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Soot precursor formation and limitations of the stabilomer grid

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Abstract

We have combined experimental and theoretical approaches to gain new insight into the mechanisms of PAH growth and soot formation. The experimental approach involves aerosol-mass spectrometry in conjunction with vacuum-ultraviolet photoionization of volatile species vaporizing from particles sampled from an Ar-diluted C₂H₂/O₂ counter-flow diffusion flame at nearly atmospheric pressure (700 Torr). We recorded aerosol mass spectra at different distances from the fuel outlet for fixed ionization energies and in a fixed position while tuning the photoionization energy. The mass spectra contain a large distribution of peaks, highlighting the importance of small building blocks and showing a variety of chemical species that extends beyond the traditional classification of PAHs based on thermodynamic stability. In addition, we performed stochastic simulations of PAH growth in the flame in order to provide better insight into the chemical composition of species associated with peaks in the measured mass spectra. These simulations were conducted using a stochastic nanoparticle simulator (SNAPS). Synthesis of experimental and simulated results showed that peaks in the observed mass spectra generally consisted of a mixture of PAH isomers. At $m/z = 154$ and 202, for example, experiments and simulations suggested that additional isomers than biphenyl and pyrene are important. Furthermore, the results highlight the importance of odd-carbon numbered species and complex growth paths. The experimental results suggest that species of higher masses can build up concentration ahead of species of lower masses. Our experimental results show, for example, that the peak at $m/z = 278$ appears closer to the burner outlet than the peak at $m/z = 202$, i.e., suggesting that a single monotonic growth mechanism is not enough.

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1. Introduction

Combustion processes are major sources of hazardous airborne pollutants, including polycyclic aromatic hydrocarbons (PAHs) and soot. However, there is a very poor understanding of the chemical

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pathways governing molecular growth from light gaseous species to large PAH molecules and soot particles [1–3]. Production of large PAHs and soot is believed to be controlled by the formation of small aromatic species, containing one to a few rings [1,2,4,5]. Hence, the formation of the first aromatic ring, i.e., benzene, has been widely studied in different flames, see, e.g., [6–11].

Developing a comprehensive description of soot formation requires an understanding of the chemistry of molecular growth beyond the first aromatic ring and identification of key intermediates. One important mechanism proposed for hydrocarbon-growth chemistry is hydrogen abstraction from the reacting hydrocarbon by a hydrogen atom, followed by acetylene (C_2H_2) addition to the hydrocarbon radical site, i.e., the so-called HACA mechanism [5,12]. Under some conditions, however, the HACA mechanism does not appear to be able to describe observed hydrocarbon growth. Keller and co-workers [13] concluded that the HACA mechanism does not promote growth of large PAHs. In addition, the HACA mechanism has also been reported to be too slow to account for experimentally observed growth rates; see, e.g., the works by Violi's group [14,15].

Other suggested growth paths include addition of methyl (CH_3) [16], vinyl (C_2H_3) [17], and phenyl (C_6H_5) [18] radicals. Some studies have stressed the role of the propargyl (C_3H_3) recombination reaction in the formation of the first aromatic ring [2,10,19]. Propargyl and vinylacetylene (C_4H_4) have also been included in growth mechanisms leading to the formation of the second aromatic ring to produce naphthalene [20]. Shukla and Koshi [17,21,22] concluded that several growth pathways should be incorporated in the construction of mechanisms aimed at describing wide ranges of combustion conditions.

Mass spectrometry is a measurement approach that can provide some insight into the chemistry leading to PAH and soot formation [23]. Various setups, using different ionization sources, have been successfully applied for detection and characterization of molecules up to masses of a few hundred u. Öktem et al. [24] combined mass spectrometry, scanning mobility particle sizing, and transmission electron microscopy for an analysis of a flat premixed ethylene/oxygen/argon flame. They found support for aromatics dominating early growth stages, whereas aliphatics contributed significantly at later stages.

Faccinnetto et al. [25] observed two manifolds of peaks when they studied mass spectra from deposits on absorbing filters in the soot inception region of a low-pressure premixed methane/oxygen/nitrogen flame. The high-mass peak was attributed to PAHs with carbon numbers from 30 to 62, and the authors suggested the formation of large PAHs to be related to the formation of

the first soot particles. Keller et al. [13] also observed a second manifold in this mass range. However, this second manifold of peaks was not observed in the recent work by Skeen et al. [26], in which particles sampled from counter-flow flames of acetylene/oxygen/argon, ethylene/oxygen/argon, and propane/oxygen/argon were focused onto a copper block. The block was heated to ~ 550 – 650 K to vaporize volatile species in the particles. Skeen et al. [26], however, observed species with ionization energies higher than what is expected from the thermodynamically most stable isomers identified by Stein and Fahr [27]. This finding provides evidence for the importance of kinetics as opposed to thermodynamic stability for molecular growth mechanisms. The current study is a continuation of the work published by Skeen et al. [26] and focuses on improving the understanding of soot precursors and growth paths in the mass range of ~ 150 – 250 u. This paper presents a synthesis of experimental observations and simulations that provide new insight into the chemical composition of prominent masses in this mass range and demonstrate that peaks in the mass spectra generally consist of a mixture of PAH isomers. Both experiments and simulations showed a variety of chemical species that extends beyond the traditional classification of PAH species based on thermodynamic stability. Consequently, this work represents a significant step in building a more accurate and comprehensive understanding of PAH growth and will greatly benefit further study of soot formation.

2. Experimental details

The experimental setup has been described elsewhere [26], and a detailed description is not provided here. Briefly, a counter-flow diffusion flame is enclosed in a chamber maintained at 700 Torr. The two sides of the counter-flow burner are separated by 14 mm. Ar-diluted C_2H_2 gas ($0.0021 \text{ g cm}^{-2} \text{ s}^{-1} C_2H_2$ and $0.0347 \text{ g cm}^{-2} \text{ s}^{-1} \text{ Ar}$) was supplied through a 14-mm ID tube on the fuel side, and Ar-diluted O_2 ($0.0053 \text{ g cm}^{-2} \text{ s}^{-1} O_2$ and $0.0232 \text{ g cm}^{-2} \text{ s}^{-1} \text{ Ar}$) passed through an identical tube on the oxidizer side. The fuel and oxidizer tubes are surrounded by outer tubes of 20-mm ID, through which Ar shielding flows help to stabilize the flame. The resulting soot-formation flame was greenish with a thin orange layer close to the fuel outlet side. The maximum (radiation corrected) flame temperature, measured using a fine-wire Type-B thermocouple, was about 2100 K.

Intermediates were sampled along the vertical centerline of the flame using a horizontally positioned quartz microprobe with a tapered tip of 180 μm ID and maximum OD of 3 mm. The

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