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Simultaneous measurements of acetylene and soot during the pyrolysis of ethylene and benzene in a shock tube

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Abstract

Acetylene is one of the most important precursors of soot and contributes to soot growth by the hydrogen-abstraction acetylene-addition (HACA) mechanism. In this work, we undertake time-resolved simultaneous measurements of acetylene and soot behind reflected shock waves at temperatures of 1600–2200 K and pressures of 3–5 bar. Acetylene mole fraction time-histories are measured from the absorption of a quantum-cascade laser operating around 13.6 μm. The soot volume fraction, particle size and number densities are calculated from the extinction and scattering of a cw Nd:Yag laser at 532 nm. Acetylene and soot are generated from the pyrolysis of 1% benzene in argon, 2.35% ethylene in argon, and binary mixtures of ethylene with propane/methane in argon. We note that acetylene time-histories exhibit a two-stage growth during the pyrolysis of benzene, which can be correlated to the initial rapid increase of soot volume fraction and a later plateauing. In comparison to ethylene pyrolysis, the pyrolysis of benzene results in larger values of the soot volume fraction, particle diameter and number density. We compare the measured data against the values simulated using the method-of-moments routine in Chemkin-Pro and a detailed PAH mechanism based on KM2 [1] and AramcoMech 1.3 [2]. Large discrepancies are observed between the measured and predicted values of the soot parameters. The data obtained from our experiments may assist future validation and development of soot mechanisms.

Keywords: Soot; Acetylene; Shock tube; Laser absorption; Scattering

1. Introduction

Understanding the process of soot/particulate formation and the measurements of soot properties are important in many areas of research [3,4]. The study of particle formation is relevant to the production of high-performance metal oxides and nanostructures such as graphene, fullerene and

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carbon nanotubes. These nanoparticles are commonly used to manufacture many everyday items such as inks, dyes, plastics and tires. On the other hand, soot emissions are harmful to human health and the environment. Soot is an air pollutant and contributes to global warming. Furthermore, the deposition of soot can accelerate melting of snow, ice and glaciers. Soot is formed as a result of the incomplete combustion of hydrocarbons, and acetylene is one of its major precursors, playing a significant role in the formation of the first aromatic ring and the growth of polycyclic aromatic hydrocarbons (PAH) which participate in soot nucleation [5]. Acetylene can also contribute to soot surface growth via the hydrogen-abstraction-C_2H_2-addition (HACA) mechanism.

Soot formation has primarily been studied in flames [6–10]. PAH and soot chemical mechanisms are most commonly validated against flame data [1,11]. Modeling chemical reactions in a flame can be complicated due to the coupling of molecular transport and heat transfer with chemistry. Shock tubes, however, are considered ideal experimental devices for isolating the chemical behavior from physical processes. The gaseous sample behind a reflected shock wave is almost stationary. Initial temperature and pressure are also more easily determined behind a reflected shock wave. Despite these advantages, the soot experiments in a shock tube can be quite challenging. The scattering collection solid angle in shock tubes is typically very small because the viewports tend to be less than an inch in diameter. Measurements at multiple angles are also restricted due to the limited number of viewports. Furthermore, most of the studies in shock tubes report 2–3 ms of test time, which might be insufficient to study the later stages of soot formation [3]. Lastly, soot experiments in shock tubes can be extremely time consuming as it is necessary to clean the shock tube after every run. Owing to such drawbacks, the laser scattering measurements are more challenging and less common in shock tubes than in open flames. The majority of previous shock tube soot studies are limited to the measurements of soot volume fraction inferred from the light extinction by soot particles [12–16]. In particular, there is very little data from shock tubes on soot particle size and number density, which can be obtained from simultaneous measurements of the extinction and scattering of light by soot particles. Graham et al. [17] were the first to measure scattering from soot in a shock tube. They studied soot from the pyrolysis of various aromatic hydrocarbons. Soot particle size and soot yield during fuel rich oxidation and pyrolysis of toluene, benzene and various aliphatic hydrocarbons have been studied by Kellerer et al. [18,19], while the morphology of soot particles in a shock tube has been characterized only by di Stasio et al. [20] by measuring the scattering signal at multiple angles during the pyrolysis of ethylene. De Iuliis et al. [21] have reported soot yield, particle size and number densities during the pyrolysis of ethylene and toluene in a shock tube. To our knowledge, none of the previous shock tube studies reported simultaneous measurements of gaseous species and soot particles.

This work reports simultaneous measurements of acetylene and soot in shock tube experiments. These simultaneous measurements are expected to provide deeper insights into soot chemistry and tighter bounds to tune the chemical mechanisms. Scattering and extinction from soot are measured behind reflected shock waves during the pyrolysis of the diluted mixtures of benzene, ethylene and binary mixtures of ethylene with propane and methane. The data are used to calculate the soot volume fraction, soot induction time, particle size and number density. Measurements are compared with the predictions from AKP mechanism (S. Park, M. Sarathy, H. Im, S. Chung; personal communication, 2015, KAUST), which is a modified version of the KM2 mechanism [1] updated using the base chemistry from AramcoMech 1.3 [2]. Detailed comparisons with the model and the explanation of the reaction mechanism are beyond the scope of this study. Additional simulations using AKP and preliminary comparisons with the predictions from the KM2 [1] and NBP [22] mechanisms are presented in the Supplemental Material.

2. Theory

Soot volume fraction is obtained using

$$f_v = \frac{(1/L)ln(I_o/I_t)\lambda}{6\pi E(m)}. \quad (1)$$

Here, L is the absorption path length (14.2 cm, the inner diameter of the shock tube), λ is the absorption wavelength (532 nm), and I_o and I_t are the incident and transmitted intensities, respectively. The soot refractive index for absorption, $E(m)$, is 0.24 at 532 nm when calculated using the equations by Chang and Charalampopoulos [6]. It is assumed that the extinction is primarily caused by absorption, and scattering can be neglected. The verification of this assumption is provided in the Supplemental Material (Section S3).

The volume equivalent diameter, d_p, of the soot particle is inferred from the scattering and extinction measurements using

$$d_p = \lambda\left(\frac{4E(m)C_{vv}}{\pi^2 F(m)K_e}\right)^{1/3}. \quad (2)$$

Here, soot refractive index for scattering, $F(m)$, is 0.44 at 532 nm [6]. The extinction coefficient, K_e, is $(1/L)\ln(I_o/I_t)$. The scattering coefficient, C_{vv}, is obtained assuming Rayleigh scattering theory. The scattering signal is calibrated using the signal from pure propane, as its scattering cross section is well known to be 9.68×10^{-27} cm^2 Sr^{-1} at 514.5 nm [20].