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<td><strong>Author(s)</strong></td>
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A High-Pressure Rapid Compression Machine Study of
n-Propylbenzene Oxidation in Air and its Comparison
with Shock Tube Data and with n-Butylbenzene
Oxidation

D. Darcy\textsuperscript{a}, H. Nakamura\textsuperscript{b}, C.J. Tobin\textsuperscript{a}, M. Mehl\textsuperscript{c}, W.K. Metcalfe\textsuperscript{a}, W.J. Pitz\textsuperscript{c},
C.K. Westbrook\textsuperscript{c}, H.J. Curran\textsuperscript{a},\textsuperscript{*}

\textsuperscript{a}Combustion Chemistry Centre, NUI Galway, Ireland
\textsuperscript{b}Institute of Fluid Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi
980-8577 Japan
\textsuperscript{c}Lawrence Livermore National Laboratory, Livermore, CA 94551

Abstract

This study presents new ignition delay data recorded in a rapid compression machine over a wide range temperature, pressure and fuel/air ratio. This data is an extension of that recorded previously (D. Darcy, C.J. Tobin, K. Yasunaga, J.M. Simmie, J. Würmel, T. Niass, O. Mathieu, S.S. Ahmed, C.K. Westbrook, H.J. Curran, Combust. Flame, 159 (2012) 2219-2232.) for the oxidation of n-propylbenzene in a high-pressure shock tube. The data was obtained for equivalence ratios of 0.29, 0.48, 0.96, and 1.92, at compressed gas pressures of 10, 30 and 50 atm, and over the temperature range of 650–1000 K. Experimental data was also obtained at 50 atm for all equivalence ratios in our new heated high-pressure shock tube and this is also presented here. Agreement between the data obtained in both the rapid compression machine and in the shock tube facilities showed excellent complementarity. A previously published chemical kinetic mechanism has been updated in attempt to simulate ignition delay times at the lower temperature conditions of this study by adding the appropriate species and reactions including alkyl-peroxyl and hydroperoxy-alkyl radical chemistry. In general, good agreement was obtained between the model and experiments and consistent trends were observed.

\textsuperscript{*}address: Combustion Chemistry Centre, School of Chemistry, NUI Galway, Ireland. Phone: 00353-91-493856. Email: henry.curran@nuigalway.ie
URL: http://c3.nuigalway.ie/(H.J. Curran)
and these are discussed. Comparisons are also made with experimental data obtained for $n$-butylbenzene over the same range of conditions and common trends are highlighted. It was found that, in general, $n$-butylbenzene was faster to ignite over the lower temperature range of 650–1000 K.

**Keywords:**
rapid compression machine, shock tube, oxidation, ignition, propylbenzene, ignition delay times, butylbenzene

1. Introduction

Heightened awareness of dwindling fuel supplies and of pollutant emissions have resulted in the our need to understand the chemistry behind the oxidation of modern transportation fuels. Unfortunately, due to the complex nature of these fuels, they being comprised of hundreds of different individual components, it is difficult to do so. For this reason the combustion community study separate fuel components to understand their oxidation and surrogate fuels are designed to mimic the combustion of these more complex fuels by using one compound to represent each component type (alkane, alkene, cycloalkane, aromatic, etc.) in a gasoline or diesel fuel. Figure 1 shows the typical composition of both of these fuel types.

![Figure 1: Typical compositions of common transportation fuels](image)

This study focuses on the alkylaromatic component, where we study the oxidation of $n$-propylbenzene. Our aim is to build upon a previously published study in which the high- to intermediate-temperature oxidation of $n$-propylbenzene was
studied in our heated high-pressure shock tube [1]. The fuel was studied at equivalence ratios ($\phi$) of 0.29, 0.48, 0.96, and 1.92, over the temperature range of approximately 1000–1500 K and at reflected shock pressures of 1, 10 and 30 atm. Additionally, the chemical kinetic mechanism of Dagaut et al. [2, 3] was modified to include pressure-dependent rate constant expressions for the main unimolecular decomposition pathways for $n$-propylbenzene oxidation together with the substitution of the NUI Galway C$_0$–C$_4$ sub-mechanism [4, 5, 6, 7, 8]. Moreover, some secondary benzylic hydrogen atom abstraction rates were updated based on estimates using analogies with primary allylic hydrogen atoms [1].

Further updates to this mechanism including the inclusion of a full $n$-heptane sub-mechanism have been described previously [9], starting with the $n$-heptane mechanism developed by Mehl et al. [10]. This mechanism was modified, and some of the main changes were the inclusion of newly estimated abstraction reaction rate constants for secondary benzyl hydrogen atoms which were assigned to match the rates adopted in the base chemistry for abstraction reactions on secondary allylic hydrogens [1]. Beta-decomposition reactions of the phenyl-propyl radicals were also updated in which reaction rate constants for analogous reactions from Mehl et al. [11] and Park et al. [12] were included.

Another important addition to the mechanism was the addition of reactions to account for the formation and consumption of $n$-propenylbenzene. These reactions included hydrogen elimination from the phenyl-propyl radicals which occurs at high temperatures, and the addition of phenyl-propyl radicals to molecular oxygen followed by concerted H$^\cdot$O$_2$ elimination in the low-temperature range. Analogous rate constants to those used for pentenyl radical addition to molecular oxygen presented in the mechanism of 1-pentene developed by Mehl et al. [11] were used.

Other previous studies of $n$-propylbenzene oxidation [2, 13, 14, 15] have been described in our previous publications [1, 9].

In this study we have investigated the low-temperature chemistry (650–1000 K) range for $n$-propylbenzene oxidation. In particular, we provide ignition delay time measurements for $n$-propylbenzene measured in our rapid compression machine (RCM) and compare these times to both obtained previously in our high-pressure shock tube (HPST) and to a previously published chemical kinetic mechanism. Additionally 50 atm data was obtained in both our RCM and in our HPST, for all temperatures and equivalence ratios listed above.

Moreover, the experimental data presented here for $n$-propylbenzene is compared to that obtained previously for $n$-butylbenzene oxidation under similar conditions [16]. This data has been submitted for publication in a complementary
study [16]. This data is has been obtained over the same temperature and pressure range and at similar fuel/air equivalence ratios to ensure its viability as a comparison.

2. Experimental

2.1. Rapid Compression Machine

The RCM used in this study is a clone of the original NUI Galway RCM which is characteristically different to most other RCMs in that it has a twin-opposed piston configuration as described previously [17], resulting in a fast compression time of approximately 16 ms. Additionally, creviced piston heads are used to improve the post compression temperature distribution in the combustion chamber [18, 19]. The design for these creviced piston heads was originally devised at MIT [20, 21, 22], who found that the temperature field obtained using creviced pistons is almost homogeneous compared to that obtained using flat piston heads which is predicted to lead to far greater gas in-homogeneities in the post-compressed combustion chamber. A computational fluid dynamics (CFD) study carried out at NUI Galway [23] supports this view.

In our RCM it is possible to reach different compressed gas temperatures by (i) varying the diluent gas used, typically we use CO\textsubscript{2}, N\textsubscript{2} or Ar, (ii) varying the compression ratio, in our case by using different sized piston heads and (iii) using different initial temperatures. We used two different sized piston heads in this study, one larger set where we achieve a compression ratio of approximately 13:1 and another smaller set which achieve an approximate compression ratio of 9.5:1. The ‘effective compression ratio’ is lowest in argon and highest in carbon dioxide as the diluent gas, due to their relative thermal diffusivities. Using pure CO\textsubscript{2} as the diluent allowed us to measure times at the lowest temperatures, while the use of Ar allows much higher temperatures to be studied due to its higher thermal diffusivity, while pure N\textsubscript{2} lies in between these two.

The reaction chamber is wrapped in double-stranded heating tape (Flexelec, 1250 W) which is insulated, and allows the variation of the initial temperature to a maximum of 140 K. By changing (i) the diluent gas composition, (ii) the piston heads and (iii) using the heating system it was possible to study a compressed gas temperature range of 600–1000 K. However, the ignition limit of \textit{n}-propylbenzene resulted in the minimum temperature achievable in this study of approximately 750 K. The heating system is also installed on the manifold and mixing tanks, to ensure that \textit{n}-propylbenzene, which has a saturation vapour pressure of 0.5 kPa at 25°C [24], did not condense in the experiments.
The manifold is heated by first attaching “type K” thermocouples at various locations along the manifold. Flexelec heating tapes are wrapped around the manifold and these were covered with Zetex 1000 insulation tape. The thermocouples were connected to both the heating tapes via a Cal 9900 thermostat and a Pico TC-08 USB thermocouple data logger (which in turn was connected to a PC).

Pressure-time profiles are measured using a pressure transducer (Kistler 603B) and transferred via an amplifier (Kistler 5018) to an oscilloscope (Picoscope 4424) and ultimately recorded digitally on computer using the Picolog PC software. The ignition delay time, defined as the time from the end of compression to the maximum rate of pressure rise during ignition, is measured using two vertical cursors on the oscilloscope. In general, it was found that the ignition delay times were reproducible to within 15% of one other at each compressed temperature. The compressed gas pressure was measured using two horizontal cursors.

The time for compression is fast, \( \approx 16 \text{ ms} \), with most of the rapid rise in pressure and temperature taking place in the last 2–3 ms of compression; therefore heat losses during compression are small but do exist. For a period following compression the gases experience a high degree of heat loss owing to the swirl experienced and the high temperature of the gas within the chamber. Heat losses continue from the core gas during the constant volume period. A typical pressure-time trace obtained on the rapid compression machine is shown in Fig. 2. The reactive pressure trace is represented by the solid line while the non reactive trace is depicted by the red dashed line.

The compressed gas temperature, \( T_C \), was calculated using the initial temperature, \( T_i \), pressure, \( p_i \) and reactant composition and the experimentally measured compressed gas pressure, \( p_C \), defined as the maximum pressure immediately after compression, and employing the adiabatic compression/expansion routine in Gaseq [25], which uses the temperature dependence of the ratio of specific heats, \( \gamma \), according to the equation:

\[
\ln \left( \frac{p_C}{p_i} \right) = \int_{T_i}^{T_C} \frac{\gamma}{\gamma - 1} \frac{dT}{T}
\]

while assuming frozen chemistry during compression. The compressed gas temperature is then plotted against the measured ignition delay time to obtain overall reactivity profiles of \( n \)-propylbenzene.

2.2. High-Pressure Shock Tube

Ignition delay times were measured at high temperature using our new HPST facility. Our previous shock tube [1] was was unable to withstand the 50 bar re-
Figure 2: Typical pressure trace obtained from the NUIG rapid compression machine; $\phi = 2.0$, $p_C = 10.146$ atm, $T_C = 842$ K, ignition delay time = 41.7 ms. Solid line represents reactive mixture while the dashed line represents the non-reactive mixture.

Reflected shock pressures presented here and thus a new HPST facility was designed to withstand reflected shock pressures of approximately 100 bar.

The dimensions of the new shock tube are the same as those for the previous shock tube (9.0 m in length; 63.5 mm in internal diameter). A double-diaphragm section divides the shock tube into a 3 m long driver section and a 5.7 m driven section. Aluminum plates were used as the diaphragm, where diaphragms of various thicknesses are chosen depending on the desired final shock pressure and vary in thickness from 0.8-2.0 mm. A helium (99.99% pure; BOC) and nitrogen (99.99% pure; BOC) mixture were used as the driver gas, where the mixing ratio was chosen depending on the desired final shock pressure and test duration and varied from approximately 75:25 to 100:0 (He:N$_2$). Six pressure transducers on the sidewall (PCB; 113A24), located at known distances from the endplate, and one at the endwall (Kistler; 603B) were used to measure the velocity of the incident shock wave, which was used to calculate temperature of mixtures behind the reflected shock wave using Gaseq [25]. Pressures behind the reflective shock wave was measured using the pressure transducer located at the endwall. Pressure traces were obtained using two digital oscilloscopes (TiePie Handyscope HS4). The ignition delay time was defined as the interval between the rise in pressure due to the arrival of the incident shock wave at the endwall and the maximum.
rate of rise of the pressure signal. Some example pressure traces are shown in Figure 3; in this figure two pressure traces achieved at $\phi = 1.92$ and 50 atm are illustrated. A facility effect was observed in the experiments which resulted in a maximum of $3\%$ / ms increase in pressure before ignition for all experiments.

A heating system was designed and installed on the driven section and manifold of the shock tube to ensure that n-propylbenzene, which has a saturation vapor pressure of 0.5 kPa at 25°C [24], was present in the gaseous phase for the duration of the experiment and that no condensation of the fuel occurred.

2.3. Mixture Preparation

The gas mixtures and the initial conditions studied are documented in Table 1.
Table 1: Composition of mixtures studied

<table>
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<th>φ</th>
<th>% fuel</th>
<th>% O₂</th>
<th>% Diluent</th>
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<td>1.92</td>
<td>3.25</td>
<td>20.32</td>
<td>76.43</td>
</tr>
<tr>
<td>0.96</td>
<td>1.65</td>
<td>20.65</td>
<td>77.70</td>
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<td>0.48</td>
<td>0.83</td>
<td>20.83</td>
<td>78.34</td>
</tr>
<tr>
<td>0.29</td>
<td>0.50</td>
<td>20.89</td>
<td>78.61</td>
</tr>
</tbody>
</table>

Gases used, nitrogen (CP Grade) 99.99%, argon (Research Grade) 99.99%, oxygen (Medical Grade) 99.5%, were supplied by BOC Ireland and were used without further purification. n-Propylbenzene was obtained from Tokyo Chemicals Ltd at 99% purity (GC grade) and used without further purification.

As n-propylbenzene is a liquid fuel at room temperature mixtures were prepared by a direct injection method. In this method the fuel was injected via an injection port on the top of the heated mixing tanks using a gas-tight syringe (SGE Analytical Science, 5ml volume, 008760). The determined amount of fuel was added based on its appropriate weight and the partial pressure of fuel was measured using an MKS pressure transducer and digital readout followed by the addition of oxygen and nitrogen to the desired partial pressures.

All mixtures were left for at least one hour before use in both the RCM and in the HPST to ensure homogeneous charge composition.

3. Results

3.1. Chemical Kinetic Model

The chemical kinetic model used here is derived from the one published previously by Dagaut et al. [2, 3] and has been modified in our previous publications [1, 9]. Additional modifications have been made here to ensure good agreement with the lower temperature chemistry present in this study. These modifications included...........(MARCO)

RCM experiments were simulated using CHEMKIN-PRO [27]. For the ignition calculations in an RCM, the calculation uses a volume profile generated from the non-reactive pressure trace. The volume history used for the simulation is representative of the heat losses during the experiments and assumes an ‘adiabatic core expansion’ approach described by Mittal et al. [28]. All non-reactive pressure traces are available as Supplemental Material.

HPST simulations were also carried out using CHEMKIN-PRO, with the initial conditions of reflected shock temperature and pressure were used assuming
constant volume conditions. The 3% / ms increase in pressure witnessed in the experiments was simulated in a similar manner to the rapid compression machine simulations where a volume profile was generated to account for this pressure increase. We observed very little variation between predicted ignition delay times using (i) adiabatic, constant volume simulations, and (ii) including the 3% / ms pressure rise due to the relatively short (≤2 ms) measurement times of these experiments. It is important to account for these facility effects for longer ignition times but as the experimental data obtained in this study are within this range adiabatic simulations suffice, see Fig 4.

Figure 4: Simulations carried out at φ= 0.48, 50 atm. Solid line represents simulations assuming adiabatic, constant volume conditions while dashed line represents simulations accounting for a 3% pressure increase per millisecond gradient over the entire temperature range.

Figures 5 and 6 show comparisons between the simulations and the experimental data. In these figures solid symbols represent shock tube experiments while open symbols represent RCM experiments. Solid lines are used on the graphs to show adiabatic simulations while the dashed lines illustrate the simu-
lations using volume histories from the RCM to account for the facility effects of the RCM. There is reasonable agreement observed between model and experiment throughout the study which indicates that the chemical kinetic mechanism captures the general trend in reactivity of these fuel mixtures.

3.2. n-Propylbenzene oxidation results

The results obtained for the oxidation of n-propylbenzene are described below. All RCM data is shown in comparison with shock tube data as this study is an investigation of the entire temperature range and we can show the relationship between the HPST and the RCM data. Error bars of ± 15% in ignition delay times have been included for both HPST and RCM data to account for uncertainties in these results. Tables of our experimental data can be found in the Supplemental Material.

3.2.1. Influence of compressed pressure on ignition delay time

The effect of pressure on ignition delay times was studied at four different fuel / air equivalence ratios (0.29, 0.48, 0.96 and 1.92), Fig. 5. Ignition delay times of n-propylbenzene oxidation versus inverse temperature at an equivalence ratio of 0.29 and at pressures of approximately 1, 10, 30 and 50 atm are shown in Fig. 5(a). At these conditions, fuel reactivity increases with increasing pressure, that is shorter ignition delay times were measured for higher pressures. The same trends are observed for fuel/air mixtures at equivalence ratios of 0.48, 0.96 and 1.92 at the same reflected shock pressures, Figs. 5(b) – 5(d). This indicates a consistent trend of reactivity of n-propylbenzene with pressure throughout this study. These results are typical of the effect of pressure on ignition delay time for other hydrocarbons [29].

Interestingly no negative temperature coefficient behavior is observed for n-propylbenzene. This is consistent with the observations of Roubaud et al. [14] in their study of the oxidation of a wide variety of alkyl-aromatic compounds.
Figure 5: Effect of varying reflected shock pressure on n-propylbenzene reactivity; ■ – 1 atm, ● – 10 atm, ▲ – 30 atm, ▼ – 50 atm. Solid symbols: Shock tube, Open symbols: RCM. Simulation; – – – RCM simulations including facility effects, —— Adiabatic simulations
3.2.2. Influence of equivalence ratio on ignition delay time

The effect of equivalence ratio on ignition delay times was determined for four fuel/air mixture compositions at 10, 30 and 50 atm, Fig. 6. The effect of equivalence ratio at pressures of 10 atm at the four equivalence ratios studied (0.29, 0.48, 0.96 and 1.92) is shown in Fig. 6(a).

At intermediate temperatures fuel-rich mixtures ignite faster than fuel-lean ones. This behaviour at intermediate temperatures is attributed to the chain branching sequence \( \text{RH} + \text{HO}_2 = \text{R} + \text{H}_2\text{O}_2 \) followed by \( \text{H}_2\text{O}_2 (+ \text{M}) = \text{OH} + \text{OH} (+ \text{M}) \), where RH is the fuel components. In the present experiments, the equivalence ratio is increased by increasing the fuel concentration ([RH]) which enhances the
rate of this branching sequence that produces two reactive \( \dot{O}H \) radicals. This effect is also seen at 30 and 50 atm, Fig 6(b) – 6(c). Traditional low temperature behaviour including an NTC region was not observed for pure \( n \)-propylbenzene experiments. This behaviour is well captured by the kinetic model.

At high temperatures, the difference between the mixtures is much smaller relative to that at the low and intermediate temperatures. However, if one looks closely enough at the relative slopes of the data it can be concluded that there is a convergence of the all data sets at the highest temperatures studied for 10 atm experiments, Fig 6(a). In the case of the 30 and 50 atm experiments and judging by the relative slopes of each data set this convergence of data will occur at a higher temperature than is achievable in this study due to the short ignition delay times observed in the experiments. We believe the convergence of the data is because the equivalence ratio is altered via changes in fuel concentration with the oxygen concentration remaining constant within these experiments. This results in very little effect of the main chain branching reaction at higher temperatures.

\[
\dot{H} + \dot{O}_2 = \dot{O} + \dot{OH}
\]

which leads to a small influence on the reactivity due to changes in equivalence ratio.

4. Discussion

As the simulations achieved using the chemical kinetic mechanism agree reasonably well with the experimental data it is now possible to use this mechanism to explore the important chemistry determining the reactivity of this fuel.

A flux analysis was carried out at \( \phi = 0.96 \) and 10 atm for a series of temperatures (750, 1000 and 1400 K) and 15% fuel consumed, these being most representative for the experimental conditions studied. This was performed to investigate the important reactions occurring at varying temperatures for \( n \)-propylbenzene oxidation.

In this flux analysis (Fig. 7) we can discuss the most common reactions occurring at various temperatures and compare how they vary in different temperature regimes, the numbers in black font represent the fuel flux at 1500 K, while red numbers represent the flux at 1000 K and blue numbers represent the flux at 750 K.

At 1000 K (numbers in red font), which is an intermediate temperature, the main consumption pathways for \( n \)-propylbenzene are abstraction reactions on the
Figure 7: Flux analysis carried out for $n$-propylbenzene oxidation at $\phi = 0.96$, 10 atm and 15% fuel conversion. Numbers represent the percent of fuel flux that goes through a particular species. Black numbers represent flux at 1400 K, Red numbers represent flux at 1000 K and Blue numbers represent flux at 750 K.

alkyl chain, mainly by $\cdot$OH radicals. A strong selectivity on the ethyl-benzyl (allylic) site is observed, accounting for 52.2% on the total abstraction rate. The primary site (designated by A in the species PBZJA), is the least targeted by abstraction and, due to the weakness of the allylic C–C bond in PBZJA formed, it rapidly decomposes to benzyl radicals and ethylene. Additionally the radical is consumed via radical addition to molecular oxygen followed by a concerted elimination reaction forming 1-propenylbenzene and HO$_2$ radical. This occurs to a much lesser extent (2.3%) at 1000 K compared to the $\beta$-scission reaction which forms ethylene and benzyl radicals (11.6%).

The homolytic decomposition of the fuel to benzyl and ethyl radicals is an important consumption pathway even at this relatively low temperature of 1000 K,
although this only accounts for approximately 4% of the fuel consumption as the energy barrier for this reaction is relatively high at this temperature.

When abstraction occurs on the secondary site (forming PBZJB), the radical is mainly consumed via addition to molecular oxygen followed by the concerted elimination pathway, showing a selectivity of 2:1 towards the formation of 2-propenylbenzene versus 1-propenylbenzene and HO₂ radicals. Additionally the PBZJB radical can decompose directly to form both the 1-propenylbenzene (0.5%) and 2-propenylbenzene radicals (3.4%) together with hydrogen atoms, but this is much less important compared to the radical addition / concerted elimination route which generates 8.7% 2-propenylbenzene and 4.9% 1-propenylbenzene respectively.

The predominant ethyl-benzyl radicals (labeled as PBZJC), are mainly consumed (20.5%) via reaction with HO₂ radicals leading to the formation of benzaldehyde and hydroxyl and ethyl radicals. Because of the intrinsic stability of ethyl-benzyl radicals, their addition to molecular oxygen and subsequent concerted elimination leading to HO₂ radical formation is less favored compared to a secondary site, and only 1.5% of the initial PBZJC formed follows this pathway, an amount much lower than its decomposition to methyl radical and styrene (16.1%) or via the direct decomposition to form 2-propenylbenzene and a hydrogen atom (14.1%).

At 750 K, the major consumption pathways are very similar to those observed at 1000 K. This is expected as traditional low-temperature behaviour including an NTC region was not observed. The main difference at 750 K was that no homolytic decomposition of the fuel to benzyl and ethyl radicals is observed as the lower energy in the system at 750 K makes it harder to break the C–C bond. Additionally the addition to molecular oxygen and subsequent molecular elimination pathway occurs to a larger extent (15.1% at 750 K compared to 0.9% at 1000 K) at these lower temperatures (750 K) as the decompositions tend not to occur at lower temperatures due to the associated energy barriers.

At high temperature (1400 K), unimolecular decomposition of the fuel dominates and abstraction reactions (now mostly involving hydrogen atoms) are less selective, attacking with a similar rate at all of the three sites on the alkyl chain (650 K: PBZJA / PBZJB / PBZJC 13.1 / 27.3 / 59.6% 1000 K: PBZJA / PBZJB / PBZJC 13.8 / 26.0 / 52.2%, 1400 K: PBZJA / PBZJB / PBZJC 11.2 / 16.5 / 22.5%). Abstraction reactions are followed by β-scission reactions leading primarily to ethylene and benzyl radicals, styrene and a methyl radical and 2-propenylbenzene and a hydrogen atom.
4.1. Sensitivity Analyses

Using Chemkin-Pro, a brute force sensitivity analysis of different reaction rate constants was computed at the 750 and 1400 K, representing the two extremes of temperatures of this work, at 10 atm and $\phi = 0.96$. As it was observed in the flux analysis that the main reaction pathways at 750 and 1000 K were very similar it was decided that a sensitivity analysis at 1000 K was redundant. The analyses were performed by increasing and decreasing both the forward and reverse rate constants by a factor of two, with sensitivities expressed using the formula:

$$\ln S = \frac{\ln(\tau_+ / \tau_-) / \ln(k_+ / k_-)}{\ln(2 / 0.5)} = \frac{\ln(\tau_+ / \tau_-)}{\ln(2 / 0.5)}$$  \hspace{1cm} (1)$$

A positive sensitivity coefficient indicates an inhibiting reaction while a negative sensitivity coefficient relates to a reaction promoting reactivity, Fig. 8. This analysis was carried out on the main reactions involving the decomposition of the fuel and its subsequent radicals along with a selection of reactions which are known to be sensitive in these regions.

As expected, at lower temperatures the most sensitive reaction involving the fuel is hydrogen atom abstraction from the benzylic site by H$\dot{\text{O}}_2$ radicals to form ethyl-benzyl radicals and H$_2$O$_2$. These reactions are not as sensitive at the higher temperatures as there is competition from the unimolecular decomposition of n-propylbenzene to form benzyl and an ethyl radical which only occurs at higher temperatures, this reaction is by far the most sensitive reaction involving the fuel at higher temperatures and as has been shown from the flux this reaction also dominates the consumption of the fuel (1400 K: 46.7%, 750 K: 0%). This reaction promotes reactivity as it leads to the formation of ethyl radicals which can react with molecular oxygen to form ethylene and an hydroperoxyl (H$\dot{\text{O}}_2$) radical. Additionally the benzyl radical reacts with the hydroperoxyl radical to form C$_6$H$_5$CH$_2$\dot{O} radical and an hydroxyl radical which helps promote reactivity as it can abstract hydrogen atoms from relatively stable molecules, for example n-propylbenzene.

The reason these reactions only occur at higher temperatures is due to the energy barrier required to break this C–C bond, 78.4 kcal mol$^{-1}$, which is too high to be overcome at lower temperatures.

The ethylbenzyl radical is responsible for other sensitive reactions at 750 K. These reactions are related to the PBZCO$\dot{\text{O}}$ radical which is formed by the addition the ethylbenzyl radical to molecular oxygen. The decomposition of this radical to form 2-propenylbenzene and a hydroperoxyl radical inhibits reactivity as it competes with the isomerization step in the chain branching sequence
which forms an alkylhydroperoxide (named PBOOH-C-A in this mechanism). This alkylhydroperoxide further decomposes to form benzaldehyde, an ethyl and a, hydroxyl radical. Thus, the isomerization step results in the formation of very reactive \( \dot{OH} \) radicals compared to relatively unreactive \( \dot{HO}_2 \) radicals formed in the competing channel.

As mentioned earlier the main promoting reaction at high temperatures involving the fuel is the unimolecular decomposition to form ethyl and benzyl radicals. This competes with hydrogen atom abstraction reactions at temperatures greater than approximately 1000 K for the consumption of the fuel which results in these abstractions either inhibiting or not affecting reactivity at all.

The reaction of fuel molecules with hydrogen atoms competes with hydrogen atom reactions with molecular oxygen in the high temperature chain-branching reaction \( \dot{H} + O_2 = \dot{O} + OH \) and as such all of these reactions inhibit reactivity. The sensitivity coefficient of is so high namely –0.716 at 1400 K it has been removed.
from the sensitivity plot to improve clarity for the other reactions plotted.

At intermediate and low temperatures the reaction of hydrogen atoms with molecular oxygen results in the formation of a hydroperoxyl radical. At high temperatures the reaction forms $\ddot{O} + \dot{OH}$ and is the dominant chain-branching reaction. This is shown in Fig. 8 as at 750 K the system is far less sensitive to $\dot{H} + O_2 = \ddot{O} + \dot{OH}$ than it is at 1400 K where it is the most sensitive reaction.

\[
\dot{H} + O_2(\text{+M}) \rightarrow \text{H} \dot{O}_2(\text{+M})
\]

\[
\dot{H} + O_2 \rightarrow \ddot{O} + \dot{OH}
\]

At lower temperatures the majority of the sensitive reactions relating to the fuel are hydrogen atom abstractions while at 1400 K the most sensitive reactions are unimolecular decompositions of the fuel and subsequent reactions of the daughter radicals.

5. Comparison with n-Butylbenzene

Additionally our experimental data has been compared with n-butylbenzene data from a supplementary publication of Nakamura et al. [16]. This experimental data was carried out to correspond with the data from this paper. n-Butylbenzene was studied in both the RCM and shock tube over the temperature range of 650–1600 K at pressures of 1, 10, 30 and 50 and at equivalence ratios of 0.3, 0.5, 1.0 and 2.0. The equivalence ratios differ slightly from our n-propylbenzene data due to a calculation error in our experiments. Table 2 shows mixture compositions of n-butylbenzene used in this study.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>% fuel</th>
<th>% $O_2$</th>
<th>% Diluent</th>
</tr>
</thead>
<tbody>
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<td>2.0</td>
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<tr>
<td>0.3</td>
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Figures 9–11 show these comparisons. Experiments at 1 atm reflected shock pressure were only possible to be carried out in the shock tube and as such have been discussed in detail in a previous publication so this study will focus only on the higher pressure conditions [1]. In these graphs n-propylbenzene is represented by black symbols (solid symbols: ST, open symbols: RCM) and lines (solid line:
adiabatic simulation, dashed line: facility effect simulation) while \( n \)-butylbenzene is represented by red symbols and lines.

![Graphs showing temperature vs. ignition delay time for \( n \)-propylbenzene and \( n \)-butylbenzene at various equivalence ratios (\( \phi \)).]

**Figure 9:** A comparison of \( n \)-propylbenzene and \( n \)-butylbenzene at various equivalence ratios (\( \phi \)) and at 10 atm. ■ – \( n \)-propylbenzene data, • – \( n \)-butylbenzene data. Solid symbols: Shock tube, Open symbols: RCM. Simulation; —— Adiabatic simulations.

At a pressure of 10 atm, Figs. 9(a) – 9(d), it is clear that \( n \)-propylbenzene and \( n \)-butylbenzene experience similar high-temperature chemistry as both the experimental data and the mechanism predictions show the same ignition delay times above 1100 K. At lower temperatures the reactivity of \( n \)-butylbenzene becomes stronger which results in faster ignition delay times observed in both experiments and model predictions. The longer alkyl side chain of \( n \)-butylbenzene is important at low and intermediate temperatures which allows more facile intra-molecular
hydrogen atom isomerization reactions in the case of $n$-butylbenzene compared to $n$-propylbenzene. It is interesting to note is that only at fuel-rich conditions do we observe any negative temperature coefficient behaviour for $n$-butylbenzene and it is not observed at all for $n$-propylbenzene, Fig. 9(d).

Figure 10: A comparison of $n$-propylbenzene and $n$-butylbenzene at various equivalence ratios ($\phi$) and at 30 atm. ■ = $n$-propylbenzene data, ◦ = $n$-butylbenzene data. Solid symbols: Shock tube, Open symbols: RCM. Simulation; –—— RCM simulations including facility effects, ——— Adiabatic simulations.

Similar trends are observed at 30 atm pressure Figs. 10(a) - 10(d) in which $n$-propylbenzene shows longer ignition delay times at lower temperatures while at higher temperatures there is a convergence of the data where it seems to have almost identical reactivity. This is understandable as the main chain branching at higher temperatures is:

20
\[ \text{H} + \text{O}_2 = \text{O} + \text{OH} \]

Which is dependent upon the concentration of molecular oxygen which is independent of the fuel concentration. As the O\(_2\) concentration is quite similar in both mixtures the high temperature reactivity is quite similar. Once again at lower temperatures while both fuel mixtures have similar compositions at the varying equivalence ratios, \(n\)-butylbenzene has a longer alkyl side chain which is important at lower temperatures which is dominated by chain branching and chain propagation reactions. The alkyl group dominates in terms of reactivity because of the aromatic groups stability with the butyl side chain able to undergo a wider range of hydrogen abstractions and thus create more radicals to drive reactivity at low temperatures in comparison to the smaller propyl chain of \(n\)-propylbenzene.

At 50 atm reflected shock pressures similar trends are observed to those which have already been discussed in which as the temperature decreases the \(n\)-butylbenzene shows higher reactivity as opposed to \(n\)-propylbenzene. Once again NTC-like behaviour is observed for \(n\)-butylbenzene while this is not prevalent for \(n\)-propylbenzene conditions.
Figure 11: A comparison of \( n \)-propylbenzene and \( n \)-butylbenzene at various equivalence ratios \( (\phi) \) and at 50 atm. ■ – \( n \)-propylbenzene data, ● – \( n \)-butylbenzene data. Solid symbols: Shock tube, Open symbols: RCM. Simulation; – – – – RCM simulations including facility effects, —— Adiabatic simulations.
6. Conclusions

A comprehensive study of $n$-propylbenzene at low temperatures was carried out in a rapid compression machine over a wide range of temperatures, pressures and fuel/air equivalence ratios. Ignition delay times were measured at temperatures in the range 650–1000 K, at reflected shock pressures of 10, 30 and 50 atm and at equivalence ratios of 0.29, 0.48, 0.96 and 1.92. These ignition delay times were compared to complimentary high pressure shock tube experiments measured previously [1] to discover trends in reactivity over the entire temperature range of approximately 650–1600 K.

It was found that an increase in reflected shock pressure resulted in shorter ignition delay times, that is higher reactivity for all equivalence ratios investigated, which is typical of the influence of pressure on fuel reactivity. The effect of equivalence ratio is as expected in that fuel rich mixtures have shorter ignition delay times indicating higher reactivity than fuel lean mixtures throughout the range although at higher temperatures the reactivity begins to converge as noted in previous publications.

It was noted that $n$-propylbenzene does not show typical low temperature chemistry namely with the absence of NTC behaviour. The reasons behind this are linked to the resonantly stabilized benzene and have been discussed.

The kinetic reaction model devised by Diéwart and Dagaut [3] and modified previously [1, 9] was again improved to successfully capture the lower temperature chemistry present in these experiments. Improvements included...

The simulations performed using this improved model captured the experimental data reasonably well and as such validated the model while the experimental data gave an insight into the trends in reactivity in terms of reflected shock pressure, temperature and equivalence ratio.

A comparison was made between $n$-propylbenzene and $n$-butylbenzene data obtained over the same range of conditions. A consistent trend was observed throughout the data in which the reactivity of both fuels are very similar while at high temperatures but $n$-butylbenzene was shows higher reactivity than $n$-propyl-benzene at lower temperatures.

7. Acknowledgments

NUIG acknowledge the financial support of the Saudi Arabian Oil Company. The LLNL work was performed under the auspices of the US Department of
References


[16] Hisashis n-BBZ paper????


