

Probing PAH formation from cyclopentene pyrolysis in a single-pulse shock tube

PITON CARNEIRO Leticia, HAMADI Alaa, CANO ARDILA Fabian-Esneider, SAID Abid, CHAUMEIX Nabih, COMANDINI Andrea
ICARE-CNRS
Orleans, Loiret, France

Abstract

The thermal decomposition of cyclopentene and cyclopentene+acetylene is studied in a shock-tube coupled to gas chromatography/mass spectrometry techniques under highly argon-diluted conditions with the goal of providing new experimental information about the polycyclic aromatic hydrocarbon (PAH) formation from cyclic C₅ species. Experiments are carried out at a residence time of 4 ms, a pressure of 20 bar, and temperatures ranging from 940 to 1650 K. An ongoing detailed chemical kinetic model for PAH chemistry is updated to successfully capture the fuel decomposition, the formation of small hydrocarbons, and the concentration of the main PAH products. Cyclopentene mainly decomposes into linear pentadiene and cyclopentadiene. In all the datasets, small hydrocarbons mainly come from the consumption of pentadiene, and the channels leading to PAHs basically originate from reactions of cyclopentadienyl radical with cyclopentadiene, other cyclopentadienyl radical, methyl, propargyl, and indenyl. The comparison between experimental and simulated results data is overall satisfactory, but updates are still needed to better predict toluene, indene, and acenaphthylene measurements.

1 Introduction

One of the main challenges for the development of next-generation combustion devices is the reduction in pollutant emissions, in particular soot and their precursors, the polycyclic aromatic hydrocarbons (PAHs). The combination of experimental and detailed kinetic modeling allows the understanding of the reaction pathways governing the PAH formation in combustion systems, and it consequently contributes to the development of clean technologies. Cyclic C₅ intermediates constitute essential building blocks for the growth to larger molecular structures. In particular, the role of cyclopentadiene and cyclopentadienyl radical is nowadays well established. Several proposed routes have also addressed the conversion of cyclopentadienyl radical to aromatic species in the literature. The reactions of cyclopentadienyl radical with methyl radical, acetylene, and another cyclopentadienyl radical are possible pathways to benzene [1–3], benzyl radical [4,5], and naphthalene formation [6–8], respectively. One of the precursor molecules for cyclopentadiene is cyclopentene through the reaction $\text{C}_5\text{H}_8 = \text{C}_5\text{H}_6 + \text{H}_2$. Thus, studies on cyclopentadiene may provide fundamental information on the

chemistry of the key C₅ intermediates. However, only two kinetic studies focused on the pyrolysis of cyclopentene in the literature. King [9] measured the kinetic parameters of the cyclopentene thermal decomposition reaction into 1,3-cyclopentadiene and hydrogen. More recently, Herbinet et al. [10] performed atmospheric-pressure pyrolysis experiments in a jet-stirred reactor in the temperature range 773-1048 K. Pyrolytic products up to naphthalene were measured using three complementary analytical methods, while a kinetic model describing the formation of aromatics was proposed.

The goal of this study is to carry out single-pulse shock tube pyrolysis experiments using argon diluted mixtures containing 100 ppm and 300 ppm cyclopentene at a nominal pressure of 20 bar over a temperature range of 940–1650 K. In addition, experiments on the pyrolysis of 100 ppm cyclopentene + 500 ppm acetylene are completed. Indeed, the study of the cyclopentene + acetylene reaction is of particular interest as it investigates the effect of acetylene addition on toluene formation and subsequently indene. Based on the newly obtained species profiles up to three-ring products, the sub-mechanism of cyclopentene is updated in our on-going kinetic model for PAH chemistry [11]. The joint experimental observations and kinetic modeling interpretations provide answers for three major questions: 1. the thermal decomposition of cyclopentene and the main decomposition products; 2. the influence of cyclopentadienyl radical on aromatic species; 3. and the effect of acetylene on cyclopentene reactivity and PAH speciation.

2 Experimental Set-up

Pyrolysis experiments are carried out with the high-purity single-pulse shock tube facility at ICARE, Orléans. The shock tube has a 78-mm inner diameter and 6-m long driven section, and 120-mm inner diameter and 3.7-m long driver section. Both sections are separated via a double diaphragm section. A 150 L dump tank is located ahead of the diaphragm. The details of the experimental facility and the procedures have been described in our previous publications ([11] and previous publications). The inner surface of the driven section is cleaned every day to remove carbon deposit and is pumped below 10⁻⁵ mbar prior each experiment.

The incident shock velocity is measured using four pressure sensors (CHIMIE METAL A25L05B) mounted on the sidewall at the end part of the driven section. The pressure–time profiles are measured by a PCB Piezotronics pressure sensor located at the end-wall of the driven section. The reflected shock wave pressure (P_5) and temperature (T_5) are determined by solving the conservation equations. The uncertainty in the calculated T_5 is within ± 30 K. The reaction time is around 4 ms in the current experimental configuration. The post-shock gas products are sampled with an air-actuated valve and are analyzed using an Agilent 7890B gas chromatograph (GC) and a Thermo Trace GC/DSQ mass spectrometer. The Agilent GC is equipped with a flame ionization detector (FID) detector and a thermal conductivity detector (TCD) connected respectively to a DB-17ms column for measurement of heavy species and to a Molsieve 5A column for measurement of inert compounds and for verifying the absence of air. The Thermo Trace GC is equipped with an FID detector connected to an HP Plot Q column for measuring light species up to mono-aromatics. The mass spectrometry is connected to the Thermo GC for identification of unknown products in the sampled mixtures. Known mixtures of the expected products are used for GCs' calibration [11].

The reaction mixtures are prepared in 136 L electropolished stainless steel cylinder according to Dalton's law of partial pressure and is maintained for at least 12 h before experiments to ensure homogeneity. The detailed experimental conditions and the exact compositions of the experimental mixtures are listed in **Table 1**. Cyclopentene is provided by Sigma-Aldrich, and the purity is 96%. Other used gases, including acetylene (>99.5%), the bath gas argon (>99.9999%) and the driven gas helium (>99.995%), are supplied by Air-Liquide.

Table 1: Experimental conditions and compositions of the gas mixtures used in this study.

Fuel mixture	X _{CYC5H8} (Mole %)	X _{C2H2} (Mole %)	X _{AR} (Mole %)	T ₅	P ₅	Reaction time
Neat cyclopentene	0.0108	—	0.9892	934-1647 K	20 bar	4 ms
Neat cyclopentene	0.0326	—	0.9674	943-1624 K	20 bar	4 ms
Cyclopentene+C ₂ H ₂	0.0111	0.0517	0.9372	940-1657 K	20 bar	4 ms

3 Kinetic modeling

A PAH kinetic model is developed in our previous serial works (latest version has been published in [11]) based on the latest version of the CRECK model [12]. Updates are made based on the theoretical calculations and reported models in literature to better capture the fuel decomposition reactivity and intermediates formation. The main reactions added and updated are described below.

The unimolecular decomposition of cyclopentene to pentadiene is updated from Dayma et al. [13] kinetic model. The recombination reaction of $c\text{-C}_5\text{H}_5 + \text{C}_3\text{H}_3$ producing styrene is added from Yuan et al. [14] model. The pathway to produce indene (C_9H_8) through the addition of $c\text{-C}_5\text{H}_5$ to C_5H_6 is adopted from Vervust et al. [15] work. The combination reaction between $c\text{-C}_5\text{H}_5$ and C_2H_2 can produce the heptatrienyl radical ($c\text{C}_7\text{H}_7$) and then $c\text{C}_7\text{H}_7$ can react with another C_2H_2 to form C_9H_8 . The corresponding rate constants were taken from the theoretical calculations by Fascella et al. [16]. The pathway to produce naphthalene (C_{10}H_8) from the self-recombination reaction of $c\text{-C}_5\text{H}_5$ is taken from Long et al. [17] theoretical calculations. Slavinskaya and Frank [18] proposed that phenanthrene can be formed from the reaction between indenyl (C_9H_7) and $c\text{-C}_5\text{H}_5$, which is adopted in the current model.

Based on the shock tube experiments, the fuel pyrolytic process is simulated using a closed homogeneous batch reactor in COSILAB [19]. Constant p_5 of 20 bar and a nominal reaction time of 4 ms are used in simulating the speciation measurements with the current kinetic model. The constant pressure assumption typically used in simulating the speciation results from single-pulse shock tube experiments has been proven in our previous works.

4 Results and discussion

Figure 1 shows the experimental and simulated mole fraction profiles of small intermediates and aromatics in the pyrolysis of neat cyclopentene and cyclopentene+C₂H₂. The results for the 300 ppm cyclopentene are not presented here due to the lack of space. The model can satisfactorily predict the profiles for the major products for both datasets, with under-prediction of ethane (Figure 1e), 1,3-butadiene (Figure 1i), toluene (Figure 1m), indene (Figure 1p), and acenaphthylene (Figure 1r), and an over prediction of C_5H_6 (Figure 1k) and C_6H_6 (Figure 1l) peaks. It is also noteworthy that the addition of acetylene has almost no influence on CYC_5H_8 speciation. We can notice a slight increment in the toluene and indene experimental peak mole fractions, and a more considerable increase in the phenylacetylene mole fractions (Figure 1n). On the other hand, naphthalene formation is slightly inhibited by the presence of acetylene (Figure 1q).

The fuel molecule, CYC_5H_8 , is consumed mainly through unimolecular decomposition reactions leading to the formation of linear pentadiene (LC_5H_8) and cyclopentadiene (C_5H_6). Among the small hydrocarbon intermediates, CH_4 is abundantly produced from H-atom abstraction reactions on C_5H_6 by CH_3 , while CH_3 is mainly formed from the reaction $\text{H} + \text{C}_3\text{H}_4\text{-P} = \text{CH}_3 + \text{C}_2\text{H}_2$ and the decomposition

reaction LC_5H_8 ($\text{LC}_5\text{H}_8 = \text{CH}_3 + \text{C}_4\text{H}_5$). Ethane (C_2H_6) is exclusively produced from the self-recombination of CH_3 . Three C_3 species ($\text{C}_3\text{H}_4\text{-A}$, $\text{C}_3\text{H}_4\text{-P}$ and C_3H_6) are detected in the experiments. The ROP analysis shows that $\text{C}_3\text{H}_4\text{-A}$ is mainly formed through $\text{H} + \text{CYC}_5\text{H}_8 = \text{C}_3\text{H}_4\text{-A} + \text{C}_2\text{H}_5$ at low temperatures, and the unimolecular decomposition reaction of C_5H_6 into acetylene and allene at high temperatures. $\text{C}_3\text{H}_4\text{-P}$ is predominantly produced from the isomerization of $\text{C}_3\text{H}_4\text{-A}$, and slightly through the unimolecular reaction $\text{C}_5\text{H}_6 = \text{C}_2\text{H}_2 + \text{C}_3\text{H}_4\text{-P}$. C_3H_6 is produced from the unimolecular decomposition of LC_5H_8 through the reaction $\text{LC}_5\text{H}_8 = \text{C}_2\text{H}_2 + \text{C}_3\text{H}_6$, and from the reaction through $\text{H} + \text{LC}_5\text{H}_8 = \text{C}_2\text{H}_3 + \text{C}_3\text{H}_6$. C_4H_6 mainly comes from the reaction $\text{H} + \text{LC}_5\text{H}_8 = \text{CH}_3 + \text{C}_4\text{H}_6$, and partly from the recombination reaction $\text{CH}_3 + \text{C}_3\text{H}_3$. The consumption of C_4H_6 through reaction with H leads to the formation of C_2H_4 and C_2H_3 , which subsequently decompose to C_2H_2 . The $\text{CYC}_5\text{H}_8 + \text{H}$ reactions are most important pathways for C_2H_4 formation. On the other hand, there are numerous formation pathways for C_2H_2 formation throughout the temperature range. C_5H_6 is exclusively formed from CYC_5H_8 unimolecular decomposition.

The thermal decomposition of CYC_5H_8 also leads to various single-aromatic structures. C_6H_6 is mainly produced through $\text{C}_5\text{H}_5 + \text{CH}_3$ reactions and propargyl self-recombination reactions. Toluene is mainly formed through the recombination reactions of propargyl with 1,3-butadiene (C_4H_6) and but-2-yn-1-yl radical ($\dot{\text{C}}\text{H}_2\text{C}\equiv\text{CCH}_3$). $\text{C}_2\text{H}_2 + \text{C}_5\text{H}_6 \Rightarrow \text{C}_7\text{H}_8$ has minor contribution to toluene formation. Since the model under-predicts the experimental results for toluene, the above-mentioned reaction needs further analyses based on the recent theoretical studies available in the literature. Styrene ($\text{C}_6\text{H}_5\text{C}_2\text{H}_3$) is majorly produced through $\text{C}_5\text{H}_6/\text{C}_5\text{H}_5 + \text{C}_3\text{H}_3$ reactions, and slightly through $\text{C}_6\text{H}_5 + \text{C}_2\text{H}_4$ reaction. Phenylacetylene ($\text{C}_6\text{H}_5\text{C}_2\text{H}$) is exclusively formed through $\text{C}_6\text{H}_5 + \text{C}_2\text{H}_2/\text{C}_2\text{H}$ reactions.

Regarding polyaromatic hydrocarbons, indene is formed mainly by the reactions $\text{C}_6\text{H}_5 + \text{C}_3\text{H}_3\text{-P}/\text{C}_3\text{H}_3$ through 1-phenyl-propyne and phenylallene intermediates [11], and in minimal part through $\text{C}_7\text{H}_7 + \text{C}_2\text{H}_2$ [20]. The addition of *c*- C_5H_5 to C_5H_6 has no contribution to indene formation according to the model. The model underpredicts indene profiles (Figure 1p) which suggests that the adopted reaction rates are not correct or the need for additional alternative reaction pathways. Naphthalene (C_{10}H_8) is predominantly formed through *c*- C_5H_5 self-recombination. The interactions of indenyl with propargyl and *c*- C_5H_5 lead to the formation of acenaphthylene (C_{12}H_8) and phenanthrene ($\text{PC}_{14}\text{H}_{10}$), respectively. Anthracene ($\text{AC}_{14}\text{H}_{10}$) is mostly formed from phenanthrene isomerization.

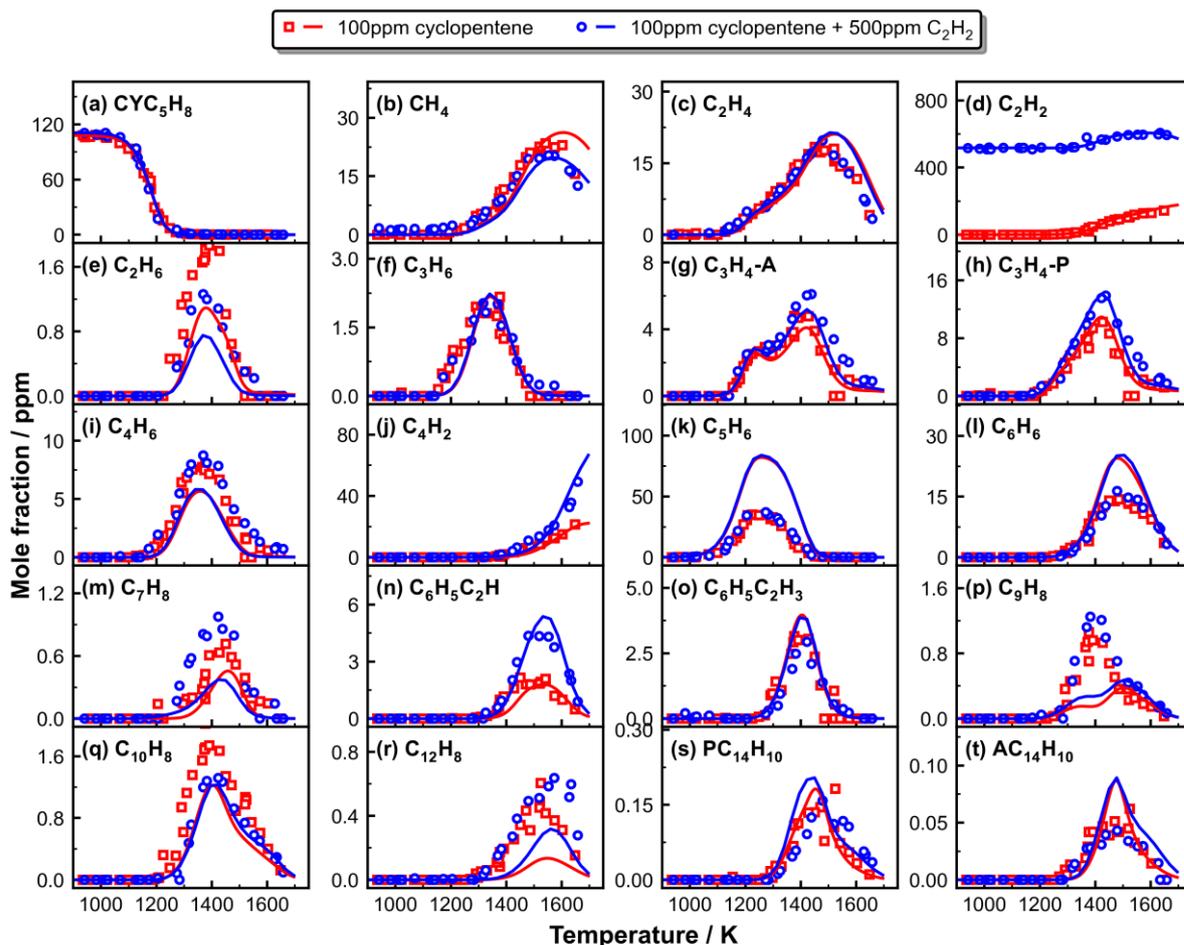


Figure 1: Measured (symbols) and simulated (lines) mole fraction profiles of small hydrocarbons in the pyrolysis of 100ppm cyclopentene and 100ppm cyclopentene+ 500ppm acetylene.

5. Conclusions

This work investigates the pyrolysis of cyclopentene in a single-pulse shock tube coupled to gas chromatographic techniques. The detailed PAH kinetic model successfully captures the concentration of major PAHs, as well as the small species produced in neat cyclopentene and cyclopentene+C₂H₂ pyrolysis. Both the model and the experimental results show that the addition of acetylene has minor influence on the speciation of cyclopentene. The initial analyses show that pentadiene plays an important role in the formation of small hydrocarbons, and C₅H₆ and c-C₅H₅ play a vital role in the formation of the sing-aromatic benzene and the larger polyaromatic hydrocarbons (naphthalene and phenanthrene). Further developments will be done to improve the prediction of the model for toluene, indene, and acenaphthylene.

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