

Towards Understanding Autoignition Chemistry of Fuel – Air(Oxygen) Mixtures Important for New IC-Engine Technologies Using a Novel High-Pressure Reactor Interfaced with a Synchrotron Photoionization Time-of-Flight Mass-Spectrometer

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Autoignition of a homogenous or nearly homogenous fuel – air mixture during the compression stroke plays crucial role in modern internal-combustion (IC) engine technologies e.g. homogeneous charge compression-ignition (HCCI) and stratified-charge compression-ignition (SCCI) engines, which promise to combine high efficiencies with ultra-low emissions. Ignition timing in these engines is determined by autoignition of a fuel – air mixture during compression and not an external means like a spark in petrol engines or fuel injection in diesel engines. Consequently, autoignition chemistry and reaction kinetics play crucial roles in development of new IC-engine technologies. One especially important but not well-understood regime to understand and predict autoignition is low-temperature combustion, which largely determines when autoignition occurs.

In the first steps of the generally accepted fuel radical oxidation mechanism under low-temperature combustion conditions, a fuel radical adds to O₂ forming RO₂ that can isomerize *via* internal H-atom transfer to form a QOOH radical. This QOOH radical can then decompose to relatively unreactive alkene + HO₂ products or form oxygen heterocycle + OH products in a chain-propagation channel. Under high [O₂] conditions, the carbon-centered QOOH can efficiently react with a 'second' O₂ forming an OOOOH radical that, after internal abstraction and subsequent dissociation, forms the OH radical and a ketohydroperoxide (KHP). Further decomposition of the labile KHP produces an oxy-radical (QO) and OH, effectively leading to the release of two OH radical chain-carriers per fuel radical, resulting in chain-branching. Chain-branching precedes autoignition. Some decomposition channels of the labile KHP may not lead to chain-branching, complicating the situation significantly.

In this work product formation in photolytic low-temperature (500 K – 700 K) Cl-atom initiated oxidation of *n*-butane and neopentane was investigated using multiplexed photoionization time-of-flight mass spectrometry (MPIMS) employing the Advanced Light Source synchrotron radiation for ionization. Oxidation was initiated by excimer-laser photolysis of a Cl-atom precursor at 193 or 248 nm. Both high (760 – 1550 Torr) and low (4 – 10 Torr) pressure flow reactors were coupled to the MPIMS in order to investigate the effect of pressure and [O₂] on product yields and kinetics. These experiments probe the time-resolved and isomer-specific formation of products in the initial kinetic steps of oxidation. Experimental results obtained using the high-pressure reactor were simulated using NUI Galway C5 model and will be shown and discussed in the presentation.

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