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# Theoretical analysis of QOOH combustion reaction pathways

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## Abstract

QOOH radicals are key intermediates in the chain of reactions leading to the autoignition of hydrocarbons and oxygenated organic compounds. They are thought to undergo two main reactions: OH elimination to form a cyclic ether and $HO_2$ elimination to form an alkene. However, theoretical analysis of various substituted hydroperoxyalkyl radicals has found two new pathways: OH transfer and internal H abstraction assisted OH elimination. To determine the importance of these new pathways, their barrier heights for several substituted alkanes were calculated using various quantum chemical theories and compared to those of the well-known pathways. Several cases revealed possible competition with the well-known pathways. Further studies will need to calculate rate coefficients and branching fractions for these pathways to understand their role in autoignition.

## Introduction

QOOH species are hydroperoxyalkyl radicals that are largely responsible for chain propagation in low-temperature hydrocarbon oxidation. Understanding the reactions QOOH undergoes is very important as chain propagation drives autoignition chemistry (Figure 1).

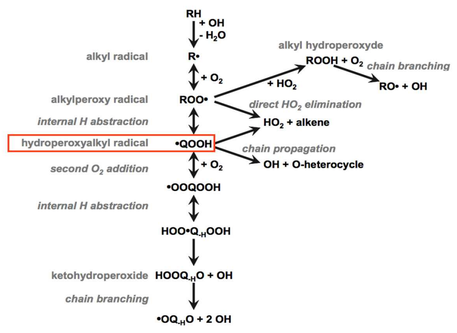
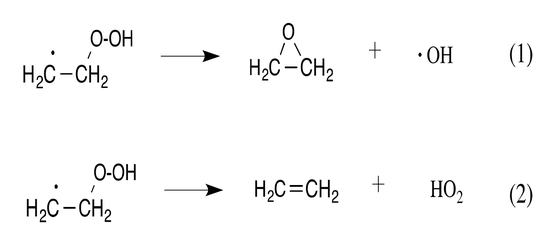



**Fig. 1.** Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.

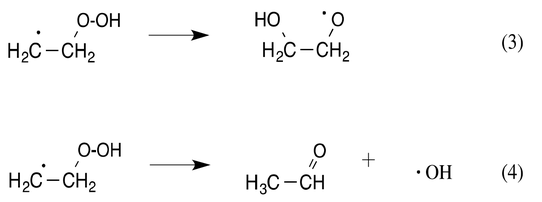
In order to optimize new fuel or engine models, these reactions must be fully explored. These elementary reactions, however, are very hard to observe experimentally due to fast propagation—making it easy to miss important pathways or short-lived intermediates.

KinBot is a software that can predict gas-phase combustion reactions—allowing the modeling of several reaction pathways in much less time and with fewer holes that may be found experimentally or using less efficient computational methods.

QOOH radicals are generally thought to undergo OH elimination to form a cyclic ether (1) or $HO_2$ elimination to form an alkene (2).




However, KinBot has found two new reactions that have not yet been observed or investigated computationally—OH transfer (3) and internal H abstraction assisted OH elimination (4).




To understand whether these findings are specific to just certain QOOH radicals and how the energy of these new pathways compares to the already known ones, I calculated barrier heights for several substituted alkanes using various quantum chemical theories.

## Methods

To determine the barrier height for various substituted alkanes (Figure 2), saddle points were located using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), and CBS-CB3 quantum chemical theories. The saddle points were proven to connect the proposed reactants and products by following the pathways along the intrinsic reaction coordinates (IRC). Besides the above methods, I also calculated highly accurate energies at the UCCSD(T)-F12/cc-pVQZ//M06-2X/6-311++G(d,p) level of theory for each species.

I proposed a range of substitutions to represent various effects:

- $CH_3$ 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

## Methods (Continued)

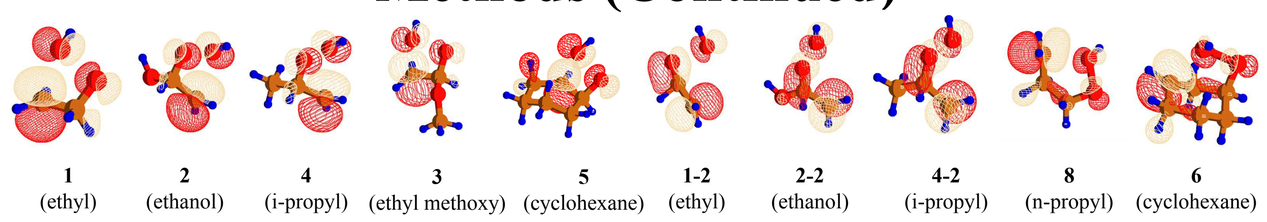



**Figure 2.** Geometries and highest occupied molecular orbitals (HOMOs) of tested transition states for various QOOH species. Species 1-2, 2-2, and 4-2 represent transition states of 1, 2, and 4, respectively, that undergo H transfer rather than OH transfer.

## Results

Schematic potential energy surfaces comparing calculated energy barriers of new OH-transfer pathways (reaction types (4), (8), (1), (5), (6) and (2)) and those of common $HO_2$ and OH elimination pathways from using B3LYP, M06-2X, CBS-CB3, and UCCSD(T)-F12 levels of theory. Drawn barriers represent E + ZPE values in kcal/mol relative to the respective alkyl + $O_2$ entrance channels.

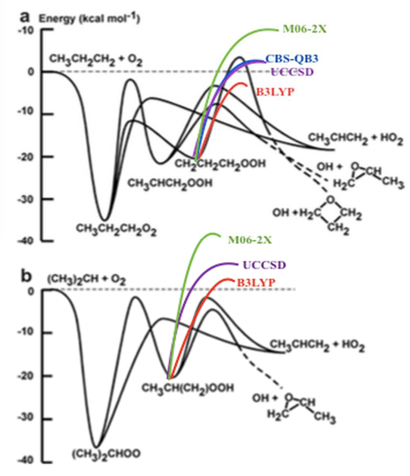



**Figure 3.** N-propyl and i-propyl systems, base figure from H. Huang et al. 2010. $Ts8_{B3LYP}$= -0.3, $Ts8_{M06\text{-}2x}$=10.6, $Ts8_{CBS\text{-}QB3}$=3.2, $Ts8_{UCCSD}$=3.1; $Ts4_{B3LYP}$= 3.4, $Ts4_{M06\text{-}2x}$=16.8, and $Ts4_{UCCSD}$=7.7.

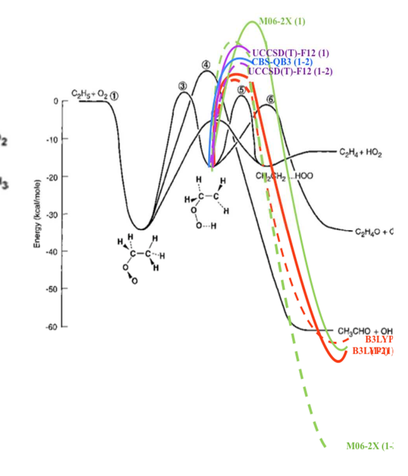



**Figure 4**. Ethyl system, base figure from Miller, Klippenstein, and Robertson 2000. $Ts1_{B3LYP}$= 7.6, $Ts1_{M06\text{-}2x}$=20.8, and $Ts1_{UCCSD}$=13.

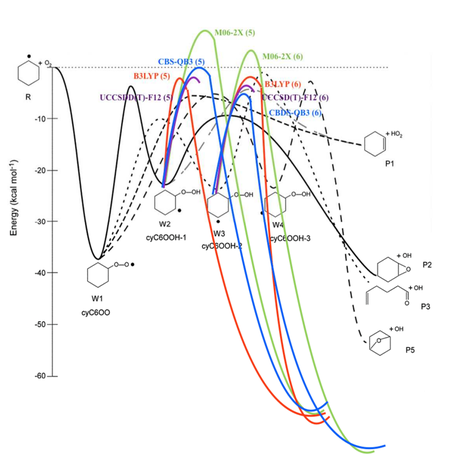



**Figure 5.** Cyclohexane systems, base figure from Adam M. Knepp et al. 2007. $Ts5_{B3LYP}$= -1.9, $Ts5_{M06\text{-}2x}$=9.6, $Ts5_{CBS\text{-}QB3}$= -0.8, $Ts5_{UCCSD}$= -1.6; $Ts6_{B3LYP}$= -1.4, $Ts6_{M06\text{-}2x}$=5.1, $Ts6_{CBS\text{-}QB3}$= -1.4, and $Ts6_{UCCSD}$= -2.9.

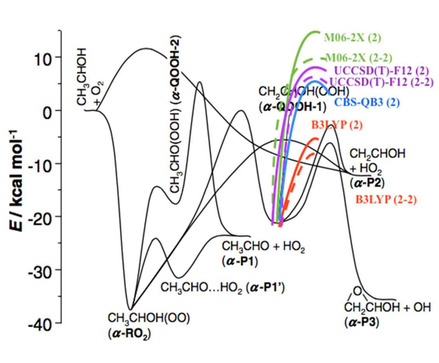



**Figure 6.** Ethanol system, base figure from J. Zádor et al. 2009.

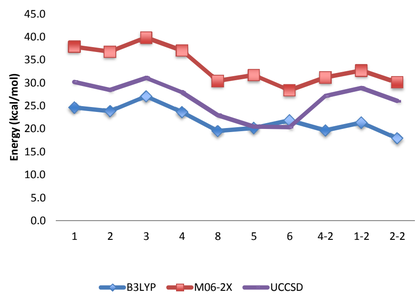



**Figure 7.** Comparison of transition state energy barriers of QOOH species and theory comparison.

| QOOH species | T1 diagnostic |
|---|---|
| 1 | 0.06796031 |
| 2 | 0.06753011 |
| 3 | 0.05482162 |
| 4 | 0.06642278 |
| 5 | 0.08806678 |
| 6 | 0.06676244 |
| 8 | 0.06884315 |
| 1-2 | 0.07095351 |
| 2-2 | 0.06592696 |
| 4-2 | 0.06485461 |

**Figure 8**. T1 diagnostics for transition structures of QOOH species. Large values (>0.02) suggest uncertainty of calculations are fairly high.

## Discussion

Pathways following internal H abstraction assisted OH elimination were frequently lower in energy than OH-transfer pathways. While the ethanol and propyl systems were higher in energy than the common pathways, those of cyclohexane and ethyl were comparable in energy. However, large T1 values suggest high uncertainty in our calculations. Future studies will need to calculate rate coefficients and branching fractions for these pathways to understand their role in autoignition.

## References

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Knepp, A.M.; Meloni, G.; Jusinski, L.E.; Taatjes, C.A.; Cavallotti, C.; Klippenstein, S. J. Theory, measurements, and modeling of OH and $HO_2$ formation in the reaction of cyclohexyl radicals with $O_2$. *Phys. Chem. Chem. Phys*., 2007, 9, 4315-4331.

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