

The comparison of two growth mechanism of polycyclic aromatic hydrocarbons (PAHs) from benzene precursor

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Introduction

Recently well-graphited and quasi-aligned carbon nanotubes (CNTs) have been produced with benzene in laboratory^[1], the thermal analysis–MS coupling technique was applied to clarify the growth mechanism of CNTs. A surprising fact was that no possible hydrocarbon species derived from benzene was detected, indicating that the C-C bond was not broken in experimental conditions. As results, the six-membered-ring growth mechanism was reasonably put forward^[2]. Based on the above studies, the kinetic model, benzene as reactant without ring-opening used to study the growth mechanism of PAHs, was proposed and growth mechanism of the whole process (including the process of dehydrogenation, condensation and fused ring) were studied theoretically using quantum chemistry calculation PM3 method in this paper.

Construction of molecular model and computational method

Two competitive growth reaction paths (Fig. 1), according to the experimental results, were designed to account for the growth mechanism of CNTs. The geometry optimization calculations were performed for every molecule. All transition states were confirmed by frequency analysis. There was the only imaginary frequency corresponding to dissociation bond for each transition state. Every reaction step of two constructed paths was interpreted in terms of the main microscopic feature of bond order, Mulliken population, net charge, frontier orbital energy etc. The growth cycle would continue from the product of Growth Cycle 1 according to the same mode of reaction.

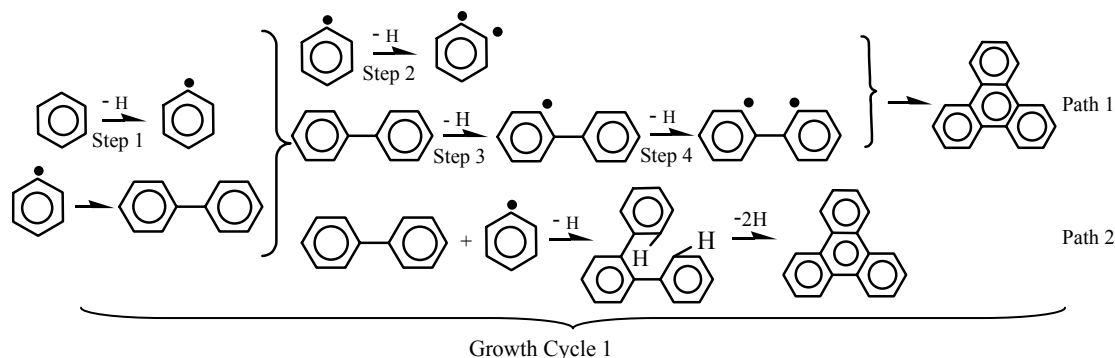


Fig. 1 The Growth Cycle 1 of reaction mechanism from benzene precursor

Results and Discussion

The activation energies of every step along the growth cycle of PAHs (Fig.2), derived from the energy difference between transition state and reactant or intermediate according to transition state theory of Eyring^[3], were calculated. Correspondingly, the product PAHs were from C₁₈H₁₂

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to $C_{48}H_{22}$, the growth process from benzene without ring-opening went through Cycle 1~6. It is concluded that path 1 was main reaction path before Cycle 5, and path 2 would become main reaction along the process of reaction. Restriction of the growth rate of PAHs was controlled by the elimination reaction of H atom from benzene (Step 1) in the whole reaction process. The activation energy of rate-determining step was $307.60 \text{ kJ}\cdot\text{mol}^{-1}$. It was proposed that the energetically favored path should only involved path 2, which was a growth scheme of the larger PAHs in size.

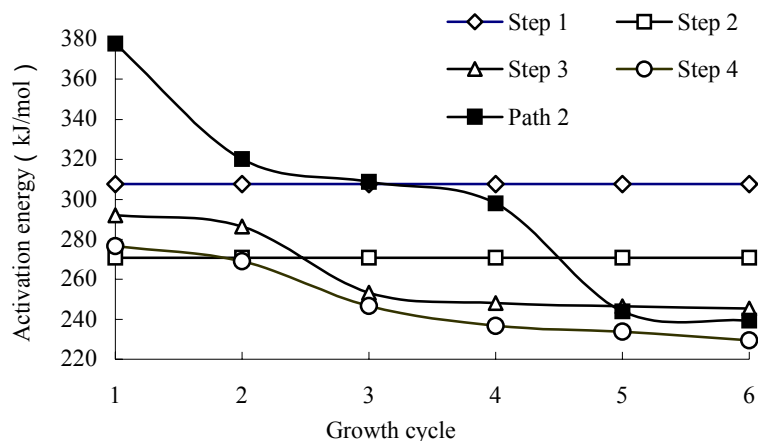


Fig. 2 Activation energy profiles of different steps from Growth Cycle 1~6 of Path 1 and Path 2

In addition, considering average C-H bond length, together with Mulliken population, we found that the average C-H bond length increased with increase in the ring numbers of the fused ring compounds. Correspondingly, the Mulliken population of C-H bond decreased along with the condensation process. These results implied that the growth reaction activity increased along with the process of growth reaction because of the weakened intensity of C-H bond.

The calculation results showed that the plane orientation of PAHs would be formed gradually along with the fusing of the aromatic ring. And the partial experimental results^[2] confirmed the relevant trends of PAHs growth mechanism discussed above. The growth mechanism had been clearly illuminated, which started from the dissociation of C-H bonds of benzene or PAH without ring-opening.

References

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