3E06

Quantum chemical molecular dynamics simulations of fullerene self-assembly from benzene

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Fullerenes can be formed by evaporation of carbon vapor[1] and also in fuel-rich flames of certain hydrocarbons[2, 3]. Fullerene formation in diffusion flames of hydrocarbons (benzene) diluted with argon and burning in oxygen offers advantages for practical operation[3]. Experimental results show that fullerene formation is sensitive to changes in operating conditions, such as fuel/oxygen ratio and chamber pressure[3]. Despite the advances in refining the fullerene formation conditions in combustion processes, the chemical formation mechanisms involved have still not been elucidated at the atomic level, preventing a rational approach towards systematic improvement of reaction conditions. To elucidate their atomistic self-assembly mechanism, quantum chemical molecular dynamics simulations on carbon vapor model systems initially consisting of C_2 molecules have been performed[4]. In the present work, we will present high-temperature quantum chemical molecular dynamics simulations on model hydrocarbon systems initially consisting of benzene molecules to shed light on their atomistic self-assembly mechanism. The simulations were carried out using density functionally tight binding (DFTB) method[5]. In this work, the effects of hydrogen, carbon to hydrogen ratio, and temperature on the fullerene formation from benzene molecules are discussed in detail.

Simulations are performed at a temperature of 3000 K considering 36 benzene molecules in a cubic periodic cell. Some of them lead to form closed cages, giant fullerenes consisting of ~140-180 C atoms. Hydrogen is removed from the system randomly on a regular basis to mimic the oxidation of six-membered rings by oxygen. As a representative of successful trajectories, the details of trajectories forming fullerene molecules is discussed below. The fullerene formation details such as carbon hybridization statistics, ring formation statistics, and some selected snapshots are presented in Fig.1, Fig. 2 and Fig. 3, respectively. All other trajectories also followed qualitatively very similar routes like this one.

It is apparent from Fig. 1 as the simulation proceeds, the number of sp^2 type carbons increases at the cost of sp type carbons. Implying that at the beginning of the simulations the system contains mainly long chains and with time these chains interacts with each other to form small clusters containing 5/6/7 membered rings and thus increasing sp^2 type carbons. This behavior is observed until (~ 49.00 ps) a stable structure containing 5/6/7 membered rings is formed; in the present case a closed cage is formed and almost all chains are consumed. After that, i.e., ~ 49.00 ps onwards these sp and sp^2 curves become stable implying that only some rearrangements are occurring in the formed cluster and almost no conversion between sp and sp^2 types carbons. An important point here to be mentioned is that the conversion rate was much slower until (up to 10 ps) some hydrogen was present in the system and it becomes much faster when there is no or very less number of hydrogen is present. Thus the presence of hydrogen may delay or even prevent the growth process as well as the cage formation. For the same reason the rate of the growth of number of rings before 10 ps is much less as shown in Fig. 2 and after that the number of 5/6/7 membered rings increase rapidly until (~ 49.00 ps) some stable structure is formed. After 49.00 ps onwards the variation of number of ring is again much less or almost none. In case of unsuccessful trajectories the formed clusters fails to get desired curvature although 5/6/7 membered rings are formed.

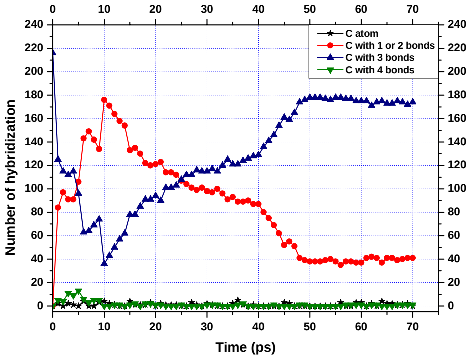


Fig. 1 Variation of hybridization types with time for a successful trajectory at 3000 K.

The formation process of fullerene from benzene can be distinguished as the following stages. **Ring opening**: Within first few time steps of simulations the benzene rings which have lost some of their hydrogen opens up to from chain consisting of sp type carbons or form biphenyl type molecules due to presence of neighboring benzene molecules as sown in Fig. 3 (0.48 ps, 2.08 ps). **Nucleation:** Although as the simulations proceeds these biphenyl molecules are lost and they form longer chains or long chains attached with small clusters containing 5/6 membered rings (4.75 ps, 5.62 ps). So far the benzene rings with C_6H_6 structure more or less do not take part in the reaction (5.62 ps). **Ring condensation:** When further hydrogen is removed from the system, few small clusters attached with long chains appeared and with time these clusters try to form almost a single big cluster via their long chains. Up to this, only few 5/6/7 membered rings are formed (10.02 ps). *Thus the presence of hydrogen slows significantly down the growth process.* Finally when all the hydrogen is removed from the system, quite rapid growth of the cluster is observed (15.02 ps). At this stage a single cluster with large number of 5/6/7 membered rings is formed and long chains are attached with this cluster. From now on, ring condensation at the cluster borders and its rearrangements occurs rapidly and appearance of 5 membered ring supply desired curvature to the cluster to push it towards a cage closure stage (35.04 ps). **Cage closure:** Finally, the cluster attains sufficient curvature to catch the C atoms on the other side and forms a close cage (49.00 ps), a giant fullerene with 156 C atoms in this case.

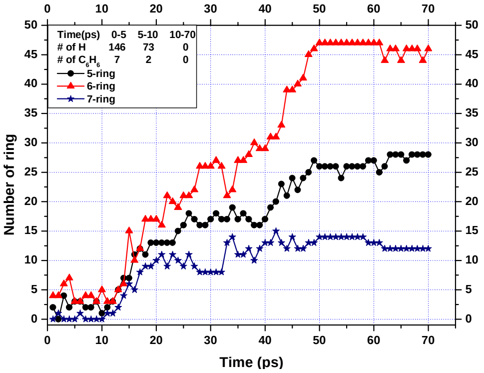
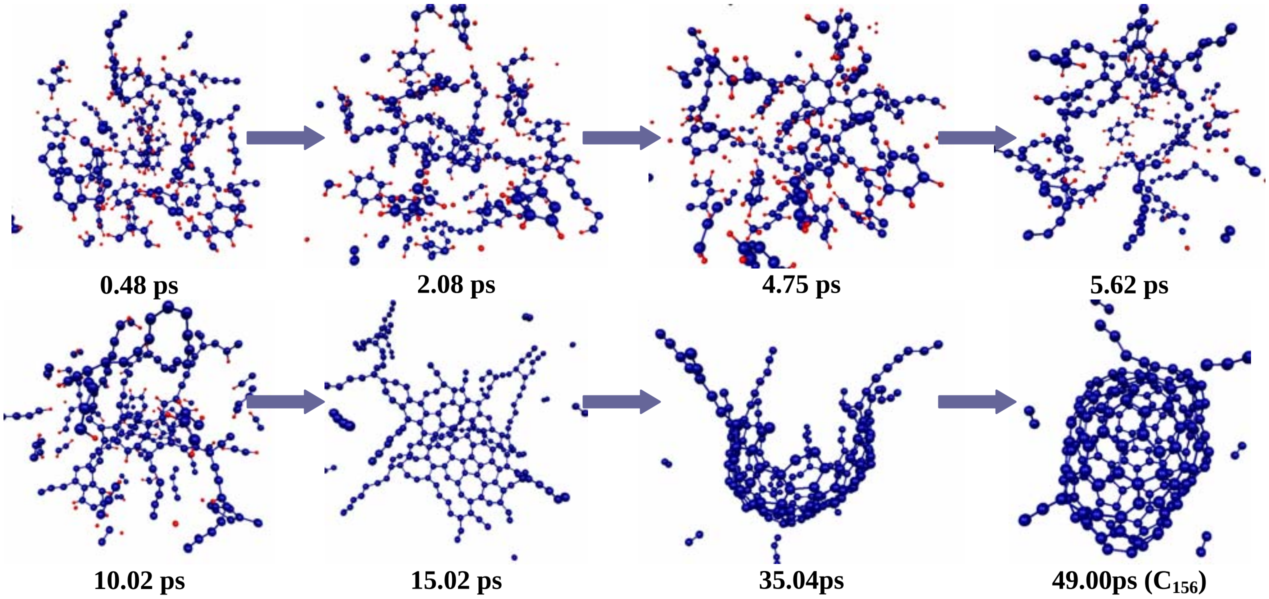


Fig. 2 Details of ring formation of a successful trajectory at 3000 K. The model system contains 216 C atoms.

These simulations show that fullerene can be formed from an ensemble of benzene molecules through four distinct stages. It is also found that the loss of hydrogen and carbon density of the model systems are important factors for the self-assembly of fullerene molecules from benzenes. The presence of hydrogen delays the fullerene formation process.



0.48 ps **2.08 ps** **4.75 ps** **5.62 ps**

10.02 ps **15.02 ps** **35.04ps** **49.00ps (C_{156})**

Fig. 3 Some representative snapshots of a successful trajectory simulated at 3000 K. Time is given at the bottom in ps. At 49.00 ps a cage containing 156 C atoms was formed.

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