A Theoretical Study of PAH Growth by Phenylacetylene Addition

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ABSTRACT

Although there were significant advancement on polycyclic aromatic hydrocarbon (PAH) formation, current mechanisms are still limited in providing an integrated and accurate scheme of PAH yield in combustion conditions, thus more detailed and comprehensive understandings are necessary. This work provides a systematic investigation of PAH growth by phenylacetylene addition. A combination of the density functional theory (DFT/B3LYP/6-311+G(d,p)) and the complete basis set method (CBS-QB3) is performed to calculate the potential energy surfaces. The reaction system is initiated by the H elimination reaction of phenylacetylene + H $\rightarrow$ o-ethynylphenyl + H₂, then the addition reaction of phenylacetylene and o-ethynylphenyl can produce PAHs with 1, 2, 3, and 4 rings. The temperature- and pressure-dependent reaction rate coefficients are calculated via a combination of conventional Transition State Theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory with solving Master Equation in the temperature range of 500–2500 K and at the pressure range of 0.01–10 atm. There are 263 species and 65 reactions in this reaction system. It shows that the rate constants of this reaction system are highly temperature-dependent, and slightly sensitive to the pressure at temperature lower than 1300 K. To evaluate the yield distributions of various PAH products in the whole reaction network, a closed 0-D batch reactor model in Chemkin is used to calculate the C₆H₅C₂H-C₂H₂-H-Ar reaction system. The results showed that the prevailing products of this system are 3-ring PAHs with side chain structures. Compared with the traditional HACA pathways, the investigated reaction system presents higher efficiency in large PAH formations, which could subsequently promote the formation of soot particles. The phenylacetylene and o-ethynylphenyl reaction network emphasizes the importance of species with side chain, and it enriches current PAH growth pathways aside from the addition of small species such as C₂H₂.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a series of organic compounds with multiple aromatic rings and have been found to be related to the formation of new stars and the earliest forms of life.¹ Both natural and anthropogenic sources contribute to PAHs emission on the Earth. PAHs along with its derivatives such as nitro-PAHs, sulfur-PAHs have negative impacts on human health due to their carcinogenicity and mutagenicity.²⁻³ Numerous studies have shown that a certain degree of exposure to PAHs would lead to a substantial risk of lung and skin cancers and nervous systems.⁴⁻⁶ Therefore, it necessitates further understandings of the scheme of PAH formation and its sequential growth.⁷

PAHs mainly form from incomplete combustion of hydrocarbon fuels, and are known as soot precursors.⁸⁻¹⁶ The hydrogen-abstraction/acetylene(C_2H_2)-addition (HACA) mechanism initially proposed by Frenklach et al.¹⁰ is widely used to describe PAH growth, and is the framework of most of the current PAH reaction mechanisms. In the HACA mechanism, the close-shell PAH is first activated by dehydrogenation reaction to form PAH radical, followed by acetylene addition reaction. However, several research groups have revealed that the production of large PAHs is underestimated via the HACA pathways.^{9, 14, 17} Parker et al. showed that the signals of anthracene and phenanthrene (PAH with 3-ring structure) were not detected in the reaction of 1- and 2-naphthyl radical (PAH with 2-ring structure) and acetylene at combustion-like temperature.¹⁸ Recently, Liu et al. checked the PAH formation in a jet-stirred reactor fueled with $C_6H_6/C_2H_2/O_2/N_2$ at 1400 K.¹⁹ The signal intensities of naphthalene and acenaphthylene were high, but the anthracene and phenanthrene signals had not been observed. These experimental observations might be explained by the site effect in HACA frame. Our previous study showed that the H abstraction and C_2H_2 addition reactions in HACA frame were greatly sensitive to the

site position (ortho-, meta- and para-position) relative to the existing C₂H chain and surface site type (zig-zag, free-edge and armchair).¹⁴ Correspondingly, the PAH with five-membered ring is the dominant product in large PAH reaction system instead of the PAH fully constituted by benzene rings (phenanthrene and pyrene). Therefore, other efficient mechanisms leading to large PAH formation need further investigations.^{11, 15, 20-21}

Recombination reaction of active molecules has been proved to be an efficient PAH formation pathway beyond HACA mechanism at some flame conditions. Mebel et al.²² showed that naphthalene could be formed from the recombination of two cyclopentadienyl radicals. The formation of PAHs with two or three benzene rings from the self-reaction and cross-reactions of fulvenallenyl were possible as discussed by Silva et al.²³ Shukla and Koshi²⁴ suggested that a phenyl addition/cyclization pathway was more efficient for PAH formation and growth in benzene pyrolysis, as compared with the HACA pathway. Similar to cyclopentadienyl and fulvenallenyl, the reaction activity of phenylacetylene (C₆H₅C₂H, or A1C₂H) was high due to the triple bond. Once the adjacent carbon relative to the ethynyl chain on C₆H₅C₂H is connected to an aromatic ring, it is likely to form a new benzene ring (such as C₆H₅C₂H+phenyl→Phenanthrene+H). Phenylacetylene is abundant in sooting flames with mole fraction close to that of benzene, and mainly forms from the addition reaction of phenyl radical and C₂H₂ (phenyl + C₂H₂ → phenylacetylene + H).²⁵⁻²⁷ Shukla et al.²⁸ detected that phenylacetylene was abundant among the pyrolysis products of acetylene and ethylene at 1485 K. In the high-temperature pyrolysis (HTP) reactor of natural gas, the formation of phenylacetylene was found to be favored.²⁹ Both phenylacetylene and phenylacetylene radical (C₆H₄C₂H) are the vital precursors of naphthalene in the HACA mechanism. For example, the naphthalene forms from the pathway of C₆H₅C₂H (+H) → C₆H₄C₂H (+C₂H₂) → naphthyl (+H) → naphthalene.

Therefore, it is well-reasoned to investigate the possibility of large PAH formation directly from the self-reaction of $C_6H_5C_2H$ and $C_6H_4C_2H$ due to the ethynyl chain and their high concentrations.

This work aims to systematically explore PAH growths by the addition reaction of $C_6H_5C_2H$ and $C_6H_4C_2H$ without the consideration of other carbon sources (i.e., acetylene). The density functional theory (DFT) combined with the complete basis set (CBS) method was utilized to search the potential energy surfaces. Subsequently, the reaction rate coefficients of each elementary reactions are evaluated by Rice-Ramsperger-Kassel-Marcus with solving the Master Equation (RRKM-ME) calculations and Transition State Theory (TST) calculations. Finally, the yields of all products are calculated in a 0-D batch reactor and compared with the HACA mechanism to evaluate its importance at combustion relevant temperatures.

2. Computational Details

The whole reaction network includes 263 species and 290 elementary reactions in this study. Each chemical species and transition state are marked as “CS” and “TS”, respectively. The structures of all species including minima (CSs) and transition states (TSs) were optimized using the DFT with B3LYP hybrid functional 6-311+G(d,p) basis set (DFT/B3LYP/6-311+G(d,p)).³⁰ To improve the accuracy of energy calculation, the sums of electronic and zero-point energies were refined with CBS-QB3 method.³¹ If not specified, the energies shown in this paper were calculated at the CBS-QB3 level.

Intrinsic reaction coordinate (IRC) calculations³² at DFT B3LYP 6-311 G+(d,p) level were performed to affirm that the calculated TSs connects the corresponding reactant and product. IRCmax calculations³³ were conducted to refine the energy barriers of the entrance reactions at

CBS-QB3 level. The Gaussian 09 program package with the version of D.01 was applied to calculate all the quantum calculations.³⁴

The temperature- and pressure-dependent rate constants and product branching ratios were discussed using RRKM-ME and TST calculations in the temperature range of 500–2500 K and pressure range of 0.01–10 atm. The internal rotation was regarded as a 1-dimensional (1-D) unsymmetrical hindered rotor. The rotation constants and torsional potential energies were obtained by scanning the dihedral angles from 0° to 360° at an increment of 20° at DFT/B3LYP/6-311+G(d,p) level.

All RRKM-ME calculations were conducted in Multiwell code (version 2019).³⁶⁻³⁸ The maximum energy was given as 300,000 cm⁻¹ in MultiWell calculation. The vibrational and translational temperatures were considered to be the same. The collisional energy transfer was described by an exponential model ($\langle E_{\text{down}} \rangle = 260 \text{ cm}^{-1}$). The bath gas collider was argon, and the corresponding Lennard-Jones parameters σ and ε/k_B were equal to 3.47 Å and 114 K, respectively. The Lennard-Jones parameters of other species were assumed to be equal to that of phenanthrene, as their sizes were close. The number of stochastic trials was set as 1×10^6 . The statistical fluctuation was checked to be within 3%. It should be noted that only the reaction system with one entrance channel can be handled by Multiwell. Therefore, the whole network was divided into several sub-reaction systems according to the entrance channels.

To simulate the yield distributions of various PAH products in the whole reaction network, a closed zero-dimensional batch reactor in Chemkin-Pro software was used. The reaction time in this 0-D batch reactor was set as 10 ms, and the temperature ranged from 1000 to 2500 K at an increment of 100 K. Based on the experimental data in a premixed ethylene flame¹⁷, the mole

fractions of the initial reactants $\text{C}_6\text{H}_5\text{C}_2\text{H}$, H , and C_2H_2 and argon (Ar) were set as 193 ppm, 100 ppm, 0.045, 0.954707, respectively. Meanwhile, the PAH growths starting from $\text{C}_6\text{H}_5\text{C}_2\text{H}$ by following HACA pathway¹⁴ was simulated at the same condition, to check the competitiveness of $\text{C}_6\text{H}_5\text{C}_2\text{H}/\text{C}_6\text{H}_4\text{C}_2\text{H}$ reaction channel in terms of the formation of large PAHs containing 3 or 4 rings.

3. Results and discussion

There are three isomers of $\text{C}_6\text{H}_4\text{C}_2\text{H}$, which can be produced via the H abstraction reaction of $\text{C}_6\text{H}_5\text{C}_2\text{H}$ (CS1) + $\text{H} \rightarrow \text{C}_6\text{H}_4\text{C}_2\text{H}$ (CS2) + H_2 , depending on the site of the abstracted H. The structure of CS2 was selected in this paper because of its higher possibility of producing larger PAHs.¹⁴ All possible addition reactions between CS1 and CS2 are explored, thus each carbon atom of CS1 is possible to attach the unsaturated carbon atom of CS2 . Each reaction pathway will be discussed in detail based on their potential energy surfaces (PESs). In Figure 1, the PES of the entrance reactions and their high-pressure limit reaction rate constants are shown.

Figure 1. Potential energy surface (a) and reaction rate constants (b) of the entrance reactions of CS1 ($\text{C}_6\text{H}_5\text{C}_2\text{H}$) and CS2 ($\text{C}_6\text{H}_4\text{C}_2\text{H}$). Energies (kcal/mol) are calculated at CBS-QB3 level, and high-pressure limit rate constants are calculated using TST.

For the two initial reactants, the active carbon atom in CS2 that labeled as A0 can attack each carbon atoms A1-A5 in CS1 (shown as the inset in Figure 1a). Considering the symmetry, there are five pathways in the CS1+CS2 reaction system, and they are named as P1, P2, P3, P4, and P5, respectively. The energy barriers of the addition reactions range from 1.6 to 5.7 kcal/mol. All entrance reactions are exothermic, with the release energies ranging from 40.3 to 61.2 kJ/mol. The forward reaction rate constant of CS1+CS2→P4-CS1 reaction is the highest among all entrance reactions due to the low energy barrier and favored entropy change.

The reaction energy of the exothermic process in the first step of reaction pathway P4 (CS1+CS2→P4-CS1) is the highest (61.2 kJ/mol), and the reverse reaction rate constant is the lowest. This makes the production of P4-CS2 is dominant among 2-ring products, evidenced in later discussions.

Due to the complexity of the studied reaction system, only PESs of important channels were discussed in detail. The full versions of the PESs can be found in the supplementary material (SM). Note that all reactions (including the reactions described in SM) have been considered in the kinetic analysis.

3.1 Analysis of potential energy surfaces

3.1.1 Reaction pathway 1

Figure 2 shows the potential energy surface of reaction pathway 1 (P1). There are four types of reactions: (1) H transfer; (2) H elimination; (3) cyclization; and (4) C-C bond rotation. The

products of P1 are P1-CS4, P1-CS9, P1-CS19, P1-CS22, P1-CS28, P1-CS36, P1-CS37, and P1-CS44. P1-CS4 is formed by H elimination reaction with the energy barrier of 32.3 kcal/mol via one-step dehydrogenation reaction $\text{P1-CS1} \rightarrow \text{P1-CS4} + \text{H}$. Except for P1-CS4, intermediates P1-CS5 and P1-CS6 may be isomerized from P1-CS1 by cyclization reactions ($\text{P1-CS1} \rightarrow \text{P1-CS5}$ (19.4 kcal/mol), $\text{P1-CS1} \rightarrow \text{P1-CS6}$ (22.4 kcal/mol)).

The intermediate P1-CS5 contains a 5-member ring sit between two 6-member rings, and a CH chain on the 5-member ring. Three products including P1-CS9, P1-CS19, and P1-CS22 can be formed from P1-CS5. The active C of the side chain is inclined to catch an H to form CH₂ side chain (P1-CS5 → P1-CS15 (57.7 kcal/mol)), then the super-saturated C releases an H to generate the product P1-CS9 via two channels: (1) P1-CS15 (H elimination, 7.1 kcal/mol) → P1-CS9+H and (2) P1-CS15 (H transfer, 40.9 kcal/mol) → P1-CS16 (H elimination, 28.6 kcal/mol) → P1-CS9+H. Alternatively, the released H from the previous step may migrate to the active C of the side chain in the phenyl (P1-CS16→P1-CS17 (35.3 kcal/mol)). Meanwhile, 4-ring PAHs P1-CS19 and P1-CS22 can form from P1-CS17 via the channels with their corresponding energy barriers shown: (1) P1-CS17 (cyclization, 15.7 kcal/mol) → P1-CS18 (H elimination, 20.3 kcal/mol) → P1-CS19+H and (2) P1-CS17 (H transfer, 42.6 kcal/mol) → P1-CS20 (cyclization, 39.4 kcal/mol) → P1-CS21 (H elimination, 32.5 kcal/mol) → P1-CS22+H, respectively. It is obvious that the PES of the first channel locates below the PES of the second channel, which indicates P1-CS19 is more likely to form as compared with P1-CS22. This is also evidenced by the higher-yielding of P1-CS19 compared with P1-CS22 from the kinetic analysis.

Intermediate P1-CS6 is featured with one active site on the middle benzene ring. A supersaturated H can move to this active site directly (P1-CS6 (H transfer, 56.5 kcal/mol) → P1-CS39) or indirectly (P1-CS6 (H transfer, 57.2 kcal/mol) → P1-CS38 (H transfer, 6 kcal/mol) → P1-CS39). Once P1-CS39 is formed, the cyclization reactions are easy to produce a new 5-, or 6-member ring. Figure 2b shows the reaction pathways from the 3-ring PAH P1-CS39 to 4-ring PAHs: P1-CS19, P1-CS28, P1-CS36, P1-CS37 (pyrene), and P1-CS44. P1-CS19 is produced via two channels: P1-CS39 (H transfer, 38.4 kcal/mol) → P1-CS50 (H transfer, 40.5 kcal/mol) → P1-CS51 (H transfer, 45.3 kcal/mol) → P1-CS52 (cyclization, 20.2 kcal/mol) → P1-CS55 (H

elimination, 28.4 kcal/mol) $\rightarrow$ P1-CS19+H and P1-CS39 (H transfer, 38.4 kcal/mol) $\rightarrow$ P1-CS50 (H transfer, 40.5 kcal/mol) $\rightarrow$ P1-CS51 (cyclization, 58.6 kcal/mol) $\rightarrow$ P1-CS56 (H transfer, 12.5 kcal/mol) $\rightarrow$ P1-CS57 (H elimination, 32.9 kcal/mol) $\rightarrow$ P1-CS19+H. These two channels are mainly composed of H transfer, cyclization, and H release reactions. The energy barrier of the reaction P1-CS51 $\rightarrow$ P1-CS52 in the first channel is lower than that of the competing reaction P1-CS51 $\rightarrow$ P1-CS56 in the second channel by 13.3 kcal/mol, thus the first channel is expected to contribute more to the formation of P1-CS19. P1-CS28, the precursor of pyrene in HACA mechanism, can form via the hydrogen elimination reactions P1-CS39 $\rightarrow$ P1-CS28+H (22.3 kcal/mol) and P1-CS50 $\rightarrow$ P1-CS28+H (31.4 kcal/mol). The product yield of P1-CS43, P1-CS36 and P1-CS44 are expected to be minor as the PES of their formation lie above the others in Figure 2b. Therefore, further discussions for P1-CS43, P1-CS36, and P1-CS44 formation are not given in this study. P1-CS37 (pyrene) is an important product in this system and it forms via the following 7 channels: (1) P1-CS39 (cyclization, 37.5 kcal/mol) $\rightarrow$ P1-CS40 (H elimination, 27.2 kcal/mol) $\rightarrow$ P1-CS41+H (H transfer, 15.4 kcal/mol) $\rightarrow$ P1-CS37+H, (2) P1-CS39 (cyclization, 37.5 kcal/mol) $\rightarrow$ P1-CS40 (H elimination, 24.0 kcal/mol) $\rightarrow$ P1-CS42+H (H transfer, 8.0 kcal/mol) $\rightarrow$ P1-CS45+H (H transfer, 1.4 kcal/mol) $\rightarrow$ P1-CS37+H, (3) P1-CS39 (cyclization, kcal/mol) $\rightarrow$ P1-CS40 (H transfer, 37.5 kcal/mol) $\rightarrow$ P1-CS46 (H transfer, 21.4 kcal/mol) $\rightarrow$ P1-CS47 (H elimination, 14.8 kcal/mol) $\rightarrow$ P1-CS37+H, (4) P1-CS39 (cyclization, 37.5 kcal/mol) $\rightarrow$ P1-CS40 (H transfer, 29.2 kcal/mol) $\rightarrow$ P1-CS48 (H transfer, 17.4 kcal/mol) $\rightarrow$ P1-CS49 (H elimination, 17.1 kcal/mol) $\rightarrow$ P1-CS37+H, (5) P1-CS39 (H transfer, 38.4 kcal/mol) $\rightarrow$ P1-CS50 (H transfer, 40.8 kcal/mol) $\rightarrow$ P1-CS51 (H transfer, 45.3 kcal/mol) $\rightarrow$ P1-CS52 (cyclization, 42.8 kcal/mol) $\rightarrow$ P1-CS53 (H transfer, 8.7 kcal/mol) $\rightarrow$ P1-CS54 (H elimination, 30.1 kcal/mol) $\rightarrow$ P1-CS37+H, (6) P1-CS39 (H transfer, 38.4 kcal/mol) $\rightarrow$ P1-CS50 (H transfer, 40.8 kcal/mol) $\rightarrow$ P1-CS51 (H

transfer, 45.3 kcal/mol) $\rightarrow$ P1-CS52 (cyclization, 42.8 kcal/mol) $\rightarrow$ P1-CS53 (H transfer, 15.3 kcal/mol) $\rightarrow$ P1-CS49 (H elimination, 17.1 kcal/mol) $\rightarrow$ P1-CS37+H, and (7) P1-CS39 (H transfer, 38.4 kcal/mol) $\rightarrow$ P1-CS50 (H transfer, 40.8 kcal/mol) $\rightarrow$ P1-CS51 (cyclization, 6.4 kcal/mol) $\rightarrow$ P1-CS49 (H elimination, 17.1 kcal/mol) $\rightarrow$ P1-CS37+H. Although more pathways leading to the formation of P1-CS37, the yielding of P1-CS37 is not high due to their high energy barriers in the formation pathway compared to other pathways, especially at lower temperatures.

3.1.2 Reaction pathway 2

Figure 3 introduces the reactions of the P2, leading to the formation of P2-CS2, P2-CS29, P2-CS6, P2-CS9, P2-CS15, P2-CS16, and P2-CS21. P2-CS2 is formed by H elimination from a super-saturated C (P2-CS1 $\rightarrow$ P2-CS2+H, 29.8 kcal/mol). Main 3-ring PAH product P2-CS29 can be formed from the following three pathways: (1) P2-CS1 (cyclization, 31.5 kcal/mol) $\rightarrow$ P2-CS3 (H transfer, 39.7 kcal/mol) $\rightarrow$ P2-CS23 (H transfer, 13.9 kcal/mol) $\rightarrow$ P2-CS28 (H elimination, 20.5 kcal/mol) $\rightarrow$ P2-CS29 + H, (2) P2-CS1 (cyclization, 31.5 kcal/mol) $\rightarrow$ P2-CS3 (H transfer, 48.6 kcal/mol) $\rightarrow$ P2-CS32 (H transfer, 6.7 kcal/mol) $\rightarrow$ P2-CS33 (H elimination, 24.3 kcal/mol) $\rightarrow$ P2-CS29 + H, and (3) P2-CS1 (H transfer, 24.7 kcal/mol) $\rightarrow$ P2-CS5 (C-C bond rotation, 5.1 kcal/mol) $\rightarrow$ P2-CS31 (cyclization, 2.0 kcal/mol) $\rightarrow$ P2-CS28 (H elimination, 20.5 kcal/mol) $\rightarrow$ P2-CS29 + H pathways. Starting from P2-CS1 in the third pathway, H transfer needs lower energy barrier (P2-CS1 $\rightarrow$ P2-CS5, 24.4 kcal/mol) compared to that of the competing cyclization reaction (P2-CS1 $\rightarrow$ P2-CS3, 31.5 kcal/mol). Thus, in terms of the energy barriers, the pathway P2-CS1 $\rightarrow$ P2-CS5 $\rightarrow$ P2-CS31 $\rightarrow$ P2-CS28 $\rightarrow$ P2-CS29 + H may be prior than the other two among the above pathways.

Figure 3. Potential energy surface of reaction pathway 2 (P2), energies (kcal/mol) are calculated at CBS-QB3 level.

Branching from P2-CS1, the rotation of the C-C bond between two phenyls is highly inclined to occur due to the relatively lower energy barrier (P2-CS1→ P2-CS30, 9.4 kcal/mol), followed by a cyclization reaction to generate P2-CS4 with 3-ring structures (P2-CS30→P2-CS4, 19.1 kcal/mol). The subsequent reactions of P2-CS4 were shown in Figure 3b, and mainly featured by H transfer, H elimination, and cyclization reactions. P2-CS6 is formed via reaction P2-CS4→ P2-CS6 + H₂ (H elimination, 86.7 kcal/mol), where two H atoms release simultaneously. If only one H released, non-planar structure P2-CS16 can be formed via P2-CS4→ P2-CS16 + H (75.5 kcal/mol). There are two pathways leading to the formation of P2-CS9, which is the isomer of P2-CS29: P2-CS4 (H transfer, 58.5 kcal/mol) →P2-CS7 (H transfer, 7.2 kcal/mol) →P2-CS8 (H elimination, 18.7 kcal/mol) →P2-CS9+H and P2-CS4 (H elimination, 64.3 kcal/mol) →P2-CS17+H (H transfer, 16.4 kcal/mol) →P2-CS18+H (H transfer, 2.0 kcal/mol) →P2-CS9+H. Another product P2-CS21 is generated from P2-CS19 via H elimination and transfer reactions, that is the pathway of P2-CS4 (H elimination, 64.3 kcal/mol) →P2-CS17 (H transfer, 35.6 kcal/mol) →P2-CS19+H. The energy barrier of 2-H atoms elimination reaction P2-CS19→P2-CS21+H₂ is 41.3 kcal/mol, which is lower than the value in the similar 2-H atoms elimination reaction P2-CS4→ P2-CS6 + H₂ (86.7 kcal/mol) and 1-H atom elimination reaction (P2-CS4→P2-CS17+H, 64.3 kcal/mol). This further confirmed the conclusion that the energy barrier of 2-H elimination reaction is greatly sensitive to the structure in our previous study¹³. The last product in P2 reaction system is P2-CS15 containing three benzene rings and one five-member ring, three channels can lead to its formation: (1) P2-CS4 (H transfer, 54.7 kcal/mol) →P2-CS10 (H transfer, 43.8 kcal/mol) →P2-CS11 (cyclization, 2.8 kcal/mol) →P2-CS12 (H elimination, 22.6 kcal/mol) →P2-CS13+H (H transfer, 1.3 kcal/mol) →P2-CS15+H, (2) P2-CS4 (H transfer, 43.8 kcal/mol) →P2-CS10 (43.8 kcal/mol) →P2-CS11 (cyclization, 2.8 kcal/mol) →P2-CS12 (H transfer, 4.7

kcal/mol) $\rightarrow$ P2-CS14 (H elimination, 10.3 kcal/mol) $\rightarrow$ P2-CS15+H, and (3) P2-CS4 (H elimination, 64.3 kcal/mol) $\rightarrow$ P2-CS17+H (H transfer, 35.6 kcal/mol) $\rightarrow$ P2-CS19+H (H transfer, 35.3 kcal/mol) $\rightarrow$ P2-CS20+H (cyclization, 104 kcal/mol) $\rightarrow$ P2-CS13+H (H transfer, 1.3 kcal/mol) $\rightarrow$ P2-CS15+H. The high energy barrier difference in two similar cyclization reactions (P2-CS20 $\rightarrow$ P2-CS13, 104 kcal/mol and P2-CS11 $\rightarrow$ P2-CS12, 2.8 kcal/mol) indicates that the cyclization reaction is unlikely to happen if there is a unsaturated C atom near the targeted C atom.

3.1.3 Reaction pathway 3

Figure 4 shows the potential energy surface of reaction pathway 3 (P3), where the products P3-CS2, P3-CS6, P3-CS8, and P3-CS12 form. Specifically, P3-CS2 forms from the dehydrogenation reaction P3-CS1 $\rightarrow$ P3-CS2+H with the energy barrier of 34.0 kcal/mol. P3-CS8 can be formed from: (1) P3-CS1 (cyclization, 34.5 kcal/mol) $\rightarrow$ P3-CS4 (H transfer, 46.2 kcal/mol) $\rightarrow$ P3-CS15 (H transfer, 6.7 kcal/mol) $\rightarrow$ P3-CS16 (H elimination, 22.2 kcal/mol) $\rightarrow$ P3-CS8+H, (2) P3-CS1 (H transfer, 26.9 kcal/mol) $\rightarrow$ P3-CS5 (cyclization, 3.6 kcal/mol) $\rightarrow$ P3-CS7 (H elimination, 17.6 kcal/mol) $\rightarrow$ P3-CS8+H, (3) P3-CS1 (H transfer, 26.9 kcal/mol) $\rightarrow$ P3-CS5 (H transfer, 42.7 kcal/mol) $\rightarrow$ P3-CS9 (cyclization, 43.9 kcal/mol) $\rightarrow$ P3-CS10 (H transfer, 18.4 kcal/mol) $\rightarrow$ P3-CS7 (H elimination, 17.6 kcal/mol) $\rightarrow$ P3-CS8+H, and (4) P3-CS1 (cyclization, 34.5 kcal/mol) $\rightarrow$ P3-CS4 (H transfer, 40.9 kcal/mol) $\rightarrow$ P3-CS14 (H transfer, 18.4 kcal/mol) $\rightarrow$ P3-CS7 (H elimination, 17.6 kcal/mol) $\rightarrow$ P3-CS8+H pathways. Among these pathways, P3-CS1 $\rightarrow$ P3-CS5 $\rightarrow$ P3-CS7 $\rightarrow$ P3-CS8+H is expected to be dominant due to the low energy barrier in each elementary reaction step. This is confirmed by the following kinetic analysis. Specifically, the H transfer from benzene ring to ethynyl chain (P3-CS1 $\rightarrow$ P3-CS5, 26.9 kcal/mol) happens firstly, followed by the cyclization reaction (P3-CS5 $\rightarrow$ P3-CS7, 3.6 kcal/mol). Subsequently, P3-CS8 with 3-ring structure forms from H elimination reaction (P3-CS7 $\rightarrow$ P3-CS8+H, 17.6 kcal/mol).

Meanwhile, P3-CS6 is unlikely to form due to the high energy barrier in reaction P3-CS5→P3-CS6 (50.8 kcal/mol), as compared with the competing reaction P3-CS5→P3-CS7 (3.6 kcal/mol). Alternatively, P3-CS5 may lead to the main product P3-CS12 via H transfer reaction (P3-CS5→P3-CS9, 42.7 kcal/mol), cyclization reaction (P3-CS9→P3-CS11, 15.6 kcal/mol), and H elimination reaction (P3-CS1→P3-CS12+H, 24.9 kcal/mol).

Figure 4. Potential energy surface of reaction pathway 3 (P3), energies (kcal/mol) are calculated at CBS-QB3 level.

3.1.4 Reaction pathway 4 and 5

The reaction pathway P3 only contributes to the production of PAHs with 2 and 3 rings, while P1 and P2 can contribute to the production of PAHs with 2, 3, and 4 rings. As for P4 and P5, as

shown in Figure 5, it contributes to the 1-, 2-, and 3-ring PAHs formation. In P4, there is only one channel $P4-CS1 \rightarrow P4-CS2 \rightarrow P4-CS3$, comprising of H elimination reaction ($P4-CS1 \rightarrow P4-CS2$, 43.5 kcal/mol) and cyclization reaction ($P4-CS2 \rightarrow P4-CS3$, 14.8 kcal/mol). P5-CS3 and P5-CS4 can be formed in P5 reaction system. After the addition reaction of $CS1+CS2 \rightarrow P5-CS1$, either P5-CS1 undergoes the cyclization reaction to generate P5-CS3 via $P5-CS1 \rightarrow P5-CS3$ (49.1 kcal/mol), or the C-C bond close to phenyl between these two benzene rings breaks down to form the di-substituted species (P5-CS2) and phenyl (P5-CS2a) via $P5-CS1 \rightarrow P5-CS2$ (41.5 kcal/mol). The two side chains of P5-CS2 can cyclize to P5-CS4 with the energy barrier of 30.5 kcal/mol.

Figure 5. Potential energy surface of reaction pathway 4 & 5 (P4 & P5), energies (kcal/mol) are calculated at CBS-QB3 level.

3.2 Kinetic analysis

3.2.1 Reaction rate coefficient and product yield

The reaction rate coefficients in each sub-systems (P1, P2, P3, P4, and P5) were evaluated individually via RRKM-ME calculations and shown in Table S1 in the supplementary material. The kinetic results show that the product yield in each sub-system are nearly independent on pressure. P3-CS2, P3-CS8 and P3-CS12 channels are selected to show the impact of pressure on the product yield in P3 reaction system at different temperatures. As shown in Figure 6, the yields of product P3-CS2, P3-CS8 and P3-CS12 at different pressures are highly overlapping above 1300 K. The formation of P3-CS8 is slightly favored at higher pressure, while P3-CS2 presents the opposite trend. This trend is also observed in Mebel's work.³⁹ For further details, the branching ratios of the major products are assembled in Table 1.

Figure 6. Product yield of P3-CS2 (a), P3-CS8 (b), and P3-CS12 (c) in P3 reaction system at various temperatures and pressures via RRKM-ME calculations.

Table 1. Product branching ratios of the $\text{C}_6\text{H}_5\text{C}_2\text{H}-\text{C}_2\text{H}_2-\text{H}-\text{Ar}$ reaction network at various temperatures and pressures.

P = 0.01 atm						
Temperature (K)	3-ring PAHs				2-ring PAHs	
	P1-CS9	P2-CS29	P3-CS8	P3-CS12	P1-CS4	P4-CS1
1000	0.00	13.44	79.25	0.00	4.13	3.17
1100	0.00	14.50	80.52	0.01	4.67	0.30
1200	0.00	15.16	79.59	0.04	5.17	0.04
1300	0.03	15.78	78.35	0.14	5.68	0.01
1400	0.25	16.42	76.87	0.40	6.05	0.00
1500	1.25	17.09	75.05	0.92	5.68	0.00
1600	3.87	17.80	72.86	1.75	3.71	0.00
1700	6.72	18.53	70.34	2.85	1.55	0.00
1800	8.38	19.29	67.63	4.10	0.59	0.00
1900	9.40	20.05	64.92	5.35	0.27	0.00
2000	10.18	20.80	62.38	6.45	0.17	0.00
2100	10.83	21.53	60.14	7.31	0.17	0.00
2200	11.40	22.21	58.27	7.88	0.22	0.00
2300	11.87	22.82	56.79	8.16	0.31	0.00
2400	12.25	23.35	55.70	8.19	0.45	0.00
2500	12.52	23.79	54.98	8.00	0.63	0.00
P = 0.1 atm						
Temperature (K)	3-ring PAHs				2-ring PAHs	
	P1-CS9	P2-CS29	P3-CS8	P3-CS12	P1-CS4	P4-CS1
1000	0.00	13.43	79.27	0.03	4.15	3.12
1100	0.00	14.48	80.45	0.09	4.68	0.29
1200	0.00	15.14	79.43	0.23	5.16	0.04
1300	0.04	15.77	78.07	0.48	5.64	0.01
1400	0.26	16.42	76.50	0.87	5.94	0.00
1500	1.34	17.10	74.70	1.41	5.44	0.00
1600	4.14	17.81	72.64	2.10	3.31	0.00
1700	7.00	18.53	70.35	2.89	1.22	0.00
1800	8.55	19.27	67.98	3.75	0.43	0.00
1900	9.51	20.03	65.62	4.64	0.19	0.00
2000	10.26	20.78	63.31	5.50	0.13	0.00
2100	10.90	21.50	61.11	6.32	0.15	0.00
2200	11.46	22.18	59.06	7.06	0.21	0.00
2300	11.92	22.79	57.21	7.72	0.31	0.00
2400	12.28	23.33	55.58	8.30	0.45	0.00
2500	12.53	23.78	54.18	8.80	0.63	0.00
P = 1 atm						

Temperature (K)	3-ring PAHs				2-ring PAHs	
	P1-CS9	P2-CS29	P3-CS8	P3-CS12	P1-CS4	P4-CS1
1000	0.00	13.43	79.43	0.29	4.11	2.70
1100	0.00	14.49	80.28	0.47	4.53	0.22
1200	0.00	15.18	79.26	0.70	4.83	0.03
1300	0.04	15.87	78.08	0.99	5.01	0.00
1400	0.32	16.62	76.86	1.36	4.84	0.00
1500	1.55	17.40	75.48	1.80	3.76	0.00
1600	4.36	18.12	73.49	2.31	1.72	0.00
1700	6.87	18.76	70.96	2.88	0.52	0.00
1800	8.34	19.44	68.50	3.52	0.19	0.00
1900	9.31	20.18	66.16	4.24	0.10	0.00
2000	10.04	20.93	63.88	5.03	0.10	0.00
2100	10.60	21.69	61.68	5.89	0.13	0.00
2200	10.96	22.43	59.56	6.82	0.19	0.00
2300	11.10	23.17	57.57	7.83	0.28	0.00
2400	10.97	23.91	55.73	8.92	0.40	0.00
2500	10.52	24.67	54.07	10.12	0.53	0.00
P = 10 atm						
Temperature (K)	3-ring PAHs				2-ring PAHs	
	P1-CS9	P2-CS29	P3-CS8	P3-CS12	P1-CS4	P4-CS1
1000	0.00	13.16	81.27	1.06	3.48	1.03
1100	0.00	14.37	81.53	1.36	2.68	0.06
1200	0.00	15.47	81.59	1.46	1.46	0.01
1300	0.03	16.50	81.30	1.60	0.57	0.00
1400	0.12	17.46	80.40	1.80	0.21	0.00
1500	0.46	18.36	79.00	2.08	0.10	0.00
1600	1.33	19.17	77.01	2.43	0.05	0.00
1700	2.99	19.84	74.28	2.86	0.03	0.00
1800	5.05	20.41	71.14	3.38	0.02	0.00
1900	6.64	21.07	68.23	4.02	0.03	0.00
2000	7.11	22.02	65.96	4.86	0.04	0.00
2100	6.31	23.37	64.30	5.94	0.06	0.00
2200	4.61	25.17	62.83	7.28	0.08	0.00
2300	2.79	27.37	60.87	8.86	0.07	0.00
2400	1.54	29.95	57.84	10.55	0.06	0.00
2500	0.97	33.07	53.58	12.24	0.05	0.00

The 0-D batch reactor simulation results indicate that the majority of the products in the whole system are 3-ring PAHs (yield > 90%), 2-ring PAHs are second to it, and the yield of 4-ring PAHs are too low to be shown here. P1-CS4 and P4-CS1 are the main 2-ring products. P1-CS9, P2-CS29,

P3-CS8 and P3-CS12 are the dominant 3-ring products. Among all products, it is apparent that P3-CS8 and P2-CS29 are prevailing at all pressures and temperatures investigated, they occupy around 90% of the total output. As temperature increases from 1000 K to 2500 K, the production of P3-CS8 decreases around 25%; meanwhile, the production of P2-CS29 is almost doubled. Pressure has small impact on the production of P3-CS8: as pressure increases from 0.01 atm to 10 atm, it increases from 79.25% to 81.27% at 1000 K, and decreases from 54.98% to 53.58% at 2500 K. As for P2-CS29, its production changes from 13.44% to 13.16% at 1000 K when pressure increases from 0.01 atm to 10 atm; while at 2500 K, its production increases from 23.69% to 33.07% with the same pressure increment.

The production of P3-CS12 and P1-CS9 are next to that of P3-CS8 and P2-CS29. The yields of P3-CS12 monotonically increase with temperature and pressure, and is up to 12.24 % at 2500 K and 10 atm. The yields of P1-CS9 present a similar temperature trend at 0.01 atm and 0.1 atm, but becomes an irregular inversed “U” shape at 1 atm and 10 atm. It is also observed that the formation of P1-CS9 is suppressed at higher pressure. When pressure increases from 0.01 atm to 10 atm, its production yield decays from 12.52% to 0.97% at 2500 K.

3.2.2 The competitiveness of $C_6H_5C_2H$ reaction system

To check the competitiveness of the investigated $C_6H_5C_2H$ reaction system in terms of large PAHs formation, a comparison with HACA mechanism was carried out. The mole fractions of PAHs with different sizes evaluated using HACA mechanism [14] and $C_6H_5C_2H$ reaction system respectively are compared in Figure 7. It is notable that the predicted concentration of PAHs with 3 and 4 rings using the HACA mechanism is not observable, which may be explained by the low efficiency of C_2H_2 addition reaction in large PAH formation. In the HACA mechanism, two PAHs are not allowed to be combined into a larger PAHs, and only the addition of C_2H_2 can increase the

of rings on PAHs. On the contrast, the formation of PAHs with 3 and 4 rings is greatly number enhanced by considering the $C_6H_5C_2H$ reaction network, especially at higher temperatures and pressures. It is because the $C_6H_5C_2H$ reaction network supplies the possibility that the increase of rings can be rapidly achieved by the recombination reaction of PAHs radical and PAH with side chain. The reaction active site on $C_6H_4C_2H$ may be occupied by C_2H_2 molecule, which may decrease the production of 3-ring PAHs via $C_6H_5C_2H$ reaction network. Therefore, we further evaluate the mole fraction of products using the combination of $C_6H_5C_2H$ reaction network and HACA mechanism at different temperatures. The comparison results illustrated in Fig. S7 in the supplementary material showed that the 3-ring PAHs is dominantly fomed by the proposed $C_6H_5C_2H$ reaction network.

Figure 7. Comparison of HACA mechanism and the $C_6H_5C_2H$ reaction network in the production of PAHs with different sizes at various temperatures when $P = 1$ atm. The insert shows the main structures of 3-ring PAHs in the products.

Temperature plays an important role in the yield of products. If the reaction accomplishment degree can be evaluated by the consumption amount of the initial reactant ($C_6H_5C_2H$, or CS1), a higher consumption of CS1 means a higher reaction accomplishment degree. As temperature

increases, the accomplishment degree of the reaction system becomes higher. At 1 atm, the reaction degrees are 12%, 61%, 77%, and 82% at 1000 K, 1500 K, 2000 K, and 2500 K, respectively. Additionally, the production of 3-ring PAHs monotonically increases as temperature in the $C_6H_5C_2H$ network. But in the HACA pathways, the production of 2-ring PAHs, which are the main products, increases with temperature before 1500 K, then decreases after 2000 K. The occurrence of the temperature at the maximum PAHs yield resulting from the equilibrium between forward and reverse reactions. Before the temperature of the maximum PAHs yield, the PAHs formation reactions are prevailing; and after this temperature, the PAHs decomposition reactions become prevailing. In our $C_6H_5C_2H$ network, the equilibrium has not reached until 2500 K. The high energy barriers should be accounted for this phenomenon.

All in all, the comparison results indicate that the consideration of the $C_6H_5C_2H$ reaction network improves the efficiency of PAHs formation, especially for larger PAHs, which subsequently promotes the formation of soot particles in combustion conditions.

4. Conclusions

In this paper, a new reaction network initiated by phenylacetylene ($C_6H_5C_2H$) addition is comprehensively investigated. The potential energy surfaces of all chemical species and transition states are calculated using a combination of the density functional theory (DFT/B3LYP/6-311+G(d,p)) and the complete basis set method (CBS-QB3), and the temperature- and pressure-dependent reaction rate coefficients are calculated using both RRKM and TST. There are 263 species and 65 reactions (from RRKM calculations) in this system. The yield distributions of the products are evaluated in a closed 0-D batch reactor model in Chemkin. It is found that there are

five reaction pathways branched from the initial addition reaction, leading to the production of PAHs including 1-, 2-, 3-, and 4-ring PAHs.

The kinetic analysis shows that the reaction rate coefficients in $C_6H_5C_2H$ reaction network are temperature-dependent and reasonably pressure-independent above 1300 K. The prevailing products of this network are 3-ring PAHs with side chain: P3-CS8, P2-CS29, P1-CS9, and P3-CS12. The yield analysis considered the whole $C_6H_5C_2H$ reaction system indicates that the yield of main product increases obviously at higher temperature due to a higher consumption of reactant.

Compared to the pathway of $C_6H_5C_2H (+H+C_2H_2) \rightarrow$ naphthalene $(+H+C_2H_2) \rightarrow$ 1-ethynylnaphthalene $(+H+C_2H_2) \rightarrow$ phenanthrene $(+H+C_2H_2) \rightarrow$ 1-ethynylphenanthrene, the $C_6H_5C_2H$ reaction system is more efficient to generate larger PAHs like 1-ethynylphenanthrene. This $C_6H_5C_2H$ reaction network supplies a new way for PAHs growth without the addition of small species such as C_2H_2 . It emphasizes the importance of species including side chains in combustion environments in PAH formation and growth.

Supporting information

Potential energy surfaces for other pathways involved in $C_6H_5C_2H$ reaction system, reaction rate coefficients, energies, vibrational frequencies, rotational constants, external symmetry number, optical isomers, electronic ground state, Lennard-Jones parameters for all optimized structures at DFT/B3LYP/6-311+G(d,p) (or CBS-QB3) level in this work. The simulated mole fraction of different PAH using HACA mechanism, $C_6H_5C_2H$ reaction network, and HACA + $C_6H_5C_2H$ reaction network at different temperatures.

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TOC Graphic