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Peri-condensed aromatics with aliphatic chains as key intermediates for the nucleation of aromatic hydrocarbons

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Abstract

Soot nucleation bridges the transition from gaseous hydrocarbons to macromolecular building blocks (nanoparticles) that eventually turn into soot. Polycyclic aromatic hydrocarbons (PAH) have often been invoked as important compounds of this process but their role has not been clearly identified. In this paper we report on a detailed analysis of the physical interactions between PAH in the range 200–450 amu using Molecular Dynamics simulations. In particular, we identified a pool of nine aromatics and studied their clustering behaviors in systems composed of thousands of homo-molecular and hetero-molecular molecules to understand the influence of molecular mass, morphology and temperature on the nucleation process. At temperatures higher than 1000 K, small clusters of PAH (2–5 molecules) are detected but they are not stable enough to accommodate the further growth into larger particles. This result raises doubts on the ability of these molecules to become soot nuclei. Molecular morphology is another important parameter for the nucleation process. Aromatics with attached aliphatic chains show considerably faster nucleation rates than the corresponding polycyclic aromatic hydrocarbons of similar mass without any chain. The collision efficiency is not increased by the aliphatic chain attachments, which may indicate that a faster nucleation process for these systems is due to the ability of these molecules to accommodate the collision energy into additional internal vibrational modes of the aliphatic chains. The results of this study provide information on the clustering behavior of PAH and can lead to the development of a more complex model to describe the physical nucleation of PAH that includes molecular masses, morphologies and temperature as main parameters to describe the transition from gas-phase species to macromolecular structures.

Keywords: Nucleation; PAH; Dimers; Clusters; Molecular Dynamics

1. Introduction

Mechanisms of soot formation have been studied for quite some time, and there is general consensus that polycyclic aromatic hydrocarbons (PAH) are key intermediates: their growth leads to nucleation of particles and the latter continue to add mass via surface growth [1–6].

The transformation from PAH to soot has been often described as a purely chemical growth by many researchers [7–16]. Aromatic precursors grow in size due to chemical reactions and by virtue of the increasing size, the species acquire the property of a condensed phase. During the

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molecular growth process, however, the magnitude of non-bonded interactions between structures can become large enough so that chemical bonding is no longer a requirement for sticking. In particular, the attractive interactions between pi electrons in aromatic systems are among the strongest non-covalent interactions in nature. Therefore, in addition to chemical growth mechanisms of PAH, various studies have been reported on physical coagulation of aromatics [17–33]. Schuetz and Frenklach [17] studied the lifetime of pyrene dimers in flame conditions using Molecular Dynamics simulations with semi-empirical force fields and concluded that the internal rotations of the colliding pair extended the lifetime of dimers. Thus the onset of PAH condensation may occur for small compounds. A similar study was reported by Wong et al. on aromatic molecules linked by aliphatic chains and peri-condensed aromatics [18], showing that the first class of molecules produces dimers faster than the equivalent condensed aromatics. Miller and co-workers [19,20] have reported detailed calculations of the intermolecular potentials for clusters of PAH from 78 to 1830 Da, showing that the binding energies rise with molecular size and asymptotically approach the experimentally value of energy for graphite of 5.0 kJ mol^{-1} (carbon atom)$^{-1}$. Recently, Totton et al. [34] used a stochastic basin hopping global optimization scheme to locate low-lying local minima on the potential energy surfaces of molecular clusters of 50 coronene and 50 pyrene molecules with mass densities lower than the bulk values of the pure crystalline PAH structures.

The majority of these studies, however, has analyzed the formation and dissociation of pairs of molecules, and compared the lifetimes of dimers with the characteristic time obtained from chemical growth rate or collision interval to assess the role of dimers as soot nuclei [17–19]. But whether dimers are stable enough to accommodate further growth toward soot nuclei is yet to be determined.

The purpose of this work is to gain insights on the physical interactions of PAH to define their principal nucleation pathways in flames. We, therefore, analyze systems composed of thousands of small aromatics to determine their clustering behavior as function of molecular mass, morphology as well as temperature, using Molecular Dynamics simulations. The results provide critical information for the development of future nucleation model.

2. Methodology

Atomistic Molecular Dynamics (MD) simulations are used to study the formation of clusters of PAH of different masses and morphologies in a wide range of temperatures. The non-bonded interactions of the potential contain a repulsion and a dispersion term expressed as Lennard–Jones (LJ) potential form, in addition to a Coulomb contribution:

$$V_{\text{non-bonded}}(r_{ij}) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + f\frac{q_i q_j}{r_{ij}} \quad (1)$$

where the electric conversion factor is $f = \frac{1}{4\pi\varepsilon_0} = 138.935485(9)$ kJ mol^{-1} nm e^{-2}. The parameters used for the LJ potential are from the work of Miller and co-workers [35]. These potentials have been used to investigate physical coagulation of aromatics in several previous studies on soot nucleation [20,35,36]. The effective atomistic electrostatic potential charges were obtained from the electronic structure calculations using Gaussian 03 program [37] with the B3LYP/6-31G** level of theory [38–40]. For the intramolecular interactions, the OPLSAA [41,42] parameters for bonds, angles, and dihedrals were used. The NVT ensemble was employed for the simulations and the constant temperature was maintained with the Nosé–Hoover thermostatting method [43] with a time constant of 0.03 ps. All calculations were performed using the Gromacs 4.0.3 program package [44] with an integration time step of 1 fs.

3. Results and discussion

As mentioned in the previous section, the goal of this study is to understand the effect of molecular mass, morphology and temperature on the clustering behavior of PAH in order to determine the feasibility of a physical nucleation pathway to describe the transition from small PAH to macromolecular structures. Figure 1 reports the structures of hydrocarbons considered in this study. Besides peri-condensed aromatics (PCAH) such as pyrene (P), coronene (C) and tri-acenaphtri-phenylene (T), (Fig. 1(a–c)), we included peri-condensed aromatics with an aliphatic branch (PCAB) such as 1,2, and 4-vinyl-3a^1,5a^1-dihydropyrenes (VP), and 1-vinylcoronene (VC) (Fig. 1 (d and e)), and aromatic molecules linked by aliphatic chains (AALH) such as 1,2-di(naphthalen-2-yl)ethane (DNE), 1,3-di(naphthalen-2-yl)propane (DNP), 2-(2-(1,9-dihydropyren-2-yl)ethyl)pyrene (DEP), and 2-(3-(1,9-dihydropyren-2-yl)-propyl)pyrene (DPP) (Fig. 1(f–i)).

Molecular Dynamics simulations of homo-molecular and hetero-molecular systems composed of 1000 molecules were carried out at four temperatures – 500 K, 750 K, 1000 K, and 1500 K. In our calculations we assumed that the majority of the collisions were bi-molecular and there was a random distribution of collisions between molecules