

Role of ring-opening reactions in low-temperature oxidation of *cis*- and *trans*-2,3-dimethyloxiranyl radicals

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The *cis*- and *trans*- isomers of 2,3-dimethyloxirane are cyclic ethers produced from unimolecular decomposition of β -QOOH and from epoxidation reactions of 2-butene + HO \dot{O} during *n*-butane oxidation. Recent isomer-resolved oxidation experiments in Doner et al. [1] detected species produced from peroxy radical-mediated reactions, including methyl vinyl ketone, diacetyl, and vinyl acetate. However, the formation pathways remain unclear as to whether the species form from O₂-addition to intact 2,3-dimethyloxiranyl radicals or to radicals produced from ring-opening. The present work examines reaction rates for the competing pathways to provide clarity and fundamental insight on the reaction mechanisms of *cis*- and *trans*-2,3-dimethyloxirane. Stereochemical-dependent potential energy surfaces for 2,3-dimethyloxiranyl radicals were calculated using AutoMech [2] and rate coefficients were computed using master equation modeling from 0.01 – 100 atm and 300 – 1000 K.

The rate calculations herein focus on the competition between reactions of α - and β - isomers of 2,3-dimethyloxiranyl (\dot{R}), namely ring-opening to \dot{R}' , including via prompt reactions, and O₂-addition to form ROO (Figure 1). The results show that, across a broad range of pressures, ring-opening rates exceed O₂-addition unless [O₂] > 10¹⁹ cm⁻³. However, prompt effects are significant for H-abstraction from *cis*- and *trans*-2,3-dimethyloxirane above ~500 K. The implication of the latter result is that thermalization of \dot{R} at combustion conditions is minimal, indicating that O₂ preferentially adds to carbon-centered radicals formed via ring-opening, even at high O₂ concentrations. Following from Dewey and Rotavera [3], inclusion of such pathways in chemical kinetics mechanisms of *n*-butane impacts $\dot{O}H$ radical populations, species profiles, and chain-branching reactions that are also relevant to other alkyl radicals.

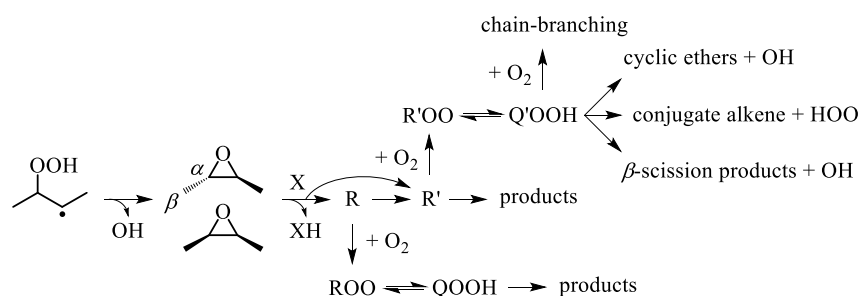


Figure 1: Prompt reactions affect competing O₂-addition and ring-opening of cyclic ether radicals.

References

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