AUTOIGNITION OF n-DECANE/n-BUTYLBENZENE/ n-PROPYLECYCLOHEXANE MIXTURES AND THE EFFECTS OF THE EXHAUST GAS RECIRCULATION

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In the present work, the autoignition of single-component and binary mixtures composed of n-decane, n-butylbenzene, and/or n-propylcyclohexane has been investigated using shock-tube techniques. In addition, the effects of the presence of the exhaust gas recirculation (EGR) components on the autoignition behavior of a 4:3:3 molar n-decane:n-butylbenzene:n-propylcyclohexane surrogate mixture have been investigated experimentally. The experiments have been performed at highly diluted conditions in argon bath gas, over a wide range of temperatures (1250–1750 K), equivalence ratios (ϕ = 0.2–1.5), and nominal pressures of 10–20 bar. A chemical kinetic model was developed to simulate the newly obtained experimental data by blending sub-models from the literature. In particular, the experimental and numerical analyses suggest that the observed increase in the ignition delay times in the presence of EGR is mainly due to the dilution levels and not to the chemistry of the fuel. Additional kinetic analyses were performed to compare the high-temperature autoignition properties of the different components considered herein.

Keywords: Ignition delay time; n-Butylbenzene; n-Decane; n-Propylcyclohexane; Shock tube; Surrogate

INTRODUCTION

Among the various strategies developed to reduce NOx and particulate matter emissions from diesel engines, the use of homogeneous charge compression ignition (HCCI) and exhaust gas recirculation (EGR) provides substantial benefits to the engine performance. In fact, by improving the homogeneity inside the combustion chamber compared to the traditional diesel engines, the soot formation from the local fuel-rich pockets is substantially reduced in the case of HCCI engines. In addition, lower temperatures are attained during the combustion process due to both the improved homogeneity and the dilution of the intake gases by EGR. This aspect determines a drastic reduction in the NOx emissions, although it leads to increased concentrations of CO and unburned hydrocarbons.

The development of optimized HCCI engines necessitates accurate chemical kinetic models for both the fuel decomposition and the consequent formation of pollutants. On the other hand, real fuels are composed of hundreds of components and such complexity poses...
serious limitations to the development of detailed kinetic models. Thus, surrogate mixtures containing few species representative of the main classes of hydrocarbons in the real fuels are commonly used in practical applications. In particular, diesel fuels for HCCI engines are composed of three major classes of compounds, i.e., the paraffins, the aromatics, and the naphthenes. In the present investigation three hydrocarbon compounds representative of the above mentioned classes are considered, i.e., n-decane, n-butylbenzene, and n-propylcyclohexane.

The proposed components have been studied in detail as single reactants. Numerous investigations have focused on the chemistry of n-decane; thus, only the works relevant to the present study will be reported. In particular, the autoignition properties of n-decane/air mixtures have been investigated over a wide range of temperatures (635–1300 K) and pressures (9–80 atm) using shock tube and rapid compression machine techniques (Kumar et al., 2009; Pfahl et al., 1996; Shen et al., 2009; Zhukov et al., 2008). In addition to the experiments in air, ignition delay time measurements have been performed for diluted mixtures in argon (Davidson et al., 2001; Horning et al., 2002; Olchanski and Burcat, 2006). In particular, the extensive work by Olchanski and Burcat (2006) include measurements performed over a wide range of equivalence ratios, for pressures between 1.8 and 10 atm, and dilution factors between 75.25% and 95%.

While the chemistry of the alkane component has been extensively studied in the past, the experimental investigations on the cyclic compounds are rather limited. The n-butylbenzene studies include species measurements in the atmospheric flow reactor at Princeton (Brezinsky et al., 1986) and in jet-stirred reactors by Diévart and Dagaut (2011) at a pressure of 10 atm and Husson et al. (2012) at atmospheric pressure. Ignition delay measurements at relatively low temperatures (below 960 K) were obtained using rapid compression machines (Husson et al., 2012; Nakamura et al., 2013; Ribaucour et al., 2000; Roubaud et al., 2000), while higher temperature shock tube studies were performed by Husson et al. (2012) and by Nakamura et al. (2013) at dilution conditions as in air. The autoignition studies cover a wide range of temperatures (640–1750 K), pressures (1–50 atm), and equivalence ratios (Φ = 0.3–2).

Concerning n-propylcyclohexane, species profiles were measured in a jet-stirred reactor by Ristori et al. (2001), while other studies focused on the flame properties (Dubois et al., 2009; Ji et al., 2011; Liu et al., 2013). The work by Dubois et al. (2009) also contains an extensive shock tube study on the ignition delay time measurements of highly diluted n-propylcyclohexane/O₂/argon mixtures (93.1% to 99.5% argon bath gas). The experimental conditions implemented in the autoignition study cover a temperature range between 1250 and 1800 K, pressures between 10 and 20 bar, and various equivalence ratios (Φ = 0.2–1.5). An additional investigation on the autoignition properties of n-propylcyclohexane was conducted by Crochet et al. (2010) using a rapid compression machine at lower temperatures (620–930 K).

Although n-decane, n-butylbenzene, or n-propylcyclohexane was used in many surrogate formulations, no studies have been performed on the proposed mixture. Herein, a shock tube technique will be used to study the autoignition of single-component and binary mixtures as a preliminary work for the subsequent investigation on the ternary mixture with and without the presence of EGR components. In particular, the proportion between the various components in the ternary mixture (4:3:3 n-decane:n-butylbenzene:n-propylcyclohexane in moles) is based on the composition in mass of an average European diesel fuel. It is important to underline the fact that the aim of the current study is not to mimic the conditions encountered in real HCCI engines, where the ignition occurs in two separate steps.
specifically associated with the low-temperature and the high-temperature chemistry of the fuel. In this case, the use of EGR techniques and the associated reduction in the overall combustion temperatures have a strong effect on the low-temperature chemistry and consequently on the total ignition delay. The experiments presented here were obtained at high temperature, highly-diluted conditions and the results cannot be compared directly to real engine studies. On the other hand, the analyses will be useful to clarify some of the aspects related to the effect of the EGR on the second stage of the ignition process, the one driven by the high-temperature chemistry. More importantly, the current investigation provides an important set of experimental data for the validation of chemical kinetic models for potential diesel surrogate mixtures.

EXPERIMENTAL AND MODELING TECHNIQUES

Experimental Apparatus

Ignition delay time measurements were obtained using a heated stainless steel shock tube. The shock tube is composed of a low pressure 5.15-m-long driven section with a 52.5-mm internal diameter and a high pressure 2-m-long driver section (114.3 mm i.d.). The whole experimental apparatus is heated to 130°C to avoid any condensation. The double diaphragm technique was used to generate shock waves by rupture of two terphane polyester diaphragms located in series between the driven and the driver sections. The driven section is equipped with four piezoelectric sensors (CHIMIE METAL A25L05B) placed along the internal wall of the tube. These sensors are characterized by a very small sensitive area (0.97 mm in diameter) and, hence, allow a very precise location of the shock wave leading to a very small error in the velocity measurement. For a shock speed of 810 m/s, the calculated error is ±0.2%. Over the whole range of the study, the error on the shock speed is less than 1%. The pressure profiles from the four sensors provide the measurement of the incident shock wave velocities. Such velocities are subsequently used together with the initial conditions to calculate the pressure and temperature conditions behind the reflected shock waves by solving the conservation equations. The estimated errors in the temperature and pressure calculations are, respectively, 1% and 1.5% based on the very low error on the shock wave speed as previously mentioned. In addition, spectrophotometric measurements were performed at the location of the last pressure transducer (10 mm from the end wall) using a HAMAMATSU R928 photomultiplier with a narrow band filter at 431 nm for the CH∗ radicals and a HAMAMATSU 1P28 photomultiplier with filter at 307 nm for the OH∗ radicals. Typical pressure and emission signals are reported in the Supplemental Content (available online). In the present work, the ignition delay time is defined as the time between the arrival of the incident shock wave at the measurement location and the time when the OH∗ profile reaches 50% of its maximum value. Similar results were obtained from the CH∗ profiles, which were consequently used to test the accuracy of the measurements. The maximum error in the ignition delay time measurement is around 25% for the lowest ignition times, while at lower temperatures where the ignition delay times are longer this value decreases to around 2%.

The nonideal effects in the shock tube were characterized using nonreactive argon gas. These experiments were performed with a quartz pressure sensor (Kistler 603B1) mounted at the end-wall perpendicularly to the flow in order to monitor the pressure in the tube during the observation time. The pressure rise was found to be around 4%/ms on average. Assuming an isentropic compression process behind the reflected shock wave, the corresponding temperature rise is about 1.6%/ms.
Reagent mixtures diluted in argon (Air Liquide, 99.999%) were prepared manometrically in a 30-L stainless steel stirred tank. The mixture preparation bench is equipped with three different capacitive pressure gauges in order to have an accurate mixture, they have an accuracy of 0.5% on the reading; the first one (MKS-631C) has a full scale of 10 Torr, the second one (MKS-631B) of 100 Torr, and the third (MKS-631D) one of 1000 Torr. Hence, the error on the molar fraction of each component corresponds to 0.5%, which leads to a 1% error on the equivalence ratio. The chemicals used in the different mixtures were n-decane (Sigma-Aldrich, 99+%), and/or n-butylbenzene (Aldrich, 99+%), and/or n-propylcyclohexane (Aldrich, 99+%). For the experiments conducted with EGR gases, the corresponding mole fraction in the reagent mixture (thus excluding the argon bath gas) is equal to 0.4, which corresponds to a typical value for HCCI engine operations. In order to choose a realistic EGR composition, PSA–Peugeot–Citroën performed tests on a diesel engine bench and analyzed the exhaust gases (Dubois, 2009). The gases were found to be constituted of: 78% N₂, 11% O₂, 6.7% CO₂, 0.2% CO, 3.9% H₂O, and 0.002% CₓHᵧ, the percentage being volumetric. The EGR composition in this study was then chosen as follows (in moles): 78% N₂ + 11% O₂ + 7% CO₂ + 4% H₂O.

**Chemical Kinetic Model**

The chemical kinetic model necessary to simulate the high temperature data obtained in the present investigation needs to include the detailed chemistry of n-decane, n-propylcyclohexane, and n-butylbenzene. The chemistry of these components is rather complicated; thus, it is beyond the scope of the present study to build a new kinetic model. On the other hand, a chemical kinetic model has been developed based on the single-component kinetic models available in the literature. In particular, the JetSurF version 2.0 model (Wang et al., 2010) represents a comprehensive model for both n-alkanes up to n-dodecane and single-ring alkylated cycloalkanes. The n-propylcyclohexane sub-model present in JetSurF has been validated against the experimental results by Dubois et al. (2009) obtained at similar conditions as the ones implemented in the present study. Thus, both the alkane chemistry, which includes the base C₀–C₄ submechanism, and the n-propylcyclohexane chemistry were taken from JetSurF version 2.0. The original model also contains a set of reactions for the formation of benzene and toluene, but this part of the model is limited. Thus, the aromatic chemistry was modified based on other contributions. In particular, the chemistry of n-propylbenzene, which includes the benzene and toluene sub-models, was selected from the work by Mzé-Ahmed et al. (2010), while the specific chemistry of n-butylbenzene was from the work by Diévart (2008).

The interactions between the chemistry of the various components are accounted for by the reactions of the components with the small radicals in the C₀–C₄ submechanism as in the original models. The blended model was tested against the n-butylbenzene data available in the literature. The analysis showed that the model is able to simulate reasonably well the high-pressure jet stirred reactor and shock tube data, although at atmospheric pressure conditions the reactivity of n-butylbenzene is overestimated. On the other hand, the simulation results obtained at the conditions studied herein are rather satisfactory and the blended model fits for the purpose of the present experimental investigation. Nevertheless, additional work will be necessary to improve the prediction capability.

The ignition delay times were calculated based on the OH⁺ profiles and estimated as equal to the time when the corresponding profile reaches 50% of its maximum value,
similarly to the experimental definition. All the simulations have been performed assuming constant volume conditions behind the reflected shock waves using Cosilab software, version 3.3.2.

RESULTS AND DISCUSSIONS

Single Components

The investigation on the single-component mixtures has been performed as a preliminary benchmark for the subsequent multi-components studies. As already mentioned, the ignition delay time measurements for n-propylcyclohexane, in highly diluted mixtures, have been reported by Dubois et al. (2009). Since the JetSurF 2.0 model has been validated against such experimental data, no additional analyses will be performed herein. Similarly, the model has been extensively validated against n-decane experimental data. On the other hand, in order to further test the kinetic model against ignition delay time measurements at conditions relevant to the present study, three experimental sets were obtained at different equivalence ratios and constant dilution equal to 99% (argon bath gas). The results are reported in Figure 1, where the modeling results are also shown. As expected, the reduction in the fuel concentrations from rich to lean mixtures leads to a decrease in the ignition delay times. Although there is a slight over-prediction of the ignition delay times at fuel-rich and stoichiometric conditions, the model correctly captures the experimental trends.

While for n-decane and n-propylcyclohexane the corresponding chemistry as described in the JetSurF model was not modified, the aromatic chemistry added for n-butylbenzene requires a more extensive validation. Thus, the n-butylbenzene experiments were conducted varying the initial conditions over a wide range of equivalence ratios, dilutions, and pressures. In particular, several experimental sets were obtained in 99% argon

![Figure 1](image-url)  
Figure 1 Ignition delay times of highly diluted n-decane/O₂ mixtures in 99% argon, nominal pressure equal to 10 bar. ◇, ---: Φ = 1.5; △, --: Φ = 1.0; □, -: Φ = 0.5.
bath gas at various equivalence ratios (Φ = 1.5, 1.0, 0.5, and 0.2) and at a nominal pressure of 10 bar (Figure 2a). Additional experiments were performed varying the percentage of argon up to 99.5% for pressures of around 20 bar (Figure 2b). As for n-decane, in both cases the reduction in the fuel concentrations from rich to lean mixtures leads to a decrease in the ignition delay times as depicted in Figures 2a and 2b for similar dilution conditions. An analogous experimental trend can be observed when the autoignition measurements conducted at different equivalence ratios (Φ = 1.0, 0.5, and 0.2) and same initial fuel mole fraction (0.1%) are compared (Figure 2c). In this case the decrease in the ignition times from stoichiometric to lean conditions is even more evident than in Figures 2a and 2b and is due to the change in the initial oxygen concentrations. In fact, in order to vary the equivalence ratio at constant fuel concentration, the O₂ mole fraction needs to be adjusted. In particular, the increased oxygen concentrations at lean conditions reduce the autoignition times of the mixtures. In Figure 2c the argon dilution for the stoichiometric mixture corresponds to 98.6%, for Φ = 0.5 to 97.2%, and finally for Φ = 0.2 it corresponds to 93.2%.
The experimental results presented in Figure 2 were used to derive an overall correlation for the ignition delay times of n-butylbenzene in the following format:

$$
\tau(\mu s) = A \times [C_{10}H_{14}]^a \times [O_2]^b \times [Ar]^c \times \exp\left(\frac{E_a}{RT}\right)
$$

where $A = (3.09 \pm 1.09) \times 10^{-8}$, $a = 0.69 \pm 0.02$, $b = -1.22 \pm 0.03$, $c = -0.24 \pm 0.05$, $E_a/R = 21950 \pm 338$ K, and where the concentrations are expressed in mol/cm$^3$ and the temperatures in K. Such an expression well fits the experimental results as shown in Figure 2d, where the normalized ignition delay data are compared to the correlation function obtained by statistical analysis ($r^2 \sim 0.965$). The normalized ignition delay time is here defined as the ratio between the ignition delay time and the relative concentrations of fuel, oxygen, and argon elevated at the corresponding coefficients ($a$, $b$, and $c$).

Figure 2 also contains the simulation results obtained using the model described in the previous sections. The model reproduces reasonably well the global activation energy of the ignition process represented by the slope of the curves. For the conditions reported in Figures 2a and 2c the simulations are in excellent agreement with the experiments, while at higher dilutions (99.5%) the model slightly over-predicts the experimental results at most equivalence ratios (Figure 2b). Overall the simulations indicate that the blended model is appropriate for the prediction of the n-butylbenzene autoignition behavior at the highly diluted conditions implemented in the present investigation.

**Binary Mixtures**

Before proceeding to the results on the ternary mixture, additional experiments were performed on binary mixtures composed of n-decane and one of the two cyclic compounds of interest, n-butylbenzene or n-propylcyclohexane. Once again, these results are important for the validation of the blended chemical kinetic model, which will be subsequently used for the simulation of the ternary mixture. For this part of the study, the mole fraction of n-decane in the fuel mixtures is equal to 0.6. The results obtained at a constant dilution factor of 99%, $\Phi = 1.5$, 1.0, 0.5, and 0.2, and nominal pressure of 10 bar are reported in Figure 3. The experiments conducted with the n-decane + n-butylbenzene mixture (Figure 3a) and the n-decane + n-propylcyclohexane mixture (Figure 3b) follow a similar trend compared to the single-component experiments, with an increment of the ignition delay times at higher equivalence ratios. A more detailed comparison between the results for single-component and binary mixtures will be presented in the next section. The simulations quite accurately reproduce the experimental global activation energy of the ignition process represented by the slope of the curves. It is also noticeable how the experimental ignition delay times are well reproduced by the model at fuel lean conditions although slightly overpredicted at rich and stoichiometric conditions. This may suggest the necessity of additional modeling work on the pyrolytic mechanisms especially in relation to the n-decane chemistry.

**Ternary Mixtures**

After considering the single-component and the binary mixtures, the ternary mixture has been studied as a base for the subsequent addition of EGR gases. Experiments have been conducted in the temperature range between 1260 K and 1740 K, at nominal
pressure of 10 bar, and equivalence ratios between 1.5 and 0.2. Selected experimental and modeling results for various equivalence ratio conditions are presented in Figure 4a. The experimental results show the expected increase in the ignition delay times at higher equivalence ratios. The experimental trends are once again well reproduced by the model, which simulates quite accurately the experimental global activation energy of the ignition process. Additional experiments have been performed in the presence of EGR gases at similar conditions to the ones implemented in the ternary mixture study \((T = 1260–1745 \text{ K}, p \sim 10 \text{ bar}, \text{ and overall equivalence ratios between 1.5 and 0.2})\). As mentioned above, the EGR gases are composed of \(\text{N}_2, \text{O}_2, \text{CO}_2, \text{and H}_2\text{O}\), and the corresponding total mole fraction is 0.4 with respect to the reagent mixture. The results, reported in Figure 4b, reproduce the similar experimental and modeling trends observed for the ternary mixture.

Nevertheless, in order to assess the influence of the EGR on the ignition delay times, a direct comparison between the different experimental results is necessary. In view of the practical relevance to HCCI engines, where the global equivalence ratio is controlled by
adjusting the flows of fresh fuel, air, and EGR gases, ignition delay data for similar overall equivalence ratios have been compared. In Figure 5, the case of stoichiometric mixtures is reported. As expected, the presence of the EGR gases increases the ignition delay of the mixture for all the conditions studied, with an average measured increment, which varies between 17.5% at \( \Phi = 1.5 \) and 50.7% at \( \Phi = 0.2 \). If all of the experimental data sets are considered, the overall average ignition delay time increase due to EGR is close to 31%. Since this value was obtained by comparing the exponential fits of numerous experimental measurements obtained using the same experimental apparatus and procedure, the 31% increase due to the EGR can be considered significant since the uncertainty on a single ignition delay time measurement can reach at most 25% for very short delays, while for longer observation times the experimental error is much lower than this value.

The experimental results demonstrate that the presence of the EGR will slow the autoignition of the mixture (Figure 5). It is then important to be able to identify the origin of this effect. Indeed, the decrease of the overall reactivity may be due to two major factors, namely, (i) the chemistry of the fuel burning process and/or (ii) the decrease in the fuel concentration due to dilution. In order to determine the relative importance of these two factors, further analyses are required. First, the overall correlation for the ignition delay times of the ternary mixture has been derived as:

\[
\tau(\mu s) = A \times [\text{fuel}]^a \times [\text{O}_2]^b \times \exp\left(\frac{E_a}{RT}\right)
\]  
(2)

where \( A = (5.28 \pm 1.54) \cdot 10^{-6} \), \( a = 0.92 \pm 0.04 \), \( b = -1.20 \pm 0.05 \), \( E_a/R = 23216 \pm 477 \, \text{K} \), and where the concentrations are once again expressed in mol/cm\(^3\) and the temperatures in K. In this expression, the coefficient for the oxygen concentration has been imposed as similar to the coefficients derived from the studies performed on the single components.
n-decane, n-butylbenzene, and n-propylcyclohexane. A variation in the assumed coefficient does not cause a substantial change in the derived parameters since the oxygen concentrations do not vary considerably over the different experimental sets. The derived correlation function fits reasonably well the normalized experimental results as shown in Figure 6a.

The correlation has been subsequently used to estimate the ignition delay times for hypothetical (ternary + O2) mixtures having initial fuel and oxygen concentrations equal to the ones present in the corresponding (ternary + EGR + O2) mixtures. The comparison between these estimates and the experimental measurements, presented in Figure 6b for stoichiometric conditions, suggests that the chemistry of the fuel decomposition is not strongly affected by the presence of the EGR gases. In fact, the ignition delay times for the ternary + EGR mixture are similar to the ones obtained when the same fuel and oxygen concentrations are introduced into Eq. (2), which was derived from the experiments without EGR gases. Thus, the effects observed in Figure 5 are mainly due to the dilution of the fuel component. Similar results have been obtained for all the experimental sets with equivalence ratios between 1.5 and 0.3, where the ignition delay times from the correlation and from the experiments agree within the experimental uncertainties, while an average variation of 37.5% has been observed for Φ = 0.2. It is not clear at the moment if such discrepancy is due to real chemical effects or to the summation of errors in the correlation for the specific conditions.

In order to further support the hypothesis that the experimental variation in the ignition delay times due to the presence of an EGR component is primarily a function of the dilution, additional modeling tests have been performed. In this case the simulations of the ternary + EGR experimental results have been compared to simulations conducted at similar conditions with the main components of the EGR gas (CO2, H2O, and N2) replaced by argon. Selected modeling results for stoichiometric conditions are presented in Figure 7. No appreciable difference between the two modeling sets has been observed for all the conditions considered in the present investigation, with a maximum discrepancy of around 5% obtained at stoichiometric conditions. This value is much lower than the average increase of 31% observed experimentally; thus, the modeling results support the above mentioned hypothesis that the presence of the EGR leads to the dilution of the fuel and the oxygen concentrations and thus to an increase in the ignition delay times.
SUPPLEMENTARY KINETIC CONSIDERATIONS

The experimental results presented in the previous sections provide a useful benchmark for the validation of chemical kinetic models for surrogate mixtures. The comparison between the different experimental sets may also be used to clarify the differences in the ignition properties of the various surrogate components. For example, in Figure 8, the stoichiometric experimental results on the binary mixtures are compared to the corresponding single-component cases. It is clear from the comparison in Figure 8a that the autoignition of n-butylbenzene is much slower compared to n-decane. The ignition delay time measurements of the binary mixture lie close to the n-decane ones although slightly

Figure 7 Ignition delay times at stoichiometric conditions; simulations on: △ ternary mixture with EGR, ✶ EGR components replaced by Ar.

Figure 8 Ignition delay times of highly diluted single-component and binary mixtures in 99% argon, nominal pressure equal to 10 bar. (a) ▼: n-butylbenzene, ○: n-decane, △: 60% n-decane + 40% n-butylbenzene (in moles); (b) ◆: n-propylcyclohexane, ○: n-decane, △: 60% n-decane + 40% n-propylcyclohexane (in moles).
higher; thus, the autoignition behavior of the mixture is mainly influenced by the n-decane chemistry.

In order to further understand the reasons of the differences observed in Figure 8a, additional kinetic analyses have to be performed. In particular, the ignition delay times are mainly sensitive to the branching reaction between H and O\textsubscript{2} to form OH + O, thus are influenced by the H atom availability. The simulated H-atoms time histories for the binary mixture and for n-butylbenzene are reported in Figure 9a for a temperature of 1530 K, which corresponds to an intermediate value in our study. Although the peaks at early times are similar, the H profile for the n-butylbenzene case drops to a lower level compared to the binary mixture case. When the hydrogen profile reaches the plateau, the secondary chemistry of the fuel plays an important role in determining the H atom concentration levels. In particular, while the scission of the alkane chain favors the formation of C1–C3 stable compounds, the oxidation of the aromatic ring proceeds mainly through the formation of the cyclopentadienyl radical, which has a strong H-scavenging effect. Other cyclic intermediate compounds act as scavenging elements, including the benzyl and the phenoxy radicals. Figure 9b shows the C2 intermediates as well as the toluene and cyclopentadiene profiles. It is clearly demonstrated that blending an alkane component to n-butylbenzene results in an increment of the small aliphatic species and a marked reduction in the ring scavenging intermediates. As a consequence, a higher H level for the binary mixture compared to n-butylbenzene is reached. The different H-atom availability should explain the dissimilarity between the ignition delay times in Figure 8a.

Different considerations apply for the n-propylcyclohexane case. As shown in Figure 8b, the autoignition of this cyclic compound is slower than n-decane while the binary mixture data lie between the two single-component profiles. On the other hand, the difference between the experimental data on n-propylcyclohexane and n-decane is reduced with respect to the case in Figure 8a relative to n-butylbenzene. Improvements in the modeling prediction for the n-decane profiles in Figure 1 are necessary in order to be able to perform a detailed kinetic examination of the comparison between n-decane and n-propylcyclohexane. On the other hand, a qualitative analysis can be performed based on the experimental and modeling results obtained herein as well as on the similarity with previous studies.

![Figure 9](image-url) Simulated time histories at Φ = 1.0, T = 1530 K, p = 10 bar, 99% argon. (a) H atoms; (b) C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{5}H\textsubscript{6}, and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}. Solid line: n-butylbenzene; dashed line: n-butylbenzene + n-decane mixture.
Figure 10 Selected reaction pathways for the decomposition of n-propylcyclohexane at $\Phi = 1.0$, $T = 1530$ K, $p = 10$ bar, 99% argon. Data at 50% fuel decay.

The n-propylcyclohexane chemistry is rather complex since the alkane ring structure makes possible numerous reaction pathways, including, for example, ring opening, dehydrogenizations, and isomerizations. Figure 10 contains few pathways for the decomposition of n-propylcyclohexane at 1530 K, 10 bar, and 99% dilution in argon for stoichiometric conditions. Three main pathways from the fuel are considered, i.e., the ring opening to form the branched intermediate A (11% of the fuel decay), the C–C $\beta$-scission occurring on the side chain forming cyclohexyl radicals and C$_3$H$_7$ (12%), and the H-atom abstraction from the ring (14%). Figure 10 clearly does not contain a detailed analysis of the chemistry of n-propylcyclohexane since it considers pathways, which account for only 37% of the fuel decay. On the other hand, such pathways are representative of the classes of reactions involving the fuel and are sufficient for the purpose of the present discussion. If all the pathways had been considered, the figure would have been too complicated and the discussion not so clear.

Without discussing the kinetic details, Figure 10 shows an important aspect of the high-temperature chemistry of n-propylcyclohexane, the fact that the major pathways involve the ring opening into linear and branched hydrocarbons, which can further decompose into smaller intermediates. The ring structure is not conserved for such pathways, which results into a substantial reduction in the importance of the ring scavenging process compared to the case of n-butylbenzene. In support of this consideration, the n-propylcyclohexane simulation results indicate that the mole fractions of toluene are essentially negligible and the ones of cyclopentadiene are much lower compared to the levels observed in Figure 9b for n-butylbenzene (maximum value of around 1 ppm for n-propylcyclohexane, 20 ppm for n-butylbenzene). This is a clear indication of the fact that the two major H-atom scavenging intermediates C$_5$H$_5$ and C$_6$H$_5$CH$_2$ are not produced in considerable amounts for the cyclic alkane. Such a result explains the marked difference between the autoignition behaviors of the two cyclic compounds considered herein.

Although the formation of the aromatic structures is reduced for the case of n-propylcyclohexane, the H-atom drop after the initial peak is significant. The modeling results indicate that, at the conditions in Figure 9, the ratio between the maximum initial H peak and the plateau level is around a factor of 4.3, which is lower than the corresponding
factor for n-butylbenzene (11.9) but still considerably high. In a previous study, Hong et al. (2011) experimentally measured the OH profile for a (n-butylcyclohexane + \text{O}_2) mixture in 99.55% argon at a temperature of 1450 K and a pressure of 2.2 atm. The authors observed a strong scavenging effect, which was not present in the n-heptane profile measured by the authors at similar conditions. By analogy, it is reasonable to expect a similar behavior in our results, i.e., a strong scavenging effect for n-propylcyclohexane compared to the one for n-decane. On the other hand, the ratio between the H peak and plateau levels for n-decane is 3.9, thus similar to the one of n-propylcyclohexane (4.3, as mentioned above). This result, when compared to the work by Hong et al. (2011), may suggest modifications in the kinetic model aimed at reducing the H-scavenging effects predicted for n-decane. These corrections would also benefit the simulation results of the n-decane profiles in Figure 1, since it would lead to shorter ignition delay times and to a reduction in the difference between the modeling and the experimental results.

CONCLUSIONS

The high-temperature autoignition of single-component, binary, and ternary mixtures composed of n-decane, n-butylbenzene, and/or n-propylcyclohexane has been studied both experimentally and numerically. The effects of the presence of an EGR component on the ignition delay times of the ternary mixture were also considered. In particular, shock tube experiments have been performed at highly diluted conditions for n-decane and n-butylbenzene. Such data constitute a relevant benchmark for the subsequent model validation. Additional experiments were performed at 99% constant dilution for n-decane + n-butylbenzene and n-decane + n-propylcyclohexane binary mixtures over a wide range of temperatures and equivalence ratios. Finally, the ternary and ternary + EGR mixtures were studied at similar conditions.

A chemical kinetic model has been developed based on models available in the literature; the simulations well reproduce both the experimental trends and the global activation energy, although the ignition delay times of fuel-rich and stoichiometric mixtures are slightly overpredicted by the model for the cases of binary and ternary mixtures.

The comparison between the experimental results shows that for similar equivalence ratios the average increase in the ignition delay times due to the EGR component is almost 31%. Further experimental analyses suggest that such an increment is mainly due to the different fuel dilution levels and not to the fuel decomposition chemistry. This hypothesis has been confirmed by additional simulation results performed using the chemical kinetic model.

Finally, additional experimental and modeling comparisons were performed in order to highlight the different autoignition properties of the various hydrocarbon components studied herein. In particular, the n-butylbenzene decomposition leads to the formation of considerable amounts of cyclic intermediates, which act as H-atom scavengers. As a consequence, the corresponding ignition delay times are much longer compared to the n-decane case. On the other hand, the difference between the n-decane and the n-propylcyclohexane measurements is reduced due to the fact that the cyclic structure is not conserved when the cycloalkane compound decomposes.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher’s website.

REFERENCES

Brezinsky, K., Linteris, G.T., Litzinger, T.A., and Glassman, I. 1986. High temperature oxidation of n-alkyl benzenes. *Proc. Combust. Inst.*, 21, 833.

Crochet, M., Minetti, R., Ribaucour, M., and Vanhove, G. 2010. A detailed experimental study of n-propylcyclohexane autoignition in lean conditions. *Combust. Flame*, 157, 2078.

Davidson, D.F., Herbon, J.T., Horning, D.C., and Hanson, R.K. 2001. OH concentration time histories in n-alkane oxidation. *Int. J. Chem. Kinet.*, 33, 775.

Diévart, P. 2008. Oxydation et combustion en milieu ultra-pauvre de carburants types gazoles. Etude expérimentale en réacteur agité et modélisation. PhD thesis. Université des Sciences et Technologies de Lille, Lille, France.

Diévart, P., and Dagaut, P. 2011. The oxidation of n-butylbenzene: Experimental study in a JSR at 10 atm and detailed chemical kinetic modeling. *Proc. Combust. Inst.*, 33, 209.

Dubois, T. 2009. Etude des mécanismes cinétiques à haute température de mélanges représentatifs de carburants dans des conditions de fonctionnement proches des moteurs HCCI. PhD thesis. Université d’Orléans, Orléans, France.

Dubois, T., Chaumeix, N., and Paillard, C.-E. 2009. Experimental and modeling study of n-propylcyclohexane oxidation under engine-relevant conditions. *Energy Fuels*, 23, 4253.

Hong, Z., Lam, K.-Y., Davidson, D.F., and Hanson, R.K. 2011. A comparative study of the oxidation characteristics of cyclohexane, methylcyclohexane, and n-butylcyclohexane at high temperatures. *Combust. Flame*, 158, 1456.

Horning, D.C., Davidson, D.F., and Hanson, R.K. 2002. Study of the high-temperature autoignition of n-alkane/O₂/Ar mixtures. *J. Propul. Power*, 18, 363.

Husson, B., Bounaceur, R., Tanaka, K., Ferrari, M., Herbinet, O., Glaude, P.A., Fournet, R., Battin-Leclerc, F., Crochet, M., Vanhove, G., Minetti, R., Tobin, C.J., Yasunaga, K., Simmie, J.M., Curran, H.J., Niass, T., Mathieu, O., and Ahmed, S.S. 2012. Experimental and modeling study of the oxidation of n-butylbenzene. *Combust. Flame*, 159, 1399.

Ji, C., Dames, E., Sirjean, B., Wang, H., and Egolfopoulos, F.N. 2011. An experimental and modeling study of the propagation of cyclohexane and mono-alkylated cyclohexane flames. *Proc. Combust. Inst.*, 33, 971.

Kumar, K., Mittal, G., and Sung, C.-J. 2009. Autoignition of n-decane under elevated pressure and low-to-intermediate temperature conditions. *Combust. Flame*, 156, 1278.

Liu, N., Ji, C., and Egolfopoulos, F.N. 2013. Ignition of non-premixed cyclohexane and mono-alkylated cyclohexane flames. *Proc. Combust. Inst.*, 34, 873.

Mzé-Ahmed, A., Hadj-Ali, K., Diévart, P., and Dagaut, P. 2010. Kinetics of oxidation of a synthetic jet fuel in a jet-stirred reactor: Experimental and modeling study. *Energy Fuels*, 24, 4904.

Nakamura, H., Darcy, D., Mehli, M., Tobin, C.J., Metcalfe, W.K., Pitz, W.J., Westbrook, C.K., and Curran, H.J. 2013. An experimental and modeling study of shock tube and rapid compression machine ignition of n-butylbenzene/air mixtures. *Combust. Flame*, 161, 49.

Olchanski, E., and Burcat, A. 2006. Decane oxidation in a shock tube. *Int. J. Chem. Kinet.*, 38, 703.

Pfahl, U., Fieweger, K., and Adomeit, G. 1996. Self-ignition of diesel-relevant hydrocarbon-air mixtures under engine conditions. *Proc. Combust. Inst.*, 26, 781.

Ribaucour, M., Roubaud, A., Minetti, R., and Sochet, L.R. 2000. The low-temperature autoignition of alkylaromatics: Experimental study and modeling of the oxidation of n-butylbenzene. *Proc. Combust. Inst.*, 28, 1701.

Ristori, A., Dagaut, P., Bakali, A.E., and Cathonnet, M. 2001. The oxidation of N-propylcyclohexane: Experimental results and kinetic modeling. *Combust. Sci. Technol.*, 165, 197.
Roubaud, A., Lemaire, O., Minetti, R., and Sochet, L.R. 2000. High pressure auto-ignition and oxidation mechanisms of o-xylene, o-ethyltoluene, and n-butylbenzene between 600 and 900 K. *Combust. Flame*, **123**, 561.

Shen, H.-P.S., Steinberg, J., Vanderover, J., and Oehlschlaeger, M.A. 2009. A shock tube study of the ignition of n-heptane, n-decane, n-dodecane, and n-tetradecane at elevated pressures. *Energy Fuels*, **23**, 2482.

Wang, H., Dames, E., Sirjean, B., Sheen, D.A., Tangko, R., Violi, A., Lai, J.Y.W., Egolfopoulos, F.N., Davidson, D.F., Hanson, R.K., Bowman, C.T., Law, C.K., Tsang, W., Cernansky, N.P., Miller, D.L., and Lindstedt, R.P. 2010. A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures. JetSurF version 2.0 Web site.

Zhukov, V.P., Sechenov, V.A., and Starikovskii, A.Y. 2008. Autoignition of n-decane at high pressure. *Combust. Flame*, **153**, 130.