Quantum Chemical Investigation on the PAH Formation via Fulvenallenyl Radicals

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The reactions of fulvenallenyl radicals have been investigated by CBS-QB3 quantum chemical calculations. The important reaction pathways were found to be analogues to the propargyl + propargyl reaction and potential surfaces are connected to the aromatic hydrocarbons (naphthalene, anthracene and phenanthrene) without barrier higher than the entrance. The reactions of fulvenallenyl and its derivative radicals are found to involve the Stone-Walse rearrangement of pentafulvalene unit. This may play some role in the annealing process of PAHs during the growth.

Elucidation of the formation mechanisms of soot as well as its precursor PAHs (polycyclic aromatic hydrocarbons) is a challenge in the chemistry of combustion. Although the substantial understanding has been made for the single aromatic-ring formation reactions thanks to the numerous experimental and theoretical investigations in a last few decades, the growth mechanisms to larger PAHs have not been well characterized though some typical sequences of reactions such as HACA [1] and PAC [2] have been proposed. In this study, recently suggested mechanisms involving the fulvenallenyl (C_7H_5) and its derivative radicals are investigated by quantum chemical calculations. Geometry optimizations and vibrational frequency calculations were performed by B3LYP/6-311G(d,p) and higher-level energy calculations was done by CBS-QB3 method.

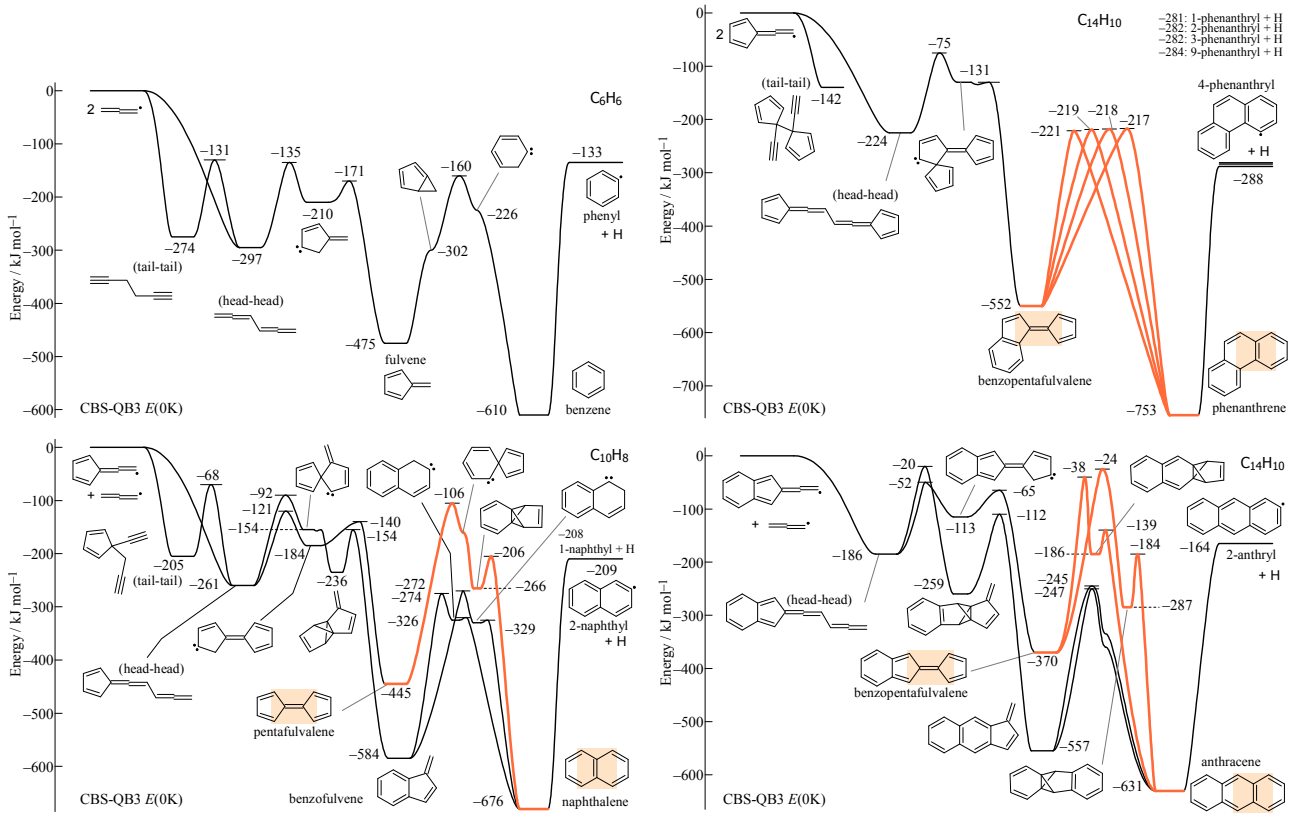
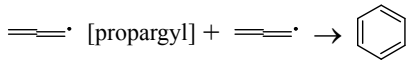


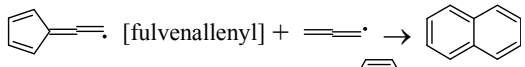
Fig. 1. Energy diagrams for the C_3H_3 (propargyl) + C_3H_3, C_7H_5 (fulvenallenyl) + C_3H_3, C_7H_5 + C_7H_7 and $C_{11}H_7$ (benzofulvenallenyl) + C_3H_3 reactions.

The calculated energy diagrams are shown in Fig 1. Major features of the self-reaction of propargyl (C_3H_3) radicals (1), which have been extensively investigated previously by Miller and Klippenstein [3], were well reproduced by the method used in this study.

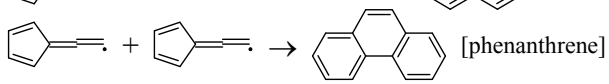


(1)

The reactions of fulvenallenyl (C_7H_5) radicals, its reaction with C_3H_3 (2) and self-reaction (3), which have been firstly suggested by da Silva and Bozzelli [4], were precisely investigated by quantum chemical calculations for the first time.



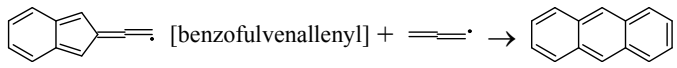
(2)



(3)

The potential energy surfaces for these reactions are quite similar to that of C_3H_3 + C_3H_3 (1) considering the analogous electronic structure of fulvenallenyl to propargyl, except that the biradical intermediates in reaction (1) were often found with the benzvalene structures. The heights of intermediate barriers, which are lower than the entrance channel, were similar to those of reaction (1) in many cases, but some barriers were significantly lowered or raised in reactions (2) and (3).

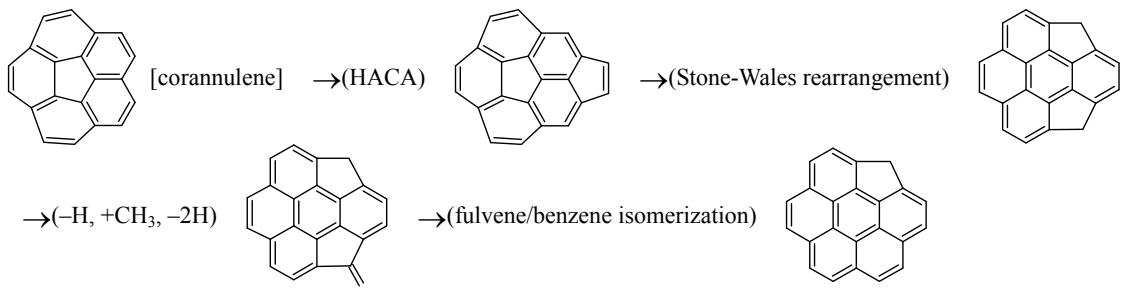
In order to extend our knowledge on the systematic trends of PAHs growth reactions, the reaction of benzofulvenallenyl radical ($C_{11}H_7$) with C_3H_3 (4) was also investigated in the present study.



(4)

It was found that the benzo-substitution of fulvenallenyl radical slightly raised the barrier height for some of fulvene-benzene type isomerization reactions.

The investigation of these reactions revealed an interesting common feature of isomerization, which is the fulvene to benzene isomerization in reaction (1). The pentafulvalene moiety in the intermediate PAHs is easily isomerize to fused two six-membered ring (naphthalene) structure. This is now well known as Stone-Wales rearrangement in the microstructures of graphene and carbon nanotubes [5]. More investigation on the general trend of this type of reactions is required since it may be the key step in the annealing process of relatively unstable PAHs with inner six-membered rings, such as reaction (5).



(5)

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