

Low-Temperature Oxidation studies of Butanone

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Ketones are as a class of compounds that may be derived from cellulosic biomass and have garnered significant interest as bio-derived transportation fuels. Butanone, in particular, has been identified as a promising transportation fuel candidate due to its high octane rating (1), and several synthetic routes from biomass have now been developed. For example, via the decarboxylation of levulinic acid, a hydrolysis product of cellulose (2), as well as direct sources via emissions from fungi (3), which grow on the drought-resistant Creosote bush found in desert regions of North America.

Whilst there have been a number of studies regarding the high-temperature combustion chemistry of butanone, advanced internal combustion engines, such as HCCI-type technology, are sensitive to the lower temperature oxidation mechanisms, derived from $R + O_2$ reactions, which are not yet well understood for ketones.

In the low-temperature (<900 K) oxidation regime, the initial step following H-abstraction from a hydrocarbon (RH) is addition of O_2 . Isomerization of the resultant oxygen-centered organic peroxy radical (ROO) to the carbon-centered QOOH radical can lead to a number of potential chain-propagating (cyclic ether + OH) and chain-terminating (alkene + HO_2) pathways.

Alternatively, following second O_2 -addition and subsequent internal H-transfer steps, the reaction sequence can yield ketohydroperoxide species – the decomposition of which leads to chain-branching via the formation of an oxy radical and two OH radicals.

In competition with these pathways are C-C β -scission channels of R and QOOH radicals, the propensity for which is influenced by the depths of the ROO and QOOH wells on the potential energy surface. Several of the butanone-derived R and QOOH radicals are resonance-stabilized with the carbonyl group, and the potential influence of resonance-stabilization of these intermediates on the yields of chain-propagation and β -scission products is explored.

Examination of the role of resonance-stabilization in butanone oxidation also aids in constraining the influence of such reactions on the oxidation mechanisms of larger, more-complex ketones.

To address the uncertainties in the low-temperature oxidation of butanone, product formation from chlorine-initiated oxidation experiments was studied at 500 and 700 K at 10 Torr using a Multiplexed Photoionization Mass Spectrometer (MPIMS) coupled to tunable synchrotron radiation from the Chemical Dynamics Beamline at the Advanced Light Source, allowing spectroscopic isomer resolution. Additional experiments utilizing partially deuterated butanone, $CD_3C(O)CD_2CH_3$, were performed to further isolate specific isomeric pathways by mass and the experimental work has been complimented by *ab initio* calculations using the automated potential energy surface exploration software, KinBot. (4)

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