



Radical–radical reactions, pyrene nucleation, and incipient soot formation in combustion

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Abstract

We present a combined experimental and probabilistic simulation study of soot-precursor. The experiments were conducted using aerosol mass spectrometry coupled with tunable vacuum ultraviolet radiation from the Advanced Light Source at Lawrence Berkeley National Laboratory. Mass spectra and photoionization efficiency (PIE) curves of soot precursor species were measured at different heights in a premixed flat flame and in a counter-flow diffusion flame fueled by ethylene and oxygen. The PIE curves at the pyrene mass from these flames were compared with reference PIE scans recorded for pyrene. The results demonstrate that other $C_{16}H_{10}$ isomers than pyrene are major components among species condensed onto incipient soot in this study, which is in agreement with the simulations. Species with mass 202 u only have a high prevalence in incipient soot particles drawn from the premixed flame, but hydrocarbon species with sizes in the range 200–400 u are important to incipient-soot formation in both flames. The simulations predict that some species form through combination reactions involving relatively large radicals and bypass traditional molecular-growth pathways through addition of small hydrocarbon species. The experimental results support this prediction; they demonstrate that these species have higher relative abundances in particles formed close to the fuel outlet than smaller, lighter molecular species and indicate that these species are important to early formation of incipient-soot precursors. The results also imply that a leading role in incipient-soot precursor formation

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is played by species with lower thermal stability than the even-carbon numbered, unsubstituted polycyclic aromatic hydrocarbons known as “stabilomers”.

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1. Introduction

Combustion-generated soot particles have significant adverse effects on climate [1–6], air quality [3], and human health [3,7–10]. Despite the need to mitigate soot-particulate emissions, however, many of the factors that control soot formation are poorly understood. A critical, but poorly understood, step in soot-formation chemistry is the transition from gas-phase species to particles [11]. Nucleation of polycyclic aromatic hydrocarbons (PAHs) is thought to play a central role in particle inception, which is supported by experimental evidence for PAH stacking in soot; see, for example, the study by Baquet et al. [12] and the review by Wang [13].

Homogeneous nucleation could be the step responsible for formation of the critical nuclei, but there is debate about the molecular size required for two PAH molecules to be physically bound long enough to nucleate a particle. Miller [14] calculated that sticking PAH collisions are only important for PAHs with masses larger than 800 u. Schuetz and Frenklach [15] calculated lifetimes for pyrene dimers, however, and found that they are stabilized by internal rotational and vibrational motion of the cluster and may survive long enough for subsequent growth to occur. Such a kinetically controlled process requires reversibility, and Eaves et al. [16] recently presented a nucleation study that accounts for reversibility. Nucleation was modeled to result from collisions mainly with benzo[a]pyrene, a species one aromatic ring larger than pyrene. These results are supported by those of Herdman and Miller [17] who calculated that the binding energies of heterodimers with reduced masses as low as 83 u can survive at 1500 K.

Sabbah et al. [18] presented evidence discounting the importance of pyrene dimerization for soot formation in flames. Their experimental results indicated that the pyrene partial pressure required for 10% conversion to the pyrene dimer at 1500 K is in excess of 40 bar, which far exceeds the pressure of most flames. They concluded that the equilibrium of the dimerization favors dissociation at high temperatures and that chemical growth to PAHs much larger than pyrene is required before homogeneous condensation can lead to significant soot formation under many combustion conditions. Kraft and co-workers [19] came to the same conclusion in their calculations of PAH clustering for

particle inception. However, these two studies focused on pyrene homodimers and equilibrium considerations. Further theoretical evidence against pyrene nucleation was presented by Elvati and Violi [20]. They pointed out that the presence of aliphatic side chains on condensed-ring structures can strengthen interactions between colliding molecules, allowing them to remain in close proximity long enough for reactions to occur. In addition, Lowe et al. [21] showed that the main parameter determining dimer stability in heterodimers is the size of the smallest monomer, and pyrene needs to stick with a hydrocarbon the size of ovalene to yield a stable complex at ~ 1000 K. Despite these indications against pyrene nucleation, it is often used as a proxy for soot formation in combustion [22–25].

There is a severe paucity of experimental data that definitively either support or eliminate nucleation of pyrene or similar-sized PAHs under atmospheric flame conditions. Many studies of incipient particle composition rely on aerosol mass spectrometry. For large hydrocarbon species, however, molecular structures cannot be identified by mass alone. Mass-resolved studies of soot constituents are often interpreted assuming observed masses are stabilomers [26–28], a class of species containing the most thermodynamically stable hydrocarbons, including pyrene [29]. These studies typically suggest pyrene and similar-sized PAHs to be important soot precursors because of the high intensities normally found in the mass range 200–400 u. The study described here was designed to (1) determine whether pyrene is the dominant species observed at mass 202 u in incipient-soot particles extracted from flames, (2) identify species at the heavier masses of 226 u, 266 u, and 278 u, which appear to be important to the first particles formed, and (3) determine formation mechanisms for these species.

2. Methods

2.1. Experimental approach

We performed experiments using a time-of-flight aerosol mass spectrometer (AMS) coupled with synchrotron vacuum-ultraviolet (VUV) radiation for photoionization. VUV photoionization limits fragmentation compared to other ionization approaches, e.g., electron impact ionization or

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