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# Graphene layer growth: Collision of migrating five-member rings

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## Abstract

A reaction pathway is explored in which two cyclopenta groups combine on the zigzag edge of a graphene layer. The process is initiated by H addition to a five-membered ring, followed by opening of that ring and the formation of a six-membered ring adjacent to another five-membered ring. The elementary steps of the migration pathway are analyzed using density functional theory to examine the region of the potential energy surface associated with the pathway. The calculations are performed on a substrate modeled by the zigzag edge of tetracene. Based on the obtained energetics, the dynamics of the system are analyzed by solving the energy transfer master equations. The results indicate energetic and reaction-rate similarity between the cyclopenta combination and migration reactions. Also examined in the present study are desorption rates of migrating cyclopenta rings which are found to be comparable to cyclopenta ring migration.

*Keywords:* Soot; PAH; Surface growth; Reaction mechanisms; HACA

## 1. Introduction

Soot formation is a persistent problem in fossil fuel combustion. About 80% of soot mass from combustion sources is estimated to originate from surface growth [1]. Recent modeling and interpretation of soot surface growth (e.g., [2–9]) has been done mostly by assumption of chemical similarity to reactions of gaseous aromatic species [10,11] and, specifically, by invoking the HACA mechanism [11–13]. This surface growth model is a repetitive reaction sequence of edge surface activation by gaseous hydrogen followed by addition of a gaseous hydrocarbon precursor (acetylene) to the surface radical site formed [12].

The initial surface HACA model was based on the armchair edges of aromatics [13], yet more recent work [14–18] has explored growth on zigzag edges, which can be formed by the filling of armchair edge boat sites. A gaseous acetylene molecule can adsorb onto an H-activated zigzag edge (i.e., add to a surface radical formed by H abstraction) and then react to form a five-membered,

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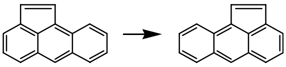
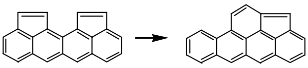
cyclopenta edge ring. Theoretical investigation of zigzag edge reactions identified the possibility of migration of cyclopenta rings along the zigzag edge,


(1)

The overall step (1) consists of a series of unimolecular transformations of the chemisorbed $C_2H_2$ surface moiety mediated by hydrogen atoms [15,17].

The previous study [17] undertook a detailed analysis of the migration reaction: energetics were examined at several levels of quantum-chemical theory (DFT, MP2, and PM3), the elementary reaction rates of the migration process were obtained by solving energy transfer master equations (with the MultiWell code [19,20]), and graphene edge growth rates and evolving surface morphologies were obtained in sterically resolved kinetic Monte Carlo (KMC) simulations by augmenting the migration kinetics with estimated rates for eight additional surface steps describing adsorption, desorption, and transformation of the cyclopenta rings. The results obtained indicate that the migration step is sufficiently fast to compete effectively with other surface processes and thus should determine the resulting surface morphology and overall rate of surface growth. It is pertinent to mention that the kinetic model with the migration step included was shown to match closely experimental measurements of surface growth rates.

As one of the consequences of rapid surface migration, the previous authors [17] suggested that two migrating cyclopenta rings could react with one another to form a relatively stable surface species such as


(2)

possibly leading to graphene layer curvature. The latter phenomenon has mechanistic implications for the evolution of soot particle surface morphology, which has been receiving increasing attention [21–24], as well as to growth of fullerenic materials and carbon nanotubes [25,26].

The present study investigates this possibility, namely, the existence of an elementary-reaction pathway of combination of "colliding" cyclopenta rings on an aromatic zigzag edge. We report the potential-energy surface (PES) for the new pathway obtained with quantum-chemical calculations and reaction rates computed on the basis of these energetics. We compare computed reaction rates of the cyclopenta ring "collision" with rates of migration, as migration was one of the dominant steps of the previous kinetic model [17]. We also examine the contribution of desorption of reaction intermediates along the migration pathway.

## 2. Computational methods

### 2.1. Energetics

Density functional theory (DFT) was used to calculate the molecular and energetic parameters of all stable species and transition states involved in the cyclopenta migration and combination reaction sequences. The substrates for the two sets of calculations were modeled by the zigzag edges of anthracene and tetracene, respectively. These are the smallest aromatic molecules of sufficient size to represent the surfaces of interest, thereby minimizing computational expense.

Geometry optimizations were performed with the B3LYP hybrid functional [27] and the 6-311G(d,p) basis set. This level of theory is the highest deemed practical for the size of molecules in question. Previous studies have shown energetic predictions of B3LYP calculations at the 6-311G(d,p) level to be in good agreement with experimental and high-level ab initio results for stable species [16,28,29]. The energies of transition states predicted by this method, however, are often underestimated by about 5 kcal $\mathrm{mol}^{-1}$ [30,31]. This shortcoming lessens the accuracy of rate constants derived from the calculated energetics yet allows for an order-of-magnitude analysis.

Force calculations were performed at each predicted stationary point to confirm the point to be an energetic minimum (no imaginary frequencies) or a saddle point (one imaginary frequency). Transition states were confirmed to connect the reactant and product stable species by visual inspection of normal modes corresponding to the imaginary frequencies calculated at the B3LYP/6-311G(d,p) level and by intrinsic reaction coordinate calculations at the B3LYP/3-21G level. Zero point energies were determined from the force calculations and scaled by a factor of 0.9668 [32]. All calculations were performed using the Gaussian 03 suite of codes [33] on an Intel Xeon cluster.

### 2.2. Kinetics

The kinetics of the reaction pathways were examined using the latest release of the MultiWell suite of codes [19,34]. MultiWell employs a stochastic approach to solution of the master equations for energy transfer in unimolecular reaction systems [19,35]. We performed computations for two models: thermal decomposition of radical intermediates, and chemically activated combination of substrate molecules with gaseous H. Microcanonical rate constants for the elementary reactions of these models were calculated with MultiWell at the RRKM level of theory.

The key inputs to MultiWell—reaction barriers, frequencies, and moments of inertia—were