

## Probing O<sub>2</sub>-Dependence of Tetrahydrofuranyl Reactions via Isomer-Resolved Speciation

Alanna L. Koritzke<sup>a</sup>, Matthew G. Christianson<sup>a</sup>, Samuel W. Hartness<sup>b</sup>,  
Nicholas S. Dewey<sup>a</sup>, Anna C. Doner<sup>a</sup>, Annabelle R. Webb<sup>a</sup>, and Brandon Rotavera<sup>a, b, \*</sup>

<sup>a</sup>University of Georgia, Department of Chemistry, Athens, Georgia, USA

<sup>b</sup>University of Georgia, College of Engineering, Athens, Georgia, USA

\*Corresponding author: [rotavera@uga.edu](mailto:rotavera@uga.edu)

Low-temperature combustion of tetrahydrofuran involves competing reactions that depend on temperature, pressure, and oxygen concentration, including ring-opening and subsequent oxidation of initial radicals ( $\dot{R}$ ), HOO-elimination yielding dihydrofuran isomers, and the formation of peroxy radicals ( $RO\dot{O}$ ). The latter species, upon isomerization, lead to hydroperoxy-substituted radicals ( $\dot{Q}OOH$ ) that undergo reaction either via unimolecular decomposition or second-O<sub>2</sub>-addition. Quantitative measurements of partially oxidized intermediates formed from each type of reaction provide critical constraints that are required for accurate modeling of combustion chemistry. To examine the influence of temperature and oxygen concentration on intermediates from tetrahydrofuran, isomer-resolved speciation measurements were conducted at 810 Torr in a jet-stirred reactor (JSR) from 500 – 1000 K. Resulting from negative-temperature coefficient behavior, species concentrations peaked at two temperatures, 600 K and 800 K, which were then selected for separate experiments to quantify O<sub>2</sub>-dependence using concentrations of  $0.37 \cdot 10^{18} - 7.40 \cdot 10^{18}$  molecules cm<sup>-3</sup>.

Utilizing vacuum-ultraviolet absorption spectroscopy and electron-impact mass spectrometry, several species related to  $\dot{R} + O_2$  reactions were detected for the first time, including explicit resolution of constitutional isomers tetrahydrofuran-3-one, butanedial, allyl formate, the latter two resulting from ring-opening reactions of  $\dot{Q}OOH$  radicals. For the majority of species, including dihydrofuran isomers, tetrahydrofuran-3-one, oxirane, and methyloxirane, a clear dependence on O<sub>2</sub> exists that is not captured quantitatively by chemical kinetics mechanisms. The latter two species arise from reactions of ring-opened  $\alpha$ -tetrahydrofuranyl radicals while the others are derived initially from  $\dot{R} + O_2$  reactions. The experiments herein provide new targets for refinement of chemical kinetics mechanisms of tetrahydrofuran. The discrepancies existing between the measured and model-predicted species profiles indicate that sub-mechanisms for important intermediates may require additional elementary reactions, such as for dihydrofuran isomers. In addition, rates for O<sub>2</sub>-addition to tetrahydrofuranyl radicals in chemical kinetics mechanisms, which employ rate rules from alkyl radicals, require scrutiny.