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Speciation of the reaction intermediates from *n*-dodecane oxidation in the low temperature regime

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Abstract

The oxidation of *n*-dodecane was studied with experiments in a pressurized flow reactor over the low temperature regime (550–830 K) at elevated pressure (0.8106 MPa) and lean equivalence ratio (0.23). *n*-Dodecane exhibited negative temperature coefficient (NTC) behavior such that fuel reactivity peaked around 700 K and then decreased with increasing temperature. Samples were extracted at a residence time of 120 ms and stable intermediates were analyzed utilizing a gas chromatograph with a flame ionization detector coupled to a mass spectrometer. While a range of species were observed, a significant portion of *n*-dodecane decomposition was attributed to a select few species. These major carbon contributing intermediates included carbon oxides (CO and CO₂), light aldehydes (formaldehyde, acetaldehyde, and propional), C₁₂ alkylated tetrahydrofurans (2-propyl-5-iso-pentyltetrahydrofuran and two other incompletely identified isomers), lactones (5-methyl-dihydro-2(3*H*)-furanone and dihydro-2(3*H*)-furanone), and alkenes (ethene and 3-dodecene). The experimental results were compared to two kinetic models. The models captured the NTC behavior; however, discrepancies in measured formaldehyde, several light unsaturated species, and carbon monoxide indicate areas for model improvement. In the low temperature branching pathway from Livermore, a reaction path was identified (hydrogen abstraction from a secondary carbon followed by molecular oxygen addition and then internal hydrogen shift from the primary carbon) which would, if more active, predict the measured intermediate species. The data from this study provide targets for the continued refinement of kinetic models for *n*-dodecane.

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1. Introduction

The United States Department of Defense Directive 4140.43 mandated the use of JP-8 jet

fuel as the universal military fuel where applicable [1]. It is desirable to optimize fuel economy, power output, fuel flexibility, and emissions for all power systems fueled with JP-8. In the evolution of advanced engines, simulations are becoming preferable to testing in developing systems. However, JP-8 is a complex fuel that contains hundreds of components, many with unknown chemistry,

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and proper simulations require resources beyond current computational abilities. To reduce these requirements, the use of surrogate fuels, mixtures of approximately 1–10 components that mimic the properties and behaviors of real fuels, has been recognized as a feasible approach for predicting combustion behavior [2]. *n*-Dodecane is a likely major component of JP-8 surrogate fuels and is the target of this study.

While analytical models of individual reactions have become more useful in developing chemical kinetic mechanisms, experimental measurements remain the benchmark for determining reaction pathways. Experimental targets such as burning velocities in flames, ignition delays in rapid compression machines (RCM) and shock tubes, and reactivity tracer species in flow reactors have been extensively used. Chemical samples from the oxidation of C_7 – C_{10} alkanes in RCM's and flow and jet-stirred reactors have been analyzed for intermediate species concentrations [e.g., 3–9]. Such measurements provide fundamental insights to the key reactions in a mechanism. Hanson and co-workers measured OH concentrations from *n*-dodecane combustion behind reflected shock waves in a shock tube [10]. Below 900 K, the negative temperature coefficient (NTC) regime was observed where reactivity decreases with increasing temperature. Gomez and co-workers measured intermediate species from methane and ethene counterflow diffusion flames doped with a JP-8 surrogate containing 30% *n*-dodecane, with temperatures in the flame ranging from 400 to 2000 K [11,12]. Major intermediates included light alkenes and alkanes. Dagaut and co-workers measured intermediates from *n*-hexadecane in a jet-stirred reactor at temperatures of 1000 K and higher [13]. Fournet and co-workers measured intermediates, including alkenes, alkynes, dienes, and aromatics, from *n*-dodecane pyrolysis in flow and jet-stirred reactors [14,15]. The difficulties of making high quality measurements during combustion of these high molecular weight hydrocarbons, due to a combination of low volatility and high reactivity, have long been documented [16].

The present study focused on the oxidation of *n*-dodecane over the low temperature regime of hydrocarbon oxidation, which is particularly important in autoignition in combustion systems. The general pathways of the oxidation of lighter *n*-alkanes, such as *n*-heptane, have been evaluated in several experimental studies and the results have been used to validate detailed kinetic models [17–19]. The key pathways should be applicable for heavier *n*-alkanes, and thus a brief summary of low temperature oxidation of *n*-alkanes is included to stress the major pathways; more detail can be found in recent reviews [20–23]. In the critical branching pathway for low temperature oxidation, the alkane undergoes hydrogen abstraction to yield an alkyl radical, which

undergoes molecular oxygen addition to produce the alkylperoxy radical. This isomerizes to form the alkylhydroperoxy radical. Further molecular oxygen addition produces the peroxyalkylhydroperoxy radical. Decomposition produces a hydroxyl radical and a ketohydroperoxide, which decomposes to produce a second hydroxyl radical and other species. The higher end of the low temperature regime is the NTC region. In this temperature regime, instead of following pathways to produce the highly reactive hydroxyl radical, the reaction proceeds to produce less reactive species including hydroperoxy radicals and alkenes. At even higher temperatures, moving through the NTC region and into the intermediate temperature regime, pathways lead from the hydroperoxy radical to hydrogen peroxide, which at high enough temperatures decomposes to form two hydroxyl radicals leading to hot ignition. While much is known, low temperature models are still under refinement.

2. Methodology

The pressurized flow reactor (PFR) facility at Drexel University was used to conduct the experiments. The PFR is a turbulent flow reactor designed to study the chemistry of hydrocarbon oxidation, in relative isolation from fluid mechanics and large temperature gradients. As detailed descriptions can be found elsewhere [24,25], the facility and methodology will only be summarized here; however, modifications to accommodate high molecular weight hydrocarbons will be described in detail. Inside the PFR, the reaction chamber consists of a 2.2 cm I.D., 40 cm long quartz reactor tube within a pressure vessel. The pressure vessel and the inside of the reactor tube are separated by an annulus that is at the same pressure as the reaction chamber. At one end of the reactor tube is the fuel mixing nozzle and the other end contains the entrance for the gas sampling probe and an integral type-K sample thermocouple. Nitrogen (purity = 99.9%) and oxygen (purity = 99.994%) are mixed to form a synthetic air free of contaminants. This synthetic air is heated to the reaction temperature. To maximize temperature uniformity along the quartz reactor tube within the pressure vessel of the PFR, experiments are conducted at high dilution in nitrogen to limit the temperature rise due to heat release and the walls of the pressure vessel are heated by three independently controlled heaters. For the present experiments, the temperature rise due to heat release varied from 11 K at maximum reactivity to 0 K at no reactivity.

The liquid fuel, *n*-dodecane (purity = 99%), was injected into the centerline of a heated nitrogen stream one meter from the reactor inlet to ensure complete vaporization and mixing. The

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