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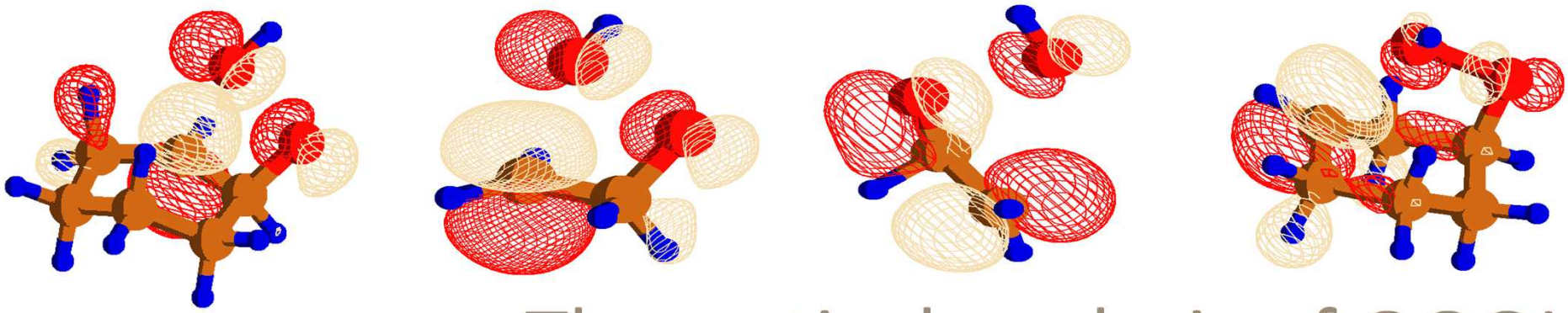

Theoretical analysis of QOOH combustion reaction pathways

Madison Fellows, Judit Zádor

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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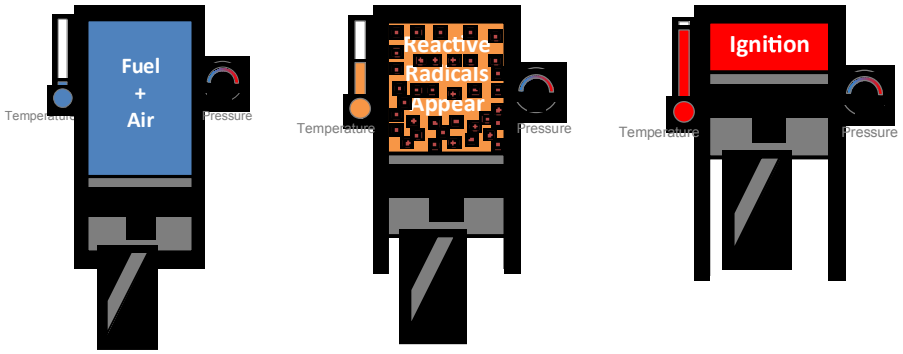
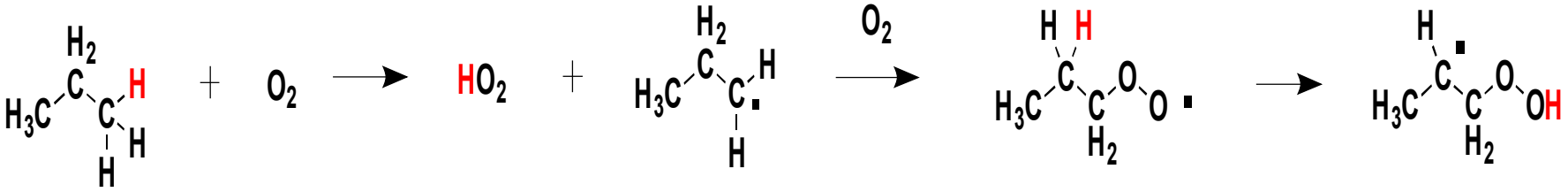
Understanding autoignition chemistry to optimize new fuel and engine models



- New efficient and clean engine technologies rely on autoignition chemistry

- Autoignition chemistry is driven by chemical chain reactions
- Initial steps of propane chain propagation
  (leading to ignition/combustion eventually)



Autoignition and QOOH: A theoretical approach

- QOOH = Chain branching → autoignition
- Reactions gets complicated!
- Pathways are fuel dependent
  → need to understand trends
- Experiments can miss short lived / unstable intermediates
- Theoretical computations can help!

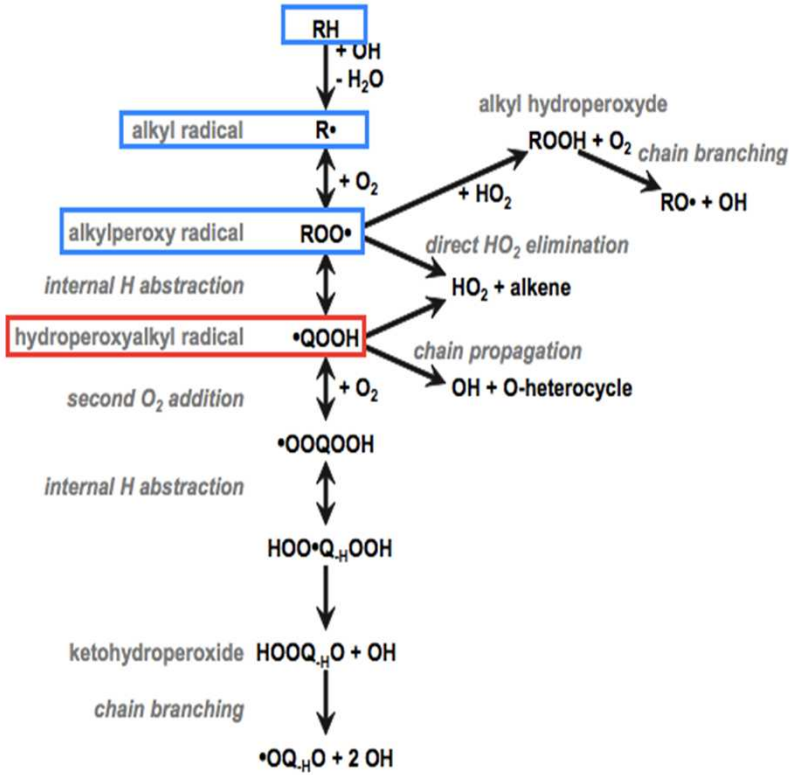
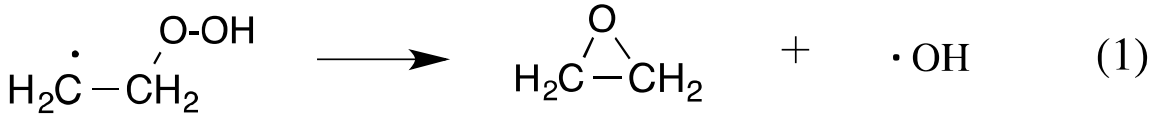


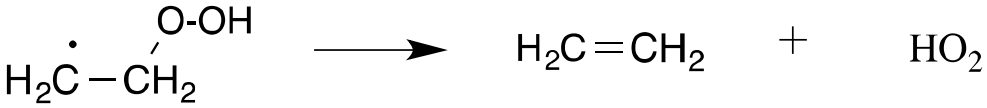
Fig. 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.

New QOOH reactions found computationally

- **Well-known pathways:** OH elimination to form a cyclic ether (1) and HO_2 elimination to form an alkene (2).

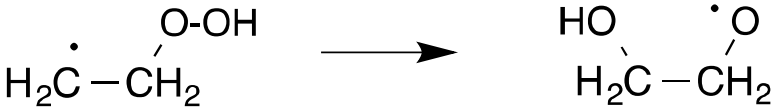


(1)

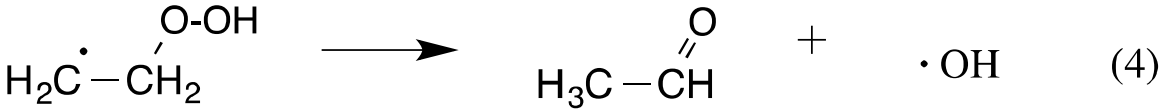


(2)

- **New pathways:** OH transfer (3) and internal H abstraction assisted OH elimination (4).



(3)

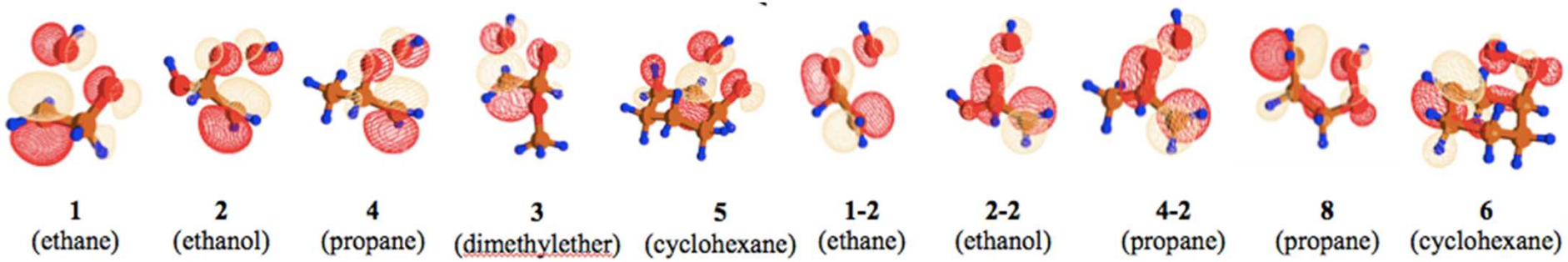


(4)

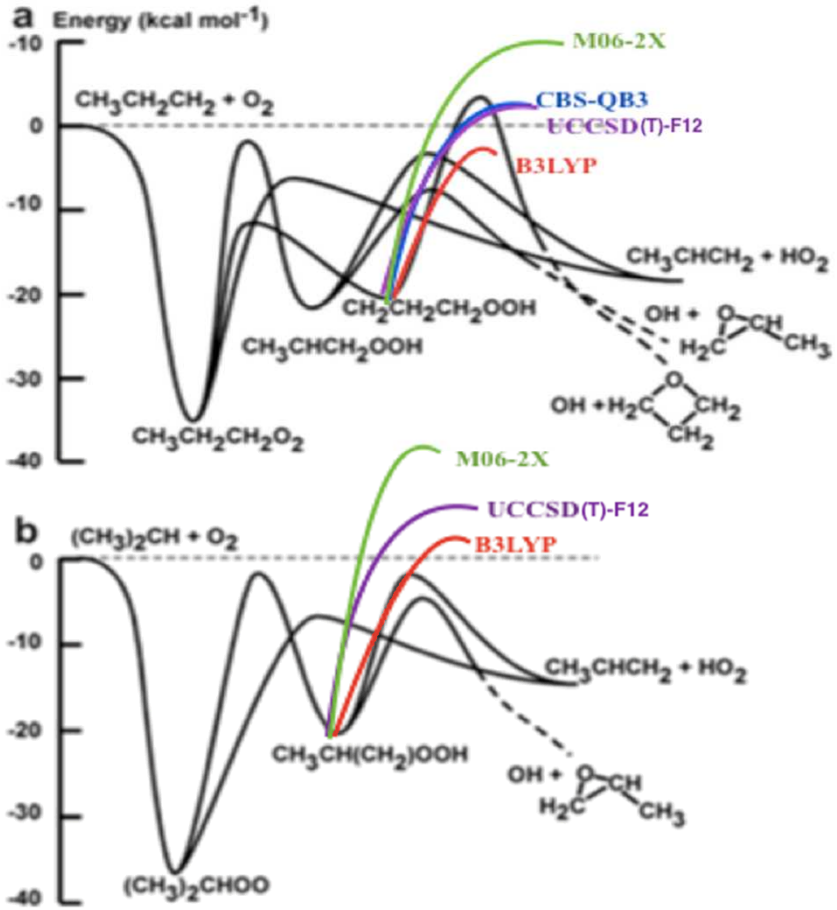
How relevant are these new pathways?

Methods:

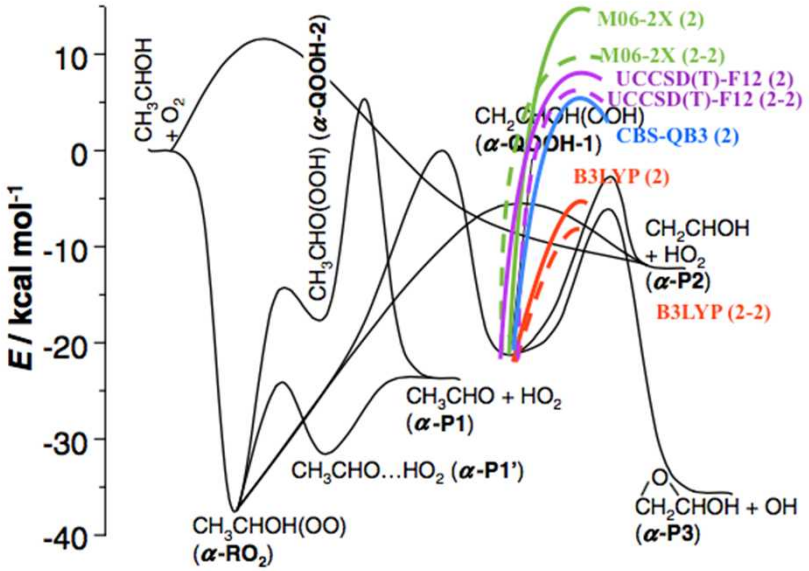
- Calculate energies of reactant and transition state of several substituted alkanes
- Compare energies using various quantum chemical theories
  - B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3 UCCSD(T)-F12/cc-pVQZ//M06-2X/6-311++G(d,p)
- Compare energies of new pathways to well-known pathways



Propyl and ethanol radical systems



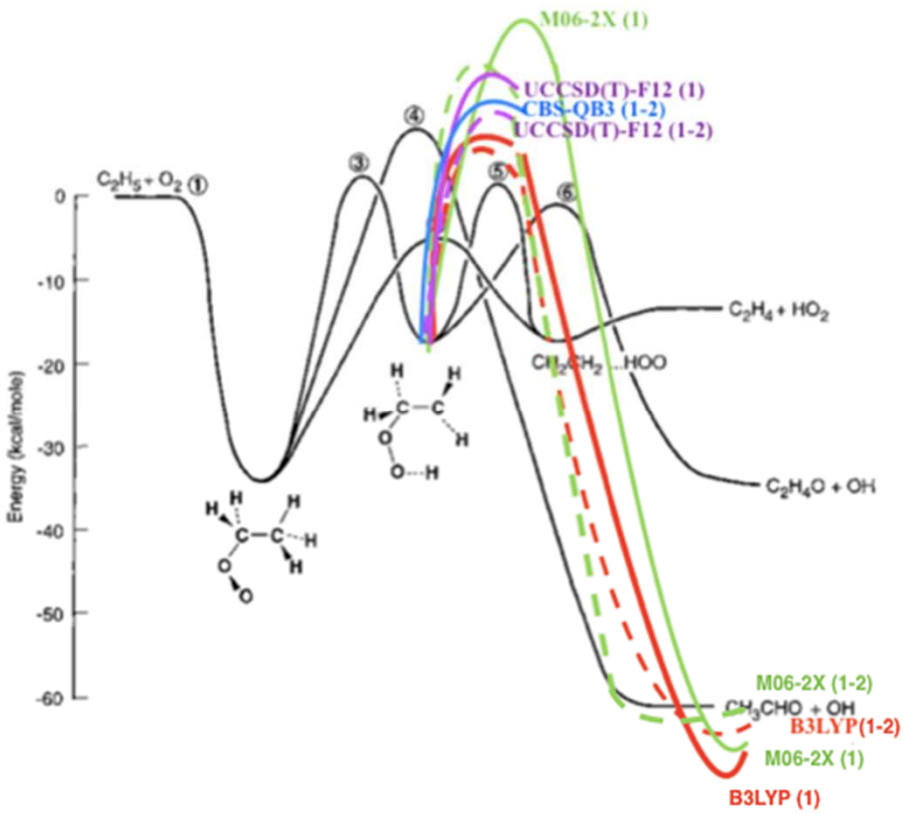
n-propyl and **i-propyl** systems undergoing OH transfer.



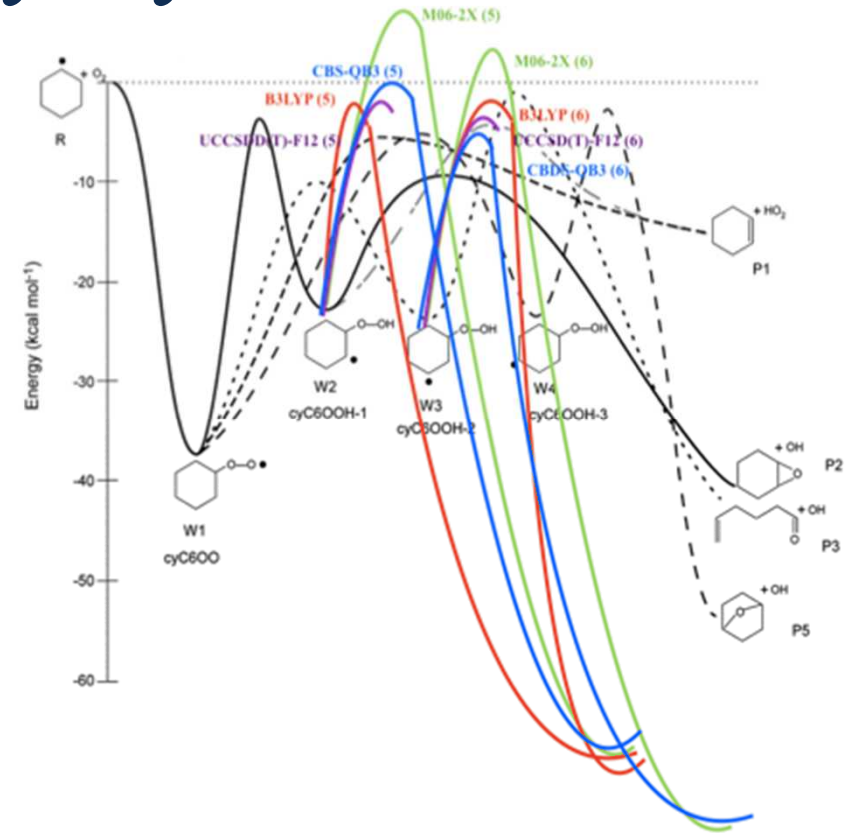
Ethanol radical system undergoing OH transfer (solid line) and H transfer (dashed line).

- OH transfer high in energy
- H transfer lower in energy
- Next-neighbor OH transfer lower in energy
- Large spread amongst methods

Ethyl and cyclohexyl systems



Ethyl system undergoing OH transfer (solid line) and H transfer (dashed line).

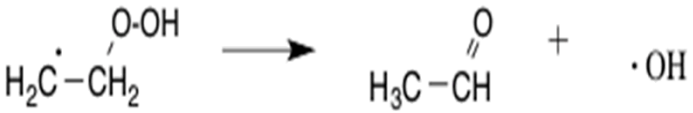


Cyclohexyl systems undergoing OH transfer.

- Pathways comparable in energy
- Cyclohexyl systems extremely exothermic

Conclusion and future studies

- New pathways comparable to known pathways
- H transfer → lower in energy (most relevant), chain propagating



- OH transfer → chain propagating, very exothermic

- Need to refine energy calculations (large T1 diagnostic)
- What are new pathways' role in autoignition?
  - Rate coefficients
  - Branching fractions

References

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