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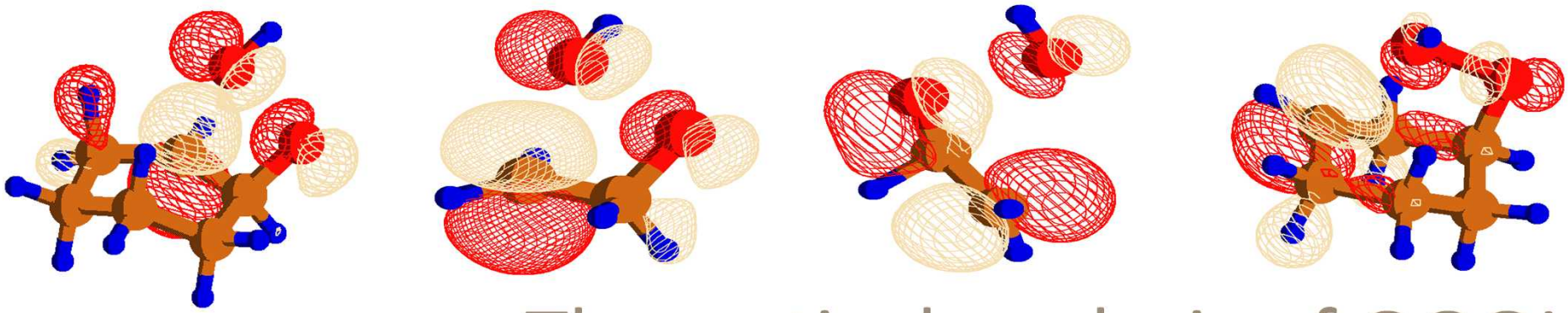

Theoretical analysis of QOOH combustion reaction pathways

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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QOOH and autoignition

- QOOH species are hydroperoxyalkyl radicals that are largely responsible for chain propagation in low-temperature hydrocarbon oxidation.
- Chain propagation → autoignition

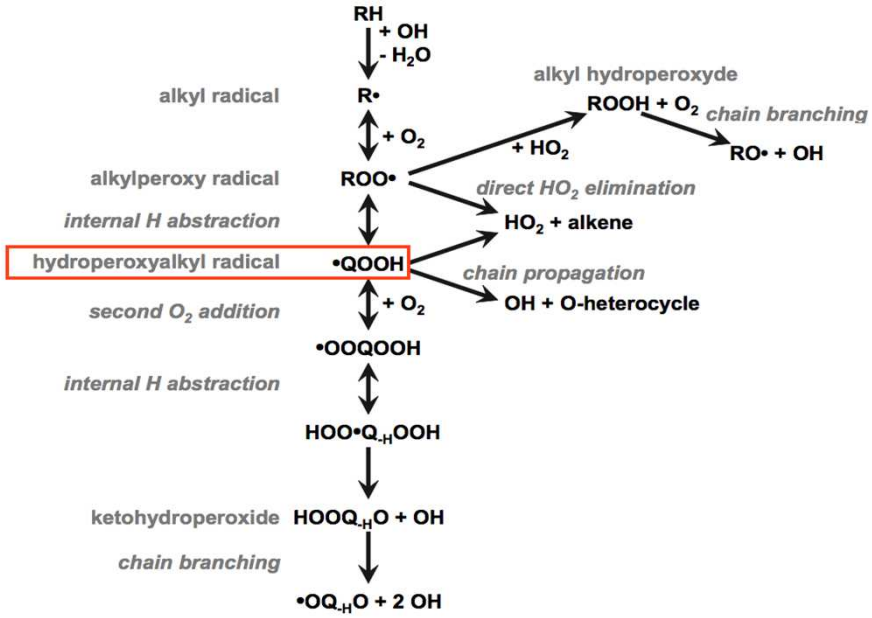
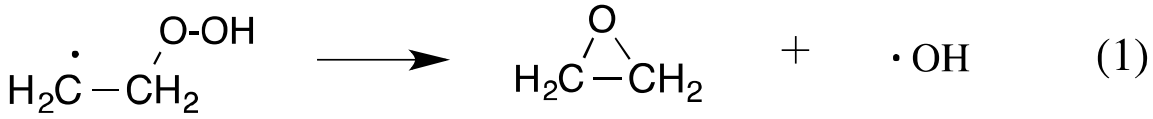


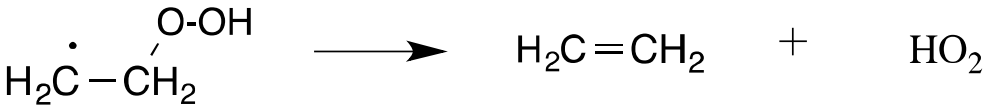
Fig. 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.

New QOOH reactions

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

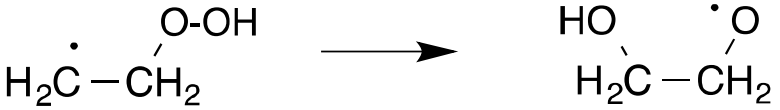


(1)

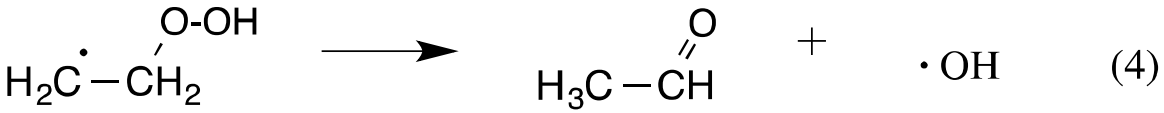


(2)

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



(3)

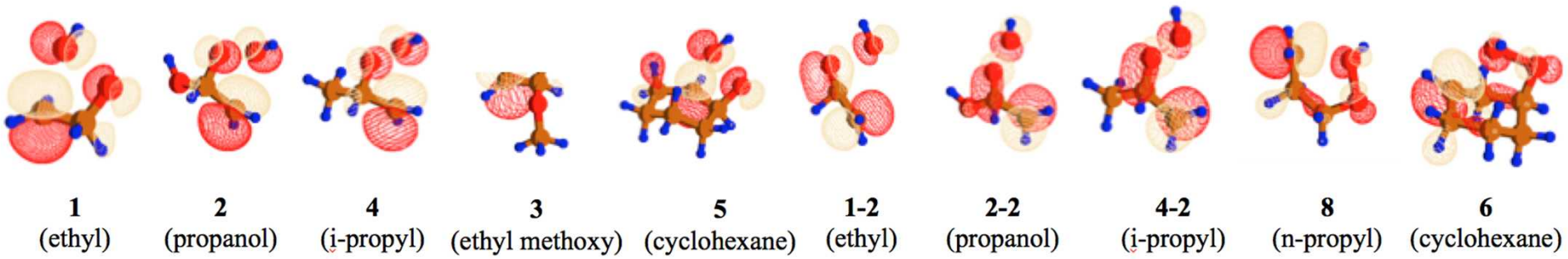


(4)

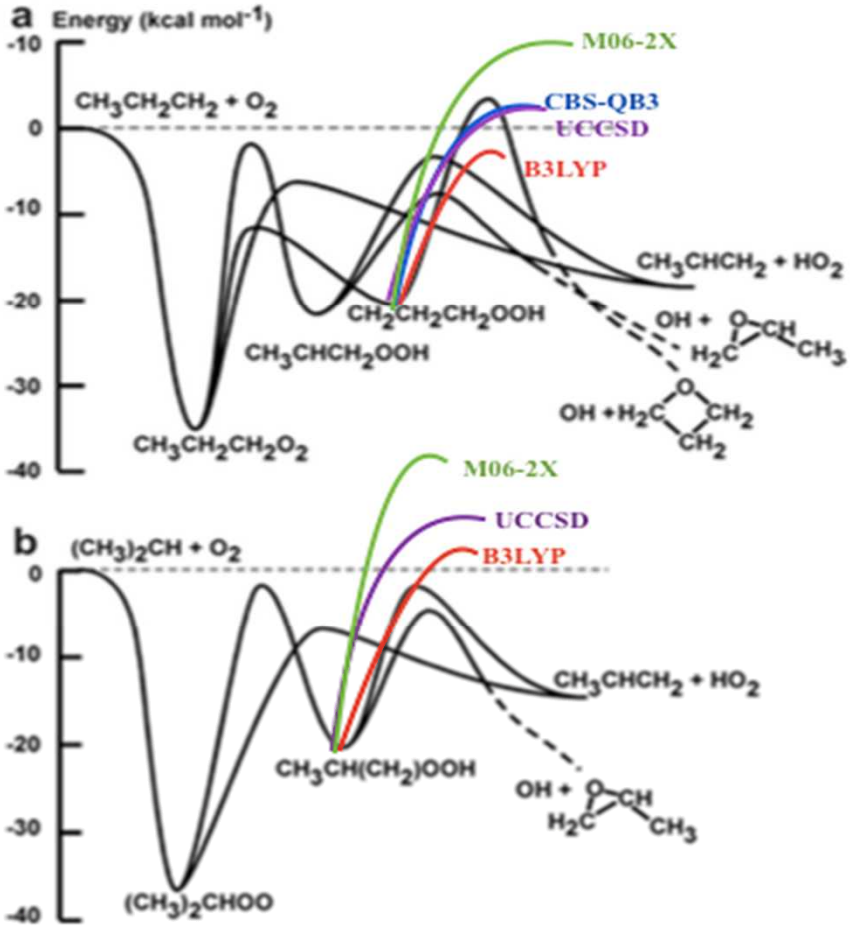
The test

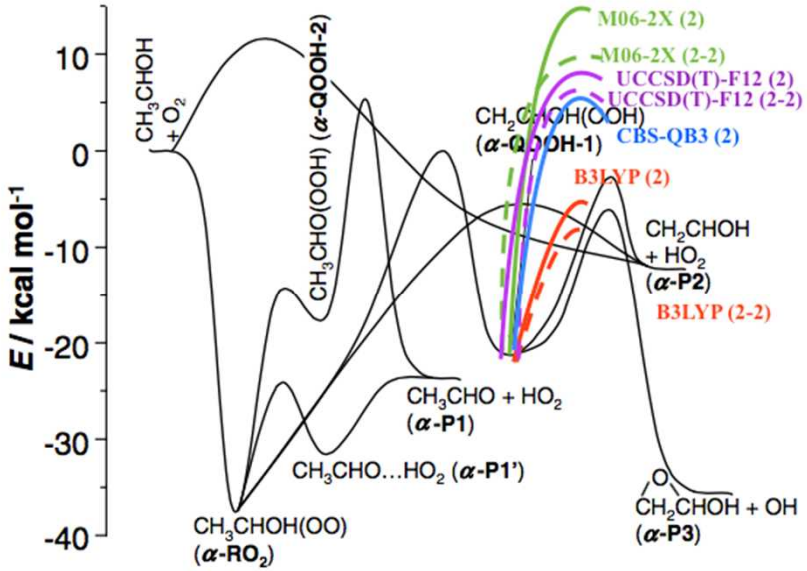
QOOH species with the following substitutions:

- CH_3 to investigate electron donating via inductive effects
- OCH_3 and OH to investigate electron donating via resonance effects
- Propyl and ethyl radical to investigate radical position
- Cyclohexane with ortho and meta radicals to investigate effects of radical position and ring strain

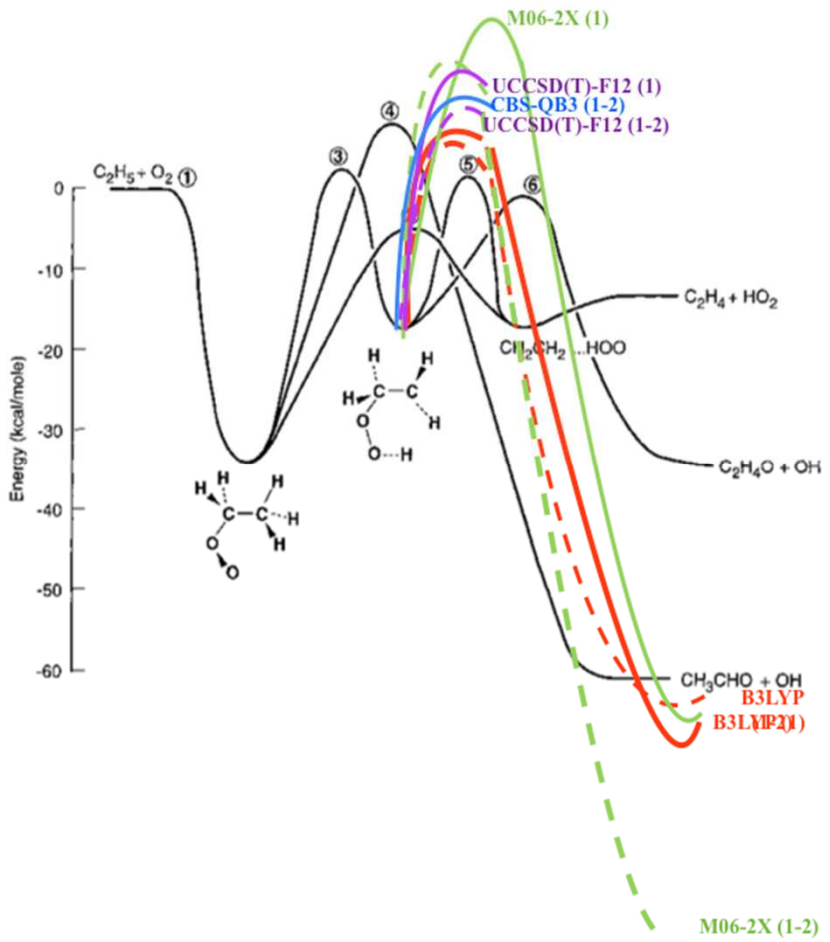


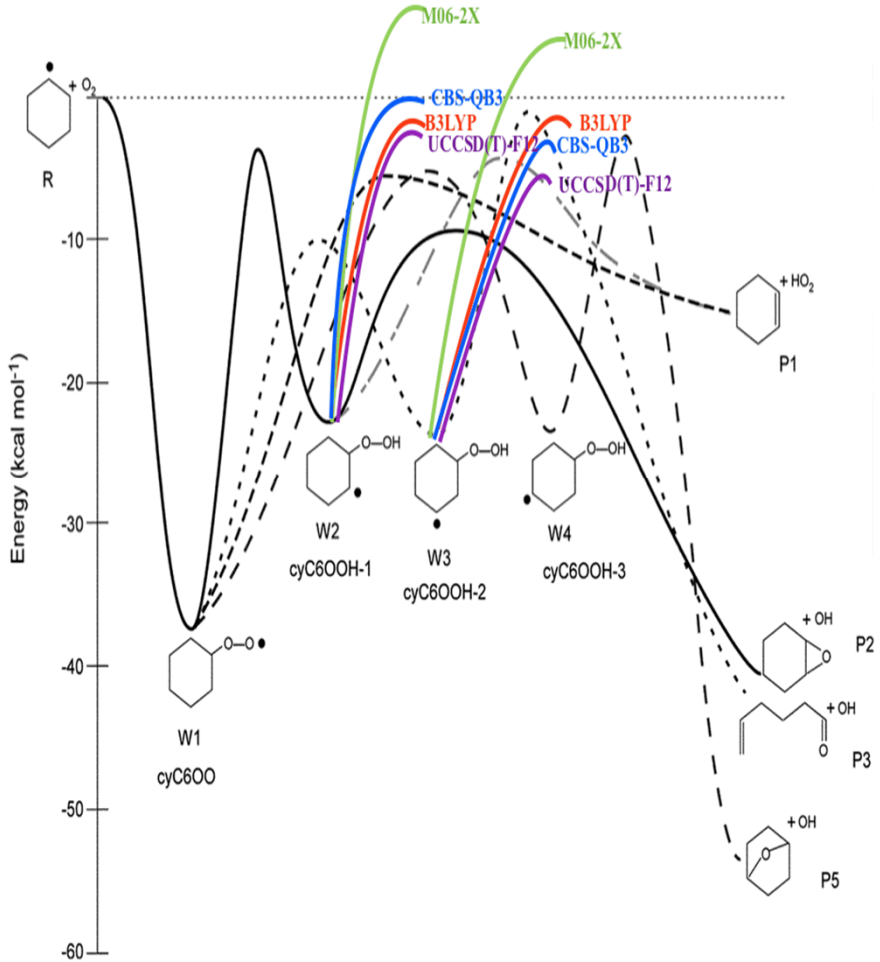
Propyl and ethanol systems





Ethyl and cyclohexane systems





Future studies

- Rate coefficients
- Branching fractions

References

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