

# Implications of Radical Ring-Opening Reactions on Ketohydroperoxide Formation: Cyclohexane and Tetrahydropyran

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The utilization of biofuels for transportation energy is most practical in blends with conventional hydrocarbons. Integration of biofuels as blending components therefore requires fundamental insight into the underlying oxidation chemistry, which at temperatures below 1000 K is governed by a degenerate chain-branching mechanism initiated by the reaction of  $O_2$  with an organic radical  $R$  formed via H-abstraction from the hydrocarbon ( $RH$ ). The  $R + O_2$  reaction forms organic peroxy radicals ( $ROO$ ), which can isomerize into carbon-centered hydroperoxyalkyl ( $QOOH$ ) radicals [1]. The propensity of hydrocarbons to undergo low-temperature chain-branching requires the second  $O_2$ -addition reaction  $QOOH + O_2$ , forming  $OOQOOH$  species, which then decompose in part through the formation of ketohydroperoxide ( $O=Q-HOOH$ ) +  $OH$ . Unlike acyclic hydrocarbons, reaction mechanisms of cyclic species include ring-opening reactions that interrupt the second  $O_2$ -addition step therein reducing chain-branching and complicating the broader reaction network.

The present study utilizes multiplexed photoionization mass spectrometry (MPIMS) to detect reaction intermediates and uniquely identify the corresponding pathways that arise from ring-opening reactions of initial cyclic  $R$  and  $QOOH$  radicals in the oxidation of cyclohexane ( $c-C_6H_{12}$ ) and tetrahydropyran ( $c-C_5H_{10}O$ ), a lignocellulosic-derived oxygenated biofuel. The experiments were conducted using  $Cl$ -initiated oxidation at 10 Torr and 1500 Torr and from 500 – 700 K. *ab initio* calculations of saddle point energies on  $R + O_2$  potential energy surfaces and unimolecular decomposition rate coefficients of  $\alpha$ -tetrahydropyranyl were conducted to complement the experiments.

The main point of contrast determined herein between cyclohexane and tetrahydropyran, in relation to chain-branching, is in ketohydroperoxide formation and is due to enhanced rates of  $R$  and  $QOOH$  ring-opening reactions at temperatures near 700 K. Cyclohexane oxidation maintains the production of ketohydroperoxide species with increased temperature, while in tetrahydropyran oxidation  $QOOH$  ring-opening into carbonyl + alkene +  $OH$  impedes the production of ketohydroperoxides. Oxygenation of biofuels (e.g. tetrahydropyran) weakens  $C-H$  and  $C-O$  bonds near the functional group, which facilitates radical ring-opening and alters  $R + O_2$  reaction pathways [2]. Complete description of reaction mechanisms for cyclic hydrocarbons requires the inclusion of ring-opening reactions that affect chain-reaction pathways, particularly ones that result in a reduction in the flux of  $QOOH + O_2$ . Accordingly, the present study aims to compare the oxidation of tetrahydropyran with the structurally analogous cyclohexane and provide constraints for modeling the reaction mechanisms of cyclic hydrocarbons by identifying intermediates and corresponding ring-opening reactions of  $R$  and  $QOOH$  radicals, the process of which contributes to reduced ketohydroperoxide formation and subsequent chain-branching.

## References

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- (2) Rotavera, B.; Savee, J.D.; Antonov, I.O.; Caravan, R.L.; Sheps, L.; Osborn, D.L.; Zádor, J.; Taatjes, C.A. *Proc. Comb. Inst.* **2016**, accepted.