



Study on Pathway of Benzo(a)pyrene Generation by Quantum Chemistry Calculations

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Density functional theory and Hatree-Fock method were employed to study the generation pathway of benzo(a)pyrene as a greatly carcinogenic substance at B3LYP and HF levels, respectively. By using 6-31G group to calculate the reaction pathways of acetylene polymerization and butenyne polymerization, we identified the transition state, intermediates and reaction energy barrier. We also calculated the energy barrier of styrene becoming butyl benzene *via* chain extension as well as the energy variation in the reaction of butyl benzene with tetrahydro-naphthalene to finally form benzo(a)pyrene. We concluded from our calculations that the aforesaid generation pathway of benzo(a)pyrene is theoretically possible and available.

Keywords: Benzo(a)pyrene, Quantum chemistry, Transition state, Reaction pathway.

INTRODUCTION

As is well-known, 3,4-benzo(a)pyrene (hereinafter referred as 'BaP') is a greatly carcinogenic substance, a polycyclic aromatic hydrocarbon comprising a benzene ring and a pyrene. Out of more than 400 currently identified carcinogenic substances, 200 or more are categorized as polycyclic aromatic hydrocarbon compounds. One of the most representative ones is but BaP. As it were 3,4-benzo(a)pyrene and many other polycyclic aromatic hydrocarbons compounds were subsequently identified in carbon black¹, processed rubber², exhaust³ of gas/diesel turbine, coal gas⁴ and smoke from tobacco leaf⁵ and cigarettes⁶. It was experimentally shown that BaP is found in the pyrolysis products of many compounds⁷⁻¹⁰. In view of the sources of polycyclic aromatic hydrocarbon, we find that only at high temperatures or when being heated would the compounds be pyrolyzed into BaP, concluding that BaP is the pyrolysis product of certain compounds. Up to date, the mechanism for polycyclic aromatic hydrocarbon generation is not so clearly understood. Some progress had been made in the mechanism studies. By using hydrogen abstraction acetylene addition (HACA) reaction, Wang and Frenklach¹¹ developed a mechanism of HACA-based polycyclic aromatic hydrocarbon generation and verified it in the premix C₂ flame (ethylene and acetylene). Nonetheless, HACA mechanism is not fully illustrated. Under some circumstances, HACA mechanism contributes way too less¹² to prediction of pyrene concentrations. Badger¹³ deduced a possible pathway of BaP generation (Fig. 1).

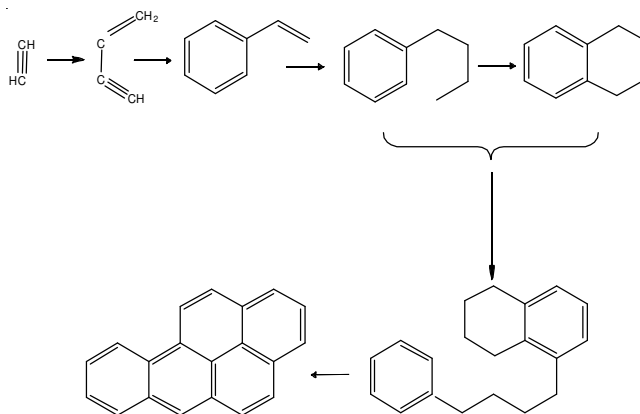


Fig. 1. Possible pathway of BaP generation from pyrolysis of certain compounds

As illustrated above, the initial reactants would be acetylene (resulting from incomplete combustion of some compounds) or ethylene. Naphthalene is however found in the pyrolysis products of those compounds⁷⁻¹⁰, such C₆-C₄ structure is deemed as a key intermediate¹⁴ in forming BaP. The compounds containing C₆-C₄ structure above, such as butadiene, ethyl benzene, phenyl butadiene, *n*-butyl benzene and naphthalene, will generate BaP during pyrolysis. The fact is that the number of reports concerning the experimental and theoretical researches of BaP generation mechanism is far from being sufficient. In this study, we used quantum chemistry

method to investigate the possible pathway of BaP generation in terms of reaction energy.

CALCULATION METHOD

Here, 6-31G group calculations were made at B3LYP and HF levels. (I) As TS or QST2 methods were used to find the transition state of acetylene polymerization into butenyne, intrinsic reaction coordinate calculation was conducted to find the reaction pathway of such polymerization. (II) As TS or QST2 methods were used to find the transition state of butenyne polymerization into styrene, IRC calculation was conducted to verify the interrelations between the transition states, products and intermediates in the reaction process. (III) The energy needed for hydrogenation of double bonds at styrene side chains, as well as the energy needed for the reaction of phenyl-ethyl and ethyl free radicals into butyl phenyl (benzene), was calculated. (IV) The butyl phenyl, tetrahydro-naphthalene and the products from the reaction of the two were calculated and optimized, frequency analysis was made to estimate the Gibbs free energy variance (ΔG) and energy variance (ΔE). In this study, all calculations were executed using Gaussian 03 package¹⁵.

RESULTS AND DISCUSSION

There are two reaction pathways for acetylene polymerizing into butenyne: one is acetylene directly polymerizing into butenyne, the other is that acetylene rearranges to vinylidene which is then polymerized with acetylene into butenyne (Figs. 2 and 3).

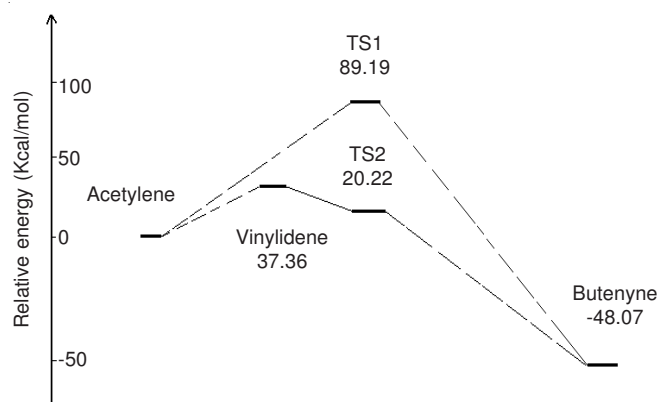


Fig. 2. Two reaction pathways for acetylene polymerizing into butenyne (B3LYP)

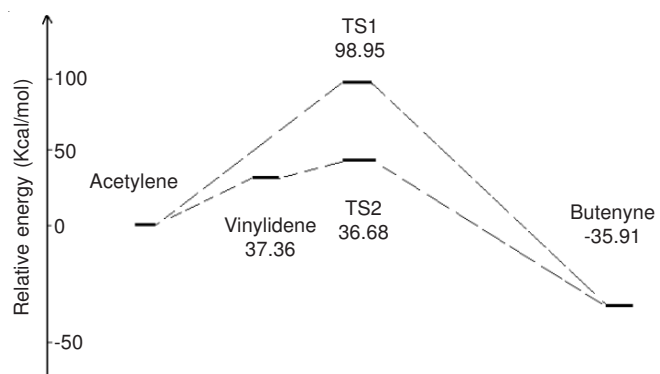
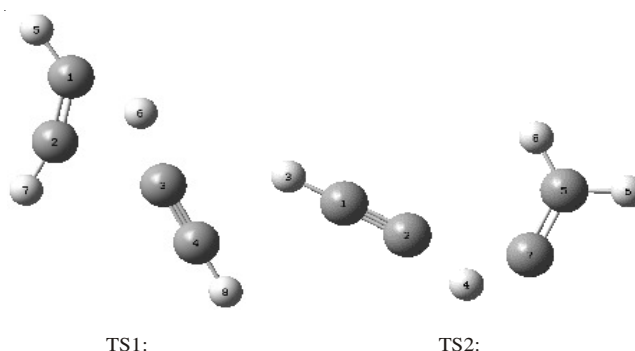


Fig. 3. Two reaction pathways for acetylene polymerizing into butenyne (HF)

For these two pathways, there are two transition states, respectively:



In order to ensure the certainty and truthfulness of transition states and intermediates, frequency analysis was made to all reactants and intermediates, finding that virtual vibration frequency for transition state TS1 is 2780.35i and for TS2, 1280.74i. The transition state is certain and true since both transition-state compounds have only one vibration mode corresponding to the frequency that is so-called virtual frequency. There are two reaction pathways for acetylene polymerization. Pathway I is: for TS1 state, the bond between H₆ atom and C₃ atom breaks and then H₆ atom migrates onto C₁ atom, making a C₂-C₃ bond.

Pathway II is: As acetylene molecules rearrange into vinylidene, C₂-H₂ bond for TS₂ state breaks and then H₂ migrates onto C₇ atom, making a C₂-C₇ bond.

For the pathway of two acetylene molecules polymerizing into butenyne, the potential barrier is on the high side (89.19 or 98.95 Kcal/mol). On the other hand, rearrangement of acetylene into vinylidene features a potential barrier of 37.36 Kcal/mol. As the polymerization of acetylene and vinylidene into butenyne is an energy-degrading process, such polymerization tends to occur more easily in comparison with acetylene-acetylene polymerization.

Butenyne's polymerization into styrene: For the reaction of butenyne to polymerize into styrene, we have hypothesized several possible reaction pathways in calculation: (1) a semi-circle formed by connecting the double-bond carbon atom of one butenyne molecule and the double-bond carbon atom of the other butenyne molecule; (2) a semi-circle formed by connecting the double-bond carbon atom of one butenyne molecule and the triple-bond carbon atom of the other butenyne molecule; (3) a circle formed by connecting the double-bond carbon atoms of two butenyne molecules and simultaneously triple-bond carbon atom of the another butenyne molecule; (4) a circle formed by connecting the double-bond carbon atoms of two butenyne molecules and their triple-bond carbon atom of the another butenyne molecule. There are yet no complete reaction pathways available for the said four possibilities and it may be taken for granted that there is a very slight chance in the existence of four pathways.

Another pathway is that one butenyne molecule undergoes electron transfer, turns triple-bond to double-bond and forms with the other butenyne an unstable circular compound. In this pathway, there are five transition states and four intermediates identified.

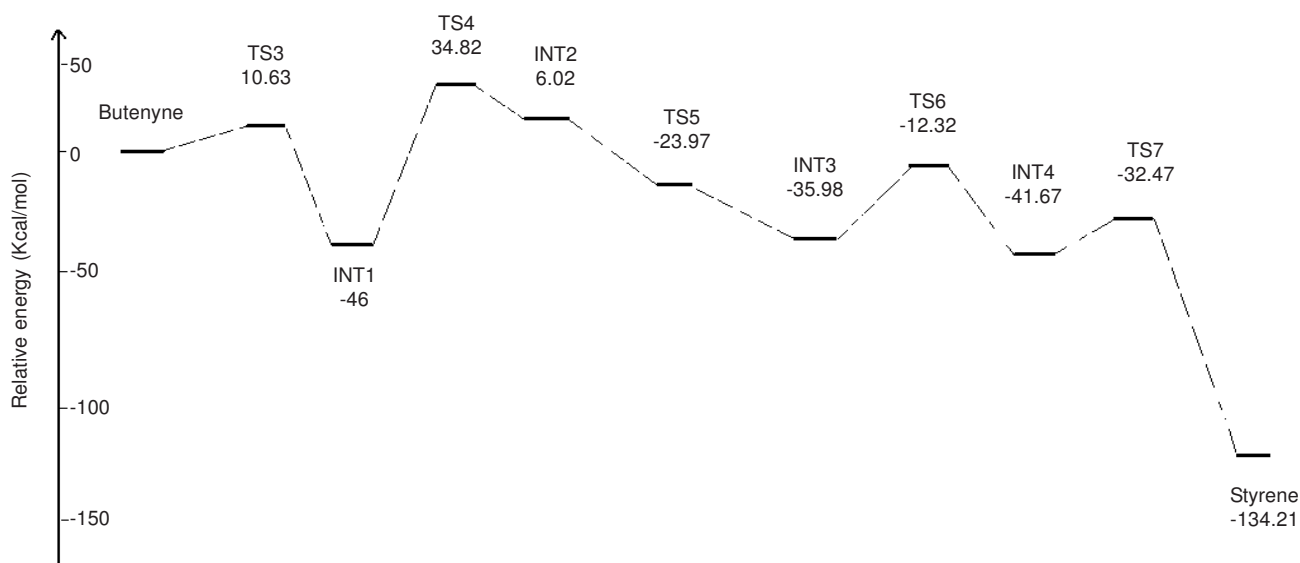
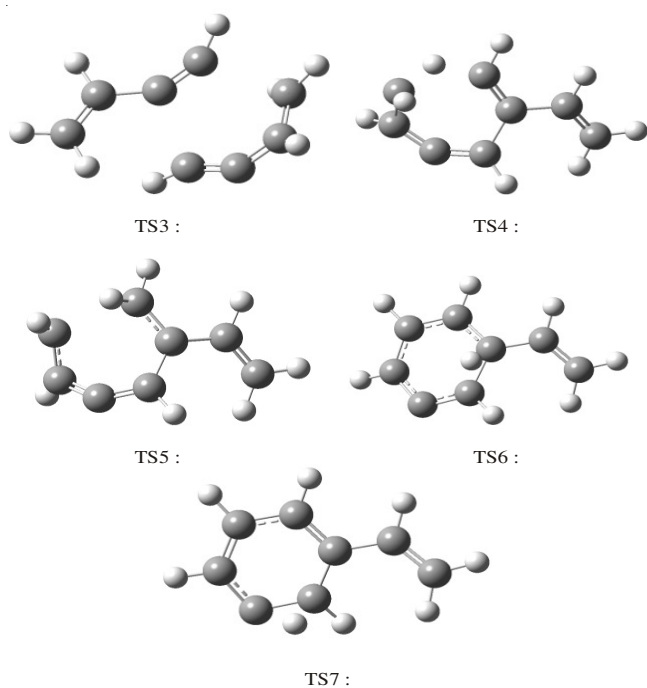


Fig. 4. Reaction pathway for butenyne's polymerization into styrene (B3LYP)



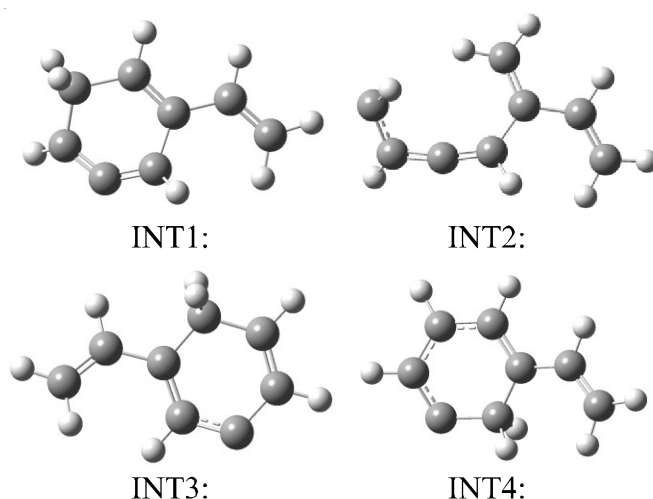
Frequency analysis was made to all reactants, transitions states and intermediates in calculations. It was found that the virtual vibration frequency for TS3 state is 512.23i; for TS4 state, 1228.68i; for TS5 state, 417.42i; for TS6 state, 1263.44i; and for TS7 state, 1091.92 i. Out of these five transition-state compounds, there is only one vibration mode corresponding to the frequency that is so-called virtual frequency, indicating that the transition state is certain and true. Given the fact that the vibration frequencies for intermediates are of positive values, we can conclude that such intermediates are at the stable point of potential energy surface. IRC calculations consolidated the relevance between reactants, transition states and products. As indicated by vibration analysis, the forward displacement vectors for the transition-state virtual vibration mode all point to products, while the reverse displacement vectors all points

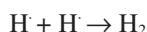
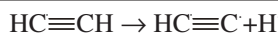
to reactants. It was demonstrated that these stagnation points are in correct reaction pathways.

In the pathway of butenyne's polymerization into styrene, the reaction energy is generally on the decrease. As there is some ring break involved between INT1 and TS4, the potential energy barrier is as high as up to 80.82 Kcal/mol. In other reaction steps, such as the ring closing, hydrogen atom migration and forming of hydrogen bond for TS4-INT2-TS5, the potential barrier is on the low side, representing an energy-degrading process. TS6-INT4-TS7-styrene merely involves hydrogen bond migration. And during TS7-styrene phase, the potential barrier is low and massive energy is released forming a stable-structured styrene.

Styrene's chain extension: Since the reactions starting from styrene's chain extension are a larger reaction system concerning free radical reaction and the reaction between butyl benzenete and trahydro-naphthalene, thermodynamic calculations are hereby conducted.

The double bonds at styrene side chains add with hydrogen to form ethyl benzene. The said hydrogen originates from acetylene generated during compound pyrolysis or from free radical reactions of other small molecules/compounds:





At high temperatures, ethyl benzene becomes phenyl-ethyl free radicals, which then react with ethane-originated ethane free radicals to form butyl benzene:



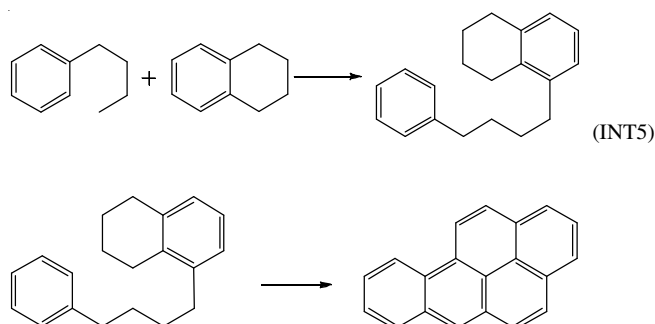
	E (a.u.)	ΔE (Kcal/mol)	G (a.u.)	ΔG (a.u.)
H	-0.499		-0.511	
C ₂ H ₆	-79.73		-79.754	
C ₂ H ₅ ·	-79.077		-79.105	
		96.636		0.138

	E (a.u.)	ΔE (Kcal/mol)	G (a.u.)	ΔG (a.u.)
H·	-0.497		-0.509	
C ₂ H ₆	-79.11		-79.134	
C ₂ H ₅ ·	-78.501		-78.53	
		70.281		0.095

	E (a.u.)	ΔE (kcal/mol)	G (a.u.)	ΔG (a.u.)
H	-0.499		-0.511	
C ₆ H ₅ -C ₂ H ₅	-309.44		-309.478	
C ₆ H ₅ -C ₂ H ₄ ·	-308.767		-308.805	
		109.187		0.162

Neither the generation of ethane free radicals nor the generation of ethyl phenyl free radicals is a spontaneous process. Moreover, the energies needed for their generations are close as 100 Kcal/mol or so (Table-3).

Energy calculation for reaction of ethyl benzene with tetrahydro-naphthalene (Tables 4 and 5): Ethyl benzene reacts with tetrahydro-naphthalene to generate the intermediate INT5, which further forms into BaP.



Ethyl benzene and tetrahydro-naphthalene can convert into each other and the energy difference between the two is slight, as less as 10.67 or 12.55 Kcal/mol. For the reaction of ethyl benzene with tetrahydro-naphthalene to become INT5, the variance between energies of reactants and products is as

TABLE-4
ENERGY VARIANCE AND GIBBS FREE ENERGY FOR THE REACTION OF ETHYL BENZENE WITH TETRAHYDRO-NAPHTHALENE TO FORM BaP (B3LYP)

	E (a.u.)	ΔE (Kcal/mol)	G (a.u.)	ΔG (a.u.)
H ₂	-1.163		-1.177	
Tetralin	-388.012		-388.052	
Butylbenzene	-389.192		-389.239	
		-10.67		0.009
INT5	-776.021		-776.088	
		12.55		0.027
Benzopyrene	-768.971		-769.022	
		45.358		0.004

TABLE-5
ENERGY VARIANCE AND GIBBS FREE ENERGY FOR THE REACTION OF ETHYL BENZENE WITH TETRAHYDRO-NAPHTHALENE TO FORM BaP (HF)

	E (a.u.)	ΔE (Kcal/mol)	G (a.u.)	ΔG (a.u.)
H ₂	-1.114		-1.128	
Tetralin	-385.326		-385.365	
Butylbenzene	-386.46		-386.505	
		-12.55		0.012
INT5	-770.645		-770.71	
		16.94		0.032
Benzopyrene	-763.862		-763.911	
		62.12		0.031

small as 12.55 or 16.94 Kcal/mol, representing an energy-releasing process. For the reaction of INT5 to form BaP, the energy variance is 45.358 or 62.12 kcal/mol representing an energy-absorption process. The ΔG values for the two reactions above are however positive, representing a non-spontaneous reaction. From the energy variances before and after reactions, it is concluded that these two reactions are easy to occur at high temperatures.

Conclusion

With quantum chemistry calculation, we obtained the specific reactions pathways for acetylene's polymerization into butenyne and for butenyne polymerization into styrene, as well as the transition states, intermediates and reaction energy barriers involved. By calculation, we also obtained the energy variances involved in the styrene chain extension, the mutual conversion between butyl benzene and tetrahydro-naphthalene and the reaction of butyl benzene with tetrahydro-naphthalene to form BaP. From the energy barriers and energy variances involved in each reaction step, we can conclude that the Badger's pathway of BaP generation at high temperatures or when being pyrolyzed is theoretically possible and available.

ACKNOWLEDGEMENTS

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