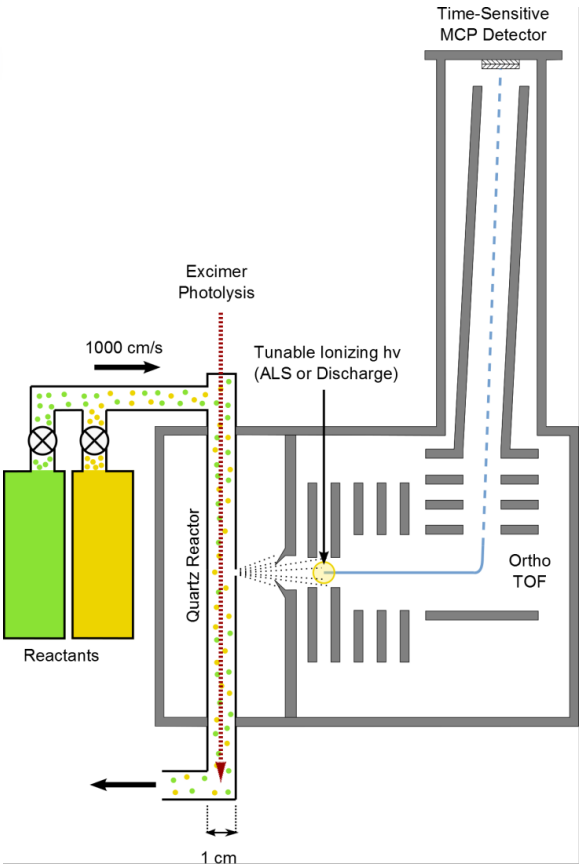


All observed products from singlet PES → 100% from ISC?

GC experiments not capable of directly observing free radicals

- Recent quantum chemical calculations support formation of some of these products on singlet C_5H_8O PES

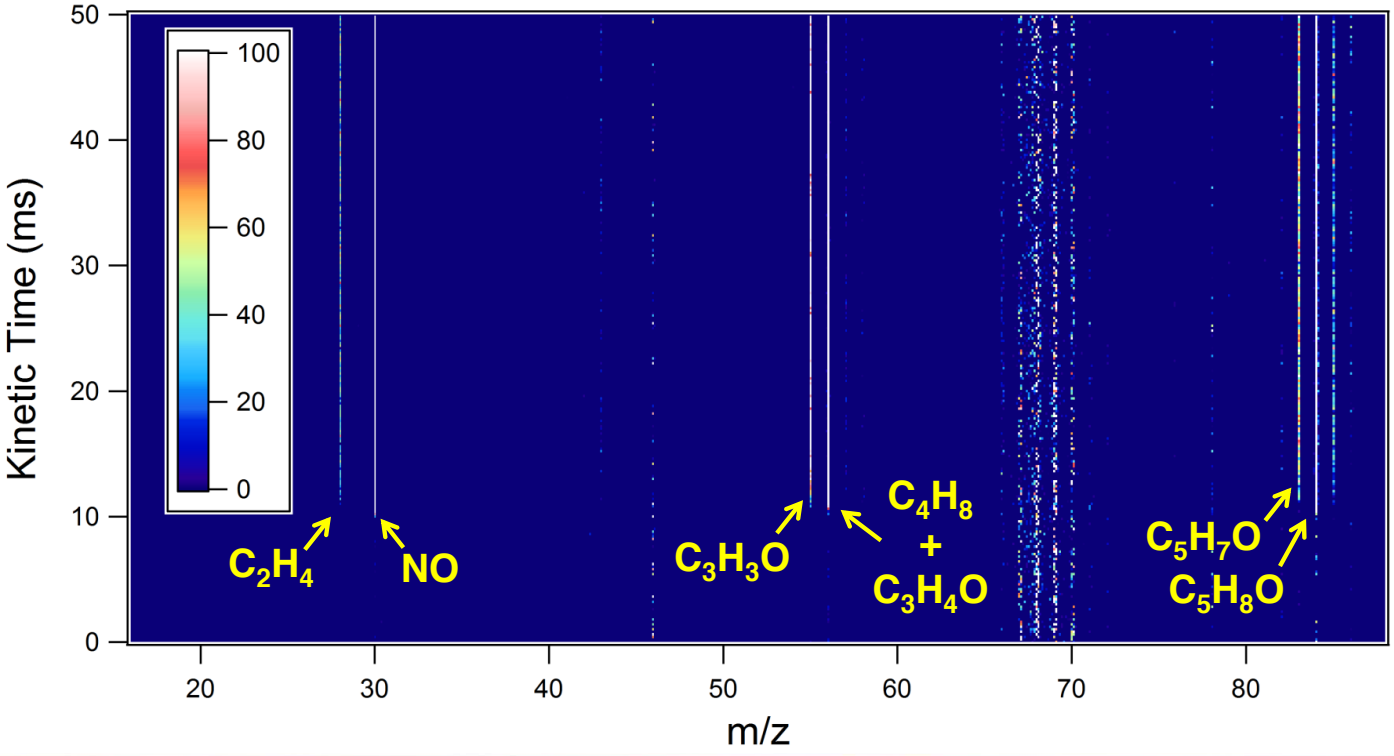
Multiplexed Synchrotron Photoionization Mass Spectrometry



- Reaction initiated by 351 nm photolysis of cyclopentene / NO_2 / He flow; 4 Torr, 298 K
- Products sampled and ionized by tunable synchrotron VUV radiation (Advanced Light Source)
- 50 kHz time-of-flight detection – full mass spectrum every 20 μs
- Three-dimensional dataset, I(*m/z*, *t*, *E*):
  - mass-to-charge (*m/z*)
  - time relative to photolysis (*t*)
  - photoionization energy (*E*)

Time-Resolved Mass Spectrum

$O(^3P)$ + cyclopentene
10.6 eV / 300 K / 4 Torr



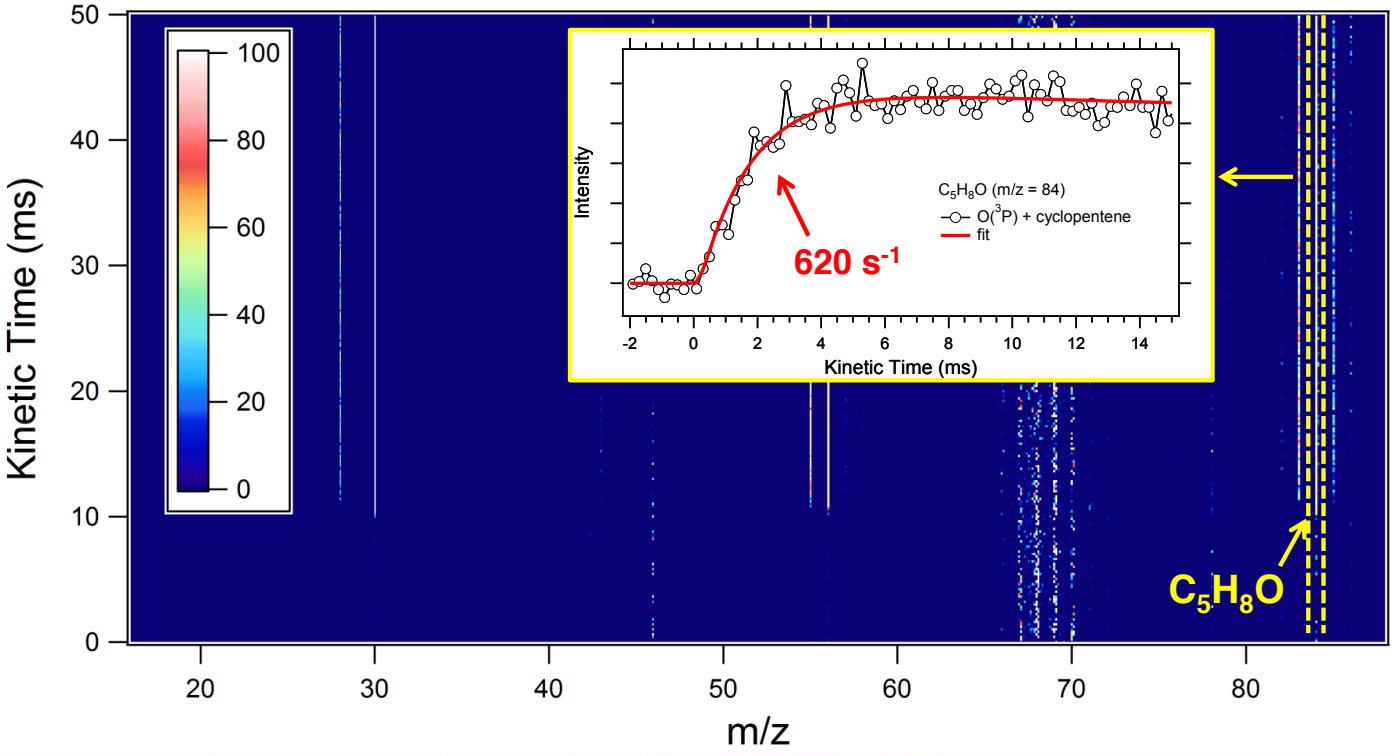
Time-Resolved Mass Spectrum

$O(^3P)$ + cyclopentene
10.6 eV / 300 K / 4 Torr

$[c\text{-}C_5H_8] = 2.6 \times 10^{13}$ cm^{-3}
$k(O(^3P) + c\text{-}C_5H_8) = 2.1 \times 10^{-11}$ cm^3 s^{-1}
$[NO_2] = 1.0 \times 10^{13}$ cm^{-3}
$k(O(^3P) + NO_2) = 1.0 \times 10^{-11}$ cm^3 s^{-1}

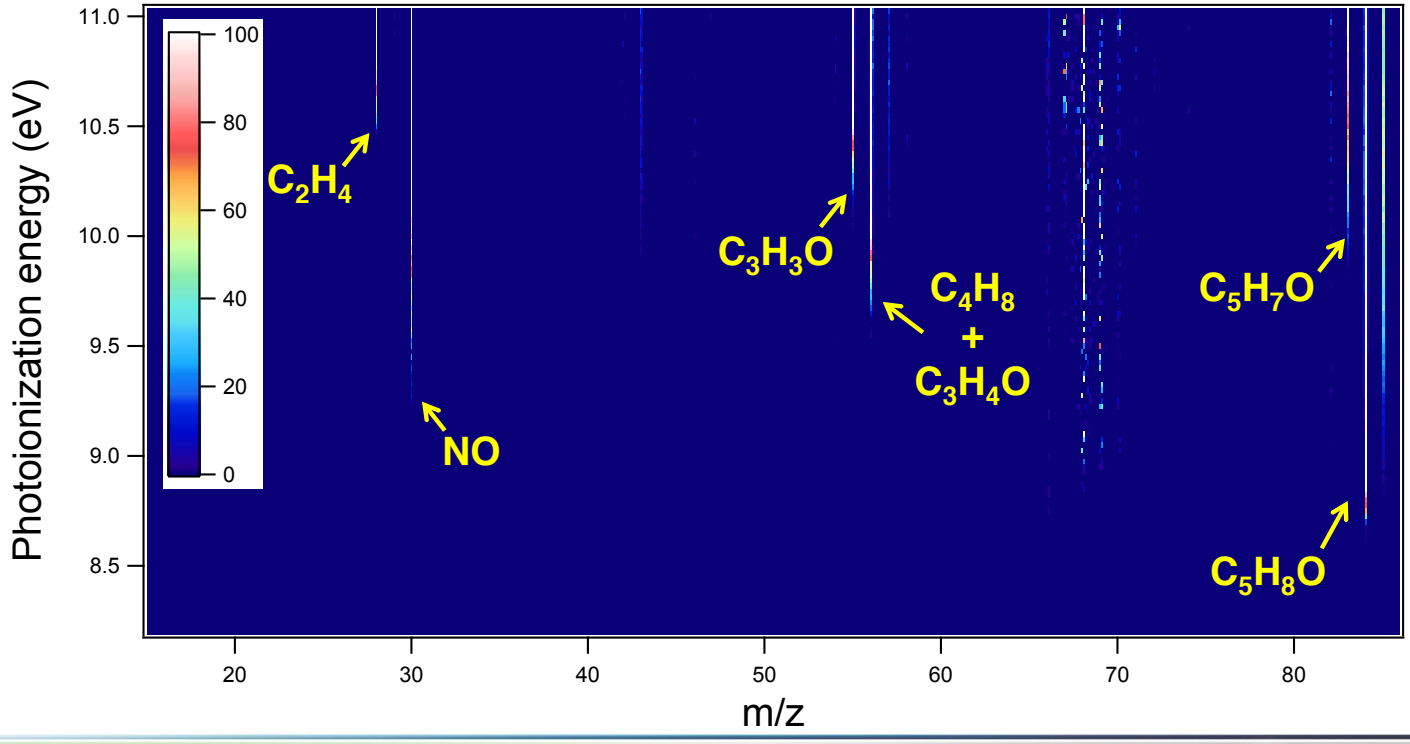
All observed time-resolved products are consistent with direct formation from $O(^3P)$ + cyclopentene

~ 650 s^{-1} total loss rate for $O(^3P)$

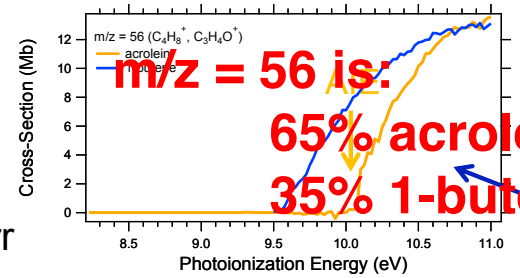


Photoionization Spectra

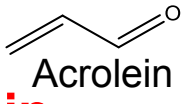
$O(^3P)$ + cyclopentene
0 - 100 ms / 300 K / 4 Torr



Photoionization Spectra

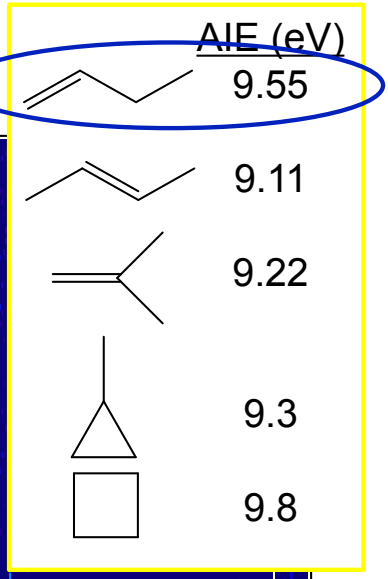


m/z = 56 is:
65% acrolein
35% 1-butene

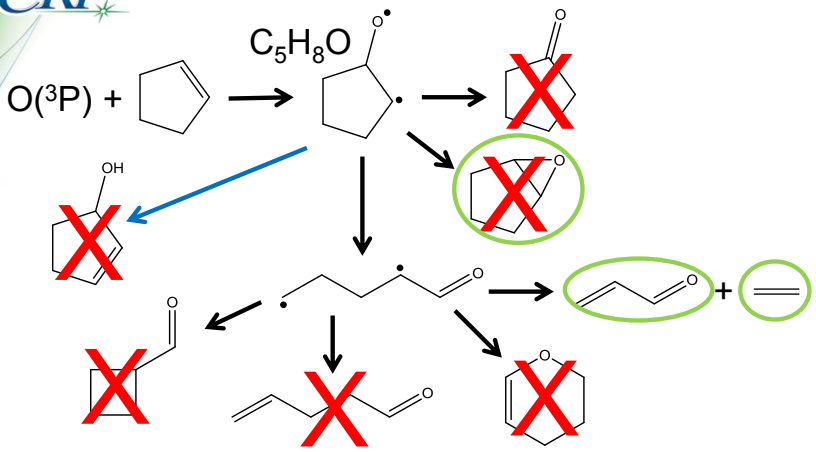


AIE = 10.11 eV

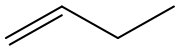
$O(^3P)$ + cyclopentene
0 - 100 ms / 300 K / 4 Torr

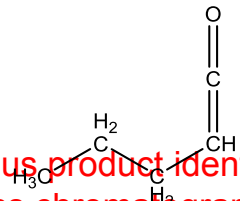


C_5H_8O

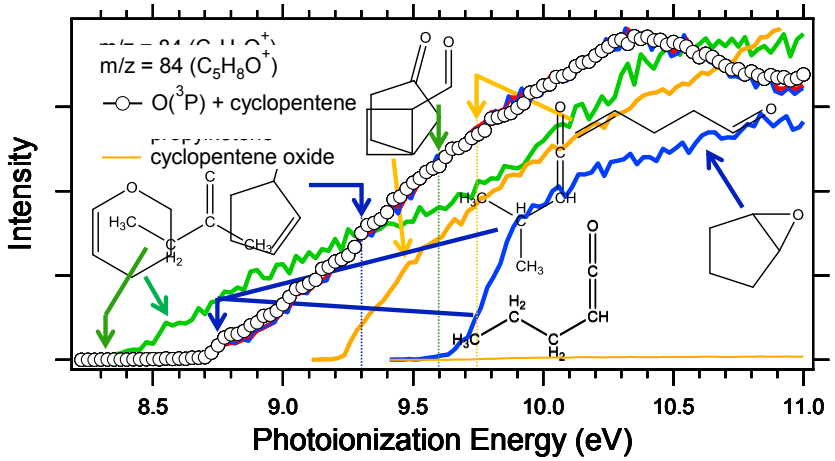


New Products:

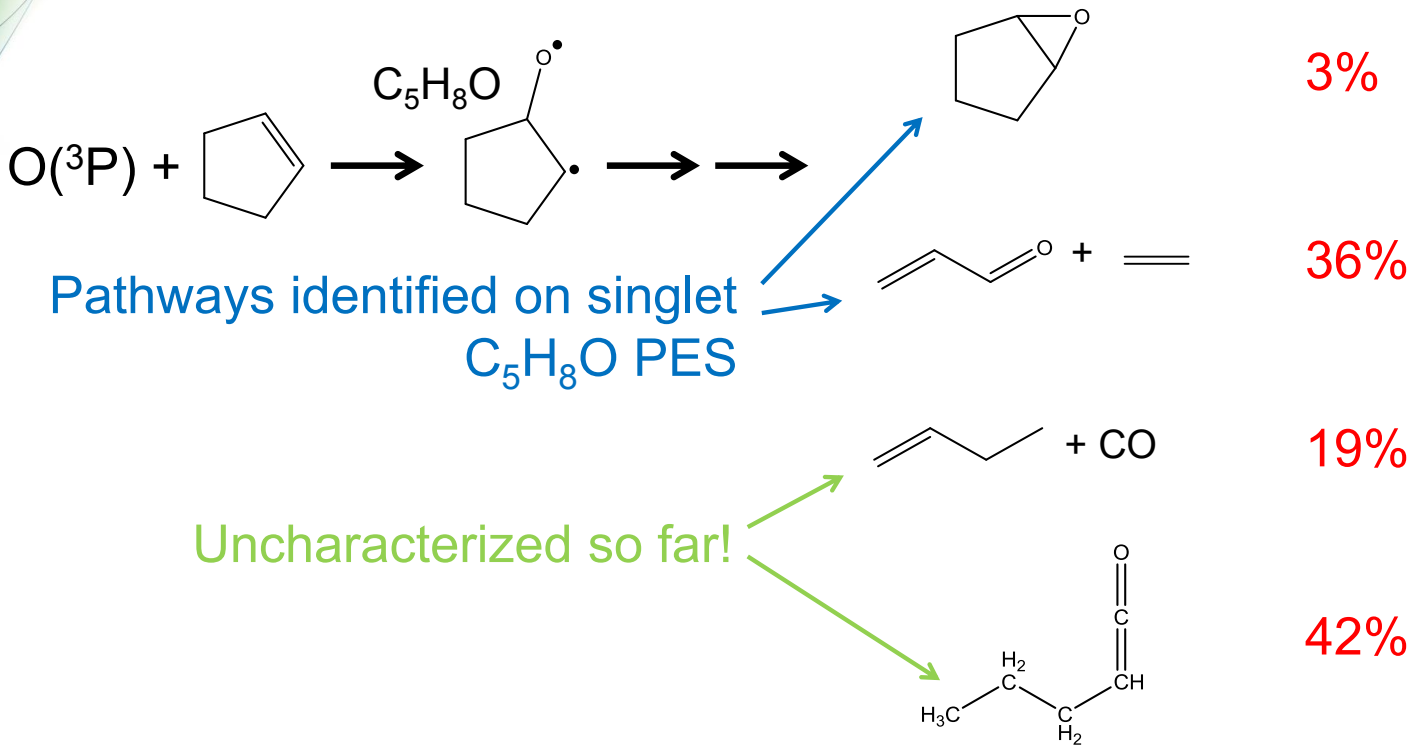




Previous product identification done with gas chromatography – probably not sensitive to ketenes!



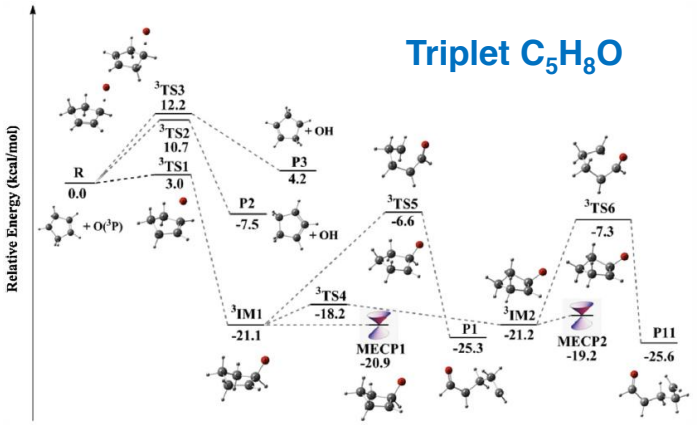
Branching Fractions



Do all products arise from intersystem crossing on C_5H_8O PES?

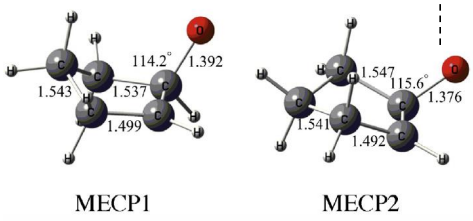
Previous C_5H_8O PES Calculations

- Guided by products identified via gas chromatography (Cvetanovic et al.)
  - No product formation on triplet PES, implies 100% of reaction proceeds through ISC



CCSD(T)//MP2/6-311G(d,p)

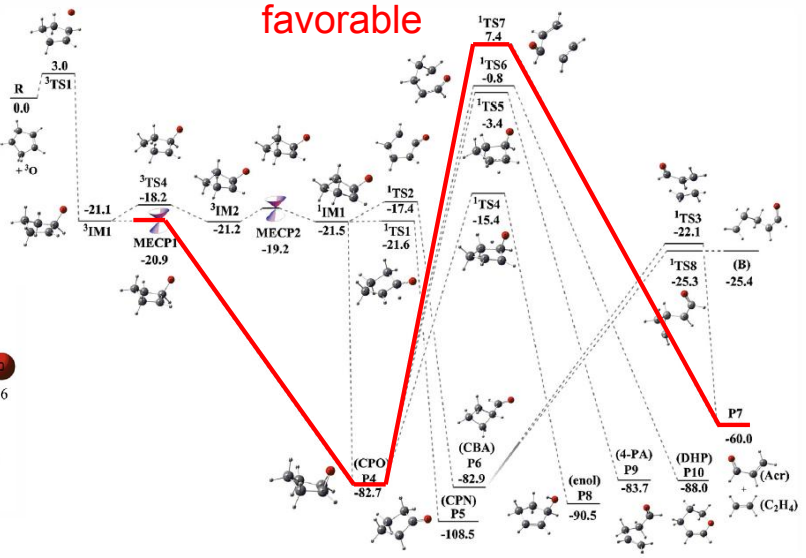
minimum energy crossing points occur near initial adduct



MECP1 MECP2

No pathways to 1-butene + CO or propylketene

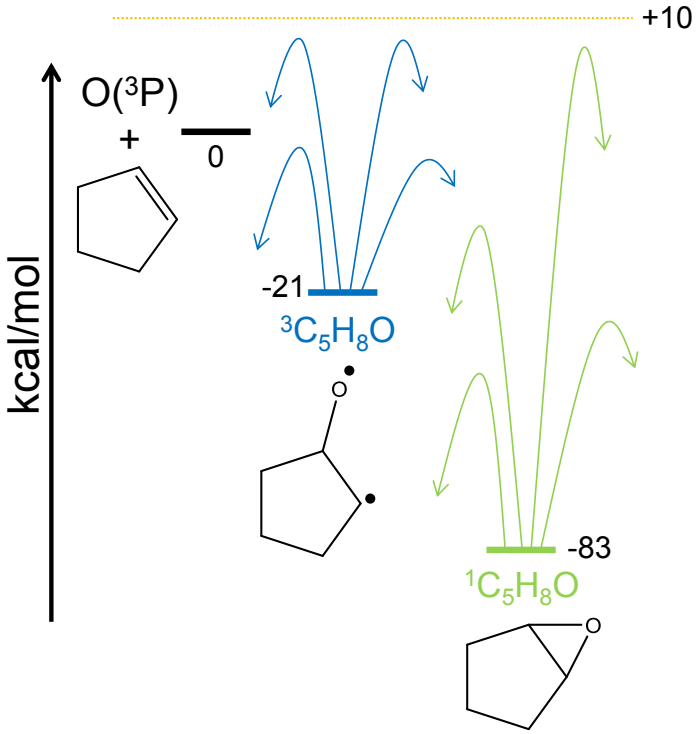
Existing pathway to acrolein + ethene does not seem favorable



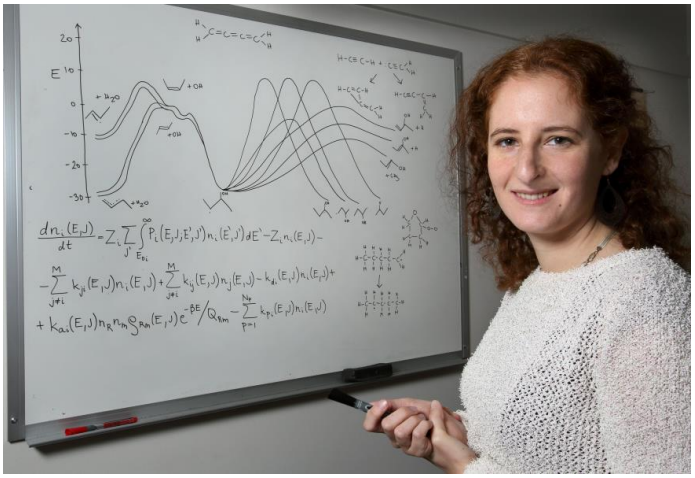
H. Zhao *et al.*, *J. Mol. Graph. Mod.* **51**, 184 (2014).

New PES Exploration Using Kinbot

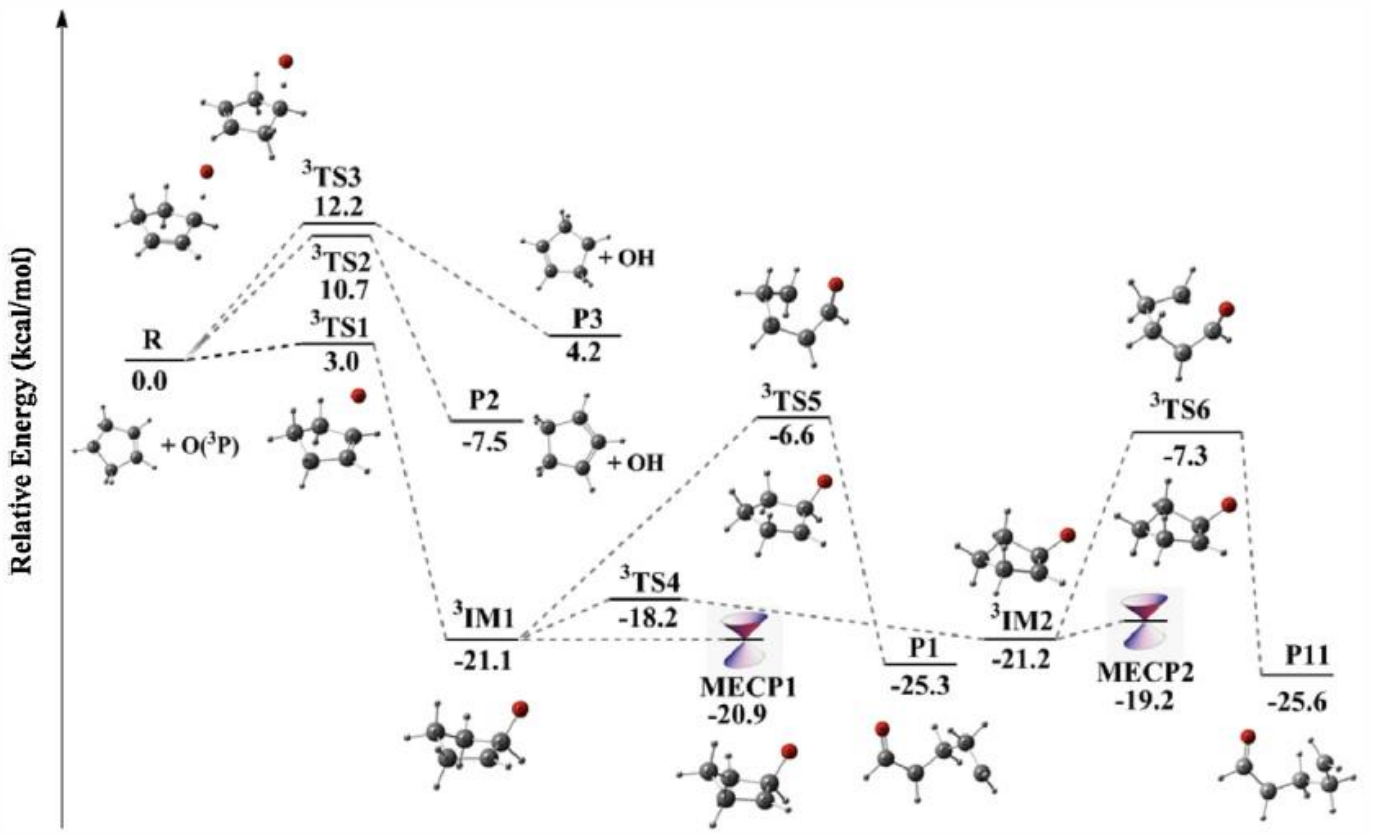
- Systematic exploration of potential energy surfaces!
- Scheme for exploring lowest-lying triplet and singlet C_5H_8O PESs:



Judit Zádor (Sandia)

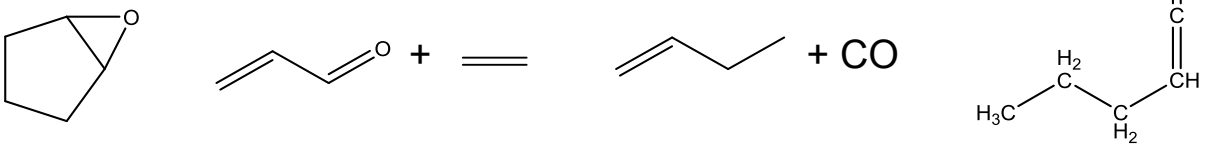


Preliminary Kinbot Results



Conclusions / Future Directions

- New take on products formed by O(^{3}P) + cyclopentene – gas chromatography not sensitive to certain compounds



3% 36% 19% 42%

- Evidence for competition between unimolecular and bimolecular processes – different than linear unsaturated hydrocarbons!

Acknowledgements

Sandia National Laboratories

Xiaohu Li
Ahren Jasper

Bruce Rude
Kevin Wilson
Musa Ahmed
Sarah Farrell

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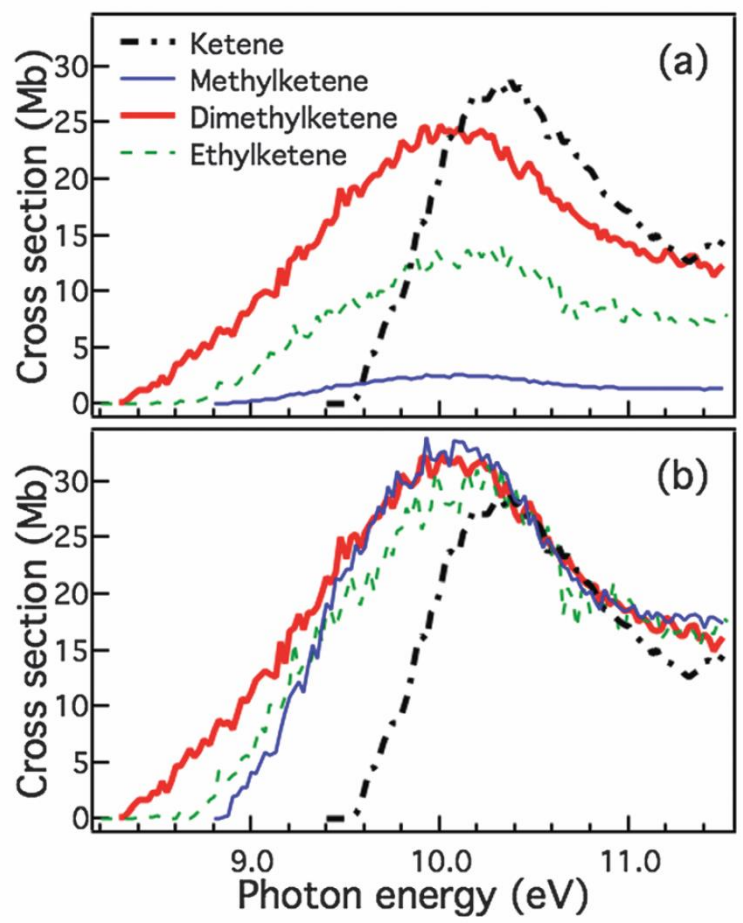
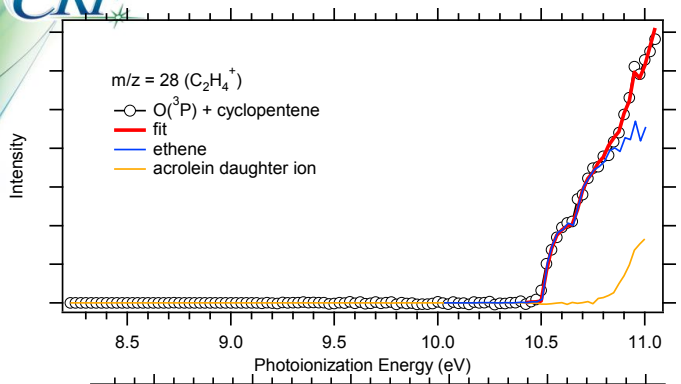
CRF

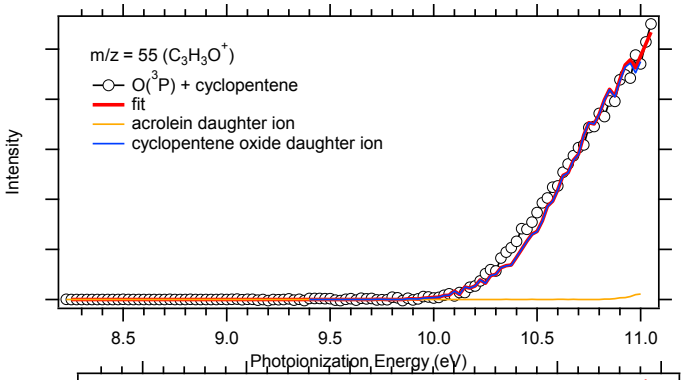
	E_{rel} (CBS-QB3)
^{3}acrolein + ^{1}ethene	-3.6 kcal/mol
^{1}acrolein + ^{3}ethene	-6.6 kcal/mol
^{3}1-butene + ^{1}CO	-29.9 kcal.mol
^{1}1-butene + ^{3}CO	42.9 kcal/mol
^{3}cyclopentene oxide	-31.8
^{3}propylketene	-46.1 kcal/mol

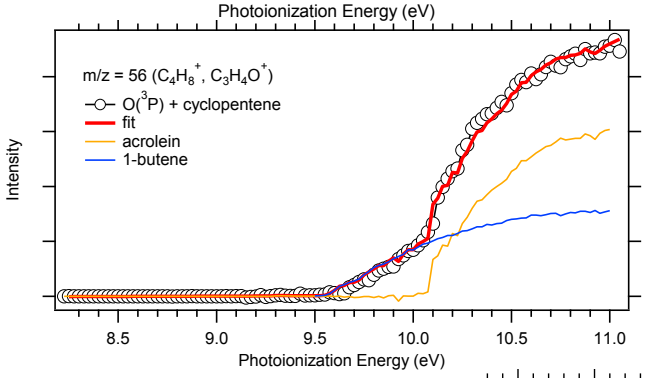
Ketene Photoionization Spectra

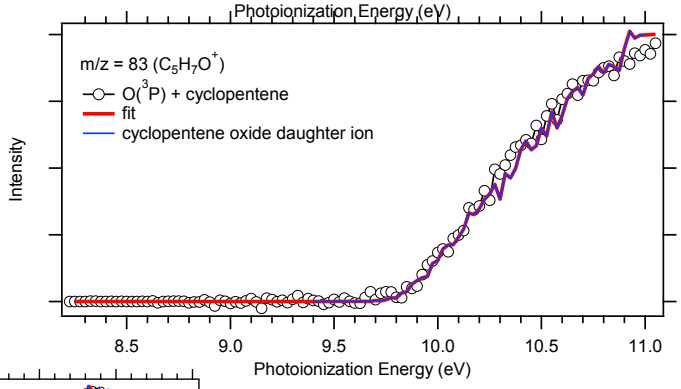


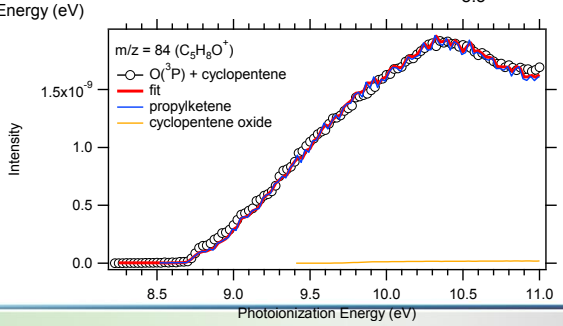
Photoionization Spectra



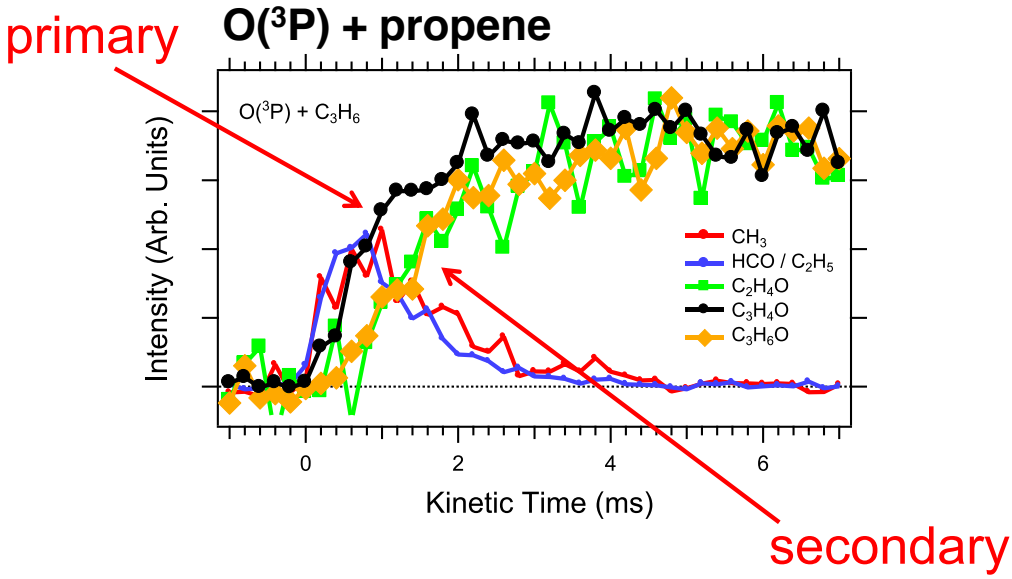








Primary vs. Secondary Products



- Kinetic modeling also used to support assignment