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An updated experimental and kinetic modeling study of \(n\)-heptane oxidation

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Abstract

This work presents an updated experimental and kinetic modeling study of \(n\)-heptane oxidation. In the experiments, ignition delay times of stoichiometric \(n\)-heptane/air mixtures have been measured in two different high-pressure shock tubes in the temperature range of 726–1412K and at elevated pressures (15, 20 and 38 bar). Meanwhile, concentration versus time profiles of species have been measured in a jet-stirred reactor at atmospheric pressure, in the temperature range of 500–1100 K at \(\phi = 0.25, 2.0\) and 4.0. These experimental results are consistent with those from the literature at similar conditions and extend the current data base describing \(n\)-heptane oxidation.

Based on our experimental observations and previous modeling work, a detailed kinetic model has been developed to describe \(n\)-heptane oxidation. This kinetic model has adopted reaction rate rules consistent with those recently developed for the pentane isomers and for \(n\)-hexane. The model has been validated against data sets from both the current work and the literature using ignition delay times, speciation profiles measured in a jet-stirred reactor and laminar flame speeds over a wide range of conditions. Good agreement is observed between the model predictions and the experimental data. The model has also been compared with several recently published kinetic models of \(n\)-heptane and shows an overall better performance. This model may contribute to the development of kinetic mechanisms of other fuels, as \(n\)-heptane is a widely used primary reference fuel. Since the sub-mechanisms of \(n\)-pentane, \(n\)-hexane and \(n\)-heptane have adopted consistent reaction rate rules, the model is more likely to accurately simulate the oxidation of mixtures of these fuels. In addition, the successful implementation of these rate rules have indicated the possibility of their application for the development of mechanisms for larger hydrocarbon fuels, which are of great significance for practical combustion devices.

Keywords: \(n\)-heptane, kinetic model, oxidation, shock tube, jet-stirred reactor

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Introduction

The oxidation of \( n \)-heptane has been widely studied as it is a primary reference fuel (PRF) and is a representative normal alkane. It is also an important component of toluene reference fuel (TRF) and ethanol toluene reference fuel (ERF) [1], which has been used as a surrogate gasoline fuel for research of combustion processes in internal combustion engines [2]. Experiments have been performed which have focused on different properties of fuel oxidation over a wide range of conditions, such as ignition delay times in shock tubes [3-8] and rapid compression machines [9-12], species versus time and/or temperature profiles measured in jet-stirred reactors [13-17] and flow reactors [18-21], laminar flame speeds [22-26] and spatial distribution of species in flames [27-30]. Moreover, a series of experiments have been performed in engines [31-35] to study homogeneous charge compression ignition (HCCI), engine knock, exhaust gas recirculation (EGR), NOx emission control, etc. Since 1979 [4] efforts have been made to develop a kinetic model for \( n \)-heptane oxidation at both low temperature and high temperature to provide further insight into this process. In 1989, Westbrook \textit{et al}. developed a detailed chemical kinetic mechanism to describe the oxidation of \( n \)-heptane and iso-octane [36]. This mechanism adopted both low- and high-temperature chemistry, and was validated through comparisons with experimental data from shock tube, turbulent flow reactor and jet-stirred reactors. Later, Chevalier developed a computational technique to automatically develop detailed kinetic mechanisms, which were used to study the influence of fuel, fuel mixtures and fuel additives on knock tendency [37]. Ranzi \textit{et al}. proposed a semi-detailed kinetic model for \( n \)-heptane oxidation [38], while Côme used a computer package to develop the kinetic models for the oxidation of both \( n \)-heptane and iso-octane [39].

Curran \textit{et al}. [40] carried out a comprehensive kinetic modeling study of \( n \)-heptane oxidation in a systematic way. The important reactions during the oxidation of \( n \)-heptane were categorized into 25 different reaction classes, including 10 reaction classes to describe high-temperature oxidation and 15 classes to describe the low-temperature regime. Although approximate treatments were assigned to some less important reactions such as the consumption of the heptene isomers, the overall performance of the mechanism was very good. This mechanism has been improved and further validated, with good performance over the pressure range of 3 to 50 atm, in the temperature range of 650 to 1200 K and at equivalence ratios of 0.3 to 2.0. More importantly, this model set a successful frame for the kinetic mechanism development of other larger \( n \)-alkanes [41]. A more recent study carried out by Mehl \textit{et al}. [42] on the kinetic modeling of gasoline surrogate components and mixtures under engine conditions has further refined and adopted this mechanism. Moreover, this mechanism also forms the basis for the mechanism development in this work.

There has been a continual interest among the research community in developing a better understanding of \( n \)-heptane oxidation both experimentally and theoretically. For example, Herbinet \textit{et al}. performed an experimental study in a jet-stirred reactor [16]. In addition to traditional gas chromatography, the experiments also used synchrotron vacuum ultraviolet photoionization mass spectrometry as the diagnostic technique to identify the unstable species such as radicals, which is an
example of the new experimental methods being applied to this kind of study. Herbinet et al. also
generated a kinetic mechanism using the software EXGAS [43], which satisfactorily reproduced the
mole fraction profiles of most of the species identified in the experiments.

Meanwhile, new reaction pathways are being adopted into the kinetic model to better describe the
oxidation process of \textit{n}-heptane. Recently, Pelucchi et al. proposed an improved kinetic model for \textit{n}\\-heptane [44], by emphasizing new reaction classes producing organic acids, diones and ketones in the
low temperature regime. The mechanism was validated over a wide range of conditions including both
low and high-temperature ranges. Good agreement was observed between simulations and experimental
data from the literature for ignition delay time measurements [5, 42, 45], species profiles measurements
taken in a jet-stirred reactor [14-16] and in a flow reactor [20], as well as laminar flame speeds [26].
Meanwhile, the experimental database of \textit{n}-heptane is being extended to cover a wider range of
conditions. Seidel et al. performed an experimental and kinetic modeling study of a fuel-rich, premixed
\textit{n}-heptane flame at 40 mbar, and successfully identified over 80 species generated at this condition [30].
Based on previous work, a detailed kinetic model was developed. Reduced kinetic mechanisms are also
being proposed, such as the work by Cai and Pitsch [46], who proposed an optimized chemical
mechanism for gasoline surrogates which was validated under extensive conditions and it showed a
very good performance compared to experimental ignition delay measurements.

This current study is based on a continuity of effort in experimental and kinetic modeling studies
of hydrocarbon fuels that we have published previously [47-58]. In this work, the ignition delay times
of \textit{n}-heptane in air are firstly measured in two different high-pressure shock tubes to provide more
experimental ignition delay time data at elevated pressures. Moreover, the experimental conditions of \textit{n}\\-heptane oxidation in a jet-stirred reactor have been extended to extremely rich (\(\phi = 4.0\)) and very lean
(\(\phi = 0.25\)) conditions, while the other conditions remain consistent with those published previously. To
reflect the improvements in the chemical kinetics and thermodynamics as well as their impact, a
detailed kinetic model of \textit{n}-heptane oxidation has been developed based on our previous work,
including our updated base mechanism [47-50, 53, 56-58], the sub-mechanisms of the pentane isomers
[51, 55] and \textit{n}-hexane [54]. In the development of this mechanism, the new reaction classes and
reaction rate rules with modifications, which have been successfully applied to the pentane isomers and
\textit{n}-hexane, have been adopted. The thermodynamic database has also been updated with recently
published optimized group values [52]. The model has been validated using the experimental data sets
obtained in this work, as well as those from the literature for ignition delay times, species profile
measured in jet-stirred reactors and also for laminar flame speed measurements. Moreover, comparisons
are made between the current model and those from recent publications. The significant reaction
pathways for the oxidation of \textit{n}-heptane are revealed by further analysis of the simulations.
Experimental Methods

PCFC Shock tube
The Physico-Chemical Fundamentals of Combustion (PCFC) shock tube at Aachen University has been designed similar to the high-pressure shock tube at NUIG. It has an inner diameter of 63.5 mm and an overall length of about 7.5 m with a 3 m driver section. Due to physical space limitations the driver section is curved with a bending radius of 1 m. The diaphragm section can house up to two pre-scored aluminum diaphragms. All parts coming into contact with fuel/air mixtures are made of stainless steel (316Ti), except for the aluminum diaphragms. Shock velocities and pressure profiles are recorded in the measuring section close to the endwall of the driven section with up to 8 PCB 113B22 pressure sensors. Signals are recorded using a digital oscilloscope with a sampling rate of 25 MHz. Fuel/air mixtures are prepared in a separate 40 L Teflon coated stainless steel mixing vessel. Partial pressures are used to prepare the desired gas mixtures. Static pressures are monitored with two STS ATM. 1st pressure sensors with measuring ranges of 500 mbar and 5 bar, respectively. The shock tube, manifold and mixing vessel can be electrically heated to 150 °C in order to avoid fuel condensation. In this study, initial temperatures of 40 °C are sufficient due to the relatively high vapor pressure of \(n\)-heptane. Temperatures are monitored with type T thermocouples due to their lower measuring uncertainty compared to conventional type K ones. High purity grade gases for reactive mixture preparation (\(N_2\) and \(O_2\)) were provided from Praxair and Westfalia. Helium and compressed air were used as driver gases. The reflected shock conditions were calculated using the initial conditions of pressure and temperature and mixture composition and the measured shock velocity with an in-house code which is based on the shock and detonation toolbox [59] in Cantera [60]. An uncertainty analysis has been performed for the PCFC shock tube and is provided as Supplementary material. Maximum uncertainties in the reflected shock temperatures are estimated to amount to 1.1% in the reflected shock temperature and 3.5% in the reflected shock pressure. Depending on the fuel reactivity this can induce uncertainties of up to 15% in the measured ignition delay time for the range studied.

NUIG Shock tube
High-temperature (above 1000 K) ignition delay times for stoichiometric mixtures of \(n\)-heptane at compressed pressures of 15 bar in a 21\% \(O_2\) : 79\% \(N_2\) bath gas were measured in the National University of Ireland, Galway (NUIG) high-pressure shock tube [61], with an inner diameter of 63 mm. The methodology used to measure ignition delay times in this facility has recently been described in our work on \(n\)-hexane [54], and thus will not be described further here. Again, \(n\)-heptane was supplied by TCI UK in high purity (> 99.0\%), while oxygen (99.5\%) and nitrogen (99.95\%) were supplied by BOC Ireland.
Jet-stirred reactor

The oxidation of \( n \)-heptane was studied in a jet-stirred reactor at LRGP in Nancy (France). This reactor can be considered to be perfectly stirred [62] and has frequently been used for numerous gas phase kinetic oxidation studies of hydrocarbons and oxygenated compounds [63]. Experiments were performed at a constant pressure of 1.067 bar, at a residence time of 2 s, at temperatures ranging from 500 to 1100 K, and at four equivalent ratios of \( \phi = 0.25, 1.0, 2.0 \) and 4.0. The fuel was diluted in helium resulting in an \( n \)-heptane concentration of 0.5%. The fuel was provided by Sigma-Aldrich (purity of 99%). Helium and oxygen were provided by Messer with purities of 99.99% and 99.999%, respectively.

The reactor is made of fused silica, and consists of a fused silica sphere (volume = 95 cm\(^3\)) into which diluted reactant enters through an injection cross located at its center. It is operated at constant temperature and pressure and it is preceded by an annular pre-heating zone in which the temperature of the gases is increased to the reactor temperature before entering it. The gas mixture residence time inside the annular pre-heater is very short compared to its residence time inside the reactor (a few percent). Both the spherical reactor and the annular pre-heating zone are heated using resistance wires coiled around their walls. The temperature is controlled using type K thermocouples. The reaction temperature was measured using another independent type K thermocouple which was located in a glass finger at the center of the reactor (which is actually the intra annular part of the preheater). The uncertainty in the temperature measurement is ±5 K.

A Coriolis flow controller is used to feed \( n \)-heptane, and two mass flow controllers are used to meter the helium and oxygen flow rates. The fuel is mixed with helium and evaporated in a heat exchanger. Oxygen is added at the reactor inlet. The accuracy in flow rates given by the manufacturer (Bronkhorst) is 0.5%. This results in a small uncertainty of 2.00 ± 0.01 s in the residence time.

Product species are analyzed directly by gas chromatography using a heated transfer line between the reactor outlet and the chromatograph sampling. The temperature of the line is heated to 160 °C to avoid product condensation during transfer. Three gas chromatographs are used for the quantification of the different species. The first chromatograph, equipped with a Carbosphere packed column, a thermal conductivity detector (TCD) and a flame ionization detector (FID), is used for the quantification of \( \text{O}_2 \), \( \text{CO} \), \( \text{CO}_2 \), methane, ethylene, acetylene and ethane. The second is fitted with a PlotQ capillary column, a methanizer, and an FID is used for the quantification of molecules from methane to reaction products containing up to 5 carbon atoms and 1 or 2 oxygen atoms maximum. The third is fitted with a HP-5 capillary column and an FID is used for the quantification of molecules which contain at least 5 carbon atoms. Calibrations are performed by injecting standards where available or by using the effective carbon number method when standards were unavailable. The maximum relative error in mole fractions is estimated to be ±5% for species which are calibrated using standards and ±10% for species calibrated using the effective carbon number method [64-65]. The identification of reaction products is performed using a gas chromatograph equipped with a PlotQ or an HP-5 capillary column and coupled to a mass spectrometer (quadrupole). The mass spectra of all of the detected reaction products are included in the
NIST 08 Mass Spectra Database [66]. For certain species, single-photon-ionization mass spectrometry (SPI-MS) [67] is used for higher accuracy, as shown in the experimental data sets provided in the Supplementary material.

Chemical Kinetic Mechanism

The kinetic model used in this work consists of 1268 species and 5336 reactions. The sub-mechanism for C0–C4 fuels is taken from AramcoMech 2.0 [57-58]. This mechanism has been widely validated for a series of fuels including hydrogen, syngas [48], methane, methanol [56], formaldehyde, ethane, ethylene, acetylene, ethanol, acetaldehyde [47], dimethyl ether [53] and propene [49-50]. The sub-mechanisms for the three pentane isomers and for n-hexane have also been published recently [51, 54-55]. On the basis of the above mechanisms, an n-heptane sub-mechanism has been developed in this work. Table 1 shows the nomination of some representative species in the n-heptane sub-mechanism.

Figure 1 shows the reaction pathways for n-heptane oxidation considered in this work, which are similar to those considered previously [40, 51, 54]. The reaction pathways of a fuel are strongly dependent on its structure, and significantly affect the reactivity of the fuel. Compared to smaller alkanes, n-pentane shows a higher reactivity at low temperatures because its structure contains more connected secondary carbons. H-atom abstraction is favored at secondary sites compared to primary ones, where secondary pentyl peroxy radicals formed can isomerize via six-membered transition state (TS) rings into hydroperoxy pentyl radicals. Six-membered TS ring formations are faster than any other (5-, 7-, or 8-membered ones) which is mainly due to their lower ring-strain energy and formation of six-membered TS ring structures contributes considerably to the chain branching process at low temperatures, promoting fuel reactivity [51, 54-55]. Similarly, n-hexane shows a higher reactivity compared to n-pentane because six-membered TS ring structures are available for all of the four connected secondary carbons, while the reactivity of n-heptane is even higher than that of n-hexane since the ratio of secondary carbon atoms to primary ones is even higher again. However, the reaction pathways that need to be considered for n-pentane, n-hexane and n-heptane are almost identical, as shown in Fig. 1. Therefore consistent reaction rate rules can be applied to their sub-mechanisms.

A series of reaction rate rules have been adopted in our previous work on the oxidation of the pentane isomers [51, 55]. These rate rules were derived from recently published ab-initio calculations [68-73] and have been applied to the reaction classes in the low temperature regime. New reaction classes related to the alternative isomerization pathway of peroxy hydroperoxy alkyl radicals [51] have also been added. The mechanisms for the three pentane isomers predict well ignition delay times with good agreement observed compared to the experimental data [55]. Many of the rate constants for the low temperature reaction classes (e.g. \( \text{RO}_2 \rightleftharpoons \text{QOOH} \), etc.) for the pentane isomers are available from ab-initio calculations [68, 71-72], but those for the hexane isomers and larger alkanes are rare. Therefore in the kinetic modeling study of n-hexane, the reaction rate rules were derived from those calculated for n-pentane but modifications were made within their uncertainty range, which have led to
better agreement between the experimental and simulated results [54]. The refined rate rules have been used to generate the \( n \)-heptane mechanism used in this work to maintain consistency in the chemical kinetics.

The thermodynamic data of the species involved have been updated using the THERM software [74], which is based on the group additivity method proposed by Benson [75]. The group values used in the calculation have been optimized [52], and are consistent with those used for the pentane isomers and for \( n \)-hexane [51, 54-55]. The kinetic mechanism, thermodynamic data, transport data, species glossary and group values for group additivity method are available as Supplementary material. In the future, this mechanism might be updated for better performance and released with comprehensive validations. Please visit our website http://c3.nuigalway.ie/ for more details.

**High temperature mechanism**

The most significant reaction classes in the high temperature regime of \( n \)-heptane oxidation are the unimolecular decomposition of the fuel and fuel derived radicals in addition to hydrogen abstraction from the fuel by the radical pool. To derive the rate constants for the unimolecular decomposition of \( n \)-heptane, firstly the high-pressure limit rate constants of the radical recombination are estimated; then the reverse rate constants are obtained using the CHEMRev software package [76] with their pressure dependence calculated using Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) theory, which has been proven to show good agreement with the more precise Rice-Ramsperger-Kassel-Marcus/Master Equation (RRKM/ME) approach for alkane decomposition [77]. The Lennard-Jones parameters for \( n \)-heptane are from Jasper and Miller [78], which are \( \sigma = 4.42 \) Å and \( \varepsilon = 213 \) cm\(^{-1} \) in a bath gas of N\( \text{2} \). The pressure dependent rate constants for the decomposition of the fuel-derived radicals: \( \dot{C}_7H_{15}-1, \dot{C}_7H_{15}-2 \) and \( \dot{C}_7H_{15}-3 \) are adopted from [79].

H-atom abstraction from the fuel by \( \dot{O}H \) radicals is the most significant reaction class involving the fuel with the radical pool over a wide temperature range. The rate constants for these reactions have been adopted from the values reported by Sivaramakrishnan and Michael [80], who measured these reaction rates experimentally in a shock-tube using \( \dot{O}H \)-radical electronic absorption and compared the results with literature data. H-atom abstraction by \( H\dot{O}_2 \) radicals contributes little to fuel consumption at low temperatures (600–750 K) but these reactions become more important at higher temperatures (750–1300 K) because the \( H\dot{O}_2 \) molecule produced decomposes into two \( \dot{O}H \) radicals, greatly promoting reactivity. The rate constants for H-atom abstraction from the fuel by \( H\dot{O}_2 \) radicals are adopted from [81]. other reactions in the high temperature regime and their rate constants are mainly derived from the \( n \)-heptane mechanism proposed by Curran et al. [40].
**Low temperature mechanism**

The low-temperature reaction pathways are illustrated in the upper part of Fig. 1. In the low-temperature regime, the fuel derived radicals (R) add to molecular oxygen to form alkylperoxy radicals (RȮ₂). Further isomerization of RȮ₂ via ring transition states and internal hydrogen atom transfer leads to the formation of hydroperoxy-alkyl radicals (QOOH). The most important competing reaction class is the concerted elimination forming C7 olefins and HȮ₂ radicals, which becomes more competitive as the temperature increases. At low- and intermediate-temperatures this concerted elimination reaction tends to reduce reactivity, because it consumes a reactive radical (usually ᵐH) in the hydrogen abstraction reaction from the fuel, and produces an HȮ₂ radical which is less reactive. Other consumption reactions of RȮ₂ are bi-molecular reactions, but only play a minor role in the reaction flux.

For the consumption of QOOH radicals, the addition to molecular oxygen is a significant step, producing peroxy alkylhydroperoxide radicals (Ȯ₂QOOH) as the precursor of ketohydroperoxides. ᵐH radicals are produced from both the formation and decomposition of ketohydroperoxides, which make this reaction sequence the major chain branching process at low temperatures. Meanwhile, the consumption of QOOH radicals also has other channels. As the O–O bond in the hydroperoxy group is weak, the consumption of QOOH radical can produce small molecule products or cyclic ethers and release an ᵐH radical, which contributes to the chain propagation process. The beta-scissions of C–O bonds that produce olefins and HO₂ radicals are only available for certain structures such as C₇H₁₄OOH₁-₂ and are thus less important.

The equilibrium between RȮ₂ and QOOH radicals significantly influences fuel reactivity at low- and intermediate-temperatures. The concerted elimination reaction of RȮ₂ leads to chain propagation while the addition of QOOH radicals to O₂ ultimately contributes to chain branching. Other significant reaction classes that can affect this equilibrium include the addition of ᵐ to O₂, the formation of cyclic ethers and the formation of ketohydroperoxides. The modified reaction rate rules for the above mentioned reaction classes are consistent with those proposed for n-hexane [54], as shown in Table 2. Detailed discussions of the comparison of rate rules and the refinements can be found elsewhere [51].

The red open arrows in Fig. 1 denote the reaction classes induced by the alternative isomerization pathways of ᵐQOOH radicals. These reaction classes have been proposed in our previous work [51, 54], with their reaction rate constants taken by analogy with those possible for RȮ₂ radicals. Although the adoption of alternative isomerization pathways has proven to have a limited effect upon model predictions for n-hexane [54], these reaction classes have been included for n-heptane to reflect the complexity of the low temperature chemistry, which become more important for the oxidation of branched alkanes [51].
Results and discussion

High pressure shock tube data

The ignition delay times for the oxidation of stoichiometric \( n \)-heptane/air mixtures at different pressures have been measured in the PCFC high pressure shock tube, see solid symbols in Fig. 2, over the temperature range of 688–1412 K, which includes the low, intermediate and high temperature regimes. The new data sets are consistent with those reported in previous work [82-83] which are depicted as half-filled symbols and open symbols respectively, showing a significant pressure effect reflected by the decrease in ignition delay times and the shifting of the negative temperature coefficient (NTC) region towards higher temperatures [5] at higher pressures. Furthermore, simulation results using the kinetic mechanism presented in this study are shown. Shock tube ignition delay times are simulated using the constant volume closed homogenous batch reactor code in CHEMKIN PRO [84]. It is assumed that the changes in conditions induced by facility effects in the region near the endwall can be treated as an isentropic compression/expansion by an effective volume change as in the RCM. These CHEMKIN PRO input files and the experimental data are available as Supplementary material. In the following descriptions, the ignition event in the simulation is defined as the maximum pressure rise unless the experimental data sets taken from literatures define the ignition delay differently.

It is important to note that the different data sets have been obtained in different facilities. This is a critical aspect regarding the level of confidence of the experimental results. By considering results taken at the same conditions but from different facilities, a higher level of confidence can be attributed to the experimental results. This has motivated a repeat of experiments in this study at conditions that have been reported previously.

Another aspect of this investigation is the treatment of facility effects. The conditions such as pressure and temperature behind the reflected shock are ideally constant. However, in the real process both the pressure and temperature behind the reflected shock increase with time due to boundary layer effects inside the shock tube and the non-ideal opening of diaphragms. This leads to pressure and temperature gradients influencing the ignition process. As a result, the measured ignition delay times may be shorter than those assuming ideal conditions. More detailed discussion on these shock tube facility effects can be found in [85]. In general, these effects become stronger with smaller inner diameter tubes and longer measuring times. In Fig. 2 the results of shock tubes with inner diameters of 50 mm [83], 63.5 mm (this study) and 140 mm [82] are shown. In [82] an average pressure gradient of \( p/p_0 = 3\%/\text{ms} \) is given for the 140 mm tube. The PCFC tube has an average pressure gradient of 8\%/ms due to the smaller inner diameter. This pressure gradient has been determined from non-reactive measurements (Fig. 3). Pressure gradients of the 50 mm tube have previously been reported to amount to around 10\%/ms [85].

At high pressures, where ignition delay times are well below 1 ms, these different pressure gradients hardly have an effect on ignition delay times and in this case the simulations can be performed assuming a truly constant volume reactor. For longer measuring times above 1 ms, facility effects are
taken into account by assuming a volume change reflecting the experimentally observed constant
increase in pressure as appropriate, depending on the shock tube as discussed above. Comparing the
experimental results with the kinetic simulation including a proper treatment of the facility induced
increase in pressure and temperature, it becomes obvious that the mechanism is able to predict the
measured ignition delay times within 15%, which is within the experimental uncertainty.

It can be seen in Fig. 2 that the model predicts well the measured ignition delay times when the
facility effect is considered (solid lines). The previous and current results appear inconsistent in ignition
delay times at 38 bar, because both the current experiments and simulations were not performed at
precisely 38 bar as in [82] (see the experimental data in the Supplementary material). Therefore the
inconsistency is caused by the pressure effect. By using the specific experimental temperatures and
pressures in our simulations, the model can successfully reproduce both the current and the previous
experimental results. It is worth noting that the simulations using varying volume traces obtained from
the experimentally measured non-reactive pressure profiles are very similar to those assuming an
average constant increase in pressure of 8%/ms, which is consistent with the average pressure gradient
of 7–8%/ms assumed for the PCFC shock tube. The dashed lines in Fig. 2 represent the simulations
with the current mechanism using unmodified rate rules, which tend to under-predict ignition delay
times over the entire temperature range. This trend is similar to those observed in the kinetic and
modeling study of n-hexane [54].

As an additional input to the ignition delay times at higher temperature, Fig. 4 shows the ignition
delay times measured in the high-pressure shock tube at NUIG for n-heptane oxidation at \( \phi = 1.0 \) and
15 bar in the temperature range 1058–1298 K. The agreement between the experimental (points) and
modeling results (solid line) are good, which further validates the high temperature n-heptane chemistry.
The dashed line shows model simulations with unmodified rate rules. The slight difference between the
predictions indicates that those modifications have only a minor effect in this temperature regime.

The mechanism has also been validated using shock tube ignition delay time data from the
literature. Campbell et al [86] used a shock tube to measure ignition delay times for n-heptane oxidation
in the temperature range 651–823 K and at pressures between 6.1 and 7.4 atm at \( \phi = 0.75 \) in 15%
\( \text{O}_2/5\%\text{CO}_2/\text{Ar} \) and in 15% \( \text{O}_2/\text{Ar} \) mixtures. Both first-stage (cool flame) and second-stage (total)
ignition delay times were measured, providing critically needed targets for further validation of kinetic
models. Figure 5 shows the experimental and modeling results for that study [86] which used the LLNL
mechanism [42], and the predictions using the current model as well as several other models [16, 30,
46]. It can be seen that the current mechanism generally shows a better performance in predicting both
the first and the second stage ignition delay times.

Shen et al. [45] measured ignition delay times for several \( n \)-alkane/air mixtures in a heated shock
tube. The experimental results for \( n \)-heptane, which were measured at \( \phi = 0.25, 0.5 \) and 1.0 at multiple
pressures are shown in Fig. 6. These results show the varying reactivity of \( n \)-heptane depending on
temperature, pressure and equivalence ratio, which have been well captured by the current model. Here
the maximum in excited OH radical concentration is defined as the ignition delay event, which is consistent with that reported in [45]. Some discrepancies can be seen at conditions such as $\varphi = 0.5$ at 13 atm. However, the relevant experimental data is not completely consistent with those under similar conditions shown in Fig. 7. Therefore these discrepancies can be partly attributed to the uncertainties of some specific data points from the literature. Ciezki and Adomeit investigated the ignition delay times for $n$-heptane/air mixtures in a high pressure shock tube for equivalence ratios of 0.5 to 3.0, at pressures between 3.2 and 42 bar in the temperature range of 660–1350 K [5]. These experimental data have been the benchmark for validating $n$-heptane oxidation mechanisms [16-17, 30, 40, 42, 44] for many years. Figure 7 shows a comparison of the experimental results reported by Ciezki and Adomeit and the predictions using the current mechanism, which indicates that it captures well the trend of the reactivity with the varying equivalence ratio, pressure and temperature ranges. The comparison of the predictions using the current mechanism and several other recently published ones [16, 30, 42, 44, 46] are shown in Fig. 8 (a), (b), (c), (d) and (e) respectively.

A brute force sensitivity analysis was performed using CHEMKIN PRO [84] at $\varphi = 1.0$, $p = 20$ bar, $T = 720$ K, and at 820 K and 1000 K respectively to determine the reactions that are most significant for the ignition process, Fig. 9. In the analysis, the rate constants of each reaction were increased and decreased by a factor of two ($k_+$ and $k_-$), and the simulations were performed using two mechanisms adopting these changes to obtain the ignition delay times ($\tau_+$ and $\tau_-`). The sensitivity coefficient ($S$) is then defined as follows:

$$S = \frac{\ln(\tau_+/\tau_-)}{\ln(k_+/k_-)} = \frac{\ln(\tau_+/\tau_-)}{\ln(2/0.5)}$$

From the definition above, it can be concluded that a reaction with a positive sensitivity coefficient inhibits reactivity while that with a negative sensitivity coefficient promotes reactivity.

At low temperatures, the consumption of the fuel is mainly initiated by H-atom abstraction from the fuel by OH radicals, followed by propagation via addition to $O_2 \rightarrow$ isomerization to $\cdot$OOH $\rightarrow$ addition to $O_2$, and the branching process via the formation and decomposition of ketohydroperoxides which produce OH radicals, promoting reactivity. Therefore at low temperatures, the reactivity is dominated by chain branching from the fuel, depicted in Fig. 9 (a). Hydrogen and other small species chemistry is only of minor importance. The most significant reactions promoting reactivity are those leading to the formation and decomposition of ketohydroperoxides. However, the formation of ketohydroperoxides via the isomerizations of $\cdot$OOOH radicals is not sensitive, because at low temperatures this reaction class dominates the consumption of $\cdot$OOOH radicals, while other consumption pathways such as the beta-scissions of $\cdot$OOOH radicals cannot compete with their addition to molecular oxygen, even when their A factors are reduced by a factor of two. The newly adopted alternative isomerization reactions of $O_2$OOOH radicals only show minor contributions as discussed in a previous work [54].
*n*-Heptane composes only primary and secondary carbon atoms. H-atom abstraction from fuel by the radical pool mainly occurs at secondary carbon sites because the C–H bonds are weaker compared to those on primary carbons. For the same reason, the hydrogen atoms on secondary carbons are favored for the internal H-atom transfer/abstraction process in the isomerization of RȮ2 to QOOH radicals. Meanwhile, the isomerization of RȮ2 to QOOH radicals prefers six-membered ring transition states since they have the lowest ring strain energies. These preferences of relevant reaction classes are also reflected in Fig 9 (a). For example, the most sensitive reaction promoting reactivity is the addition of Ĉ7H16OOH2-4 radicals to O2. These are produced through the sequence of hydrogen abstraction from a secondary carbon → addition to O2 → isomerization via a six-membered transition state ring and internal abstraction of a secondary H-atoms. The decomposition of the relevant ketohydroperoxide, C7KET24, also significantly promotes reactivity. Similarly, the additions of Ĉ7H14OOH3-5 and Ĉ7H14OOH4-2 radicals to O2 also contribute significantly to reactivity, with certain differences caused by the branching ratios of hydrogen abstraction reactions from the fuel. On the other hand, the concerted (olefin + HȮ2 radical) elimination reactions are the most inhibiting at low temperatures. Although HȮ2 radicals can abstract hydrogen atoms from the fuel, these reactions are considerably endothermic and contribute little to fuel consumption at low temperatures. In addition, H-atom abstraction from the fuel by HȮ2 radicals produces H2O2 which only decomposes easily into OH radicals at higher temperatures (~850 K). As has been discussed above, the equilibrium between RȮ2 and QOOH radicals significantly influences fuel reactivity at low temperatures. This is consistent with Fig. 9 (a) since the concerted elimination reactions of RȮ2 play a key role in reducing reactivity, while the addition of QOOH to O2 greatly increases it. The predicted reactivity of *n*-heptane (Fig. 2) and *n*-hexane [54] become lower when modified reaction rate rules are used, which can be mainly attributed to the enhanced concerted elimination reactions in the modification [54].

Figure 9 (b) shows the results of the sensitivity analysis performed in the NTC region at 820 K. With an increase in temperature, there is an increased competition between chain branching and chain propagation/termination reactions. Under these conditions, the addition of QOOH radicals to O2 and the concerted elimination reactions of RȮ2 radicals continue to be important promoting and inhibiting reaction classes, respectively. However, the chemistry of small molecules starts to become important. The most important reaction promoting reactivity is the decomposition of H2O2, while the most inhibiting reaction is the chain termination reaction HȮ2 + HȮ2 = H2O2 + O2. This is because in this reaction two HȮ2 radicals are consumed to produce just one H2O2 molecule leading to the formation of two reactive ŌH radicals, whereas if one HȮ2 radical reacts with any stable species two radicals and two H2O2 molecules will be produced leading to the formation of four reactive ŌH radicals. Moreover, even though the decomposition of H2O2 into ŌH radicals promotes reactivity, this reaction is endothermic and only becomes significant at higher temperatures. At 820 K, HȮ2 radicals can also be converted into more reactive ŌH radicals via reaction with ĈH3 and CH3Ȯ2 radicals, promoting reactivity as shown in Fig. 9 (b), or inhibit reactivity through the chain-termination reaction producing
H$_2$O$_2$ and O$_2$. However, the temperature can increase to temperatures above 900 K after the first stage ignition, making the decomposition of H$_2$O$_2$ much easier and promoting reactivity. The sensitivity coefficients shown in Fig. 9 (b) reflect the influences of different reactions integrated over the entire ignition process. It indicates that the production and consumption reactions of HO$_2$ radicals play a significant role in the NTC region, and are sensitive to the increase in temperature leading to ignition.

The relatively large sensitivity coefficient of H-atom abstraction from primary carbon atoms indicates the branching ratio of this reaction class is also important in controlling reactivity. As discussed above, H-atom abstraction occurs preferentially from secondary carbon atoms. However, the concerted elimination reaction that inhibits reactivity also favors secondary alkylperoxy radicals, since there are more hydrogen atoms on beta carbons. On the other hand, primary alkylperoxy radicals, C$_7$H$_{15}$-1O$_2$, only have two hydrogen atoms on the beta carbon leading to the concerted elimination reaction, and therefore there is less competition from this reaction class in the sequent chain branching process. Besides H$_2$/O$_2$ and C$_1$ chemistry, the reactions of other small molecules also become sensitive. For example, the concerted elimination of n-propyl peroxide radical (nC$_3$H$_7$O$_2$) inhibits reactivity. These small molecule radicals are mainly produced from the β-scission of fuel-derived radicals or from low-temperature products of the chain branching process.

The chemistry of small molecule species is even more important in the high-temperature regime, as shown in Fig. 9 (c). As the temperature increases, the decomposition of H$_2$O$_2$ is further enhanced and becomes the dominant reaction promoting reactivity. Correspondingly, H-atom abstraction from fuel by HO$_2$ radicals, which converts HO$_2$ radicals into H$_2$O$_2$, greatly promotes reactivity. On the other hand, the duplicated chain terminating reactions of HO$_2$ radicals are the most inhibiting reactions, as discussed above. The unimolecular decomposition of the fuel and β-scission of the fuel-derived radicals show positive or negative sensitivity coefficients depending on the reactivity of the different smaller hydrocarbon species produced. The low-temperature chain branching reactions are not observed to be sensitive in Fig 9 (c) due to the high temperature conditions. A series of reactions between small molecule hydrocarbon radicals and HO$_2$ radicals are shown in Fig. 9 (c). In general, those converting HO$_2$ into OH radicals directly or indirectly promote reactivity, while those converting HO$_2$ into O$_2$ inhibit reactivity.

Jet stirred reactor

The jet-stirred reactor experiments were performed at 1.06 bar, at a residence time of 2s and at equivalence ratios of 0.25, 2.0 and 4.0 in order to extend the relevant experimental database to very lean (φ = 0.25) and very rich (φ = 4.0) conditions. Detailed compositions of the mixtures are listed in Table 3, with over 40 species being identified. The intermediates include C$_1$–C$_2$ alcohols, C$_1$–C$_4$ aldehydes, C$_1$–C$_4$ alkanes, C$_2$–C$_7$ alkenes, small molecular dienes and alkynes, C$_7$ cyclic ethers, as well as other oxygenated species such as acids and unsaturated aldehydes, which can be produced from the low-temperature oxidation process. The simulation has been performed using the perfectly-stirred reactor.
module within CHEMKIN PRO [84] employing the transient solver, with an end-time of 20 s. Figures 10–12 present the model versus experimental results at equivalence ratios of 0.25, 2.0 and 4.0, respectively. The experimental data sets are available in the supplementary material.

The NTC behavior of \( n \)-heptane under different conditions is reflected in the experimental results. In general, the experimental trends are well captured by the model, except for the under-prediction in reactivity at \( \phi = 0.25 \) at a temperature of approximately 750 K, indicating that the current mechanism can capture the overall chemical behavior of \( n \)-heptane under most conditions studied in the present work. Good agreement is observed between the experimental results and the predictions for major intermediates, with the deviations in the peak concentrations being mostly within a factor of two of the experiments. However, the deviations for oxygenated species at low temperatures, such as those shown in Fig 10 (j), Fig 11 (b) and Fig 11 (f), suggest that the consumption pathway of the low-temperature chemistry products can be further refined. In the current mechanism, the Korcek mechanism [87] which produces acids from ketohydroperoxides has also been considered, with the rate constants adopted from Pelucchi et al. [44]. However, the effects of adopting this reaction class are very slight, as the concentrations of the acids are under-predicted at all conditions studied in this work, especially for the leanest mixture which requires further investigation. This might be due to the fast decomposition of ketohydroperoxides in the current model which requires further investigation of the detailed reaction pathways that consume ketohydroperoxides. The dashed lines present the simulations using the mechanism with unmodified rate rules. It can be see that the new modifications have only a slight effect upon the predicted mole fraction profiles of major species. The dashed lines are overlapping with the solid lines for many cases.

It is worth noting that two important classes of intermediates are reasonably well predicted by the model, that is, heptenes and \( C_7 \) cyclic ethers. As shown in Fig 10–12 (m), the heptene isomers are largely produced from the concerted elimination reactions of \( R\tilde{O}_2 \) radicals, to which ignition delay times are sensitive, showing different effects depending on the temperature range, as discussed earlier. The overall agreement between the model and experimental results of 1-, 2- and 3-heptene are better predicted using the modified rate rules adopted here, yet the branching ratio may need to be further refined. Another possible reason for the deviations, especially those at intermediate temperatures, may be attributable to the consumption pathways of these alkenes. The experimental and simulated mole fraction profiles of five different \( C_7 \) cyclic ethers are shown in Figs. 10–12 (n)–(o). These species are produced from the chain propagating reactions of \( \tilde{Q}OOH \) radicals forming cyclic ethers and \( \tilde{O}H \) radicals. Although this reaction class is not seen to be sensitive according to our analysis presented above, its significance for the consumption of \( R\tilde{O}_2 \) radicals cannot be neglected, as will be shown in the rate of production analysis below. Using the modified rate rules adopted here, in general the predicted mole fraction profiles agree better with the experimental results. Even at \( \phi = 0.25 \), where the performance of the model is not as good as at the other equivalence ratios, the predicted peak concentration of cyclic ethers match the magnitude of the measured values.
Figures 13 and 14 present the validation of the model against experimental data from previous studies [16-17] in the same jet-stirred reactor. The experimental conditions are similar having a fuel concentration of 0.5% using helium as the diluent gas. The pressure was 1.06 bar with the residence time of 2s. The equivalence ratios were 1.0 and 3.0, respectively. The agreement of the predicted mole fraction profiles with the measured ones is good for the major species. Figures 13 (d) and Fig. 13 (f) show the mole fraction profiles of cyclic ethers and the heptene isomers. The cyclic ethers are well-predicted, while the heptenes are over-predicted within a factor of two. Similar trends are seen in Fig. 14 (d) for the $\varphi = 3.0$ condition, as the concentrations of the two cyclic ethers are well predicted, while the agreement for 1- and 2-heptene shown in Fig. 14 (f), are better than those at the stoichiometric condition. However, certain deviations are observed at low temperatures for oxygenated species at $\varphi = 3.0$, such as acetaldehyde and propanal shown in Fig 14 (c) and (e). Figure 15 shows the validations at higher pressures, which uses the experimental data from Dagaut et al. [14]. The model can in general reproduce well the species mole fraction profiles. The predicted mole fraction profiles of the heptane isomers agree better with the experimental results as shown in Fig. 15 (f) compared to those at 1.06 bar, while certain deviations between the experimental and modeling results can be observed for some smaller alkenes such as ethylene and propene as shown in Fig. 15 (b) and Fig. 15 (c). These observations indicate that the consumption pathways for the primary oxidation products of $n$-heptane may need further refinement, possibly by firstly considering their pressure dependence.

Simulations have also been performed using the mechanisms proposed by Mehl et al. [42], Herbinet et al. [16], Pelucchi et al. [44] Seidel et al. [30] and Cai et al. [46] and compared with those of the current mechanism. The experimental data sets are taken from [16]. Comparisons are shown in Fig. 16, with each row comparing the simulated results using the current mechanism compared to the target mechanism, which indicates that the current mechanism has an overall better performance. Rate of production analyses have been performed for $n$-heptane oxidation in the jet-stirred reactor using helium diluted at 0.5% fuel, at a residence time of 2 s, at $\varphi = 1$, and at $T = 650, 850$ and 1000 K in order to reflect the significant reaction pathways over the entire temperature range. Based on the results at the three different temperatures, a reaction pathway diagram has been generated following two principles and is shown in Fig. 17. Considering the neatness of the diagram, the first principle is that, the reaction pathways with contributions of less than 10% at all three temperatures are not shown. Some of the remaining pathways may have very low contributions at either low or high temperatures due to their dependence on temperature; e.g. the addition of fuel derived radicals to oxygen. Therefore the second principle is that, if a reaction pathway has a contribution of less than 6%, the contributions of the sequent reaction pathways of its product are not shown. The arrows denote reaction pathways, with their contributions under different temperatures indicated using different fonts: red italic denotes $T = 650$ K, black bold denotes $T = 850$ K and blue underlined denotes $T = 1000$ K.

At all three temperatures, fuel consumption occurs mainly via H-atom abstraction by the radical pool, with a slight change in the branching ratios leading to different fuel derived radicals (R). An
analysis of the branching ratio for abstraction by different radicals indicates that the contribution of H-atom abstraction by OH radicals to fuel consumption is 95.8% at 650 K, 78.1% at 850 K and 43.5% at 1000 K, while that by H atoms is 3.1% at 650 K, 9.1% at 850 K and 52.7% at 1000 K. This reflects the inhibited chain propagating process due to increasing temperature, as well as the enhanced β-scission of fuel derived radicals which readily produce H atoms in the sequent dehydrogenation reactions. This overall trend can also be observed from the change in flux distribution with increasing temperature. Unlike those of OH radicals and H atoms, the contributions to fuel consumption of H-atom abstraction by HO₂ radical is 0.7% at 650 K, 9.1% at 850 K and 2.2% at 1000 K. This trend is consistent with the discussions on sensitivity analysis for ignition delay time in that H-atom abstraction from the fuel by HO₂ radicals plays an important role at intermediate temperatures (~850–1300 K). The production of R radicals is depicted in the upper left part of Fig. 17, and the consumption is shown in the order of 1-, 2-, 3- and 4-heptyl vertically. In general, the chain propagation and chain branching processes in the consumption of each fuel radical are depicted from left to right in Fig.17; the left edge shows the reaction classes such as the β-scission and isomerization reactions of alkyl radicals, followed by chain propagation reactions including the addition of alkyl radicals to O₂, concerted elimination of RÖ₂ radicals producing an HÖ₂ radical and an olefin, which competes with the isomerization of RÖ₂ into ÕOOH radicals. In the middle part of Fig.17, the multiple consumption channels of ÕOOH are shown, including ÕOOH radical addition to O₂, the formation of cyclic ethers and also the β-scission reactions producing smaller molecule products. On the right edge, the chain branching step is reached via the formation of ketoxydperoxide species and bi-hydroperoxy alkyl radicals. The formation and decomposition of the former produce two OH radicals in total, while the decomposition of the latter also releases two OH radicals. The further decomposition pathways of these species are not depicted here in order to reduce the size of the figure. Alternative isomerization reactions are more important for Õ₂QOOH radicals where the hydroperoxy groups are on primary carbon atoms. This is because the C–H bonds are stronger and are not favored by the internal H-atom transfer process. Although for n-heptane, the alternative isomerization reaction leads to chain branching which can also be reached via the formation of ketoxydperoxides, this additional pathway may be important for branched alkanes when the formation of ketoxydperoxides is not possible [51]. At 650 K, the chain branching process dominates, with the production of ketoxydperoxides and bi-hydroperoxy alkyl radicals at the right end of Fig.17. The β-scission pathway of each fuel derived radical can be neglected. The concerted elimination reactions of RÖ₂ have lesser contributions compared to those of the isomerization into ÕOOH radicals. However, ignition delay time predictions are very sensitive to these concerted elimination reactions where an increase in their rate reduces reactivity, as shown in Fig 9. On the other hand, the flux leading to cyclic ethers is quite high. For each RÖ₂ radical, the 1,4 H-atom transfer channel is favored over the other isomerization pathways, and the sequent formation of five membered ring cyclic ethers dominates the consumption of the corresponding ÕOOH radicals. However, the reactivity of the system is in-sensitive to the formation of cyclic ethers.
because these chain propagation reactions produce OH radicals which are much more reactive than the
H₂O₂ radicals produced from the concerted elimination reactions of RO₂ radicals at low temperatures. As
the temperature increases to 850 K, the chain propagation pathways become more dominant and there is
little flux to chain branching and QOOH radical addition to O₂. An obvious feature in the reaction
pathways is that the concerted elimination reactions largely consume RO₂ radicals, especially secondary
RO₂ radicals since there are more hydrogen atoms on the beta carbons. Meanwhile, the formation of
cyclic ethers is also enhanced. As has been discussed previously, the production of 1-heptyl radicals
promotes reactivity, with this class of reaction showing a relatively large sensitivity coefficient at
intermediate temperatures. This may be partly explained by the consumption channels of different fuel
radicals shown in Fig. 17. While the concerted elimination reaction dominates the consumption of 2-, 3-
and 4-heptyl radicals, the isomerization reactions contribute about 69% in total to the consumption of 1-
heptyl radicals. Therefore the production of 1-heptyl radicals, compared to the other heptyl radicals,
increases the chain branching process, and thus promotes reactivity. At the higher temperature condition
of 1000 K, the only important consumption pathways for alkyl radicals are β-scissions, simultaneously
producing smaller hydrocarbon radicals and olefins. Therefore the chemistry of these smaller
hydrocarbon species becomes important in controlling the reactivity of the system. The addition of alkyl
radicals to molecular oxygen has only a minor contribution to the overall flux of the system.

Rate of production analyses have also been performed at ϕ = 0.25 and ϕ = 4.0 at T = 650 K to
determine the influence of equivalence ratio upon the oxidation of n-heptane through the reaction
pathways shown in Fig. 17. The contributions have been marked with numbers in red frames and
numbers with red backgrounds for ϕ = 0.25 and ϕ = 4.0 at T = 650 K, respectively. As shown by the
experimental conditions in Table 3, the concentration of the fuel remains constant, while that of oxygen
varies with increasing equivalence ratio. As a result, the reactions involving oxygen are enhanced at ϕ =
0.25 and inhibited at ϕ = 4.0. This is reflected in Fig. 17 in that the additions of Ṛ and QOOH radicals
to molecular oxygen, especially the latter, have higher contributions at the fuel-lean condition. For
easy, the addition of C₇H₁₄OOH₄ radicals to oxygen account for 89.2%, 67.2% and 35.5% to its
consumption at ϕ = 0.25, 1.0, and 4.0, respectively, shown at the bottom of Fig. 17. For the
consumption of QOOH radicals, the lower contribution of the addition to O₂ with an increase in
equivalence ratio leads directly to the higher contribution of cyclic ether formation. Meanwhile, the
equilibrium between RO₂ and QOOH radicals is also affected. As the consumption of QOOH radicals is
actually inhibited by the lack of O₂ at the fuel-rich condition, the isomerization of QOOH radicals back
to RO₂ radicals and the consumption of RO₂ radicals via other reaction pathways are promoted. Figure
17 shows that the production of 3-heptene from C₇H₁₅-O₂ radical contribute 15.3%, 32.9% and 45.7%
to its consumption at ϕ = 0.25, 1.0, and 4.0, respectively. According to the results and discussions of the
sensitivity analysis shown in Fig. 9, these changes lead to a lower reactivity at fuel-rich conditions,
which is consistent with the fuel consumption values shown in Figs. 10–12 (b). On the other hand, the
branching ratios in the production of different fuel derived radicals are very similar at all of the three
equivalence ratios. This is because H-atom abstraction from the fuel occurs mainly via OH radicals, with only minor contributions from the other radicals, but varies with equivalence ratio. Similarly, the branching ratios of different consumption channels of O₂QOOH radicals are also highly consistent despite of the varying equivalence ratio, since they are mainly consumed via isomerization and sequent decomposition.

Laminar flame speed predictions

The current mechanism has been validated using the laminar flame speed data reported in [24-26]. The comparisons are shown in Figs. 18–20. The simulation used the premix code in CHEMKIN PRO [84]. Considering the high temperature condition in the flame, the current mechanism has been reduced by removing most of the reactions involving low-temperature species. This reduced mechanism, or the high temperature version of the current mechanism, is also available as Supplementary material and at the C3 website: http://c3.nuigalway.ie/.

Dirrenberger et al. measured adiabatic laminar burning velocities of n-heptane at 1 atm using a flat flame adiabatic burner [26]. The heat flux method was used to determine burning velocities at conditions for which the net heat loss of the flame is zero. Figure 18 shows the experimental data sets reported for n-heptane flame speeds, which were measured at 298 K, 358 K and 398 K [26]. The model predicts well the flame speeds except for the under-prediction at fuel-rich conditions, which is similar to the deviations between the experimental and modeling results presented in the original paper [26]. Sileghem et al. measured the laminar burning velocities of n-heptane using the heat flux method for a flat flame adiabatic burner at atmospheric pressure and at multiple initial temperatures from 298 K to 358 K [25]. Good agreement can be seen between the experimental data and the simulations using the current model for all data sets at initial temperature from 298 K to 358 K (Fig. 19). Only slight under-predictions can be seen at the initial temperature of 358 K. The deviations are mostly within the reported uncertainty range (± 1.4 cm/s for equivalence ratio = 1.3 and ±1 cm/s for the other equivalence ratios).

The current mechanism has been further validated against flame speed data at elevated pressures. Kelly et al. performed experimental study on laminar flame speeds and Markstein lengths studies for C₅–C₈ n-alkane mixtures in air at pressures of up to 10 atm [24]. Figure 20 shows the measured n-heptane flame speeds at an initial temperature of 353 K and at pressures of 1, 2, 5, and 10 atm, respectively. The predicted flame speeds agree well with the experimental results at all pressures, with slight under-predictions at 5 atm which are within the reported uncertainty range of ± 2 cm/s. This indicates that the pressure dependence of the high temperature chemistry is reasonable in the current mechanism.
Conclusions

In this work, the oxidation of n-heptane has been firstly investigated experimentally. A detailed chemical kinetic model has been developed to numerically describe these experimental observations. Good agreement is observed between the model predictions and measured ignition delay times. In general, the model also satisfactorily captures the trend in the mole fraction profiles of most species measured in a jet-stirred reactor over a very wide range of equivalence ratios (0.25, 2.0 and 4.0). A good performance of the current mechanism is also indicated via further validations and comparisons to several recently published n-heptane mechanisms. The reaction rate rules used in this mechanism are consistent with those used for the pentane isomers [51, 55] and n-hexane [54] sub-mechanisms. Therefore good consistency in kinetic can be expected, which is important regarding simulations for fuel mixtures. The reaction rate rules have been shown to lead to reasonably good predictions and may thus be used in the development of mechanisms of larger alkanes.

Acknowledgments

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References


Table 1. Nomination of some representative species in $n$-heptane sub mechanism.

<table>
<thead>
<tr>
<th>Species</th>
<th>Structure</th>
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<tbody>
<tr>
<td>$nC_7H_{16}$</td>
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</tr>
<tr>
<td>$\cdot C_7H_{15}$-1</td>
<td>![Image]</td>
</tr>
<tr>
<td>$C_7H_{14}$-1</td>
<td>![Image]</td>
</tr>
<tr>
<td>$C_7H_{15}O_2$-2</td>
<td>![Image]</td>
</tr>
<tr>
<td>$\cdot C_7H_{14}OOH_2$-4</td>
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<tr>
<td>$C_7H_{14}$-O$_2$-5</td>
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</tr>
<tr>
<td>$C_7H_{14}OOH_2$-$4O_2$</td>
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</tr>
<tr>
<td>$\cdot C_7H_{13}$Q13-5</td>
<td>![Image]</td>
</tr>
<tr>
<td>$C_7$KET1-3</td>
<td>![Image]</td>
</tr>
<tr>
<td>$C_7$KET1-3O</td>
<td>![Image]</td>
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<tr>
<td>Reaction</td>
<td>Rate rules</td>
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<tr>
<td>$\text{RO}_2 \rightleftharpoons \text{QOOH}$</td>
<td>Table 6 in [68]</td>
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<tr>
<td>Cyclic ether formation</td>
<td>Table 3 in [72]</td>
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<tr>
<td>Concerted $\text{H}_2\text{O}_2$ elimination</td>
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<tr>
<td>Second addition to $\text{O}_2$</td>
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Table 3. The detailed composition of the reactant mixtures in jet-stirred reactor experiments.

<table>
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<tr>
<th>$\varphi$</th>
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<td></td>
<td>$n$-heptane</td>
<td>$O_2$</td>
<td>He</td>
</tr>
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<td>4.00</td>
<td>0.50</td>
<td>1.38</td>
<td>98.13</td>
</tr>
<tr>
<td>2.00</td>
<td>0.50</td>
<td>2.75</td>
<td>96.75</td>
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<tr>
<td>0.25</td>
<td>0.50</td>
<td>22.00</td>
<td>77.50</td>
</tr>
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</table>
Figure 1. Reaction pathways considered in the model development of this work. The reaction pathways induced by the alternative isomerization of peroxy hydroperoxalkyl have been marked with open arrows.

F = fuel, R = fuel derived radical, RO2 = alkyl peroxy radical, QOOH = hydroperoxalkyl radical, ROOH = alkyl hydroperoxide, RO = alkoxyl radical, C-ETH = cyclic ether, O2OOOH = peroxy alkylhydroperoxide radical, HOOPOOH = dihydroperoxalkyl radical, KET = keto-hydroperoxide, C-ETH-OOH = hydroperoxy cyclic ethers, EROOH = olefinic hydroperoxalkyl, E = alkene, ER-O = olefinic alkoxy radical, prd = decomposition products
Figure 2. Experimental (symbols) and modeling results (lines) for \(n\)-heptane ignition delay times at multiple conditions (in air, \(\phi = 1.0\)). Half-filled symbols are experimental data from [82], while solid symbols are experimental data measured in this work. Open symbols are experimental data from [83]. Solid and dashed lines are predictions with and without the modifications in the rate rules, respectively.
Figure 3. An example non-reactive pressure trace

\[ \frac{d(p/p_0)}{dt} = 8\% /\text{ms} \]
Figure 4. Experimental (symbols) and modeling results (lines) for ignition delay times of stoichiometric $n$-heptane/air mixture at 15 bar. Solid and dashed lines are predictions with and without the modifications in the rate rules, respectively.
Figure 5. Experimental (symbols) [86] and modeling results (lines) for n-heptane/15%O2/5%CO2/Ar mixture ignition delay times at multiple conditions. Solid lines are predictions using current mechanism and dashed lines are predictions using mechanisms from (a) [42], (b) [16], (c) [30], (d) [46].
Figure 6. Experimental (symbols) [45] and modeling results (lines) for n-heptane/air mixture ignition delay times at multiple conditions.
Figure 7. Experimental (symbols) [5] and modeling results (lines) for \textit{n}-heptane/air mixture ignition delay times at multiple conditions.
Figure 8. Comparisons of the predicted ignition delay times at multiple conditions using the current mechanism and several other ones proposed recently. Experimental data (symbols) are from [5]. Solid lines are predictions using current mechanism. Dashed lines are predictions using mechanisms from: (a) [42], (b) [16], (c) [44], (d) [30], (e) [46].
Figure 9. Sensitivity analysis on the ignition delay time of $n$-heptane at $T = 720$ K, 820 K and 1000 K, $p = 20$ bar. Negative sensitivity coefficients indicate decreases in ignition delay times.
Figure 10. Experimental (symbols) and modeling results (lines) for \( n \)-heptane oxidation in jet-stirred reactor at 1.06 bar with residence time = 2 s, \( \phi = 4.0 \), 0.5% fuel diluted by helium. Solid and dashed lines are predictions with and without the modifications in the rate rules, respectively.
Figure 11. Experimental (symbols) and modeling results (lines) for \( n \)-heptane oxidation in jet-stirred reactor at 1.06 bar with residence time = 2 s, \( \phi = 2.0 \), 0.5% fuel diluted by helium. Solid and dashed lines are predictions with and without the modifications in the rate rules, respectively.
Figure 12. Experimental (symbols) and modeling results (lines) for \( n \)-heptane oxidation in jet-stirred reactor at 1.06 bar with residence time = 2 s, \( \phi = 0.25 \), 0.5% fuel diluted by helium. Solid and dashed lines are predictions with and without the modifications in the rate rules, respectively.
Figure 13. Experimental (symbols) [16] and modeling results (lines) for \(n\)-heptane oxidation in jet-stirred reactor at 1.06 bar with residence time = 2 s, \(\phi\) = 1.0, 0.5% fuel diluted by helium.
Figure 14. Experimental (symbols) [17] and modeling results (lines) for \( n \)-heptane oxidation in jet-stirred reactor at 1.06 bar with residence time = 2 s, \( \phi = 3.0 \), 0.5% fuel diluted by helium.
Figure 15. Experimental (symbols) [17] [14] and modeling results (lines) for $n$-heptane oxidation in jet-stirred reactor at 10 bar with residence time = 1 s, $\varphi = 1.0$, 0.1% fuel diluted by nitrogen.
Figure 16. Comparisons of experimental results (symbols) [16] and predictions using the current mechanism and several other ones proposed recently. Solid lines are predictions using current mechanism. Dashed lines are predictions using mechanisms from: Row (a) [42], Row (b) [16], Row (c) [44], Row (d) [30], Row (e) [46].
Figure 17. Reaction flux for $n$-hexane oxidation in jet stirred reactor at $p = 1.06$ bar with 0.5% fuel in helium, $\tau = 2s$. The contributions of the reactions are marked. Red italic, black bold and blue underlined numbers are at $\varphi = 1.0$, $T = 650$ K, 850 K and 1000 K, respectively. Numbers with red frames and red backgrounds are at $\varphi = 0.25$ and $\varphi = 4.0$ at $T = 650$ K.
Figure 18. Experimental (symbols) [26] and modeling results (lines) for the laminar flame speed of $n$-heptane in air at 1 atm and different initial temperatures.
Figure 19. Experimental (symbols) [25] and modeling results (lines) for the laminar flame speed of \( n \)-heptane in air at 1 atm and different initial temperatures.
Figure 20. Experimental (symbols) [24] and modeling results (lines) for the laminar flame speed of $n$-heptane in air at initial temperature of 353 K and different pressures.