



n-Heptane cool flame chemistry: Unraveling intermediate species measured in a stirred reactor and motored engine



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ABSTRACT

This work identifies classes of cool flame intermediates from *n*-heptane low-temperature oxidation in a jet-stirred reactor (JSR) and a motored cooperative fuel research (CFR) engine. The sampled species from the JSR oxidation of a mixture of *n*-heptane/O₂/Ar (0.01/0.11/0.88) were analyzed using a synchrotron vacuum ultraviolet radiation photoionization (SVUV-PI) time-of-flight molecular-beam mass spectrometer (MBMS) and an atmospheric pressure chemical ionization (APCI) Orbitrap mass spectrometer (OTMS). The OTMS was also used to analyze the sampled species from a CFR engine exhaust. Approximately 70 intermediates were detected by the SVUV-PI-MBMS, and their assigned molecular formulae are in good agreement with those detected by the APCI-OTMS, which has ultra-high mass resolving power and provides an accurate elemental C/H/O composition of the intermediate species. Furthermore, the results show that the species formed during the partial oxidation of *n*-heptane in the CFR engine are very similar to those produced in an ideal reactor, *i.e.*, a JSR.

The products can be classified by species with molecular formulae of C₇H₁₄O_{*x*} (*x* = 0–5), C₇H₁₂O_{*x*} (*x* = 0–4), C₇H₁₀O_{*x*} (*x* = 0–4), C_{*n*}H_{2*n*} (*n* = 2–6), C_{*n*}H_{2*n*–2} (*n* = 4–6), C_{*n*}H_{2*n*+2}O (*n* = 1–4), C_{*n*}H_{2*n*}O (*n* = 1–6), C_{*n*}H_{2*n*–2}O (*n* = 2–6), C_{*n*}H_{2*n*–4}O (*n* = 4–6), C_{*n*}H_{2*n*+2}O₂ (*n* = 0–4, 7), C_{*n*}H_{2*n*}O₂ (*n* = 1–6), C_{*n*}H_{2*n*–2}O₂ (*n* = 2–6), C_{*n*}H_{2*n*–4}O₂ (*n* = 4–6), and C_{*n*}H_{2*n*}O₃ (*n* = 3–6). The identified intermediate species include alkenes, dienes, aldehyde/keto compounds, olefinic aldehyde/keto compounds, diones, cyclic ethers, peroxides, acids, and alcohols/ethers. Reaction pathways forming these intermediates are proposed and discussed herein. These experimental results are important in the development of more accurate kinetic models for *n*-heptane and longer-chain alkanes.

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1. Introduction

Auto-oxidation processes are ubiquitous in natural and engineered systems, including the oxidation of cell membranes, atmospheric degradation of volatile organic compounds, and fuel ignition in engines. In fuel ignition processes, the auto-oxidation reac-

tion is often initiated by H-atom abstraction from the fuel (*e.g.*, a hydrocarbon) to form hydrocarbon radicals. The subsequent O₂ addition to the hydrocarbon radicals, intramolecular H-atom migration, further O₂ addition, and decomposition of oxidized intermediates yields a highly complex species pool [1]. The competition between radical chain propagation, chain termination, and chain branching pathways controls unique ignition-related phenomena, such as the so-called “cool flame”, the negative-temperature-coefficient (NTC) regime, and two-stage ignition [2]. The pioneering work from Downs and Wheeler [3,4] showed that reactive

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intermediates (e.g., peroxides) are responsible for end-gas auto-ignition and knock in internal combustion engines. Recent studies have shown that low-temperature oxidation reactions significantly influence heat release and ignition in homogenous charge compression (HCCI) engines [5]. Therefore, probing the pool of reactive intermediates in the low-temperature oxidation process is required to understand relevant fuel/engine phenomena.

A substantial body of literature exists that describes the details of the auto-ignition of the most common transportation fuel surrogate (i.e., *n*-heptane) under conditions relevant to modern and future engine concepts. These studies report fuel conversion, stable products, and a number of intermediates under various conditions in jet-stirred reactors (JSRs) [6–11], flow reactors [12–14], flames [15–23], and motored engines [24,25]. Reviewing this existing *n*-heptane oxidation data reveals that a comprehensive analysis of the pool of reactive intermediates is still scarce, especially under low-temperature and high-pressure conditions; preventing an in-depth understanding of relevant mechanistic pathways and key rate coefficients for reactions controlling ignition and pollutant formation [26]. Assigning plausible, let alone correct structures, to such reactive intermediate species is challenging, both on experimental and theoretical grounds, because all relevant molecular conformations would have to be identified. There is some recent progress in this direction, albeit for dimethyl ether (DME) oxidation [27].

Dagaut et al. studied the oxidation of *n*-heptane in a JSR covering the low- and high-temperature oxidation regimes (500–1150 K) at 10 and 40 bar [8]. The intermediates with the molecular formula of C_nH_{2n} ($n=2-7$), CH_2O , C_2H_4O , CH_3OH , CH_3CHO , and $C_7H_{14}O$ were detected by gas chromatography (GC). Sahetchian et al. [25] detected the heptyl-ketohydroperoxide during the oxidation of *n*-heptane in a motored CFR engine. Boehman et al. [24] also investigated the auto-ignition of *n*-heptane in a motored engine and analyzed the exhaust composition. Oxygenated intermediates of CH_2O , C_2H_4O , C_4H_8O , $C_4H_6O_2$, C_5H_8O , $C_5H_{10}O$, $C_4H_8O_2$, $C_5H_{10}O_2$, $C_6H_{10}O_2$, and $C_7H_{12}O_2$ were detected by Fourier transform infrared (FTIR) spectroscopy and GC analysis. Recent work by Herbinet et al. [9] addressed the low-temperature oxidation of *n*-heptane in a JSR at atmospheric pressure. As shown in Table 1, a detailed GC analysis of the intermediate species pool was performed. The authors also analyzed the intermediate species by synchrotron vacuum ultraviolet radiation photoionization time-of-flight molecular-beam mass spectrometry (SVUV-PI-MBMS), which enabled the detection of a large number of intermediates, including keto-hydroperoxides that are important for auto-ignition [27–35] and radicals [29,36,37]. The SVUV-PI-MBMS data provided new insight into the low-temperature oxidation chemistry of *n*-heptane. However, the limited mass resolution of the mass spectrometer hindered a full separation of the intermediate species, as shown in Table 1.

This study attempts to further clarify the intermediate species pool from *n*-heptane low-temperature oxidation in a JSR at atmospheric pressure and in a cooperative fuel research (CFR) engine at elevated in-cylinder pressure. The products were analyzed using SVUV-PI-MBMS, and a complementary experimental setup comprising an atmospheric pressure chemical ionization (APCI) Orbitrap mass spectrometer (OTMS). The elemental C/H/O composition of the intermediates during *n*-heptane JSR oxidation was confirmed by the APCI-OTMS, and the species pool from *n*-heptane low-temperature oxidation in the CFR engine was found to be in agreement with that observed in the JSR. The results of this studies allowed to categorize the intermediate species, deduce their probable structures, and propose their formation mechanisms. In addition, the results indicate that combining SVUV-PI-MBMS and APCI-OTMS can be effective at analyzing the intermediate species pool from low-temperature oxidation products of long-chain alka-

nes. Furthermore, the unique ionization process and high mass resolution of the APCI-OTMS is proven to be highly valuable in low-temperature oxidation studies. Moreover, the combination of an ideal reactor (i.e., JSR) and a real engine (i.e., CFR) reveals that common low-temperature reaction mechanisms exist in both fundamental and practical combustion devices.

2. Experimental method

In this work, one JSR (i.e., JSR-1) was coupled to the time-of-flight molecular-beam mass spectrometer with synchrotron vacuum ultraviolet radiation as the photoionization source [38]. The mass spectrometer has a sensitivity of 1 ppm, a mass resolving power of ~ 3500 , and a dynamic range of six orders of magnitude. The experiments were performed at Terminal 3 of the Chemical Dynamics Beamline of the Advanced Light Source at the Lawrence Berkeley National Laboratory. Details of the experimental setup and the experimental procedure can be found in the literature [38]. Stoichiometric *n*-heptane (1%)/ O_2 (11%)/Ar (78%) mixtures were investigated at quasi-atmospheric pressures of 0.933 bar and a residence times of 2 s. The reactor temperature was measured by a K-type thermocouple located in the vicinity of the sampling cone. The sampling probe introduces temperature inhomogeneity in the reactor; the temperature uncertainty of gas sampled from the reactor is ± 20 K. The distribution of reactive intermediates at varying reactor temperatures was obtained by measuring the photoionization spectra. Furthermore, the photon energy was scanned to measure the photoionization efficiency spectra (PIE), which contains the information of the species ionization thresholds.

Another JSR (i.e., JSR-2) was coupled with a Thermo LTQ Velos Orbitrap mass spectrometer equipped with an IonMax APCI ion source at King Abdullah University of Science & Technology (KAUST), Saudi Arabia. Stoichiometric *n*-heptane (1%)/ O_2 (11%)/Ar (78%) mixtures were again investigated at atmospheric pressure and a residence times of 2 s. The Orbitrap automated gain control (AGC) target was set to 1×10^6 charges for full scan and the microscan was set to 500 ms. The mass scan covered the range of 50–300 u. The calibration of the LTQ-Orbitrap mass analyzer was performed in positive ESI ionization mode, according to the manufacturer's guidelines. The Orbitrap mass spectrometer was operated using XCalibur software. Analytes were detected in the Orbitrap at a mass resolving power of 100,000, a sensitivity range of 1–5 ppm, and mass accuracy < 5 ppm. A diagram of the JSR, combined with Orbitrap mass spectrometer, is presented in Fig. 1. The sampling method was similar to that used by Dagaut et al. [39]. For on-line analysis, the products were sampled using a quartz tube (of 4 mm diameter for the tubes body and 0.5 mm at the tip) at the outlet of the reactor and ionized by the APCI. Subsequently, the ions were transferred into the system using a skimmer with a positive mode for analysis. In addition to the on-line analysis, off-line measurements were also performed. For off-line analysis, the gas mixture from the outlet of JSR-2 passed through a U-tube and was condensed by liquid nitrogen for one hour to increase the signal-to-noise (S/N) ratio. Please note that using liquid nitrogen to condense products in a hydrocarbon oxidation experiment should be done carefully because oxygen may also condense, thereby creating a potentially explosive mixture. The products were then collected by dissolving them in methanol and injecting them into an APCI ionization source with a syringe. The comparison showed that intermediates from both on-line and off-line analysis were in good agreement.

For JSR-1, tunable synchrotron vacuum ultraviolet light was used in a single photon ionization technique. A neutral species is ionized when the photon energy is higher than the molecule's ionization energy, resulting in the parent molecule peak (M^+) and/or its fragments. The APCI used with JSR-2 is a soft ionization

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