

•QOOH decomposition and the •QOOH + O₂ reaction: Direct experimental investigation and theory

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The carbon-centered hydroperoxyalkyl radicals, often referred to as •QOOH, play a central role in the autoignition kinetics of alkanes at low temperatures (<~800 K), because they participate in important chain propagating and chain branching reactions. The formation of these radicals in the gas-phase by internal H-abstraction from the corresponding peroxyalkyl radicals (ROO•) was postulated at least as early as 1965¹ based on product studies. With the advancement of computational and theoretical chemistry the pathways leading to these highly unstable radicals have been established.^{2,3} •QOOHs are ubiquitous in every complex chemical model describing low-temperature autoignition of alkanes or related compounds, yet, these ephemeral species have never been observed directly, nor have their kinetics been studied in isolation.

In this work we present the first direct measurements on the kinetics of a •QOOH radical. The *tert*-butyl hydroperoxy radicals are generated from *tert*-butylhydroperoxide by abstracting one of the nine methyl hydrogens by a photolytically generated Cl-atom. The fate of this •QOOH radical and its reaction with molecular oxygen was monitored in two low-pressure experimental setups at room temperature. In one experiment we probed the OH radicals, which are direct products from the thermal decomposition of this •QOOH radical, in a reaction flow cell by multipass direct absorption at 2.87 μm wavelength to obtain time-resolved absolute OH concentrations. We additionally performed multiplexed synchrotron photoionization mass spectrometry (MPIMS) experiments at the Chemical Dynamics Beamline at the Advanced Light Source to obtain mass-, isomer- and time-resolved profiles of the chemical species involved, providing further, complementary insight into the chemical mechanism. Finally, the chemical system was described using high-level theoretical calculations, employing *ab initio* transition-state master-equation methods as well as a small chemical model to account for the secondary chemistry in the experiments.

Our combined experimental and theoretical effort enabled us to make the first direct investigation of a •QOOH species: we measured rate coefficients and branching fractions of its decomposition reaction and of its reaction with O₂. This information, in turn, can be used to constrain both our theoretical approaches and larger chemical models.

References

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