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

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Abstract

With the goal of improving our capabilities to model surrogate fuels, in particular in relation to PAH and soot formation, the pyrolysis of n-heptane is studied in a single-pulse shock tube over a broad range of temperatures (900-1700 K) at 20 bar nominal pressure and 4 ms residence time. Three different initial fuel mole fractions were considered, 100, 500, and 2000 ppm of n-heptane in argon. Fuel and intermediate species, including aromatics up to phenanthrene, are measured using gas chromatography and mass spectrometry. An ongoing detailed chemical kinetic model for PAH chemistry has been updated to successfully capture the fuel decomposition, the formation of small hydrocarbons, and the concentration of the main PAH products. Major reaction pathways to PAHs are discussed as well as the role of important intermediate species.

1   Introduction

N-Heptane has been extensively used as a primary reference fuel for gasolines and as a single-component surrogate for diesels. Due to these practical interests, the pyrolysis of n-heptane has been broadly investigated through various experimental configurations and techniques regarding the fuel properties and speciation measurements; some of the recent works include [1–7]. On the other hand, the information on the formation mechanisms of polycyclic aromatic hydrocarbons (PAHs) in heptane combustion is still scarce. Understanding PAHs formation in combustion processes provides a base for the development of the soot formation kinetic models, which are essential elements used for the implementation of solutions for improved combustion efficiency and reduced emissions. Pyrolytic conditions offer a suitable environment to study the fuel decomposition and the build-up of PAHs.

As all the previous pyrolytic studies available in the literature are centered on the decomposition of n-heptane and the formation of small hydrocarbon products, the present article aims on providing shock tube pyrolysis datasets of species profiles, ranging from small hydrocarbons to three-ring aromatics, for different heptane mixtures, at conditions relevant to modern combustion devices (~20 bar, 900-1770 K). The kinetic model developed in our serial works, whose latest version has been published in [8], has been updated to simulate the newly obtained experimental profiles and interpret the results. With the

combination of experimental measurements and modeling analysis, kinetic insights revealing the aromatic species formation from n-heptane pyrolysis will be presented.

2   Experimental Set-up

n-Heptane pyrolysis experiments are carried out with the high-purity single-pulse shock tube facility at ICARE, Orléans. A detailed description of the shock tube apparatus can be found in prior publications ([8] and previous works). Briefly, the single-pulse shock tube apparatus consists of the driven section (length: 6 m; inner diameter: 78 mm) and the driver section (length: 3.7 m; inner diameter: 120 mm), separated by a double diaphragm. The shock tube operates in a single pulse fashion as equipped with a dump tank (volume 150 L) situated close to the diaphragm section. Experiments are performed behind reflected shock waves, where stable species are withdrawn from the shock tube using an air-actuated valve and analyzed by gas chromatography/gas chromatography–mass spectrometry techniques. The temperature and pressure conditions are calculated solving the conservation equations once the incident shock wave velocity is measured from the signals of four pressure sensors located in the end-section of the shock tube. The estimated error in T_5 is 30K. The experiments are conducted with helium (Air Liquide, purity >99.995 %) as the driver gas and dilute mixtures of n-heptane (Sigma–Aldrich, purity ≥99.5%) in argon bath gas (Air Liquide, purity >99.9999 %). This study includes three argon-diluted fuel mixtures of different n-heptane mole fractions (101 ppm, 500 ppm and 2000 ppm).

The Agilent GC, designed to measure the PAHs up to four rings, is equipped with a flame ionization detector (FID) coupled to a DB-17ms column for heavy species separation, and a thermal conductivity detector coupled to a Molseive 5A column for monitoring air absence and dilution by helium. An external valve box heated to 320°C, coupled to the GC, is used for sample storage and injection. The Thermo Trace GC is also equipped with an FID detector, connected to an HP Plot Q column for measuring light species up to mono-aromatics. A DSQ mass spectrometer aids in species identification. The detectors are calibrated using standard-mixtures and gas-phase mixtures. The uncertainties in the species mole fractions is 5% for the small species and 10%-15% for the PAHs.

3   Kinetic modeling

A PAH kinetic model is developed in our previous serial works (latest version has been published in [9]) based on the latest version of CRECK model [9]. The n-heptane sub-mechanism by Zhang et al. [10] is chosen to substitute the lumped heptane chemical mechanism. The n-heptane sub-mechanism includes unimolecular decomposition and H-abstraction reactions from the fuel and the corresponding fuel radicals. Additionally, the rate coefficient of the hydrogen abstraction from C_2H_4 by H atom from the CRECK model is reintegrated [9]; in our previous model, this reaction had been modified with the value recommended by Baulch et al. [11].

Based on the shock tube experiments, the fuel pyrolytic process is simulated using a closed homogeneous batch reactor in COSILAB [12]. 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

The target of this work is to investigate PAH formation in heptane pyrolysis. For this, three different heptane mixtures with different concentrations are prepared (100, 500, and 2000 ppm). Several species ranging from small hydrocarbons to PAHs are detected and quantified. The small hydrocarbons up to toluene are shared among the three sets. Trace and significant amounts of PAHs are respectively detected

in the 500 and 2000 ppm sets, while no PAHs are observed in the 100 ppm set. Figures 1 and 2 show respectively the comparison of experimental and predicted mole fractions of small species and aromatics for the three datasets. The model does an excellent job in simulating the profiles for the major small species for all initial fuel mole fractions, with slight discrepancies observed for CH_4 (Figure 1b) and the C_3H_4 isomers (Figure 1g and h) where the initial formation is well captured but the decomposition starts at lower temperatures compared to the experiments, and for an over-prediction of the C_3H_8 (Figure 1i) C_5H_{10}-1 (Figure 1q) peaks. It is important to underline that the original model by Zhang et al. [10] has similar capabilities, as shown in Figure 3 for the experimental set at 2000 ppm initial mole fraction. Concerning the small hydrocarbons, the major difference with the current model lies in the C_4 intermediates, in particular 1,3-butadiene (Figure 1k), 1- and 2-butyne (Figure 1m and p). On the other hand, the model by Zhang et al. [10] did not target the aromatic chemistry, thus our current model is greatly improved in relation with the chemistry involved in the aromatic species. This can be observed in Figure 3r to w for the single-ring aromatics. Figure 3 also contains the simulations obtained with two well-established models available in the literature, the original CRECK model [9] and the LLNL model [14]. The LLNL model [13] shows discrepancies in predicting some of the major intermediates such as methane, ethylene, allene, propyne, and benzene although it correctly predicts the fuel decomposition. The CRECK model [9] seems to better predict methane, ethane, the C_3 products, and some of the minor C_4 intermediates, but it still does not accurately capture some of the key species profiles such as for ethylene, acetylene, and the aromatics. In addition, some of the C_4 isomers are not considered in the CRECK kinetic scheme due to the species lumping.
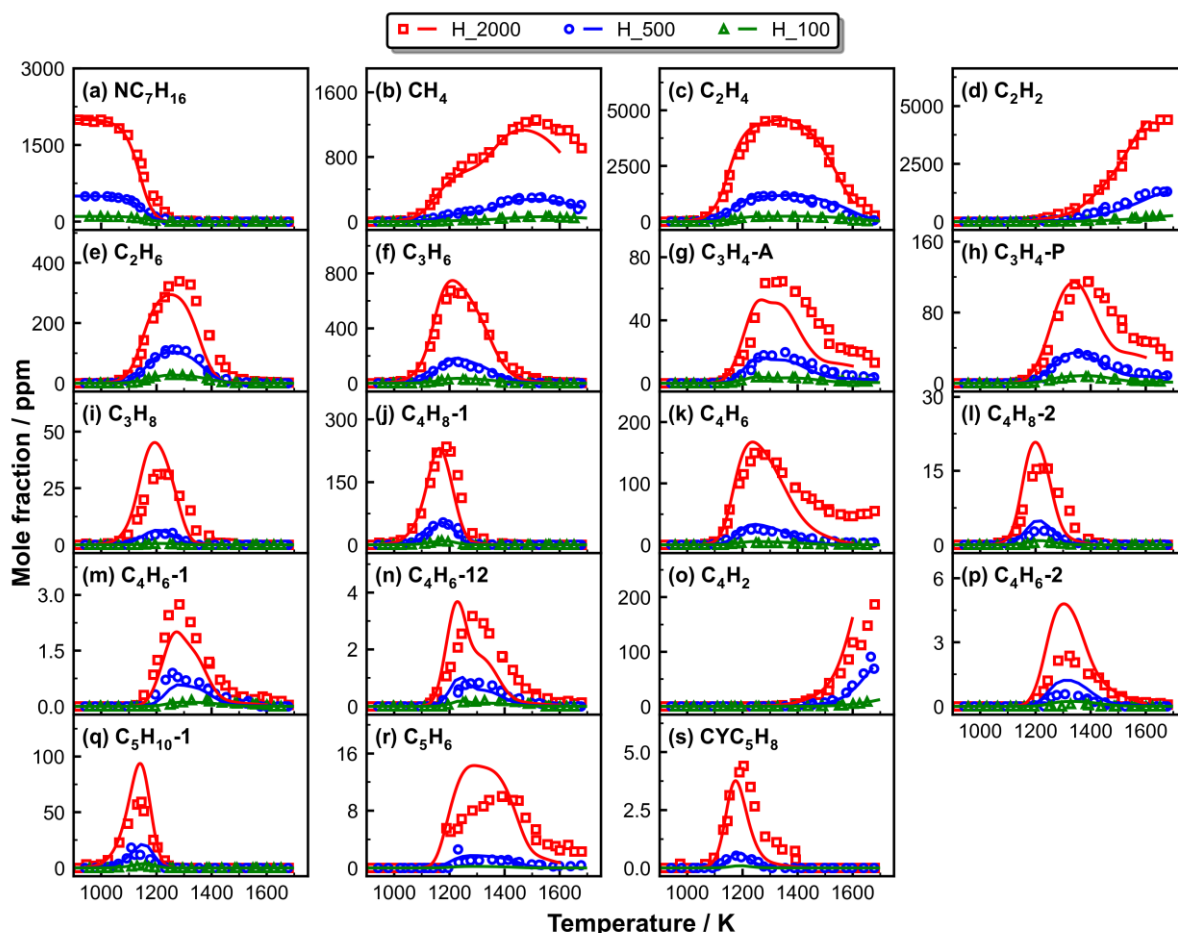
Figure 1: Measured (symbols) and simulated (lines) mole fraction profiles of small hydrocarbons in 100ppm, 500ppm, and 2000ppm heptane pyrolysis.

As already mentioned above, Figure 2 presents the experimental and modeling results for the three datasets concerning the aromatic products. Since the focus of this work is to highlight the PAH formation chemistry, only the reaction pathways leading to the formation of such aromatic intermediates will be discussed here. First at all, the model is capable to reproduce the results relatively well, although improvements in the model prediction capabilities are still required. This is mainly due to the over-prediction of the benzene profiles (Figure 2a), benzene being the precursor molecule for other PAH products. Benzene formation accounts largely on propargyl self-recombination reaction. Since the levels of C_2H_2 and C_2H_4 are high in heptane pyrolysis, strong interactions are observed between phenyl and C_2 fuels, particularly acetylene, through $C_6H_5 + C_2H_x = C_6H_5C_2H_x\text{-}1 + H$ (x=2, 4) reactions leading to phenylacetylene and styrene production, respectively (Figures 2c and d). The major sources that account for the formation of toluene (Figure 2b) are the recombination reactions of propargyl with 1,3-butadiene (C_4H_6) and but-2-yn-1-yl radical ($\dot{C}H_2C\equiv CCH_3$), respectively. Indene (Figure 2e) is formed mainly through $C_7H_7+C_2H_2$ [14] and $C_6H_5+C_3H_3\text{-}P/C_3H_3$ reaction through 1-phenyl-propyne and phenylallene intermediates [8]. The subsequent interactions of indenyl with methyl and propargyl respectively lead to the formation of the most abundant PAH species naphthalene (Figure 2f) and acenaphthylene (Figure 2g), as explained in our recent study [8,14]. Finally, phenanthrene (Figure 2h) is mainly formed through C_7+C_7 reactions at low temperatures, while through $C_6H_5C_2H+C_6H_5$ addition-elimination reactions at high temperatures.
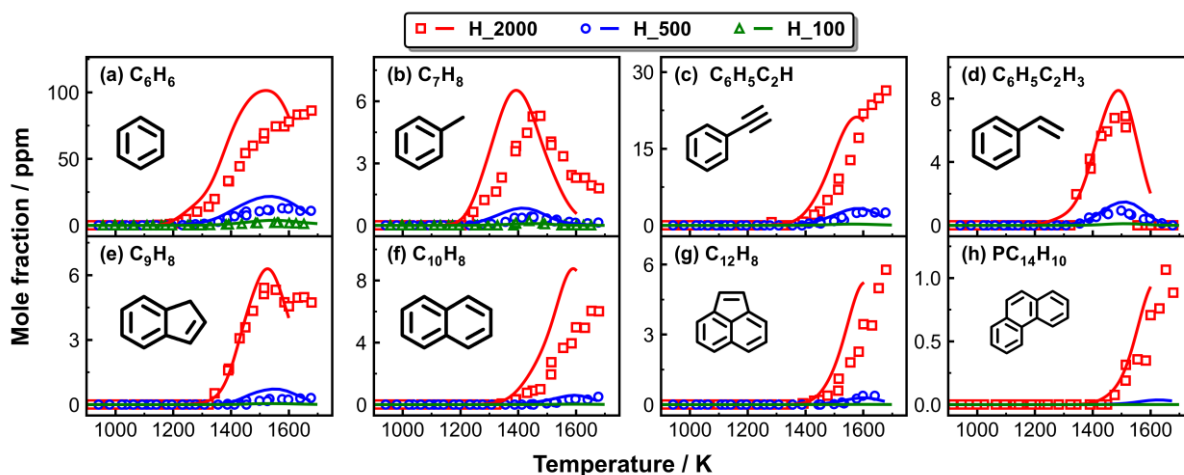
Figure 2: Measured (symbols) and simulated (lines) mole fraction profiles of MAHs and PAHs in 100ppm, 500ppm, and 2000ppm heptane pyrolysis.
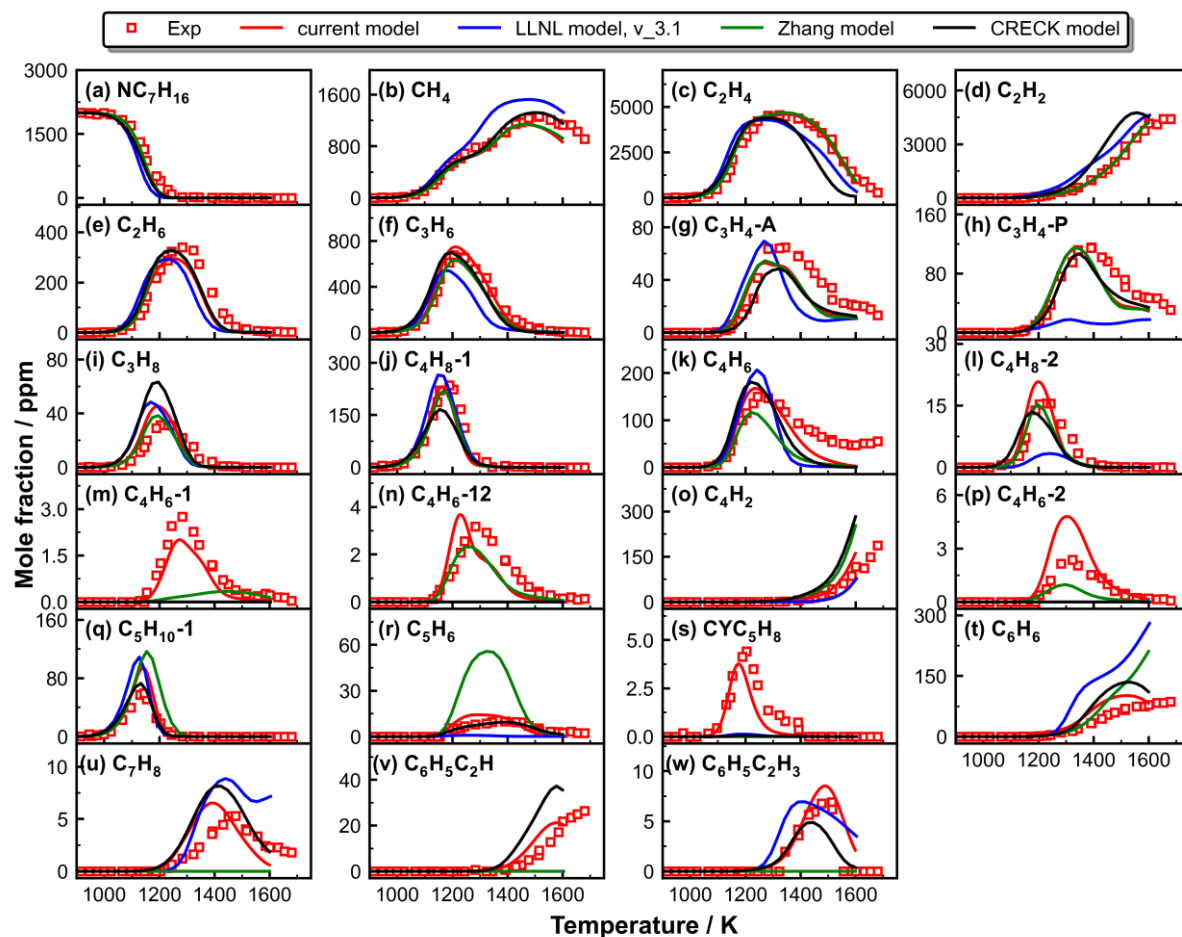

Figure 3: Species concentrations as a function of T5 from 2000 ppm heptane pyrolysis experiments at the nominal P5 of 20 bar. Symbols: measurements; Solid lines: simulations with different models (see legend)

5. Conclusions

This work investigates the pyrolysis of n-heptane in a single-pulse shock tube coupled to gas chromatographic techniques. In particular, PAH formation has been targeted as an important new addition to the literature on n-heptane chemistry. The detailed PAH kinetic model successfully captures the concentration of major PAHs, as well as the small species produced in heptane pyrolysis. Initial analyses presented in this abstract will be further developed. The results obtained can be used for improving the comprehension of PAH formation from the pyrolysis of surrogate fuels.

Acknowledgment

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