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Automated Kinetics: Recent Examples

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In Honor of the 2019 R.H. Wilhelm Award Winner, William H. Green (MIT)

2021 AIChE Annual Meeting, Boston (virtual presentation)

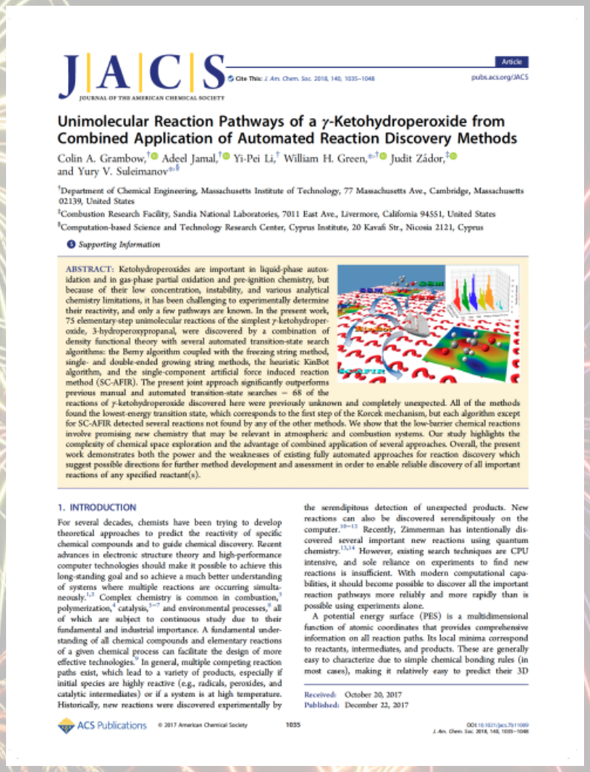
November 8, 2021

Funding:
DOE BES GPCP and
Argonne-Sandia HPCC

Congratulations, Bill!

Common themes in our research

- Automated elementary kinetics
  - 2016 Telluride Meeting



JACS — Article — pubs.acs.org/JACS

Unimolecular Reaction Pathways of a γ-Ketohydroperoxide from Combined Application of Automated Reaction Discovery Methods

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Supporting Information

ABSTRACT: Ketohydroperoxides are important in liquid-phase autoxidation and in gas-phase partial oxidation and pre-ignition chemistry, but because of their low concentration, instability, and various analytical chemistry limitations, it has been challenging to experimentally determine their reactivity, and only a few pathways are known. In the present work, 75 elementary-step unimolecular reactions of the simplest γ-ketohydroperoxide, 3-hydroperoxypropanal, were discovered by a combination of density functional theory with several automated transition-state search algorithms: the Berny algorithm coupled with the freezing string method, single- and double-ended growing string methods, the heuristic KinBot algorithm, and the single-component artificial force induced reaction method (SC-AFIR). The present joint approach significantly outperforms previous manual and automated transition-state searches — 68 of the reactions of γ-ketohydroperoxide discovered here were previously unknown and completely unexpected. All of the methods found the lowest-energy transition state, which corresponds to the first step of the Korcek mechanism, but each algorithm except for SC-AFIR detected several reactions not found by any of the other methods. We show that the low-barrier chemical reactions involve promising new chemistry that may be relevant in atmospheric and combustion systems. Our study highlights the complexity of chemical space exploration and the advantage of combined application of several approaches. Overall, the present work demonstrates both the power and the weaknesses of existing fully automated approaches for reaction discovery which suggest possible directions for further method development and assessment in order to enable reliable discovery of all important reactions of any specified reactant(s).

1. INTRODUCTION

For several decades, chemists have been trying to develop theoretical approaches to predict the reactivity of specific chemical compounds and to guide chemical discovery. Recent advances in electronic structure theory and high-performance computer technologies should make it possible to achieve this long-standing goal and so achieve a much better understanding of systems where multiple reactions are occurring simultaneously.[1,2] Complex chemistry is common in combustion,[3] polymerization,[4] catalysis,[5−7] and environmental processes,[8] all of which are subject to continuous study due to their fundamental and industrial importance. A fundamental understanding of all chemical compounds and elementary reactions of a given chemical process can facilitate the design of more effective technologies.[9] In general, multiple competing reaction paths exist, which lead to a variety of products, especially if initial species are highly reactive (e.g., radicals, peroxides, and catalytic intermediates) or if a system is at high temperature. Historically, new reactions were discovered experimentally by the serendipitous detection of unexpected products. New reactions can also be discovered serendipitously on the computer.[10−13] Recently, Zimmerman has intentionally discovered several important new reactions using quantum chemistry.[13,14] However, existing search techniques are CPU intensive, and sole reliance on experiments to find new reactions is insufficient. With modern computational capabilities, it should become possible to discover all the important reaction pathways more reliably and more rapidly than is possible using experiments alone.

A potential energy surface (PES) is a multidimensional function of atomic coordinates that provides comprehensive information on all reaction paths. Its local minima correspond to reactants, intermediates, and products. These are generally easy to characterize due to simple chemical bonding rules (in most cases), making it relatively easy to predict their 3D

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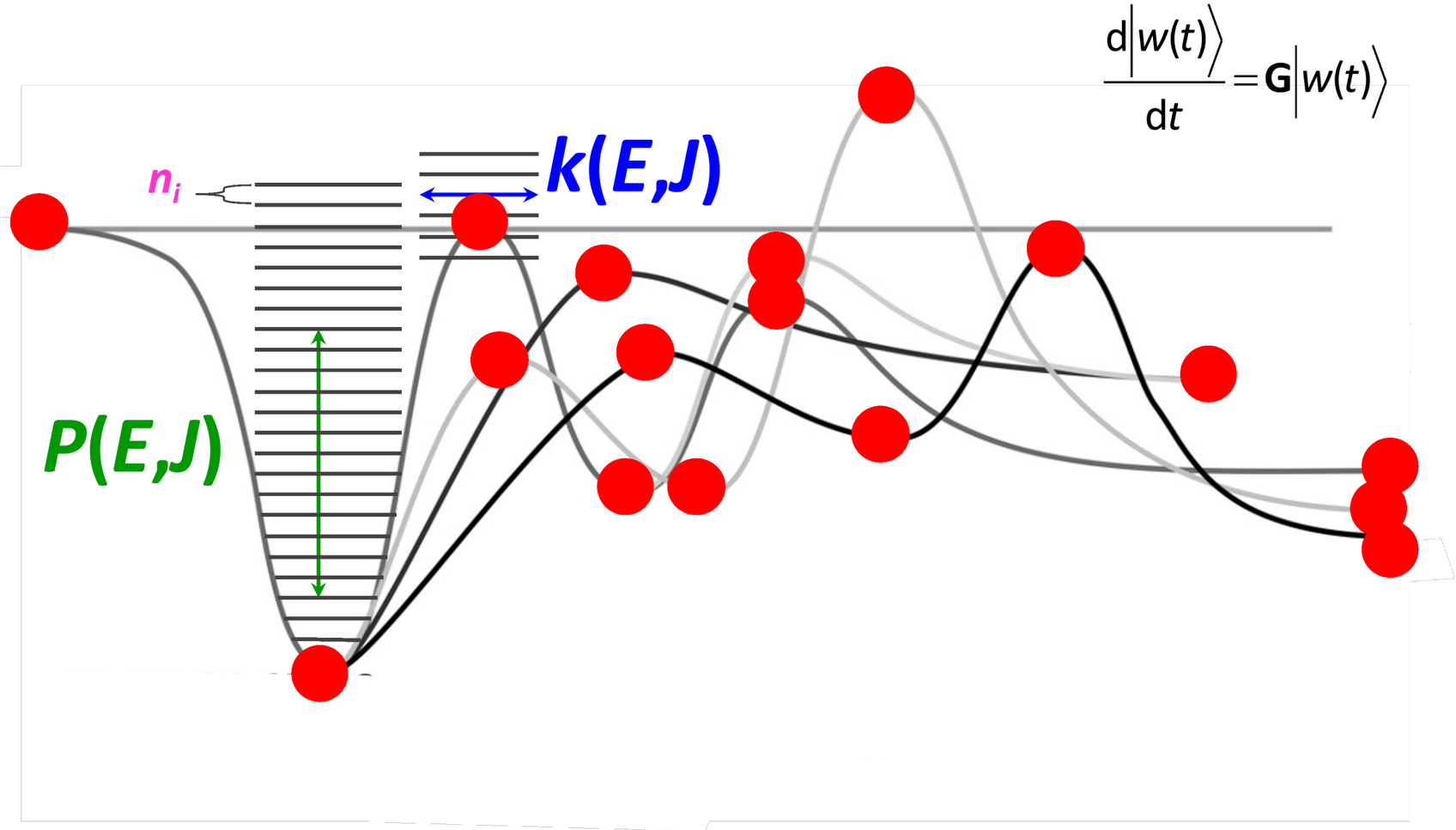
ACS Publications © 2017 American Chemical Society 1035

- Collaboration on RMG-related projects, directly and indirectly

- Working with Bill's group members
  - Visitors
  - Postdocs
  - Collaborators

Many important gas-phase reactions happen over multiple-well potential energy surfaces



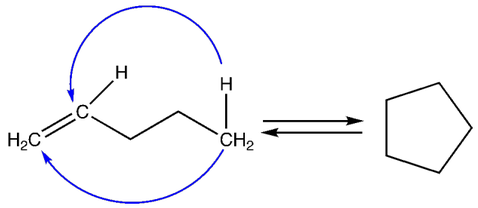
Experimental and computational tools

Ruben Van de Vijver

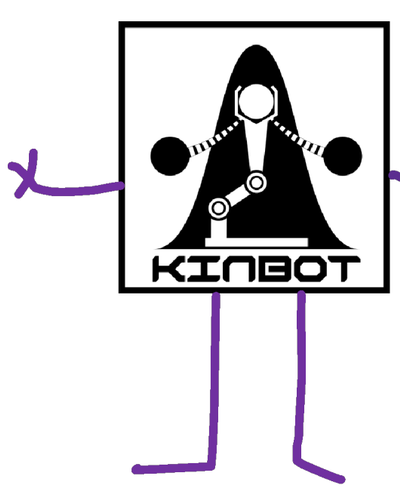
ME bits

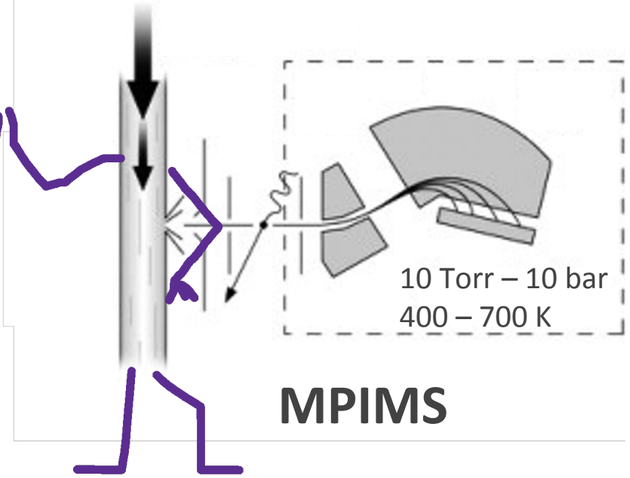
Starting structure

Pattern recognition



Endocyclic closed-shell cyclization

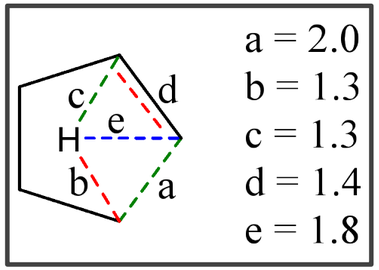




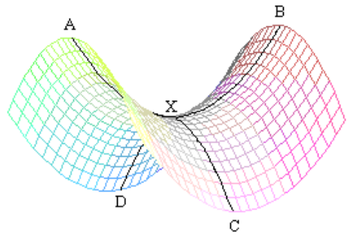
MPIMS

Product characterization

Recipe

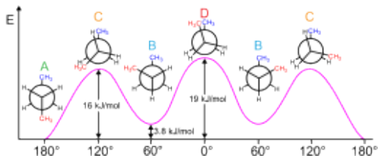


Saddle point search



Checking…

Refine and characterize



github.com/zadorlab/KinBot

Van de Vijver, Zádor, CPC, 2020, 248, 106947

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Article

Quantitative Detection of Products and Radical Intermediates in Low-Temperature Oxidation of Cyclopentane

Published as part of The Journal of Physical Chemistry virtual special issue "Cheuk-Yiu Ng Festschrift".

Leonid Sheps,* Amanda L. Dewyer, Maria Demireva, and Judit Zádor*

Cite This: *J. Phys. Chem. A* 2021, 125, 4467–4479

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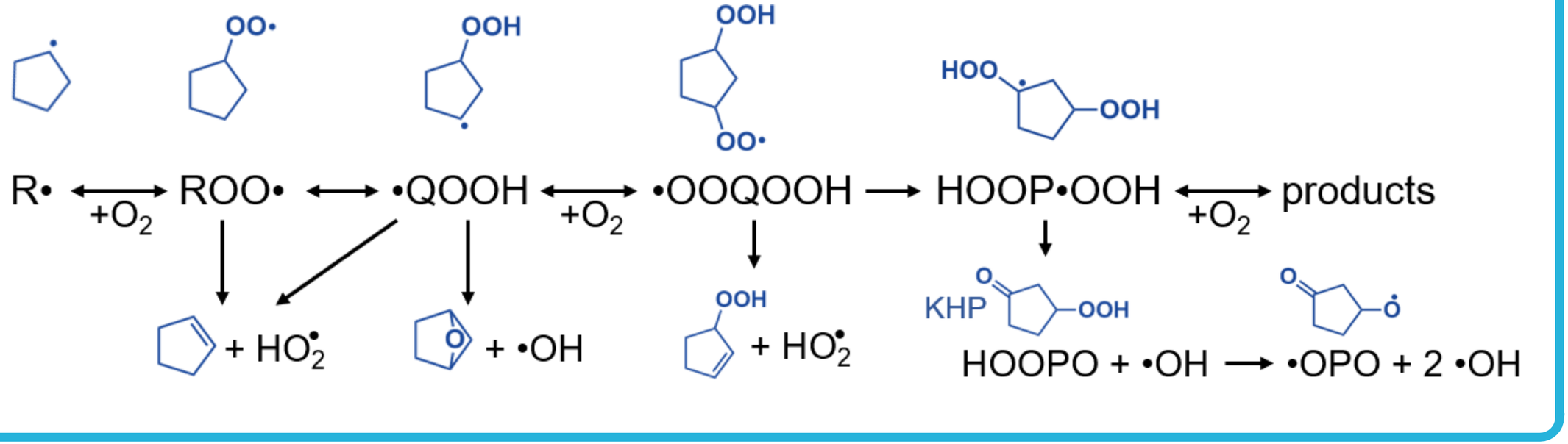
Low-temperature cyclopentane oxidation: Mechanism and prior studies

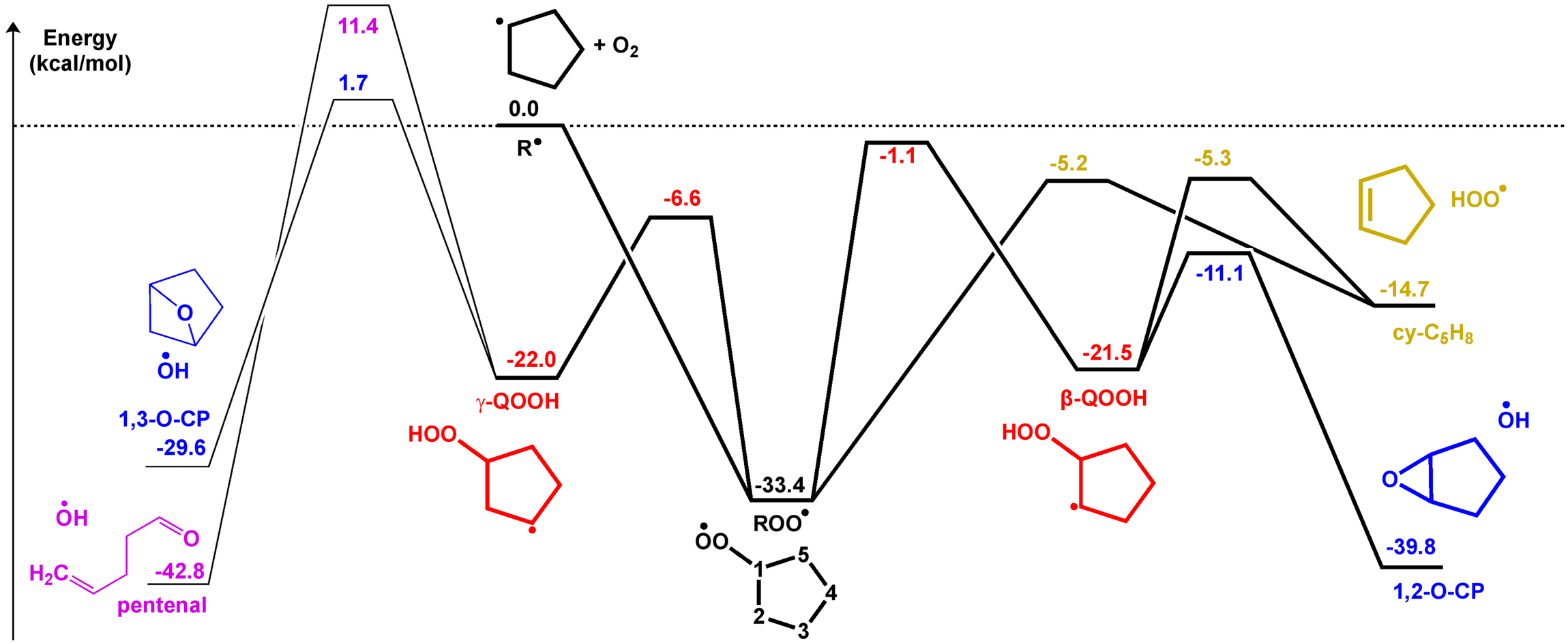


1. Wu and Bayes: 3.5 Torr, PIMS, cyclopentyl radical
2. DeSain and Taatjes: up to 723 K and 56 Torr, HO_2 detection
3. Sirjean et al.: CBS-QB3 for R + O_2 addition
4. Rashidi et al.: UCCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G(d,p) and ME for R + O_2
5. Miyoshi: R + O_2 and γ-QOOH + O_2 PESs at the CBS-QB3 level

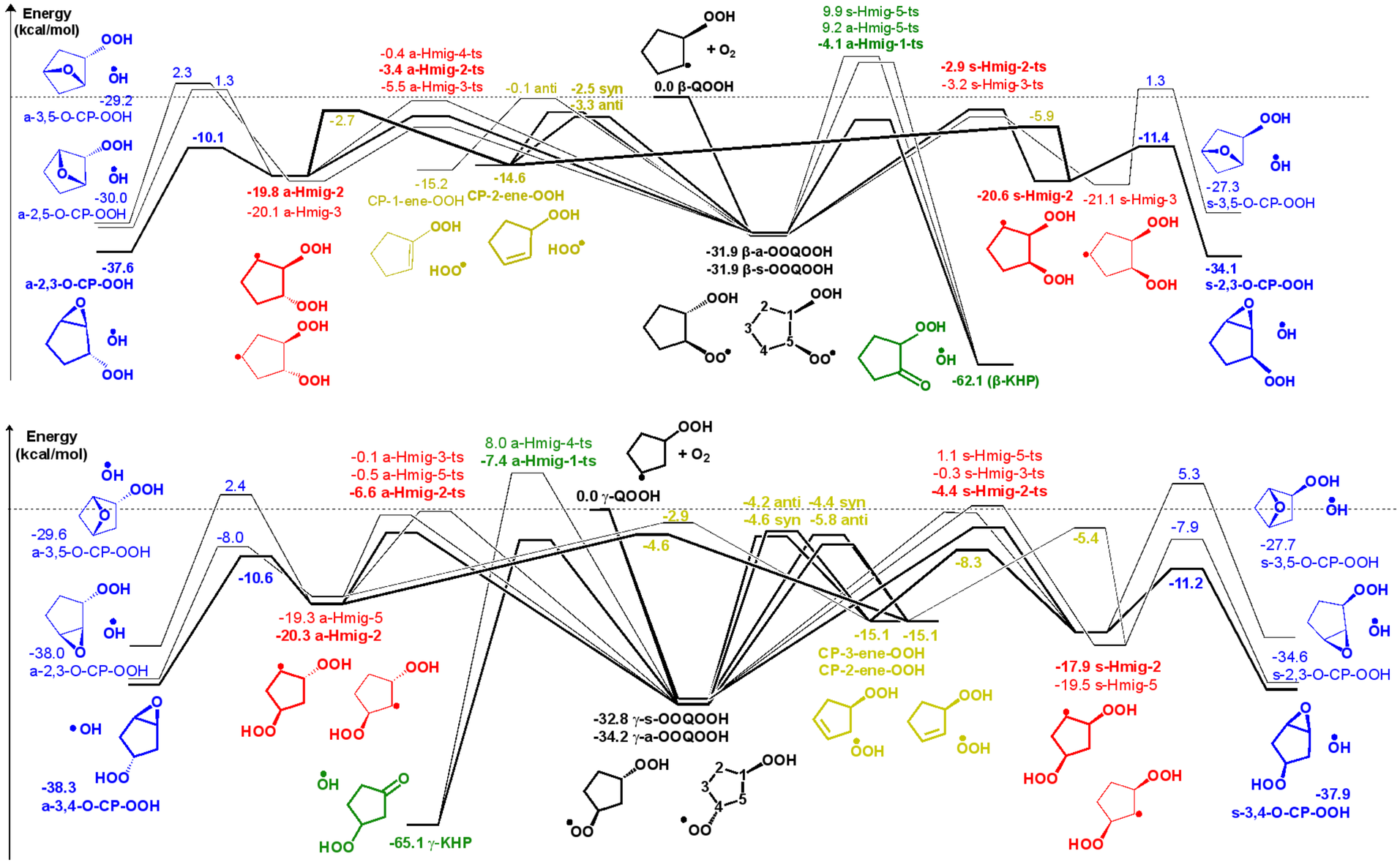
6. This work: 10 Torr–10 bar, 400–700 K, illuminating the coupled first- and second-O_2 addition reactions in unprecedented detail

1. IJCK 1986, 18, 547–554
2. JPCA 2001, 105, 6646–6654
3. JPCA 2009, 113, 6924–6935
4. CNF 2017, 183, 358–371
5. SAE Tech. Pap. Ser., 2019, 0148-7191
6. JPCA 2021, 125, 4467–4479

R + O_2 PES @ CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G**

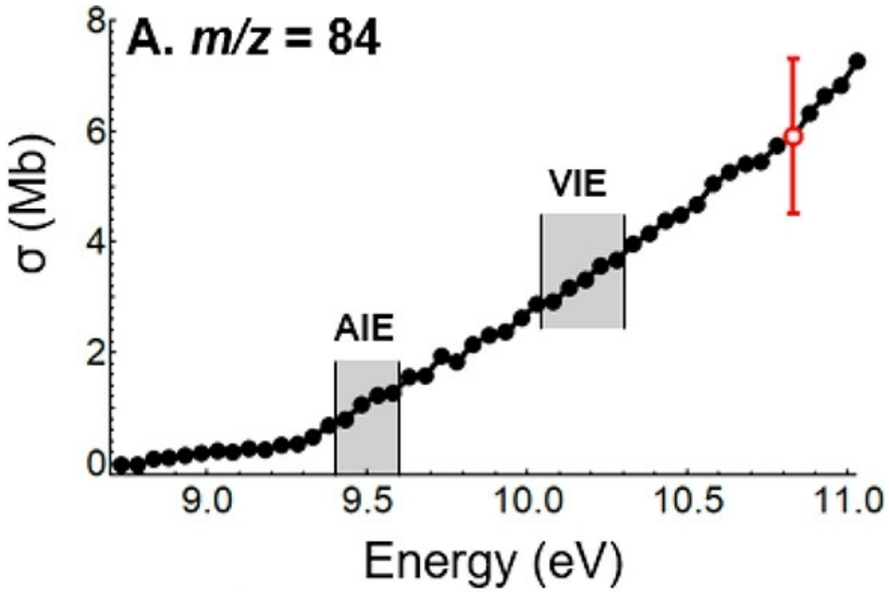


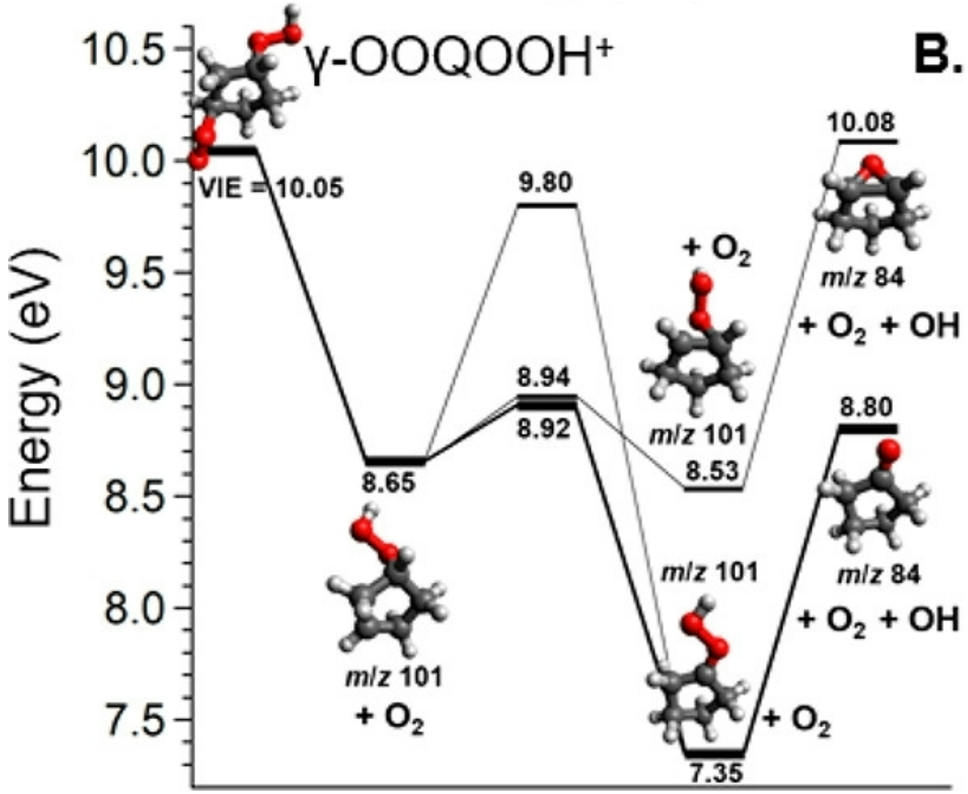
QOOH + O_2 PESs @ CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6-311++G**



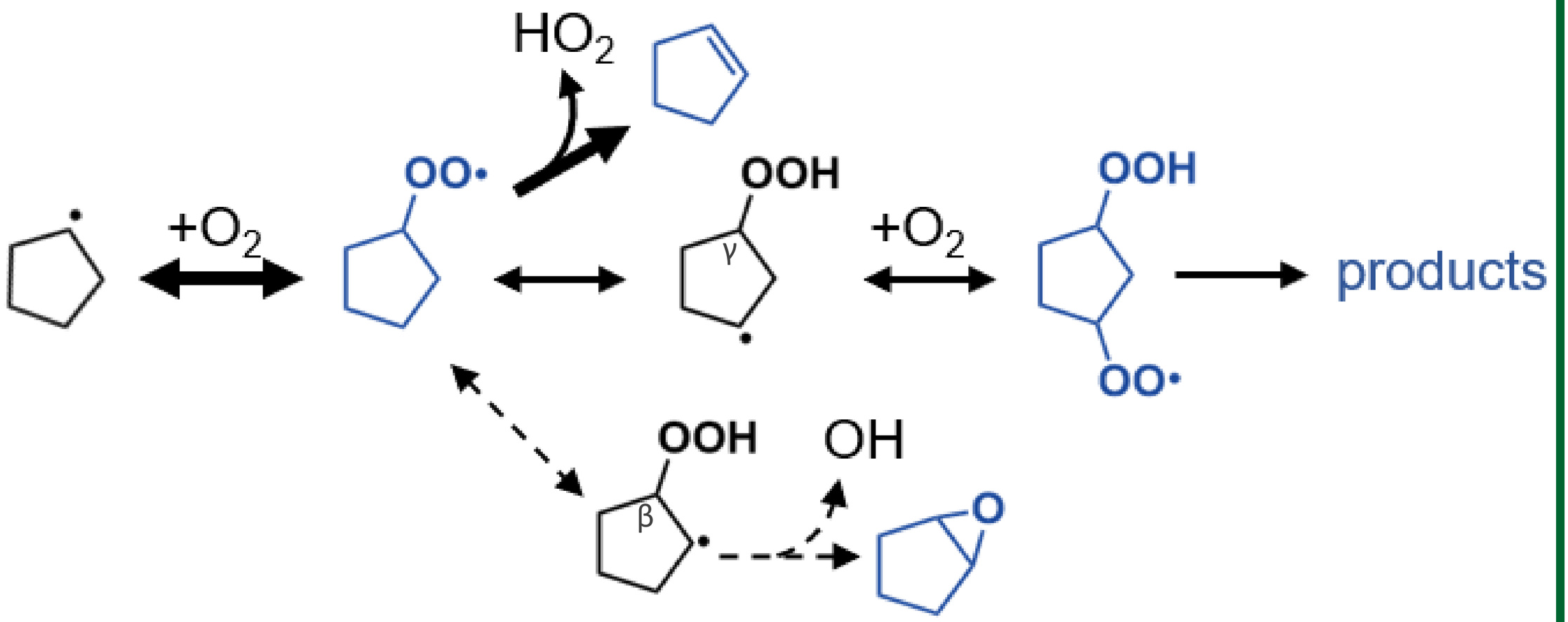
KinBot was used to explore the cation conformers and fragmentation dynamics as well

26 γ-OOQOOH conformers



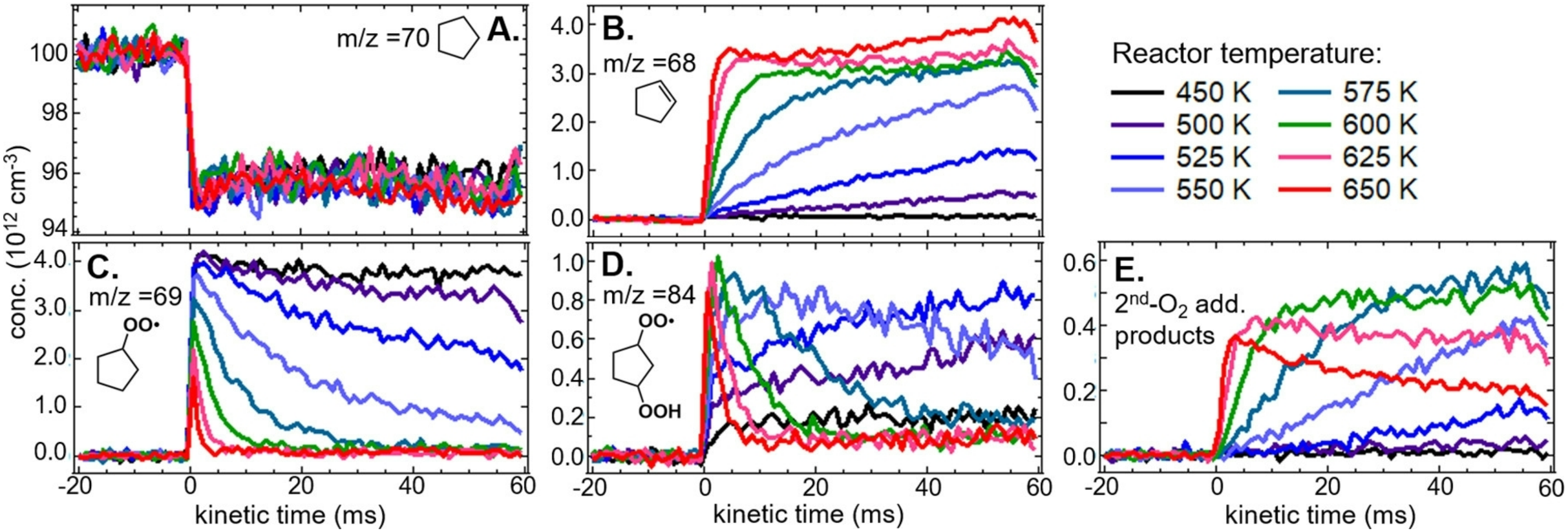


Simplified primary sub-mechanism for the oxidation of cyclopentane at P = 10 – 7500 Torr and T = 400 – 700 K



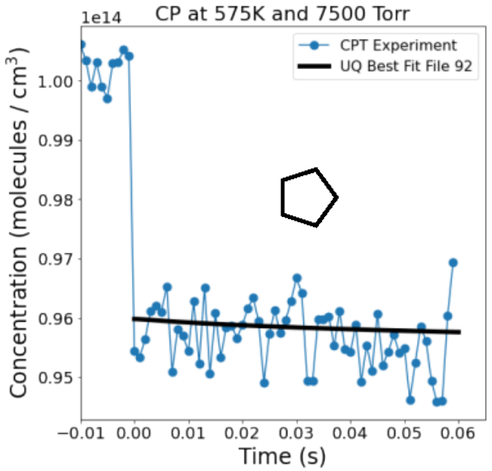
(The experimentally detected species are highlighted in blue)

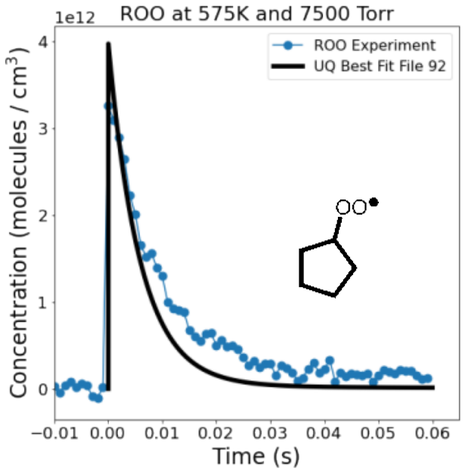
Kinetics

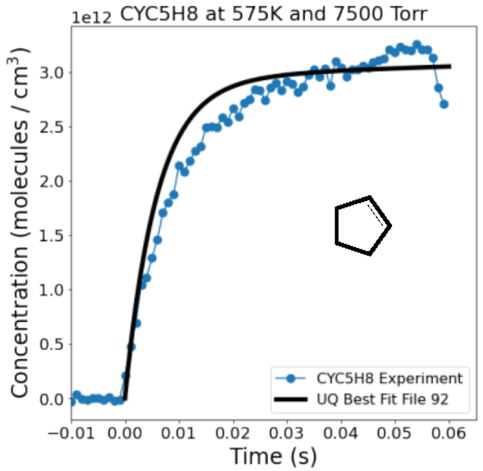

A.
m/z =70
B.
m/z =68
C.
m/z =69
OO•
D.
m/z =84
OO•
OOH
E.
2nd-O2 add.
products
conc. (10^12 cm^-3)
kinetic time (ms)
kinetic time (ms)
kinetic time (ms)
Reactor temperature:
450 K
500 K
525 K
550 K
575 K
600 K
625 K
650 K

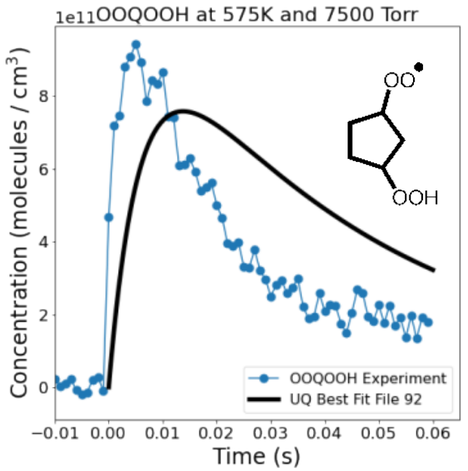
Simulations with the ME rate coefficients

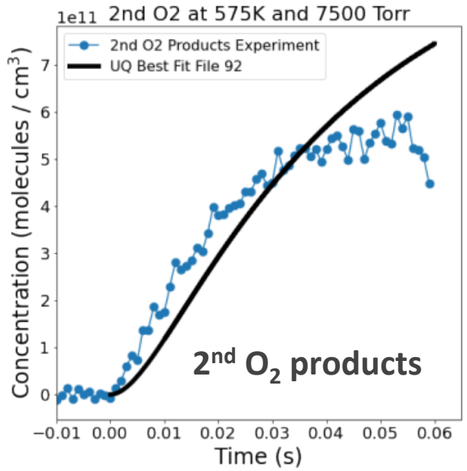
10 bar, 575 K



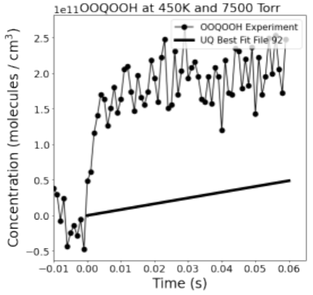


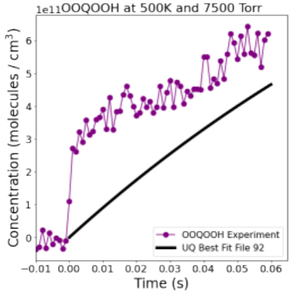


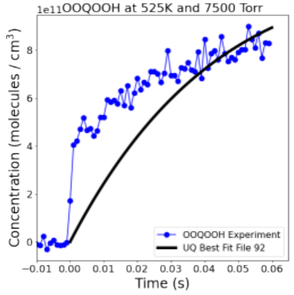


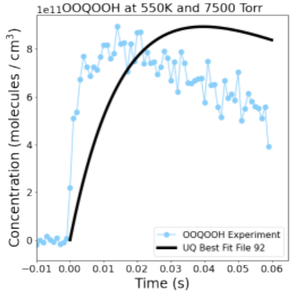


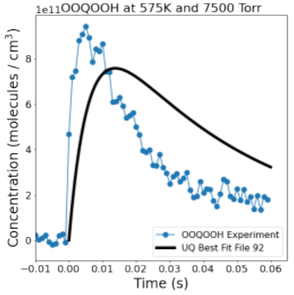
10 bar, OOQOOH, as a function of temperature

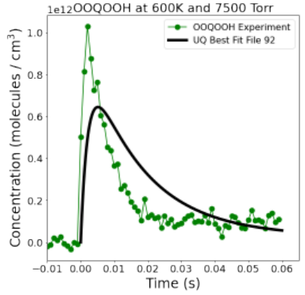


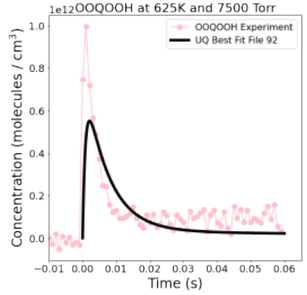


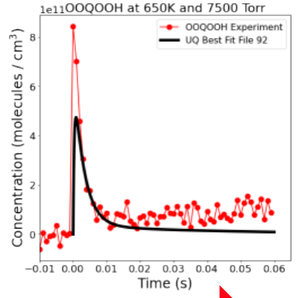


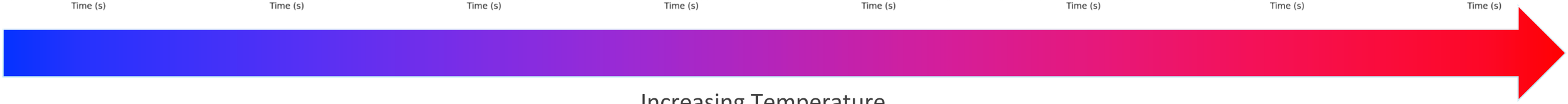






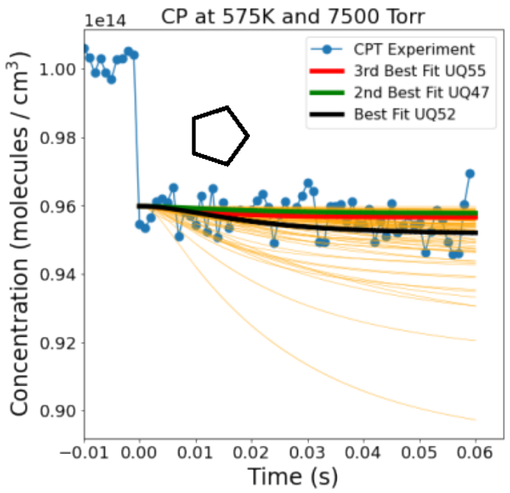


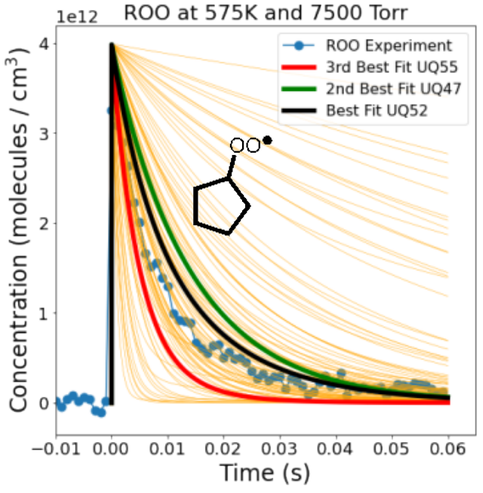


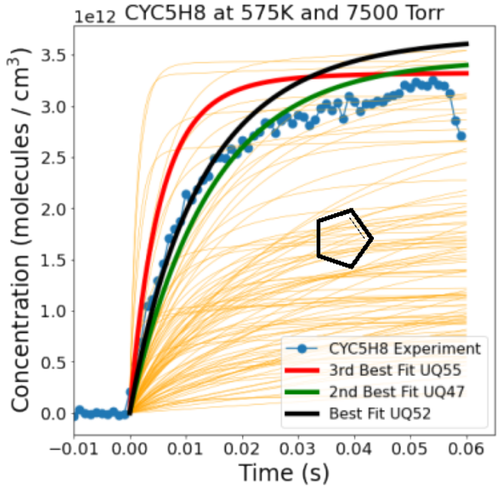


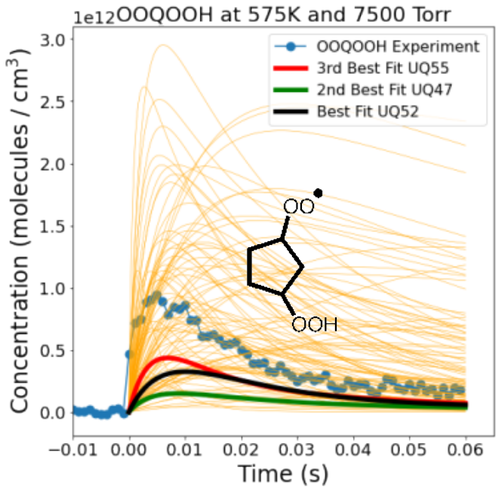
Increasing Temperature

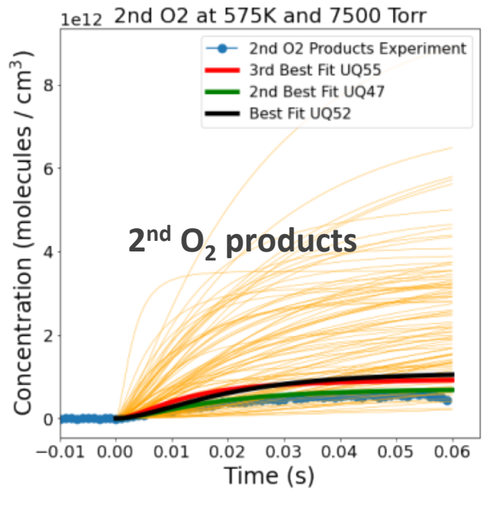
Simulations with uncertainties











Goodness of fit judged from the combined Sum Squared and Similarity Score, 1:1 Weighting

$$\cos(\theta) = \frac{A \cdot B}{\|A\|\|B\|} = \frac{\sum_{i=1}^{n} A_i B_i}{\sqrt{\sum_{i=1}^{n} A_i^2}\sqrt{\sum_{i=1}^{n} B_i^2}}$$

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Article

A New Pathway for Intersystem Crossing: Unexpected Products in the O(^{3}P) + Cyclopentene Reaction

Published as part of The Journal of Physical Chemistry virtual special issue "125 Years of The Journal of Physical Chemistry".

Krupa Ramasesha, John D. Savee, Judit Zádor,* and David L. Osborn*

Cite This: https://doi.org/10.1021/acs.jpca.1c05817

Read Online

$O(^3P)$ and its reactions with alkenes

$O(^3P)$

Troposphere

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$O(^1D) + M \longrightarrow O(^3P) + M$$

Stratosphere

$$O_2 + h\nu \longrightarrow O(^3P) + O(^3P)$$

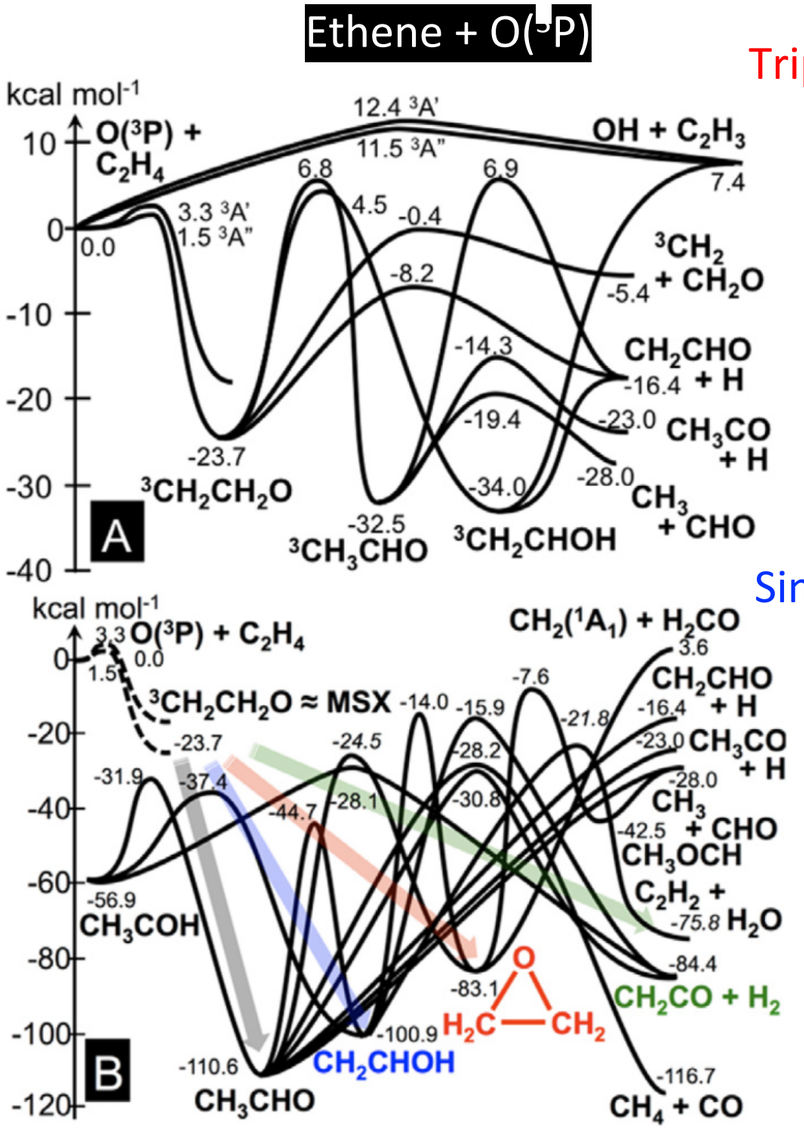
Combustion

$$H + O_2 \longrightarrow OH + O(^3P)$$

$O(^3P)$ + alkenes

Classic non-adiabatic reactions

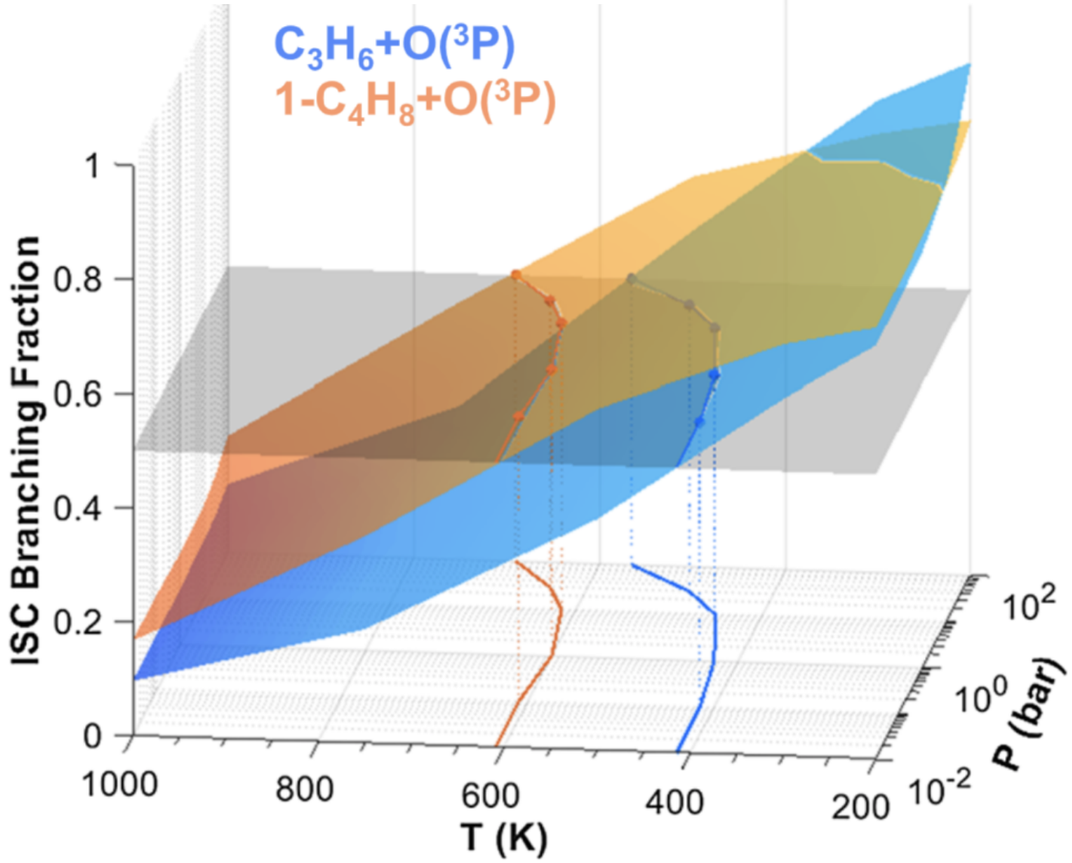
Rich in pathways



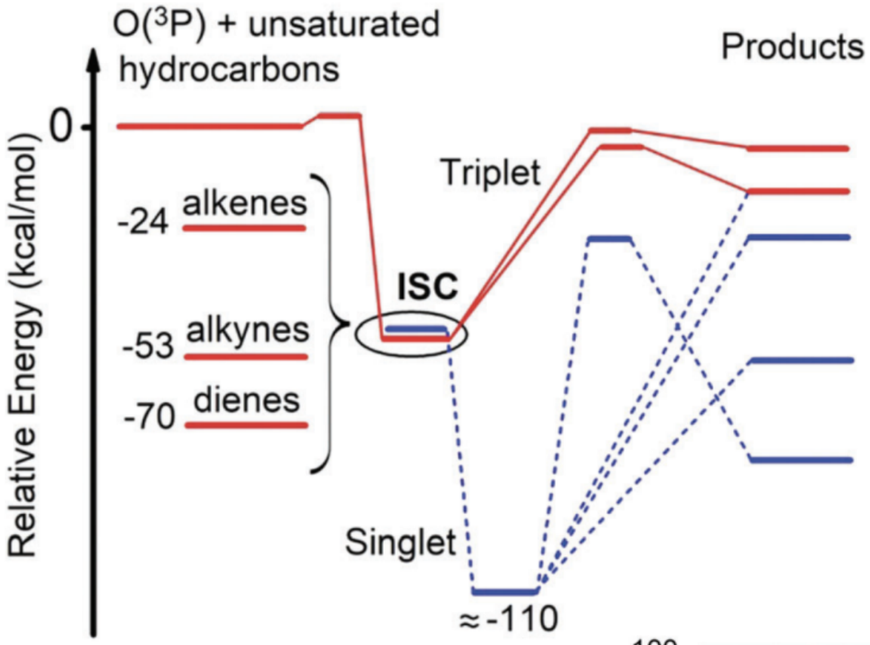
Li X, Jasper AW, Zádor J, Miller JA, Klippenstein SJ. Proc Combust Inst. 2017;36:219-27.

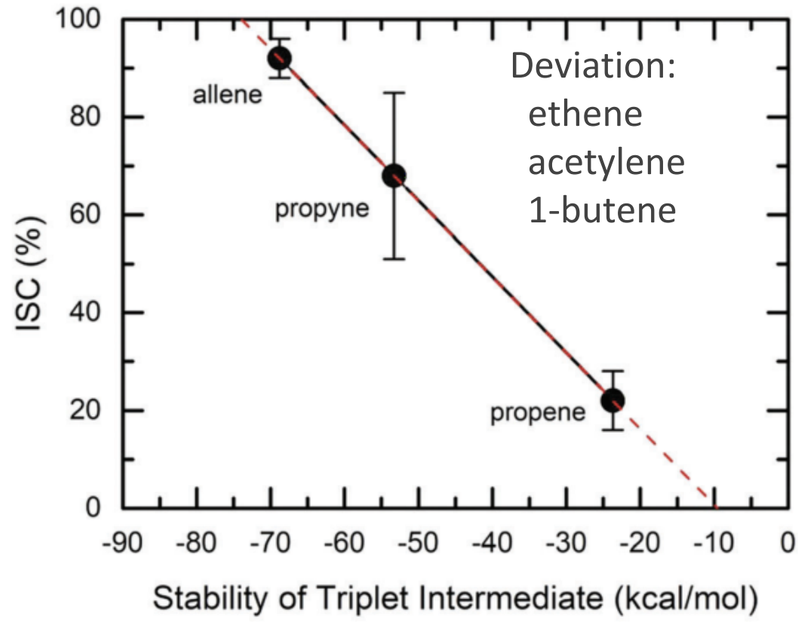
What controls ISC?

Terminal alkenes



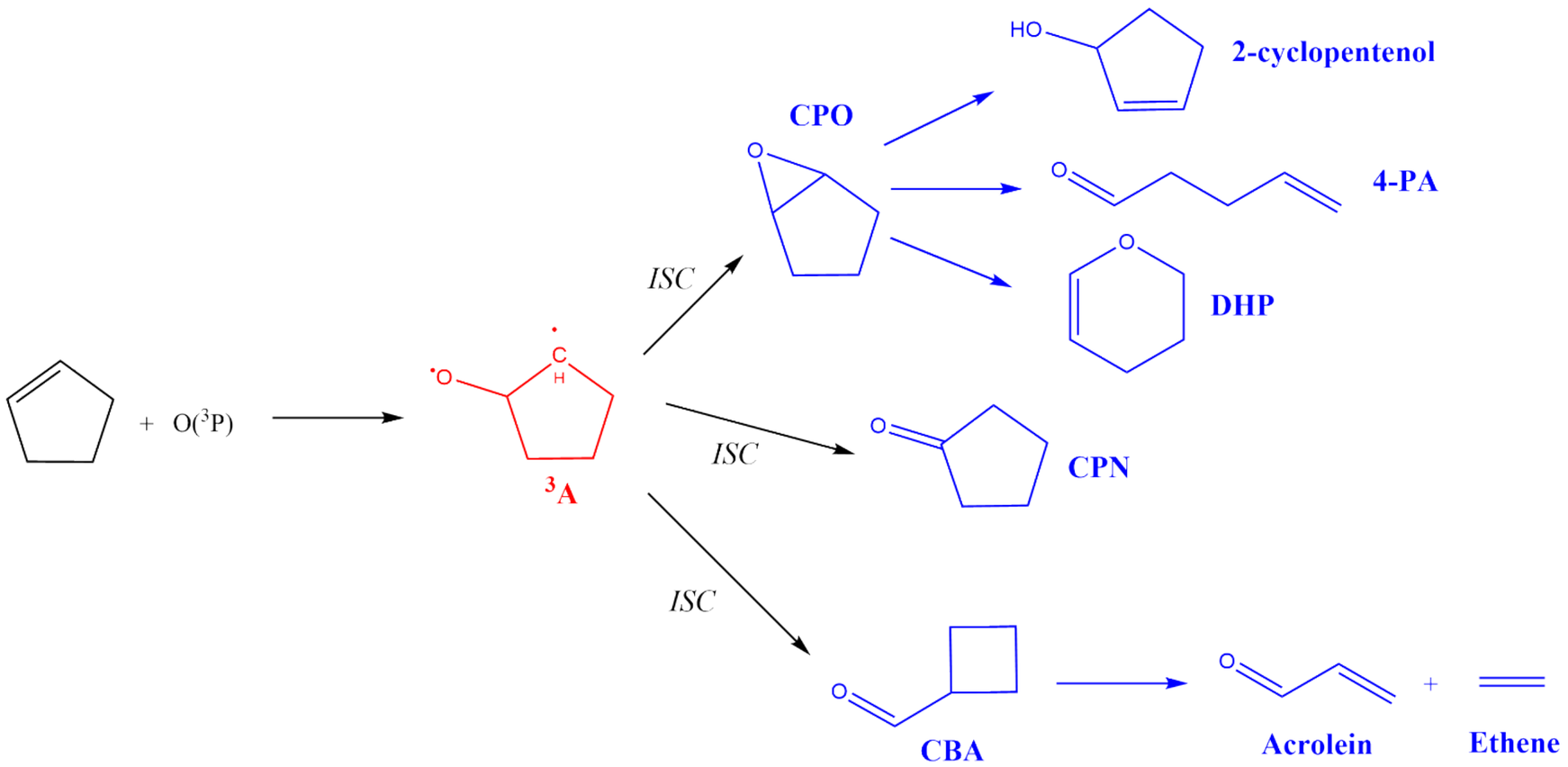
Maffei et al., Fuel, 2020





Pan et al., Chem Rev, 2017

What happens when the alkene is cyclic?



Cvetanović, R. J.; Ring, D. F.; Doyle, L. C., Reaction of Oxygen Atoms with Cyclopentene. *The Journal of Physical Chemistry* **1971**, *75*, 3056-3061.

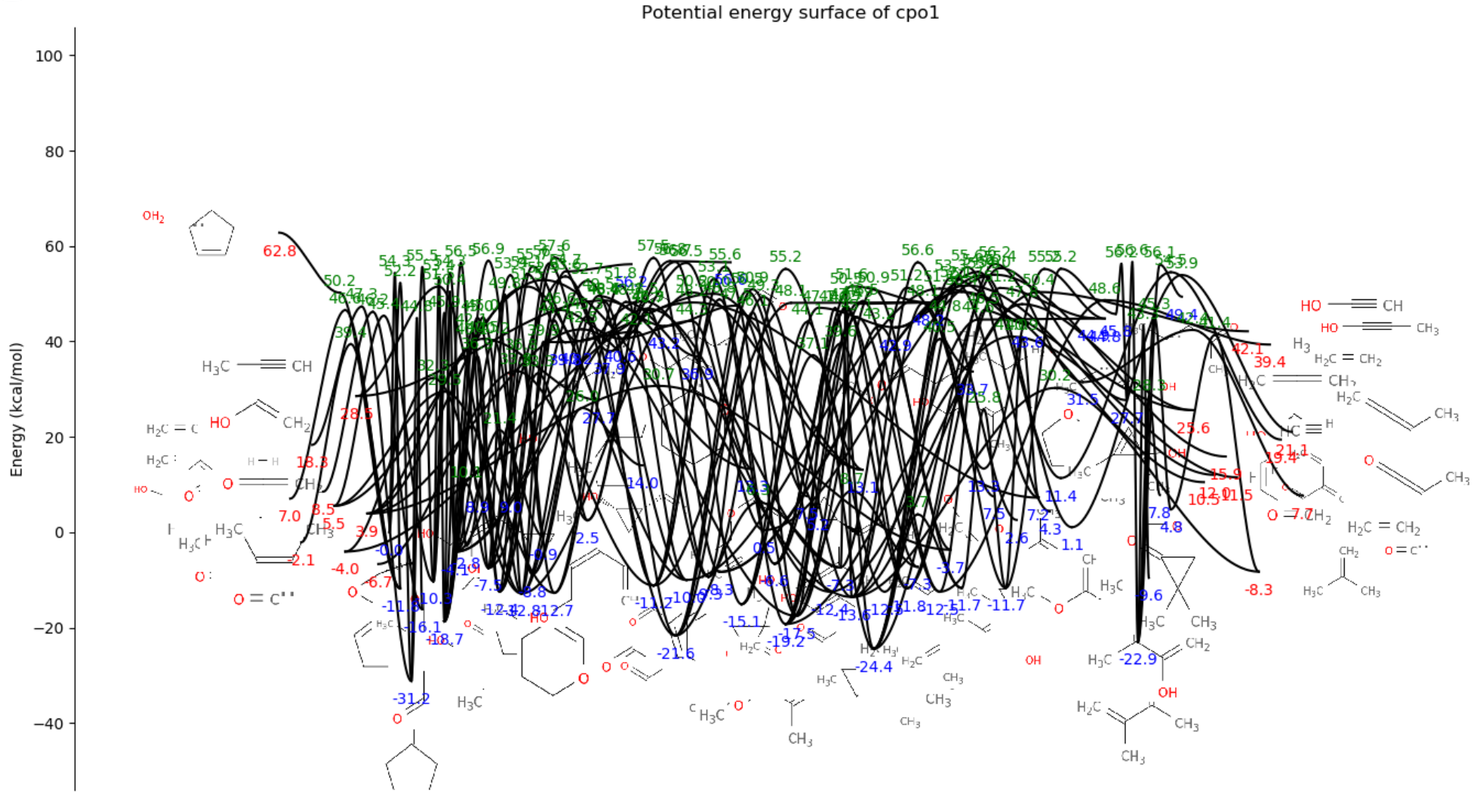
Hoyermann, K.; Nothdurft, J.; Olzmann, M.; Wehmeyer, J.; Zeuch, T., Formation and Decomposition of Chemically Activated Cyclopentoxy Radicals from the *c*-C_5h_9 + O Reaction. *The Journal of Physical Chemistry A* **2006**, *110*, 3165-3173.

Zhao, H. M.; Liu, K. H.; Song, D.; Su, H. M., Nonadiabatic Reaction Mechanisms of the O(^{3}P) with Cyclopentene. *Journal of Molecular Graphics & Modelling* **2014**, *51*, 184-192.

KinBot finds a very large number wells on both PESs

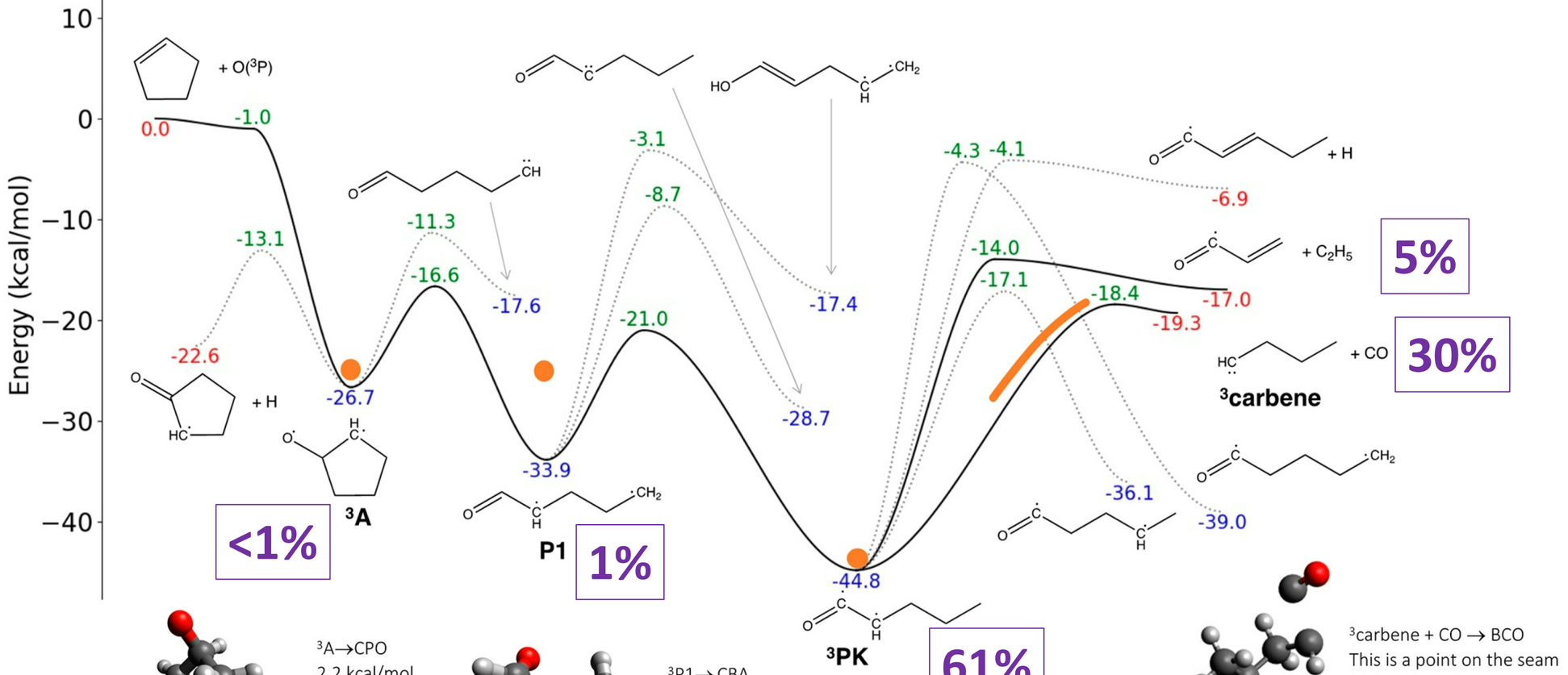
>20 wells on the triplet surface

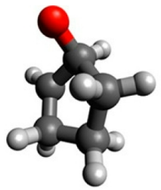
>65 wells on the singlet surface



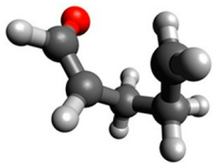
Energy- and flux-based filtering was used

Active pathways and primary yields on the triplet surface at 4 Torr and 298 K

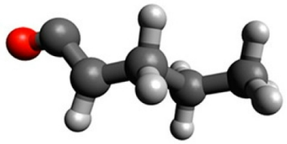




^{3}A→CPO
2.2 kcal/mol
SOC: 20.2 cm^{-1}

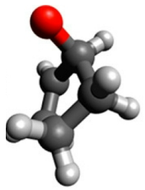


^{3}P1→ CBA
8.5 kcal/mol
SOC: 0.04 cm^{-1}



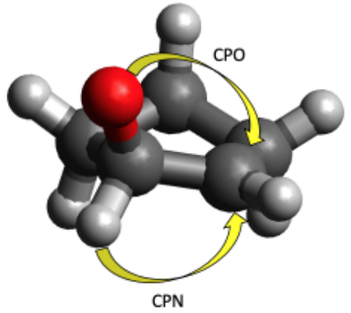
^{3}PK→^{1}PK
0.2kcal/mol
SOC: 27.9 cm^{-1}

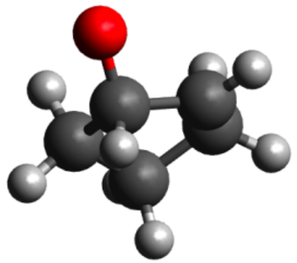
^{3}carbene + CO → BCO
This is a point on the seam
SOC: ~13 cm^{-1}

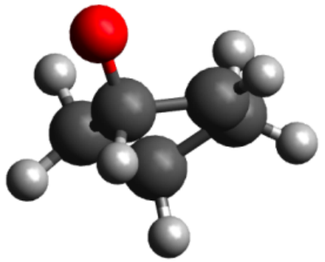


^{3}A→CPO
1.6 kcal/mol
SOC: 38.2 cm^{-1}

Prompt products from ^{3}A

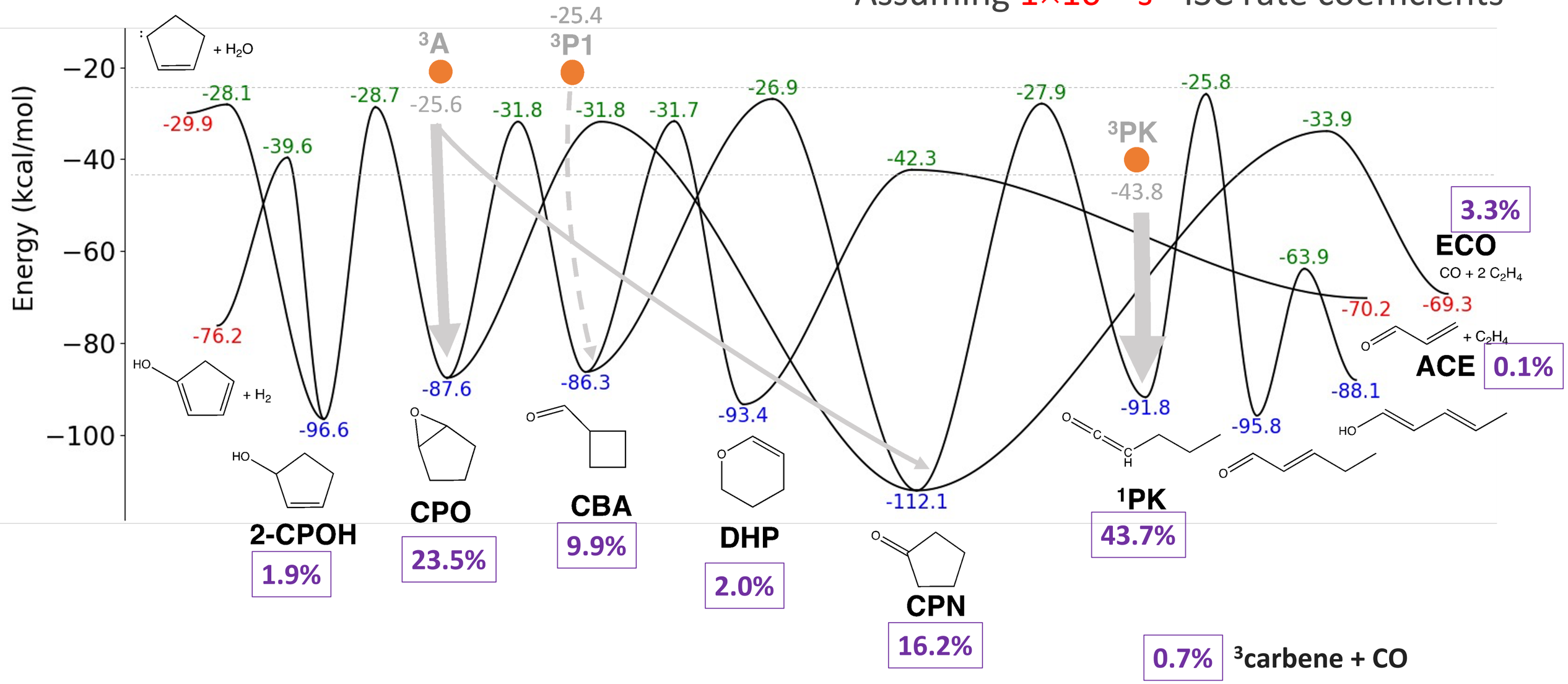






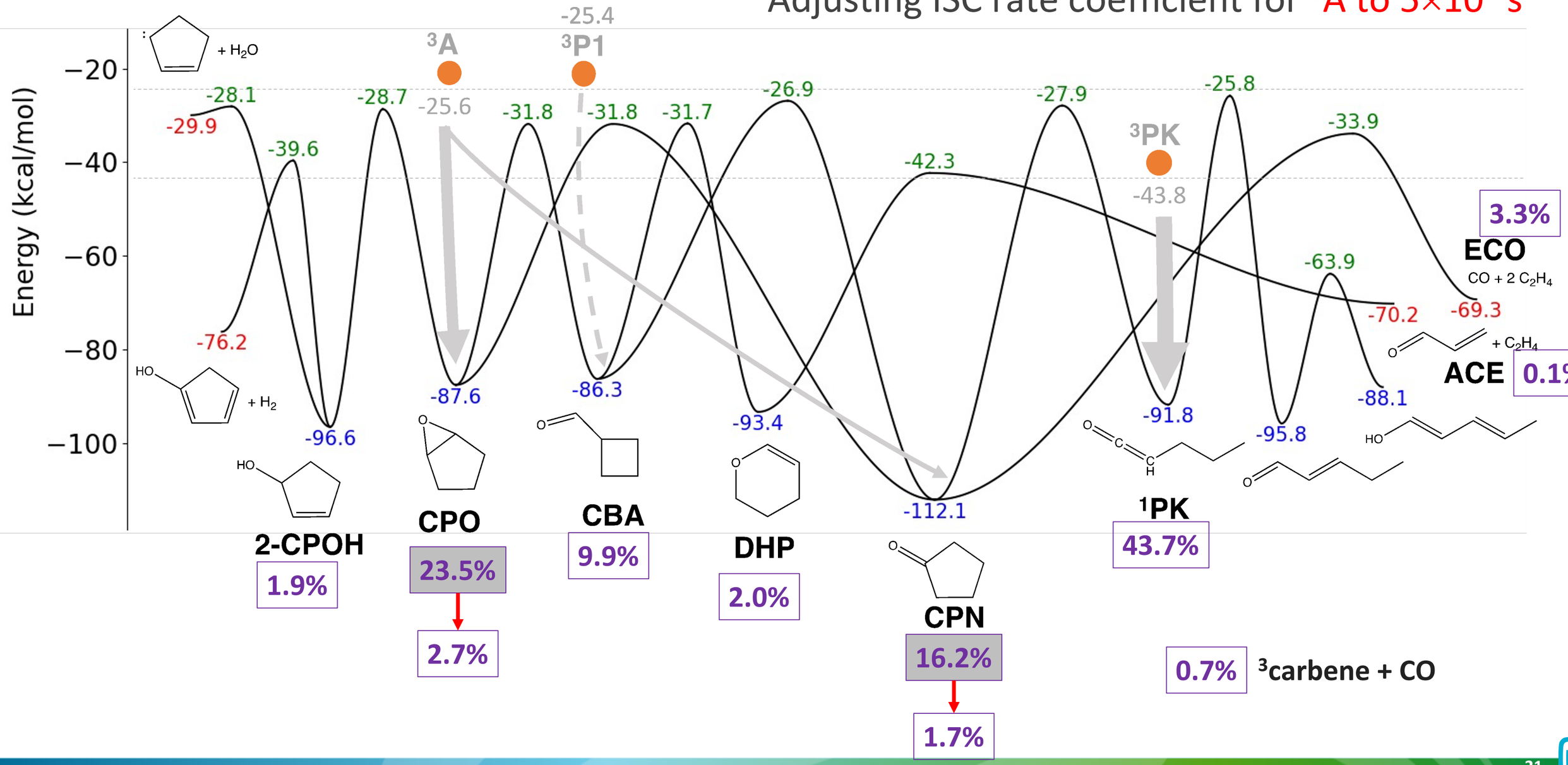
Active pathways and yields on the singlet surface after ISC

Assuming 1×10^{11} s^{-1} ISC rate coefficients



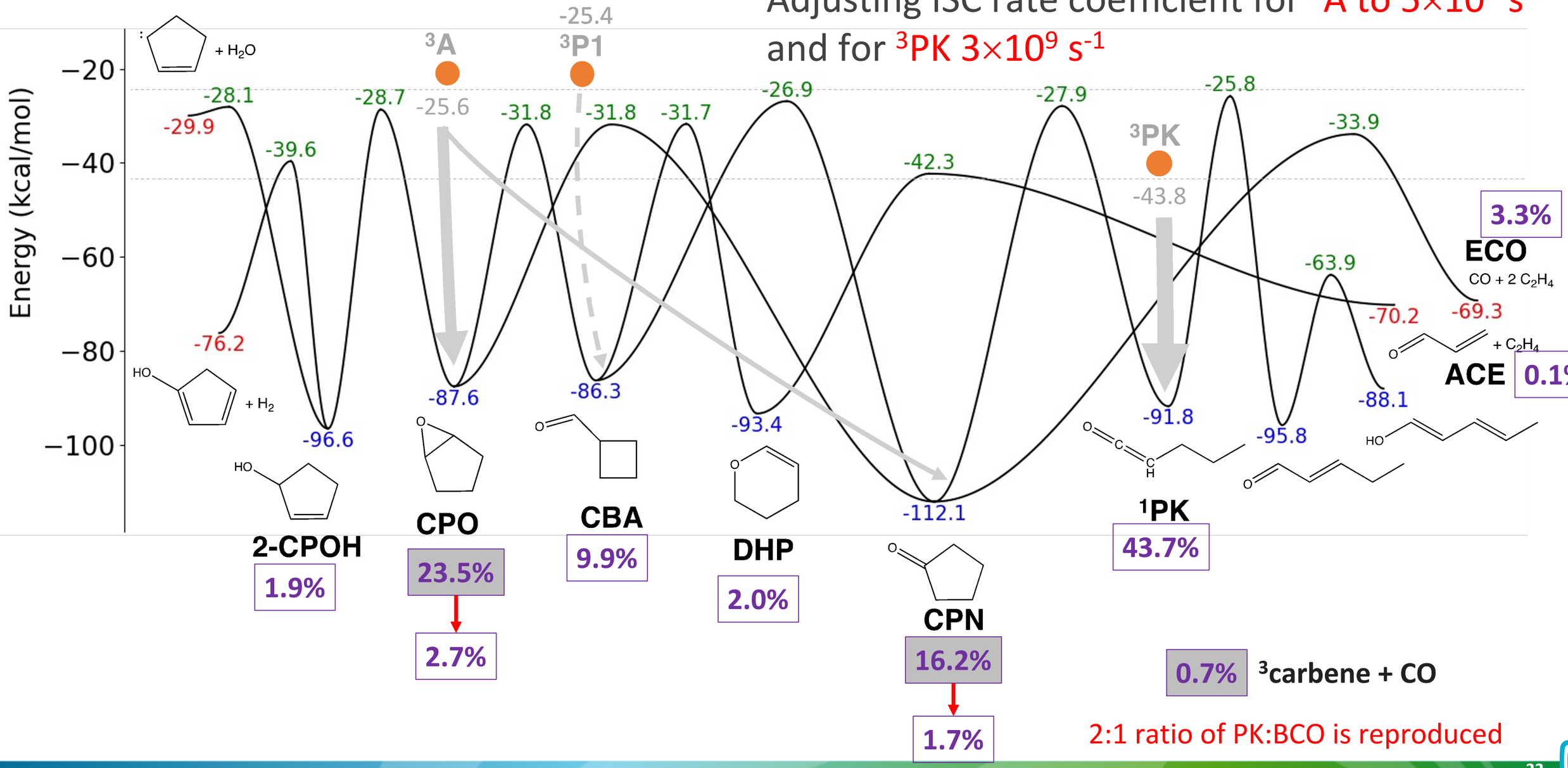
Active pathways and yields on the singlet surface after ISC

Adjusting ISC rate coefficient for ^{3}A to 5×10^9 s^{-1}



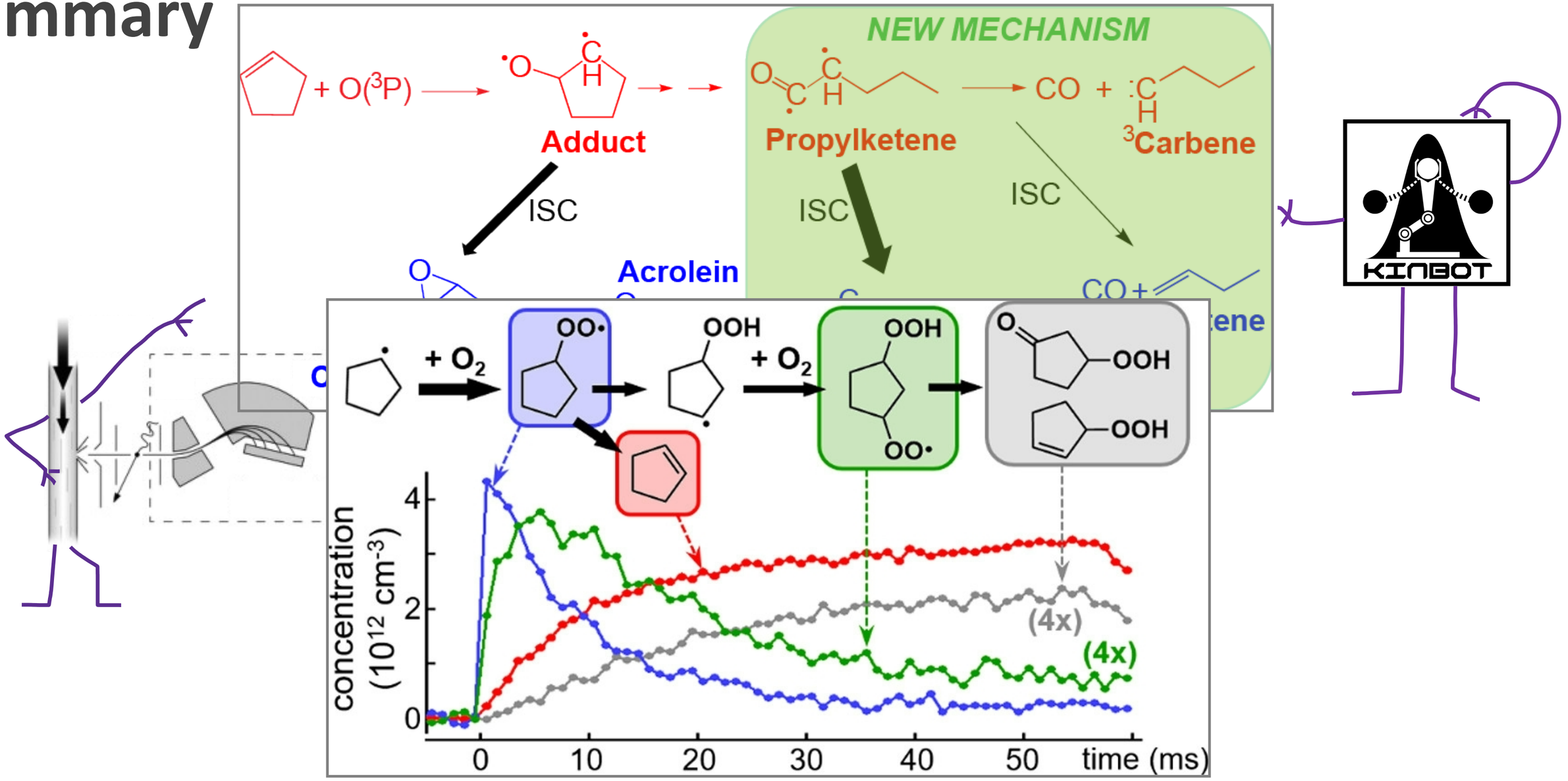
Active pathways and yields on the singlet surface after ISC

Adjusting ISC rate coefficient for ^{3}A to 5×10^9 s^{-1} and for ^{3}PK 3×10^9 s^{-1}



2:1 ratio of PK:BCO is reproduced

Summary


NEW MECHANISM
+ O(3P)
Adduct
ISC
Acrolein
Propylketene
CO +
3Carbene
ISC
ISC
CO +
+ O2
+ O2
OOH
OOH
OOH
OOH
concentration (10^12 cm^-3)
time (ms)
(4x)
(4x)
KINBOT