Cyclopentane combustion. Part II. Ignition delay measurements and mechanism validation

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Abstract

This study reports cyclopentane ignition delay measurements over a wide range of conditions. The measurements were obtained using two shock tubes and a rapid compression machine, and were used to test a detailed low- and high-temperature mechanism of cyclopentane oxidation that was presented in part I of this study (Al Rashidi et al., 2016). The ignition delay times of cyclopentane/air mixtures were measured over the temperature range of 650–1350 K at pressures of 20 and 40 atm and equivalence ratios of 0.5, 1.0 and 2.0. The ignition delay times simulated using the detailed chemical kinetic model of cyclopentane oxidation show very good agreement with the experimental measurements, as well as with the cyclopentane ignition and flame speed data available in the literature. The agreement is significantly improved compared to previous models developed and investigated for higher temperatures only. Reaction path and sensitivity analyses were performed to provide insights into the ignition-controlling chemistry at low, intermediate and high temperatures. The results obtained in this study confirm that cycloalkanes are less reactive than their non-cyclic counterparts. Moreover, cyclopentane, a high octane number and high octane sensitivity fuel, exhibits minimal low-temperature chemistry and is considerably less reactive than cyclohexane. This study presents the first experimental low-temperature ignition delay data of cyclopentane, a potential fuel-blending component of particular interest due to desirable antiknock characteristics.

Keywords

Cyclopentane, ignition delay, shock tube, rapid compression machine, kinetic modeling

1. Introduction

Recent developments in climate change policies [1] and fuel economy projections [2] portend major shifts in energy production and consumption trends. In an unprecedented occurrence, 195 countries signed the Paris Agreement whereby they pledged to reduce greenhouse gas (GHG) emissions and limit the increase in global average temperature to well below 2 °C above pre-industrial levels by the year 2020 [1]. At the same time, the global demand for energy is expected to increase as the world's population and Gross Domestic Product (GDP) increase, particularly in China and India [2]. In order for the projected increase in energy demand to be met within the constraints of legally binding climate change agreements, the fuel industry has to evolve. The latest Energy Outlook report published by British Petroleum (BP) shows that, even though conventional fossil fuels are projected to meet two-thirds of the increase in energy demand out to 2035, renewables and unconventional fossil fuels will grow faster [2]. Shale-derived fuels are among the emerging new sources of energy that are expected to grow quickly in the near future due to technological advancements [2]. These, among others, are the fuels of the future, and they are primarily composed of alkanes and cycloalkanes, followed by aromatics and bicyclic hydrocarbons [3]. The combustion chemistry of alkane fuel components is relatively well researched; however, that of cycloalkanes is not, despite the proven importance of cycloalkane functionality in the oxidation of real fuels [4]. In general, investigating fuel chemistry ultimately allows for the control of fuel efficiency and emission via targeted fuel and engine design.

The most prominent cyclic backbone in practical fuels is cyclohexane [3]. Accordingly, studies on cycloalkane combustion are mostly concerned with cyclohexane and methylcyclohexane, which are regarded as representatives of the naphthenic fraction in conventional fuels [5-10]. These studies show that cyclohexane and its derivatives are less reactive than their non-cyclic counterparts due to the conformational inhibition of ROO/QOOH isomerization pathways, which promotes the formation of non-reactive olefins [11, 12]. They also emphasize the importance of these species in soot formation mechanisms [13]. Since cycloalkane chemistry and kinetics are strongly influenced by the ring size [12], and because other cycles are also prominent in practical fuels, it is important to investigate components other than cyclohexane.

In this study, we investigate the low- and high-temperature reactivity and ignition properties of cyclopentane, a high-octane, knock-resistant cycloalkane, commonly found in gasoline and a suitable blending component [14]. Previous experimental studies of cyclopentane ignition delay are generally limited to high-temperature conditions. Daley et al. [15] measured the ignition delay of cyclopentane in a shock tube (ST) under engine-relevant conditions for lean and stoichiometric fuel/air mixtures, at pressures of 13 and 45 atm, and at temperatures between 847 and 1379 K [15]. Tian et al. [16] and Sirjean et al. [17] also provided ST ignition delay measurements of cyclopentane within the temperature range of 1100–1800 K and at pressures of up to 8.4 bar, for fuel-lean, stoichiometric and fuel-rich conditions [16, 17]. The fuel/oxidant mixtures were diluted in argon at fuel concentrations of 0.5 and 1.0% [16, 17]. The measured data were used to validate high-temperature cyclopentane oxidation mechanisms developed based on the JetSurF2.0 mechanism [16] or using the EXGAS software [17]. Davis and Law [18] measured premixed laminar flames speeds for cyclopentane/air mixtures at a range of equivalence ratios. They found that cyclopentane/air mixtures exhibited similar laminar flame speeds as *n*-pentane, *n*-hexane, and cyclohexane.

Herein, we present ignition delay experiments that span a wider range of conditions than in previous studies and are also relevant to internal combustion engines. High-temperature experiments were conducted at the high-pressure shock tube (HPST) facilities at King Abdullah University of Science and Technology (KAUST) and the National University of Ireland, Galway (NUIG), whereas the rapid compression machine (RCM) at NUIG was used to carry out measurements at low to intermediate temperatures. The new data span temperatures between 650 and 1350 K, pressures of 20 and 40 atm, and use fuel/air mixtures at equivalence ratios of 0.5, 1.0 and 2.0. A detailed kinetic oxidation model comprising low- and high-temperature reaction classes is tested against the ignition and flame speed data available in the literature, as well as the new data. Details of the kinetic model development may be found in Part 1 of this study, entitled “Mechanism development and computational kinetics”. The model was also tested against speciation data measured in a jet-stirred reactor, as detailed in [19].

2. Experimental Methods

2.1. KAUST High-Pressure Shock Tube (HPST)

High temperature ignition delay measurements (1000 – 1300 K) were performed using the HPST facility at KAUST at pressures of 20 and 40 atm. The HPST has been reported previously in literature [20]; hence, only brief overview will be given here. The driven section of the shock tube is 6.6 m long while the driver section length can be varied to a maximum length of 6.6 m. The shock tube has an inner diameter of 10 cm and the inner surface is electro-polished to reduce boundary layer effects. The driver and driven sections are separated by pre-scored aluminum diaphragms in a double-diaphragm mid-section. The double diaphragm mid-section allows better control of diaphragm burst pressures p_4 and hence an excellent control of reflected shock temperatures T_5 and pressures p_5 . The driven section is connected to a turbopump that can be used to achieve a vacuum pressure as low as 10^{-5} Torr. The test mixture consisting of cyclopentane (purchased from Sigma Aldrich with a purity of 99%), oxygen, nitrogen and/or helium (purchased from AH gases at 99.999% purity) was prepared manometrically by using a magnetically-stirred mixing vessel. For each set of measurements, the mixtures were allowed to mix for at least one hour before starting the experiments.

In order to measure the shock velocity, six piezoelectric pressure transducers are located axially along the last 3.2 m of the driven section of the shock tube. Post reflected shock conditions (T_5 and p_5) were calculated by using shock jump relations and known thermodynamic properties of test mixtures. A Kistler 603B1 pressure transducer located at 1 cm from the endwall was used to measure the sidewall pressure. Sidewall OH* emission was measured through a sapphire window at 1 cm from the endwall by using a photodetector and a narrow band-pass optical filter. A schematic of the experimental setup is shown in Fig. 1. Ignition delay time (IDT) is defined as the time between the arrival of the reflected shock wave at the sidewall optical location and the onset of ignition. Both sidewall pressure and OH* emission determinations are shown in Fig. 2 and agree within 5% of each other. The post-reflected pressure gradient (dp_5/dt) is nearly 3%/ms for the test conditions presented in this work, and this is accounted for in the simulations using a volume time history [21]. The uncertainty on the HPST experimental measurements is approximately $\pm 20\%$. Uncertainties in the reflected shock temperature and pressure are $< 1\%$ and are mainly due to errors in measuring incident shock velocity

and thermodynamic parameters. Uncertainty in the mixture (fuel/air) composition is estimated to be less than 5% and results from the error in the measured partial pressures during mixture preparation. The pressures were measured using MKS Baratron Capacitance Manometers which have a manufacture specified uncertainty of 0.12% of the reading.

Figure 1. Schematic of the KAUST high-pressure shock tube (HPST) used for ignition delay time measurements.

Figure 2. Representative pressure and OH-emission traces in the KAUST HPST obtained with a reacting mixture.

2.2. NUIG High-Pressure Shock Tube (HPST)

High-temperature ignition delay times (1000—1300 K) were measured for stoichiometric mixtures of cyclopentane in a 21% O₂ : 79% N₂ bath gas were measured behind reflected shocks within the NUI, Galway high-pressure shock tube at pressures of 13, 20, 40 and 50 atm. The fuel was supplied by Sigma Aldrich in high purity (> 99.0%), while oxygen (99.5%) and nitrogen (99.95%) were supplied by BOC Ireland. The common theory and design of shock tubes as chemical reactors has been generally well-documented in Ref. [22] and the NUIG HPST has been described in detail in Refs. [23, 24], thus only a brief description of the apparatus is presented here.

The 63.5 mm bore shock tube is comprised of a 3 m long driver section and 5.73 m long driven section, which are separated by a 3 cm long double diaphragm housing. Shocks are generated with helium. The driven gas, which contains the fuel mixture, is heated via the reflected shock and subsequent measurements are performed at the endwall of the driven section. The pressure history of the gas at the endwall is recorded by a dynamic pressure transducer that is mounted in the endwall of the driven section, from which the ignition delay time of the mixture is subsequently measured. Ignition delay

times are defined as the time difference between the arrival of the reflected shock at the endwall and the Von Neumann spike due to ignition. The thermodynamic state of the test gas behind the reflected shock wave is evaluated from the ideal normal shock equations, which require the measurement of the shock velocity at the endwall. This measurement is performed by monitoring the incident shock arrival time at six pressure transducers staggered along the axis of the driven section and interpolating the velocity of the shock along the tube, and shock attenuation is accounted for by extrapolating the collective velocity measurements to the endwall. Ignition delay measurements within the device are generally reproducible to within $\pm 15\%$, and gas temperatures behind the reflected shock are conservatively estimated to be uncertain within ± 10 K.

2.3. Rapid compression machine (RCM)

Low- to intermediate-temperature ignition delay times (675-1000 K) for fuel-lean, stoichiometric, and fuel-rich ($\phi = 0.5, 1.0,$ and 2.0 , respectively) mixtures of cyclopentane in a 21% O_2 : 79% diluent bath gas were measured within the NUI, Galway rapid compression machine at compressed pressures of 20 and 40 atm. The fuel was supplied by Sigma Aldrich in high purity ($> 99.0\%$), while oxygen (99.5%) and nitrogen (99.95%) were supplied by BOC Ireland. The details concerning the design, operating principles, and limitations of the apparatus have been well-documented in Refs.[25-27], while a description of the current reaction chamber geometry, ignition delay time collection methodology, data acquisition hardware, and data post-processing techniques are available in Ref. [24].

Briefly, the experimental platform utilizes opposed pistons to rapidly compress a test gas, and furthermore maintain the elevated compressed gas thermodynamic state for the duration of chemical interest. The test gas pressure history, monitored during each experiment, serves as the sole diagnostic during and after the compression process. Ignition delay times are defined at each condition as the time difference between the local maximum in pressure that occurs near the end of volumetric compression and the maximum rate of pressure rise due to ignition, which provides a sufficiently sensitive diagnostic for the high-fuel and oxidizer concentrations studied here so that further ignition indicators offered by spectral techniques are not necessary. The widely used

adiabatic core model was employed to evaluate the compressed gas temperatures from pressure histories. Furthermore, the adiabatic core model was also used to transiently prescribe the energy supplied to or lost from the test gases due to volumetric compression and heat losses, respectively, in order to adequately compare experimental data sets with mechanism simulations. These transport processes were isolated from chemical ones by compressing an analogous non-reactive gas for each experimental condition, and quantified by deriving the specific volume history of the adiabatic core gas from the measured pressure history of the non-reactive experiment that was then used as an inputted boundary condition for a simulated variable volume 0-D reactor. Ignition delay measurements within the RCM are generally reproducible to within $\pm 10\%$, and gas temperatures behind the reflected shock are conservatively estimated to be uncertain within ± 10 K.

3. Results and discussion

The experimental ignition delay measured in this study were used along with data available in the literature to test the cyclopentane mechanism developed in [28]. Table 1 summarizes the experimental data sets used for evaluating the present model. The pressure and temperature conditions of the individual experiments conducted in this study are provided in Tables S1-S3 in the Supplementary Material. Shock tube experiments at NUIG were conducted at the same conditions as those employed at KAUST ($\phi = 1$ and $p = 20, 40$ atm) and those used in [15] (fuel/air mixtures at $\phi = 1$ and $p = 13, 50$ atm) to assess the facility-to-facility variation in the experiments. We used the homogeneous batch reactor model of the CHEMKIN PRO software package [29] to simulate both RCM and shock tube experiments. Flame speed experiments available in the literature were simulated using the PREMIX module [29].

Table1. Summary of experimental conditions employed in cyclopentane ignition studies available in the literature as well as in this study

Reference	Technique	Pressure (atm)	Equivalence Ratio ϕ	Temperature range (K)	% Fuel	Diluent
[15]	ST	13, 45	0.25, 0.5, 1	847 – 1379	0.7, 1.4, 2.7	air
[17]	ST	8.4	0.5, 1, 2	1230 – 1840	0.5	Ar

[16]	ST	1.1, 10	0.58, 1, 2	1150 – 1850	1.0	Ar
[30]	ST	1	0.58, 1, 2	1330 – 2000	1.0	Ar
[31]*	ST	8.3	0.5, 1, 1.5	1311 – 1773	0.5, 1.0	Ar
NUIG**	ST	13, 20, 40, 50	1.0	930 – 1280	2.7	air
NUIG**	RCM	20, 40	0.5, 1, 2	675 – 934	1.4, 2.7, 5.4	air
KAUST**	ST	20, 40	0.5, 1, 2	922 – 1316	1.4, 2.7, 5.4	air

*Study of cyclopentene ignition

**This study

3.1. Mechanism tuning

The original mechanism developed in part I of this study gave good agreement between experimental and simulated high-temperature ignition delay time (IDT) data measured using a shocktube. However, discrepancies were observed between the two sets of data for RCM-measured low-temperature IDT. Figure 3 shows that, for conditions of $\phi = 1.0$, $P = 20$ atm, and at low temperatures (< 850 K), simulated ignition is up to four times slower than experimental ignition. To ameliorate the agreement between the two sets of data, the energy terms in the modified Arrhenius expressions of reactions that have high temperature-sensitivity coefficients at these conditions were varied within an interval of ± 2 kcal, the uncertainty range of energies calculated in part I [28]. The best agreement, for all investigated conditions, was obtained upon reducing the activation energies of alkyl + O₂ $\rightarrow$ olefin + HO₂, ROO $\rightarrow$ QOOH (peroxy/alkylhydroperoxide isomerization) and OOQOOH $\rightarrow$ KHP + OH (formation of ketohydroperoxide) reaction classes by 1.00, 0.60 and 1.50 kcal, respectively. The obtained simulation IDT curve is shown in Fig. 3.

Figure 3. Comparison of low-temperature IDT profiles measured experimentally to those simulated using the original [28] and tuned mechanisms at $\phi = 1.0$ and $P = 20$ atm.

3.2. RCM data and comparison to the model

Figures 4 and 5 compare the RCM-measured ignition delay of cyclopentane with the simulations that were run using effective volume histories to account for the heat loss resulting from facility effects. The measurements span equivalence ratios of 0.5, 1.0 and 2.0, pressures of 20 and 40 atm, and temperatures between 680 and 950 K. Generally, the model agrees well with the experimental data and captures the trend of ignition delay dependence on temperature, equivalence ratio, and pressure. The temperature-dependent profiles of cyclopentane ignition delay at different equivalence ratios for pressures of 20 (Fig. 4a) and 40 atm (Fig. 4b) show that reactivity increases with increasing equivalence ratio, particularly in the negative temperature coefficient (NTC) regime extending from 730 K to 840 K. The dependency on equivalence ratio becomes less important with increasing temperatures and decreasing ignition delay times, as shown in Fig. 4, due to the competition between chain branching and chain propagation, as explained in Section 3.3. The pressure-dependence of the ignition delay data is shown in Fig. 5 for pressures of 20 and 40 atm at equivalence ratios of 0.5, Fig. 5(a), 1.0, Fig. 5(b) and 2.0, Fig. 5(c). The model captures the pressure-dependence trend well and confirms that reactivity increases with increasing pressure, especially in the NTC region. In fact, for a temperature of 770 K at $\phi = 1$ and 2, ignition at 40 atm is more than ten times faster than that at 20 atm. This is consistent with what has been observed for non-cyclic

hydrocarbons [32, 33] and oxygenated species [34], and is due to higher concentrations of reactive species and faster reaction rates at higher pressures.

Figure 4. RCM-measured ignition delay profiles for cyclopentane/air mixtures at equivalence ratios of 0.5, 1.0 and 2.0 for 20 atm (a) and 40 atm (b) (dashed, solid and dotted lines represent model simulations at $\phi = 0.5$, 1.0 and 2.0, respectively).

Figure 5. RCM-measured ignition delay profiles for cyclopentane/air mixtures at pressures of 20 and 40 atm for $\phi = 0.5$ (a), 1.0 (b) and 2.0 (c) (solid and dashed lines represent model simulations at $p = 20$ and 40 atm, respectively).

Although the model is in good agreement with the experimental data, it slightly under-predicts ignition delay by up to a factor of 1.5 below 720 K for $\phi = 0.5$ and $\phi = 1.0$, and over-predicts it by up to a factor of three above 830 K. Meanwhile, at intermediate temperatures ($720 < T < 830$ K), the agreement between experiment and simulation is within 20% for stoichiometric conditions. For fuel-lean and fuel-rich conditions in the NTC temperature range, the model slightly over-predicts and under-predicts reactivity, respectively. The observed differences between experiments and simulation are due to uncertainties in experimental data, particularly at the higher temperatures characterized by short ignition delay times (i.e., below 10 ms), as well as the uncertainties in reaction kinetics. More in-depth analysis of quantities of interest is needed in order to determine the exact source of discrepancy and the culprit reactions.

3.3. Shock tube data and comparison to the model

The ST ignition delay data measurements carried out at the HPST facility at KAUST are presented in Figs. 6 and 7 along with the simulation results that were obtained using the pressure profiles corresponding to a post-reflected pressure gradient (dp_s/dt) of 3%/ms. Just as in the case of the RCM experiments, ST experiments were conducted at pressures of 20 and 40 atm, and equivalence ratios of 0.5, 1.0 and 2.0 in air. The investigated temperature range extends from 920 K to 1320 K. Fig. 6 highlights the

dependence of ignition delay on equivalence ratio, whereas Fig. 7 highlights the pressure-dependence.

Figure 6. ST-measured ignition delay profiles for cyclopentane/air mixtures at $\phi = 0.5$, 1.0 and 2.0 for 20 atm (a) and 40 atm (b) (dashed, solid and dotted lines represent model simulations at $\phi = 0.5$, 1.0 and 2.0, respectively)

Figure 7. ST-measured ignition delay profiles for cyclopentane/air mixtures at pressures of 20 and 40 atm for $\phi=0.5$ (a), 1 (b) and 2 (c) (solid and dashed lines represent model simulations at $P=20$ and 40 atm, respectively)

Figure 6 shows that the model captures the weak dependence of ignition delay data on equivalence ratio very well. It is also capable of predicting the convergence of reactivity profiles at temperatures greater near 1300 K at a pressure 20 bar. The convergence is not clearly observed at 40 bar since the temperature range at this condition does not exceed 1200 K. However, the general trend indicates convergence of reactivity at temperatures higher than 1300 K. For temperatures between 920 K and 1300 K, both experiments and simulations exhibit increasing reactivity with increasing fuel richness, similar to RCM data. However, despite the lack of data at $T > 1300$ K, we may conclude from the general profiles that at temperatures higher than those investigated in this study, the trend will be reversed with the lean mixtures being most reactive. According to Bugler et al. [32] and

Wang et al. [35], the crossover is caused by the domination of $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ chain branching pathway at higher temperatures. This pathway competes with the chain propagation pathway of $\text{RH} + \text{H} = \text{R} + \text{H}_2$ for H-atoms. Therefore, at high temperatures, the reactivity of fuel-rich mixtures having high concentrations of RH is less than that of fuel-lean mixtures [35]. The model also captures the pressure-dependence trend (Fig. 7) wherein shorter ignition delay times are observed at higher pressures due to faster rates of non-sequential elementary reactions.

In order to control for possible and unwanted facility effects in ST data measured at KAUST, high-temperature ignition experiments were also conducted using the HPST at NUI Galway at pressures of 20 and 40 atm, and an equivalence ratio of 1. Figure 7b compares the data from KAUST and NUIG, and shows that the two sets agree very well and are within uncertainty limits at 20 atm (less than 20% difference). At 40 atm, the values still agree well within the uncertainty limits, however, the differences are up to 34% due to greater uncertainties in measuring very short ($< 100 \mu\text{s}$) ignition delay times. The model over-predicts both sets of ignition delay values; however, it agrees more with the data from NUIG at high pressures and temperatures.

For all investigated conditions, the average difference between model simulations and experimental data is $\sim 35\%$. Better agreement is observed at lower temperatures and longer ignition delay times than at higher temperatures and shorter ignition delay times. However, the model under-predicts reactivity over the entire investigated temperature range. This indicates that the high-temperature chemistry of the model is likely to be slightly slower than it should be at the investigated conditions. As discussed in [19], cyclopentane reactivity is influenced to a great extent by the chemistry of allyl radicals that are produced in high concentrations at elevated temperatures via C–C scission reaction of cyclopentyl radical. These resonantly stabilized radicals can either react with HO_2 radicals to produce OH radicals in chain branching reactions, or recombine to give 1,5-hexadiene in chain termination reactions. The branching ratio between these two pathways has a strong influence on reactivity. In our model, we use pressure-dependent rate coefficients calculated by Goldsmith et al. [36] using QCISD(T)/cc-pVQZ and RRKM master equation methods for allyl + HO_2 reactions, and the experimentally

determined, pressure-dependent rate coefficients of Lynch et al. [37] for the allyl recombination reaction.

3.4. Modeling of literature data

The available studies on cyclopentane IDT are mostly limited to low-pressure and dilute conditions, and all of them were performed at temperatures higher than 900 K. The most recent paper on this subject was published by Tian et al. [16] who measured the ignition delay times of cyclopentane (CPT) in a shock tube, at pressures of 1.1 and 10 atm, equivalence ratios of 0.577, 1.0 and 2.0, and temperatures between 1150 K and 1850 K. Fuel/oxidant mixtures of 1% cyclopentane in Argon were used. They also developed a high-temperature oxidation mechanism of cyclopentane that was validated against their experimental data as well as data from Orme et al. measured at the same conditions ($\phi = 0.577/1/2$, $p = 1$ atm and 1% CPT/O₂/Ar) [30]. Their mechanism was compared to that of Sirjean et al. [17], which is the only other mechanism of cyclopentane oxidation available in the literature. Figure 8 presents the experimental data of [16] and [30] along with simulations using models from [16] and [17], as well as our own model.

Figure 8. Cyclopentane ignition delay measurements by Tian et al. [16] (solid symbols) and Orme et al. [30] (empty symbols) (dashed, dotted and solid lines represent simulations using models from [17], [16] and this study, respectively)

Figures 8a and 8b show that experimental data of [16] and [30] agree well within the experimental uncertainty at $p = 1.1$ atm and $\phi = 0.577$ and 1.0 . All three models predict the data and the reactivity trend well. However, our model over-predicts reactivity at lean conditions by up to a factor of 2, which is larger than the experimental uncertainty range. At rich conditions (Fig. 8d), all models are well within Tian et al.'s 10 atm experimental uncertainty ($\pm 15\%$). Although our model slightly over-predicts the ignition delay times measured by [16] at $\phi = 2$ and $p = 1.1$ atm (up to 35%), it agrees more with data from [30], at the same conditions, than the other two models (Fig. 8c). Note that Orme et al. [30] measure an ignition delay time that is more than two times longer than that measured by Tian et al. [16] at 1580 K, $\phi = 2.0$ and $p = 1.1$ atm. As mentioned earlier, Sirjean et al. [17] provide the only high-temperature cyclopentane oxidation mechanism in the literature besides [16]. Their mechanism was developed with the help of a kinetic model generation software called EXGAS [17]. For the reactions specific to cyclopentane, they estimated rate constants using rate constants from the literature and performed *ab initio* calculations for the beta scission of cyclopentyl radicals using the CBS-QB3 method. In addition, Sirjean et al. [17] measured the ignition delay times of 0.5% cyclopentane/ O_2 /Ar mixtures over the temperature range of 1230–1840 K, at equivalence ratios of 0.5, 1.0 and 2.0, and a pressure of 8.4 bar, using a shock tube. We simulated these experiments using our cyclopentane mechanism and the mechanism obtained using

EXGAS [17]. The results are summarized in Fig. 9. Both models concur with the experimental data equivalence ratio effect quite well. However, our model provides better prediction at stoichiometric conditions.

Figure 9. Cyclopentane ignition delay measurements by [17] at $\phi = 0.5$ (a), 1.0 (b) and 2.0 (c), and $p = 8.4$ bar (dashed and solid lines represent simulations using Sirjean et al.'s and our model, respectively)

The only available measurements of cyclopentane ignition delay in air are those reported by Daley et al. [15]. These measurements were carried out in a shock tube, at temperatures ranging between 847 and 1379 K, pressures of 13 and 45 atm, and equivalence ratios of 0.25, 0.5 and 1.0. We tested our mechanism against Daley et al.'s data under all investigated conditions. The models of [16] and [17] were also used to simulate these experiments for the purpose of comparison at engine-relevant conditions. The results are presented in Fig. 10. All three models under-predict reactivity at $\phi = 0.5$ and $\phi = 1.0$ for temperatures lower than 1200 K. However, our model is much better at simulating ignition at the investigated conditions than the models of [16] and [17] which are up to 40 times slower than the experiments, as shown in Fig. 10. Meanwhile, the

disagreement between our modeled ignition delay values and the experimental values is less than 40%. At $\phi = 0.25$, our mechanism agrees very well experimental data, with an average of about 10% difference.

Figure 10. Cyclopentane ignition delay measurements by [15] at 13 (black) and 45 atm (grey), and $p = 8.4$ bar (dashed, dotted and solid lines represent simulations using [16], [17] and our model, respectively)

In light of the observed disparities, we repeated the experiments reported by Daley et al. [15] for $\phi = 1.0$ at the same conditions using the shock tube facility at NUIG. Figure 11 shows that the two sets of data agree within their respective uncertainties (15% and 20% for Daley et al. and NUIG data, respectively), and that our mechanism slightly under-predicts reactivity at temperatures lower than 1200 K.

Figure 11. Comparison of cyclopentane ignition delay times measured in a shock tube by [15] (empty symbols) and this study (solid symbols) at 13 and 45/50 bar. Curves are simulations with present model.

In addition to the cyclopentane ignition delay data available in the literature, we tested our model against data reported for the corresponding olefin, cyclopentene. Yahyaoui et al. [31] report ignition delay times of 0.5% and 1.0% cyclopentene/O₂/Ar mixtures measured behind reflected shock waves at a pressure of 840 kPa, argon dilution of 92 – 97 %, and equivalence ratios of 0.5, 1.0 and 1.5. The agreement between our model and this data is very good, as shown in Fig. 12, particularly at 0.5% fuel concentration. At rich conditions, the model slightly over-predicts the experimental data, but the difference is within our estimated experimental uncertainty ($\pm 50\%$) based on similar shock tube studies (no experimental uncertainties reported by authors). At 1% fuel concentration and temperatures lower than 1400 K, the model over-predicts cyclopentene reactivity by up to a factor of three.

Figure 12. Cyclopentene ignition delay measurements by [31] at $\phi = 0.5, 1.0$ and 2.0 and $p = 840$ kPa for 0.5% (a) and 1% (b) fuel/oxidant mixtures (dashed, solid and dotted lines represent model simulations at $\phi = 0.5, 1.0$ and 2.0 , respectively)

Our model was also tested against flame speed data measured by Davis and Law [18] at atmospheric temperature and pressure over an equivalence ratio range of $0.7 - 1.7$. However, to minimize computational time and cost, the mechanism was reduced and the low-temperature oxidation chemistry of cyclopentane was excluded for flame speed simulations. The model was reduced using the method of direct relation graph (DRG) with expert knowledge (DRG-X) [38]. This approach assumes that some species are weakly coupled to others, such that they do not contribute significantly to the combustion process and can be removed from the mechanism without hampering the chemical fidelity. However, unlike the original DRG method [39, 40] that is restricted by a uniform error tolerance for all the species, the DRG-X allows for different reduction errors for heat release rate and species of interest. Therefore, this method results in a smaller skeletal mechanism with similar chemical fidelity compared to the original DRG method. In this work, the error tolerance was set at 0.01 for heat release, 0.1 for H and OH radicals, 0.3 for cyclopentane and 0.4 (the default value) for other species. The reduced mechanism consists of 173 species. Analogies to molecules of similar structure were made to determine polarizability and dipole moment transport properties of species in the cyclopentane sub-mechanism. Lennard-Jones collision parameters were calculated using the critical pressure, critical temperature and acentric factor according to the method proposed by Tee et al. [41].

Figure 13 shows that the reduced model predicts cyclopentane flame speeds well, particularly at lean conditions. For stoichiometric and rich conditions the model underpredicts flame speed by up to 43 % at $\phi = 1.7$. Under the investigated conditions, maximum speed is observed at $\phi = 1.1$, where the deviation between model and experiment is only 4%.

Figure 13. Experimental [18] and simulated flame speed data of cyclopentane at atmospheric temperature and pressure

In summary, our model shows very good agreement (< 50% deviation) with all the available literature data for cyclopentane and cyclopentene. It even shows much better agreement with the experimental data measured in air than the other two high-temperature cyclopentane oxidation models [16, 17]. In addition to ignition delay and flame speed data, the model was tested against species concentration profiles measured at a pressure of 10 atm, temperatures between 740 K and 1250 K, and equivalence ratios between 0.5 and 3.0, using a jet-stirred reactor [19]. The results show good agreement (< 20 % difference between model and experiments for most species), as discussed in [19].

4. Reaction path and sensitivity analyses

In order to elucidate the reaction pathways that drive cyclopentane reactivity, sensitivity and rate of production (ROP) analyses were performed for stoichiometric

fuel/air mixtures at low (700 K), intermediate (770 K) and high (1100 K) initial temperatures, for an initial pressure of 20 atm. The analyses were conducted at times corresponding to 20% fuel conversion, at temperatures of 750 K, 810 K and 1110 K for the low-, intermediate-, and high-temperature conditions, respectively.

4.1. Reaction path analyses

The dominant high and low-temperature reactivity pathways are highlighted in Figs. 14 and 15, respectively. Both figures show ROP values calculated for scenarios with various initial temperatures.

In the high-temperature regime, independently of the initial temperature, the chain of oxidation reactions starts with H-atom abstraction from the fuel forming cyclopentyl radical (CYC5H9). For 700 K and 770 K, abstraction by OH radicals is dominant: 80% and 67%, respectively, with only a minor contribution from H radicals that are not abundant at low temperatures: 2% and 3%, respectively. At 1100 K, abstraction by OH radicals is still the major path (58%), but abstraction by H becomes more important (23%). Depending on the initial temperature, the cyclopentyl radical produced may undergo C–C and C–H β -scission or O₂-addition reactions. The scission pathways are relatively important at 1100 K with contributions of 13% and 17% for the C–C and C–H scission reactions, leading to 1-penten-5-yl radical (C5H91-5) and cyclopentene (CYC5H8)+H, respectively. In addition to the C–H scission pathway, CYC5H8 is produced from CYC5H9 via the formally direct pathway of $\text{CYC5H9} + \text{O}_2 = \text{CYC5H8} + \text{HO}_2$. This pathway is particularly important at high (1100 K) and intermediate temperatures within the NTC regime (770 K), with relative contributions of 55% and 38%, respectively. C5H91-5 dissociates into ethylene (C2H4) and the resonantly stabilized allyl radical (C3H5-A) almost completely at high temperatures. At low and intermediate temperatures, this pathway is much less important, with contributions of 2% and 33%, respectively. The dominant reaction pathway for C5H91-5 at these conditions is O₂-addition. Meanwhile, cyclopentene undergoes H-atom abstraction, mainly from the two CH₂ groups at the allylic positions and less at the other CH₂ group, to produce CYC5H71-3 and CYC5H71-4 radicals with relative rates of production of 58% and 23%, respectively, when the initial temperature is 1100 K. The C–C scission pathway of

radical (CPTO2J) with relative ROPs of 76% and 57% at 700 and 770 K, respectively (shown in Fig. 14). The dominant consumption pathway of CPTO2J is the concerted elimination of HO₂ radicals, leading to cyclopentene (CYC5H8) (54% and 70% at 700 K and 770 K, respectively). The chain branching alkylperoxy/hydroperoxalkyl isomerization pathways leading to CPT1Q2J is unimportant, with an ROP of 1% at 700 K. Isomerization to CPT1Q3J is relatively important, with a contribution of 34% to the CPTO2J consumption at 700 K. CPT1Q2J is mainly converted to the cyclic ether CPTYO12 and an OH radical, whereas, CPT1Q3J mainly undergoes addition to O₂ (98% and 91% at 700 K and 770 K, respectively). The product of the addition to O₂ (CPTQ3QJ) is converted to the corresponding ketohydroperoxide CPT1*O3Q since the alternative isomerization pathways, which were found to be unimportant, were not included in the mechanism. The ketohydroperoxide then decomposes via O-O bond fission to give two sets of products.

Figure 15. Rate of production analyses performed at $p = 20$ atm, $\phi = 1.0$ and initial temperatures of 770 K (**bold**) and 700 K (*italic*) with emphasis on low-temperature oxidation pathways

4.2. Sensitivity analysis

In order to investigate the effect of parametric uncertainties in the mechanism, we carried out sensitivity analysis at $P = 20$ atm, $\phi = 1.0$ and initial temperatures of 700 K, 770 K and 1100 K. First, we selected the most important reactions using local sensitivity

analysis by ranking the $|d\ln T/dk_i|$ temperature sensitivity coefficients at a time just before ignition. Because these local sensitivity coefficients cannot account for the strong nonlinearity in the chemical mechanisms [42, 43], we also calculated brute force (BF) sensitivity coefficients given by $\log(\tau_i^+/\tau_i^-)/\log(2.0/0.5)$, where τ_i^+ and τ_i^- are the ignition delay times calculated using rate constants k_i multiplied and divided by a factor of two, respectively [44, 45]. A positive sensitivity coefficient means that a faster rate constant results in longer IDT, i.e., the system is less reactive. Figure 16 shows the results of the analysis, displaying reactions with sensitivity coefficients greater than ± 0.1 only. At 700 K and 770 K similar sensitivity trends are observed, with the most important reactivity-promoting reactions (negative coefficients) being the formation of ketohydroperoxide from CPTQ3QJ, H-atom abstraction from cyclopentane by HO₂ radicals, and CPTO2J/CPT1Q3J isomerization. The reaction path analyses discussed in Section 4.1. show that that these reactions are not dominant, even at low temperatures. However, they are involved in low-temperature chain branching, particularly the formation of ketohydroperoxide and the CPTO2J/CPT1Q3J isomerization. Therefore, ignition, temperature, and reactivity are highly sensitive to the rate coefficients of these reactions at 700 K and 770 K initial temperatures. The chain terminating concerted HO₂ elimination pathway of CPTO2J is the most important reactivity suppressing reaction at these temperatures, followed by the recombination of HO₂ radicals to form H₂O₂ + O₂, and the decomposition of ketohydroperoxide CPT1*O3Q to give CH₂CO, C₂H₄, CHO and OH. Alternatively, CPT1*O3Q may give CH₂CHO, C₂H₄, CO and OH in a pathway that favors reactivity. It should be noted that these reactions are written as single steps in the mechanism, and that the rate coefficients used are those of the rate limiting O–O scission elementary reaction with an equal branching ratio assumed to each path. Other reactions with relatively high sensitivity coefficients (i.e., suppressing reactivity) at 700 K and 770 K include the formally direct pathway of CYC5H₉ + O₂ = CYC5H₈ + HO₂. The dissociation of H₂O₂ to two OH radicals and H-abstraction by OH are also highly sensitive reactions that promote reactivity.

At 1100 K initial temperature, the low-temperature chain branching pathways of alkylperoxy and hydroperoxyalkyl radicals as well as ketohydroperoxides become unimportant, except for the formally direct pathway of CYC5H₉ + O₂ = CYC5H₈ + HO₂

which promotes reactivity at 1100 K. Meanwhile, the high-temperature cyclopentyl C–C scission pathway exhibits high positive sensitivity at 1100 K: this pathway disfavors reactivity due to the ultimate production of unreactive allyl radical and ethylene. Since high concentrations of allyl radicals (C₃H₅-A) are produced at 1100 K, as discussed in Section 4.1, reactivity becomes sensitive to the rate coefficients of allyl + HO₂ reactions, particularly the reactivity promoting C₃H₅-A + HO₂ = C₃H₅O + OH reaction that converts non-reactive allyl and HO₂ radicals to reactive C₃H₅O and OH radicals. H-atom abstraction reactions by H atoms and HO₂ radicals also show high sensitivity coefficients at 1100 K. H-atom abstraction by HO₂ radicals promotes reactivity due to the formation of H₂O₂ that breaks into two OH radicals; however, abstraction by H atoms reduces reactivity since this reaction competes with the chain branching H + O₂ = O + OH pathway for H atoms.

Figure 16. Sensitivity analyses performed at $p = 20$ atm, $\phi = 1.0$ and initial temperatures of 1100 K, 770 K and 700 K. The temperature at which the sensitivity coefficients are calculated are 860 K, 960 K, and 1200 K.

5. Effect of cyclic structure and size on reactivity

The results obtained in this study concur with the available literature regarding the reduced reactivity of cycloalkane fuels compared to the non-cyclic counterparts. Figure 17a shows experimental ignition delay data of cyclopentane, cyclohexane, *n*-pentane, and *n*-hexane obtained from this study, Silke et al. [46], Bugler et al. [32] and Zhang et al. [24], and Fig. 17b shows simulation results obtained using our model and those from [46], [32] and [24], respectively. For initial temperatures between 650 and 950 K, cyclopentane and cyclohexane are less reactive than their non-cyclic counterparts with a difference of almost two and one orders of magnitude, respectively, between both the experimental or simulated IDTs at 800 K. Yang et al. [12] show that in the case of cyclohexane this trend is attributed to the conformational inhibition of the 1,5 H-atom migration chain branching pathway of the alkylperoxy radical at low temperatures. The same was observed in this study, as well as the accompanying computational study, for cyclopentane [28]. The reaction path analysis discussed in Section 4.1. shows that even at temperatures as low as 700 K, the contributions of the 5- and 6-membered ring H-atom migration reactions to the consumption of alkylperoxy radicals is minimal (35%). The suppression of these pathways is due to the high energy barriers involved in forming the strained bicyclic transition states (refer to Part I of this study for further details). Consequently, concerted elimination leading to unreactive olefins and HO₂ radicals is favored, and overall, the low-temperature reactivity of cyclopentane is reduced. Cyclopentane is less reactive than cyclohexane in the temperature range of 650–870 K, with differences in ignition delay times of up to 20 times. Despite conformational inhibition, low-temperature cyclohexane oxidation mainly occurs via chain branching ROO/QOOH isomerization pathways [5], unlike cyclopentane, where ignition is driven by the dissociation of cyclopentenyl radicals. Moreover, for cyclopentane, the NTC region that marks the transition from low to high temperature oxidation chemistry is shifted to lower temperatures compared to *n*-pentane, *n*-hexane and cyclohexane, as a result of reduced low-temperature reactivity. Furthermore the NTC inflection region is flatter (near zero slope) for cyclopentane than for the other fuels shown in Fig. 17. Based on the works of Kalghatgi [47, 48] and Mehl [49, 50], this is indicative of high octane sensitivity fuel with high antiknock potential. Cyclopentane is characterized by a research

octane number (RON) of 103 and a motor octane number (MON) of 85 [51] which gives a sensitivity $S = \text{RON} - \text{MON}$ of 18. Therefore, cyclopentane is a promising gasoline blending candidate with great potential for increasing the antiknock quality, especially under boosted engine conditions.

Figure 17. Comparison of experimental and simulated IDT profiles of cyclopentane (this study), cyclohexane [46], *n*-pentane [32] and *n*-hexane [24]

6. Conclusions

The ignition delay times of lean, stoichiometric and rich cyclopentane/air mixtures were measured at pressures of 20 and 40 atm over a wide range of initial temperatures (650–1350 K) and fuel-to-air ratios (0.5–2.0) using two shock tubes and a rapid compression machine. This experimental data along with literature data were used as targets for the validation of a detailed mechanism, which was described in the first part of this study [28]. A pressure-dependence trend of higher reactivity at higher pressures was observed for experimental and simulated data at all investigated equivalence ratios. This trend is expected, and is consistent with the occurrence of higher reaction rate constants (for sequential elementary reactions) and collision rates at higher pressures, for a given temperature. For initial temperatures up to 1200 K, reactivity is also directly proportional to equivalence ratio, with fuel-rich mixtures being more reactive than stoichiometric and fuel lean mixtures. This trend is inverted at higher temperatures due to competition between chain propagation, H-atom abstraction, and chain branching $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ reactions for H atoms.

The simulated ignition delay profiles are within $\pm 50\%$ of the experimental data, which is twice as much as the uncertainties of experiments. Our chemical model is the first one that captures the pressure-, temperature-, and ϕ -dependent reactivity under engine-relevant conditions adequately, largely because we included a newly developed detailed description of the ROO/QOOH chemistry and cyclopentyl radical decomposition pathways. Reaction path and sensitivity analyses show that at low-, intermediate- and high- temperature conditions cyclopentane is mainly converted to cyclopentene, thus, emphasizing the importance of cyclopentene chemistry in dictating cyclopentane reactivity. The ROP analysis also shows that, even at initial temperatures as low as 700 K, low-temperature chain-branching contributes little to cyclopentane oxidation. This is probably due to the inhibition of the ROO/QOOH isomerization pathways that occur via highly strained bicyclic transition states, as discussed in Part I. Instead, ROO mostly undergoes chain terminating concerted elimination of HO₂ leading to high concentrations of cyclopentene.

Finally, we found that cyclopentane is less reactive than *n*-pentane and cyclohexane consistent with the high octane rating and high sensitivity of cyclopentane compared to the other two fuel molecules. These properties are evident in the suppressed low-temperature chemistry and minimal NTC behavior of cyclopentane, which renders it a desirable fuel blending candidate of high engine knock-resistance potential.

The results presented in this study provide the first set of experimental ignition data for cyclopentane at low-temperatures, as well as the first analysis of the low-temperature chemistry and reactivity of this compound.

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