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Time-resolved measurements of key intermediate products during cyclopentanone pyrolysis in a shock tube

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The pyrolysis of cyclopentanone, a promising biofuel candidate identified by the Department of Energy's Co-Optima program, is investigated in this work. Time resolved measurements of carbon monoxide, ethylene, and cyclopentanone are provided to gain a detailed understanding of the unimolecular decomposition pathway of the fuel. Experiments were conducted between 1156-1312 K near 9 atm with 0.1% fuel loading balanced in argon. A strategy to report species concentration with interference is presented and the measurements obtained are crucial validation targets for the development of detailed chemical kinetic mechanisms used to predict fuel chemistry.

I. Nomenclature

X = Mole fraction
σ = Absorption cross-section
L = Absorbing path length
T = Temperature
P = Pressure
α = Absorbance

II. Introduction

The world's energy demands continue to rise as the population grows, creating a need for sustainable, scalable, and energy rich fuels. In 2017, the United States consumed approximately 97.7 quadrillion BTU of energy, with 29% by the transportation sector alone [1]. The burning of petroleum and natural gas fuels by the transportation and other sectors is causing global temperatures to rise through the production of greenhouse gases [2]. Due to the rapidly increasing global temperatures and energy demands, the Department of Energy, in sponsorship with university partners, created the Co-Optimization of Fuels and Engines (Co-Optima) initiative aimed at finding renewable fuels that simultaneously increase engine performance and efficiency, and decrease greenhouse gas emissions. One such fuel identified by the Co-Optima program is the cyclic ketone cyclopentanone. This candidate fuel can be produced through the endophytic fungus, *Gliocladium roseum* [3] and is contained in oils produced through the pyrolysis of

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biomass [4]. Cyclopentanone is also an extremely attractive fuel for spark-ignition internal combustion engines, as it has the lowest autoignition reactivity of many biofuels. This autoignition resistance combined with its large lower heating value (LHV) of 31.99 MJ/kg, make cyclopentanone a very attractive blending agent in boosted internal spark ignition engines.

Previous investigation into cylcopentanone have been both theoretical and experimental in nature. Zaras et al. [5] used the G3B3 method to understand the unimolecular decomposition of cyclopentanone and used RRKM theory to calculate relevant rate constants over the temperature span of 800-2000 K. Thion et al. [6] used a jet-stirred reactor and sampled the product stream to determine major products of cyclopentanone oxidation at 1 and 10 atm. H-abstraction reactions on the fuel by H, OH, and CH_3 were also investigated; a mechanism detailing cyclopentanone oxidation was established. In a large collaborative effort, Zhang et al. [7] investigated the olefin + HO_2 elimination reactions, a crucial pathway for cyclopentanone oxidation. This study was supported with experimental validation of ignition delay times and carbon monoxide time histories over a range of equivalence ratios, temperature, and pressures.

The radical involved oxidation of cyclopentanone can have many similarities in pyrolysis. Thus, it is paramount that the pyrolysis pathway be fully understood so that parallels can be drawn to the oxidation of the fuel. Investigations into the pyrolysis of cyclopentanone are scarce [5] and no experimental validations have been provided. Therefore, in this work carbon monoxide, ethylene, and cyclopentanone time-histories are measured, and used as key validation targets for mechanism development.

III. Experimental Procedure

Shock Tube Facility

Carbon monoxide, ethylene, and cyclopentanone (CPN) time-histories were collected in a double-diaphragm, heated, shock tube facility at UCF with an internal diameter of 0.1417 m, specific details of which can be found in [8-10]. The velocity of the incident shock wave was measured through five piezoelectric pressure transducers (wired to four time interval counters). The temperature (T_5) and pressure (P_5) behind the reflected shock were calculated through quasi one-dimensional normal shock relations using the measured incident shock velocity. Eight equally spaced ports around the circumference of the tube, 2.00 cm away from the end-wall, were used for pressure and spectroscopic measurements.

Laser Measurements

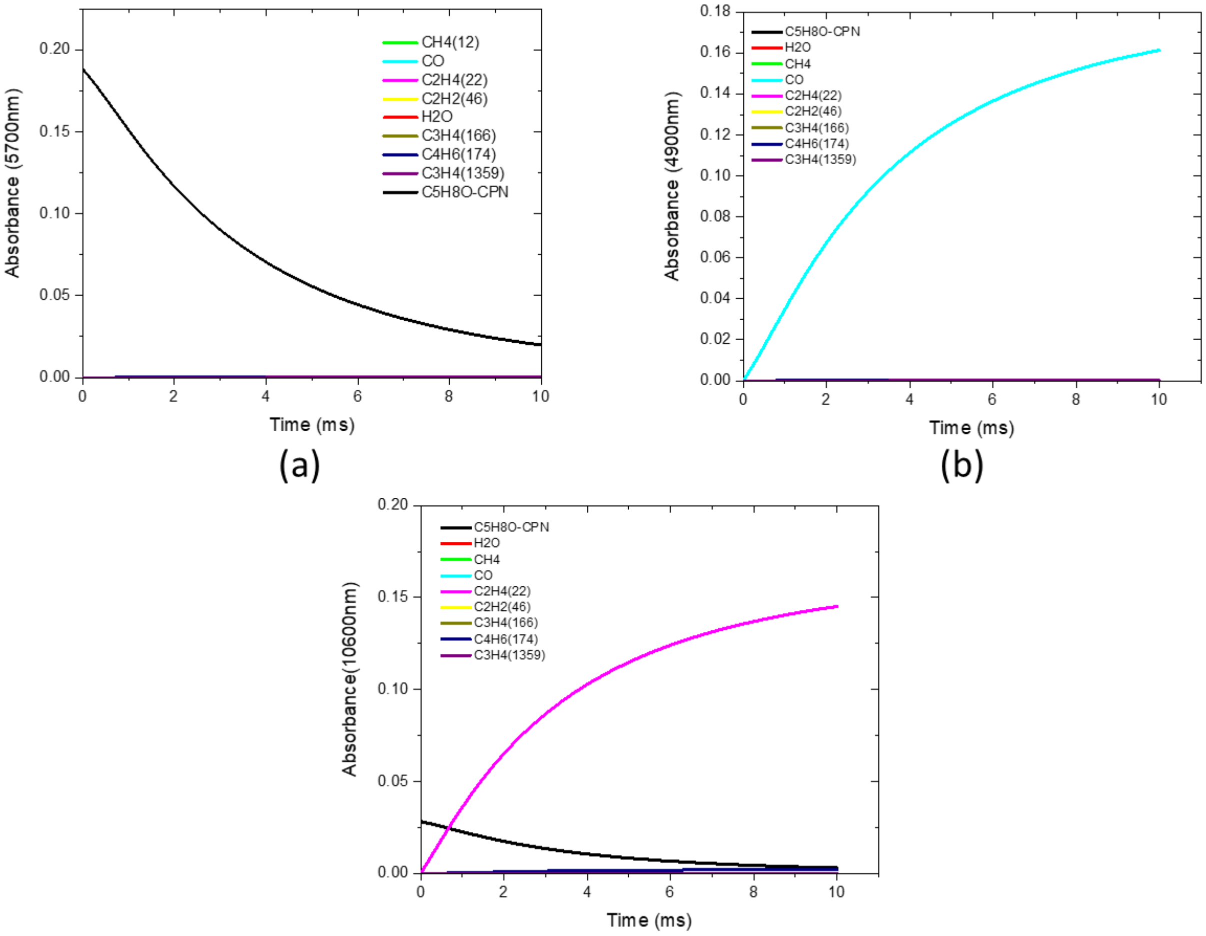
CHEMKIN-Pro simulations were conducted using a preliminary pyrolysis mechanism for cyclopentanone from MIT, the concentrations of the top intermediates formed during the pyrolysis of 0.1% CPN/99.9% Ar were found and fed into the Beer-Lambert law, eq. (1), to calculate the absorbance of each molecule at three different wavelengths, displayed in Fig. 1. Measurements of carbon monoxide were made with a continuous wave, distributed feedback quantum cascade laser centered at 2046.30 cm^{-1} from Alpes Lasers (TO3-L-50). Due to the negligible interference of other molecules, the measured absorbance is directly converted into concentration of CO through eq. (1).

$$X = \frac{\alpha RT}{PL\sigma},\ \alpha = -\ln\left(\frac{I}{I_o}\right) \tag{1}$$

$$\alpha_{949} = \alpha_{CPN} + \alpha_{C2H4} \tag{2}$$

$$X_{C2H4} = \frac{1}{\sigma_{C2H4,949}}\left(\frac{RT\alpha_{949}}{PL} - X_{CPN}\sigma_{CPN,949}\right) \tag{3}$$

Ethylene absorbance was measured with a tunable CO_2 gas laser (Access Laser L4GS) centered at 949.49 cm^{-1}. As seen in Figure 1c, CPN also has an absorption feature at the measuring wavelength for ethylene; therefore, the contribution from CPN to the measured absorbance at this wavelength must be quantified. In order to do so, a DFB QCL centered at 1749.84cm^{-1} from MIRSense was used for CPN quantification, interference free as shown in Figure 1b. The time-history of CPN can thus be calculated from eq. 1 during each experiment. To obtain the time-histories of C2H4, the contribution of C2H4 and CPN have to be taken into consideration as in eq. (2). If eq. (1) is substituted into eq. (2) for each compound, eq. (3) is obtained which subtracts out the contribution of CPN from the measured absorbance. In eq. (3) $\sigma_{C2H4,949}$is the cross-section of ethylene at its measuring wavelength (949. 49cm^{-1}), $\sigma_{CPN,949}$ is the cross-section of CPN at the ethylene measuring wavelength, X_{CPN} is the mole fraction of CPN determine through eq. (1) at 1749.84cm^{-1}, and $\alpha_{949}$is the sum of the ethylene and CPN absorbance at ethylene's measuring wavelength.



(a)

(b)

(c)

Figure 1. Absorbance of top intermediates at **(a)** wavelength for measuring CPN (1749.84cm^{-1}), **(b)** wavelength for measuring CO (2046.30cm^{-1}), and **(c)** wavelength for measuring C2H4 (949.49cm^{-1}). Cross-section (CS) for CO obtained through eq.2; CS for C2H4 obtained from [11]; CS of C2H2, H2O, and CH4 obtained through the HITRAN 2012 database [12]; CS of CH2CO (18) not found; CS of C3H4(166), C3H4 (1359), and C4H6(174) obtained from PNNL 2008 database at STP conditions

IV. Results and Discussion

The thermal decomposition of C_5H_8O in Ar was investigated behind reflected shockwaves between 1156-1312 K at pressures near 9 atm. Figure 2 shows one example of the time histories of cyclopentanone, ethylene, and carbon monoxide. Figure 2 shows an induction time of cyclopentanone at theses conditions of 0.127ms, denoted by the constant fuel concentration over this time and the zero concentration of CO and C_2H_4. After the induction period the fuel depletes at nearly a constant rate, with the small deviations toward the end of the test time being caused by beam steering at these elevated pressures. Conversely, the concentrations of CO and C_2H_4 grow with a constant rate with the ratio of C_2H_4 to CO growth about 1.7

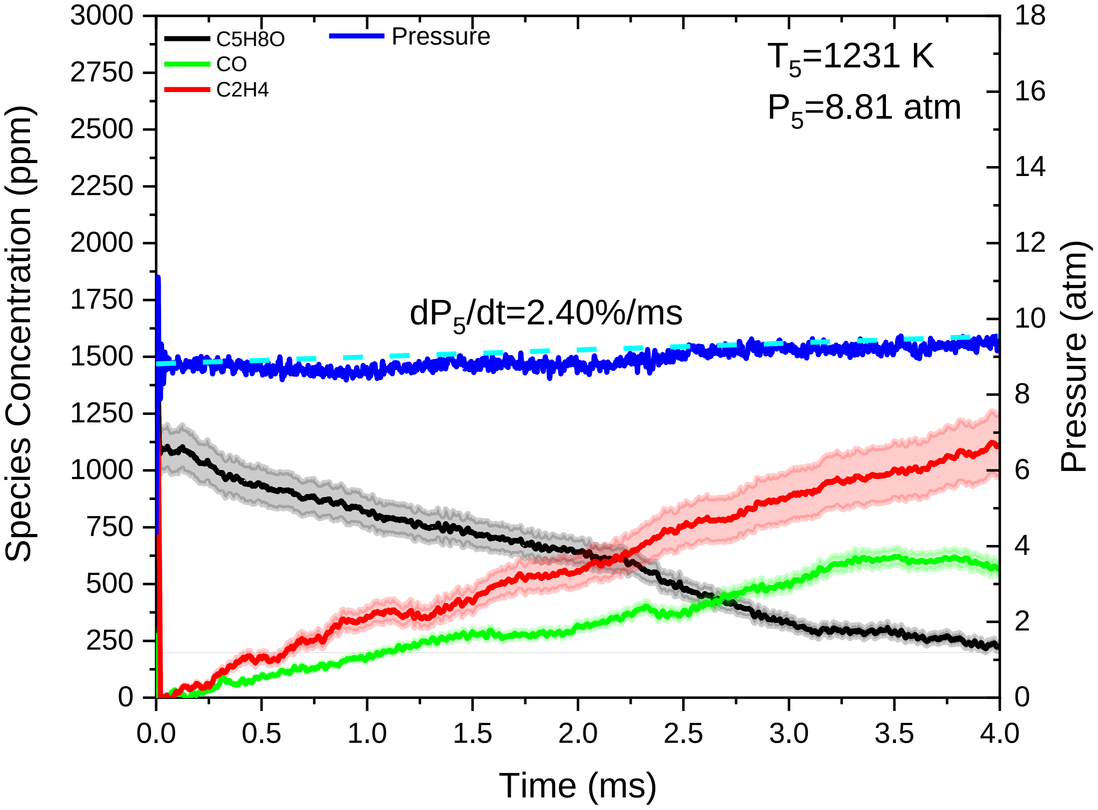


Figure 2. CO, C_2H_4, and C_5H_8O time-histories during pyrolysis of cyclopentanone

V. Summary

The unimolecular decomposition of cyclopentanone into the formation of important products, carbon monoxide and ethylene was investigated in this work. The induction time of the fuel, the time-dependent growth of the products, and the ratio of the products were measured and are extremely important quantities that can be used to extend the knowledge of this promising biofuel candidate through the development of detailed chemical kinetic mechanisms.

VI. Acknowledgements

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