Full Length Article

Homo-dimerization of oxygenated polycyclic aromatic hydrocarbons under flame conditions

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ABSTRACT

Homogeneous nucleation is identified as one of the steps responsible for the formation of the critical nuclei that define the transition from gas-phase species to soot formation particles. However, the effect of molecular properties (like size, composition, and shape) on their propensity to physically bind, for a time long enough to initiate particle nucleation, has not been thoroughly investigated. In this work, we analyze the effect of oxygen content on the homodimerization propensity of different polycyclic aromatic compounds (PACs) using molecular dynamics simulations coupled with well-tempered Metadynamics enhanced sampling. We analyzed species in two mass groups, with a molecular weight ranging from 448 μ to 696 μ, and with varying oxygen content, mostly present as ethers. The reconstructed free energy profiles show that, besides mass, the presence of oxygenated groups influences the tendency of PACs to bind, with oxygenated compounds forming dimers that are less stable than the corresponding polycyclic aromatic hydrocarbons. Although this work represents only the first step towards a model for PACs dimerization that include oxygen, these results suggest that oxygenated compounds are less likely to condense onto soot particles.

1. Introduction

Non-reactive phenomena play a crucial role in current models that describe particle inception for soot formation [1,2], whether van der Waals driven interactions are considered the main factor controlling the aggregation of soot precursors or a preliminary step conducive to the chemical linkage of gas-phase molecules [3–8]. The most widely employed mechanism for soot particle inception is the dimerization of two polycyclic aromatic hydrocarbons (PAHs), with the smallest dimerizing PAH being pyrene due to its thermodynamic stability and concentration [9,10]. Experiments have shown that the size distribution of soot particles in flames has a bimodal behavior [11]; this trend is very well reproduced by models that use dimerization as the inception step for soot particles [12,13], with the sticking coefficients related to inception computed from Lennard-Jones potential and the Hamaker constant [14].

There is, however, debate about the molecular size required for two PAH molecules to form a stable dimer. Miller [15] calculated that sticking PAH collisions are only important for PAHs with masses larger than 800 μ. Schuetz and Frenklach [9] computed the lifetimes for pyrene dimers and found that they are stabilized by internal rotational and vibrational motions of the cluster and may survive long enough, at high pressures, for subsequent growth to occur. However, recently

Eaves et al. showed the importance of reversibility during the soot inception process [16]: 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 μ can survive at 1500 K.

On the other hand, there have been concerns regarding the dimerization mechanism of pyrene and recent studies have argued against this phenomenon [18–20]. Sabbah et al. [18] presented evidence discounting the importance of pyrene dimerization for soot formation in flames. Their experimental results indicate 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 [21] came to the same conclusion in their calculations of PAH clustering for particle inception. A computation study of the equilibrium constants of the dimerization using an updated PAH interaction potential [20,22] has shown that pyrene dimerization is unlikely to play a role in nucleation [21], and an investigation of the free energy surface by Violi et al. supports this finding, showing that
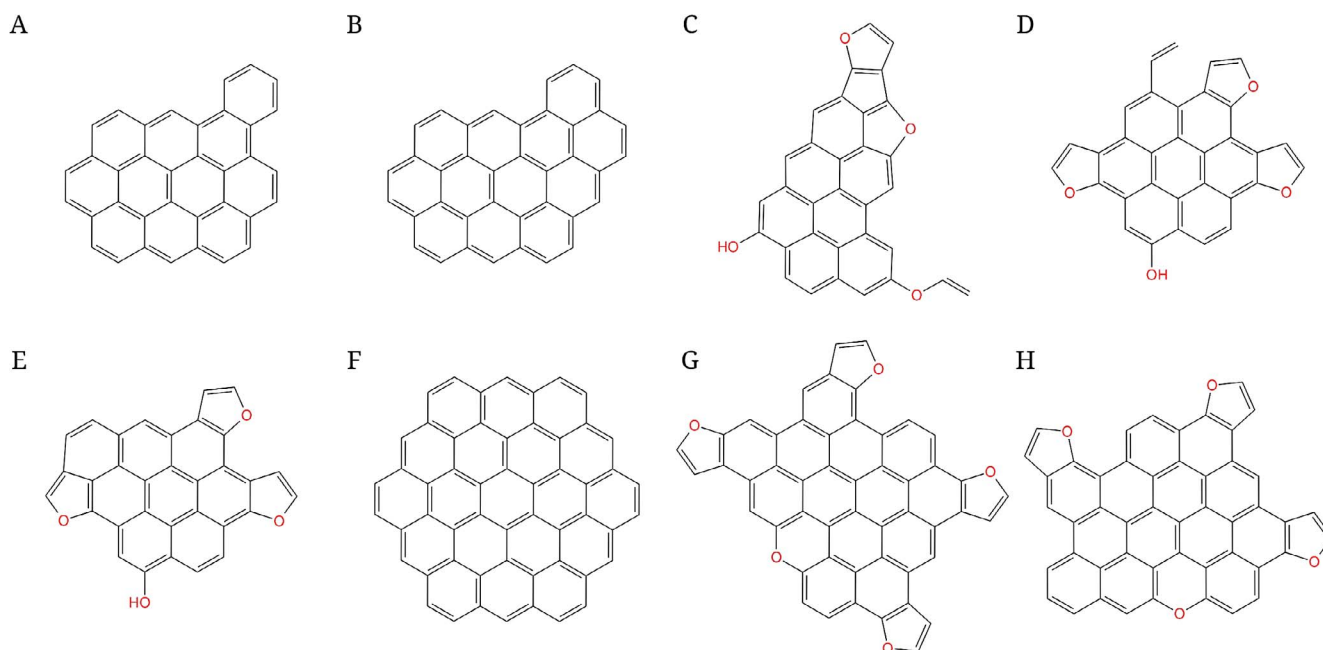

Fig. 1. Pool of molecules identified for this study.

dimerization of pyrene at high temperatures is thermodynamically unfavorable [19,23]. For this reason, dimerization of species larger than pyrene like ovalene and coronene have been suggested as contributors to the nucleation step [19,21]. Despite these findings, pyrene is often used as a proxy for soot formation in combustion [24–26]. Mass however is not the only factor that has been shown to contribute to the dimerization process. Elvati and Violi pointed out the role of aliphatic side chains on condensed-ring structures that can strengthen interactions between colliding species, allowing molecules to remain in close proximity long enough for reactions to occur [19,27,28].

To add to this picture of uncertainty, more recent works. have highlighted the importance of oxygen chemistry for the growth mechanism of polycyclic aromatic compounds, leading to compositions of the soot precursor molecules that include oxygen [28–31]. These structures have significant influence on the particle structures and growth, and hence soot. The authors, analyzed premixed flames of ethylene using a combination of molecular computations based on SNAPS code and experimental techniques that include synchrotron-coupled VUV aerosol mass spectrometry (AMS) and X-ray photoelectron spectroscopy (XPS). AMS studies revealed that these oxygenated species are present under a very wide range of combustion conditions, suggesting generic formation mechanisms [29].

Prompt by these results, in this paper we report an analysis of the impact of oxygen on the dimerization of polycyclic aromatic compounds (PACs), using molecular dynamics simulations. As system for our study, we chose the environment of an atmospheric pressure, premixed ethylene flame previously experimentally studied [29]. The results show that in these conditions, oxygen, and shape of the molecules both play a role, once relatively big molecular weights ($\sim 600\,\mu$) are reached.

2. Methodology

Biased molecular dynamics simulations were carried out to determine the propensity of molecules to dimerize, by employing the NAMD 2.12 software [32] and PLUMED 2.3 plug-in [33]. The atomistic interactions were modeled employing the Chemistry at Harvard Macromolecular Mechanics (CHARMM) force field [34]. To test the validity of this choice, as CHARMM is not a force field tuned for combustion simulations, we compared our results with the free energy (FE) of

dimerization of circumcoronene in the same conditions, since its aggregation propensity has been well studied. As additional test, we performed a series of simulations at 500 K for pyrene dimerization (not reported) in order to compare with FEs previously computed [17–19] with other force fields. A timestep of 1 fs was used to integrate the equations of motions, while the temperature was controlled with a Langevin thermostat with a damping constant of $10\,\mathrm{ps}^{-1}$. As the molecules are simulated in a non-periodic system without any long-range electrostatic method, we set the cutoff for the non-bonded interaction to smoothly taper to zero from 3.8 to 4.0 nm. Each free energy curve was computed as the average of 5 independent realizations of 100 ns, well-tempered Metadynamics runs [35]. The free energy profiles were reconstructed by adding a bias shaped like a normal distribution every 100 fs and using a bias factor of 20 to reach convergence.

3. Results

The first step for our study was to build a reasonable pool of molecules to study. To this end, we reviewed our previous work on XPS spectra of soot samples extracted from ethylene flame showing information on the functional groups of the predicted oxygenated species incorporated into particles. In those conditions, XPS data showed that alcohol/enol groups are formed early in the flame, and their concentrations decrease with increasing distance from the burner. The abundance of ethers included in soot particles instead increases with increasing distance from the burner. The fractions of C–OH, C–O–C, and C=O species at different DFFOs were determined using the O 1s spectra reported in [29]. The O/C content was based on the results of the SNapS simulations [36], by taking the higher values of the O/C distribution in order to study the differences at the extremes of the spanned range. It should be noted that, especially for soot nanoparticles, these are extremely high values [30,31] probably in part due to the lower propensity of oxygenated compounds to aggregate (see below).

Data from this analysis were used as inputs to our simulations. Indeed, we identified a pool of molecules including compounds with and without oxygen with various masses. The temperature used in our systems (1680 K) corresponds to the location in the flame where bimodal particle distribution have been detected [37]. Since dimerization of compounds of small masses does not happen at flame temperatures