

# Rate Rules for Conventional and Alternative Isomerization Pathways of Hydroperoxyalkylperoxy Radicals at the High-Pressure Limit

Samah Y. Mohamed<sup>1,\*</sup>, Alexander C. Davis<sup>2</sup>, Mariam J. Al Rashidi<sup>1</sup>, S. Mani Sarathy<sup>1</sup>

<sup>1</sup> King Abdullah University of Science and Technology, Clean Combustion Research Center, Thuwal, 23955-6900, Saudi Arabia

<sup>2</sup> Franklin and Marshall College, Lancaster, PA, 17604-3003, USA

\* Corresponding author: samah.mohamed@kaust.edu.sa

## Abstract

Understanding comprehensive low temperature oxidation chemistry is essential for accurately determining auto-ignition properties. Research efforts in this regard have focused primarily on the investigation of combustion reaction kinetics and thermodynamics, leading to more accurate rate coefficients and group values, as well as new reaction pathways that are supported by the experimental identification of new species<sup>1</sup>.

In the classical low temperature chemistry scheme, hydroperoxyalkylperoxy(OOQOOH) radicals isomerize via a conventional H-migration from the carbon connected to the OOH group to the peroxy group forming an OH radical and a ketohydroperoxide (KHP). KHP species further decompose to produce OH and alkoxy radicals. This chain branching is responsible for low-temperature reactivity. Alternatively, OOQOOH radicals can isomerize via H-migration from other sites forming P(OOH)<sub>2</sub> radicals, which can undergo further O<sub>2</sub> addition or decompose to a hydroperoxy cyclic ether + OH and/or olefinic-hydroperoxide + HO<sub>2</sub>, ultimately leading to variations in reactivity. Recently, it has been shown that the inclusion of these alternative pathways in the 2-methylhexane model increases reactivity by 40%<sup>2</sup>, with rate parameters assigned in analogy to RO<sub>2</sub> isomerization reactions.

In this work rate rules of conventional and alternative isomerization of hydroperoxyalkylperoxy radicals via 5-, 6-, 7- and 8-membered ring transition states are studied using computational methods. Effects of the chemical nature (primary, secondary or tertiary) of the peroxy and the H-abstraction sites are taken into consideration.

Geometry optimizations and frequency calculations of all reactants, products and transition states are performed using the Gaussian09 suite of programs. Initial scans of all rotors are performed using the B3LYP/6-31+G(d,p) method. The resulting lowest energy structures were further refined using B3LYP/6-311++G(2df,2pd) as well as the CBS-QB3, G3, and G4 composite methods. Rate parameters are determined using ChemRate and are fit to a three parameter Arrhenius equation over the temperature range of 300-1000 K.

The calculated rate rules are implemented in the 2-methylhexane model to elucidate the effects of using analogies on ignition properties. The calculation of branching ratios of conventional and alternative OOQOOH isomerization pathways shows that at low temperatures, below 600K, alternative pathways may be even more important than the conventional isomerization pathways, and thus, they should be included in mechanisms.

## References

1. Wang, Z.; Zhang, L.; Moshhammer, K.; Popolan-Vaida, D. M.; Shankar, V. S. B.; Lucassen, A.; Hemken, C.; Taatjes, C. A.; Leone, S. R.; Kohse-Höinghaus, K.; Hansen, N.; Dagaut, P.; Sarathy, S. M., *Combust Flame* **2016**, *164*, 386-396.
2. Mohamed, S. Y.; Cai, L.; Khaled, F.; Banyon, C.; Wang, Z.; Al Rashidi, M. J.; Pitsch, H.; Curran, H. J.; Farooq, A.; Sarathy, S. M., *J Phys Chem A* **2016**, 10.1021/acs.jpca.6b00907.