On the Combustion Chemistry of \( n \)-Heptane and \( n \)-Butanol Blends

Darshan M. A. Karwat,*† Scott W. Wagnon,‡ Margaret S. Wooldridge,†‡ and Charles K. Westbrook§

†Department of Aerospace Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
‡Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
§Lawrence Livermore National Laboratory, Livermore, California 94550, United States

Supporting Information

ABSTRACT: High-speed gas sampling experiments to measure the intermediate products formed during fuel decomposition remain challenging yet important experimental objectives. This article presents new speciation data on two important fuel reference compounds, \( n \)-heptane and \( n \)-butanol, at practical thermodynamic conditions of 700 K and 9 atm, for stoichiometric fuel-to-oxygen ratios and a dilution of 5:64 (molar ratio of inert gases to \( \text{O}_2 \)), and at two blend ratios, 80%–20% and 50%–50% by mole of \( n \)-heptane and \( n \)-butanol, respectively. When compared against 100% \( n \)-heptane ignition results, the experimental data show that \( n \)-butanol slows the reactivity of \( n \)-heptane. In addition, speciation results of \( n \)-butanol concentrations show that \( n \)-heptane causes \( n \)-butanol to react at temperatures where \( n \)-butanol in isolation would not be considered reactive. The chemical kinetic mechanism developed for this work accurately predicts the trends observed for species such as carbon monoxide, methane, propane, 1-butene, and others. However, the mechanism predicts a higher amount of \( n \)-heptane consumed at the first stage of ignition compared to the experimental data. Consequently, many of the species concentration predictions show a sharp rise at the first stage of ignition, a trend that is not observed experimentally. An important discovery is that the presence of \( n \)-butanol reduces the measured concentrations of the large linear alkenes, including heptenes, hexenes, and pentenes, showing that the addition of \( n \)-butanol affects the fundamental chemical pathways of \( n \)-heptane during ignition.

1. INTRODUCTION

There is significant interest in biofuels for the transportation sector, and the first point of entry is to blend biofuels with traditional petroleum-based fuels. Biofuels can be single component fuels (such as ethanol or butanol) or multi-component fuels (such as biodiesels derived from rapeseed or soy methyl esters). There is an immediate need to understand how biofuels change the chemistry of conventional fuels in terms of global reactivity, as well as the effects of biofuels on air pollutants, particulate, and greenhouse gas emissions. Significant effort has been made to understand the combustion chemistry of large \( n \)-alkanes, which comprise a significant fraction of complex fuel mixtures such as kerosene, gasoline, and diesel. \( n \)-Heptane (\( n \)-C\(_7\)H\(_{16}\)) has received particular attention because it is a primary reference fuel along with iso-octane (\( i \)-C\(_8\)H\(_{18}\)). \( n \)-C\(_7\)H\(_{16}\) has a high vapor pressure, allowing gas-phase studies of its chemistry, and it also exhibits chemical kinetic features such as negative temperature coefficient (NTC) behavior that distinguishes large-chain \( n \)-alkanes from many other hydrocarbons.

The global reactivity of \( n \)-C\(_7\)H\(_{16}\) has been extensively studied in shock tubes,1–7 jet-stirred reactors,8 rapid compression machines,12,19 individual species concentrations have been measured optically using laser diagnostics in shock tubes,7 and one set of measurements has been performed in a premixed laminar flame.14 These studies have provided important insights into reaction pathways and fuel consumption rates; however, as has been noted by Karwat et al.,19 there are significant differences between model predictions and experimental measurements of key intermediate species formed during the ignition delay time of \( n \)-C\(_7\)H\(_{16}\). Several chemical kinetic mechanisms have been developed to describe \( n \)-C\(_7\)H\(_{16}\) chemistry at both low and high temperatures. The most recently published mechanism,12 based on the work of Curran et al.,21 was used in the Karwat et al.19 study. Other such mechanisms include a recently updated mechanism from Côme et al.,22 and a mechanism developed by researchers at Politecnico di Milano.23

Like \( n \)-C\(_7\)H\(_{16}\) the biofuel \( n \)-butanol (\( n \)-C\(_4\)H\(_9\)OH) has garnered much interest in the recent combustion chemistry literature. Its low vapor pressure, reduced miscibility in water, and high energy density24 lend \( n \)-C\(_4\)H\(_9\)OH considerable advantages over ethanol in applications such as aviation fuel, and studies have investigated flame characteristics and
propagation,\textsuperscript{25−28} ignition,\textsuperscript{29−34} decomposition,\textsuperscript{35} pyrolysis,\textsuperscript{36,37} and elementary reaction rates.\textsuperscript{38,39} Speciation of n-C\textsubscript{7}H\textsubscript{16}OH has been explored as well in jet-stirred reactors,\textsuperscript{35,40} laminar flame configurations,\textsuperscript{27,41} and rapid compression facilities.\textsuperscript{34} When compared to a recently published chemical kinetic mechanism,\textsuperscript{33} a speciation study in a rapid compression facility by Karwat et al.\textsuperscript{34} showed excellent reproducibility of global ignition delay times, but with important differences between ethene and aldehyde measurements and predictions. A more comprehensive mechanism for n-C\textsubscript{4}H\textsubscript{9}OH has since been developed by Sarathy et al.\textsuperscript{42}

While it is apparent that speciation studies are capable of providing insights into the chemical kinetic effects of blending oxygenated biofuels with conventional hydrocarbon fuels, only two studies, both in a jet stirred reactor,\textsuperscript{43,44} have examined the chemical kinetic effects of adding n-C\textsubscript{4}H\textsubscript{9}OH to a large n-alkane. Dagaut and Togbe\textsuperscript{44} studied the oxidation kinetics of n-C\textsubscript{7}H\textsubscript{16}/n-C\textsubscript{4}H\textsubscript{9}OH blends at two blend ratios (80%/20% and 50%/50% by volume) at a residence time of 0.7 s, over a wide temperature range (500−1100 K) and constant pressure (10 atm), in highly diluted mixtures with initial fuel concentrations of 750 ppm at two fuel-to-O\textsubscript{2} equivalence ratios (0.5 and 1). They observed that fuel consumption decreased as temperature was increased between 620 and 770 K, signifying the presence of an NTC region of n-C\textsubscript{7}H\textsubscript{16} oxidation, and that n-C\textsubscript{7}H\textsubscript{16} was consumed at temperatures much lower than it would be consumed without the presence of n-C\textsubscript{4}H\textsubscript{9}OH. The n-C\textsubscript{7}H\textsubscript{16} oxidation at low temperatures thus induced n-C\textsubscript{4}H\textsubscript{9}OH to react. Furthermore, the rates of consumption of each of the components reflected the blend ratio; when n-C\textsubscript{7}H\textsubscript{16} was present in concentrations four times higher than n-C\textsubscript{4}H\textsubscript{9}OH, the rate of n-C\textsubscript{7}H\textsubscript{16} consumption was four times higher than that of n-C\textsubscript{4}H\textsubscript{9}OH, whereas in equimolar mixtures of n-C\textsubscript{7}H\textsubscript{16} and n-C\textsubscript{4}H\textsubscript{9}OH, the two components were consumed at the same rate. Dagaut and Togbe\textsuperscript{44} produced two chemical kinetic mechanisms for the study, one detailed and one reduced, and found that the reduced mechanism, which omitted reactions that left ignition predictions unaffected, predicted fast formation of CO, CO\textsubscript{2}, and H\textsubscript{2}O above 800 K.

In the study by Saisirirat et al.\textsuperscript{43} similar measurements to the Dagaut and Togbe\textsuperscript{44} study were made (along with measurements of n-C\textsubscript{7}H\textsubscript{16}/n-C\textsubscript{4}H\textsubscript{9}OH blends in a homogeneous charge compression ignition engine) but at an equivalence ratio of 0.3 and a 50%/50% blend of n-C\textsubscript{7}H\textsubscript{16} and n-C\textsubscript{4}H\textsubscript{9}OH. The authors’ analyses, using a chemical kinetic mechanism generated by merging separate mechanisms for n-C\textsubscript{7}H\textsubscript{16}OH and n-C\textsubscript{4}H\textsubscript{9}OH,\textsuperscript{44,45} showed the presence of n-C\textsubscript{4}H\textsubscript{9}OH tempered the NTC behavior of n-C\textsubscript{7}H\textsubscript{16} because the overall rate of production of OH radicals that consumed fuel molecules decreased due to the presence of n-C\textsubscript{4}H\textsubscript{9}OH, and because the overall production of OH radicals itself decreased with the presence of n-C\textsubscript{4}H\textsubscript{9}OH.

The work presented in this article uses the unique features of the University of Michigan Rapid Compression Facility as a chemical reactor and builds on previous speciation work to present the first measurements of species time-histories of n-C\textsubscript{7}H\textsubscript{16}/n-C\textsubscript{4}H\textsubscript{9}OH blends under autoignition conditions. The goal of the work is to provide insights into changes in reaction pathways and product formation in the combustion of conventional, petroleum-based fuels when blended with oxygenated alternative fuels, using n-C\textsubscript{7}H\textsubscript{16} as an example of a conventional hydrocarbon fuel and n-C\textsubscript{4}H\textsubscript{9}OH as an example of a single-component biofuel.

2. EXPERIMENTAL SETUP

2.1. University of Michigan Rapid Compression Facility. The University of Michigan Rapid Compression Facility (UM RCF), as a unique and powerful chemical reactor, has allowed fuel chemistry studies over a broad range of thermodynamic conditions. Ignition studies of reference hydrocarbon compounds such as i-C\textsubscript{8}H\textsubscript{19},\textsuperscript{46,47} simulated syngas mixtures of hydrogen and carbon monoxide,\textsuperscript{48} and oxygenated hydrocarbons\textsuperscript{29} have been performed previously using the UM RCF, and the facility has also been used to study soot formation and morphology.\textsuperscript{50,51} The UM RCF has also been used to obtain time-resolved measurements of hydroxyl radical formation during the ignition of i-C\textsubscript{8}H\textsubscript{19}/air mixtures,\textsuperscript{22} as well as quantitative measurements of the intermediate species formed during the combustion of i-C\textsubscript{8}H\textsubscript{19},\textsuperscript{53} methyl butanoate,\textsuperscript{54} n-C\textsubscript{3}H\textsubscript{7}OH,\textsuperscript{34} and n-C\textsubscript{7}H\textsubscript{16},\textsuperscript{19} using rapid gas sampling and gas chromatography.

As described in detail previously,\textsuperscript{34} the UM RCF uses a free-piston/cylinder compression process to create the thermodynamic conditions necessary for combustion chemical kinetic studies, the features of which are interrogated using optical, pressure, and sampling measurements. The five major components of the UM RCF, seen in Figure 1, are the driver section, the driven section, the test section (or test manifold), the sabot (a free piston with a tapered nosecone), and the fast-
acting hydraulic globe valve system. For each experiment, preprepared fuel/oxidizer/diluent mixtures are filled into the evacuated driven section and compressed with the sabot using high pressure gas released by the globe valve from the driver section. At the end of compression (EOC), the nosecone of the sabot seals the fuel/oxidizer/diluent mixture in the test section through an interference fit at specifically targeted temperatures and pressures achieved by varying the compression ratio and the composition of the inert gases in the test gas mixture. The majority of the pressure and temperature increases due to compression occur in the last 10 ms of the 145 ms compression stroke. After EOC, the fuel/oxidizer/diluent mixture in the test section autoignites after a period of time that is designated the ignition delay time (τ_{ign}). Details on the uniformity of the temperature and pressure conditions created in the test section can be found in Karwat et al.34

This study builds upon two previous studies, the first being a study of the combustion chemistry of n-C7H1634 and the second being a similar study of n-C4H9OH.35 The two studies serve as references to understand how the combustion chemistry of n-C7H16 and n-C4H9OH blended together are similar or contrasting to their respective chemistries in isolation. For this study, stoichiometric n-C7H16/n-C4H9OH/O2 mixtures, with an inlet/O2 ratio of 5.64 (molar basis), were studied at two molar blend ratios: 80% n-C7H16 with 20% n-C4H9OH (80–20) and 50% n-C7H16 with 50% n-C4H9OH (50–50). Mixtures were prepared manometrically using high-purity compounds (n-C7H16, Sigma-Aldrich, puriss. p.a., ≥99.5%, GC grade; n-C4H9OH, Sigma-Aldrich, purum, >99% GC grade; O2, Cryogenic Gases, Purity Plus 4.3, 99.993%, <0.4 ppm Ar, <3 ppm moisture, <10 ppm N2, <0.5 ppm hydrocarbons; inert diluents, CO2, Cryogenic Gases, Laser grade, 99.995%, GC grade. The uncertainty in the sampling time is ±11 μs. The gas samples were taken from the core of the test section (beyond the cold thermal boundary layer). Furthermore, the sampling process had no effect on the ignition events in the test section, as τ_{ign} values determined from the gas-sampling experiments were in excellent agreement with experiments where gas sampling was not used. The reactive gases, when sampled, are quenched as they expand into the vacuum of the sample chamber (P_{sample} ≈ 11 Torr). The samples are then drawn into a syringe (Hamilton Gastight 1010) through the syringe port on the sampling chamber and then introduced into the gas chromatographs for analysis. Further details on the gas sampling system can be found in Karwat et al.34

The main contributors to the uncertainty of the gas sampling measurements include the dilution of the sample by unreacted gases trapped in the dead volume of the sampling system of the sampling probe (±16%, as determined previously34) and the gas chromatography calibration uncertainties for each species. The uncertainty in the sampling time is ±0.75 ms centered on the falling edge of the sampling pulse sent to the fast-acting valves. This uncertainty is determined from the pressure time histories of the sample volume and the falling edge of the trigger signal. The gas sampling results therefore represent the average value of the intermediate species present in the test section during the sampling time.

For the current experimental setup, end-view imaging cannot be conducted simultaneously with gas sampling through the end wall. An experiment to ensure no spatial bias to the gas sampling was performed by rotating the high-speed gas sampling system by 180° to acquire a sample from the southwest corner of the test section at almost the same time during the ignition delay period as a sample acquired from the northeast corner. The sample yielded species concentrations that were within measurement uncertainties (different for each species, as seen later) with the overall species time-histories.

Intermediate species formed during the ignition delay time were quantified using three gas chromatographs (GCs) equipped with four different columns, with each column connected to a separate detector. A temperature-controlled 10-
port gas sampling valve injected the samples into the columns in the GCs. Ultra-high purity helium (Cryogenic Gases, Purity Plus, 99.999%) was used as the carrier gas for all of the GCs. n-Heptane (n-C7H16), methanol (CH3OH), acetaldehyde (CH3CHO), and propionaldehyde (C3HCHO) were detected with a Perkin-Elmer Autosystem GC with a Varian CP-PoraBOND Q (25 m × 0.53 mm × 0.7 μm) column connected to a flame ionization detector (FID). The temperature program for this GC was 30 °C for 4.5 min → 45 °C/minute → 110 °C for 9 min → 45 °C/minute → 150 °C for 20 min. Methane (CH4), ethane (C2H6), propane (C3H8), propene (C3H6), 1-butene (1-C4H8), 1-pentene (1-C5H10), 1-hexene (1-C6H12), 1,3-butadiene (1,3-C4H6), and 3-heptene (3-C7H14) were detected with a Perkin-Elmer Autosystem GC with a Varian CP-Al2O3/Na2SO4 (25 m × 0.25 mm × 0.25 μm) column connected to an FID. The temperature program for this GC was 30 °C for 4 min → 25 °C/minute → 150 °C for 7 min → 45 °C/minute → 200 °C for 2 min. The third GC, a Perkin-Elmer Clarus 500, used an Agilent DB-Wax (30 m × 0.25 mm × 0.25 μm) column connected to an FID to detect 2-heptene (2-C7H14) and n-butyraldehyde (n-C4HCHO), and a Restek ShinCarbon ST packed (2 m × 1 mm, silica steel) column connected to a thermal conductivity detector (TCD) to detect carbon monoxide (CO). The temperature program for this GC was 25 °C for 5 min → 45 °C/minute → 200 °C for 5 min. The FIDs used a hydrogen/air flame, were maintained at 300 °C, and were set with a range and attenuation of 1. The TCD was maintained at 100 °C with an attenuation of 1 and current of ±160 mA. Further purification of the helium, air, and hydrogen was applied using adsorbents to remove water, hydrocarbons, and oxygen before use in the GCs. High-purity reference chemicals (either gaseous or vapors of liquid) were used to develop the GC temperature programs used in the study, and the chromatograms were used to establish the calibrations for absolute concentration. (See Table S1, Supporting Information, for a detailed list of calibration chemicals used.) Calibration mixtures were made in the magnetically stirred mixing tank with the upper limit of concentrations calibrated for greater than the lower limit of concentrations. Calibration curves were linear in all cases, except for n-C4H9OH, which showed nonlinearities and saturation at high concentrations. Only measurements later during the ignition delay time were considered for n-C4H9OH, to remain in the linear portion of the calibration curve. A data acquisition system (NI PXI 4472) recorded voltage signals from the GC detectors with a sampling rate of 8 Hz.

3. MODEL DESCRIPTION

Kinetic modeling calculations were carried out using CHEMKIN Release 10101 (x64). The detailed chemical kinetic mechanism for n-C7H16 was taken from an updated version of the mechanism described in Mehl et al. which was based on the original mechanism of Curran et al. The n-C7H16 portion of the kinetic mechanism was taken from the recent work of Sarathy et al. The core mechanism for hydrocarbons from C1 to C4 species was taken from a recently refined mechanism from Metcalfe et al. The resulting full mechanism was previously used to carry out modeling analysis of n-C7H16 autoignition. The kinetic mechanism includes the extensive submechanism that leads to the NTC behavior that is seen for n-C7H16 at temperatures from about 650 to 850 K. This reaction pathway is initiated by the addition of molecular oxygen O2 to heptyl radicals that are produced from the n-C7H16 fuel by H atom abstraction reactions:

\[
\text{n-C7H16 + OH} \leftrightarrow \text{C7H15} + \text{H2O} \quad (R1)
\]

\[
\text{C7H15 + O2} \leftrightarrow \text{C7H15O2} \quad (R2)
\]

followed by isomerization of the C7H15O2 species via internal H atom abstraction from within the C7H15O2 species and additional reactions at low temperatures. This sequence of reactions ultimately produces two or more OH radicals, as well as other radical species, along with a modest amount of heat. The reaction sequence ceases when gas temperature reaches a level where the dissociation of the heptylperoxy radicals, the reverse of reaction R2, becomes faster than the same reaction in the addition direction. The reaction sequence produces the first stage ignition that will be seen below in Figures 2 through 5.

In contrast, although low temperature radical isomerization reaction pathways are included in the n-C7H16OH oxidation mechanism, n-C7H16OH exhibits little or no NTC behavior under the present conditions. As a result, in the kinetic model calculations described below, OH radicals are consumed by H atom abstraction reactions with n-C7H16OH

\[
\text{n-C4H9OH + OH} \leftrightarrow \text{C4H8} + \text{H2O} \quad (R3)
\]

where C4H9OH refers to any of the five radicals that can be produced by H atom abstraction from n-C7H16OH. Molecular O2 can add to all of these radicals via reactions analogous to reaction R2 above, but because of the highly strained transition state rings involved, little isomerization occurs, and there is only a minor amount of low-temperature reaction or heat release from n-C7H16OH reactions via the reaction pathways that are so productive in the oxidation of n-C7H16. The small amounts of low-temperature reactivity are insufficient to replace the OH radicals that are consumed in reaction R3, so the net effect of the addition of n-C7H16OH to n-C7H16 is to reduce the levels of...
OH and therefore reduce the levels of consumption of \( n-C_7H_{16} \) compared to \( n-C_6H_{14} \) alone, as observed below.

Somewhat in contrast with the effects of \( n-C_7H_{18} \) OH inhibiting ignition of \( n-C_8H_{18} \) in the NTC region, the presence of \( n-C_7H_{16} \) clearly sensitizes the ignition of \( n-C_7H_{18} \) in the NTC region. At temperatures from about 650 to 850 K, \( n-C_7H_{18} \) as the sole fuel is distinctly unreactive under most conditions, but when some \( n-C_7H_{16} \) is added to the \( n-C_7H_{18} \) fuel at these low temperatures, the high reactivity of \( n-C_7H_{18} \) contributes a sufficiently large amount of OH and other radical species that makes \( n-C_7H_{18} \) oxidation proceed at a rate similar to that of the \( n-C_7H_{16} \) also observed in the present study.

The interactions between \( n-C_7H_{16} \) and \( n-C_7H_{18} \) OH are very similar to those between the gasoline primary reference fuels \( n-C_7H_{16} \) and \( i-C_8H_{18} \). In the low temperature regime, \( i-C_8H_{18} \) reduces the reactivity of \( n-C_7H_{16} \) and delays its ignition, while the addition of \( n-C_7H_{16} \) increases the low temperature reactivity of \( i-C_8H_{18} \) at temperatures where \( i-C_8H_{18} \) is not ordinarily reactive at all. The high octane fuels \( (i-C_8H_{18} \text{ RON} = 100; n-C_7H_{18} \text{ OH RON} = 96) \) produce very little low temperature 

In the course of the present project, portions of the kinetic mechanism for \( n-C_7H_{16} \) were found to be insufficient to describe the present experimental results. The \( n-C_7H_{16} \) mechanism had been developed primarily on the basis of integrated system experiments such as ignition delay times in shock tubes and rapid compression machines and laminar flame speed measurements, with very few species-specific measurements to provide especially demanding validation tests. The new speciation measurements provided by the present experiments (and similar experiments using only \( n-C_7H_{16} \)) provide new and more challenging sets of validation data, and further refinements for the \( n-C_7H_{16} \) mechanism will be needed in response to these new experiments.

4. RESULTS AND DISCUSSION

4.1. Ignition Experiments and Modeling. Ignition experiments were conducted to understand the dependence of ignition delay time \( t_{\text{ign}} \) on blend ratio at a fixed temperature (700 K) and pressure (9 atm). A study of \( n-C_7H_{16} \) chemical kinetics provided baseline \( t_{\text{ign}} \) data against which the influence of the presence of \( n-C_7H_{18} \) OH was compared. It was expected that increasing the amount of \( n-C_7H_{18} \) OH would increase the ignition delay time, given the much greater low-temperature reactivity of \( n-C_7H_{18} \). Since in the baseline study the chemical kinetics of \( n-C_7H_{16} \) were studied at a temperature of 700 K and a pressure of 9 atm, yielding a \( t_{\text{ign}} \) on the order of 15 ms, the presence of \( n-C_7H_{18} \) OH would allow for several discrete sampling events (each lasting 1.5 ms, as described earlier) during the ignition delay period.

For each experiment, the effective test conditions are determined based on the pressure time-history from each experiment. Examples are provided in Figures 2 and 3. Since

![Figure 3. Results from a typical UM RCF 50–50 ignition experiment. The lower panel depicts the pressure time-history in the test section and the rate of pressure rise. The upper panel shows still images taken at 30 000 fps via end-view imaging. The color of the images has been adjusted for clarity.](image-url)
Figure 2 presents typical results from a UM RCF ignition experiment for the 80–20 blend for which imaging data were acquired. The lower panel depicts the time-histories of the pressure and rate of pressure rise in the test section. A fast Fourier transform has been applied to filter high frequency disturbances greater than 2.5 kHz generated by the impact of the sabot near EOC. The motion of the sabot compresses the test gas mixture into the test section to the first maximum. The EOC time is set to time \( t = 0 \), after which the volume in the test section is constant. The first stage of ignition occurs at \( \tau_{\text{fi}} = 12.37 \) ms, corresponding to a local maximum in \( \frac{dP}{dt} \) (circled in the lower panel of Figure 2). The pressure time-history from EOC to \( \tau_{\text{fi}} \) defines \( P_{\text{eff}} \) and \( T_{\text{eff}} \) as 9.05 atm and 703 K, respectively. After another time interval, the pressure rises abruptly again to its maximum value. The second pressure rise corresponds to autoignition of the test mixture at 19.70 ms.

The upper panel of Figure 2 shows stills from the image sequence corresponding to the pressure data of the lower panel. Intense chemiluminescence occurs only during the second stage of ignition. The chemiluminescence is attributed to CH and \( \text{C}_2 \) radicals, which have strong spectroscopic features in the blue part of the visible spectrum (CH, 431.2 nm; \( \text{C}_2 \), 473.7, 516.5, and 563.5 nm) and are generated only through the decomposition of intermediate hydrocarbons present in the test mixture. Note the uniformity of the blue emission throughout the test section, attesting to the homogeneity of the reactant mixture and the state conditions in the test section. Such uniformity gives confidence in localized sampling.

Figure 3 shows similar imaging and pressure data for a 50–50 blend. The general features of the pressure time-history are the same as observed for the 80–20 blend. However, both \( \tau_{\text{fi}} \) and \( \tau_{\text{fi}} \) increase to 21.77 and 32.39 ms, respectively, compared to 12.37 and 19.70 ms for the 80–20 blend.

As is seen in Figures 2 and 3, the addition of \( n\text{-C}_4\text{H}_9\text{OH} \) slows the ignition process. A clearer representation of the influence of \( n\text{-C}_4\text{H}_9\text{OH} \) can be seen in Figure 4, which compares the pressure time-histories obtained experimentally for the blends with the baseline (100–0) case. Also shown in Figure 4 are zero-dimensional, constant volume, adiabatic CHEMKIN simulations, using the blend reaction mechanism described earlier, of the ignition delay times for the 80–20 and 50–50 experiments. The initial pressure and temperature conditions used in the simulations corresponded to the effective pressure and temperature conditions obtained experimentally. As described previously, the effective pressure and temperature definitions adequately account for the heat transfer physics occurring in the test section of the UM RCF during the time interval leading to the first stage ignition. As the amount of \( n\text{-C}_4\text{H}_9\text{OH} \) increases in the blend, the differences between the model predictions and the experimental results increase. While experiments show that \( \tau_{\text{fi}} \) and \( \tau_{\text{fi}} \) increase by a factor of approximately three from the 100–0 to the 50–50 case, the model predicts an increase by a smaller factor of approximately two (see also Table 1). Also, it is observed experimentally that the rise in pressure during the first stage of ignition decreases with increasing concentrations of \( n\text{-C}_4\text{H}_9\text{OH} \). This is not the case with the model predictions, for even though the heat release of the first stage of ignition occurs over a slightly longer period of time with increasing concentrations of \( n\text{-C}_4\text{H}_9\text{OH} \), the computed pressure reached at the end of the first stage of ignition is nearly the same for the 100–0, 80–20, and 50–50 conditions, and the calculated pressure increase is consistently greater than the pressure rise measured experimentally.

In order to understand why ignition slows as the blend ratio increases and to compare important features of the pressure time-histories, the ignition times were normalized, and the results are presented in Figure 5. Specifically, the period of time between EOC and the first stage of ignition of each experiment was normalized by \( \tau_{\text{fi}} \) (resulting in a normalized time domain of 0 to 1), and the period of time between the first stage of ignition and autoignition (\( \tau_{\text{auto}} \)– \( \tau_{\text{fi}} \)) was normalized by \( \tau_{\text{fi}} \) and \( \tau_{\text{fi}} \) added to the first normalized time domain, so the ignition delay between the first and second stages of ignition takes place over a normalized time interval from 1 to 2.

The experimental data show that as the amount of \( n\text{-C}_4\text{H}_9\text{OH} \) in the blend increases, the first stage of ignition becomes less pronounced, indicating the amount of heat released and the pressure rise during the first stage ignition become smaller. The model simulations, also shown in Figure 5, differ from the experimental data in several ways. The predicted pressure rise in the first stage of ignition is larger than observed experimentally. The predicted rate of pressure rise at the second stage of ignition is much larger than observed experimentally. The predicted changes in the relative time between the first and second stages of ignition are unchanged for the blends, whereas the experimental data exhibit an increase in the relative time between the first and second stages of ignition with increasing amount of \( n\text{-C}_4\text{H}_9\text{OH} \).

The effects described above can be interpreted based on an understanding of the \( n\text{-C}_4\text{H}_9\text{OH} \) ignition chemistry. The main stage of autoignition occurs at approximately 900–1000 K with the decomposition of \( \text{H}_2\text{O}_2 \) which accumulates during chemical reactions at low temperatures. When the reactive mixture reaches this temperature, \( \text{H}_2\text{O}_2 \) decomposition releases a large amount of highly reactive OH radicals, and ignition occurs. Different fuels or fuel mixtures reach this \( \text{H}_2\text{O}_2 \) decomposition temperature and ignite at different times, depending on the amount of heat release and temperature increase they experience during the first stage, low temperature ignition.
heat release being approximately proportional to the ratio of n-C7H16 to n-C4H9OH. The decreasing amount of heat release with increasing blend fraction of n-C4H9OH reduces the temperature of the reactive mixture at the end of the first stage of ignition and therefore lengthens the time for the reactive mixture to reach H2O2 decomposition temperatures, thus lengthening $\tau_{\text{ign}}$. The other dominant products of the low temperature, first stage of ignition are highly reactive OH radicals that then react with all of the fuel components. Fuels that are highly reactive at low temperatures, such as n-C7H16 produce large amounts of OH, while fuels that have little low temperature reactivity produce little OH under the same conditions. The presence of n-C4H9OH in the fuel blend therefore reduces the levels of OH in the reactive mixture because there is less n-C7H16 in the reactive mixture, while the n-C4H9OH removes OH from the reactive mixture without producing new OH radicals.

Recent work by Saisirirat et al.43 reflects similar trends. In that work, the authors studied n-C7H16/n-C4H9OH blends in a homogeneous charge compression ignition engine and found that the presence of n-C4H9OH both reduced the amount of low temperature, cool flame behavior and retarded autoignition and phasing. They concluded that, since the fuel mixtures were oxidized primarily by OH radicals formed from decomposition of alkylperoxy and ketoperoxy radicals, the presence of n-C4H9OH, which decreased the rate of production of OH radicals, slowed overall reactivity.

We thus observe computationally from Table 1 and Figure 6 a nonlinear increase in $\tau_1$ and $\tau_{\text{ign}}$ as the amount of n-C4H9OH increases in the blend ratio, seen especially when the amount of n-C4H9OH in the mixture is greater than 50%. While the model adequately captures the increase in $\tau_1$ and $\tau_{\text{ign}}$ as a function of blend ratio, the model predicts slightly smaller increases than observed experimentally. Shown also in Figure 6 with the thinner lines are modeling results using the Saisirirat et al.43 mechanism, which predicts faster $\tau_1$ and $\tau_{\text{ign}}$ compared to the current mechanism as long as n-C7H16 is present in the mixture. The Saisirirat et al.43 mechanism is explored in greater detail below.

It is clear that n-C7H16 reacts much more quickly than n-C4H9OH; at a temperature of 700 K and a pressure of 9 atm, n-C7H16 reacts almost an order of magnitude faster than n-C4H9OH. However, when n-C7H16 is blended with n-C4H9OH the low-temperature reactivity of n-C7H16 forms a radical pool that stimulates n-C4H9OH to react at temperatures where it normally would not react. These results are similar to the results observed in the JSR study by Dagaut and Togbé,44 who measured the consumption of n-C4H9OH in the presence of n-C7H16, at NTC conditions, again, conditions where n-C4H9OH would not normally react. Furthermore, the amount of n-C4H9OH consumed was proportional to the amount of it present in the blend. For example, in an 80–20 molar blend, when the concentration of n-C7H16 was four times higher than that of n-C4H9OH, four times more n-C7H16 was consumed than n-C4H9OH.

The influence of n-C4H9OH on the chemical kinetics of blends is complicated and nuanced. In order to show the influence of the presence of n-C4H9OH, simulations were performed in which the n-C4H9OH was removed from the blends, thus leaving lean reactive mixtures of only n-C7H16. The simulation results are shown in Figure 4 as the 80–0 ($\phi = 0.88$, dark cyan dashed line) and 50–0 ($\phi = 0.64$, pink dashed line) mixtures. The $\tau_1$ values for these mixtures are approximately the same, while the $\tau_{\text{ign}}$ values increase with decreasing
concentrations of n-C7H16. Interestingly, when compared to the respective 80–20 and 50–50 blends, the model predicts that n-C7H16OH not only lengthens $\tau_1$ but also shortens $\tau_{inert}$ compared to the respective 80–0 and 50–0 cases when n-C7H16OH is not present in the mixture; this can be attributed to the fact that the 80–0 and 50–0 mixtures are fuel lean.

As noted earlier, such changes in ignition behavior can arise due to the less reactive component of the fuel consuming radicals that would otherwise act on the more reactive fuel and its fuel fragments. Mehl et al.20 and Vanhove et al.60 in their studies of binary blends of n-C7H16 and toluene have discussed at length the radical scavenging properties of a compound like toluene that reacts on much longer time scales than n-C7H16. Like n-C4H9OH, toluene is a single stage fuel, and easily abstractable H-atoms on the methyl group of toluene act as a radical scavenger, suppressing the reactivity of the system. Just as has been observed experimentally in this work, when n-C7H16 was mixed with toluene to create a 50–50 blend, Mehl et al.20 observed that the two-stage behavior was maintained, with the first stage and second stages of ignition being lengthened, and a lower amount of heat released during the first stage of ignition. From their chemical kinetic mechanism, they observed that lower concentrations of H2O2 were produced by the first stage of ignition. The reduced amount of heat released by the 50–50 blend served to lengthen the time delay until the second stage ignition, just as noted above for the n-C7H16/n-C4H9OH fuel blends. Vanhove et al.60 make similar conclusions, but note that the effect of the presence of a slowly reacting compound like toluene is more significant on other slowly reacting compounds, such as iso-C4H9OH, given that toluene actually increases the activation energy of iso-octane ignition. In the case of toluene being blended with n-C7H16, the mixture reactivity is still driven by n-C7H16.

An early study of a similar nonlinear interaction of ignition of mixtures of two such different fuels was reported by Westbrook for shock tube ignition of mixtures of methane and ethane.61 Ethane is the highly reactive fuel, while methane is much less reactive. At a postshock temperature of 1500 K, stoichiometric ethane/O2/Ar mixtures were predicted to ignite at 16 $\mu$s, andstoichiometric methane/O2/Ar mixtures were calculated to ignite at 270 $\mu$s. Stoichiometric mixtures of 95% methane + 5% ethane with O2 and Ar ignited at 155 $\mu$s; the replacement of only 5% of the methane by ethane reduced the ignition delay by nearly 50% of the difference in the individual ignition delay times. From the opposite direction, the addition of methane to ethane, starting at 100% ethane, increased the ignition delay time very slowly until the mixtures were about 60% methane, and further replacement of ethane by methane rapidly increased the computed ignition delay time, producing an ignition delay curve very similar to that in Figure 6 for mixtures of n-C7H16 and n-C4H9OH. Conversely, the addition of the more reactive component, n-C7H16 in the present case, rapidly lowers the ignition delay time for a small amount of n-C7H16 additive, just as was reported for the addition of small amounts of ethane to methane.61 This sensitization of the less reactive mixture by small amounts of the more reactive component is quite familiar in combustion kinetics.

4.2. High-Speed Gas Sampling Experiments. While the ignition studies provide an understanding of the global kinetics of ignition of n-C7H16 and n-C4H9OH blends, speciation measurements provide more detailed understanding of the dominant chemical pathways in the reacting test gas mixture. Sampling experiments were performed to identify intermediates formed during the ignition delay time. Figure 7 presents results from a typical sampling experiment for an 80–20 blend in which $P_{eff} = 9.1$ atm, $T_{eff} = 703$ K, $\tau_1 = 11.98$ ms, and $\tau_{inert} = 18.44$ ms. Shown are the pressure and pressure derivative time-histories in the test section, the sampling pulse used to trigger the high-speed gas sampling system, and the pressure in the sampling chamber. Since only a very small amount of sample is removed from the reacting mixture in the test section, the pressure in the test section remains unaffected by the sampling process. All the general features seen in Figure 2, which depicts an ignition experiment without sampling, are identical to those seen in Figure 7. As indicated by the pressure rise in the sampling volume, the sample is collected within 2 ms after the falling edge of the trigger signal.

Also shown in Figure 7 is the time-history of a nonigniting experiment, in which the O2 of an igniting mixture is replaced by N2. The almost identical thermal characteristics of O2 and N2 permit direct comparison of the pressure time-histories. As seen in Figure 7, the bulk of the compression process in the UM RCF occurs during the last ten ms before EOC. There is always concern about possible reaction of the test gas mixture during compression, which affects the assumptions used to define the effective thermodynamic conditions (eqs 1 and 2) of the experiment. The nonigniting experiment, however, shows a nearly identical compression process to the igniting experiment and is almost indistinguishable from the igniting experiment ($P_{eff}$ and $T_{eff}$ differ by less 0.3% and 0.1%, respectively) until the first stage of ignition. As will be seen later, even though intermediate species are observed between EOC and the first stage of ignition, signaling the decomposition of small amounts of n-C7H16, the extent of reaction is small, and the use of effective pressure and temperature definitions remains valid. Furthermore, the heat transfer physics of the experiments remain unaffected by the sampling events. Similar results are observed for the sampling experiments of 50–50 blends. Details on all of the gas sampling experiments, including mixture compositions, can be found in Table S2, Supporting Information.
The left panels of Figures 8 and 9 show the pressure time-histories for the sampling experiments for the 80−20 and 50−50 blends, respectively. All of the experiments showed nearly identical compression processes and very similar pressure time-histories after EOC. The experiments showed excellent repeatability; for the 80−20 blend, the average $P_{eff}$, $T_{eff}$, $\tau_{1}$, and $\tau_{ign}$ were 8.98 atm, 700 K, 13.45 ms, and 20.86 ms, respectively, with the corresponding standard deviations of 0.19 atm, 3.2 K, 1.51 ms, and 1.62 ms, respectively. For the 50−50 blend, the average $P_{eff}$, $T_{eff}$, $\tau_{1}$, and $\tau_{ign}$ were 9.06 atm, 701 K, 23.16 ms, and 35.16 ms, respectively, with the corresponding standard deviations being 0.06 atm, 1.3 K, 1.11 ms, and 0.98 ms, respectively. The slight differences that exist between experiments are attributed to the small variations in effective temperatures and pressures, and in mixture preparation. The temporal error bars on the speciation results represent only the uncertainty introduced by the sampling valve system and not by the statistical variation in ignition delay, which would increase the error bars in the time domain by about 5%. To compensate for the differences that remain in the sampling data, the pressure time-histories are plotted using a time domain normalized by the first stage of ignition and the second stage of ignition, as described earlier. These results can be seen in the right panels of Figures 8 and 9 for the 80−20 and 50−50 blends, respectively. The normalized pressure time-histories are virtually identical.

Figure 10 provides an example of the chromatograms obtained from the sampling experiment depicted in Figure 7. The data are for the experiment depicted in Figure 7, which was an 80−20 blend experiment with a normalized sampling time of 1.69.

Figure 8. Left panel depicts the unnormalized experimental pressure time-histories of the sampling experiments for the 80−20 blend. Note the level of repeatability of the compression process, as well as of the first and second stages of ignition and heat release. Right panel presents the normalized data where 0 represents EOC, 1 represents the first stage of ignition, and 2 represents the second stage of ignition. Shown also are the normalized times when samples were taken from the test section.

Figure 9. Left panel depicts the unnormalized experimental pressure time-histories of the sampling experiments for the 50−50 blend. Right panel presents the normalized data where 0 represents EOC, 1 represents the first stage of ignition, and 2 represents the second stage of ignition. Shown also are the normalized times when samples were taken from the test section.

Figure 10. Typical gas chromatograms obtained from the three gas chromatographs. The data are for the experiment depicted in Figure 7, which was an 80−20 blend experiment with a normalized sampling time of 1.69.

The species identified from the GC data. Although several peaks remained unidentified, for the 80−20 blend, the carbon balance for the species measured was 82 ± 14% for sampling at early times during the ignition delay period and 60 ± 10% for sampling closer to autoignition. The carbon balances were 72 ± 15% and 60 ± 10%, respectively, for the 50−50 blend. Using the calibrations for each species, the peaks were converted into
discrete measurements of intermediate species for each normalized sampling time. It is worth noting that the total amounts of carbon and oxygen in the system change very little as a function of blend ratio: for the 100−0 case, χ(C) = 0.09401 and χ(O) = 0.2980; for the 80−20 case, χ(C) = 0.09455 and χ(O) = 0.3003; for the 50−50 case, χ(C) = 0.09526 and χ(O) = 0.3054.

Radicals such as O, H, OH, and CH₃ can recombine when gases from the test section are sampled and quenched, potentially forming water vapor and small hydrocarbons that can interfere with species measurements by changing concentrations. However, predicted radical concentrations, presented in Figure 11, are very low (<40 ppm) until very close to autoignition. Radicals are thus not expected to be a source of error in the species concentration measurements presented in this work.

Figure 11. Small radical concentration predictions using the current mechanism at T₀ = 700 K, P₀ = 9 atm, ϕ = 1, at a dilution of ~5.64.

Figure 12. Experimental n-C₇H₁₆ concentration time-histories for stoichiometric 100−0 (black circles), 80−20 (green squares), and 50−50 (red triangles) blends obtained from the UM RCF at nominal conditions of 700 K and 9 atm. Also shown with lines are zero-dimensional, constant volume, adiabatic mechanism predictions using the current mechanism (100−0, thick solid black; 80−20, thick dashed green; 50−50, thick red dotted) and the Saisirirat et al.⁴³ mechanism (100−0, thin solid blue; 80−20, thin dashed purple; 50−50, thin dotted gold).

results for 100−0 (black circles) from Karvat et al.¹⁹ serving as a comparative baseline. The average experimental conditions for the 100−0 results are Pₑff = 9.02 atm, Tₑff = 701 K, χ(n-C₇H₁₆) = 0.0134, χ(O) = 0.1490, χ(N₂) = 0.2336, and χ(CO₂) = 0.6040, resulting in τ₁ = 7.94 ms and τₑff = 14.09 ms with standard deviations of 0.52 and 0.63 ms, respectively, for the first and overall stages of ignition. The nominal conditions and ignition data for the 80−20 sampling experiments were reported above and were for an average mixture composition of χ(n-C₇H₁₆) = 0.0118, χ(n-C₆H₁₀OH) = 0.0029, χ(O) = 0.1487, χ(N₂) = 0.2417, and χ(CO₂) = 0.5949. The nominal conditions and ignition data for the 50−50 sampling experiments were also reported above and were for an average mixture composition of χ(n-C₇H₁₆) = 0.0087, χ(n-C₆H₁₀OH) = 0.0087, χ(O) = 0.1484, χ(N₂) = 0.2580, and χ(CO₂) = 0.5762. The species concentrations are plotted as a function of normalized time in which 0 represents EOC, 1 represents the first stage of ignition, and 2 represents overall ignition. Measured concentrations for all species except n-C₇H₁₆ and n-C₆H₁₀OH are plotted in two ways, each providing different information on the chemical kinetics of the mixtures. On the left-hand side, the data are plotted as absolute units of mole fraction, and on the right-hand side, the data are normalized by the initial amount of n-C₇H₁₆ in the mixtures. Plotted with solid black lines, dashed green lines, and dotted red lines are the corresponding zero-dimensional, constant volume, adiabatic, mechanism predictions for the average experimental conditions of the 100−0, 80−20, and 50−50 cases, respectively. The ignition results for these simulations are also included in Table 1.

The mechanism predictions agree well with the experimental data for some species and not for others. For all intermediate species, the model predicts an abrupt production at the first stage of ignition. While concentrations were measured to be nonzero near the time of the first stage of ignition for many species, the abruptness of the rise in concentrations was not observed experimentally. This is due at least in part to the finite amount of time required for the gas sampling valves to open and shut.

Figure 12 shows the data for n-C₇H₁₆ as a function of time. Within experimental uncertainties, each of the blend mixtures results in 30−40% of the initial n-C₇H₁₆ consumed during the first stage of ignition, which is approximately a factor of 2 less than the amount predicted computationally. (Model predictions using the Saisirirat et al.⁴³ mechanism, plotted in Figure 12, also show significant consumption at the first stage of ignition. These results will be discussed below.) The experimental and modeling results are self-consistent in that heat released during the first stage of ignition is attributed to n-C₇H₁₆ consumption (caused mainly due to n-C₇H₁₆ + OH to form n-C₆H₁₅ and water). Consequently, since the experiments indicate lower n-C₇H₁₆ consumption during the first stage of ignition, there is lower heat release during the first stage of ignition, and hence, the time from first stage to autoignition increases. The converse is true of the model predictions, where more n-C₇H₁₆ is consumed during the first stage, yielding higher heat release and less time from first stage to autoignition. Many of the differences between the computationally predicted and experimentally measured intermediate species are due in part to the differences in consumption of n-C₆H₁₅ at the first stage of ignition.

Since n-C₆H₁₀OH reacts only because of the presence of n-C₇H₁₆ at a temperature of 700 K and a pressure of 9 atm, it follows that the amount of n-C₆H₁₀OH consumed is at some level proportional to the concentration of n-C₇H₁₆ consumed. Figure 13 shows these trends for n-C₆H₁₀OH, computationally. The experimental and modeling results are in fairly good agreement, particularly at later times.

Also shown in Table 1 and Figures 6, 12, and 13 are predictions using the Saisirirat et al.⁴⁸ mechanism. As observed in Table 1 and Figure 6, while the Saisirirat et al.⁴⁸ mechanism predicts slower first stages of ignition for the 100−0 and 80−20
blends, the autoignition predictions are in very good agreement (within 10–20%) with each other for cases in which \( n-\text{C}_7\text{H}_{16} \) is present in the mixture. However, key differences are observed in Figures 12 and 13, which predict greater consumption of both \( n-\text{C}_7\text{H}_{16} \) and \( n-\text{C}_4\text{H}_{9}\text{OH} \) at the first stage of ignition.

Figures 14–16 show measurements and predictions for \( \text{CH}_4 \), \( \text{C}_2\text{H}_6 \), and \( \text{C}_2\text{H}_4 \), respectively. The left-hand side (LHS) of Figure 14 compares the experimental and modeling data for the blends on an absolute basis. The current mechanism predicts slightly higher values for \( \text{CH}_4 \) compared to the experimental data. When the data are normalized by the initial amount of \( n-\text{C}_7\text{H}_{16} \) present, as seen on the right-hand side (RHS) of Figure 14, it is evident that the model predictions are a function of the amount of \( n-\text{C}_7\text{H}_{16} \) in the system. Figure 15 shows that model predictions for \( \text{C}_3\text{H}_8 \) agree well with experimental results (within less than a factor of 2) and that the rate of production of \( \text{C}_3\text{H}_8 \) slows as the amount of \( n-\text{C}_4\text{H}_{9}\text{OH} \) increases. \( \text{C}_3\text{H}_8 \) concentrations are predicted within a factor of 2 to 3 of the experimental results, as seen on the LHS of Figure 16.

Figure 16. Experimental \( \text{C}_4\text{H}_8 \) time-histories for stoichiometric 0–100, 80–20, and 50–50 blends. Also shown are predictions using the current mechanism. Experimental and simulation conditions and symbol and line details are the same as those in Figure 12.

Figure 17. Experimental \( \text{C}_3\text{H}_8 \) time-histories for stoichiometric 0–100, 80–20, and 50–50 blends. Also shown are predictions using the current mechanism. Experimental and simulation conditions and symbol and line details are the same as those in Figure 12.

Figure 18. Experimental \( \text{C}_3\text{H}_6 \) time-histories for stoichiometric 0–100, 80–20, and 50–50 blends. Also shown are predictions using the current mechanism, as well as mechanism predictions where the \( n-\text{C}_4\text{H}_{9}\text{OH} \) has been removed from the initial reactant mixture (i.e., 80–20 \( \rightarrow \) 80–0 [thin dashed dark cyan lines] and 50–50 \( \rightarrow \) 50–0 [thin dotted pink lines]). Experimental and simulation conditions and other symbol and line details are the same as those in Figure 12.

The model does predict slower formation of \( \text{C}_3\text{H}_8 \) with increasing \( n-\text{C}_4\text{H}_{9}\text{OH} \), \( \text{C}_3\text{H}_8 \) was not observed in the experiments until much later for the 80–20 and 50–50 cases. The LHS of Figure 18 shows that while \( n-\text{C}_4\text{H}_{9}\text{OH} \) decreases the amount of \( \text{C}_3\text{H}_8 \) predicted on an absolute basis, \( \text{C}_3\text{H}_8 \) concentrations are predicted to increase on a per \( n-\text{C}_7\text{H}_{16} \) basis.
It is observed experimentally that C$_4$H$_8$ concentrations do indeed decrease with the addition of n-C$_7$H$_{16}$ on an absolute basis, although the normalized experimental data do not show an increase in C$_4$H$_8$ relative to the initial amount of n-C$_7$H$_{16}$. The influence of n-C$_7$H$_{16}$ on C$_4$H$_8$ is clearer when comparing the 80–20 to the 80–0 predictions and the 50–50 to the 50–0 predictions, also presented in Figure 18. It is seen on the LHS of Figure 18 that n-C$_7$H$_{16}$ not only slows the formation of C$_4$H$_8$, but also slows its consumption, thereby causing an accumulation of C$_4$H$_8$. At the same time, the model predicts that C$_4$H$_8$ production is enhanced relative to the amount of n-C$_7$H$_{16}$ in the system.

Figure 19, which shows 1-C$_4$H$_8$ measurements and predictions, shows similar trends to C$_4$H$_8$. Although there are larger differences between the experimental and modeling results, the data show that production of 1-C$_4$H$_8$ on an absolute basis decreases with the addition of n-C$_7$H$_{16}$. While it is evident that n-C$_7$H$_{16}$ is the source of 1-C$_4$H$_8$ as seen in Figure 19 on the RHS, the 1-C$_3$H$_6$ data do not show an enhancement with the addition of n-C$_7$H$_{16}$ like C$_4$H$_8$ does. (The 0–100 simulation, the ignition results of which are shown in Table 1, shows a maximum concentration of less than 200 ppm of 1-C$_4$H$_8$ right before ignition, indicating that n-C$_7$H$_{16}$ contributes very little to 1-C$_4$H$_8$ production during the ignition delay period.) The 1,3-C$_3$H$_6$ data, seen in Figure 20, are in good agreement with model predictions, and both experimental and modeling results show that the presence of n-C$_7$H$_{16}$ suppresses 1,3-C$_3$H$_6$ formation.

Experimental and computational results for CH$_3$CHO are presented in Figure 21. As seen on the LHS, while the model predicts very little change in the concentration between the 100–0, 80–20, and 50–50 cases, experimental results point to a decrease in concentrations with increasing blend ratio. By comparison with the 50–0 and 80–0 simulations, the mechanism indicates the decrease in production of CH$_3$CHO due to decreasing amounts of n-C$_7$H$_{16}$ offset by increasing CH$_3$CHO production through n-C$_7$H$_{16}$ oxidation. The modeling results on the RHS of Figure 21 indicate an enhancement effect for increasing n-C$_7$H$_{16}$ in the reaction mixture. However, the experimental data indicate that the total amount of carbon in the system dictates the concentration of CH$_3$CHO and that n-C$_7$H$_{16}$ does not enhance CH$_3$CHO production.

It is evident from the experimental results presented in Figure 22 that there is early formation of CH$_3$OH, prior to the first stage of ignition. The model predicts a decrease in CH$_3$OH, also seen experimentally, as the n-C$_7$H$_{16}$ blend ratio increases. Both the experimental data and the model results in the RHS of Figure 22 show that CH$_3$OH is formed primarily from n-C$_7$H$_{16}$.

Although the formation of n-C$_7$H$_{16}$-CHO is one of the key decomposition pathways of n-C$_7$H$_{16}$,$^{34}$ the kinetic model shows that most of its production in these experiments at 700 K comes from the low temperature oxidation of the n-C$_7$H$_{16}$ via reactions of three different heptyl ketohydroperoxide species and a heptyl-hydroperoxide species. As is seen in Figure 23, n-C$_3$H$_3$CHO is formed earlier during the ignition delay period.
when $n$-C$_4$H$_9$OH is present in the reacting mixture. It is clear, experimentally as well as computationally, that the presence of $n$-C$_4$H$_9$OH increases $n$-C$_3$H$_7$CHO formation, as the 50−0 and 80−0 simulations show that $n$-C$_3$H$_7$CHO concentrations decrease compared to the 50−50 and 80−20 simulations. However, the model overpredicts $n$-C$_3$H$_7$CHO concentrations by an order of magnitude compared to the experimental data and indicates much larger increases in $n$-C$_3$H$_7$CHO with $n$-C$_4$H$_9$OH addition to the mixtures. Relative confidence in the reaction pathways for $n$-C$_4$H$_9$OH$^+$ and uncertainties in the low temperature $n$-C$_4$H$_8$ reaction pathways and rates indicate that the current model seriously overpredicts production of $n$-C$_3$H$_7$CHO and that further analysis is needed.

Experimental results presented in Figure 24 show that CO is produced at a slower rate when $n$-C$_4$H$_9$OH is present in the mixture. The model predicts a higher rate of production than observed experimentally; however, there is good agreement between the experimental and modeling data at later times during ignition. For CO and other species that are strongly correlated with the initial $n$-C$_4$H$_9$ present in the mixture, the higher values observed from the model predictions compared to the experimental data are likely a direct result of the higher consumption rate predicted by the model for $n$-C$_4$H$_9$. As with $n$-C$_4$H$_9$ consumption, the model predicts only slight differences in CO as a function of $n$-C$_4$H$_9$OH.

Speciation results of smaller hydrocarbons do not provide a full understanding of how kinetics are changed with fuel blends. Indeed, the size of chemical kinetic mechanisms and the multiple and interrelated production and consumption channels of small hydrocarbons such as CH$_4$ and C$_2$H$_4$ (regardless of parent fuel) make it difficult to understand how mechanisms might be revised to more accurately represent experimental data. However, some intermediate species are only produced by one component of the fuel blend. These species, discussed below, shed light on how branching fractions from the parent fuel change, how global activation energies change, and how particular chemical pathways are enhanced or suppressed.

Figures 25 and 26 show experimental measurements and computational predictions of the two smallest alkenes larger than are expected to be produced through $n$-C$_3$H$_7$OH oxidation. In Figure 25, 1-C$_5$H$_{10}$ concentrations decrease when less $n$-C$_6$H$_{12}$ is present in the fuel mixture, as expected. The model predicts higher 1-C$_5$H$_{10}$ concentrations than the experimental data by a factor of 2 to three for all cases. As seen in the computational results on the LHS of Figure 25, comparison between the 50−0 and 50−20 simulations and the 80−0 and 80−20 simulations indicates that 1-C$_5$H$_{10}$ is slightly affected by the $n$-C$_4$H$_9$OH, even though $n$-C$_4$H$_9$OH is not a direct source of 1-C$_5$H$_{10}$. The RHS of Figure 25 interestingly highlights that, even though $n$-C$_4$H$_9$OH does not produce 1-C$_5$H$_{10}$, it reduces the amount of 1-C$_5$H$_{10}$ produced from the $n$-C$_5$H$_{10}$. Similar conclusions can be made regarding 1-C$_6$H$_{12}$, where the experimental and modeling results are presented in Figure 26.

Figures 27 and 28 present results for two heptene isomers. Figures 25 and 26 show experimental measurements and computational predictions of the two smallest alkenes larger than are expected to be produced through $n$-C$_3$H$_7$OH oxidation.
symbol and line details are the same as those in Figure 12.

The model thus predicts a change in the branching fraction of \( \text{C}_7\text{H}_{14} \) decomposition with the addition of \( \text{n}-\text{butanol} \) to react at temperatures where \( \text{n}-\text{butanol} \) is not normally reactive. Several smaller hydrocarbons—including species such as methane, ethane, ethane, propane, propene, methanol, and acetaldehyde—which are formed through congruous chemical pathways of the two fuels were not significantly affected by the composition of the fuel blend. The concentrations of smaller species were well correlated with the initial amount of \( n \)-heptane in the reactant mixture, indicating \( n \)-butanol suppressed their formation only insomuch as the \( n \)-butanol displaced \( n \)-heptane in the fuel blend. However, the speciation data of several larger hydrocarbons indicate significant synergy between the chemistry of the two fuel components. Specifically, the presence of \( n \)-butanol changed the fundamental chemical pathways of \( n \)-heptane during ignition. More broadly, the suppression of large unsaturated hydrocarbon intermediate formation points toward the soot suppression tendencies of \( n \)-

observed experimentally, it is not surprising that the modeling results for 2-\( \text{C}_7\text{H}_{14} \) and 3-\( \text{C}_7\text{H}_{14} \) are much higher (20 times higher for 2-\( \text{C}_7\text{H}_{14} \) and a factor of 3 higher for 3-\( \text{C}_7\text{H}_{14} \)) than the experimental data. The experimental data indicate that 2-\( \text{C}_7\text{H}_{14} \) is suppressed by the presence of \( n \)-\( \text{C}_7\text{H}_{16} \). Computationally, however, the opposite trends are predicted. Comparison of the 50–0 and 80–0 simulations with their 50–50 and 80–20 counterparts in Figure 27 shows that \( n \)-\( \text{C}_7\text{H}_{16} \) actually increases the predicted concentrations of 2-\( \text{C}_7\text{H}_{14} \) from 3-\( \text{C}_7\text{H}_{16} \). The model thus predicts a change in the branching fractions of \( n \)-\( \text{C}_7\text{H}_{16} \) decomposition with the addition of \( n \)-\( \text{C}_7\text{H}_{16} \).

The experimental data for 3-\( \text{C}_7\text{H}_{14} \) were convolved with additional uncertainties compared to 2-\( \text{C}_7\text{H}_{14} \). The 3-\( \text{C}_7\text{H}_{14} \) calibration standard was an uncertain mixture of \( \text{cis}-3 \)-\( \text{C}_7\text{H}_{14} \) and \( \text{trans}-3 \)-\( \text{C}_7\text{H}_{14} \) and the measured areas of these two isomers were approximately equal in the chromatograms. Consequently, 3-\( \text{C}_7\text{H}_{14} \) was quantified to within a factor of 2. The upper limit of the measurements is thus represented by the open symbols in Figure 28. Predictions for 3-\( \text{C}_7\text{H}_{14} \) are of the same order of magnitude as the 2-\( \text{C}_7\text{H}_{14} \) predictions.

The differences between the experimental results and the computed results for the heptene isomers were sufficiently large that they motivate revising and revising the low temperature oxidation of \( n \)-\( \text{C}_7\text{H}_{16} \). Specifically, reaction flux analysis showed that two reaction pathways were responsible for production of the \( n \)-\( \text{C}_7\text{H}_{16} \) isomers. These reaction pathways consist of the direct reaction of heptyl radicals with molecular oxygen and the alkylperoxy radical isomerization of heptylperoxy radicals to the \( \text{C}_7\text{H}_{16} \). \( \text{OOH} \) radical, with the \( \text{OOH} \) and the radical site adjacent to each other in the \( \text{C}_7\text{H}_{16} \). These reactions are written as

\[
\text{C}_7\text{H}_{14} + \text{O} = \text{C}_7\text{H}_{14} + \text{HO}_2 \tag{R4}
\]

\[
\text{C}_7\text{H}_{14} \text{O} \rightarrow \text{C}_7\text{H}_{14} \text{OOH} \rightarrow \text{C}_7\text{H}_{14} + \text{HO}_2 \tag{R5}
\]

and our ongoing study focuses on the contributions of these reactions to ignition at low temperature conditions.

It is important to note that most large \( n \)-alkane chemical kinetic mechanisms follow similar general rate rules for fuel consumption and that the present experimental results point out the degree to which corrections to the mechanisms are necessary. The kinetics of the low temperature reactions of large olefin species, heptenes in the present case, have received very little attention in experimental and computational work, and it appears likely that greater reactivity of these olefins would correct the present differences between computed and experimental results. The low temperature chemistry of \( n \)-\( \text{C}_7\text{H}_{14} \) is the subject of current work, and the results will be reported in a forthcoming paper.

5. CONCLUSIONS

The results of this study inform an important part of our understanding on how biofuel blends affect combustion chemistry and how to develop and validate reaction mechanisms for biofuel blends. New ignition and speciation data have been presented on blends of two important reference fuel compounds, \( n \)-heptane and \( n \)-butanol, at practical thermodynamic conditions of 700 K and 9 atm and at two blend ratios. When compared with 100% \( n \)-heptane ignition results, the experimental data show that \( n \)-butanol slows the reactivity of \( n \)-heptane, and several characteristics of the first stage ignition and autoignition time-histories are affected. While there is good agreement between the experimental data and model predictions for some key features of the blend ignition data, the results also highlight the need for a more detailed understanding of some of the \( n \)-heptane reaction pathways, and new kinetic modeling work on this subject will be reported in the near future.

The speciation data revealed information not identifiable from the ignition data alone, and comparison of the speciation data on absolute and relative scales (\( \text{i.e}., \text{relative to the initial amount of} \ n \text{-heptane in the mixtures} \) provided further insights. The \( n \)-heptane caused \( n \)-butanol to react at temperatures where \( n \)-butanol is not normally reactive. Several smaller hydrocarbons—including species such as methane, ethane, ethene, propane, propene, methanol, and acetaldehyde—which are formed through congruous chemical pathways of the two fuels were not significantly affected by the composition of the fuel blend. The concentrations of smaller species were well correlated with the initial amount of \( n \)-heptane in the reactant mixture, indicating \( n \)-butanol suppressed their formation only insomuch as the \( n \)-butanol displaced \( n \)-heptane in the fuel blend. However, the speciation data of several larger hydrocarbons indicate significant synergy between the chemistry of the two fuel components. Specifically, the presence of \( n \)-butanol changed the measured concentrations of the large linear alkenes 1-pentene, 1-hexene, and 2-heptene. This discovery indicates that the presence of \( n \)-butanol changed the fundamental chemical pathways of \( n \)-heptane during ignition. More broadly, the suppression of large unsaturated hydrocarbon intermediate formation points toward the soot suppression tendencies of \( n \)-

Figure 27. Experimental 2-\( \text{C}_7\text{H}_{14} \) time-histories for stoichiometric 100–0, 80–20, and 50–50 blends. Also shown are predictions using the current mechanism, as well as mechanism predictions where the \( n \)-\( \text{C}_7\text{H}_{16} \) has been removed from the initial reactant mixture (\( \text{i.e}, \text{80–20} \rightarrow 80–0 \) [thin dashed dark cyan lines] and 50–50 \( \rightarrow 50–0 \) [thin dotted pink lines]). Experimental and simulation conditions and other symbol and line details are the same as those in Figure 12.

Figure 28. Experimental 3-\( \text{C}_7\text{H}_{14} \) time-histories for stoichiometric 100–0, 80–20, and 50–50 blends. Also shown are predictions using the current mechanism, as well as mechanism predictions where the \( n \)-\( \text{C}_7\text{H}_{16} \) has been removed from the initial reactant mixture (\( \text{i.e}, \text{80–20} \rightarrow 80–0 \) [thin dashed dark cyan lines] and 50–50 \( \rightarrow 50–0 \) [thin dotted pink lines]). Experimental and simulation conditions and other symbol and line details are the same as those in Figure 12.
butanol, where soot has significant global warming potential. From an engine design standpoint, the measurably slower reactivity of blends as compared to pure large n-alkanes, which tend to drive the reactivity of complex fuel mixtures such as kerosene, directs changes in practical engine design; for example, jet engines used in aviation might require longer combustor lengths or increased pressure ratios. The conclusions of this study thus critically inform the broader discussions of alternative fuels, including engine design and climate change policy.

**ASSOCIATED CONTENT**

3 Supporting Information

Tables of experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**

*Tel: 734-763-7470. Fax: 734-647-3170. E-mail: dippind@umich.edu.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We would like to thank the U.S. Department of Energy Basic Energy Sciences, the U.S. Department of Energy via the University of Michigan Consortium on Efficient and Clean High-Pressure, Lean Burn (HPLB) Engines, the Michigan Memorial Phoenix Energy Institute, and the Graham Environmental Sustainability Institute for their financial support. This work was also supported by the U.S. Department of Energy, Office of Vehicle Technologies, and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. DE-AC52-07NA27344. We would like to thank Dr. William Pitz and Dr. Marco Mehl for their very helpful discussions and insights into the chemical mechanism. We also thank Dr. Henry Curran, Dr. Darren Healy, Dr. John Griffiths, Dr. Guillaume Vanhove, and Dr. Rodolfo Minetti for sharing their experimental data. We would also like to thank the anonymous reviewers for providing helpful comments and suggestions.

**REFERENCES**

(55) CHEMKIN, release 10101 (x64); Reaction Design: San Diego, CA, 2010.