

Bimolecular Reactions of Cyclic Ether Radicals

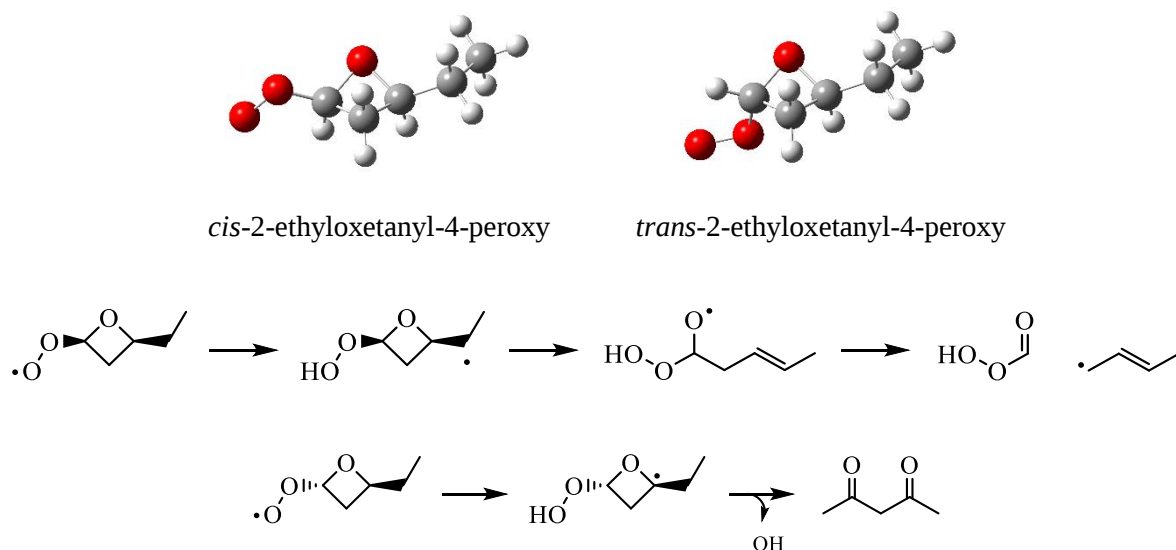
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ABSTRACT

Alkyl-substituted cyclic ethers including alkyloxiranes and alkyloxetanes are isomer-specific proxies for reaction mechanisms of carbon-centered hydroperoxyalkyl radicals ($\dot{\text{Q}}\text{OOH}$). Subsequent bimolecular reactions of cyclic ethers include H-abstraction, which creates strained, carbon-centered radicals that may form peroxy radicals following O_2 -addition. The length of the alkyl substituents and the proximity of the localized electron relative to the ether group affects the propensity for intramolecular hydrogen transfer to form a $\dot{\text{Q}}\text{OOH}$ radical that retains the cyclic ether structure. In addition, stereochemical effects, namely the position of the substituents relative to the plane of the ether group, creates stereoisomer-specific reaction pathways, some of which involve chain-branching via formation and decomposition of organic acids (e.g. performic acid) and some involve the formation of metastable dicarbonyls (e.g. 2,4-pentanedione) that, prior to Doner et al.¹ were ascribed to form exclusively via decomposition reactions of ketohydroperoxides formed from second- O_2 -addition ($\dot{\text{Q}}\text{OOH} + \text{O}_2$).

The importance of accurate and complete description of the chemical kinetics of cyclic ether lies in the ubiquitous, inadequate description of the aforementioned bimolecular reactions and the associated uncertainty that arises from mechanism truncation error². Ongoing efforts to produce high-fidelity sub-mechanisms for cyclic ethers are outlined. The approach involves isomer-resolved speciation measurements from gas-phase oxidation experiments of cyclic ethers in a jet-stirred reactor in addition to high-level quantum-chemical computation of rate coefficients and thermochemical properties of species.



¹ Doner, A. C., J. Zador, Rotavera, B. Stereoisomer-Dependent Rate Coefficients and Reaction Mechanisms of 2-ethyloxetanylperoxy Radicals. *Proc. Comb. Inst.* 40, 105578, 2024.

² Dewey, N. S. and Rotavera, B. Reaction mechanisms of alkyloxiranes for combustion modeling. *Combustion Flame* 252, 112753, 2023.

³ Copan, A. V., Moore III, K. B., Elliott, S. N., Mulvihill, C. R., Pratali Maffei, L., Klippenstein, S. J. Radical Stereochemistry: Accounting for Diastereomers in Kinetic Mechanism Development. *J. Phys. Chem. A* 128, 3711-3725, 2024.