SAND2012-1612C

•QOOH decomposition and the •QOOH + O_2 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). 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 1965[1] based on product studies. With the advancement of computational and theoretical chemistry the pathways leading to these highly unstable radicals were established.[2,3] •QOOHs are ubiquitous in every complex chemical model describing low-temperature autooxidation 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 is monitored in two low-pressure experimental setups at room temperature. In one experiment we probe OH radicals, which are direct products from the thermal decomposition of this •QOOH radical, by direct IR-absorption in a Herriott-type flow cell allowing us to obtain time-resolved information on the absolute OH yields. We additionally perform multiplexed synchrotron photoionization mass spectrometry (MPIMS) experiments to obtain mass-, isomer- and time-resolved profiles of the participating chemical species, providing further, complementary insight into the chemical mechanism. Finally, the chemical system is 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 get the first direct observations for this crucial species, and to establish directly measured rate coefficients, which in turn can be used to constrain both our theoretical approaches and larger chemical models.

References

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