A TIME-SCALE PROBLEM FOR THE FORMATION OF SOOT PRECURSORS IN PREMIXED FLAMES

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Introduction
This paper applies a previously developed tool to study the molecular transformations that occur in combustion conditions during the transition from gas phase precursors to soot particles.1,2 To help resolve issues such as identification of pathways leading to soot formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways form...
KMC/MD code. The choice of the input PAH is due to their presence in high concentrations in the PAH inventory, and to the importance that PAH with peripherally fused five-membered rings (CP-PAH), which includeacenaphthylene, have in the flame formation chemistry of soot\textsuperscript{13} and fullerenes.\textsuperscript{16} Acetylene is the most abundant building block\textsuperscript{17} and contributes to the HACA mechanism. The concentration profiles have been calculated using the CHEMKIN package\textsuperscript{18} together with a kinetic model previously developed.\textsuperscript{19}

In using these concentrations in the atomistic model, no allowance was made in the calculated hydrocarbons and H profiles for species depletion or temperature change. A detailed description of the gas-phase species involved, and the reactions that can occur in the system, together with their rates is reported elsewhere.\textsuperscript{20}

**Results and Discussion**

Homann and co-workers reported the molecular formulas of PAH in a C/H diagram for the two flames, where each point corresponds to a certain compound C$_x$H$_y$. The experimental data have been re-plotted in Figure 1 as diamond points for the aromatic\textsuperscript{7} (1a) and aliphatic\textsuperscript{8} flames (1b).

The totality of points represent the ensemble of PAH and PAH radicals with different molecular formulae. The formulae of six-ring PAH with most peri-condensed ring structures like coronene, ovalene, etc. lie on the dotted line in the diagrams. The points above the line represent PAH that are H-rich and those below that are H-poor with respect to these most condensed 6-ring structures. The authors also emphasized that large H-rich PAH play an important role in reactions, both with respect to growth and consumption, irrespective of whether they are molecules or radicals.\textsuperscript{3} As most of the PAH are pericondensed, enriched hydrogen in their structure means 4C bays or larger coves at which reactions could take place preferentially. The results obtained through the use of KMC/MD code are plotted as filled circles on the same figure. The use of the KMC/MD methodology allows us to follow the evolution of structures in a chemically specific way. The computed data are in good agreement with the experimental results in terms of H/C ratio, and show the formation of H rich compounds corresponding to open elongated PAH with bays and coves. PAH formation does not follow a narrow path in the C-H diagram but a broad band due to the variance in H content for the same number of C atoms; the molecular formulas of the PAH form a band that widens toward larger PAH. This observation indicates that with an increase in the number of C atoms, the bandwidth for the H content becomes larger. This behavior becomes more pronounced when the fuel is changed from acetylene to benzene. The KMC/MD method is able to reproduce this trend too and this is due to the different contribution of the reaction pathways to the growth of the aromatic compounds. Having a diverse molecular base and not only the reaction sequence of hydrogen abstraction and addition of acetylene molecules to the radical site previously formed may lead to a network of aromatic-aliphatic linked structures.

The results reported in Figure 1 are both relative to two conditions within the oxidation zone of the flames. We did that in order to emphasize the influence that the two environments have on the structures of the compounds formed. The relative contribution of the different types of growth reactions seems to depend on the fuel. In the case of aromatic fuels polymerization reactions can occur early since aromatics are in relatively large concentrations in the fuel, whereas in the case of aliphatic fuels such as acetylene, ethylene or methane the first aromatic ring must be formed from fuel decomposition products by a sequence of elementary reactions and therefore the concentrations of aromatic soot precursors are in lower concentrations than in the aromatic flames.

**Figure 1.** Hydrogen and carbon content for the aromatic (a) and aliphatic (b) flames.

In benzene flames, PAH are formed in concentrations about 100 times those found in aliphatic fuel flames of the same C/O ratio.\textsuperscript{21} Their maximum concentrations occur within the oxidation zone and decrease at the end of it where most of the carbon is formed. Polycyclic aromatics arise in the oxidation zone but their concentration does not decrease as rapidly in the region where molecular oxygen has been consumed. An important difference consists in unsaturated hydrocarbons present in the oxidation zone, i.e. C$_x$H$_y$ in acetylene flames, and benzene and PAH in benzene flames. During the combustion of benzene, the benzene molecule itself is an important reactant for the formation of higher molecular weight PAH. In contrast to acetylene, benzene is completely consumed, even before the end of the oxidation zone. In the vicinity of the temperature maximum benzene is no longer available as a building block for larger molecules or particles. Within a benzene flame C$_n$H$_m$ is formed as the temperature increases. At the end of the oxidation zone, C$_6$H$_6$ is present in nearly the same concentrations as those found in acetylene flames.

**Figure 2.** Intermediate compounds formed in aliphatic (a) and aromatic (b) flames.

Figure 2 reports the structures of two intermediate compounds formed in the aliphatic (2a) and aromatic flame (2b). In the first case

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the compound formed is still mainly planar and the contribution of acetylene is significant. In the lower part of the figure, the structure formed in the aromatic flame shows already three-dimensional characteristics and the contribution of aromatic hydrocarbons, such as benzene, naphthalene is prevalent.

Another important characteristic of these particles is their morphology. Ellipticity parameters are often used to characterize particle shape. In order to characterize ellipticity, the aspect ratio AR is computed

\[ AR = \frac{a}{b} \]

where a and b are the axes of the ellipse that has as its center the object’s centroid.

A series of diameters of the particles are sampled. The average of these diameters is used as the spherical diameter \( r_s \) of the configurations, and an average of the longer diameters is used as \( "a" \), and an average of the shortest ones is used as \( "b" \). A better evaluation of \( a \) and \( b \) can be obtained using the Legendre ellipse that has the same geometrical moments up to the second order as the original object area. The Legendre ellipse is often used instead of the original object. The aspect ratio of the particle, defined as \( a/b \), is reported in Figure 3 as a function of the diameter (ED) calculated for an equivalent spherical particle.

![Figure 3](image)

**Figure 3.** The aspect ratio of soot precursor molecules as a function of equivalent spherical diameter in acetylene flame (in Angstroms).

The aspect ratio of a circle is one and of an ellipse with the ratio of axes 2:1 is equal to two. The aspect ratio for the ellipse increases with an increase in the ratio of the major and secondary axes. The aspect ratio is seen to increase with increasing particle size.

The elongated shapes exhibited by the young nanoparticles is supported by “in situ” measurements on soot evolution in flames. Light scattered by nanoparticles is more depolarized than that scattered by soot particles and the depolarization ratio increases as the particle deviate from the spherical shape.\(^{21}\)

**Concluding Comments**

The paper presents the application of Kinetic Monte Carlo and Molecular Dynamic to study soot inception in aliphatic and aromatic flames. Formation of carbonaceous nanoparticles can be followed in a chemically specific way. Properties of the particles, such as H/C ratio and morphology have been computed, showing the presence of elongated shapes for young nanoparticles. The influence of two different environments, an aromatic and aliphatic flame, is assessed in terms of structures of the particles formed. The use of this approach will enable the investigation on the physical (e.g., porosity, density, sphericity) as well as chemical (e.g., H/C, aromatic moieties, number of cross-links) properties.

**Acknowledgments**

This research is funded by the University of Utah Center for the Simulation of Accidental Fires and Explosions (C-SAFE), funded by the Department of Energy, Lawrence Livermore National Laboratory, under subcontract B341493. The calculations presented in this paper were carried out at the Utah Center for High Performance Computing, University of Utah that is acknowledged for computer time support. The code used is one based on the LLNL code (2).

**References**