

Reaction Mechanisms of R and QOOH Radicals Produced in Low-Temperature Oxidation of Butanone

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Butanone ($\text{H}_3\text{CC}(=\text{O})\text{CH}_2\text{CH}_3$) is a potential biofuel derived from biochemical and catalytic processes utilizing a range of different platform chemicals including 2,3-butanediol, produced from microbial fermentation, and levulinic acid. The presence of the carbonyl group in butanone introduces resonance stabilization in R and QOOH radicals, a characteristic that impacts combustion-relevant reaction mechanisms. Resonance stabilization alters the competition between chain-branching, chain-propagation, and chain-termination in low-temperature autoignition chemistry, which is initiated by $\text{R} + \text{O}_2$ reactions. Ignition delay time experiments of Burke et al. (*Comb. Flame*, 2016) confirm inhibited chain-branching in the low- and intermediate-temperature regimes for butanone relative to *n*-butane. The present work examines product formation and related mechanisms in butanone oxidation and concludes that chain-propagation pathways remain relevant at temperatures below 700 K.

Multiplexed photoionization mass spectrometry (MPIMS) measurements of Cl-initiated butanone oxidation were conducted at 10 Torr and temperatures of 500 K and 700 K to study reaction mechanisms under conditions where QOOH-mediated product formation dominates. Pseudo-first-order conditions using low initial radical concentrations and high oxygen concentrations ($[\text{R}]_0 \sim 10^{12}$ molecules cm^{-3} and $[\text{O}_2] \sim 10^{16}$ molecules cm^{-3}) were utilized in order to favor $\text{R} + \text{O}_2$ over other reactions of the initial radical. Two isotopologues were employed: butanone and butan-2-one-1,1,1,3,3-d5 ($\text{D}_3\text{CC}(=\text{O})\text{CD}_2\text{CH}_3$). Photoionization spectra from both sets of experiments identify 10 distinct species relevant to understanding low-temperature butanone oxidation. Concentration measurements were made relative to the methylvinylketone (but-3-en-2-one) product, which is formed with monotonically positive temperature dependence via several $\text{R} + \text{O}_2$ reactions. Other relevant species quantified include carbonyl species, diacetyl and 3-oxobutanal, and two cyclic ether species, tetrahydrofuran-3-one and 1-oxiranyl-2-ethanone, all of which are formed coincident with OH in chain-propagation reactions via QOOH unimolecular decomposition. Several species arising from C–C β -scission of initial R radicals of butanone, e.g. butan-2-one-1-yl, were also quantified, including methyl, ethene, formaldehyde, ketene, and acetaldehyde.

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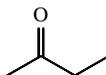


Fig. 1. Molecular structure of butanone.

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