



Additional chain-branching pathways in the low-temperature oxidation of branched alkanes



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ABSTRACT

Chain-branching reactions represent a general motif in chemistry, encountered in atmospheric chemistry, combustion, polymerization, and photochemistry; the nature and amount of radicals generated by chain-branching are decisive for the reaction progress, its energy signature, and the time towards its completion. In this study, experimental evidence for two new types of chain-branching reactions is presented, based upon detection of highly oxidized multifunctional molecules (HOM) formed during the gas-phase low-temperature oxidation of a branched alkane under conditions relevant to combustion. The oxidation of 2,5-dimethylhexane (DMH) in a jet-stirred reactor (JSR) was studied using synchrotron vacuum ultraviolet photoionization molecular beam mass spectrometry (SVUV-PI-MBMS). Specifically, species with four and five oxygen atoms were probed, having molecular formulas of $C_8H_{14}O_4$ (e.g., diketo-hydroperoxide/keto-hydroperoxy cyclic ether) and $C_8H_{16}O_5$ (e.g., keto-dihydroperoxide/dihydroperoxy cyclic ether), respectively. The formation of $C_8H_{16}O_5$ species involves alternative isomerization of $OOQOOH$ radicals via intramolecular H-atom migration, followed by third O_2 addition, intramolecular isomerization, and OH release; $C_8H_{14}O_4$ species are proposed to result from subsequent reactions of $C_8H_{16}O_5$ species. The mechanistic pathways involving these species are related to those proposed as a source of low-volatility highly oxygenated species in Earth's troposphere. At the higher temperatures relevant to auto-ignition, they can result in a net increase of hydroxyl radical production, so these are additional radical chain-branching pathways for ignition. The results presented herein extend the conceptual basis of reaction mechanisms used to predict the reaction behavior of ignition, and have implications on atmospheric gas-phase chemistry and the oxidative stability of organic substances.

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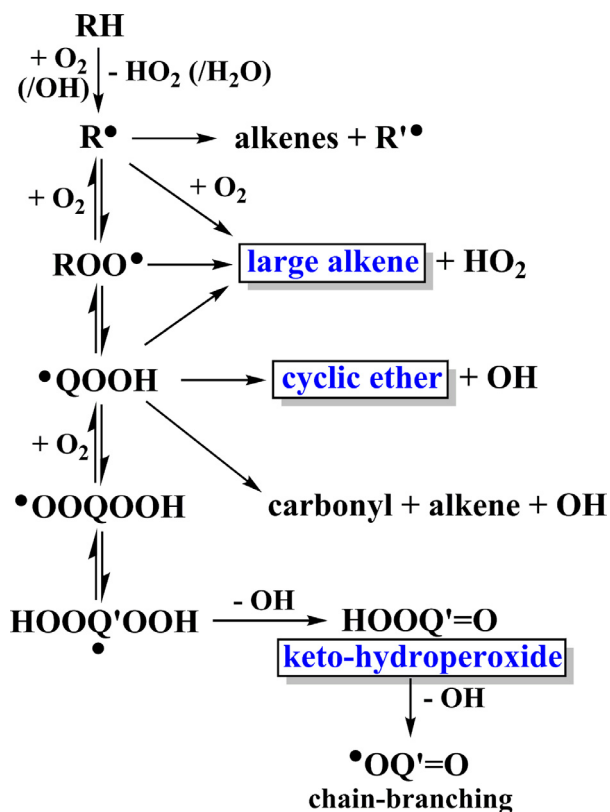
1. Introduction

The low-temperature auto-oxidation of hydrocarbons occurs in many natural and engineered systems. Gas-phase auto-oxidation determines the fate of volatile organic compounds (VOCs) in the atmosphere under low- NO_x conditions [1–4], ultimately leading to the

formation of extremely low volatility organic compounds (ELVOCs) [1,5,6]. In combustion systems, low-temperature auto-oxidation of hydrocarbon fuel leads to ignition [7–13], a governing parameter in the design of engines. In the liquid phase, auto-oxidation contributes to the degradation of organic substances such as lipids, lubricants, plastics, and foods [14–20]. Simulations attempting to predict the ignition properties of a hydrocarbon fuel in engines or the distribution of atmospheric pollutants must accurately represent the complex auto-oxidation pathways and branching ratios to various products [21–24].

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Scheme 1. Classical scheme for the low-temperature oxidation of hydrocarbons. The annotated species with blue and box were detected in this work. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The auto-oxidation process begins with radical initiation and proceeds by a series of O_2 addition and intramolecular H-atom migration reactions that eventually lead to radical chain-branching, propagation, or termination [7–12], as presented in Scheme 1 (see Supporting Information, SI, for detailed description). This scheme dating back to the mid 20th century [7,8] laid the foundation for the first mathematical models for predicting ignition [13,25]. At present, the scheme remains largely unchanged in high fidelity chemical kinetic simulations used to improve the efficiency and emissions of combustion systems [11,26–29].

The classical low-temperature auto-oxidation reaction scheme presented in Scheme 1 has been confirmed via gas-phase measurements of the key intermediates such as hydroperoxyalkyl radicals [30], alkylhydroperoxides [31,32], large alkenes [32–35], cyclic ethers [31,34,36,37], and keto-hydroperoxides [33,35,38–42]. Experiments on liquid-phase auto-oxidation by Korcek and coworkers [43–46] identified the presence of monohydroperoxides, dihydroperoxides, and keto-hydroperoxides, while recent computational studies [47,48] have shown that subsequent decomposition pathways of keto-hydroperoxides to acids are favorable. The recent experimental study on dimethyl ether oxidation [42] confirms this mechanism, i.e., the formation of carbonic acid.

The majority of studies on low-temperature hydrocarbon auto-oxidation use propane [37] or *n*-butane [32], as these prototypical *n*-alkanes display the cool-flame and negative temperature coefficient (NTC) characteristics observed in larger alkanes. *n*-Heptane and *iso*-octane are also commonly used surrogate compounds to understand the ignition chemistry of real gasoline fuels [23,24].

In this work, we used a jet-stirred reactor (JSR) to investigate the auto-oxidation of 2,5-dimethylhexane (DMH), a lightly methyl substituted alkane that is in the typical carbon number range of gasoline

fuel. This molecule was chosen because the presence of primary, secondary, and tertiary carbon hydrogen bonds was expected to yield more complexity in the low-temperature reaction scheme (as discussed later). Furthermore, DMH is a model compound to study the combustion properties of lightly branched alkanes, which are major components of typical petroleum derived and synthetic fuels [49,50].

Product species measured in our experiments provide further confirmation of the classical low-temperature oxidation scheme. However, we also observe more highly oxygenated species that are not part of the classical scheme. A detailed kinetic analysis was conducted to rationalize formation pathways leading to these species. We show that these new species are additional radical chain-branching intermediates, suggesting the presence of an extended auto-oxidation reaction mechanism for DMH at conditions of relevance to auto-ignition in engines. Our experimental evidence of an extended auto-oxidation scheme also has implications on atmospheric gas-phase chemistry and on the oxidative stability of liquid hydrocarbons.

2. Experimental and theoretical method

In this study, a spherical fused-silica JSR was coupled to a high resolution ($m/\Delta m \sim 2500$) time-of-flight molecular-beam mass spectrometer (MBMS, refers to Fig. S1 in SI) with synchrotron vacuum ultraviolet (SVUV) radiation as the photoionization (PI) source [42]. The mass spectrometer has a sensitivity range of 1 ppm, and a dynamic range of several orders of magnitude. The SI presents detailed information on the experimental method and a diagram of the set-up in Fig. S1. The experiments were performed at Terminal 3 of the Chemical Dynamics Beamline of the Advanced Light Source at the Lawrence Berkeley National Laboratory, USA. The SVUV-PI-MBMS enables detection of reactive oxidation intermediates, e.g., peroxides [31,42,51]. The stoichiometric DMH (1%)/ O_2 /Ar mixtures were investigated under quasi-atmospheric pressures and residence times of 0.933 bar and 2 s, respectively. A K-type thermocouple from Thermocoax was fixed at the vicinity of the sampling cone to measure the reactor temperature. The thermocouple is coated with Inconel alloy 600, which is not expected to catalyze the oxidation reaction under the conditions studied here. Experiments conducted without the thermocouple in place detected similar species distributions in the reactor. The uncertainty in reactor temperature is ± 20 K, which was obtained by measuring the temperature distribution inside the JSR with a movable thermocouple. The photoionization spectra were measured at varying reactor temperatures to obtain the distribution of reactive intermediates. Furthermore, photoionization efficiency spectra (PIE) were measured to obtain species' ionization thresholds to aid identification [52]. Absolute mole fractions are not presented due to the absence of photoionization cross sections for many of the detected species.

The mass resolution and the resolution of photoionization spectroscopy for species this large preclude the unambiguous identification of the observed molecules simply by a combination of mass and photoionization spectra. However, we can limit the conceivable range of chemical pathways based on the knowledge of global hydrocarbon oxidation chemistry; for example, no significant molecular weight growth by carbon-carbon bond formation occurs at these stoichiometries and temperatures. The present approach is to combine existing knowledge on low-temperature oxidation mechanisms, chemical kinetics, and theoretical calculations to support the interpretation of experimental data.

The identification of species at certain mass-to-charge (m/z) signals is performed by first postulating potential structures based on the classical low-temperature reaction scheme. For m/z signals that cannot be explained by the classical scheme, the mechanism was extended based on kinetics analysis. We propose new pathways that lead to the probable structures. Experimentally measured PIE spectra for several pure components (e.g., C_8 alkenes and cyclic ethers) [34]

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