

Temperature- and pressure-dependent competition among reaction pathways from first- and second-O₂ additions in THF oxidation

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An important part of the reactivity of organic peroxy radicals (ROO) is the isomerization by internal H-abstraction to carbon-centered radicals (QOOH), which play key roles in diverse systems ranging from combustion chemistry to the Earth's atmosphere. In atmospheric chemistry, consecutive internal H shifts and O₂ addition steps to QOOH influence the creation and aging of aerosol particles, with implications for air quality, health, and the climate.¹ In combustion, the competition between QOOH decomposition and second O₂ addition governs the extent of radical chain branching that eventually leads to ignition.²⁻³ Detailed knowledge of fuel oxidation chemistry is needed to optimize the performance of advanced engine designs, which rely on autoignition in the low-temperature regime, $T < 800\text{K}$.

We performed a combined experimental and computational study of the autoignition chemistry of tetrahydrofuran (THF), a prototypical cyclic ether that is a building block of several proposed biofuels. We probed numerous reaction intermediates and products of THF oxidation using synchrotron-based time-resolved photoionization mass spectrometry at $T = 400 - 700\text{ K}$ and $P = 10 - 2000\text{ Torr}$, and interpreted our results with aid from quantum chemical calculations of the relevant potential energy surfaces. The main active pathways in THF oxidation at low pressures are decomposition of ROO and QOOH to form HO₂ + 2,3-dihydrofuran and OH + butanedial. However, second-O₂ addition to QOOH becomes increasingly important at elevated P due to collisional stabilization of the OOQOOH adduct. Surprisingly, OOQOOH decomposition yields relatively unreactive HO₂ + dihydrofuranyl hydroperoxide, contrary to common assumptions of second-O₂ addition as a chain-branching step. Our experimental results, including the direct probing of OOQOOH and its decomposition products, help constrain a low- T THF oxidation mechanism and provide key benchmarks for the modeling of THF combustion.

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