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Reaction Mechanisms of a Cyclic Ether Intermediate: *cis*-2,3-dimethyloxirane

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Abstract

Oxiranes are a class of cyclic ethers formed in abundance during low-temperature combustion of hydrocarbons and biofuels, either via chain-propagating steps that occur from unimolecular decomposition of β -hydroperoxyalkyl radicals (β -QOOH) or from reactions of HO \dot{O} with alkenes. *cis*- and *trans*- isomers of 2,3-dimethyloxirane are produced as intermediates from *n*-butane oxidation. While rate coefficients for β -QOOH \rightarrow 2,3-dimethyloxirane + $\dot{O}H$ are reported extensively, subsequent reaction mechanisms of the cyclic ethers are not. As a result, chemical kinetics models commonly adopt simplified consumption mechanisms of 2,3-dimethyloxirane isomers by convoluting several elementary reactions into a single step, which may introduce mechanism truncation error – model uncertainty derived from missing chemistry.

The present work provides insight on reaction mechanisms of *cis*-2,3-dimethyloxirane in support of ongoing efforts to minimize mechanism truncation error. Reaction mechanisms are inferred from the detection of products during Cl-initiated oxidation of *cis*-2,3-dimethyloxirane using multiplexed photoionization mass spectrometry conducted at 10 Torr and temperatures of 650 K and 800 K. Several species were identified from ring-opening of α - and β -*cis*-2,3-dimethyloxirane radicals. Neither of the two conjugate alkene isomers from $\dot{R} + O_2$ reactions were detected. Products were also identified from decomposition of alternative QOOH radicals, namely resonance-stabilized ketohydroperoxide-type radicals. The present work provides the first analysis of *cis*-2,3-dimethyloxirane reaction mechanisms and reveals that consumption pathways of alkyl-substituted oxiranes formed as intermediates during hydrocarbon and biofuel combustion are complex and may require expanded sub-mechanisms.

Keywords: cyclic ether, primary intermediate, *n*-butane, MPIMS, QOOH