FULLY-INTEGRATED MOLECULAR DYNAMICS – KINETIC MONTE CARLO CODE: A NEW TOOL FOR THE STUDY OF SOOT PRECURSOR GROWTH IN COMBUSTION CONDITIONS

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Introduction

Formation of soot and other carbonaceous material during the incomplete combustion of hydrocarbons is one of the least resolved problems; despite essential progress in understanding single processes, the comprehensive theory and models that predict the formation of these compounds fall short of predicting many of the experimental observations.

The transformation from low molecular weight organic gas phase species to particulate matter is not well understood since high molecular weight carbonaceous species formed during this process are difficult to analyze with certainty by conventional methods. Recent advances in experimental and modeling investigations in combustion have shown that a much larger amount of carbonaceous material, besides soot and GC-identifiable PAHs, is emitted in form of organic carbon (tar-like material) than were thought some years ago.[1-2] Following recent experimental characterization of this material,[1-2345-6] we developed a kinetic mechanism in which high molecular mass aromatic compounds are postulated to form by the reactive polymerization of small PAH [7-9]. The mechanism involves a sequence of chemical reactions between aromatic compounds with 6 π-electron, i.e. benzene, naphthalene, and cyclo-penta fused compounds i.e., acenaphthylene, indene. The distinguishing features of this mechanism and its importance in explaining experimental observations is reported elsewhere,[8] together with a detailed quantum mechanic analysis of the first steps of the reaction sequence.

The work presented here adds one step more to the study of this process. The aim of this paper is to introduce a new tool for examining the molecular transformations from gas phase precursors to soot-like material. This new approach combines two common methods: Kinetic Monte Carlo (KMC) and Molecular Dynamics (MD). In the new code, KMC and MD are fully integrated in such a way that any reaction process for the KMC time step is much larger than the time required for relaxation during MD. The kinetic rates are calculated using high-level quantum chemical methods. The code is employed to study a low-pressure laminar premixed benzene/oxygen/argon flame and some preliminary results are reported for the H/C ratio of soot precursors. The use of this new code can provide at the long term potential for information on soot precursor characteristics.

Computational details

The Fully-Integrated KMC/MD code combines the strengths of two common simulation methods: Kinetic Monte Carlo (KMC)[10] and Molecular Dynamics (MD)[11]. This approach allows sampling long time-scales, where the time-duration between Monte Carlo events can be arbitrarily long (depending on the kinetics, model. etc), while in molecular dynamics, we require time steps which are a small fraction of the atomic vibrational period. So the combination of the two techniques spans two time- and equilibrium scales, MD allows for relaxation as well as processes very far from equilibrium, while the KMC part allows much larger time-scale changes to the system, provided that the system is at equilibrium.

Structure simulation

The sequence of steps repeated in the Fully-Integrated KMC/MD code are reported in Figure 1.
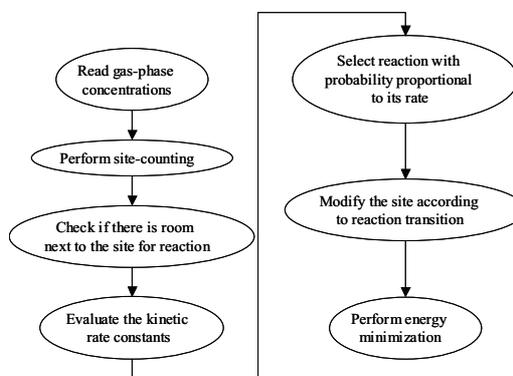
Figure 1. Sequence of steps repeated in the KMC/MD code

The code first reads the gas-phase concentrations (typically from the user or another application), then performs a site-counting procedure to identify every atom with a local environment which fits the definition of each site, including proximity conditions. The sites included into the code are described elsewhere[12].

As a next step the code evaluates the kinetic rate constants on a per-site basis as well as the reaction rates. Kinetic parameters for the possible reactions among the species present in the systems have been evaluated using the Transition State Theory (TST),[13] and the Evan–Polanyi linear free-energy formula[14] within the reaction class TST formalism, to provide activation energies of reactions in a given reaction class. The potential energy information were calculated using the hybrid density functional B3LYP method[15] (i.e. B3LYP/6-31G(d,p).[16]).

The Evan–Polanyi linear free-energy formula was used to derive the activation energies in a given reaction class, such as H-abstraction reaction rates were calculated.[17]

After this step, the code selects a reaction with probability proportional to its rate, and then perform modification of the site according to the reaction transition. Reaction sites have been defined in the context of the empirical bond-order potentials of Brenner,[18] which is able to capture many of the essential features of chemical bonding in hydrocarbons. The analytical function is a highly parametrized version of Tersoff's empirical-bond-order formalism[19].

The last step is represented by the molecular dynamics calculation and it consists in the energy minimization of the newly obtained structure. High molecular mass compound growth is here modeled in the environment of a low-pressure laminar premixed benzene / oxygen / argon flame[20].

Results and Discussion

Starting from a gas-phase bulk containing acenaphthylene, naphthalene and H, the calculations follow the growth of an individual substrate (in this case naphthalene) to which compounds from the bulk are added..

In order to show the importance of Molecular Dynamics module in this method, we analyze the structure reported in Fig.2.
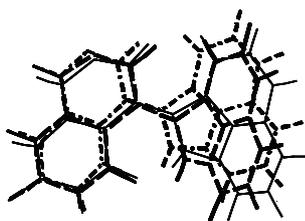
Figure 2. Structural modification during relaxation.

The compound $C_{22}H_{13}$ represents an intermediate produced during the molecular growth process. The figure shows the changes that occur to the structure after a relaxation of few ps using the molecular dynamics module, which allows the structure to reach a relaxed local minimum. The dashed line shows the change that occur after 1 ps, and the solid line reports the structure after 2 ps. The importance of this module is straightforward. The calculations lead insight into proximity conditions and site dependencies for cyclodehydrogenation reactions.

After the application of the Molecular Dynamics, new reactions and reaction sites are identified, and the Kinetic Monte Carlo module is applied for a given interval to calculate the new structures formed. Examples of structural evolutions of high molecular mass compounds are shown in Fig. 3 for the system selected (starting compound is naphthalene). Structure 2 ($C_{64}H_{38}$) is formed from Structure 1 through H abstraction and further addition of 2 molecules of naphthalene and 1 acenaphthalene. After further H abstraction and naphthalene addition, Structure 3 ($C_{94}H_{50}$) is produced.
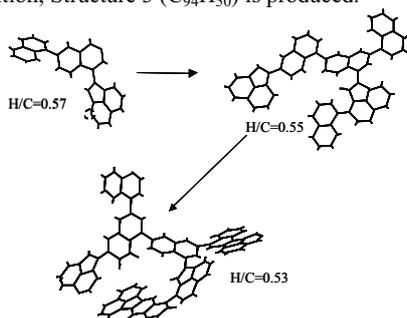
Figure 3. Structural evolution of aromatics

The introduction of ring closure reactions by dehydrogenation in the kinetic scheme allows the formation of curved structures. The H/C ratio of the structures slowly decreases going from 0.57 for the first structure to 0.53 for the last in the present limited simulation.

Evidences for molecules such as shown in Fig.3 is provided by Homann and co-workers,[21] who analyzed large PAH molecules and radicals in a similar benzene flame.

The combination of the polymerization mechanism together with KMC/MD code allow us to build compounds with H/C ratios in the range identified by the authors. This would not be possible with a mechanism that allows only the formation of fused aromatic. More than that this approach can provide information on the chemical structure of the compounds during their growth.

Further work such as a larger number of simulations can give statistical information about the system, i.e. H/C and molecular weight distribution, and morphology as a function of the time.

Conclusions

This paper is directed at the development of a new tool for examining the molecular transformations from gas phase precursors to soot. A new code, named Fully-Integrated KMC/MD, has been developed and employed to analyze possible growth pathways that lead to high molecular mass compounds. This code puts the two simulation procedures (KMC and MD) on an equal footing and involves alternating between MD and MC steps during the simulation. The code was used to analyze some experimental results obtained by Prof. Homann's research group. The environment chosen for this analysis is a low-pressure laminar premixed benzene/oxygen/argon flame. The open structures obtained with the reaction scheme presented above and the code provide an explanation for the H/C ratios of soot precursors and young soots being greatly higher than those of polybenzenoid structures of equal molecular weight. Also, the curvature introduced by forming five- and six-membered rings is the most noticeable feature of these structures.

The knowledge of the structures of soot precursor compounds is important to further progress with respect to the question about soot formation models by applying the KMC/MD code to follow the time-evolution of a statistical ensemble of molecules, as well as the time-evolution of extremely large molecules.

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