

Shock tube study of 5 membered cyclic hydrocarbon oxidation

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Abstract

Cyclic hydrocarbons may exhibit different combustion characteristics to each other and their linear counterparts. This shock tube study measured the ignition delay times of cyclopropane, cyclopentane, cyclopentene, cyclopentadiene and dicyclopentadiene behind reflected shock waves, across a temperature range of 1300 to 2200 K. The roles played by ring size, the cyclic structure, the degree of fuel saturation, fuel and O₂ concentration, and the reflected shock temperatures and pressures were examined.

Introduction

The structural differences between cyclic and linear hydrocarbons could cause cyclic hydrocarbons to display combustion characteristics that differ from that of their linear counterparts. This study examines the combustion characteristics of cyclic molecules by determining the ignition delay times of cyclopropane, cyclopentane, cyclopentene, cyclopentadiene and dicyclopentadiene, plus oxygen, mixtures in argon behind reflected shock waves.

Some work has already been carried out on these compounds including a study by Slutsky *et al.* [1] that determined the ignition delay times of cyclopropane mixtures in argon at 1200 – 1600 K at a reflected shock pressure of 6 atm. A study by Drummond *et al.* [2] gave ignition delay times for cyclopropane plus oxygen mixtures behind reflected shock waves in the temperature range of 1055 – 1490 K with pressures ranging from 3.5 to 5.0 atm. Some omissions and errors, discussed later in more detail, make comparisons with these studies difficult.

A cyclopentadiene study by Burcat *et al.* [3] produced ignition delay times for mixtures with fuel concentrations varying from 0.5 to 2.5 % and oxygen varying from 3.3 to 16.6 %. The temperature ranged from 1278 – 2110 K and the experimental pressures were between 2.43 and 12.45 atm. A model was created and used to simulate both the ignition delay times and product distribution of samples quenched before ignition.

The kinetics and oxidation mechanism of cyclopentadiene were examined very recently by monitoring O atoms and CO molecules behind reflected shock waves by Murakami *et al.* [4].

Experimental

The stainless steel shock tube used to carry out this work consisted of a 0.63 m long, 160 cm in diameter, driver section that was separated from a 6 m long, 10.24 cm in diameter, test section by a polycarbonate diaphragm that was allowed to burst under pressure with

the assistance of a cross shaped cutting device that petaled the diaphragm. This shock tube was fully characterized [5] in line with a previous account of shock tube characterisation [6] and validated against recent experiments on n-heptane oxidation from the Stanford group [7].

Four PCB pressure transducers, located at distances of 0.49486, 0.63589, 0.23689 and 0.02994 m from the endwall and connected to 3 time counters (1 × Phillips PM6666 & 2 × Fluke PM6666), were used to calculate the incident shock velocity as the shock wave moved down the tube and these values were extrapolated to calculate the shock velocity at the endwall. This value, along with the initial pressure, p_1 , and initial temperature, was used to calculate the temperature, T_5 , and pressure, p_5 , behind the reflected shock wave.

Emissions were observed using an end on detection diagnostic that consisted of a PDA55 (switchable gain, amplified silicon detector) located behind either a 431 nm (for CH* emission) or 312 nm (for OH* emission) narrow bandpass filter with spectral bandwidths of 10 nm. The filter and the PDA were aligned behind a 7.5 mm wide fused silica window located in the endwall.

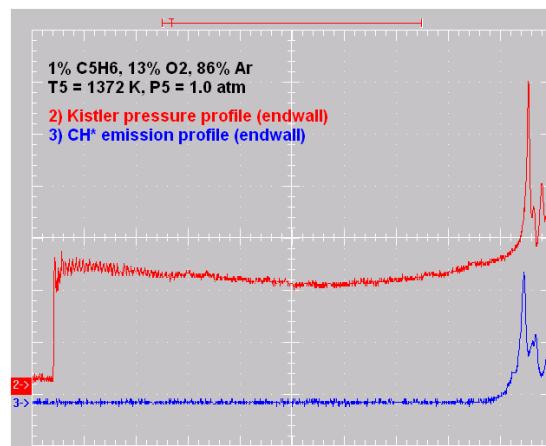


Figure 1: Typical endwall pressure sensor and CH* emission profile

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A Kistler pressure transducer mounted flush with the endwall signalled the shock wave arrival at the endwall, Fig. 1, and the beginning of the ignition delay period. The end of the ignition delay period was defined as the maximum rise in the rate of emission, Fig 1. The following gases were obtained from BOC Ireland Ltd. and were used without further purification; helium (CP grade), argon (99.9995 %) and oxygen (99.5 %). Cyclopropane (99+ %), cyclopentane (99+ %), cyclopentene (determined to be > 99.5 % pure by gas chromatography; Agilent 6890GC) and dicyclopentadiene (determined to be 99.5 % pure by GC analysis) were obtained directly from Aldrich Chemical Co. Ltd. The dicyclopentadiene was heated at 40°C to produce cyclopentadiene and allow the collection, via distillation, of the pure monomer. The cyclopentadiene was analysed by GC and was determined to be 99.4 % pure. No deterioration occurred over the timespan taken to run experiments on each mixture. The gas, cyclopropane, and all of the liquids used were subjected to several freeze-pump-thaw degassing cycles before being used. Test mixtures were made up in a 35 L stainless steel tank using standard manometric methods and stirred for 2 hours before use. In order to check the validity of this method some mixtures were left overnight to mix by diffusion while others were left overnight after mixing for 2 hours. In both cases the results obtained were consistent with the original values.

Specific objectives

The mechanisms by which cyclic hydrocarbons break down may be dramatically different from each other, due to factors such as ring size, the number of rings present and the degree of saturation. They may also exhibit very different combustion characteristics to their linear counterparts [8] due to the actual ring structure. This study aims to provide ignition delay times for cyclic fuels that encompass different ring sizes, a varied number of rings and different degrees of saturation. Mixture compositions were varied to allow relevant comparisons to be made, Table 1.

Results and Discussion

Cyclopropane

The following mixtures, Table 1, were prepared using the experimental method described previously and their ignition delay times, defined as the time interval between shock wave arrival at the end wall and the maximum rise in the rate of emission, were measured, Fig. 1. In all cases, except the cyclopropane study at 4.0 atm, CH* emission was the parameter observed. For the cyclopropane experiments at 4.0 atm OH* emission was examined.

Cyclopropane mixtures with equivalence ratios, ϕ , of 0.5, 1.0 and 2.0 and a constant fuel composition of 1.0 % were examined, Fig. 2. From left to right as the equivalence ratio decreases, and the O₂ concentration increases from 2.25 to 4.50 to 9.00 %, there is a substantial decrease in the ignition delay times of the

mixtures. In another set of experiments cyclopropane mixtures with identical equivalence ratios of 0.5, 1.0 and 2.0, created by altering the fuel concentration while keeping the O₂ constant at 4.5 %, were examined, Fig. 3. Again the ignition delay times decrease as the equivalence ratio decreases but in this case the effect is much less dramatic. Altering the O₂ concentration produces a much greater effect on the ignition delay times of a mixture than that observed when the fuel concentration is altered by a corresponding amount.

A study by Drummond *et al.* [2] examined cyclopropane plus O₂ mixtures behind reflected shock

	Fuel %	O ₂ %	Ar %	ϕ	p_5 (atm)
Cyclopropane	1.0	2.25	96.75	2.0	1.0
	1.0	4.50	94.50	1.0	1.0
	1.0	9.00	90.00	0.5	1.0
	0.5	4.5	95.00	0.5	1.0
	1.0	4.5	94.50	1.0	1.0
	2.0	4.5	93.50	2.0	1.0
Cyclopentane	2.0	9.0	89.00	1.0	4.0
	1.0	3.75	95.25	2.0	1.0
	1.0	7.50	91.50	1.0	1.0
Cyclopentene	1.0	13.00	86.00	0.577	1.0
	1.0	3.50	95.50	2.0	1.0
Cyclopentadiene	1.0	7.00	92.00	1.0	1.0
					4.0
	1.0	13.00	86.00	0.538	1.0
	1.0	3.25	95.75	2.0	1.0
Dicyclopentadiene	1.0	6.50	92.50	1.0	1.0
	1.0	13.00	86.00	0.5	1.0
	1.0	13.00	86.00	1.0	1.0

Table 1: Mixture compositions, equivalence ratios and experimental p_5 .

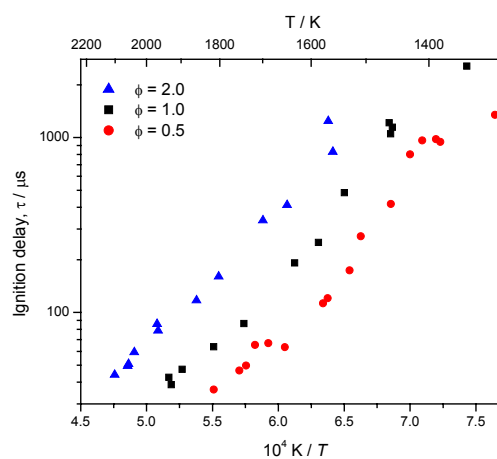


Figure 2: Ignition delay times versus T^{-1} for 1 % cyclopropane, \blacktriangle $\phi = 2.0$, 2.25 % O₂, \blacksquare $\phi = 1.0$, 4.50 % O₂, \bullet $\phi = 0.5$, 9.00 % O₂ in Ar, $p_5 = 1.0 \pm 0.1$ atm.

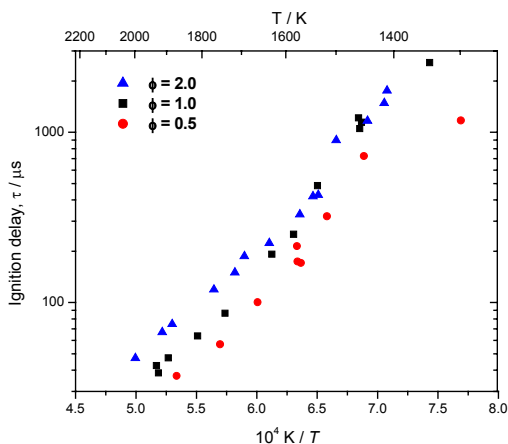


Figure 3: Ignition delay times versus T^{-1} for cyclopropane: \blacktriangle 2.0 % ($\phi = 2.0$), \blacksquare 1.0 % ($\phi = 1.0$), \bullet 0.5 % ($\phi = 0.5$), $O_2 = 4.5$ %, in Ar, $p_5 = 1.0 \pm 0.1$ atm.

waves. The ignition delay time is not clearly defined for the cyclopropane experiments but it is stated that measurements were determined from OH absorption records. A plot of:

$$\tau p_5 [C_3H_6]^{-1} [O_2]^4 \text{ versus } T^{-1}$$

was used to produce a correlation of all cyclopropane results. The mixture compositions defined on the graph were not consistent with oxidant:fuel ratios stated elsewhere. In addition, it was stated that a constant p_1 of 65 torr had been used to produce a T_5 range from 1055 to 1490 K and a p_5 range from 3.5 to 5.0 atm for all the cyclopropane experiments. However it is impossible for this initial pressure to produce the temperatures shown while the p_5 values remain within this range.

On the assumption that the p_1 value was incorrect a more suitable value was chosen and the ignition delay times were calculated for a 2 % cyclopropane, 9.0 % O_2 in Ar mixture. This calculation produced p_5 values from 3.5 to 4.2 atm for the relevant temperatures. These values were plotted against ignition delays, measured as stated previously using OH* and not CH* emission, that were produced in *this study* for the same mixture at a reflected shock pressure of 4.0 ± 0.1 atm, Fig. 4. The 4.0 atm ignition delays were also compared to a 1 % cyclopropane, 4.5 % O_2 in Ar mixture that was compressed to a p_5 of 1.0 atm and examined using CH* emission as the criterion of ignition, Fig. 5. As expected a decrease in ignition delay is observed as the reflected shock pressure increases.

A study by Slutsky *et al.* [1] produced ignition delay times for airlike, $\phi = 1.0$, cyclopropane mixtures in Ar, behind reflected shock waves of $p_5 = 5.9 \pm 1.0$ atm. As the exact mixture composition is not stated, and *this shock tube* cannot produce p_5 's > 4.0 atm, it was impossible to reproduce the delay times observed by

Slutsky. Those delay times are shorter than those produced in *this study* for a $\phi = 1.0$, 1 % cyclopropane, mixture with $p_5 = 1.0 \pm 0.1$ atm and correspondingly shorter than those produced for a $\phi = 1.0$, 2 % cyclopropane, mixture with $p_5 = 4.0 \pm 0.1$ atm, Fig. 5. The differences produced by different definitions of the ignition delays times are negligible.

Cyclopropane and Propene

In order to examine the effect played by ring opening on the combustion of cyclopropane a 1.0 % propene, 4.5 % O_2 in Ar mixture, $\phi = 1.0$, was examined at reflected shock pressures of 1.0 atm and compared to a similar 1.0 % cyclopropane, 4.5 % O_2 in Ar mixture, $\phi = 1.0$, Fig. 6. The ignition delay times for these two C_3H_6

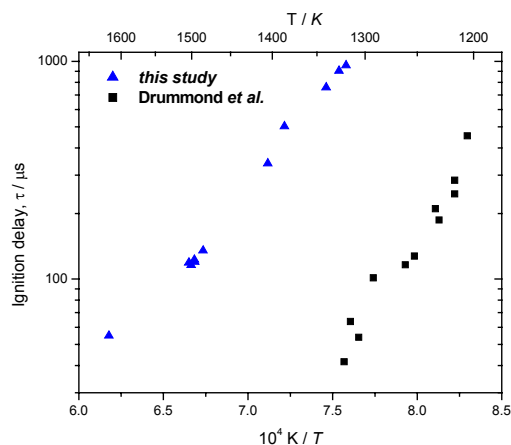


Figure 4: 2 % cyclopropane, 9.0 % O_2 in Ar; $\phi = 1.0$: Ignition delay times versus T^{-1} for \blacktriangle *this study*, $p_5 = 4.0 \pm 0.1$ atm; \blacksquare Drummond *et al.* [2], $p_5 = 3.5 - 4.2$ atm;

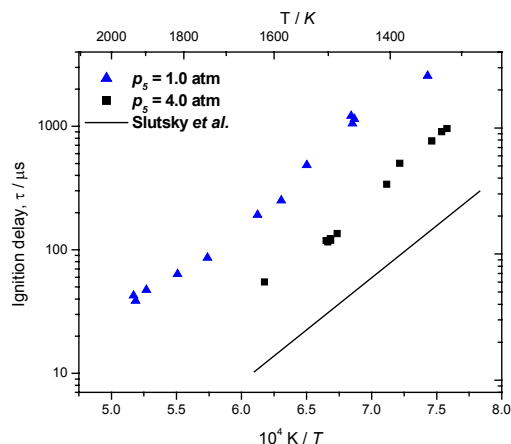


Figure 5: Ignition delay times versus T^{-1} for \blacktriangle 1% cyclopropane, 4.5 % O_2 in Ar, $p_5 = 1.0$ atm; \blacksquare 2 % cyclopropane, 9.0 % O_2 in Ar, $p_5 = 4.0$ atm, — Slutsky *et al.*, $\phi = 1.0$ airlike cyclopropane mixture in Ar, $p_5 = 5.9 \pm 1.0$ atm

mixtures are essentially the same and could mean that the ring-opening step is not the rate-determining step in the ignition of cyclopropane.

5 membered rings

A number of cyclopentane in O₂ mixtures, with $\phi = 2.0$, 1.0 and 0.577 and the fuel concentration constant at 1.0 %, were examined at a reflected shock pressure of 1.0 atm, Fig. 7. As expected the ignition delay times decrease moving from left to right corresponding to an increase in O₂ from 3.75 to 7.50 to 13.00 %.

The same set of experiments were carried out with three $\phi = 2.0$, 1.0 and 0.538 cyclopentene mixtures in

which the fuel concentration had again been held constant at 1.0 %, Fig. 8. Again there is a decrease in the ignition delay times as the O₂ concentration is increased to produced lower equivalence ratios. For both cyclopentane and cyclopentene the largest change in ignition delay times occurs when the O₂ concentration is increased from a $\phi = 2.0$ to $\phi = 1.0$ mixture.

The 1.0 % cyclopentene, 7.0 % O₂ was examined at reflected shock pressures of 4.0 ± 0.1 atm and the ignition delays were compared to those with $p_5 = 1.0 \pm 0.1$ atm, Fig. 9. As expected the ignition delay times decrease as the reflected shock pressure increases.

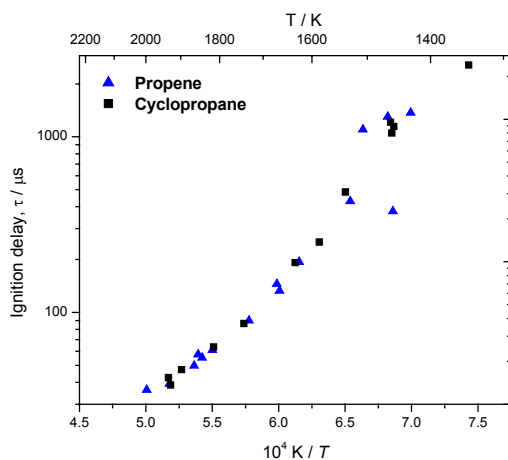


Figure 6: Ignition delay times versus T^{-1} for
 ▲ 1% cyclopropane, 4.5 % O₂ in Ar;
 ■ 1% propene, 4.5 % O₂ in Ar; $\phi = 1.0$,
 $p_5 = 1.0 \pm 0.1$ atm.

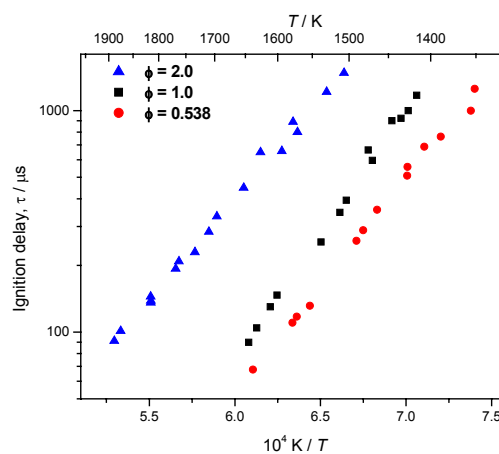


Figure 8: Ignition delay times versus T^{-1} for
 1 % cyclopentene, ▲ $\phi = 2.0$, 3.50 % O₂,
 ■ $\phi = 1.0$, 7.00 % O₂, ● $\phi = 0.538$, 13.00 % O₂,
 in Ar, $p_5 = 1.0 \pm 0.1$ atm.

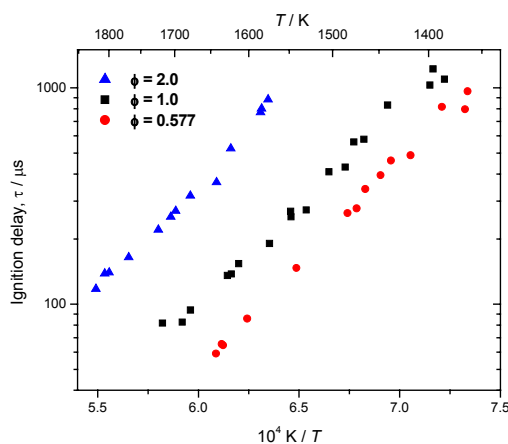


Figure 7: Ignition delay times versus T^{-1} for
 1 % cyclopentane, ▲ $\phi = 2.0$, 3.75 % O₂,
 ■ $\phi = 1.0$, 7.50 % O₂, ● $\phi = 0.577$, 13.00 % O₂,
 in Ar, $p_5 = 1.0 \pm 0.1$ atm.

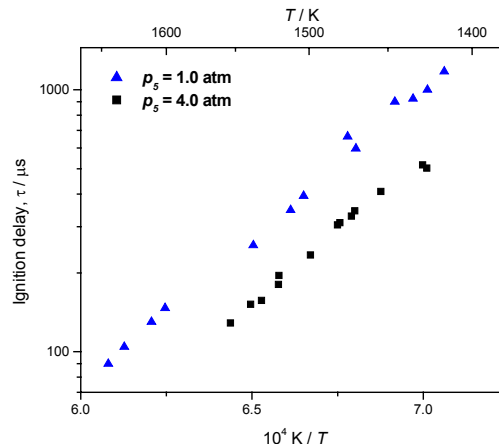


Figure 9: Ignition delay times versus T^{-1} at reflected
 shock pressures of ▲ 1.0 ± 0.1 and ■ 4.0 ± 0.1 atm,
 for 1.0 % cyclopentene, 7.0 % O₂ in Ar, $\phi = 1.0$.

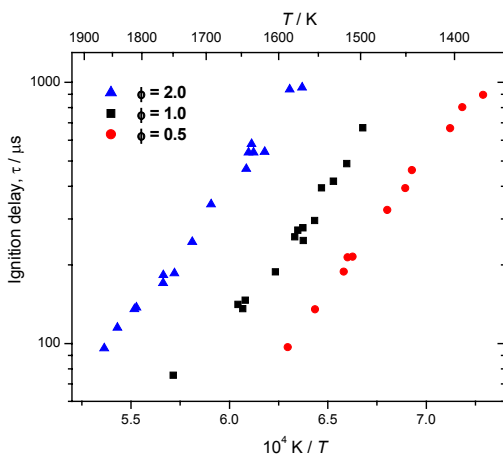


Figure 10: Ignition delay times versus T^{-1} for 1 % cyclopentadiene, $\blacktriangle \phi = 2.0$, 3.25 % O_2 , $\blacksquare \phi = 1.0$, 6.50 % O_2 , $\bullet \phi = 0.5$, 13.00 % O_2 , in Ar, $p_5 = 1.0 \pm 0.1$ atm.

The ignition delay times for three cyclopentadiene plus O_2 mixtures in Ar were observed at $p_5 = 1.0 \pm 0.1$ atm, Fig. 10. The mixtures had a constant fuel composition of 1.0 % while the O_2 concentration was varied to give $\phi = 2.0$, 1.0 and 0.5. A similar trend to that displayed by cyclopropane, cyclopentane and cyclopentene was observed in that increasing the O_2 concentration to give a smaller equivalence ratio leads to decreased ignition delay times, with the largest decrease occurring as ϕ is changed from 2.0 to 1.0.

A study by Burcat *et al.* [3] examined the ignition delay times of cyclopentadiene plus O_2 mixtures in Ar. Fuel concentrations varied from 0.5 to 2.5 % and the O_2 concentration changed from 3.3 to 16.6 %. Experiments were carried out at temperatures from 1278 to 2110 K and pressures from 2.43 to 12.45 atm and the results were summarized by the equation:

$$\log_{10} \beta = -12.5 + 7,540 / T$$

$$\text{where } \beta = \tau [C_5H_6]^{-0.06} [O_2]^{0.95} [Ar]^{-0.29}$$

Equation 1

The relevant calculations were made for the ignition delay times produced for the 1 % cyclopentadiene, 6.5 % O_2 in Ar mixture at $p_5 = 1.0 \pm 0.1$ atm and these values were compared to a representative sample of the Burcat data, Fig. 11. The values from *this study* show good agreement with those calculated by Burcat.

5 membered rings and dicyclopentadiene

Four of the fuels studied were compared at $\phi = 1.0$ with the fuel concentration constant at 1.0 % and $p_5 = 1.0 \pm$

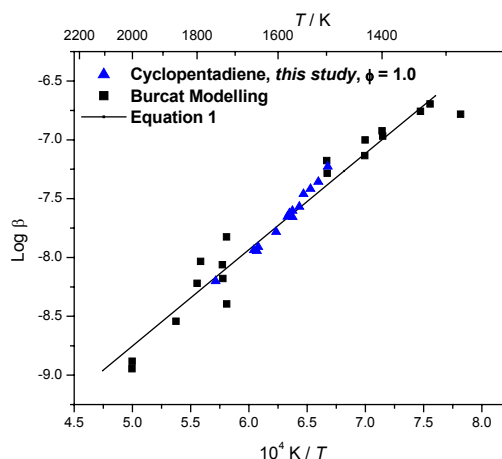


Fig 11: \blacktriangle 1.0 % cyclopentadiene, 6.5 % O_2 in Ar, \blacksquare Burcat modeling, — Equation 1.

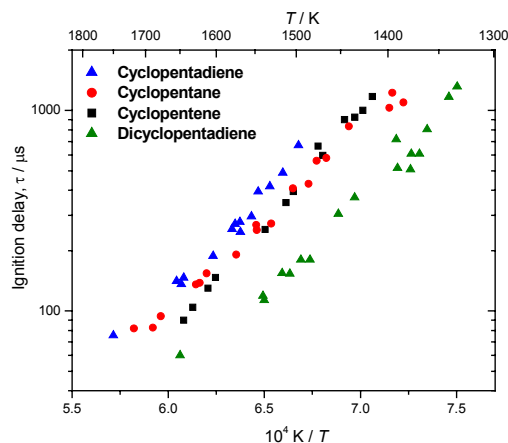


Figure 12: Ignition delay times versus T^{-1} for \blacktriangle 1.0 % cyclopentadiene, 6.5 % O_2 ; \bullet 1.0% cyclopentane, 7.5 % O_2 ; \blacksquare 1.0% cyclopentene, 7.0% O_2 ; \blacklozenge 1.0 % dicyclopentadiene, 13.0% O_2 ; in Ar, with $p_5 = 1.0 \pm 0.1$ atm, $\phi = 1.0$.

0.1 atm, Fig. 12. As the O_2 concentration was varied (cyclopentadiene = 6.5 % O_2 , cyclopentane = 7.5 % O_2 , cyclopentene = 7.0 % O_2 and dicyclopentadiene = 13.0 % O_2) the general trend of increased O_2 concentration yielding shorter ignition delay times was observed. This was not so obvious in the cases of cyclopentane ($O_2 = 7.5\%$) and cyclopentene ($O_2 = 7.5\%$) where the delay times were very similar.

Another comparison was carried out on these fuels at $p_5 = 1.0 \pm 0.1$ atm in which the fuel concentration was held at 1.0 %, the O_2 at 13.0 % and the Ar concentration at 86.0%, Fig. 13. In this case the ignition delay times of all four fuels were very similar.

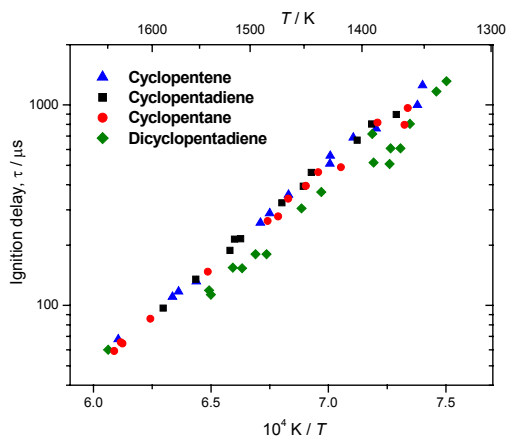


Figure 13: Ignition delay times versus T^{-1} for ▲ cyclopentene, ■ cyclopentadiene ● cyclopentane, ◆ dicyclopentadiene, fuel = 1.0 %, $O_2 = 13.0\%$ in Ar, $p_5 = 1.0 \pm 0.1$ atm.

Conclusions

It is impossible to determine with any confidence the conditions at which Drummond *et al.* produced the ignition delay times for cyclopropane. The results produced for the same fuel by Slutsky *et al.* agree with the results from *this study* in that the general trend of ignition delay times shortening with increasing reflected shock pressure is displayed, Fig. 5. However the exact pressure at which the results were obtained cannot be reproduced in our present shock tube and the mixture concentrations used by Slutsky *et al.* can only be estimated.

The cyclopropane results produced in *this study* display the larger changes caused to ignition delay times when the equivalence ratio is altered by varying the O_2 , instead of the fuel, concentration, Figs. 2 & 3. The trend of higher reflected shock pressures giving shorter ignition delay times is also illustrated, Fig. 5. The two C_3H_6 isomers, cyclopropane and propene, yield very similar ignition delay times under the same conditions, perhaps signifying that the rate determining step in cyclopropane is not the ring opening step, while also emphasising the role played by identical O_2 concentrations, Fig 6.

The $\phi = 2.0$, 1.0 and 0.5 mixtures of cyclopentane, cyclopentene and cyclopentadiene in Ar exhibited similar traits in that the ignition delay times decreased as the O_2 concentration was increased when ϕ went from 2.0 to 1.0 to 0.5, Figs. 7, 8 & 10. For all three the largest decrease in ignition delay times occurred as ϕ was changed from 2.0 to 1.0.

The $\phi = 1.0$ cyclopentadiene results agreed well with a plot of $\text{Log} [\tau * [C_5H_6]^{-0.06}[O_2]^{0.95}[Ar]^{-0.29}]$ versus T^{-1} produced by Burcat *et al.* for ignition delay times of cyclopentadiene plus O_2 mixtures in Ar, Fig. 11. Again the cyclopentene ignition delay times decreased as a mixture was examined at reflected shock pressures of 1.0 and then 4.0 atm, Fig. 9.

Stoichiometric, $\phi = 1.0$, mixtures of cyclopentane, cyclopentene, cyclopentadiene and dicyclopentadiene in which the fuel concentration had been maintained constant at 1.0% generally displayed ignition delay times that shortened as the O_2 concentration increased, Fig. 12. The results for cyclopentane and cyclopentene were very similar.

Mixtures of cyclopentane, cyclopentene, cyclopentadiene and dicyclopentadiene in Ar in which the fuel had been held constant at 1.0 % and the O_2 concentration at 13.0 %, displayed very similar ignition delay times emphasising that it may be the concentration of O_2 present rather than the actual equivalence ratio that is significant.

Acknowledgements

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