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.

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The products can be classified by species with molecular formulae of $C_7H_{14}O_x$ ($x=0-5$), $C_7H_{12}O_x$ ($x=0-4$), $C_7H_{10}O_x$ ($x=0-4$), C_nH_{2n} ($n=2-6$), C_nH_{2n-2} ($n=4-6$), $C_nH_{2n+2}O$ ($n=1-4, 6$), $C_nH_{2n}O$ ($n=1-6$), $C_nH_{2n-2}O$ ($n=2-6$), $C_nH_{2n-4}O$ ($n=4-6$), $C_nH_{2n+2}O_2$ ($n=0-4, 7$), $C_nH_{2n}O_2$ ($n=1-6$), $C_nH_{2n-2}O_2$ ($n=2-6$), $C_nH_{2n-4}O_2$ ($n=4-7$), and $C_nH_{2n}O_3$ ($n=3-6$). 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.

Keywords: *n*-heptane; auto-oxidation; peroxides; synchrotron VUV photoionization mass spectrometry; APCI Orbitrap mass spectrometry

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 reaction is often initiated by H-atom abstraction from the fuel (*e.g.*, a hydrocarbon) to form hydrocarbon radicals. The subsequent O_2 addition to the hydrocarbon radicals, intramolecular H-atom migration, further O_2 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 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.

Table 1. Intermediate species measured during *n*-heptane oxidation in a JSR by Herbinet *et al.* [9], Rodriguez *et al.* [33], and this work. The intermediates labeled in bold were also detected in the JSR and CFR engine experiments by an atmospheric pressure chemical ionization (APCI) Orbitrap mass spectrometer (OTMS).

m/z	Herbinet <i>et al.</i> ^a	Herbinet <i>et al.</i> ^b	Rodriguez <i>et al.</i> ^c	This work ^d
28	C ₂ H ₄	C ₂ H ₄	C ₂ H ₄	C ₂ H ₄
30	--	CH ₂ O	CH ₂ O	CH ₂ O
32	--	CH ₄ O		CH ₄ O
34	--	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
42	C ₃ H ₆	one peak	C ₃ H ₆ /C ₂ H ₂ O	C ₃ H ₆ /C ₂ H ₂ O
44	C ₂ H ₄ O	C ₂ H ₄ O	C ₂ H ₄ O	C ₂ H ₄ O
46	--	--		CH ₂ O ₂ /C ₂ H ₆ O
48	--	--	CH ₄ O ₂	CH ₄ O ₂
54	C ₄ H ₆	--		C₄H₆
56	C ₄ H ₈ /C ₃ H ₄ O	one peak	C ₄ H ₈	C₄H₈/C₃H₄O
58	C ₃ H ₆ O	one peak	C ₃ H ₆ O	C₃H₆O/C₂H₂O₂
60	C ₂ H ₄ O ₂	one peak		C ₂ H ₄ O ₂ /C ₃ H ₈ O
62	--	--	C ₂ H ₆ O ₂	C ₂ H ₆ O ₂
68	C ₅ H ₈	--		C₅H₈/C₄H₄O
70	C ₅ H ₁₀ /C ₄ H ₆ O	one peak		C₅H₁₀/C₄H₆O
72	C ₄ H ₈ O	one peak	C ₄ H ₈ O	C₄H₈O/C₃H₄O₂
74	C ₃ H ₆ O ₂	--	C ₃ H ₆ O ₂	C ₃ H ₆ O ₂
76	--	--	C ₃ H ₈ O ₂	C ₃ H ₈ O ₂
82	--	--		C₆H₁₀/C₅H₆O
84	C ₆ H ₁₂ /C ₅ H ₈ O	one peak		C₆H₁₂/C₅H₈O/C₄H₄O₂
86	C ₅ H ₁₀ O	one peak		C₄H₆O₂/C₅H₁₀O
88	--	--	C ₄ H ₈ O ₂	C ₄ H ₈ O ₂
90	--	--		C ₃ H ₆ O ₃ /C ₄ H ₁₀ O ₂
94	--	--		C₇H₁₀
96	C ₇ H ₁₂	--		C₇H₁₂/C₆H₈O/C₅H₄O₂
98	C ₇ H ₁₄ /C ₆ H ₁₀ O	one peak		C₇H₁₄/C₆H₁₀O/C₅H₆O₂
100	C ₆ H ₁₂ O/C ₅ H ₈ O ₂	one peak		C₆H₁₂O/C₅H₈O₂
102	--	--	C ₅ H ₁₀ O ₂	C ₅ H ₁₀ O ₂ /C ₆ H ₁₄ O
104	--	--		C ₄ H ₈ O ₃
110	C ₇ H ₁₀ O	one peak		C₇H₁₀O
112	--	one peak		C₇H₁₂O/C₆H₈O₂
114	C ₇ H ₁₄ O	one peak		C₇H₁₄O/C₆H₁₀O₂/C₅H₆O₃
116	C ₆ H ₁₂ O ₂	one peak	C ₆ H ₁₂ O ₂	C ₆ H ₁₂ O ₂ /C ₅ H ₈ O ₃
118	--	--		C ₅ H ₁₀ O ₃
126	--	C ₇ H ₁₀ O ₂		C₇H₁₀O₂
128	C ₇ H ₁₂ O ₂	C ₇ H ₁₂ O ₂	C ₇ H ₁₂ O ₂	C₇H₁₂O₂
130	--	one peak	C ₇ H ₁₄ O ₂	C₇H₁₄O₂/C₆H₁₀O₃
132	--	--		C ₇ H ₁₆ O ₂ /C ₆ H ₁₂ O ₃ /C ₅ H ₈ O ₄
142	--	--		C₇H₁₀O₃
144	--	C ₇ H ₁₂ O ₃		C₇H₁₂O₃
146	--	C ₇ H ₁₄ O ₃	C ₇ H ₁₄ O ₃	C₇H₁₄O₃
158	--	--		C₇H₁₀O₄
160	--	--		C₇H₁₂O₄
162	--	--		C₇H₁₄O₄
178	--	--		C₇H₁₄O₅

^a GC analysis, ^b SVUV-PI-MBMS analysis, ^c GC, Cavity Ring Down Spectroscopy (CRDS), SVUV-PI-MBMS, and laser photoionization mass spectrometer analysis, ^d SVUV-PI-MBMS analysis.

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 alkanes. 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%)/O₂ (11%)/Ar (78%) mixtures were investigated at quasi-atmospheric pressures of 0.933 bar and a residence times of 2s. 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%)/O₂ (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.

Fig. 1. Schematic representation of experimental setup for the JSR-2 experiment at KAUST.

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 method, which generally produces less fragments in first-order mass analysis compared to other gas phase ionization techniques such as electron ionization (EI). It typically produces singly-charged ions and is well suited for low polarity and nonpolar compounds [40, 41]. As mention above, the analyte was in either gaseous (on-line analysis) or liquid (off-line analysis) form. In both cases, ionization was accomplished using an atmospheric pressure corona discharge to ionize water vapor which transfers a proton to the analyte. APCI settings were as follows: vaporizer temperature: 473 K, sheath gas flow rate: 30 (arb. unit), the aux gas flow rate: 15 (arb. unit), sweep gas flow rate: 0 (arb. unit), capillary temperature 548 K, and corona needle current: 7 μ A. The mass spectrum was recorded for a minute and an average signal was obtained from the scans. The APCI spectra provides an easily identifiable protonated molecular ion peak $[M+H]^+$, which allows for determination of the molecular mass [42, 43].

Similar to the off-line analysis of the intermediates formed in JSR-2, exhaust gas from *n*-heptane oxidation in a motored CFR engine at KAUST was analyzed. The original carburetor was replaced with a port fuel injector (PFI), which sprays fuel onto the hot intake valve to ensure complete vaporization. The engine characteristics and operating conditions are presented in Table 2. The intake temperature of 27 °C may have an influence on fuel vaporization at the intake port. However,

temperature increase during the compression stroke would assist fuel vaporization in the bulk charge. Any resulting mixture fraction stratification is not expected to affect the qualitative discussion reported in this work. The CFR engine is a variable compression ratio engine designed and used for the measurement of fuel's octane number. The present experiment uses this apparatus as a high-pressure, variable-volume homogeneous reactor, similar to a homogenous charge compression ignition (HCCI) engine. The engine was operated to study oxidation products from low-temperature reactivity, and hence ignition was avoided [44-48].

Table 2. CFR engine specifications and test conditions.

Engine type	Single Cylinder
Injection system	Port fuel injection
Bore	82.55 mm
Stroke	114.3 mm
Connecting rod length	254 mm
Compression ratio	8.3
Engine speed	600 RPM
Fuel/air Eq. ratio	0.3
Intake pressure	98 kPa
Inlet air temperature	27±1 °C

The intake air to the engine flows through a mass flow meter and is preheated to the set point temperature. *n*-Heptane was injected before the intake valve through a PFI. The fuel was supplied to the injector from a fuel tank pressurized by helium. The mixture formed is assumed to be thoroughly homogeneous at the start of compression. The engine was not connected to an emission analyzer, and the fuel flow through the injector was not measured. Therefore, the equivalence ratio was set using a lambda sensor while operating the engine under normal hot ignition and combustion conditions. The assumption was that complete combustion occurred when the compression ratio was increased to a point where Crank Angle (CA) 50 occurred at top dead center (TDC). This approach is not ideal when operating the engine in HCCI mode due to reduced combustion efficiency. However, the aim of this experiment is to detect species pool during low-temperature oxidation in engine relevant conditions. The compression ratio was then reduced to a point where hot ignition was avoided, and allowed to motor until the coolant temperature reached a steady value before the samples were collected. Low temperature fuel reactivity was determined from first law heat release analysis using the in-cylinder pressure that was recorded using a Kistler pressure transducer at a resolution 0.05° degree of crank

angle. The cylinder pressure, temperature history and heat release rate are presented in Fig. 2. We assumed an adiabatic core to perform the heat release analysis.

Fig. 2. The cylinder pressure, temperature history, and heat release rate during *n*-heptane low-temperature oxidation in the CFR engine. The CFR engine specifications and test conditions are presented in Table 2.

The exhaust gas mixture from the CFR engine passed through a U-tube immersed in acetone-dry ice mixture for one hour to condense the intermediate species. Our test shows that the coolant of liquid nitrogen or acetone-dry ice mixture has no effect on the result. The samples were dissolved in methanol and analyzed by the APCI-OTMS.

3. Results and discussion

Table 1 presents the species produced in JSR-1 and measured by the SVUV-PI-MBMS from 490-600 K. Within this temperature range, the conversion of *n*-heptane increases from 0% at 490 K to 60% at 600 K, which is prior to the regime where typical negative-temperature-coefficient (NTC)

behavior is observed. Compared to the earlier work of Herbinet *et al.* [9], this study observed a more comprehensive intermediate species pool because of the higher mass resolution of the mass spectrometer and higher fuel concentration. The intermediates labeled in bold in Table 1 were also measured by APCI-OTMS during *n*-heptane oxidation in JSR-2 and in the CFR engine. We note that intermediates with molecular weight below 50 u were not measured by the APCI-OTMS. In general, the species pool detected in JSR-1, JSR-2, and the CFR engine are similar. The temperature for the start of the low-temperature heat release in the CFR engine is around 600 K. This is slightly higher than the temperature where low-temperature reactivity occurs in the JSR (i.e., 500-550 K). A higher temperature is required in the engine to observe low-temperature oxidation products due to the lower residence time and lower equivalence ratio. In both the JSR and CFR engine, the conditions correspond to the low-temperature oxidation regime, before the start of NTC reactivity. The presence of common intermediates indicates that low-temperature oxidation proceeds through multiple O₂ addition pathways even under engine relevant conditions. Compared to the high-pressure oxidation data of *n*-heptane by Dagaut *et al.* [8] and Boehman *et al.* [24], this study presents a more detailed analysis of the intermediate species pool. In addition, the CFR engine measurements provide new insights into the high-pressure low-temperature oxidation chemistry of *n*-heptane.

The measured 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_nH_{2n} (n=2-6), C_nH_{2n-2} (n=4-6), C_nH_{2n+2}O (n=1-4, 6), C_nH_{2n}O (n=1-6), C_nH_{2n-2}O (n=2-6), C_nH_{2n-4}O (n=4-6), C_nH_{2n+2}O₂ (n=0-4, 7), C_nH_{2n}O₂ (n=1-6), C_nH_{2n-2}O₂ (n=2-6), C_nH_{2n-4}O₂ (n=4-7), and C_nH_{2n}O₃ (n=3-6). The intermediate species include mainly alkene, dienes, aldehyde/keto compounds, olefinic aldehyde/keto compounds, diones, cyclic ethers, peroxides, acids, and alcohols/ethers.

The focus of this work is primarily directed toward understanding the occurrence of intermediates with the molecular formulae of C₇H₁₄O_x (x=0-5), C₇H₁₂O_x (x=0-4), and C₇H₁₀O_x (x=0-4), which highlight the first, second, and third sequential O₂ addition reaction mechanism and the bimolecular reactions of these intermediates. As a secondary aspect, smaller intermediates with less

than seven carbon atoms, will be discussed. The ionization energy onset from the measured PIE curve of a specific m/z is compared with the ionization energy of the potential molecule. Literature ionization energies were adopted from the NIST database [49] or quantum calculations by Battin-Leclerc et al. [9, 32, 33]. In Battin-Leclerc's work, zero-point-energy-corrected adiabatic ionization energy of the lowest energy conformer was calculated from the composite CBS-QB3 method using Gaussian program. The uncertainty of ionization energy from the calculation is estimated to be within ± 0.1 eV. However, recent work of Moshhammer et al. [27] has shown that the uncertainty in calculated ionization energy is larger when not all probable conformers are considered. Our experimental uncertainty of ionization energy is estimated to be ± 0.05 eV. However, it is difficult to interpret the PIE curves of a large molecule due to the large number of possible isomers with overlapping PIE curves. In this work, we did not carry out ionization energy calculations, so the discussion focuses on probable structures based on the mechanistic and kinetic analysis.

3.1 Intermediates with the same carbon skeleton of *n*-heptane

3.1.1 C₇H₁₄O_x intermediates (x=0-5)

A detailed reaction scheme for the low-temperature oxidation of alkanes was proposed in recent work by Wang *et al.* [30, 31] on 2,5-dimethylhexane and 2-methylhexane. The reaction scheme includes the first, second, and third stage O₂ addition reactions, which produce intermediates with the same carbon number as that of the respective fuel, *e.g.*, C_nH_{2n}O_x (n is the carbon number of the fuel, x=0-5). Scheme 1 presents an analogous reaction mechanism for *n*-heptane. The important intermediates (C₇H₁₄O_x, x=0-5) are highlighted in blue and boxed. They include heptenes (C₇H₁₄, m/z 98), C₇ cyclic ethers (C₇H₁₄O, m/z 114), C₇ olefinic hydroperoxides (C₇H₁₄O₂, m/z 130), C₇ keto-hydroperoxides and/or hydroperoxy cyclic ethers (C₇H₁₄O₃, m/z 146), C₇ olefinic dihydroperoxides (C₇H₁₄O₄, m/z 162), and C₇ keto-dihydroperoxides and/or dihydroperoxy cyclic ethers (C₇H₁₄O₅, m/z 178). The production of these various intermediates depends on the radical pool comprising R, ROO, QOOH, OOQOOH, P(OOH)₂, and OOP(OOH)₂, whose reaction mechanisms vary with temperature (*i.e.*, O₂ addition, decomposition, and isomerization). As temperature increases, exothermic O₂

addition reactions are thermodynamically unfavorable, while the endothermic decomposition reactions are favored.

Scheme 1. Reaction scheme for *n*-heptane low-temperature oxidation. Represented intermediates (*i.e.*, C₇H₁₄O_x, x=0-5) are boxed and highlighted in blue.

The C₇H₁₄O_x (x=0-5) intermediates from *n*-heptane oxidation in JSR-1 using SVUV-PI-MBMS are shown in in Figs. 3a and 3b, while those from JSR-2 and the CFR engine using APCI-OTMS are shown in Figs. 3c and 3d. The JSR-1 SVUV-PI-MBMS results in Fig. 3a observed all C₇ intermediates, with the exception of C₇H₁₄O₄. The protonated molecular peaks for C₇H₁₄, C₇H₁₄O₄, and C₇H₁₄O₅ were not detected during the off-line JSR-2 APCI-OTMS measurement (Fig. 3c, solid lines), but the latter two species were detected by the on-line JSR-1 APCI-OTMS measurement (Fig. 3c, red dashed lines). The CFR engine APCI-OTMS measurement detected the protonated molecular peaks of C₇H₁₄O_x (x=1-5). In general, the analysis observed the molecular formula corresponding to the six C₇ intermediates in Scheme 1 and the APCI-OTMS measurement confirms the elemental C/H/O composition of these intermediates.

Fig. 3. Mass spectra of intermediates with $C_7H_{14}O_x$ ($x=0-5$) molecular formula. The mass spectra in panels (a) and (b) correspond to the JSR-1 SVUV-PI-MBMS measurements at 530 K and 600 K, respectively, and a photon energy of 9.6 eV. The signal of $C_7H_{14}O_5$ is increased by a factor of 20 for clarity in Fig. 3a. The mass spectra in panel (c) correspond to the JSR-2 APCI-OTMS off-line measurements at 535 K (black line) and on-line measurements of $C_7H_{14}O_3$, $C_7H_{14}O_4$, and $C_7H_{14}O_5$ at 542 K (red dashed line). (d) is for CFR engine APCI-OTMS measurements.

Comparing the signals in Figs. 3a and 3b indicates that the accumulation of C_7H_{14} (heptenes) and $C_7H_{14}O$ (C_7 cyclic ethers) is favored at higher temperature (*e.g.*, 600 K), while that of $C_7H_{14}O_3$ and $C_7H_{14}O_5$ is favored at lower temperature (*e.g.*, 530 K). These phenomena are further supported by the temperature-dependent signal profiles of the $C_7H_{14}O_x$ intermediates shown in Fig. 4a-4c. The temperature-dependent behavior of C_7H_{14} (heptenes) and $C_7H_{14}O$ (C_7 cyclic ethers) is in agreement with previous studies on *n*-heptane oxidation [8, 9, 11]. For C_7H_{14} , the three linear isomers, *i.e.*, 1-heptene, 2-heptene and 3-heptene, were detected by Zhang *et al.* [11], and their maximum concentration follows the order 1-heptene < 2-heptene < 3-heptene. The clear ionization onset of C_7H_{14} in Fig. S1a at 8.8 eV agrees well with the ionization energy (IE) of 3-heptene (8.77 eV [49]) and 2-

heptene (8.84 eV [49]). The IE of 1-heptene is 9.34 eV [49], for which the onset is not clear from the PIE curve in Fig. S1a. This may be attributed to the signal overlap with 3-heptene and 2-heptene. For $C_7H_{14}O$, C_7 cyclic ethers with three-, four-, and five-membered rings were previously detected [8, 9, 11], and the most abundant isomer is 2-methyl-5-ethyl-tetrahydrofuran. The calculated ionization energy for *trans*-2-methyl-5-ethyl-tetrahydrofuran and *cis*-2-methyl-5-ethyl-tetrahydrofuran is 9.05 and 9.08 eV [9] respectively, which agrees well with the IE onset at 9.0 eV in this work (Fig. S1b). It is noted that $C_7H_{14}O$ could also include the signal of heptanal and/or heptanone isomers. For example, 2-heptanone (IE: 9.3 eV [49]) and 3-heptanone (IE: 9.1 eV [49]) were detected in the GC analysis [9].

Fig. 4. Temperature-dependent signal profiles of intermediates with the same carbon number of *n*-heptane at 9.6 eV. The reaction temperature is not corrected, which has an uncertainty of ± 20 K.

Unlike heptenes and C_7 cyclic ethers, the signal intensity of $C_7H_{14}O_3$ and $C_7H_{14}O_5$ reaches a maximum at 540 K and then decreases rapidly at higher temperatures (Fig. 4a and 4b). The instability of these molecules at higher temperatures suggests that they contain hydroperoxy groups. The temperature-dependent behavior of $C_7H_{14}O_3$ agrees with C_4 - C_7 keto-hydroperoxide intermediates measured during oxidation of *n*-butane [28], *n*-pentane [32], hexane isomers [34], and *n*-heptane [9, 33]. The distinct IE onset of $C_7H_{14}O_3$ intermediate in Figure S1c is 9.0 eV, which is in good agreement with that reported by Herbinet *et al.* [9]; they calculated the adiabatic ionization energy of several C_7 keto-hydroperoxide, such as 3-hydroperoxy-1-heptanal (IE: 9.32 eV), 4-hydroperoxy-2-heptanone (IE: 9.57 eV), and 5-hydroperoxy-3-heptanone (IE: 9.31 eV). However, none of these corresponds to the clear IE onset at 9.0 eV.

Interpreting the PIE curve becomes challenging for large molecules and any discrepancy may be attributed to several aspects. First, the large number of probable isomers of $C_7H_{14}O_3$ keto-hydroperoxide makes the PIE curve very complex [30, 31]. Second, the numerous conformers of each isomer increase the uncertainty in the IE calculation [27]. Last, the C_7 hydroperoxy cyclic ether from Scheme 1 has the same molecular formula as C_7 keto-hydroperoxide, and both current and previous [9] experiments cannot separate these two types of intermediates. Thus, the temperature-dependent signal profile and PIE curve of $C_7H_{14}O_3$ may also contain a contribution from hydroperoxy cyclic ethers.

Peroxide intermediates with five oxygen atoms were not detected in previous studies of C_4 - C_7 alkanes [9, 33, 34, 50], but they were observed in recent studies of 2-methylhexane [31], 2,5-dimethylhexane [30], and many other organic species [51]. In this work, the temperature-dependent signal profile of $C_7H_{14}O_5$ (Fig. 4a) was found to be similar to that of $C_7H_{14}O_3$ (Fig. 4b), which is in agreement with the observations in 2-methylhexane [31] and 2,5-dimethylhexane [30] low-temperature oxidation. According to Scheme 1, the probable structures of the $C_7H_{14}O_5$ intermediates are keto-dihydroperoxides (KDHP) and/or dihydroperoxy cyclic ethers (DHPCE). The PIE curve of $C_7H_{14}O_5$ intermediates is shown in Fig. S1d.

According to Scheme 1, the $C_7H_{14}O_2$ intermediates are olefinic hydroperoxides (OHP), which contain one hydroperoxy group; therefore, the temperature-dependent signal profile at this mass should be similar to those of $C_7H_{14}O_3$ and $C_7H_{14}O_5$. However, as shown in Fig. 4c, the signal profile changed after 550 K, indicating that other $C_7H_{14}O_2$ intermediates might be produced at higher temperatures. For example, $C_7H_{14}O_2$ intermediates could also contain one carbonyl and one hydroxyl group (*e.g.*, carbonyl alcohol). The decomposition of keto-hydroperoxides ($C_7H_{14}O_3$) forms keto-alkoxyl radicals, whose secondary reaction with *n*-heptane and/or other stable intermediates may produce a $C_7H_{14}O_2$ carbonyl alcohol *via* hydrogen abstraction.

Fig. S1e shows a clear IE onset for $C_7H_{14}O_2$ at 9.1 eV. Rodriguez *et al.* [33] calculated the adiabatic IEs of seven probable C_7 OHPs, whose IEs are in the range of 8.83-9.24 eV. In obvious

agreement with the measured IE onset are the IEs of *trans*-hept-2-enyl-1-hydroperoxide (IE: 9.05 eV), *cis*-hept-2-enyl-4-hydroperoxide (IE: 9.10 eV), *cis*-hept-3-enyl-2-hydroperoxide (IE: 9.02 eV), and *cis*-hept-2-enyl-1-hydroperoxide (IE: 9.19 eV). They also calculated the IEs for several C₇ carbonyl alcohols [33]. Their IEs range from 9.07 to 9.44 eV, so they could also be ionized at 9.6 eV in Fig. 4c. Thus, it is plausible that the signal of C₇H₁₄O₂ receives a contribution from C₇ carbonyl alcohols, especially at higher temperatures. Another probable structure for the C₇H₁₄O₂ intermediate is heptanoic acid; however, its IE of 10.14 eV [33] is much higher and is unlikely to contribute to the signal intensity at 9.6 eV in Fig. 4c.

Apart from these C₇ intermediates, other intermediates with the same nominal *m/z* were also detected, such as C₅H₆O₂ and C₆H₁₀O at *m/z* 98, C₆H₁₀O₂ at *m/z* 114, and C₆H₁₀O₃ at *m/z* 130. The appearance of these C₅ and C₆ intermediates is more evident at higher temperatures (*i.e.*, 600 K in Fig. 3b versus 530 K in Fig. 3a).

3.1.2 C₇H₁₂O_x intermediates (x=0-4)

Figure S2 shows the C₇H₁₂O_x (x=0-4) intermediates measured by SVUV-PI-MBMS and APCI-OTMS from *n*-heptane JSR and CFR engine oxidation. The SVUV-PI-MBMS and APCI-OTMS results are in good agreement with each other, and confirm the elemental C/H/O composition of these intermediates; mass peaks corresponding to C₅H₄O₂ and C₆H₈O at *m/z* 96 and C₆H₈O₂ at *m/z* 112 were also detected. Similar to the C₅H₆O₂, C₆H₁₀O, C₆H₁₀O₂, and C₆H₁₀O₃ intermediates in Fig. 3a and 3b, the appearance of C₅H₄O₂, C₆H₈O, and C₆H₈O₂ is more evident at higher temperatures (*i.e.*, 600 K versus 530 K). The temperature-dependent signal profiles of the C₇H₁₂O_x (x=0-4) intermediates are presented in Fig. 4d and 4e. The energy scan for these intermediates is shown in Fig. S3a-S3e in the Supplemental Material.

The temperature-dependent signal profiles of the C₇H₁₂O₄ intermediates (*m/z* 160) are similar to those of C₇H₁₄O₃ and C₇H₁₄O₅. Consistent with our previous work [30, 31], it is proposed that this molecule contains one hydroperoxy group and two carbonyl groups (*e.g.*, diketo-hydroperoxides), or one hydroperoxy group, one carbonyl group, and one cyclic ether group (*e.g.*, keto-hydroperoxy cyclic

ether). These could be produced by OH radical-assisted water elimination from the $C_7H_{14}O_5$ intermediates (*i.e.*, keto-dihydroperoxides and/or dihydroperoxy cyclic ethers); or *via* H-atom abstraction from $C_7H_{14}O_5$ intermediates at carbon sites not connected to the hydroperoxy group, and subsequent cyclization to form $C_7H_{12}O_4$ intermediates. Here, two other pathways are proposed for the production of $C_7H_{12}O_4$ intermediates, as shown in Scheme 2 and 3. Due to the complexity of the reaction system, only specific examples in Scheme 2 and 3 are presented to show the reaction pathways and probable functional groups of the $C_7H_{12}O_x$ ($x=1-4$) intermediates.

The first new sequence proposed is *via* H-atom abstraction from $C_7H_{14}O_3$ intermediates (*i.e.*, C_7 keto-hydroperoxides and hydroperoxy cyclic ethers), O_2 addition to the radical site, and subsequent decomposition; for example, Scheme 2 presents H-atom abstraction from 4-hydroperoxy-2-heptanone (C7KET24) and subsequent reactions that lead to $C_7H_{12}O_x$ ($x=1-4$) intermediates. We note that 4-hydroperoxy-2-heptanone is one of the most abundant keto-hydroperoxides in *n*-heptane oxidation [11]. For simplification, only H-atom abstractions from carbon sites ‘c’, ‘d’, and ‘f’ of 4-hydroperoxy-2-heptanone are presented. Scheme 2 shows seven $C_7H_{12}O_4$ intermediates, *e.g.*, diketo-hydroperoxides ($C_7H_{12}O_4-1$ and $C_7H_{12}O_4-7$) and keto-hydroperoxy cyclic ethers ($C_7H_{12}O_4-2$ to $C_7H_{12}O_4-6$) that could result from these reactions.

Scheme 2. H-atom abstraction of 4-hydroperoxy-2-heptanone (C7KET24) by OH radical and subsequent reactions leading to C₇H₁₂O_x (x=1-4). H-atom abstractions at carbon site c, d, and f are presented. The C₇H₁₂O, C₇H₁₂O₂, C₇H₁₂O₃, and C₇H₁₂O₄ species are labeled with bold line, bracket, wedge, and wave line, respectively. C₇H₁₂O₂-1 was detected by Herbinet *et al.* [9] while the rest C₇H₁₂O_x (x=1-4) intermediates are probably formed but no definite evidence exists.

A second proposed pathway to produce the C₇H₁₂O₄ intermediates involves H-abstraction from cyclic ethers (C₇H₁₄O), subsequent O₂ addition and isomerization reactions, and decomposition. Scheme 3 presents the H-atom abstractions of 2-methyl-5-ethyl-tetrahydrofuran (C₇H₁₄O2-5) and subsequent reactions that may lead to C₇H₁₂O_x (x=1-4) intermediates. The most favorable H-abstraction sites is at carbon site ‘b’ and ‘e’ [52] of 2-methyl-5-ethyl-tetrahydrofuran, to produce two 2-methyl-5-ethyl-tetrahydrofuran radicals (*i.e.*, C₇H₁₄O2-5b (2-methyl-5-ethyl-tetrahydrofuran-2-yl radical) and C₇H₁₄O2-5e (2-methyl-5-ethyl-tetrahydrofuran-5-yl radical) in Scheme 3). Only reactions initiated from C₇H₁₄O2-5e are considered in Scheme 3, and the products from C₇H₁₄O2-5b are similar. To produce the C₇H₁₂O_x (x=1-4) intermediates, the first step is O₂ addition to C₇H₁₄O2-5e, which is estimated to be competitive with the β-C-O scission of C₇H₁₄O2-5e. The estimated rate constant of C₇H₁₄O2-5e β-C-O scission is 5×10³ s⁻¹ at 500 K and 2.3×10⁵ s⁻¹ at 600 K [52]. Assuming the rate

constant of O_2 addition to $C_7H_{14}O_2$ -5e is $6 \times 10^{12} \text{ cm}^3/\text{mol/s}$ [53], the apparent first-order rate constants of the O_2 addition to $C_7H_{14}O_2$ -5e is estimated to be $\sim 1.5 \times 10^7 \text{ s}^{-1}$ for the range 500 K - 600 K under the present experimental condition. Therefore, we expect that O_2 addition is favored over β -C-O scission of $C_7H_{14}O_2$ -5e, and the oxidation reaction mechanism for $C_7H_{14}O_2$ -5e in Scheme 3 appears plausible. Keto-hydroperoxy cyclic ethers (e.g., $C_7H_{12}O_4$ -9), and hydroperoxy di-cyclic ethers (e.g., $C_7H_{12}O_4$ -8, $C_7H_{12}O_4$ -10, and $C_7H_{12}O_4$ -11) could also be produced from this reaction mechanism.

Scheme 3. H-atom abstraction of 2-methyl-5-ethyl-tetrahydrofuran ($C_7H_{14}O_2$ -5) by OH radical and subsequent reactions lead to $C_7H_{12}O_x$ (x=1-4). H-atom abstraction at carbon site e is presented. The $C_7H_{12}O$, $C_7H_{12}O_2$, $C_7H_{12}O_3$, and $C_7H_{12}O_4$ species are labeled with bold line, bracket, wedge, and wave line, respectively. These $C_7H_{12}O_x$ (x=1-4) intermediates are probably formed but no definite evidence exists.

$C_7H_{12}O_3$ species (m/z 144) could be produced by H-atom abstraction from the $C_7H_{14}O_3$ intermediates in Scheme 2 (e.g., $C_7H_{12}O_3$ -1 to $C_7H_{12}O_3$ -5, olefinic keto-hydroperoxide), and C_7 cyclic ethers in Scheme 3 (e.g., $C_7H_{12}O_3$ -6 to $C_7H_{12}O_3$ -11, olefinic hydroperoxy cyclic ether). The olefinic keto-hydroperoxide $C_7H_{12}O_3$ species may also be produced by H-atom abstraction from olefinic

hydroperoxide $C_7H_{14}O_2$ intermediates at the carbon sites not connected to the hydroperoxy group, followed by O_2 addition, and subsequent decomposition.

Furthermore, heptenes (C_7H_{14}) are important intermediates during *n*-heptane low-temperature oxidation. Following the low-temperature reactions in Scheme 1, the oxidation of heptenes, such as 1-heptene in Scheme 4, also produces $C_7H_{12}O_3$ intermediates (*e.g.*, $C_7H_{12}O_3$ -12 to $C_7H_{12}O_3$ -15, olefinic keto-hydroperoxides, and olefinic hydroperoxy cyclic ethers). Here only H-atom abstraction at the allylic site of 1-heptene and subsequent reactions are shown. The $C_7H_{12}O_3$ intermediates from this reaction mechanism contain one hydroperoxy group, which causes them to have similar temperature-dependent behavior as C_7 keto-hydroperoxides. However, Fig. 4d shows high signal present for $C_7H_{12}O_3$ intermediates at 600 K, indicating that other intermediates without a hydroperoxy group may be produced. Another probable structure of $C_7H_{12}O_3$ intermediates could include two carbonyl groups and one hydroxyl group, suggesting that they may be produced from $C_7H_{11}O_3$ radicals by abstracting H-atoms from *n*-heptane or other intermediates. The $C_7H_{11}O_3$ radicals could be produced from $C_7H_{12}O_4$ intermediates (*e.g.*, diketo-hydroperoxide and keto-hydroperoxy cyclic ether) *via* the dissociation of the $-O-OH$ bond in the hydroperoxy group. Nevertheless, bimolecular reactions involving $C_7H_{11}O_3$ intermediates to form $C_7H_{12}O_3$ are unlikely to be significant because the concentration of $C_7H_{11}O_3$ radicals is unlikely to be large.

Scheme 4. H-atom abstraction of 1-heptene (C₇H₁₄-1) by OH radical and subsequent reactions leading to C₇H₁₂O_x (x=0-3) intermediates. H-atom abstraction at carbon site ‘c’ are presented. The C₇H₁₂O, C₇H₁₂O₂, and C₇H₁₂O₃ species are labeled with bold line, bracket, and wedge, respectively. These C₇H₁₂O_x (x=0-3) intermediates could be reasonably formed but no definite evidence exists.

The signal intensity of C₇H₁₂O₂ species (*m/z* 128) in Fig. S2a and S2b is much higher than those of C₇H₁₂O₃ and C₇H₁₂O₄ species, indicating that they are important intermediates of *n*-heptane oxidation. These species were observed in a recent *n*-heptane oxidation study and were reported as C₇ diones [9]. Products with the same carbon skeleton as the fuel, and containing two carbonyl groups, have been reported in various hydrocarbon oxidation studies [9, 32, 33, 54]. Recently, Ranzi *et al.* [55] and Pelucchi *et al.* [56] proposed a probable pathway to the formation of diones, *e.g.*, H-atom abstraction from a keto-hydroperoxide at the α -position to the hydroperoxyl group followed by β -scission (*e.g.*, formation of 2,4-heptandione (C₇H₁₂O₂-1) in Scheme 2). Including these pathways in kinetic models improved predictions of C₄ and C₇ diones in *n*-butane [55] and *n*-heptane [56] low-temperature oxidation. Improvements were also observed in the prediction of C₅ diones in *n*-pentane

oxidation [57], but discrepancies still existed. The PIE curve of $C_7H_{12}O_2$ intermediate measured in this work agrees with that reported by Herbinet *et al.* [9] (Fig. S3c). They calculated the adiabatic ionization energy of the most probable C_7 diones, *e.g.*, 1,3-heptandione (IE: 9.32 eV), 2,4-heptadione (IE: 9.40 eV), and 3,5-heptandione (IE: 9.37 eV).

The lower IE onset at 9.1 eV in Fig. S3c indicates that other intermediates may exist. Another probable pathway for the formation of the $C_7H_{12}O_2$ intermediate is proposed here. First, as shown in Scheme 2, H-atom abstraction from C_7 keto-hydroperoxides at sites β -, γ -, and/or δ - to the hydroperoxyl group, followed by cyclization, produces keto cyclic ethers (*e.g.*, with one carbonyl and one cyclic ether group), such as $C_7H_{12}O_2$ -2 and $C_7H_{12}O_2$ -3. Second, reactions involving C_7 cyclic ethers also lead to the formation of diones (*e.g.*, $C_7H_{12}O_2$ -4) and keto cyclic ethers (*e.g.*, $C_7H_{12}O_2$ -5), as shown in Scheme 3. The production of diones from cyclic ether oxidation was observed by Vanhove *et al.* [58] and Antonov *et al.* [59] in tetrahydrofuran oxidation. It should be noted that $C_7H_{12}O_2$ intermediates with two double bonds and one hydroperoxy group, such as $C_7H_{12}O_2$ -6 in Scheme 4, may also be produced. Recent work on neopentane low-temperature oxidation performed by Eskola *et al.* [60] suggested that a chemically activated $QOOH+O_2$ reaction might be a source for 2,2-dimethylpropanedial in parallel to keto-hydroperoxide. This pathway may also lead to $C_7H_{12}O_2$ species in *n*-heptane low-temperature oxidation.

The $C_7H_{12}O$ intermediates (m/z 112) could be heptenones (*e.g.*, $C_7H_{12}O$ -1 in Scheme 2 and $C_7H_{12}O$ -4 in Scheme 3), cyclic ethers with one double bond (*e.g.*, $C_7H_{12}O$ -2 and $C_7H_{12}O$ -3 in Scheme 3, and $C_7H_{12}O$ -5 and $C_7H_{12}O$ -6 in Scheme 4), and/or heptenals, which could be produced from C_7 keto-hydroperoxides, C_7 cyclic ethers, and C_7 heptenes. They could also result from H-atom abstractions of $C_7H_{14}O_2$ intermediates (*e.g.*, C_7 olefinic hydroperoxides) at the carbon sites not connected to the hydroperoxy group and subsequent cyclization. The C_7H_{12} intermediates (m/z 96) could be heptadienes and could be produced by H-atom abstractions from heptenes and subsequent reactions [61]. One example for 1,3-heptadiene formation is presented in Scheme 4.

3.1.3 $C_7H_{10}O_x$ intermediates ($x=0-4$)

The SVUV-PI-MBMS and APCI-OTMS measurement also detected $C_7H_{10}O_x$ ($x=0-4$) intermediates during *n*-heptane JSR and CFR engine oxidation (Fig. S4). In addition to these C_7 intermediates, the APCI-OTMS also observed the protonated molecular peak of C_6H_8O at m/z 95, $C_6H_6O_2$ at m/z 111, $C_8H_{14}O_2$ at m/z 143, and $C_8H_{14}O_3$ at m/z 159. The temperature-dependent signal profiles of these $C_7H_{10}O_x$ ($x=0-4$) intermediates appear in Fig. 4f-h, and the energy scans for intermediates with these m/z ratios are shown in Fig. S5. Following the same logic of the H-atom abstraction and subsequent reactions of the $C_7H_{14}O_x$ intermediates, these $C_7H_{10}O_x$ intermediates could be produced by H-atom abstraction from $C_7H_{12}O_x$ intermediates and subsequent reactions similar to those in Schemes 3-5. For example, one of the probable $C_7H_{10}O$ structures, 2-methyl-5-ethyl-furan, has been detected using GC analysis [9], which could be produced from $C_7H_{12}O$ -3 in Scheme 3.

3.2 Intermediates with less than seven carbon atoms

3.2.1 C_nH_{2n} ($n=2-6$), $C_nH_{2n-2}O$ ($n=2-6$), and $C_nH_{2n-4}O_2$ ($n=4-6$) intermediates

Figure 5a and 5b presents the mass spectra of *n*-heptane oxidation with a photon energy of 10.5 eV, highlighting species with nominal m/z 28, 42, 56, 70, 84, 98, and 112. The intermediates formed at two different temperatures (*i.e.* 530 K and 600 K) were analyzed. The reaction process at 530 K corresponds to lower fuel conversion and higher concentrations of the initial oxidation intermediates, such as the peroxides with the same carbon chain as that of the fuel; while the reaction process at 600 K corresponds to higher fuel conversion and higher concentrations of stable intermediates. The general features of the mass spectra at the two temperatures were found to be the same, except that the formation of $C_4H_4O_2$ and $C_6H_8O_2$ is more evident at 600 K. The protonated mass peaks at m/z 56, 70, 84, 98, and 112 were also observed by the APCI-OTMS sampled from *n*-heptane oxidation in JSR-2 and the CFR engine (Fig. 5c and 5d). The results from the CFR engine are similar to the JSR data, except that the alkenes were not observed.

Fig. 5. Mass spectra of intermediates with m/z 28, 42, 56, 70, 84, 98, and 112. The mass spectra in panels (a) and (b) are for JSR-1 SVUV-PI-MBMS measurements at reaction temperature of 530 K and 600 K, respectively, and a photon energy of 10.5 eV. The mass spectra in panel (c) correspond to the JSR-2 APCI-OTMS measurements at reaction temperature of 535 K. (d) is for CFR engine APCI-OTMS measurements.

These products include five alkenes (C_nH_{2n} , $n=2-6$), which were also identified using GC analysis [9] as ethylene (C_2H_4), propene (C_3H_6), 1-butene (C_4H_8), 1-pentene (C_5H_{10}), and 1-hexene (C_6H_{12}). We note that the signals of m/z 56 and 70 contain the fragments of n -heptane at 10.5 eV; the signals of these two species are also measured at a lower photon energy of 10 eV, which does not cause the fragmentation of n -heptane. Fig. 5a and 5b show that the signals of these alkenes increase with temperature from 530 K to 600 K, except for C_6H_{12} . Radical β -C-C scission is expected to be important pathway for alkene formation; for example, consider the β -C-C scission of QOOH radicals (see Scheme 1). Scheme 5 presents the decomposition of γ -QOOH radicals, resulting from the intramolecular H-atom isomerization of ROO radicals *via* six-membered ring transition states, which

are the most abundant QOOH radicals in *n*-heptane oxidation. The calculated rate constant from Villano *et al.* [62] shows that the β -C-C scission of γ -QOOH to olefin + aldehyde + OH is competitive at 600 K with cyclization to form cyclic ethers containing a four-membered ring. As shown in Scheme 5, β -C-C scission of γ -QOOH radicals leads to the formation of C₂-C₆ alkenes. Similarly, β -C-C scission of γ -P(OOH)₂ radicals (that contain one and/or two hydroperoxy group(s) in the γ -position to the radical site) also produces alkenes. Moreover, H-atom abstraction from the γ -site relative to the hydroperoxy group in keto-hydroperoxides form γ -QOOH radicals with a carbonyl functional group. Their decomposition could also produce alkenes; for example, β -C-C scission of the C7KET24-f radical (4-hydroperoxy-2-heptanone-6-yl radical) in Scheme 2 produces propene. Another source for alkenes could be decomposition of cyclic ether radicals following H-atom abstraction from cyclic ethers. One example for this reaction pathway to propene is shown in Scheme 3 for the C₇H₁₄O₂-5e radical (2-methyl-5-ethyl-tetrahydrofuran-5-yl radical).

Scheme 5. Decomposition of γ -QOOH to cyclic ether and OH, and olefin + aldehyde + OH. Rate constant at 600 K presented from Villano *et al.* [62].

Furthermore, intermediates with the molecular formula C_nH_{2n-2}O (n=2-6) were detected. It is obvious that C₂H₂O is ketene, while other species could be alkenyl keto/aldehydes containing a double

bond and a carbonyl group. For example, GC analysis [9] observed C₃-C₆ alkenyl keto/aldehydes, *e.g.*, prop-2-enal (acrolein, C₃H₄O), 3-buten-2-one and 2-butenal (C₄H₆O), 1-penten-3-one (C₅H₈O), and 1-hexen-3-one (C₆H₁₀O). These products could be produced from the reactions of aldehydic and keto radicals, such as bimolecular reactions with O₂ and/or β-C-C scission. H-atom abstraction from aldehydes and ketones, decomposition of keto-hydroperoxides, and H-atom abstraction from cyclic ethers and subsequent decomposition are all potential sources of aldehydic and keto radicals.

Figure 5 also presents the signals of intermediates with a molecular formula of C_nH_{2n-4}O₂ (n=4-6), detected especially at 600 K in the SVUV-PI-MBMS experiment. These three intermediates were not reported in the previous *n*-heptane oxidation study [9], and their structure and reaction mechanism remains unclear. In the detailed product analysis of *n*-butane oxidation [54], *m/z* 84 was detected and the molecular formula was assigned as C₄H₄O₂; the authors concluded that this species could be a furanone with the carbonyl group conjugated to the double bond.

3.2.2 C_nH_{2n}O (n=1-6) and C_nH_{2n-2}O₂ (n=2-6) intermediates

Figure 6 presents the mass spectra obtained for *n*-heptane oxidation in JSR-2 and the CFR engine, highlighting species with nominal *m/z* 30, 44, 58, 72, 86, 100, and 114. When using SVUV-PI-MBMS with JSR-1 at 10.5 eV, the spectrum of 530 K and 600 K in Fig. 6a and 6b shows all these intermediates except *m/z* 30. The existence of *m/z* 30 is confirmed at 11 eV in Fig. 6a and 6b (blue dashed line). The signal intensity of C₇H₁₆ was so strong at 10.5 eV that it interfered with the analysis of the other intermediates; thus, the mass peak at 10 eV is presented as a red dashed line in Fig. 6a and 6b. This provide better resolution for the distribution of other intermediates, such as C₅H₈O₂, C₆H₁₂O, and C₇H₁₆. The formation of these intermediates is more effective at higher temperatures (600 K versus 530 K, Fig. 6a and 6b). The intermediates from *n*-heptane JSR-2 and CFR engine oxidation measured by the APCI-OTMS are in agreement with the SVUV-PI-MBMS analysis, except that the protonated molecular peaks of C₂H₂O₂, C₃H₆O, and C₃H₄O₂ were not detected.

Fig. 6. Mass spectra of intermediates with m/z 30, 44, 58, 72, 86, 100, and 114. The mass spectra in panel (a) and (b) correspond to SVUV-PI-MBMS on-line analysis during *n*-heptane JSR oxidation at reaction temperature of 530 K and 600 K, respectively. The black line represents mass spectra at 10.5 eV. The mass spectra of m/z 30 measured at 11 eV are denoted in blue dashed line. The mass spectra of m/z 100 measured at 10 eV are denoted in red dashed line. (c) Orbitrap mass spectrometry off-line analysis during *n*-heptane JSR oxidation at reaction temperature of 535 K. (d) Orbitrap mass spectrometry off-line analysis during *n*-heptane CFR engine oxidation.

These intermediates can be categorized into two classes, *i.e.*, $C_nH_{2n}O$ ($n=1-6$) and $C_nH_{2n-2}O_2$ ($n=2-6$). $C_nH_{2n}O$ ($n=1-6$) intermediates could be C_1 - C_6 aldehydes and/or keto compounds. Previous GC analysis [9] detected acetaldehyde (C_2H_4O), propanal (C_3H_6O) and acetone (C_3H_6O), butanal (C_4H_8O) and 2-butanone (C_4H_8O), pentanal ($C_5H_{10}O$) and 2-pentanone ($C_5H_{10}O$), as well as 2-hexanone ($C_6H_{12}O$). These aldehyde and/or keto compounds could be produced from decomposition of C_7 keto-hydroperoxides by breaking the $-O-OH$ bond in the hydroperoxy group. In this process, OH and keto-alkoxy radicals are formed; the latter easily decompose *via* β -C-C scission [63]. For

example, the pathway (a) in Scheme 6 shows that β -C-C scission close to the carbonyl group (*i.e.* the C_b-C_c bond) produces the aldehyde/keto compound and their radicals, whereas β -C-C scission away from the carbonyl group (*i.e.* the C_c-C_d bond) produced diones and alkyl radicals.

Scheme 6. Decomposition of the most probable C₇ keto-hydroperoxide to release OH radical and keto-alkoxyl radical. Subsequent β -C-O scission of keto-alkoxyl radical forms C_nH_{2n}O (n=1-5), C_nH_{2n-2}O₂ (n=3-6), keto and/or aldehyde radicals (C_nH_{2n-1}O, n=2-6), and alkyl radical (C_nH_{2n+1}, n=1-4).

The tendency of C₇ keto-alkoxy radical to produce aldehyde/keto compounds or diones merits further discussion. Reactions (1) and (2) shown below correspond to pathway (g) in Scheme 6; the rate constants are $3.3 \times 10^9 \text{ s}^{-1}$ and $2.3 \times 10^8 \text{ s}^{-1}$ at 600 K for reactions (1) and (2) [9], respectively, which indicate that the formation of aldehyde/keto compound and their radicals are more favorable than the production of diones.

The carbon adjacent to the alkoxy group is a primary carbon in reaction (2), while those for reactions (a)-(e) in Scheme 6 are secondary carbons. To estimate rate coefficients to produce diones from reactions (a)-(e) in Scheme 6, reaction (3) should be more suitable than reaction (2). The rate constant of reaction (3), calculated by Rauk *et al.* [64] at 600 K, is $2.9 \times 10^9 \text{ s}^{-1}$, which is comparable to that of reaction (1). Therefore, formation of diones and alkyl radicals may also become important, and decomposition of the C_7 keto-hydroperoxide could directly produce not only aldehyde and/or keto compounds, but also diones. As shown in Fig. 6, the SVUV-PI-MBMS detected intermediates with the molecular formula $C_nH_{2n-2}O_2$ ($n=2-6$), which may correspond to the C_2 - C_6 diones.

In addition, the experimental results show evidence that enols are produced in *n*-heptane oxidation. Figure S6 presents clear IE onsets at 9.3 eV for C_2H_4O , 8.8 eV for C_3H_6O , and 8.5 eV for C_4H_8O . These indicate the formation of vinyl alcohol (IE: 9.33 eV [49]), propenols (IE: 8.64-8.7 eV [49]), and butenols (IE: 8.34-8.44 eV [49]). These enols are quite common in low-pressure flames [65-67] but were seldom detected during alkane low-temperature oxidation. Further work is needed to understand their low-temperature formation mechanism. Organic acid assisted keto-enol tautomerizations may convert the C_2 - C_4 aldehydes to the corresponding enols [68].

3.2.3 $C_nH_{2n+2}O$ ($n=1-4, 6$) and $C_nH_{2n}O_2$ ($n=1-6$) intermediates

Figure 7 shows the SVUV-PI-MBMS mass spectrum of m/z 32, 46, 60, 74, 88, 102, and 116 during *n*-heptane oxidation in JSR-1 at 11.8 eV (a, b) and 10 eV (c, d). The mass peaks of $C_nH_{2n+2}O$ intermediates, including CH_3OH , C_2H_6O , C_3H_8O , and $C_4H_{10}O$ could be methanol, ethanol and/or dimethyl ether, propanols and/or ethyl methyl ether, and butanols and/or C_4 ethers. The ionization energies of ethanol and propanols are above 10.1 eV; the signals of C_2H_6O and C_3H_8O observed in the spectrum measured at 10 eV in Fig. 7c and 7d could therefore come from the ionization of dimethyl

ether (IE: 10.025 eV [49]) and ethyl methyl ether (IE: 9.72 eV [49]). In addition to the $C_nH_{2n+2}O$ intermediates, $C_nH_{2n}O_2$ intermediates from C_1 to C_6 were observed and their energy scans are presented in Fig. 8. The IE onsets in Fig. 8c-8d at 11.25, 10.55, 10.36, and 10.18 eV for CH_2O_2 , $C_2H_4O_2$, $C_3H_6O_2$, and $C_4H_8O_2$, respectively, are in reasonable agreement with those of formic acid (IE: 11.33 eV [49]), acetic acid (IE: 10.65 eV [49]), propanoic acid (IE: 10.44 eV [49]), and butanoic acid (IE: 10.17 eV [49]).

Fig. 7. Photoionization mass spectra of m/z of 32, 46, 60, 74, 88, 102, and 116 recorded during n -heptane JSR oxidation at (a) 530 K and 11.8 eV, (b) 600 K and 11.8 eV, (c) 540 K and 10 eV, and (d) 600 K and 10 eV.

For $C_3H_6O_2$ and $C_4H_8O_2$ in Fig. 8c and 8d, further onsets were observed at 9.45 and 9.3 eV, respectively. In a recent study of n -pentane low-temperature oxidation, Rodriguez *et al.* [32] observed the $C_3H_6O_2$, $C_4H_8O_2$, and $C_5H_{10}O_2$ intermediates and proposed that they could be olefinic hydroperoxides. The calculated ionization energies of allylhydroperoxide ($C_3H_6O_2$, IE: 9.55 eV), but-

1-enyl-3-hydroperoxide ($C_4H_8O_2$, IE: 9.29 eV), and but-2-enyl-1-hydroperoxide ($C_4H_8O_2$, IE: 9.32 eV) are close to the measured IE onset of $C_3H_6O_2$ and $C_4H_8O_2$ intermediates. The IE onset for $C_5H_{10}O_2$ in Fig. 8e is 9.3 eV and that of $C_6H_{12}O_2$ in Fig. 8f is 9.2 eV, which are both close to those of the C_3 and C_4 olefinic hydroperoxides, and much lower than the ionization energies of various acid isomers, such as pentanoic acid of 10.08 eV [32] and hexanoic acid of 10.21 eV [33]. Therefore, these two intermediates could be olefinic hydroperoxides. This interpretation seems to be supported by the calculated ionization energy of pent-1-enyl-3-hydroperoxide (IE: 9.18 eV) and pent-2-enyl-1-hydroperoxide (IE: 9.25 eV) for $C_5H_{10}O_2$ [32], and hex-1-enyl-3-hydroperoxide (IE: 9.26 eV), *cis*-hex-3-enyl-2-hydroperoxide (IE: 9.19 eV), and hex-2-enyl-1-hydroperoxide (IEs: 9.12 and 9.19 eV) for $C_6H_{12}O_2$ [33]. We note that $C_2H_4O_2$ is also ionized at 10 eV (Fig. 7c and 7d) and an IE onset below 10.55 eV is observed, which indicates other isomers of $C_2H_4O_2$ may exist.

Fig. 8. Photoionization efficiency spectra of $C_nH_{2n}O_2$ ($n=1-6$) measured at 530 K. The inserted line helps clarify the ionization energy onset.

In combustion processes –especially in the transport sector – organic acids are important exhaust emissions [69, 70]. Acetic acid and propanoic acid have been detected during alkane oxidation [9, 34, 54, 71], but formic acid is seldom reported [54]. It was observed as an intermediate in dimethyl ether low-temperature oxidation [27, 38, 72, 73]. However, the reaction mechanism for formic acid is still dispute [27, 74, 75].

OH radical addition to formaldehyde, and subsequent decomposition, was considered to be an important route for formic acid formation [76] and had been included in the kinetic models [11, 77].

However, experimental and theoretical calculations have shown that this channel is negligible compared to H-atom abstraction from formaldehyde by OH radicals [78-80]. The Korcek mechanism of γ -keto-hydroperoxide has been suggested to produce acids during the gas-phase oxidation of hydrocarbons [55, 56, 81], and the recent experiment suggests that Korcek reaction may happen in dimethyl ether oxidation [27, 38]. Pelucchi *et al.* [56] showed that the Korcek reaction of γ -keto-hydroperoxide in *n*-heptane oxidation could produce organic acids, ranging from formic acid to pentanoic acid. However, they increased the Korcek reaction rate constant [55] by a factor of three to predict acetic and propanoic acid formation. These Korcek reactions were also included in an *n*-pentane kinetic model to predict acetic acid at 1 and 10 atm in a JSR [57]. Interestingly, the acetic acid concentration was significantly underestimated, even when the rate constant of the Korcek reaction calculated by Jalan *et al.* [81] was increased by a factor of 10. Dames *et al.* [82] studied propane ignition in a rapid compression machine (RCM). They stated that under the lowest temperature RCM experiments (~ 700 K), decomposition of γ -keto-hydroperoxide ($\text{HOOCH}_2\text{CH}_2\text{CHO}$) to $\text{OH} + \text{OCH}_2\text{CH}_2\text{CHO}$ dominates by three orders of magnitude. Only at and below 400 K does cyclic peroxide (CP) formation (*i.e.*, the Korcek mechanism) become competitive with the aforementioned channel. Thus, they did not include the formation of CP and its subsequent reactions to formic acid and acetic acid. To assess the potential importance of the Korcek reactions under the present conditions, we calculated the branching fractions of the decomposition of $\text{HOOCH}_2\text{CH}_2\text{CHO}$ to $\text{OH} + \text{OCH}_2\text{CH}_2\text{CHO}$ (OQ'O), CP, formic acid, and acetic acid from 500-700 K and at 1 atm. The rate coefficients as the basis of the simulated data in Fig. 9 are taken from quantum chemistry calculations by Goldsmith *et al.* [83]. The branching ratio to CP, formic acid, and acetic acid is 7%, 0.6%, and 0.1% at 500 K, respectively, and these numbers drop to 1%, 0.2%, and 0.06% at 600 K. Apparently, the Korcek reaction is not sufficient to lead to substantial organic acid formation under our conditions. Thus, there are likely other channels for organic acid formation during the gas-phase oxidation of alkanes.

Fig. 9. Branching fraction for rate constants for thermal $\text{HOOCH}_2\text{CH}_2\text{CHO}$ decomposition at 1 atm.

Smaller olefinic hydroperoxides were recently reported during oxidation of *n*-pentane [32] and of *n*-heptane and *n*-decane [33], and their reaction mechanism is not fully understood. Rodriguez *et al.* [32] proposed that olefinic hydroperoxides arise not only from the oxygen addition process, but also through the recombination of HO_2 radicals with the olefinic radicals. Given that C_3 - C_6 olefins were detected (Fig. 5) and that H-atom abstraction from them forms olefinic radicals, this reaction mechanism may explain the formation of C_3 - C_6 olefinic hydroperoxides.

3.2.4 $\text{C}_n\text{H}_{2n+2}\text{O}_2$ ($n=0-4, 7$) and $\text{C}_n\text{H}_{2n}\text{O}_3$ ($n=3-6$) intermediates

Figure 10 shows the SVUV-PI-MBMS mass spectrum of m/z 48, 62, 76, 90, 104, 118, and 132 during *n*-heptane oxidation in JSR-1 at reaction temperature of 540 K (Fig. 10a) and 600 K (Fig. 10b) at 10 eV. The blue dashed line shows the mass spectrum at 11 eV for m/z 34. These intermediates correspond to $\text{C}_n\text{H}_{2n+2}\text{O}_2$ ($n=0-4, 7$) and $\text{C}_n\text{H}_{2n}\text{O}_3$ ($n=3-6$). The species with molecular formulae of H_2O_2 , CH_4O_2 , $\text{C}_2\text{H}_6\text{O}_2$, $\text{C}_3\text{H}_8\text{O}_2$, $\text{C}_4\text{H}_{10}\text{O}_2$, and $\text{C}_7\text{H}_{16}\text{O}_2$ could be hydrogen peroxide, methyl peroxide, ethyl peroxide, propyl peroxide, butyl peroxide, and heptyl peroxide, while $\text{C}_3\text{H}_6\text{O}_3$, $\text{C}_4\text{H}_8\text{O}_3$, $\text{C}_5\text{H}_{10}\text{O}_3$, and $\text{C}_6\text{H}_{12}\text{O}_3$ could be C_3 - C_6 keto-hydroperoxides. For example, the PIE curves for H_2O_2 (Fig. S7a), CH_4O_2 (Fig. S7b), $\text{C}_2\text{H}_6\text{O}_2$ (Fig. S7c), $\text{C}_3\text{H}_8\text{O}_2$ (Fig. S7d) could support the interpretation of the measured signals as hydrogen peroxide [84], methyl peroxide [28], ethyl peroxide [28], and propyl peroxide [71], respectively. The PIE curve of $\text{C}_4\text{H}_8\text{O}_3$ in Fig. S7e is consistent with that of the C_4 keto-hydroperoxide [28] below 10 eV. The discrepancy above 10 eV may be caused by fragmentation of larger molecules. The comparison in Fig. S7f with C_5 keto-hydroperoxide [32] is also satisfactory, although the profile shows high noise. Evidence supporting that the aforementioned C_2 - C_7 intermediates could be

peroxides is their fast consumption when the temperature increases from 540 K to 600 K (Fig. 10).

Fig. 10. Photoionization mass spectra of m/z of 34, 48, 62, 76, 90, 104, 118, and 132 during *n*-heptane JSR oxidation at reaction temperature of 540 K (a) and 600 K (b). The black line are mass spectra at 10 eV. The mass spectra of m/z 34 at 11 eV are denoted in blue dashed line.

The C_1 - C_4 , and C_7 alkyl peroxides could be produced from the disproportionation of C_1 - C_3 alkyl peroxy radicals, and C_7 alkyl peroxy radicals with HO_2 radicals. As shown in Scheme 1 and Scheme 6, the H-atom abstraction of *n*- C_7H_{16} forms C_7 alkyl radicals, and the decomposition of the keto-hydroperoxide forms C_1 - C_4 alkyl radicals. The subsequent O_2 addition to these alkyl radicals produces C_1 - C_4 , and C_7 alkyl peroxy radicals. The reaction mechanism for C_3 - C_6 keto-hydroperoxides is not clear. They may be produced from the combination of smaller radical species and/or from the β -C-C scission of the γ - $\text{P}(\text{OOH})_2$ radicals. One example is shown below.

3.2.5 $\text{C}_n\text{H}_{2n-2}$ ($n=4-6$) and $\text{C}_n\text{H}_{2n-4}\text{O}$ ($n=4-6$) intermediates

Further intermediates observed during *n*-heptane oxidation in the JSR and CFR engine are m/z 54, 68, 82 and 96. These species were measured by SVUV-PI-MBMS at 530 K and 600 K in the JSR (Fig. S8a and S8b), and by APCI-OTMS at 535 K in both the JSR and the CFR engine (Fig. S8c and S8d). The data from all three experiments are in good agreement, and species can be classified into $\text{C}_n\text{H}_{2n-2}\text{O}_2$ ($n=4-6$) and $\text{C}_n\text{H}_{2n-4}\text{O}$ ($n=4-6$). The signals at C_4H_6 , C_5H_8 , and C_6H_{10} could be from C_4 - C_6

dienes. For example, 1,3-butadiene and 1,3-pentadiene were observed in the GC analysis for *n*-heptane oxidation [9]. The C₄H₄O, C₅H₆O, and C₆H₈O intermediates have not been reported in the literature, and they may have two double bonds and one cyclic ring, as for example in furan which could contribute to C₄H₄O. For *m/z* 96, the species with molecular formula of C₅H₄O₂ was also observed.

4. Conclusions and perspective

In this work, the low-temperature oxidation of *n*-heptane was studied in two separate JSRs and a CFR engine. The intermediate pool of species was experimentally probed using SVUV-PI-MBMS and APCI-OTMS. The resulting spectra from both experimental systems are in good agreement, and the combination of these two diagnostic methods clarified the elemental composition of oxidation intermediates. This work demonstrates, for the first time, a similarity in the distribution of intermediate species from *n*-heptane oxidation in an engine and an ideal reactor.

The species pool includes intermediates with the same carbon skeleton as the fuel, such as C₇H₁₄O_x (*x*=0-5), C₇H₁₂O_x (*x*=0-4), and C₇H₁₀O_x (*x*=0-4), highlighting the first, second, and third sequential O₂ addition reaction mechanism and bimolecular reactions of these intermediates. Large numbers of C₁-C₆ intermediates were observed, resulting from the decomposition of C₇ intermediates. The intermediates can be classified into alkenes, dienes, aldehyde/keto compounds, olefinic aldehyde/keto compounds, diones, cyclic ethers, peroxides, acids, and alcohols/ethers. While many observed signals could be rationalized using the unambiguous elemental C/H/O composition and PIE curves with respective onsets, it must be realized that the enormous wealth of species now accessible with these highly discriminative techniques presents more challenges, regarding the vast number of potential structures and conformers that may contribute to the measured mass spectra. The qualitative data of the oxidation intermediates, especially those with the same carbon skeleton of *n*-heptane are valuable. However, the number of isomeric structures increases exponentially with the number of atoms in the molecule, and thus the hundreds of structural variations that are addressed in this work cannot be determined and quantified as easily [37]. Furthermore, the photoionization cross sections of many intermediates are not known. Significant advances in knowledge are needed to obtain

quantitative information from the current experimental data set. Here, plausible pathways have been discussed, in part by analogies drawn from previous work, and a fuller understanding of the contributing routes to low-temperature alkane oxidation is emerging. Even for one of the most common reference fuels such as *n*-heptane, we demonstrate that the intermediate pool composition is significantly more complex than postulated in any model, that previously undetected classes of species exist in long-chain alkane oxidation, and that these species matter under engine conditions. Furthermore, kinetic model development using the present experimental information is needed to show the potential role of these highly oxygenated species, especially at low temperatures.

Recent collaborations between the Combustion Chemistry Center at NUI Galway, Lawrence Livermore National Laboratory, and the Clean Combustion Research Center at KAUST aim at improving kinetic models of alkanes with updated thermodynamics, reaction pathways, kinetics, and rate rules. The methodology has been successfully adopted in the kinetic modeling of pentane isomers [53], *n*-hexane [85, 86], *n*-heptane [11], 2-methylhexane [31, 87], and iso-octane [88]. This methodology was also adopted to optimize the rate rules for a set of normal alkanes from *n*-heptane to *n*-undecane, and was demonstrated to improve the predictive accuracy for all the considered fuels [89]. The experimental results in this work provide additional insights into the sequential third O₂ addition to P(OOH)₂ radicals and subsequent reactions, bimolecular reactions of C₇ intermediates, *e.g.*, C₇H₁₄O_x (x=0-5) and C₇H₁₂O_x (x=0-4), and the formation of C₂-C₆ diones from the decomposition of the C₇ keto-alkoxy radicals. However, these pathways were seldom considered in the aforementioned kinetic models, or those from other teams [33, 56, 82, 90]. Our next goal is to include these pathways in an *n*-heptane kinetic model [11], and to test their effect on the species distribution in *n*-heptane JSR oxidation and on *n*-heptane ignition delay measurements in shock tubes and rapid compression machines. As shown previously by Moshhammer et al. [27, 38] on low-temperature oxidation of dimethyl ether, identification of newly detected intermediates [27] and subsequent quantification [38] of some of these species involved significant experimental and theoretical work. Similarly, extensive theoretical and experimental work is needed here to reveal the role of enols, acids, and olefinic

peroxides in low-temperature oxidation mechanisms.

Supplemental material

PIE curves for $C_7H_{14}O_x$ ($x=0-3, 5$), $C_7H_{12}O_x$ ($x=0-4$), $C_7H_{10}O_x$ ($x=0-4$), $C_nH_{2n}O$ ($n=2-4$), $C_nH_{2n+2}O_2$ ($n=0-3$), $C_nH_{2n}O_3$ ($n=4$ and 5) intermediates. Temperature-dependent signal profiles of $C_7H_{12}O_x$ ($x=0-4$), $C_7H_{10}O_x$ ($x=0-4$), C_nH_{2n-2} ($n=4-6$), and $C_nH_{2n-4}O$ ($n=4-6$).

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Figure Captions

(Color figures in electronic version only)

Table 1. Intermediate species measured during *n*-heptane oxidation in a JSR by Herbinet *et al.* [9], Rodriuez et al. [33], and this work. The intermediates labeled in bold were also detected in the JSR and CFR engine experiments by an atmospheric pressure chemical ionization (APCI) Orbitrap mass spectrometer (OTMS).

Fig. 1. Schematic representation of experimental setup for the JSR-2 experiment at KAUST.

Table 2. CFR engine specifications and test conditions.

Fig. 2. The cylinder pressure, temperature history, and heat release rate during *n*-heptane low-temperature oxidation in the CFR engine. The CFR engine specifications and test conditions are presented in Table 2.

Scheme 1. Reaction scheme for *n*-heptane low-temperature oxidation. Represented intermediates (*i.e.*, $C_7H_{14}O_x$, $x=0-5$) are boxed and highlighted in blue.

Fig. 3. Mass spectra of intermediates with $C_7H_{14}O_x$ ($x=0-5$) molecular formula. The mass spectra in panels (a) and (b) correspond to the JSR-1 SVUV-PI-MBMS measurements at 530 K and 600 K, respectively, and a photon energy of 9.6 eV. The signal of $C_7H_{14}O_5$ is increased by a factor of 20 for clarity in Fig. 3a. The mass spectra in panel (c) correspond to the JSR-2 APCI-OTMS off-line measurements at 535 K (black line) and on-line measurements of $C_7H_{14}O_3$, $C_7H_{14}O_4$, and $C_7H_{14}O_5$ at 542 K (red dashed line). (d) is for CFR engine APCI-OTMS measurements.

Fig. 4. Temperature-dependent signal profiles of intermediates with the same carbon number of *n*-heptane at 9.6 eV. The reaction temperature is not corrected, which has an uncertainty of ± 20 K.

Scheme 2. H-atom abstraction of 4-hydroperoxy-2-heptanone (C_7KET24) by OH radical and subsequent reactions leading to $C_7H_{12}O_x$ ($x=1-4$). H-atom abstractions at carbon site c, d, and f are presented. The $C_7H_{12}O$, $C_7H_{12}O_2$, $C_7H_{12}O_3$, and $C_7H_{12}O_4$ species are labeled with bold line, bracket, wedge, and wave line, respectively. $C_7H_{12}O_2-1$ was detected by Herbinet *et al.* [9] while the rest $C_7H_{12}O_x$ ($x=1-4$) intermediates are probably formed but no definite evidence exists.

Scheme 3. H-atom abstraction of 2-methyl-5-ethyl-tetrahydrofuran ($C_7H_{14}O_2-5$) by OH radical and subsequent reactions lead to $C_7H_{12}O_x$ ($x=1-4$). H-atom abstraction at carbon site e is presented. The $C_7H_{12}O$, $C_7H_{12}O_2$, $C_7H_{12}O_3$, and $C_7H_{12}O_4$ species are labeled with bold line, bracket, wedge, and wave line, respectively. These $C_7H_{12}O_x$ ($x=1-4$) intermediates are probably formed but no definite evidence exists.

Scheme 4. H-atom abstraction of 1-heptene ($C_7H_{14}-1$) by OH radical and subsequent reactions leading to $C_7H_{12}O_x$ ($x=0-3$) intermediates. H-atom abstraction at carbon site 'c' are presented. The $C_7H_{12}O$,

$C_7H_{12}O_2$, and $C_7H_{12}O_3$ species are labeled with bold line, bracket, and wedge, respectively. These $C_7H_{12}O_x$ ($x=0-3$) intermediates could be reasonably formed but no definite evidence exists.

Fig. 5. Mass spectra of intermediates with m/z 28, 42, 56, 70, 84, 98, and 112. The mass spectra in panels (a) and (b) are for JSR-1 SVUV-PI-MBMS measurements at reaction temperature of 530 K and 600 K, respectively, and a photon energy of 10.5 eV. The mass spectra in panel (c) correspond to the JSR-2 APCI-OTMS measurements at reaction temperature of 535 K. (d) is for CFR engine APCI-OTMS measurements.

Scheme 5. Decomposition of γ -QOOH to cyclic ether and OH, and olefin + aldehyde + OH. Rate constant at 600 K presented from Villano *et al.* [62].

Fig. 6. Mass spectra of intermediates with m/z 30, 44, 58, 72, 86, 100, and 114. The mass spectra in panel (a) and (b) correspond to SVUV-PI-MBMS on-line analysis during *n*-heptane JSR oxidation at reaction temperature of 530 K and 600 K, respectively. The black line represents mass spectra at 10.5 eV. The mass spectra of m/z 30 measured at 11 eV are denoted in blue dashed line. The mass spectra of m/z 100 measured at 10 eV are denoted in red dashed line. (c) Orbitrap mass spectrometry off-line analysis during *n*-heptane JSR oxidation at reaction temperature of 535 K. (d) Orbitrap mass spectrometry off-line analysis during *n*-heptane CFR engine oxidation.

Scheme 6. Decomposition of the most probable C_7 keto-hydroperoxide to release OH radical and keto-alkoxyl radical. Subsequent β -C-O scission of keto-alkoxyl radical forms $C_nH_{2n}O$ ($n=1-5$), $C_nH_{2n-2}O_2$ ($n=3-6$), keto and/or aldehyde radicals ($C_nH_{2n-1}O$, $n=2-6$), and alkyl radical (C_nH_{2n+1} , $n=1-4$).

Fig. 7. Photoionization mass spectra of m/z of 32, 46, 60, 74, 88, 102, and 116 recorded during *n*-heptane JSR oxidation at (a) 530 K and 11.8 eV, (b) 600 K and 11.8 eV, (c) 540 K and 10 eV, and (d) 600 K and 10 eV.

Fig. 8. Photoionization efficiency spectra of $C_nH_{2n}O_2$ ($n=1-6$) measured at 530 K. The inserted line helps clarify the ionization energy onset.

Fig. 9. Branching fraction for rate constants for thermal $HOOCH_2CH_2CHO$ decomposition at 1 atm.

Fig. 10. Photoionization mass spectra of m/z of 34, 48, 62, 76, 90, 104, 118, and 132 during *n*-heptane JSR oxidation at reaction temperature of 540 K (a) and 600 K (b). The black line are mass spectra at 10 eV. The mass spectra of m/z 34 at 11 eV are denoted in blue dashed line.