

**SHOCK TUBE MEASUREMENTS OF IGNITION DELAY TIMES FOR
N-DECANE AND DECENES: THE INFLUENCE OF THE DOUBLE
BOND**

By

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Abstract

In order to understand the influence of double bond and its position on decene isomer oxidation, shock tube measurements has been performed to investigate the autoignition of n-decane, 1-decene, and 5-decene within a temperature range of 650-1300 K. Mixtures comprised of these C10 speices in air at equivalence ratios of 0.5, 1 and 1.5 were studied at an initial pressure of 20 atm. A stoichiometric case at an elevated initial pressure of 40 atm was also carried out for comparison. Although no previous study exists for direct comparison, the experimental results agree with the trends of previous studies for various alkenes and alkanes. For 5-decene, with the double bond centrally located, the ignition delay data illustrates slightly increased reactivity at higher temperatures and a significantly lower reactivity for temperatures lower than 950 K when compared to both n-decane and 1-decene. 1-Decene results show similar reactivity to n-decane at high temperatures and slightly slower reactivity at low temperatures. Chemical kinetic model predictions are compared to the shock tube results and possible reaction pathways are discussed. Only the high temperature trends for decene isomer reactivity were captured due to the limitations of models available in the literature. The results of this experimental work should serve as an important reference for understanding alkene oxidation and provide quantitative targets for the future development of kinetic models.

1 Introduction

1.1 Demand for cleaner fuels

Fossil-based gasoline, diesel, and kerosene (jet fuel) have been the dominant fuels utilized in automobiles, trucks, and aircrafts for a century. Today, nearly 84% percent of all automobile motor fuel consumed in the US is gasoline and it is predicted that this situation will remain the same in the following decades, except for a slight increasing of usage of diesel [1], with the advancement of clean diesel engine technology. The air pollution and carbon emissions brought by the use of fossil fuels poses significant threat to the wellness of environment and public health and has become a global issue drawing the attention of leaders all over the world. In the 2015 United Nations Climate Change Conference, 126 countries signed the Paris Agreement, in which an ambitious goal was set to lower carbon emission. The increasing pressure on the regulation of automobile emissions demands the development of cleaner fuels and better internal combustion engines for increased efficiency and lower emissions. While internal combustion engine technology has been highly developed, the science of fuel combustion has not been fully understood by researchers and there is still potential to improve the efficiency of internal combustion engines. Since gasoline, diesel, and many alternative fuels mainly consist of hydrocarbons, understanding the chemical kinetics for hydrocarbon oxidation is crucial for providing a guidance for the improving of engine performance, the development of alternative fuels and the reducing harmful emission brought by the combustion.

1.2 Ignition delay

In diesel engines, autoignition initiates combustion after the fuel is injected; while in gasoline spark-ignition engines, autoignition is not desired since it causes engine knock, which is a phenomenon that significantly compromises efficiency and might even lead to severe engine damage. Ignition delay, denoting the time from the injection of fuel to the start of combustion, is a crucial property to characterize the reactivity of fuels. A shorter ignition delay is desired in diesel engines to ensure higher efficiency and lower emissions, whereas a longer ignition delay is needed in a spark-ignition engine to avoid the engine knock effect [2]. The quality of diesel and gasoline are indicated by Cetane Number (CN) and Octane Number (ON), respectively. Diesel with higher Cetane number will have a shorter ignition delay in conventional diesel engines, which indicates higher fuel reactivity. That is to say, the higher the cetane number the faster the autoignition response occurs and the more thoroughly the combustion of fuel will occur, resulting in better diesel engine performance. In contrast, higher octane numbers allow the fuel to withstand high compression for longer periods without autoigniting, reducing the chance of engine knock in a spark-ignition engine. As a very important characteristic of fuels, ignition delay is affected by both internal factors such as the composition of fuel and external factors such as the pressure, temperature and equivalence ratio of the fuel/air mixture. The effect of various factors on the ignition delay of three C10 hydrocarbon fuel species has been studied in this work and will be shown in the experimental result section.

1.3 Hydrocarbon composition of fuels

The hydrocarbon composition of gasoline and diesel have been researched in various studies [1]-[3]. An estimated composition of gasoline and diesel fuels is shown in Figure 1.1. Commercial gasoline is a mixture of thousands of species distilled from crude oils, which primarily consists of n- and iso-alkanes (35%-80%), aromatics (10%-50%), alkenes (2%-20%), and cycloalkanes (3-10%) [3]. Although alkanes and aromatics are the most abundant constituents of gasoline, alkenes are found in important proportions. In typical North American diesel fuels, which mainly consist of n- and iso-alkanes (25%-50%), cycloalkanes (20%-40%), and aromatics (15%-40%), alkenes are found in smaller amounts [4]. Additionally, alkenes are major intermediates of the oxidation of alkanes [5]. Furthermore, it is also worth noting that unsaturated fatty acid esters, in which double bonds structure can also be found abundant and similar in structure and reactivity to alkenes, have been identified to be the major constituent of biofuel. Biofuel is a promising type of clean alternative fuel derived from feedstock oils. There has been a drastic increase globally in the production and adoption of biofuels, as mentioned in a thorough review of biofuels done by Oehlschlaeger et al. [6]. It is clear that unsaturated fuel constituents account for an important part of all types of fuels people use every day. The major characteristic of alkenes in terms of chemical structure is the existence of double bond. It is well known that double bond position plays a very important role in determining the physical properties and chemical properties of a molecule. Therefore, the position of double bond in alkene isomers can have an effect on fuel performance. However, the experimental work and chemical kinetics of alkene oxidation has been investigated in only a very limited number of papers and even less studies have looked into the effect of double

bond position on alkene oxidation. Thus, a deeper understanding of alkene oxidation would contribute to a clearer picture of the autoignition process of hydrocarbon fuels and potentially further to the development of cleaner fuels and engines.

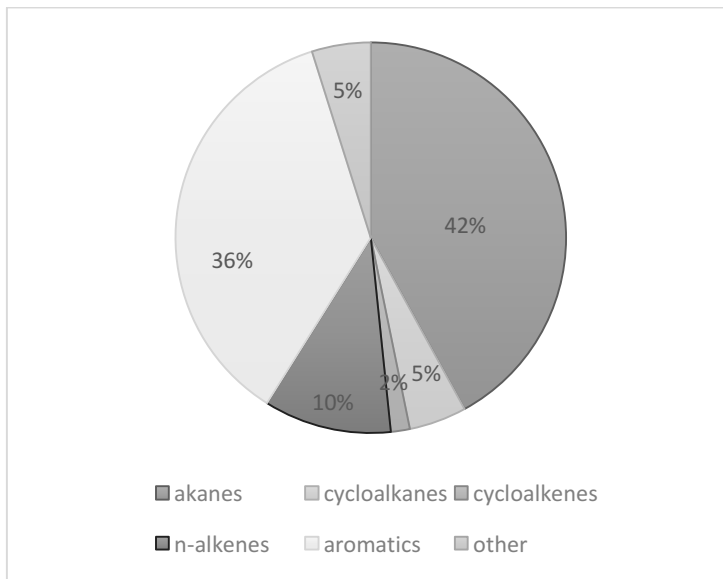


Figure 1.1: Percentage of different hydrocarbons in gasoline.

1.4 Goal and structure of this thesis

In this work, the main effort has been concentrated on investigating the effect of a double bond on C10 species, through an study of n-decane, 1-decene and 5-decene by means of shock tube experiments and chemical kinetics modeling. The chemical structures of the species investigated are shown in Figure 1.2.



Figure 1.2: Chemical structure of n-decane, 1-decene and 5-decene.

A brief introduction to the shock tube technique and chemical reaction pathways for hydrocarbon fuels at different temperatures are given in the experimental approach and modelling method section, respectively. A discussion of the experimental and modeling results are provided in discussion section.

1.5 Previous work

Numerous studies related to the autoignition and oxidation of alkanes have been published. A detailed list of previous experimental and modelling work on the oxidation of C7 or larger n-alkanes at high and low pressures was introduced by Shen et al. [7]. Yet there are much fewer studies focused on alkene oxidation. In 1981, the low-temperature oxidation of 1-pentene and 2-pentene was studied by Baldwin and Walker [8]. A similar study on 1-pentene were conducted by Prabhu [9] in a pressurized flow reactor facility at 6 atm over a temperature range of 600-800 K and equivalence ratio of 0.4. Later, Minetti et al. [10] researched the pre-ignition of n-pentane and 1-pentene in rapid compression machine (RCM) in a temperature range of 600-900 K. The first kinetic modeling work was published by Ribaucour et al. [11], taking advantage of the experimental data measured by Minetti et al. [10]. In 2002, Heyberger et al. [12] published a paper detailing the

development of alkene oxidation models using experimental data from a shock tube for temperature from 1200 to 1670 K, pressure from 6.6 to 8.9 atm, equivalence ratio from 0.5 to 2. Yahyaoui et al. [13] conducted an experimental and modeling study of 1-hexene oxidation using the shock tube technique for a temperature range from 1270 to 1700 K, pressure of 0.2 MPa, and equivalence ratio of 0.5, 1 and 1.5. Comparisons between C5 alkane and alkene oxidation has been conducted by Mehl et al. [14] by using the ignition delay data at both low and high temperature.

Although a few studies have centered on the oxidation properties of alkenes, fewer papers have focused on the effect of double bond position on the oxidation of alkenes. A list of previous experiments investigating this topic is given in Table 1.1. In 1968, Salooja [15] investigated on the ignition properties of 1-, trans- and cis-2-butene in a flow reactor. Later, the combustion of the n-pentene isomers in cool flame region was studied by Hughes and Prodhan [16]. They discovered that 1-pentene is more reactive than the other two isomers, cis-2 and trans-2 pentene, and thus have a shorter ignition delay. The oxidation of 1-pentene was investigated by Prabhu [9]. Their experimental results indicated that hydrogen abstraction reactions dominate over radical addition reactions when the carbon number is large in the terminal alkene. More recently, Tanaka [17] carried out premixed combustion experiments of 1-, trans-2 and trans-3-heptene using a rapid compression machine (RCM). Similarly, the oxidation and autoignition of 1-, 2-, and 3-hexene has been studied by Vanhove et al. [18] with RCM. The results of Tanaka and Vanhove both showed that the double bond position of alkenes has an effect on their ignition characteristics. Zhang et al. [19] focused on the double bond position in the alkyl chain of a fatty acid ester. Mehl et al. [20] carried out ignition experiments on the isomers of pentene and hexene in both a high-

and low-pressure shock tube. They developed kinetic mechanism for unsaturated components utilizing both the previous experimental data of Tanaka et al. and Vanhove et al. in lower temperature range and shock tube data in higher temperature range. Hellier et al. [21] performed diesel engine experiments testing a series of octene isomers. Their results indicated that change in location of the double bond from trans-2-octene to 1-octene increases the ignition delay. The most recent work was finished by Fridlyand et al. [22] on the oxidation of 1-, cis-2-, cis-5-decene. Comparison between previous work on decene oxidation and results of this work will be presented in experimental result section.

Table 1.1: Previous works on the effect of double bond position in alkene.

| Year | Authors | Device | Fuel | Conditions | | |
|------|-----------|---------------|---|------------|----------|-------------------------|
| | | | | T[K] | P[atm] | ϕ |
| 1968 | Salooja | Flow reactor | 1-,trans- and cis-2-butene | - | - | - |
| 1973 | Hughes | Reaction | 1-, cis-2-, trans-2-pentene | 553-603 | 0.11- | 1:1 with O ₂ |
| 1996 | Prabhu | Flow reactor | 1-pentene | 600-800 | 6 | 0.4 |
| 2003 | Tanaka | RCM | 1-, trans-2-, trans-3-heptene | 318 | 11.6 | - |
| 2005 | Vanhove | RCM | 1-, 2-, 3-hexene | 630-850 | 6.71- | 1 with air |
| 2009 | Zhang | CFR engine | C9 fatty acid esters | 250-991 | - | 0.26 with air |
| 2011 | Mehl | Shock Tube | 1-, trans-2-pentene | 993-1770 | 7.8-10.8 | 0.5,1,2 with air |
| | | | 1- hexene, trans-2-hexene, trans-3-hexene | 990-1460 | 8.5-12.1 | 1 with air |
| 2013 | Hellier | Diesel engine | 1, trans-2, cis-3, and trans-3-octene | 366-1900 | <35 | - |
| 2015 | Fridlyand | Shock Tube | 1, cis-2, cis-5, trans-5-decene | 850-1500 | 40-65 | 1 with air |

2 Experimental Approach

2.1 Shock tube introduction

Shock tube experiments (ST) and Rapid Compression Machine (RCM) techniques are the most common methodologies for investigating the fuel oxidation properties. A shock tube is a metal tube in which high-pressure and low-pressure sections are divided by a diaphragm. When the diaphragm is ruptured, a strong shock wave will be generated and propagate into the lower pressure section, causing a rapid increase in temperature and pressure in the lower pressure section. Consequently, a premixed fuel/oxidizer mixture filled in the lower pressure section can be autoignited. The ignition delay, time duration between shock heating and autoignition, can be measured using pressure and optical sensors. A rapid compression machine is a device in which a single piston stroke can simulate the compression that would occur in an engine. Shock tubes are able to provide a higher temperature range and shorter ignition delays than RCMs. A traditional RCM is good for low to intermediate temperatures and longer ignition delays (~10 ms and longer). Comparing with other methods, shock tube has the merit of completely covering a wide range of pressure and temperature, as such adopted as the only method for investigating decene autoignition in this work. The design and operation of a high pressure shock tube was well described by Tranter et al. [22].

A shock tube must be able to withstand high pressures, since experiments may take place in a very extreme conditions of up to 1000 atm. Like the apparatus shown in Figure 2.1, a typical shock tube consists of a driver section, a diaphragm, a driven section and a test section.

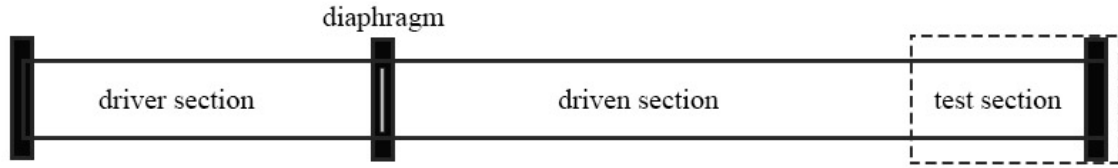


Figure 2.1: Configuration of a typical shock tube.

2.1.1 Driver section

The driver section holds compressed driver gas used to generate shock wave. The pressure of gas in this section must be extremely high in order form the shock wave. Gases with very low reactivity are always adopted as driver gas, such as helium, so that the reaction won't be affected by the driver gas.

2.1.2 Driven section

The driven section is the component filled with premixed vaporized fuel/oxidizer of interest (from a mixing tank). In order to allow the shock wave to be fully developed, it is suggested that the length of the driven section need to be as least 20 times of the diameter of the tube [24].

2.1.3 Diaphragm

The diaphragm is a metal or plastic piece separating the driver section and the driven section. The rupture of diaphragm can be achieved by several ways, either spontaneously or by some kind of mechanical mechanism. One way to do it is to use some explosive mechanism to burst the diaphragm. The drawback of this method is the fragment of the diaphragm may interfere the measurements of sensors. The diaphragm can also be ruptured by spring loaded plunger or cutter as described by Crede [24]. Another way to achieve

rupture of diaphragm is through strain-induced failure caused by the high pressure of the driver section.

2.1.4 Test section

The test section is part of the driven section, close to the end wall of the shock tube, where the shock wave is fully developed and measurements are made. All experimental data including pressure and temperature are collected by different sensors in the test section. The correct installing of transducer in the shock tube wall is crucial in order to eliminate any unwanted vibrations and noises. A proper thread seal is needed to maintain the correct pressure in the test section, which can be achieved by using deformable metal seals.

2.2 Operation principles

Autoignition experiments in this thesis were carried out in the high-pressure shock tube facility in the Combustion and Energy Systems Lab at Rensselaer Polytechnic Institute. This shock tube has been used in multiple previous works on fuel combustion and was described by Shen et al. in [25]. The inner diameter of the shock tube is 5.7 cm. The length of driver section and driven section are 2.6 m and 4.1 m respectively. The external heated initial temperature is up to 473 K. The accessible range of temperature during shock tube experiment is over 650 K and a typical fuel/air combustion experiment has a temperature range from 650 K to 1300 K. The accessible range of pressure is 1-200 atm. The uncertainty in initial temperature behind the shock is $\pm 1-1.5\%$ and the uncertainty in pressure behind the shock is $\pm 1-2\%$. In this experiment, helium or a mixture of helium and nitrogen was used as the driver gas. The rupture of diaphragms was achieved by filling the driver section

with high pressure gas, causing strain failure of the diaphragms. Also, the diaphragms were designed to open into four pieces without fragments which might compromise the experiment outcome. Diaphragm with different thickness were used to control the reflected shock pressure. Mixing and stirring of decene/air mixture was done in a designated stainless steel mixing tank and then dumped into the pre-vacuumed driven section. The mixture need to be stirred for at least 30 minutes in order to be well mixed. As shown in Figure 2.3, five pressure transducers were installed uniformly next to the end wall. With their signal sent to counter timers, the time interval of the passing incident shock from one point to the next was measured and the incident shock velocity can be determined. The method used to identify ignition delay time is called the reflected shock method. Ignition delay, in the shock tube situation, is measured as the time interval between the reflection of the shock wave and the start of the combustion. The time point when shock was reflected can be captured by a Kistler piezoelectric pressure transducer mounted close to the end wall, where pressure was measured quantitatively. OH• radical is a good indicator of combustion, since its concentration increases sharply at ignition [3]; thus, the start point of combustion was indicated by the increase of electronically excited OH• emission, which was monitored by a filtered photodetector installed at the center of the end wall. A typical output of a pressure transducer and photodetector are shown in Figure 2.2, where it can be seen that how ignition delay is determined.

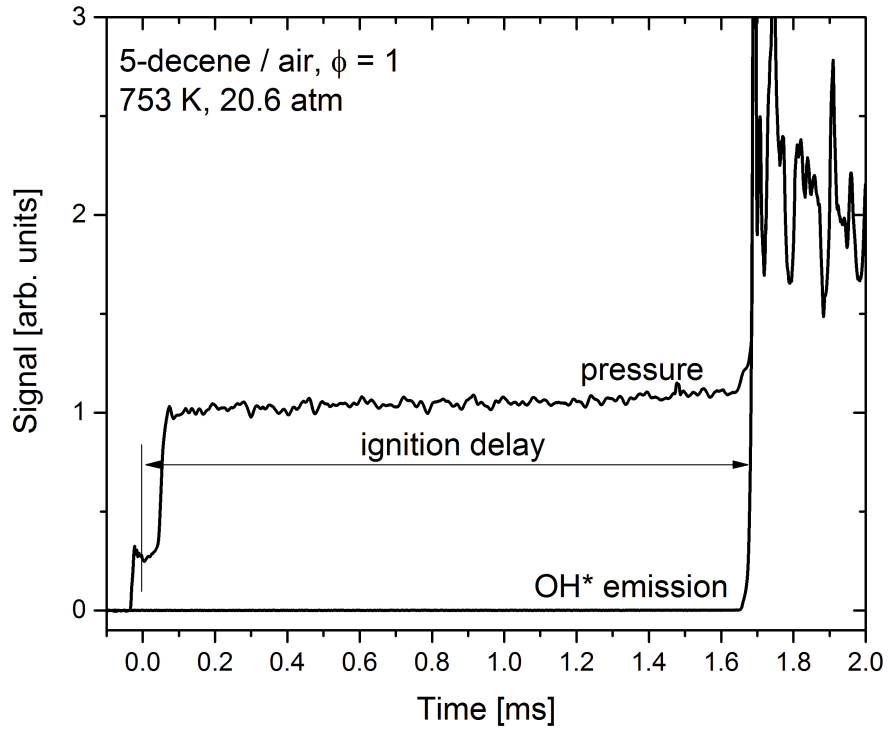


Figure 2.2: Ignition delay measurement.

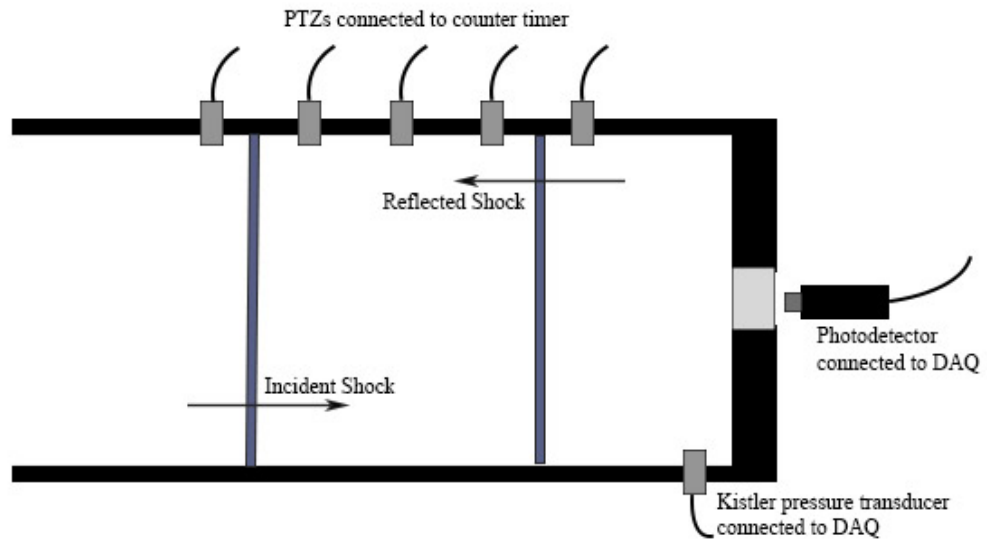


Figure 2.3: Schematic of RPI shock tube test section.

3 Experimental Results

3.1 Observations

Autoignition delay times of n-decane, 1-decene and 5-decene/air mixtures were measured in shock tube experiments with equivalence ratios of 0.5, 1, 1.5, pressure of 20 atm and temperature range of 700-1200 K. Air, in this case, is defined as mixture of 21% O_2 and 79% N_2 . Another set of stoichiometric experiments of the same mixtures at elevated pressure of 40 atm were also carried out for comparison. Experimental results at different equivalence ratios are plotted in Figure 3.1-3.4. Observations can be made that ignition delay increases with a decreasing equivalence ratio and is shorter at elevated pressure and temperature. While ignition delay generally increases with decreasing temperature, a slight decrease of ignition delay can be observed as temperature decrease from approximately 900 to 800 K at an initial pressure of 20 atm. This transition region is referred as the negative temperature coefficient (NTC) region. An interesting inversion in reactivity can be observed between 5-decene and 1-decene when temperature was increased. In high-temperature region ($T > 950$ K), 1-decene display very similar ignition delay time to n-decane and 5-decene has ignition delay consistently shorter than that of 1-decene and n-decane. In a low-temperature region ($T < 950$ K), 5-decene shows significantly longer ignition delay than that of 1-decene and n-decane and 1-decene has a slightly longer ignition delay than n-decane. It also appeared that the low-temperature reactivity was more significantly affected by the double bond position.

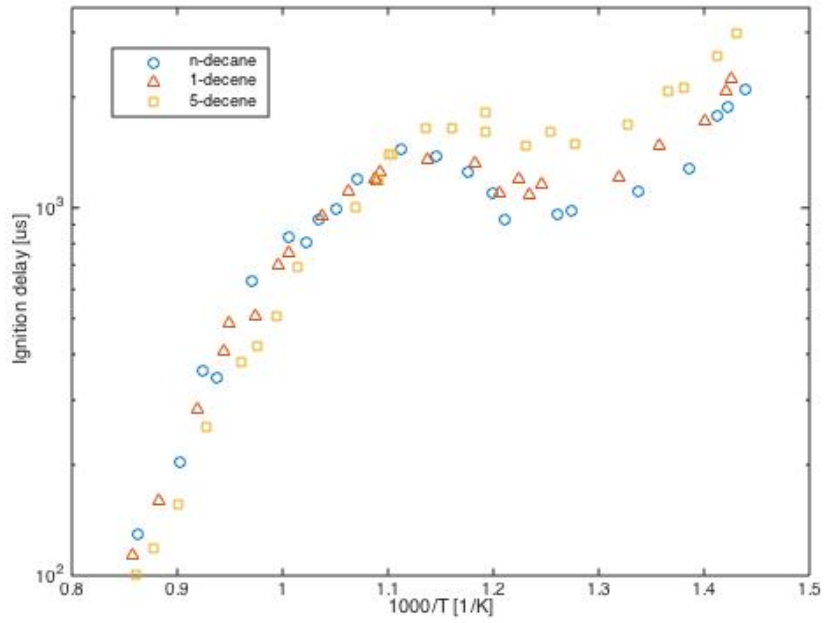


Figure 3.1: Ignition delay for n-decane, 1-decene and 5-decene when $\phi = 1$, $P=20\text{atm}$.

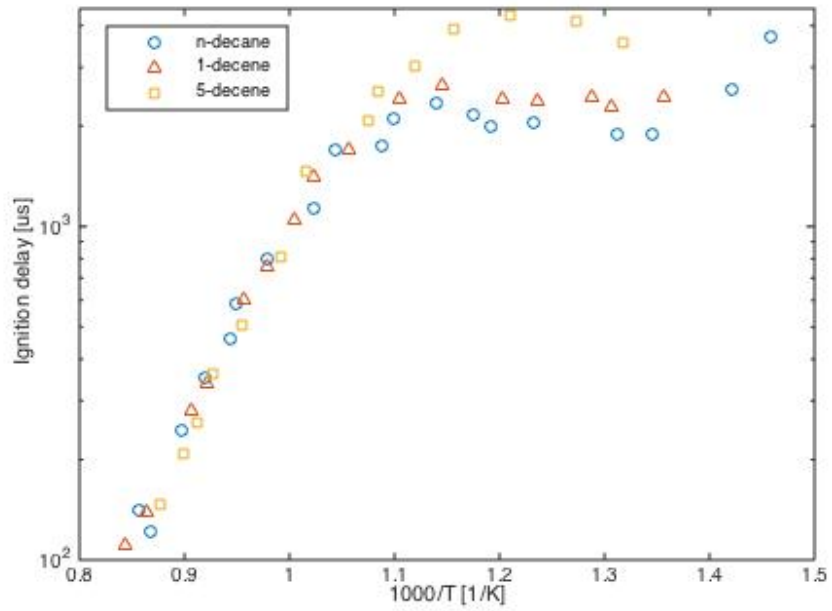


Figure 3.2: Ignition delay for n-decane, 1-decene and 5-decene when $\phi = 0.5$, $P=20\text{atm}$.

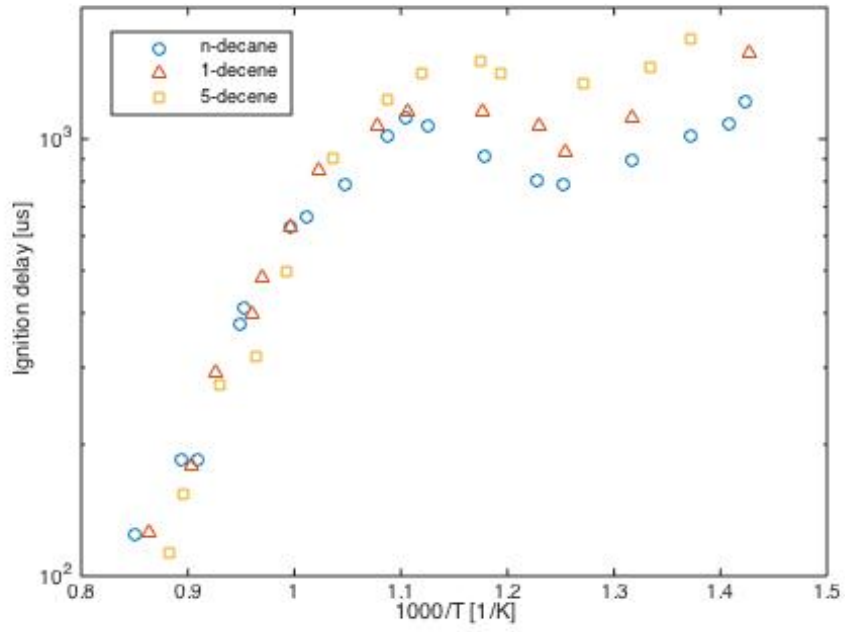


Figure 3.3: Ignition delay for n-decane, 1-decene and 5-decene when $\phi = 1.5$, $P=20\text{atm}$.

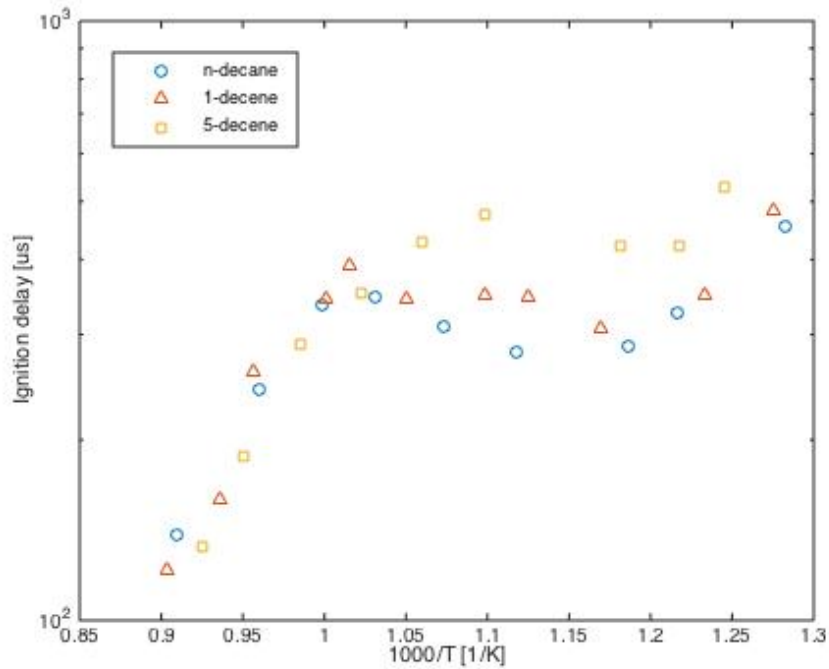


Figure 3.4: Ignition delay for n-decane, 1-decene and 5-decene when $\phi = 1$, $P=40\text{atm}$.

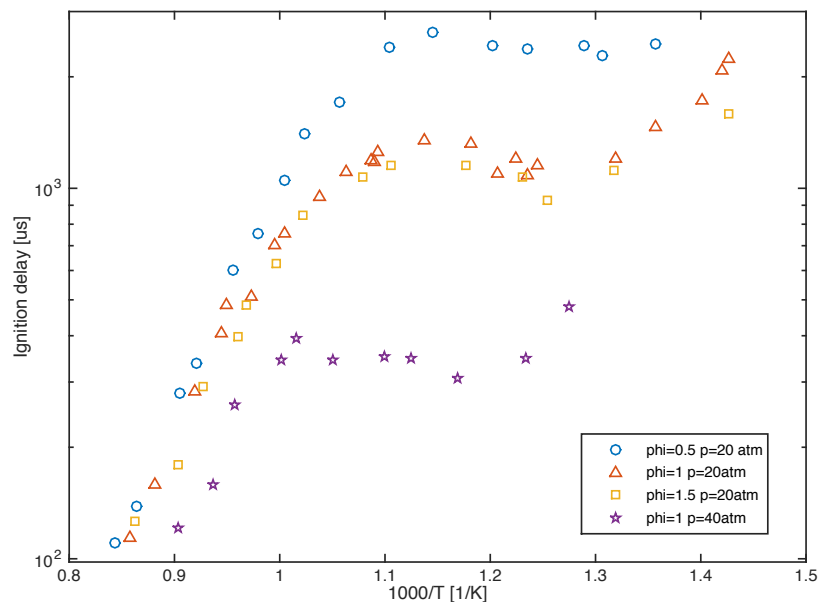


Figure 3.5: Comparison between various equivalence ratios and pressure for 1-Decene.

3.2 Comparison to previous work

The experimental results in this study showed very similar trends to previous works investigating alkene oxidation. In the transition from high temperature to low temperature (NTC), NTC behavior was observed in previous studies on alkene and alkane oxidation. The trend of ignition delay at high temperature in this study is consistent with the result presented by Fridlyand et al.[23], who conducted shock tube speciation experiments on four decene isomers, 1, cis-2, cis-5 and trans-5, at high temperature (850-1500K) and pressure. He observed that 5-decene has a significantly increased fuel consumption compared to 1-decene and 2-decene and concluded that decenes with a more center located double bond tend to be more reactive at high temperature. Hellier et al. [21] looked into the effect of double bond position for four isomers of octane, 1, trans-2, cis-3 and trans-3.

All combustion experiments were carried out in a single-cylinder direct-injection diesel engine. They concluded that as the double bond moved toward the center, the ignition delay time showed an increasing trend, which is consistent with the results of this study at lower temperatures. In the work by Mehl et al. [20], the ignition delay of hexene isomers were studied using both a shock tube in high temperature range and a rapid compression machine in an intermediate temperature range. Their experiment results displayed the same trend as this study and the inversion of reactivity as temperature increases was also observed.

4 Modeling of chemical kinetics

Chemical kinetics models used to simulate the ignition of 1-decene and 5-decene were generated by Fridlyand et al. [23] with the use of the Reaction Mechanism Generator (RMG), which is a software developed by Massachusetts Institute of Technology (MIT) for auto generation of chemical kinetic models. A detailed description of the implementation process was also included in [23]. CHEMKIN-Pro was used to conduct the simulations at the shock tube experimental conditions. The chemical kinetics reaction mechanisms for hydrocarbon combustion have been studied in many papers. A general mechanism for hydrocarbon oxidation under HCCI condition was discussed by Westbrook [26]. Chemical kinetics models of all classes of hydrocarbon have been reviewed by Simmie [29]. Chemical models for the oxidation of short and long alkenes can found in references [12] and [30], respectively. Westbrook et al. has developed the detailed chemical kinetics mechanisms for the oxidation of n-alkanes from C8 to C16 [27]. A detailed chemical kinetics mechanism for oxidation of n-hexene isomers was developed by Mehl et al. [28].

4.1 Chain reactions: initiation, propagation, branching and termination

Chain reaction is the dominating process in the oxidation of hydrocarbon fuels [26]. Once started, chain reaction can be viewed as repetitions of different elementary reactions. The repetition does not end until all the reactants are fully reacted. Intermediate species appearing in the elementary reactions are defined as chain carriers, which are usually free radicals. Elementary chain reactions can be generally classified as chain initiation, chain branching, chain propagation and chain terminating [31].

4.1.1 Chain initiation

Chain initiation, often occurring at the start of chain reaction, is defined as the reactions that generate free radicals from stable species, such as one situation decene decomposition:



A more general expression for decomposition of hydrocarbon is [26]:



4.1.2 Chain branching

Chain initiation is a special case of chain branching, which happens when a reaction generates more free radicals than it consumes, as in the most important chain branching reaction in high-temperature combustion [26]:



One $\text{H}\cdot$ radical consumed, forming another two radicals and consuming molecular oxygen. Chain branching is the most important type of elementary reaction for characterizing the reaction rate at a certain condition, as such is closely related to the length of fuel ignition delay. Generally, if the oxidation of a hydrocarbon is dominated by chain branching, the chain reaction will end sooner and result in a shorter ignition delay.

4.1.3 Chain propagation

Chain propagation is defined as elementary reactions in which the number of free radicals is conserved. For example, the addition of $\text{OH}\cdot$, which consume one free $\text{OH}\cdot$ radical and generate another radical:



4.1.4 Chain termination

Elementary reactions, in which free radicals are consumed and stable molecules are generated, are defined as chain termination reactions. As a simple illustration [26]:



All the illustrations given above is based on single reactions. But in reality, a large set of reactions together may be viewed as one category these types of reactions. For instance, the Waddington mechanism, which happens during low-temperature oxidation, consists of a sequence of reactions, which initially consumes an $\text{OH}\cdot$ and ultimately generates a new $\text{OH}\cdot$. Although some of the reactions in the Waddington mechanism cannot be treated as chain propagating, the whole process qualified as a chain propagating process. There are many such examples in the general scheme for hydrocarbon fuel combustion.

4.2 A general reaction scheme for hydrocarbon combustion

A general scheme for pathways of chain reaction for hydrocarbon fuel oxidation is shown in Figure 4.1, which was summarized based on the result of [26]-[30]. Given that thousands of elementary reactions that take place during the oxidation of hydrocarbon, this scheme only represents the important categories of reactions that occur. Note that, at different temperatures a different part of this scheme will dominate resulting in the differences in ignition delay and its dependence on temperature, pressure, mixture, and fuel. Each one of the reactions in this scheme will be introduced in the following sub-sections

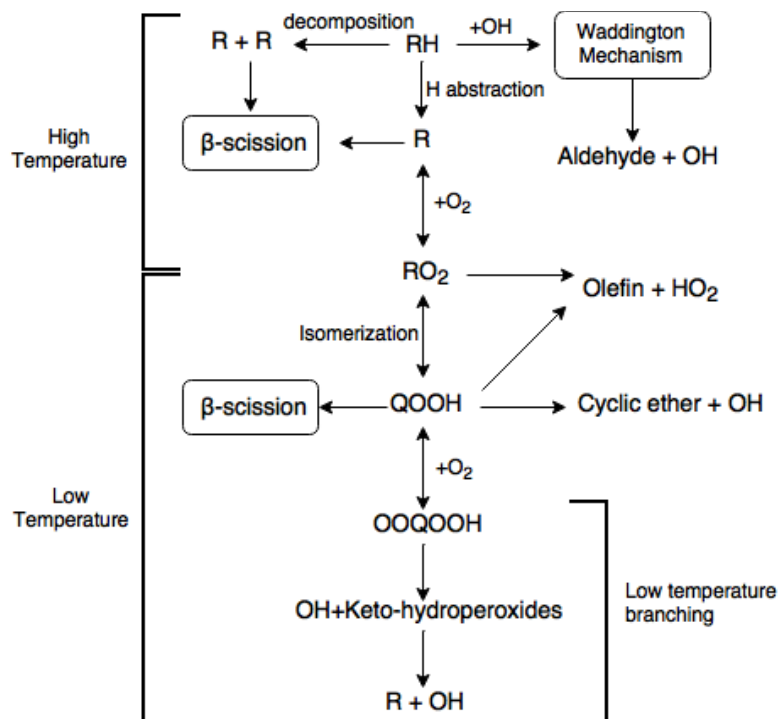


Figure 4.1: General reaction scheme for hydrocarbon fuels at low and high temperature.

4.2.1 Common reaction pathways

The most common chain initiations are the decomposition reactions, in which fuel molecules are fragmented into smaller molecules, and the abstraction of H atoms, in which alkyl radical is generated [26]:



where X could be a radical or stable (e.g., O_2).

4.2.2 High-temperature reaction pathways

At high temperature, chain reaction is generally dominated by chain branching reactions, including decomposition of fuel molecules and beta-scission of radicals. As one of the most

important chain branching reactions, beta-scission break the C-C bond in a large free radical, forming a smaller radical and an olefin. As an example, beta-scission of alkyl radical [26]:



4.2.3 Intermediate and low temperature reaction pathways

At intermediate to low temperature, more chain propagating reactions take part in the chain reaction.

1. Alkyl radical addition to O₂

As one major intermediate pathway, this reaction serves as a premise for internal isomerization and further low temperature branching pathways [26]:

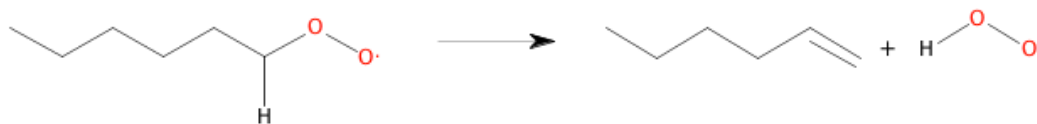


2. Internal isomerization

RO₂· radical may undergo internal isomerization [26]:



A possible propagating reaction, known as the elimination of HO₂·, may happen to RO₂· radical before internal isomerization [26]:

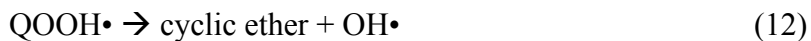


$\text{HO}_2\cdot$ elimination may also happen to $\text{QOOH}\cdot$ after isomerization [26]:



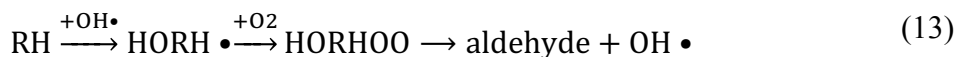
4.2.4 Generation of cyclic ethers

Another chain propagating process may happen to the product of internal isomerization of $\text{RO}_2\cdot$ [26]:



4.2.5 Waddington mechanism

As mentioned before, Waddington mechanism is a chain propagating process occur to the fuel molecule only at low temperature, in which one $\text{OH}\cdot$ is consumed and eventually generate one $\text{OH}\cdot$ [26]:



4.2.6 Addition of QOOH to O₂

A second O₂ may add to the product of isomerization QOOH, forming an OOQOOH radical. Further isomerization may happen after that [26]:



4.2.7 Low-temperature branching

At low temperature, after a series of chain propagating reactions, the chain finally get branched and smaller alkyl radicals are generated.

5 Modeling Results

Simulation results carried out by CHEMKIN-Pro utilizing existing chemical kinetic models are shown below in Figure 5.1-5.5 along with comparison to the experimental data. Since the chemical kinetics model used for 1-decene and 5-decene, developed by Fridlyand et al. [23] can only model the higher temperature condition ($> 900\text{K}$), as the model does not contain low-temperature chemistry, the more interesting low-temperature trends are not be seen in the modelling predictions. A LLNL model published by Sarathy et al. [32] was used to simulate n-decane oxidation, which is able to capture full curve at high and low temperature but clearly does not provide quantitative predictions for ignition delay.

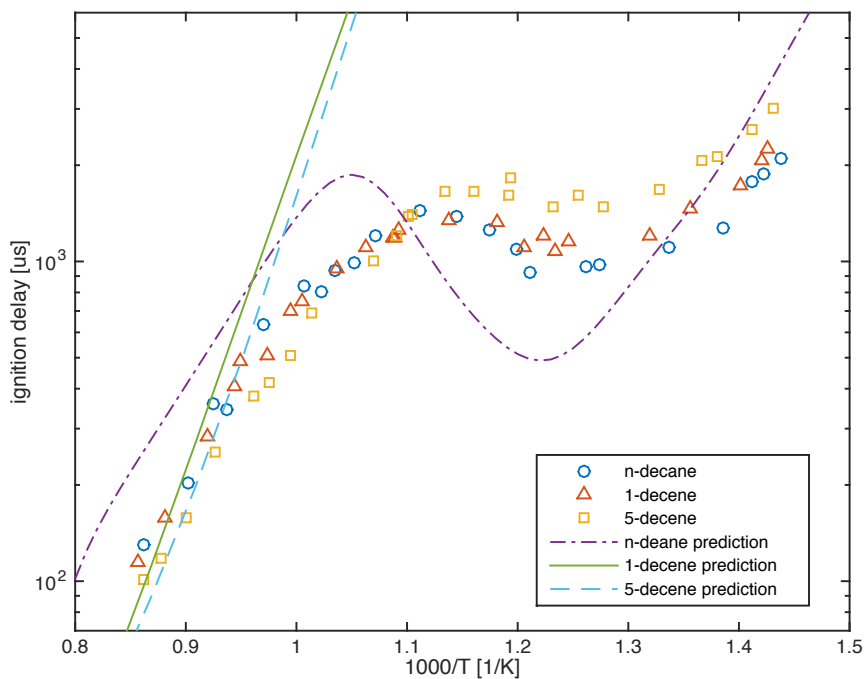


Figure 5.1: Ignition delay comparison with modeling predictions when $\phi=1$, $P=20\text{atm}$.

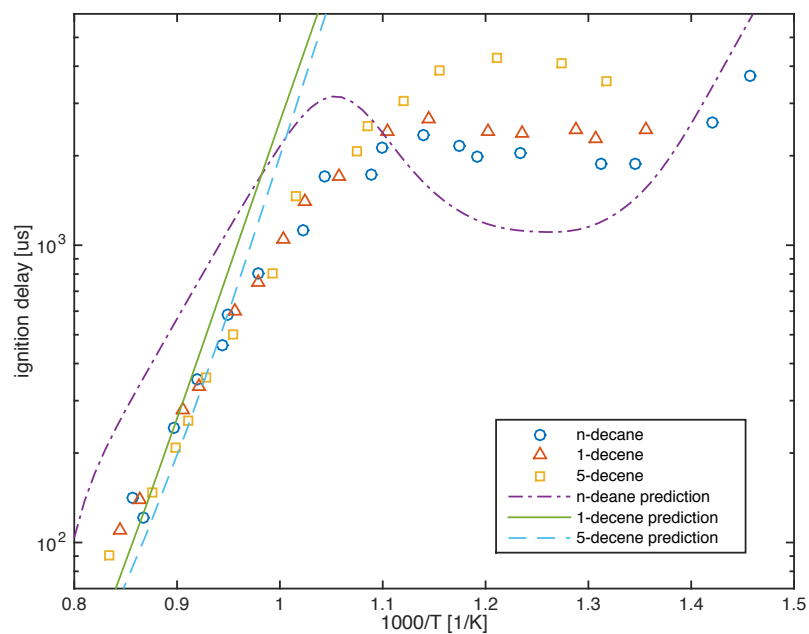


Figure 5.2: Ignition delay comparison with modeling predictions when $\phi=0.5$, $P=20\text{atm}$.

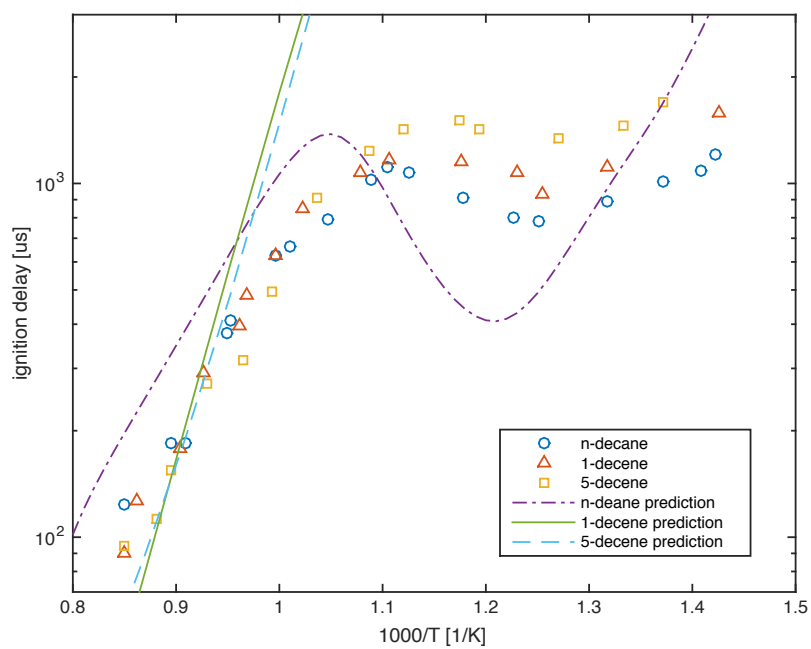


Figure 5.3: Ignition delay comparison with modeling predictions when $\phi = 1.5$, $P=20\text{atm}$.

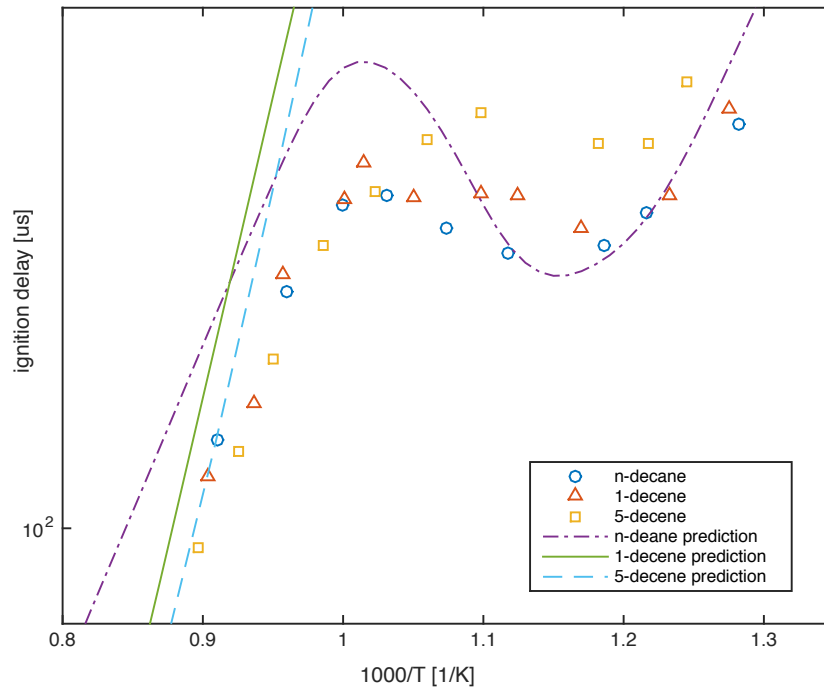


Figure 5.4: Ignition delay comparison with modeling predictions when $\phi = 1$ $P=40\text{atm}$.

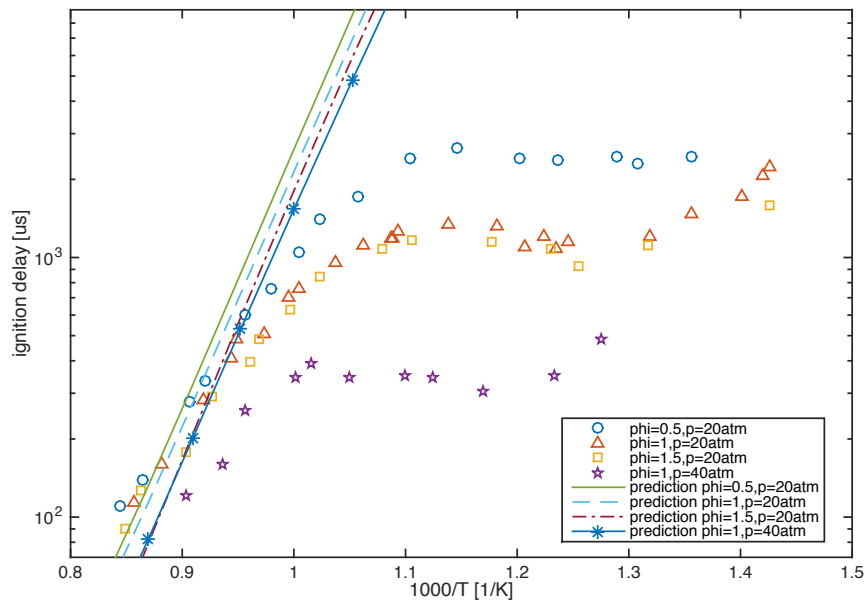


Figure 5.5: Ignition delay comparisons with different equivalence ratio and pressure for 1-decene.

5.1 Comparison to experiment

For the n-decane model, the trend of ignition delay generally coincide with the experimental data but the predicted ignition delay differs with the experimental data in the high and intermediate temperature with the model having longer ignition delay at high temperature and shorter ignition delay at intermediate temperature than experiment. Differences between predicted data and experimental data are expected, since the kinetic model is complex and not grounded in experimental results. The negative temperature coefficient (NTC) behavior at intermediate temperature is captured for n-decane with reasonable prediction for the temperature range for this behavior but with an over prediction for the magnitude for the NTC behavior. For 1-decene and 5-decene, it is clear that the trend of ignition delay at intermediate temperature and high temperature is not captured, but the tendency of decreasing ignition delay with larger equivalence ratio was correctly predicted. The predicted ignition delay only coincide with the experimental data when temperature is higher than 1000 K.

6 Discussion

Chemical reaction schemes could provide a reasonable explanation for the variation of ignition delay at different conditions including temperature, pressure and equivalence ratio, as shown in presented experimental results. At high temperature, reactions were dominated by the chain-branching reactions. Given that C-H bonds and C-C bonds on an allylic position are weaker than C-H and C-C bonds in a structure without double bonds, as shown in Figure 6.1.

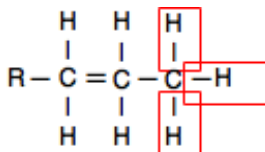


Figure 6.1: The position of allylic C-H bonds.

As such, the centrally located double bond in 5-decene can cause adjacent allylic C-H and C-C bonds to be weaker and the carbon chain easier to break than 1-decene. Therefore, the chain branching process is accelerated, resulting in shorter ignition delay time for 5-decene compared to 1-decene. In the low-temperature region, the reaction pathways become significantly more complex and, as introduced in section 4, more low-temperature chain propagating reactions get involved. The O_2 addition to R radical reaction has an equilibrium constant in favor of the forming of RO_2 at low temperature, which helps to start the low temperature part of the reaction scheme. During the generation of RO_2 and isomerization product ROOH , propagating reactions such as the elimination of $\text{OH}\cdot$ elimination and the forming of cyclic ether can happen, which will compete with the low temperature branching. Additionally, the low-temperature Waddington mechanism also serves to inhibit the chain branching progress. In sum, the chain branching reactions may

get slowed down by numerous chain propagating reactions favored only at low and intermediate temperature, resulting in longer reaction time than high temperature oxidation. Several possible situations may account for lower reactivity of 5-decene compared to 1-decene and n-decane in a low temperature region. The weaker allylic C-H bonds in 5-decene may cause the OH• elimination of RO₂ and ROOH much easier than that of 1-decene and n-decane, causing more chain propagation to compete with chain branching. The existence of double bond in 1-decene and 5-decene can limit the possible internal isomerizations of RO₂, causing n-decane to react faster than the decenes. These chemistries cause the ignition delay at low temperature to follow the order: n-decene<1-decene<5-decene.

7 Conclusion

Experimental data was presented for the ignition delay of n-decane, 1-decene and 5-decene, in order to examine the influence of double bond position in C10 alkenes at both low temperature and high temperature using shock tube. The experimental results show that decene with a more center-located double bond tend to display a shorter ignition delay than 1-decene and n-decane at high temperature. The ignition delay for 1-decene is almost the same as that of n-decane. An inversion in reactivity occur when the temperature drops below 900 K, resulting the ignition delay following the order: n-decene<1-decene<5-decene. Comparison was made with experimental results of previous works on alkene oxidations, experimental results in this work showed consistency with the trends observed in other studies. Double bond position in decenes is shown to play a very important role in determining low-temperature ignition delay. It is suggested that competition between chain branching and chain propagating is the major factor that affect the ignition delay. At high temperature, the center located double bond in 5-decene boost chain branching by providing weaker allylic C-H bonds, leading to shorter ignition delay. However, at lower temperature region where more chain propagation involved, the weak allylic C-H bond serves to facilitate some chain propagating reactions, such as the HO₂• elimination, slowing down the overall reaction speed and resulting in longer ignition delay.

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Appendix A: Experimental result data

Table A.1: Ignition delay times for n-decane.

n-decane/air, $\phi=1$

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 21.6 | 695 | 1.438849 | 2089 |
| 21.4 | 703 | 1.422475 | 1874 |
| 22.1 | 708 | 1.412429 | 1783 |
| 22.8 | 722 | 1.385042 | 1276 |
| 21.5 | 748 | 1.336898 | 1111 |
| 21.4 | 785 | 1.273885 | 978 |
| 22 | 793 | 1.261034 | 962 |
| 20.2 | 826 | 1.210654 | 930 |
| 21.6 | 834 | 1.199041 | 1090 |
| 21.7 | 851 | 1.175088 | 1255 |
| 22.3 | 873 | 1.145475 | 1379 |
| 19.7 | 899 | 1.112347 | 1448 |
| 19.4 | 934 | 1.070664 | 1199 |
| 18.4 | 951 | 1.051525 | 989 |
| 22.2 | 967 | 1.034126 | 932 |
| 21.7 | 978 | 1.022495 | 802 |
| 21.6 | 994 | 1.006036 | 834 |
| 21.6 | 1030 | 0.970874 | 631 |
| 18.9 | 1067 | 0.937207 | 344 |
| 18.4 | 1082 | 0.924214 | 360 |
| 19.4 | 1109 | 0.901713 | 203 |
| 19.8 | 1159 | 0.862813 | 130 |

n-decane/air, $\phi=0.5$

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 22 | 686 | 1.457726 | 3718 |
| 22.4 | 704 | 1.420455 | 2574 |
| 21.8 | 743 | 1.345895 | 1881 |
| 20.5 | 762 | 1.312336 | 1882 |
| 20.3 | 811 | 1.233046 | 2043 |
| 21 | 839 | 1.191895 | 1983 |
| 21.5 | 851 | 1.175088 | 2160 |
| 20.4 | 878 | 1.138952 | 2343 |
| 21.3 | 910 | 1.098901 | 2116 |
| 21.3 | 919 | 1.088139 | 1738 |
| 20.5 | 958 | 1.043841 | 1698 |

| | | | |
|------|------|----------|------|
| 19.9 | 978 | 1.022495 | 1128 |
| 20.8 | 1021 | 0.979432 | 802 |
| 19.4 | 1053 | 0.949668 | 584 |
| 19.6 | 1059 | 0.944287 | 463 |
| 19.8 | 1088 | 0.919118 | 354 |
| 19 | 1115 | 0.896861 | 243 |
| 18.9 | 1153 | 0.867303 | 122 |
| 18.2 | 1167 | 0.856898 | 141 |

n-decane/air, phi=1.5

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 20.6 | 703 | 1.422475 | 1212 |
| 22.4 | 710 | 1.408451 | 1084 |
| 21.1 | 729 | 1.371742 | 1013 |
| 21.2 | 759 | 1.317523 | 891 |
| 20.3 | 799 | 1.251564 | 784 |
| 21.5 | 815 | 1.226994 | 803 |
| 19.3 | 849 | 1.177856 | 912 |
| 20.1 | 888 | 1.126126 | 1069 |
| 20.2 | 905 | 1.104972 | 1118 |
| 19.5 | 919 | 1.088139 | 1019 |
| 20.2 | 955 | 1.04712 | 790 |
| 20.1 | 989 | 1.011122 | 664 |
| 19.5 | 1003 | 0.997009 | 626 |
| 19 | 1049 | 0.953289 | 410 |
| 18.3 | 1054 | 0.948767 | 376 |
| 18.3 | 1100 | 0.909091 | 184 |
| 18.8 | 1118 | 0.894454 | 185 |
| 18.2 | 1177 | 0.849618 | 124 |

n-decane/air, phi=2

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 24.1 | 705 | 1.41844 | 1100 |
| 23.4 | 736 | 1.358696 | 854 |
| 21.4 | 766 | 1.305483 | 723 |
| 20.1 | 788 | 1.269036 | 650 |
| 21.6 | 801 | 1.248439 | 684 |
| 18.5 | 844 | 1.184834 | 784 |
| 20 | 866 | 1.154734 | 982 |
| 19.1 | 896 | 1.116071 | 1000 |
| 20.1 | 947 | 1.055966 | 817 |
| 18.2 | 1022 | 0.978474 | 429 |

| | | | |
|------|------|----------|-----|
| 18.9 | 1057 | 0.946074 | 262 |
| 19.4 | 1142 | 0.875657 | 121 |

n-decane/air, phi=1

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 42.8 | 780 | 1.282051 | 453 |
| 41.9 | 822 | 1.216545 | 325 |
| 42.2 | 843 | 1.18624 | 287 |
| 40.7 | 895 | 1.117318 | 280 |
| 41.4 | 932 | 1.072961 | 308 |
| 39.3 | 970 | 1.030928 | 347 |
| 38.4 | 1001 | 0.999001 | 335 |
| 37 | 1042 | 0.959693 | 242 |
| 36.8 | 1099 | 0.909918 | 139 |

Table A.2 Ignition delay times for 1-decene.

1-decene/air, phi=1

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 22.7 | 701 | 1.426534 | 2240 |
| 21.8 | 704 | 1.420455 | 2072 |
| 21.2 | 714 | 1.40056 | 1719 |
| 22.6 | 737 | 1.356852 | 1467 |
| 22.9 | 758 | 1.319261 | 1206 |
| 22.9 | 803 | 1.24533 | 1154 |
| 20.3 | 810 | 1.234568 | 1079 |
| 18.7 | 817 | 1.22399 | 1201 |
| 20.2 | 829 | 1.206273 | 1100 |
| 21.1 | 846 | 1.182033 | 1321 |
| 21.7 | 879 | 1.137656 | 1348 |
| 20.4 | 915 | 1.092896 | 1254 |
| 20.4 | 918 | 1.089325 | 1181 |
| 20.6 | 920 | 1.086957 | 1191 |
| 21.8 | 941 | 1.062699 | 1107 |
| 20.7 | 964 | 1.037344 | 951 |
| 21.5 | 995 | 1.005025 | 753 |
| 22.7 | 1005 | 0.995025 | 700 |
| 21.1 | 1027 | 0.97371 | 509 |
| 20 | 1054 | 0.948767 | 484 |
| 19.8 | 1059 | 0.944287 | 408 |
| 19.1 | 1088 | 0.919118 | 282 |

| | | | |
|------|------|----------|-----|
| 20.3 | 1134 | 0.881834 | 159 |
| 19.2 | 1167 | 0.856898 | 114 |

1-decene/air, phi=0.5

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 21.8 | 737 | 1.356852 | 2454 |
| 20.6 | 765 | 1.30719 | 2287 |
| 22.1 | 776 | 1.28866 | 2434 |
| 22 | 809 | 1.236094 | 2387 |
| 21.1 | 832 | 1.201923 | 2422 |
| 20.7 | 873 | 1.145475 | 2644 |
| 20.7 | 906 | 1.103753 | 2408 |
| 20.7 | 946 | 1.057082 | 1705 |
| 20.9 | 977 | 1.023541 | 1402 |
| 20.9 | 996 | 1.004016 | 1046 |
| 18.5 | 1021 | 0.979432 | 755 |
| 18.5 | 1046 | 0.956023 | 604 |
| 20.4 | 1086 | 0.92081 | 336 |
| 19.1 | 1104 | 0.905797 | 279 |
| 17.3 | 1157 | 0.864304 | 139 |
| 19.3 | 1185 | 0.843882 | 110 |

1-decene/air, phi=1.5

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 24.7 | 701 | 1.426534 | 1581 |
| 22.7 | 759 | 1.317523 | 1118 |
| 21.2 | 797 | 1.254705 | 930 |
| 22.1 | 813 | 1.230012 | 1075 |
| 19.9 | 850 | 1.176471 | 1149 |
| 22.2 | 904 | 1.106195 | 1159 |
| 20 | 927 | 1.078749 | 1077 |
| 21.9 | 978 | 1.022495 | 846 |
| 18.7 | 1003 | 0.997009 | 627 |
| 20.2 | 1032 | 0.968992 | 482 |
| 22.6 | 1041 | 0.960615 | 396 |
| 20.6 | 1079 | 0.926784 | 292 |
| 19 | 1106 | 0.904159 | 179 |
| 20.6 | 1159 | 0.862813 | 126 |
| 19.5 | 1178 | 0.848896 | 90 |

1-decene/air, phi=1

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|--------|----------|
|---------|-------|--------|----------|

| | | | |
|------|------|----------|-----|
| 43.7 | 784 | 1.27551 | 481 |
| 42.4 | 811 | 1.233046 | 348 |
| 43.5 | 855 | 1.169591 | 307 |
| 39.7 | 889 | 1.124859 | 346 |
| 40.5 | 910 | 1.098901 | 350 |
| 42.7 | 952 | 1.05042 | 344 |
| 39.3 | 985 | 1.015228 | 392 |
| 37.1 | 999 | 1.001001 | 343 |
| 36.1 | 1045 | 0.956938 | 259 |
| 37.7 | 1068 | 0.93633 | 159 |
| 36.2 | 1107 | 0.903342 | 121 |

Table A.3 Ignition delay times for 5-decene.

5-decene/air, $\phi=1$

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 21.7 | 699 | 1.430615 | 2999 |
| 22.5 | 708 | 1.412429 | 2583 |
| 22.2 | 724 | 1.381215 | 2119 |
| 22.9 | 732 | 1.36612 | 2065 |
| 20.6 | 753 | 1.328021 | 1681 |
| 21 | 783 | 1.277139 | 1489 |
| 21.1 | 797 | 1.254705 | 1612 |
| 20 | 812 | 1.231527 | 1479 |
| 21.3 | 838 | 1.193317 | 1828 |
| 20.4 | 839 | 1.191895 | 1610 |
| 18.9 | 862 | 1.160093 | 1651 |
| 21.4 | 881 | 1.135074 | 1653 |
| 20.5 | 905 | 1.104972 | 1401 |
| 19.3 | 908 | 1.101322 | 1389 |
| 20.5 | 917 | 1.090513 | 1201 |
| 21.4 | 935 | 1.069519 | 1008 |
| 18.4 | 986 | 1.014199 | 689 |
| 18.6 | 1006 | 0.994036 | 508 |
| 20.4 | 1025 | 0.97561 | 419 |
| 19.3 | 1041 | 0.960615 | 380 |
| 20.2 | 1079 | 0.926784 | 254 |
| 20.7 | 1111 | 0.90009 | 157 |
| 20 | 1140 | 0.877193 | 118 |
| 19.8 | 1161 | 0.861326 | 101 |

5-decene/air, phi=0.5

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 22.8 | 759 | 1.317523 | 3539 |
| 22 | 785 | 1.273885 | 4098 |
| 20.4 | 826 | 1.210654 | 4280 |
| 21.5 | 865 | 1.156069 | 3894 |
| 20.3 | 893 | 1.119821 | 3042 |
| 21.5 | 922 | 1.084599 | 2527 |
| 21.2 | 931 | 1.074114 | 2074 |
| 19.6 | 984 | 1.01626 | 1455 |
| 19.4 | 1008 | 0.992063 | 806 |
| 20.1 | 1047 | 0.95511 | 503 |
| 19 | 1078 | 0.927644 | 361 |
| 18.8 | 1097 | 0.911577 | 258 |
| 19.5 | 1113 | 0.898473 | 209 |
| 19.2 | 1141 | 0.876424 | 147 |
| 17.5 | 1199 | 0.834028 | 91 |

5-decene/air, phi=1.5

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 23.6 | 729 | 1.371742 | 1703 |
| 22.8 | 750 | 1.333333 | 1460 |
| 23.4 | 787 | 1.270648 | 1339 |
| 23.2 | 838 | 1.193317 | 1416 |
| 23.5 | 851 | 1.175088 | 1515 |
| 23 | 893 | 1.119821 | 1421 |
| 21 | 920 | 1.086957 | 1232 |
| 22.3 | 965 | 1.036269 | 908 |
| 21.6 | 1007 | 0.993049 | 497 |
| 22.2 | 1037 | 0.96432 | 318 |
| 20.8 | 1076 | 0.929368 | 273 |
| 19.8 | 1117 | 0.895255 | 154 |
| 20.1 | 1134 | 0.881834 | 113 |
| 19.4 | 1178 | 0.848896 | 94 |

5-decene/air, phi=1

| P [atm] | T [K] | 1000/T | tau [us] |
|---------|-------|----------|----------|
| 43.5 | 803 | 1.24533 | 530 |
| 42.4 | 821 | 1.218027 | 422 |
| 43.5 | 846 | 1.182033 | 420 |
| 41.3 | 910 | 1.098901 | 474 |
| 40.8 | 943 | 1.060445 | 429 |
| 40.9 | 978 | 1.022495 | 352 |

| | | | |
|------|------|----------|-----|
| 39.1 | 1015 | 0.985222 | 288 |
| 39.3 | 1052 | 0.95057 | 188 |
| 38.7 | 1081 | 0.925069 | 133 |
| 37.5 | 1115 | 0.896861 | 93 |