Computational study of polycyclic aromatic hydrocarbons growth by vinylacetylene addition

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Abstract: The growth of polycyclic aromatic hydrocarbons (PAH) can proceed via multiple chemical mechanisms. The mechanism of naphthyl radical and vinylacetylene (C_4H_4) addition reaction has been systematically investigated in this computational study. A combination of DFT/B3LYP/6-311+G(d,p), CCSD/6-311+G(d,p) and CBS-QB3 methods were performed to calculate the potential energy surfaces. It revealed that the products, including phenanthrene, anthracene, a PAH with a five-membered ring structure, and PAH with a C_4H_3 radical substitution, can be formed in A₂-1 (1-naphthyl)+ C_4H_4 and A₂-2 (2-naphthyl) + C_4H_4 reaction networks. The reaction rate constants at 0.1-100 atm were evaluated by RRKM theory by solving the master equation in the temperature range of 800-2500 K, which showed that the rate constants of reactions A₂-1 (A₂-2)+ C_4H_4 →product+H are highly temperature-dependent but nearly pressure-independent. The distribution of products was investigated in a 0-D batch reactor, wherein the initial reactant concentrations were taken from experimental measurements. The results showed that adduct intermediates were the main products at low temperature ($T < 1000$ K), and the phenanthrene and PAH with C_4H_3 radical substitution became the dominant products at temperatures where PAHs and soot form in flames ($T > 1000$ K). It was observed that a significant amount of phenanthrene is formed from PAH with a C_4H_3 radical substitution with the assistance of H atom. Reaction pathway sensitivity analysis for the PAH radical+ C_4H_4 reaction system was performed and showed that the new benzene rings are more likely to be generated near the zig-zag edge surface site instead of the free edge. For the development of a PAH mechanism, the analogous treatment of rate constants for larger PAH radical + C_4H_4 reaction system are discussed. The formation rate of naphthalene from the reaction of phenyl+ C_4H_4 was found to be very close to that of phenanthrene from the reaction of naphthyl+ C_4H_4 , suggesting that the analogous treatment of the rates is reasonable in PAH mechanisms.

Keywords: PAHs, soot, nucleation, mechanism, kinetics.

1. Introduction

The chemistry of polycyclic aromatic hydrocarbons (PAHs) draws significant attention in combustion, atmospheric, and material carbon science. One reason for this interest is because PAH chemistry has improved the production efficiency of 2-D and 3-D carbon materials, which present outstanding thermal conductivity as well as mechanical and electrical properties, via a chemical vapor deposition (CVD) method [1-3]. However, controlling the quality of the formed 2-D and 3-D materials in commercial application remains a challenge, due to a lack of fundamental knowledge about the formation mechanism of PAHs [4, 5]. Furthermore, the formation mechanism of PAHs is a major concern in the combustion community, since PAHs formed during incomplete combustion of hydrocarbon are regarded as soot precursors [6-8]. Developing accurate models of PAH and soot formation is important for many reasons, including the development of cleaner combustion engines [9, 10] and understanding the formation of interstellar dust [11, 12].

The growth of PAHs, starting with benzene (A_1) in flames, has long been modeled by the hydrogen-abstraction/acetylene-addition (HACA) framework originally proposed by Frenklach and coworkers [13]. Following a more extensive approach, Mebel et al. [14] discussed the branching ratio of products in a benzene + acetylene reaction system. The results confirmed that naphthalene (A_2) was the dominant product of the HACA framework over a wide range of temperatures and pressures. On the other hand, recent experimental and theoretical results indicate that the HACA pathway does not explain the addition of new benzene rings (such as naphthalene to phenanthrene) on PAHs. Parker et al. [15] investigated the reaction of 1- and 2-naphthyl radical and acetylene at combustion-like temperatures using photoionization mass spectrometry. The results revealed that the dominant product was acenaphthylene produced via a HACA-based reaction scheme, while anthracene and phenanthrene were not detected. Liu et al. [16] further investigated the possible reasons for these observations, and suggested that the site effect should account for this phenomenon. They found that the H abstraction and C_2H_2 addition reactions on the ortho-position (relative to the existing C_2H substitution) and bay surface site, were kinetically unfavored, when compared to other site options, due to the relatively high energy barrier and orientation hindrance effect. In this way, the incremental addition of new benzene rings is unlikely to occur when the reactant PAH is as large as, or larger than, naphthalene, and PAHs with five-membered rings are the preferred products in the HACA framework. The non-radical based PAH- C_2H_2 pathway, in which C_2H_2 attacks the close-shell PAH molecule followed by an H_2 release, can introduce a new benzene ring on armchair and bridge surface sites of PAHs [7]. This pathway describes possible PAHs growth in regions where radical concentration is very low, such as in the post-flame region and interstellar space. However, the majority of PAHs are formed in sooting flame, where radical species are abundant [8, 17]. Raj et al. [18] investigated the role of PAH growth initiated by propargyl (C_3H_3) addition onto naphthalene and the naphthyl radical, and concluded that the new benzene ring may form if C_3H_3 attacks the zig-zag site of PAH. However, the low concentration of C_3H_3 may limit its

application in some flames. Therefore, other radical-based pathways responsible for the addition of new benzene rings on PAH molecules should be explored.

One likely mechanism to produce new benzene rings is the addition reaction of vinylacetylene (C_4H_4) and PAH radicals, since a second addition of other carbon species is not required during the cyclization process. C_4H_4 is abundant in combustion environments, including premixed ethylene, benzene, toluene, and gasoline flames [19-22]. The measured mole fraction of C_4H_4 is up to 2×10^{-3} , comparable to C_2H_2 [19-22]. Correlations between C_4H_4 and PAH formation are greater under CVD process conditions. A significant amount of PAHs, including naphthalene, phenanthrene, and pyrene, were detected by Norinaga et al. in a CVD process with acetylene as the carbon source [23]. They analyzed the concentration of gas-phase compounds further, and their results showed that the major active species was C_4H_4 with a mole fraction of 3×10^{-1} .

Among the addition reactions of C_4H_4 with aromatic species, the phenyl+ C_4H_4 reaction has received special attention [24-29]. The phenyl+ C_4H_4 reaction was first considered in the PAHs mechanism by Appel et al. [27], and modelling results showed that phenyl+ C_4H_4 reaction is the main route of naphthalene formation in ethylene flames. Subsequently, the addition reactions of C_4H_4 with PAHs radical have been merged into PAH mechanisms, assuming reaction rate coefficients to be equal to that of phenyl+ $C_4H_4 \rightarrow$ naphthalene+H [28, 30-33]. The rate coefficients of the reaction phenyl+ $C_4H_4 \rightarrow$ naphthalene+H come primarily from two sources. One was suggested by Appel et al. [27] with the expression of $2.5 \times 10^{29} \times T^{-4.43} \times \exp(-26400/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Application examples include the PAHs mechanisms proposed by Pang et al. [32] and Chernov et al. [28]. However, the rate coefficient may be problematic, as the pre-exponential factor at 1000 K is $1.6 \times 10^{16} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is beyond the physical collision limit ($\sim 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The other one was suggested by Aguilera-Iparraguirre et al. [34] using density functional theory (DFT) and transition state theory (TST) calculation. The rates is used in the PAH mechanism proposed by Wang et al. [33]. Here, the reaction rate coefficients of $C_4H_4 +$ phenyl $\rightarrow$ naphthalene + H were assumed to be equal to that of the entrance elementary reaction step (C_4H_4 molecule attaches to the phenyl radical). Such treatment may exaggerate the role of C_4H_4 in PAHs growth, as the formation of other isomers and the H loss from the $C_6H_5C_4H_4$ intermediate are probable. This is evidenced by the experimental study of Zhao et al. [26], in which trans-1-phenylvinylacetylene and the 4-phenylvinylacetylene were also the main products in the reaction of phenyl+ C_4H_4 . The formation of trans-1-phenylvinylacetylene and 4-phenylvinylacetylene is interesting, as they are suitable precursors for the chemical coalescence inception pathway due to their high reactivity and concentration in flame.

Chemical coalescence inception pathways are the other driving force for determining whether appreciable amounts of PAHs with radical substitutions can be produced from PAH radical + C_4H_4 reaction in sooting flames. Furthermore, it is notable that phenyl radical only consists of free edges, but larger PAH radicals contain free

edge and zig-zag surface sites at least. Therefore, the accuracy of the analogy treatment of reaction rates from phenyl+C₄H₄ reaction to PAH radical + C₄H₄ reactions requires further investigation, as the kinetics are highly sensitive to the type of targeted surface site instead of the size of PAHs in growth and oxidation processes [35-39]. Thus, obtaining reliable reaction rate coefficients and yield distribution of products in PAH radical + C₄H₄ reaction system is crucial to better understand PAH formation in flames and materials production.

The addition reaction of C₄H₄ with PAH radicals has received little attention. To the best of our knowledge, only the addition reactions between C₄H₄ and 1-naphthyl/2-naphthyl were recently assessed by Zhao et al. [40], with an emphasis on the PAH formation at low temperatures (70-180 K) relevant to conditions on Titan. Naphthalene (A₂) is the simplest PAH with free-edge and zig-zag surface sites, providing an opportunity to explore the site effect of PAH radical + C₄H₄ reactions using high-level theoretical procedures. In this study, the addition reactions of C₄H₄+1-naphthyl radical (A₂-1) and C₄H₄+2-naphthyl radical (A₂-2), are systematically investigated with an emphasis on PAH formation at flame temperatures. The potential energy surfaces (PES) are explored by a combination of density functional theory (DFT) B3LYP/6-311+G(d,p), CCSD(T)/6-311+G(d,p), and CBS-QB3 methods. Reaction rate coefficients were subsequently determined by RRKM theory by solving the master equation at various temperatures and pressures. Based on the kinetic parameters, the potential yield distributions of products are investigated at combustion conditions via a 0-D batch reactor. Finally, reaction pathway sensitivity analysis and the analogous treatment for kinetic parameters in other PAH radical + C₄H₄ reaction systems for PAH mechanism development are discussed.

2. Calculation details

In this study, the close-shell and open-shell structures were optimized at the DFT B3LYP 6-311 G+(d,p) level, with restricted wave function and unrestricted wave functions respectively [41-43]. The same method was utilized to obtain frequency information with a correction factor of 0.967, which was originally obtained for the DFT B3LYP 6-311 G+(3df,2p) method [44]. To improve energy accuracy, the sum of electronic and zero-point energy was refined with the CBS-QB3 method, a single-determinant reference state method. The root-mean-square deviation of CBS-QB3 energy for hydrocarbon molecule was 1.49 kcal/mol [45]. T1 diagnostics were performed at the CCSD(T)/6-311+G(d,p) level with DFT structures to assess whether the CBS-QB3 method was suitable for the energy calculation. A larger T1 value means that a multiple-determinant reference state method should be applied to calculate the energy. Here, the threshold value of T1 was considered as 0.02 for close-shell structures, and 0.045 for open-shell structures [21, 46, 47]. T1 diagnostics results indicated that the energies of 27 molecules among the 150 molecules in this study should be described by a multiple-determinant reference state method. Energy calculations using the multiple-determinant reference state CASPT2 method can be used for these structures. The strength of the CASPT2 method is its ability to give exact spin states, but its application for large

molecule is limited by the computational cost. The number of active orbitals used in CASPT2 calculation should be larger than the minimum required to describe the strong (static) correlation, otherwise its accuracy may be lower than the CBS-QB3 method [48]. Our case showed that 500 GB memory was not sufficient for the CASPT2 (6,6) calculation, not to mention the more active orbitals calculation. In this study, all energies were given at the CBS-QB3 level and used in rate calculation, although the energies of species with high T1 diagnostic values may not be entirely reliable. Fortunately, the energies of these species were of lesser importance in this study, as the pathways where these structures existed were significantly less competitive than other pathways in the kinetic analysis. All T1 diagnostics values are listed in Table S1 in the supplementary material. In addition, two transition states of the entrance reactions (C_4H_4 attaches to naphthyl radical) failed to converge in the CCSD(t)/6-31+G(d') step in CBS-QB3 calculations due to spin contamination. To make our comparisons more rigorous, the energy barriers for all competing entrance reactions were taken from the DFT/B3LYP/6-311+G(d,p) level in rate calculations. All quantum chemistry calculations were performed using a Gaussian 09 software package with version D.01.

Based on the obtained quantum chemistry results, including vibrational frequencies, energy barriers, moments of inertia, and other molecular parameters, we evaluated the global reaction rate coefficients (e.g., $A_2-1 + C_4H_4 \rightarrow$ Product A + H) via RRKM theory by solving the master equation. The MultiWell suite of codes (MultiWell-2017.1) was utilized for the kinetic calculations. PES results showed that the investigated A_2-1 (or A_2-2) + C_4H_4 reactions were multi-well bimolecular reactions, as illustrated by (1). Three steps were taken to evaluate the global reaction rate coefficients. Specifically, the rate coefficient of $Intermediate1 \rightarrow A_2-1$ (or A_2-2) + C_4H_4 reaction was determined by initiating the Intermediate1 with thermal energy distribution. Subsequently, the rate coefficients of recombination reaction A_2-1 (or A_2-2) + $C_4H_4 \rightarrow Intermediate1$ were calculated via the combination of its reverse reaction rate coefficients and equilibrium constants. Finally, the global reaction rate coefficients of A_2-1 (or A_2-2) + $C_4H_4 \rightarrow$ Product A + H were evaluated by multiplying the yield of Product A and the rate coefficients of A_2-1 (or A_2-2) + $C_4H_4 \rightarrow Intermediate1$. The yield of Product A was obtained by initiating the Intermediate1 with chemical activation energy distribution. The simulation time was long enough for the reaction to reach the equilibrium. In this way, the yield of Product A was a constant under the given temperature and pressure conditions.

The reaction rate coefficients were evaluated in the temperature range of 800-2500 K and pressure ranges of 0.1-100 atm. In MultiWell calculations, the maximum energy was set as 300,000 cm⁻¹. The translational and vibrational temperatures were set to be equal. The sums and densities of states were calculated by exact count with an energy grain size of 10 cm⁻¹. Both the temperature-independent exponential-down model with $\langle \Delta E_{\text{down}} \rangle = 260 \text{ cm}^{-1}$ [49], and the temperature-dependent exponential down model $\langle \Delta E_{\text{down}} \rangle = 200 \times (T/300 \text{ K})^{0.85} \text{ cm}^{-1}$ [50] were used to describe the collisional energy transfer. In A₂-1 + C₄H₄ (C1) reaction systems, the calculated yields of various products with these two collisional energy transfer models were almost the same, as presented in Fig. S1 in the supplementary material. In this study, the temperature-independent exponential-down model with $\langle \Delta E_{\text{down}} \rangle = 260 \text{ cm}^{-1}$ was employed for other reaction cases. Argon was selected as the bath gas collider. The Lennard-Jones parameters σ and ϵ/k_B of Argon were equal to 3.47 Å and 114 K, respectively. In addition, the Lennard-Jones parameters of the PAH structures were assumed to be equal with that of phenanthrene (A₃), as the values are mainly determined by molecule size [51]. The symmetry numbers of all local structures were determined according to the study by Ducan [52]. The real frequencies below 100 cm⁻¹ were carefully examined, and all internal rotations were treated as 1-D hindered rotations [35]. The torsional potential energy and the rotation constant as a function of dihedral angle were obtained via the relaxed potential energy surface scans at the DFT/B3LYP/6-311 G+(d,p) level, and are shown in Table S7 in the supplementary material. A dihedral angle step of 20° was used in the scan calculation. The number of stochastic trials changed from 1×10⁶ to 1×10⁷ to keep statistical fluctuations below 3%.

A 0-D batch reactor in Chemkin-Pro software was used to investigate the yield distribution and the formation rate of new benzene in A₂-H-C₄H₄-H₂-N₂ (A₁-H-C₄H₄-H₂-N₂) reaction system, with A₂ (A₁), H, C₄H₄, H₂ and N₂ as the initial reactants. The mole fractions of A₂ (A₁) and C₄H₄ were set as 6.18×10⁻⁵ and 4.0×10⁻⁴ respectively, as measured in a premixed sooting ethylene flame by Castaldi et al. [17]. The mole fractions of H, H₂ and N₂ were assumed to equal 1.0×10⁻⁴, 1×10⁻², and 0.9894382 (N₂ = 1 - A₂ - C₄H₄ - H - H₂), respectively. The reaction network and corresponding kinetics considered in A₁-H-C₄H₄-H₂-N₂ reaction system are listed in Table 1. The kinetic information for A₂-H-C₄H₄-H₂-N₂ reaction system comes from this study, as shown in Table 2. It should be noted that A₂-1 and A₂-2 are generated via the H abstraction reactions (A₂+H → A₂-1+H₂ and A₂+H → A₂-2+H₂) in the A₂-H-C₄H₄-H₂-N₂ reaction system. The H abstraction reaction rate constants came from [16]. The residence time in 0-D batch reactor is set as 10 ms, and investigated temperature ranges from 1000-1750 K.

3. Results and discussion

A₂-1 and A₂-2 exist simultaneously in the flame, and their concentrations are determined by the H abstraction reactions of A₂ with H, OH, CH₃ and other active radicals. In this study, both A₂-1+C₄H₄ and A₂-2+C₄H₄ reactions

were studied. Each C atom on the C₄H₄ molecule is active, due to the double and triple bonds, and can attack active C atoms on PAH molecules. In this way, there are eight entrance channels, if the possibilities of all reaction are considered. To simplify the complicated A₂-1+C₄H₄ and A₂-2+C₄H₄ reaction systems in a reasonable manner, we first investigated the rates of every entrance reaction. As shown in Fig.1 (a), the rate coefficients of A₂-1+C₄H₄ entrance reactions with C(2) and C(3) atoms on C₄H₄ molecule as the target sites are lower than that of C(1) and C(4) atoms by at least one order of magnitude at 1500 K. The result is mainly due to the difference in the energy barriers. The energy barriers of addition reactions involving C(2) (8.1 kcal/mol) and C(3) (7.2 kcal/mol) are more than twice that of reactions involving C(1) (3.1 kcal/mol) and C(4) (2.3 kcal/mol). The kinetic feature of A₂-2+C₄H₄ is similar to that of A₂-1+C₄H₄, as shown in Fig.1 (b). Kinetic results indicate that PAH radicals attacked by the C(1) and C(4) atoms on C₄H₄ molecule are more favorable than by the C(2) and C(3) atoms. In this study, we only discuss the reaction possibilities of A₂-1+C₄H₄ and A₂-2+C₄H₄ reactions with C(1) and C(4) atoms on C₄H₄ molecules as the target sites, namely A₂-1+C₄H₄ (C1), A₂-1+C₄H₄ (C4), A₂-2+C₄H₄ (C1), and A₂-2+C₄H₄ (C1) reaction systems. It should be noted that a complex is first formed between A₂-1 and C₄H₄ fragments in the study by Zhao et al. [40]. This process was also checked by IRC calculations in this study, as shown in Fig.S2. The complexes with relative strong van-der-Waals force were not found except in A₂-1+C₄H₄ (C4) system at the DFT/B3LYP/6-311+G(d,p) level. The existence of such complexes mainly influences the kinetic rate in the low temperature region (e.g., T < 300 K), and does not affect the kinetic results at flame temperature due to the short lifetime; therefore, the formation of complexes has been ignored in this study. Two examples of similar treatments can be seen in phenyl+C₄H₄ reactions [29, 34].

3.1 Potential energy surface and yield distribution

3.1.1 A₂-1+C₄H₄ (C1) reaction system

The PES of the A₂-1+C₄H₄ (C1) reaction system is shown in Fig. 2. The entrance reaction of A₂-1 and C₄H₄ (C1) produced the adduct CS2, which split into six channels. Two channels involve the H elimination from the C₄H₄ substitution on adduct CS2 via pathways CS2→CS10_P+H (46.2 kcal/mol) and CS2→CS11_P+H (54.8 kcal/mol). Here, the energy barrier of H elimination from the C₄H₄ substitution was much higher than from the aromatic rings. Examples include reactions CS6→CS7_P+H (13.8 kcal/mol) and CS14→CS7_P+H (28.6 kcal/mol). Alternatively, the adduct CS2 may undergo a six-member ring closure to CS3 (CS2→CS3, 42.4 kcal/mol). CS3 is a structure with one bare C atom and two adduct H atoms, and may lead to the formation of phenanthrene (CS7_P) via two pathways: CS3→CS5→CS6→CS7_P+H and CS3→CS9→CS14→CS7_P+H. Both pathways involve two H migration reactions and one H elimination reaction. In the former pathway, one adduct H atom first migrates to the adjacent saturated C atom (CS3→CS5, 54.6 kcal/mol), then migrates to unsaturated C atoms (CS5→CS6, 7.2 kcal/mol). In the latter pathway, the other adduct H atom first migrates to

the ortho-position saturated C atom (CS3→CS9, 29.0 kcal/mol), then migrates to the unsaturated C atom (CS9→CS14, 46.2 kcal/mol). It was noted that the energy barrier of H transfer reaction CS9→CS14 (46.2 kcal/mol) was higher than that of the similar reaction CS5→CS6 (7.2 kcal/mol) by 6.4 times, although they share almost the same reaction features. The higher energy barrier in CS9→CS14 reaction may result from the larger coulomb force between the H atom (donor) and the unsaturated C atom (acceptor) [21]. In addition, a phenanthrenyl radical (CS15) may form from the 2-H elimination reaction, but this process is kinetically unsupported due to the relatively high energy barrier (77.7 kcal/mol).

In terms of the energy barrier, the adduct CS2 is more likely to form the CS4 structure, which is featured with H transfer from the benzene ring to the bare β -C atom on the C₄H₄ substitution (CS2→CS4, 34.3 kcal/mol), as shown in Fig.2. The CS4 structure can lead to the products CS10_P and CS7_P through channels of CS4→CS8→CS16→CS10_P+H, and CS4→CS8→CS16→CS18→CS19→CS6→CS7_P+H. The reaction step of CS4→CS8 is a C-C rotation process, followed by H transfer from C₄H₄ to the unsaturated C atom on the benzene ring (CS8→CS16, 29.0 kcal/mol). It should be noted that the intermediate CS16 can also form directly from CS2 via H transfer on the C₄H₄ substitution. The subsequent H elimination reaction from the β -C atom on the substitution site (CS16→CS10_P+H, 44.6 kcal/mol) produces CS10_P. Alternatively, product CS7_P forms after the cyclization reaction (CS16→CS18, 42.1 kcal/mol), intermolecular H transfer reactions (CS18→CS19, 41.7 kcal/mol and CS19→CS6, 37.4 kcal/mol), and H elimination reaction (CS6→CS7_P+H, 13.8 kcal/mol). H migration on the adduct CS2 from the terminal C atom to the unsaturated C atom on the C₄H₄ substitution leads to the formation of the CS12 structure, with an energy barrier of 58.4 kcal/mol (CS2→CS12). This process causes the middle C-C double bond to become a C-C single bond, and the terminal C atom becomes active. Benefitted from these features, the subsequent C-C rotation reaction (CS12→CS13, 4.7 kcal/mol) and cyclization reaction (CS13→CS6, 2.4 kcal/mol) proceed rapidly once CS12 forms, due to the low energy barrier. Here, the intermediate CS13 bridges the product CS17_P and product CS7_P via the channel of CS17_P+H→CS13→CS6→CS7_P+H, which proves to be an important conversion channel for A₃ formation in the following kinetic analysis.

With these quantum chemistry results, the yields of product in this reaction network were calculated using RRKM theory by solving the master equation. As shown in Fig.3 (a), the formation of products in A₂-1+C₄H₄ (C1) reaction system is greatly sensitive to temperature. When the temperature is below 1000 K, the reactions trend toward remaining at the CS2 adduct intermediate due to the relatively high energy barrier in further isomer reactions. At higher temperatures, the main products are PAH with a C₄H₃ radical substitution (CS10_P and CS11_P), and the closed-ring product CS7_P is the minor product. This matches well with the yield distribution

in phenyl+C₄H₄ reaction systems [25]. The results also indicate that it is unreasonable to treat closed-ring products, such as CS7_P as the sole products in a PAH radical + C₄H₄ reaction in mechanism [33]. With CS6 or CS14 as the initial well, the mole fraction of the reactant (CS7_P+H) is still 100 % when the reaction reaches equilibrium, indicating that the formation of CS7_P in this reaction system can be regarded as an irreversible process. On the other hand, the formation of CS10_P and CS11_P is highly reversible. The kinetic characteristics of reactions CS10_P+H→products and CS11_P+H→products were investigated. In this way, the rate constants of reverse reactions can be evaluated. The results shown in Fig.3 (b)-(c) suggest that CS11_P+H and A₂-1+C₄H₄ are the dominant products in CS10_P+H→products reaction, and CS10_P+H and A₂-1+C₄H₄ are the dominant products in CS11_P+H→product reaction. Considering that the conversion between A₂-1+C₄H₄, CS10_P+H, and CS11_P+H is a rapid process due to the high reaction rate at flame temperatures, because of its irreversibility, the yield of CS7_P may be higher when the reaction system reaches equilibrium. Evidenced from Fig.3 (a)-(c), the formation of CS17_P+H can be ignored in this reaction network. However, the formation of CS17_P+H is favorable in the following A₂-1+C₄H₄ (C4) reaction system. The yield distribution of CS17_P+H→products reaction with CS13 as the initial well was examined. The results shown in Fig. 3 (d) confirm that the conversion of CS17_P+H toward CS7_P+H is a rapid process caused by the low energy barrier in the channel CS17_P+H→CS13→CS6→CS7_P+H.

3.1.2 A₂-1+C₄H₄ (C4) reaction system

The adduct CS20 forms when the C4 atom on C₄H₄ attaches to A₂-1 and splits into four pathways, as shown in Fig.4. Unlike the above A₂-1+C₄H₄ (C1) reaction system, the CS20 cannot cyclize to the third six-membered ring (like CS2→CS3 reaction). It produces directly CS17_P by H elimination from the C4 atom on the substitution (CS20→CS17_P+H, 44.5 kcal/mol). This provides a competitive pathway for A₃ formation, namely A₂-1+C₄H₄ (C4)→CS20→CS17_P+H→CS13→CS6→CS7_P+H. Alternatively, the other H elimination from the C4 atom on the substitution generates the conformer CS65_P species. The energy barrier of CS20→CS65_P+H (44.2 kcal/mol) is close to that of CS20→CS17_P+H. The H transfer from the benzene ring on CS20 to the β-C atom on the C₄H₄ substitution is another probable reaction (CS20→CS29, 35.1 kcal/mol) with a lower energy barrier, compared to CS20→CS17_P+H reaction. Once formed, CS29 can lead to the formation of CS7_P and a phenanthrenyl radical (CS33) via the pathways of CS29→CS30→CS31→CS32→CS7_P+H, CS29→CS30→CS31→CS38→CS7_P+H, and CS29→CS30→CS31→CS32→CS33+H. The three pathways are generally similar, and include a C-C rotation reaction (CS29→CS30, 3.6 kcal/mol), a cyclization reaction (CS30→CS31, 7.6 kcal/mol), H transfer reactions (CS31→CS32, 41.1 kcal/mol or CS31→CS38, 44.5 kcal/mol), H elimination (CS32→CS7_P+H, 26.8 kcal/mol or CS38→CS7_P+H, 27.9 kcal/mol), and an H₂ elimination reaction (CS32→CS33+H₂, 77.3 kcal/mol).

Of the three pathways, starting from CS20, the C-C bond rotation reaction of CS20→CS21 occurs with a low energy barrier (4.7 kcal/mol). The C₄H₄ substitution rotates slightly toward the zig-zag surface site of the intermediate CS21, which makes possible the formation of a five-membered ring, though the reaction of CS21→CS22 (20 kcal/mol), and a six-membered ring though the reaction of CS21→CS34 (33.7 kcal/mol) possible. The energy barrier of the five-membered ring formation is lower than that of the six-membered ring formation by 13.7 kcal/mol. This means that the formation of the CS22 structure with a five-membered ring may be favorable. The CS22 is a non-planar structure caused by three superfluous H atoms. The H elimination and C₂H₂ releasing reactions produce more stable chemical structures at flame temperatures. Here, H elimination from the benzene ring gives the product CS37_P. Other H elimination reactions and C₂H₂ releasing reactions for CS22 are studied in the pathways of CS22→CS23→CS24→CS25→CS26→CS27+H (green dash in Fig.4) and CS22→CS23→CS28+C₂H₂ (green dash in Fig.3). The PES of both pathways lie above the others in Fig.4, indicating that the formation of products CS27 and CS28 can be ignored. This is confirmed in the following kinetic analysis.

The yield distribution of products in the A₂-1+C₄H₄ (C4) reaction system is shown in Fig. 5. Similar to the A₂-1+C₄H₄ (C1) reaction system, the adduct intermediate CS20 survives with high yield value when the temperature is below 1000 K. At higher temperatures, the main products are CS7_P, CS17_P, CS37_P, and CS65_P in the reaction of A₂-1+C₄H₄ (C4). The yield of CS7_P, CS17_P, CS37_P, and CS65_P increase rapidly in the temperature range of 800-1300 K; their yield curves are different at higher temperature. The yields of CS17_P and CS65_P increase slightly and converge to 43% at higher temperatures. In contrast, the yields of CS7_P and CS37_P peak at 1200 K with values of 11.4% and 41.4%, respectively, and they decrease linearly in the temperature range of 1200-2500 K. The formation of the minor product CS35_P can be ignored as the yield is less than 0.1% in the whole temperature region. Once formed, the open-ring products, including CS17_P, CS37_P, and CS65_P, are likely to return to the reaction network with an H addition, due to high reaction reversibility. As shown in Fig.5 (b)-(d), CS17_P+H, CS37_P+H, and CS65_P+H reactions share similar yield features. The results show that the self-conversion between CS17_P+H, CS37_P+H, and CS65_P+H are preferred, and the formation of CS7_P is only favorable in the temperature range of 1000-1700 K where the yield value is large than 5%. The conversions from CS17_P+H, CS37_P+H, and CS65_P+H to reactant A₂-1+C₄H₄ are kinetically unsupported, and the peak yield value of A₂-1+C₄H₄ is only 1%. Combined with the channel CS17_P+H→CS13→CS6→CS7_P+H (shown in Fig. 2), where the CS17_P is quickly consumed to form CS7_P, it can be expected that a significant amount of CS7_P may be converted from other products with the assistance of the H atom in the entire A₂-1+C₄H₄ (C1+C4) reaction system.

3.1.3 A₂-2+C₄H₄ (C1) reaction system

The discussions above focus on reactions with A₂-1; here the focus is on reactions with A₂-2. The PES of A₂-2+C₄H₄ (C1) reaction system is shown in Fig.6. When the C1 atom of C₄H₄ attacks the active carbon on the benzene ring, the adduct CS40 forms and splits into six different reaction channels. Two of the six channels lead to the formation of CS54_P and CS55_P via H elimination reactions, those are CS40→CS54_P+H (47.9 kcal/mol) and CS40→CS55_P+H (54.9 kcal/mol). Two other channels, starting from CS40, converge at CS50 with the C₄H₄ substitution. Specifically, CS50 forms from the channels of CS40→CS48→CS49→CS50 and CS40→CS50. The former channel involves an H transfer from the end C atom to the bare C atom on the C₄H₄ substitution (CS40→CS48, 35.9 kcal/mol), C-C rotation between benzene moiety and C₄H₄ moiety (CS48→CS49, 4.4 kcal/mol), and H transfer from C₄H₄ substitution to the bare C atom on benzene (CS49→CS50, 44.5 kcal/mol). The latter channel CS40→CS50 (55.5 kcal/mol) is the H transfer step occurring on the C₄H₄ moiety. In this reaction network, CS50 leads to the formation of the open-ring CS54_P structure and the closed-ring CS7_P structure. The H elimination reaction (CS50→CS54_P+H, 41.4 kcal/mol) generates the product CS54_P. Alternatively, the product CS7_P can form from the channels of CS50→CS51→CS52→CS32→CS7_P+H and CS50→CS51→CS53→CS43→CS7_P+H, which are featured with a cyclization reaction (CS50→CS51, 39.9 kcal/mol), the H transfer reaction on the benzene ring, and the H elimination reaction.

The first step in the fifth channel (green line in Fig.6) beginning from CS40, is the H migration on the adduct CS40 from the terminal C atom to the bare C atom on the C₄H₄ substitution (CS40→CS45, 58.5 kcal/mol). The energy barrier and the vibration mode of the transition state in this reaction are almost the same as that in the reaction CS2→CS12 in the A₂-1+C₄H₄ (C1) reaction system. Once CS45 forms, the rotation of the C-C bond occurs rapidly, due to the low energy barrier (CS45→CS46, 3.7 kcal/mol). Subsequently, H elimination from CS46 may produce a CS56_P structure (CS46→CS56_P+H, 44.8 kcal/mol). In terms of the energy barrier, the cyclization reaction (CS46→CS47, 1.8 kcal/mol) is more likely, followed by the H elimination reaction (CS47→CS7_P+H, 19.9 kcal/mol), to form the more stable structure CS7_P. The last channel, starting from CS40, is labeled as the orange line in Fig. 4. Here, the cyclization reaction (CS40→CS41, 41.7 kcal/mol) produces the intermediate CS41, featured with two superfluous H atoms and a bare C atom. These features drive the subsequent channels of CS41→CS42→CS43→CS7_P+H and CS41→CS31→...→CS7_P+H, consisting of H transfer reactions and H elimination reactions.

In the A₂-2+C₄H₄ (C1) reaction system, the CS54_P and CS55_P species, formed by H elimination from the adduct intermediate CS40, are the dominant products in the temperature range of 1100-2500 K, as shown in Fig.7

(a). In this case, the yields of CS7_P and CS56_P are 0.8 % and 0.02 % at 1500 K, indicating that the reactions $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS7_P+H and $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS56_P+H are too slow to compete with reactions $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS54_P+H and $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS55_P+H. The entrance well in reactions $A_2-2+C_4H_4$ (C1) $\rightarrow$ products, CS54_P+H $\rightarrow$ products, and CS55_P+H $\rightarrow$ products are the same (CS40), which is the main reason that the yield distribution is similar in each reaction, as shown in Fig (b)-(c). The results shown in Fig (b)-(c) also indicate that the reaction $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS54_P+H and $A_2-2+C_4H_4$ (C1) $\rightarrow$ CS55_P+H are highly reversible, evidenced by the high yield of $A_2-2+C_4H_4$ in the reaction of CS54_P+H $\rightarrow$ products and CS55_P+H $\rightarrow$ products. Although the yield of CS56_P is kinetically unsupported, it is still helpful to explore the yield distribution in reaction CS56_P+H $\rightarrow$ products as the species CS56_P has nearly identical structural features as CS17_P. As shown in Fig. (d), CS7_P is the dominant product of the reaction CS56_P+H $\rightarrow$ products in the temperature range studied, resulting from the low energy barrier in the channel of CS56_P+H $\rightarrow$ CS46 $\rightarrow$ CS47 $\rightarrow$ CS7_P+H.

3.1.4 $A_2-2+C_4H_4$ (C4) reaction system

Generally speaking, the reaction network for the $A_2-2+C_4H_4$ (C4) system shown in Fig.8 is similar to that for $A_2-1+C_4H_4$ (C4) (Fig.4) and $A_2-2+C_4H_4$ (C1) (Fig.6) systems. The adduct intermediate CS57 can lead to the formation of CS7_P via the channels of CS57 $\rightarrow$ CS58 $\rightarrow$ CS45 $\rightarrow$... $\rightarrow$ CS7_P+H, CS57 $\rightarrow$ CS59 $\rightarrow$ CS58 $\rightarrow$ CS45 $\rightarrow$... $\rightarrow$ CS7_P+H, CS57 $\rightarrow$ CS61 $\rightarrow$ CS62 $\rightarrow$ CS43 $\rightarrow$... $\rightarrow$ CS7_P+H, and CS57 $\rightarrow$ CS64 $\rightarrow$ CS44 $\rightarrow$ CS9 $\rightarrow$... $\rightarrow$ CS7_P+H, where the H transfer reactions (CS57 $\rightarrow$ CS58, 66.7 kcal/mol, CS62 $\rightarrow$ CS43, 45.5 kcal/mol, and CS9 $\rightarrow$ CS14, 46.2 kcal/mol) and rotation of C-C double bond (CS58 $\rightarrow$ CS45, 44.8 kcal/mol) are the rate limiting steps. The formation of the open-ring structure CS60_P from CS57 is also a reaction possibility, and it is kinetically supported, due to the relatively low energy barrier (CS57 $\rightarrow$ CS60_P, 40.4 kcal/mol) and pathway simplicity. In this reaction system, the H elimination from ring closure structure CS61 is included, which produces CS63_P, featured with one unsaturated C atom and one superfluous H atom on the same benzene ring. By considering this, it is possible to compare the competitiveness between two reaction pathways. One is the H elimination from intermediates like CS61 with moderate thermal stability, followed by H transfer reaction or H elimination to evolve to a structure with higher thermal stability at combustion temperatures. The other pathway is that the H transfer reaction occurs first, followed by H elimination, to generate a product like CS7_P.

Compared with other reaction systems, the yield distribution in $A_2-2+C_4H_4$ (C4) systems is more concise, as shown in Fig.9 (a)-(b). At flame temperature ($T > 1200$ K), the reaction $A_2-2+C_4H_4$ $\rightarrow$ products mainly produces CS60_P, as shown in Fig.9 (a). In turn, $A_2-2+C_4H_4$ is the dominant product in reaction CS60_P+H $\rightarrow$ products, as

shown in Fig. 9 (b). The yield of CS63_P is lower than 0.01%, meaning that the pathway $\text{CS61} \rightarrow \text{CS63_P} + \text{H} \rightarrow$ steady product is not as competitive as the pathway $\text{CS61} \rightarrow \text{intermediate} \rightarrow \text{steady product} + \text{H}$.

The formation of anthracene (CS71_P) is also possible in $\text{A}_2\text{-2} + \text{C}_4\text{H}_4$ reaction system if the C_4H_4 molecule attaches to the active C atom with a different rotation angle, as shown in Fig. 10. Specifically, CS71_P can be formed from the pathways $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{CS66} \rightarrow \text{CS67} \rightarrow \text{CS68} \rightarrow \text{CS69} \rightarrow \text{CS70} \rightarrow \text{CS71_P} + \text{H}$ and $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{CS72} \rightarrow \text{CS73} \rightarrow \text{CS74} \rightarrow \text{CS75} \rightarrow \text{CS76} \rightarrow \text{CS70} \rightarrow \text{CS71_P} + \text{H}$. In the former pathway, the highest energy barrier exists in the H transfer reaction ($\text{CS69} \rightarrow \text{CS70}$) with the value of 41.6 kcal/mol, which is lower than the energy barrier of corresponding competing reaction ($\text{CS69} \rightarrow \text{CS68}$, 45.7 kcal/mol). This means that anthracene is likely to form from the $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{CS66} \rightarrow \text{CS67} \rightarrow \text{CS68} \rightarrow \text{CS69} \rightarrow \text{CS70} \rightarrow \text{CS71_P} + \text{H}$ pathway in terms of energy barrier. In contrast, CS71_P formation via the latter pathway is unlikely. The energy barriers of elementary reaction steps, involving the formation of new C-C bond ($\text{CS73} \rightarrow \text{CS74}$, 31.2 kcal/mol) and the dissociation of the existing C-C bond ($\text{CS74} \rightarrow \text{CS75}$, 39.9 kcal/mol), are much higher than that of the corresponding competing reactions ($\text{CS73} \rightarrow \text{CS72}$, 19.5 kcal/mol, $\text{CS74} \rightarrow \text{CS73}$, 36.2 kcal/mol). The yield distribution results support the PES analysis. As shown in Fig. 11 (a) and Fig. 11 (c), anthracene (CS71_P+H) is predominantly formed from the former pathway, especially in the temperature range of 900-1400 K where the yield of CS71_P+H is beyond 5 %. Similar to the aforementioned reaction system, the primary products in this reaction system are the CS60_P and CS54_P, which are produced via H-atom abstraction from the intermediates CS66 and CS77, respectively. The secondary H-assisted isomerization of the CS60_P predominantly yields the reactants at high temperature, and produces reactants and anthracene equally around 1000 K as shown in Fig. 11 (b). This indicates that the anthracene may be the preferred product in $\text{A}_2\text{-2} + \text{C}_4\text{H}_4$ reaction system, as compared to phenanthrene in low temperature region. When the temperature is above 1000 K, the secondary H-assisted isomerization CS54_P in this reaction network is unlikely due to the relative lower reaction rate in pathways $\text{CS72} \rightarrow \text{A}_2\text{-2} + \text{C}_4\text{H}_4$ and $\text{CS72} \rightarrow \text{CS73} \rightarrow \text{CS74} \rightarrow \text{CS75} \rightarrow \text{CS76} \rightarrow \text{CS70} \rightarrow \text{CS71_P} + \text{H}$, as shown in Fig. 11 (d). It should be noted that secondary H-assisted isomerization of CS54_P is a rapid process via the channel $\text{CS54_P} + \text{H} \rightarrow \text{CS40}$, as shown in Fig. 6-7.

Apart from the above reaction networks, direct H abstraction reactions including $\text{A}_2\text{-1} + \text{C}_4\text{H}_4 \rightarrow \text{A}_2 + \text{i-C}_4\text{H}_3$, $\text{A}_2\text{-1} + \text{C}_4\text{H}_4 \rightarrow \text{A}_2 + \text{n-C}_4\text{H}_3$, $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{A}_2 + \text{i-C}_4\text{H}_3$, and $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{A}_2 + \text{n-C}_4\text{H}_3$ were considered as shown in Table S3-S5 in the supplementary materials. Furthermore, a comparison of rate constants for $\text{phenyl} + \text{C}_4\text{H}_4 \rightarrow \text{benzene} + \text{n-C}_4\text{H}_3$ [25] and $\text{A}_2\text{-2} + \text{C}_4\text{H}_4 \rightarrow \text{A}_2 + \text{n-C}_4\text{H}_3$ was carried out to extrapolate the rate constants to larger PAH. The rate deviation is within 30 % in the temperature range of 800-2500 K, indicating that the kinetic parameters of H abstraction reactions are suitable for larger PAH radical + C_4H_4 reaction system.

3.2 Kinetic analysis

3.2.1 Reaction rate constants

Based on the quantum chemistry results above, the reaction rate constants were evaluated in the temperature range of 800-2500 K, using RRKM theory with solving master equation. The pressures used are 0.1, 1, 10, and 100 atm. The corresponding reaction rate constants are listed in Table 2 in the form of an Arrhenius expression. Verification of this method for calculating rate constants for thermal decomposition reaction and biomolecular addition reactions has been reported in previous studies [7, 35, 53]. Generally, the deviation between calculated rate constants and reported experimental values is within a factor of three at various temperatures and pressures. To the best of our knowledge, there is no experimental data on rate constants for the reaction of $A_2-1(A_2-2) + C_4H_4$. Comparisons between $A_2-1(A_2-2) + C_4H_4$ and $A_1-(\text{phenyl}) + C_4H_4$ were carried out to check the kinetic similarity. The theoretical high-pressure limit rate constant for $A_1- + C_4H_4$ reaction was evaluated by Mebel et al. [25] at the G3(MP2,CC) level. As shown in Fig. 12 (a), the reaction rates of $A_2-1 + C_4H_4$ were very close to that of $A_2-2 + C_4H_4$, the deviation was within 3 % at 1500 K. This means that the C_4H_4 addition to PAH radical was insensitive to the type of surface site at least for free and zig-zag edges. The rate constants for $A_2-1(A_2-2) + C_4H_4$ were also lower than that the $A_1- + C_4H_4$ reaction by a factor of 1.48 at 1500 K. Such deviation was probably due to differences in energy barriers calculated by G3(MP2,CC) and DFT/B3LYP/6-311+G(d,p) methods. As shown in Table S6 of supplementary material, the maximum difference in energy barriers is 2.9 kcal/mol for the $A_2-2 + C_4H_4$ entrance reaction, which may introduce 1.65 time rate coefficient uncertainty at 1500 K. In addition, the different molecular characteristics between phenyl and naphthyl radical could lead to rate deviations. The pressure dependence of the global rate constants is shown in Fig.12 (b). The rate coefficient curves at 0.1, 1, 10, and 100 atm nearly overlap for the reactions $A_2-1 + C_4H_4 (C_1) \rightarrow CS10_P + H$, $A_2-1 + C_4H_4 (C_1) \rightarrow CS11_P + H$, and $A_2-1 + C_4H_4 (C_1) \rightarrow CS7_P + H$, respectively. Similar pressure behavior was also observed in $A_2-1 + C_4H_4 (C_4)$, $A_2-2 + C_4H_4 (C_1)$, and $A_2-2 + C_4H_4 (C_4)$ reaction systems. Therefore, it can be concluded that the rate constants of PAH radical + $C_4H_4 \rightarrow \text{product} + H$ type reaction are nearly independent of pressure.

3.2.2 Yield distribution in 0-D reactor

The yield distributions of products were discussed with PES analysis for each sub-system above. Due to the high reversibility of some reactions, it was necessary to examine the yield distribution in the entire $A_2-H-C_4H_4-H_2-N_2$ (A_2 , H, C_4H_4 , H_2 , N_2 are the reactant) reaction system, including all reactions listed in Table 2. As shown in Fig. 11, the yield distribution was highly sensitive to the 0-D reactor temperature. The low yield of A_3 indicated that A_3 formation was unlikely to occur in the $A_2-H-C_4H_4-H_2-N_2$ reaction framework at 1000 K, and adduct

intermediates CS2 and CS40 were the main products, as illustrated in Fig. 13 (a); this is because the energy barriers of H elimination reactions and isomer reactions from CS2 and CS40 species were relatively high. The formation of A₃ and PAH with C₄H₃ radical substitutions are more favorable at higher temperatures. As shown in Fig. 13 (b)-(d), the mole fractions of A₃ and PAH with C₄H₃ radical substitution CS10_P were close, and the values top two among all intermediates and products when the temperature was higher than 1250 K. The results confirmed the above analysis, that the yield of A₃ may be high in the entire A₂-H-C₄H₄-H₂-N₂ reaction system because its reaction rate is irreversible. The predicted yield distribution of products at 1500 K is in good agreement with the experimental results for the naphthyl radical + C₄H₄ reaction, obtained at 1450±10 K, where the mass peak of dominant product was 178 (CS10_P and A₃). It is also observed that the concentration ratio between phenanthrene (A₃) and anthracene (CS71_P) increases at higher temperature. For example, the ratio is equal to 1.2 at 1000 K and increases to 18.2 at 1750 K. This is consistent with the PAH experimental results showing that the concentration of anthracene in sooting flame is negligible when compared to phenanthrene [17, 27].

The A₃ formation by A₂-1 + C₄H₄ → A₃ + H and A₂-2 + C₄H₄ → A₃ + H reactions in PAHs mechanism proposed by Wang et al. [33] and Chernov et al. [28] are discussed here to test the robustness of the rate constants used in the mechanism. As shown in Fig. 13 (a)-(d), the predicted mole fraction of A₃, using reference rate constants [28, 33], was less sensitive to temperature. For example, the mole fraction of A₃ predicted with the rate constant suggested by Chernov et al. at 1750 K, was higher than that at 1000 K by 6.06 times. However, the gap was as great as 165 times in this study. The second feature is that the rate constants used in the PAH mechanism were significantly higher, especially at low temperatures. For example, the mole fraction of A₃, predicted with the rate constant suggested by Chernov et al., was higher than the rate constants reported here by a factor of 88.7, 17.8, 6.3, and 3.3 at 1000, 1250, 1500, and 1750 K, respectively.

As discussed in the PES analysis, the reaction pathway was significantly different when C₄H₄ attacks the bare C atom near the free edge (A₂-2) and zig-zag edge surface sites (A₂-1). To check the site effect on A₃ formation in such a reaction system, the sensitivity of A₃ formation was performed. Each specific reaction network is individually removed from the entire reaction system; then the importance of the specific reaction network can be evaluated by comparing the mole fractions of A₃ calculated with and without removing the specific reaction network. As shown in Fig.14, the calculated mole fraction of A₃, removing the A₂-1 + C₄H₄ reaction network (shown in Fig.2 and Fig.4) is lower by 73.3% than when no reaction is removed. The value becomes 16.2% when the A₂-2 + C₄H₄ reaction network (shown in Fig.6 and Fig.8) is removed. Therefore, A₂-1 + C₄H₄ → A₃ + H (zig-zag edge) is the main pathway leading to A₃ formation, instead of A₂-2 + C₄H₄ → A₃ + H (free edge). In other words, the new benzene ring is more likely to form near the zig-zag edge surface site. In addition, the A₂-1 + C₄H₄ → A₃ + H and A₂-2 + C₄H₄ → A₃ + H reactions were removed, and only 5.4% reduction was observed. This indicates that the majority of A₃ (94.6%) is generated by a rapid and effective conversion from other products

and intermediates, further confirmed the analysis that an accumulated total yield of A₃ may be high due to the irreversibility of the A₃+H reaction and the high reversibility of other products + H reactions.

The PAH kinetics module is rapidly being employed in transportation fuel mechanisms for soot prediction, but due to computational costs, it is necessary to simplify the reaction pathways for engine CFD simulations. With the above strategy, the sensitivity analysis for each A₃ formation pathway was carried out for pathway simplification. The results, shown in Fig. S3-S4 in supplementary material, indicate that the pathways linked to CS10_P, CS17_P, CS37_P, CS60_P, and CS65_P should be maintained to describe the formation of A₃, and that other pathways can be ignored. The reaction pathways filtered by sensitivity analysis are marked with an asterisk in Table 1. The fitted rate constants for one-step A₃ formation process (A₂-1+C₄H₄→A₃+H and A₂-2+C₄H₄→A₃+H reactions) are provided in Table S2 in the supplementary material.

3.2.3 Discussion on analogous treatment of kinetics

To extend the kinetic rate parameters to the larger PAH radical + C₄H₄ reaction system, the formation of A₂ from the A₁-H-C₄H₄-H₂-N₂ reaction system, and A₃ from the A₂-H-C₄H₄-H₂-N₂ reaction system, are discussed here. The corresponding kinetic parameters used in the A₁-H-C₄H₄-H₂-N₂ reaction systems are listed in Table 1. In simulations, the mole fractions of the A₁, H, and C₄H₄ in the A₁-H-C₄H₄-H₂-N₂ reaction system are the same as that of A₂, H, and C₄H₄ in the A₂-H-C₄H₄-H₂-N₂ reaction system. In this way, it is possible to compare the concentration of A₂ formed in A₁-H-C₄H₄-H₂-N₂ reaction system with that of A₃ formed in A₂-H-C₄H₄-H₂-N₂ reaction system, to check the kinetic dependence along with reactant size. The kinetic features of the two process are generally similar, as shown in Fig.15. A₃ forms more quickly than A₂ by a factor of 2.9 at 1000 K, and it is slower than A₂ by a factor of 1.5 and 2.2 at 1500 K and 2000 K. The deviation may be the results of slightly different rate constants, as discussed above for Fig. 10 (a). Also, the formation of other A₂ isomers was not considered in the A₁-H-C₄H₄-H₂-N₂ reaction systems, but the formation of all A₃ isomers was considered in the A₂-H-C₄H₄-H₂-N₂ reaction systems. This may be a potential reason for the deviation at 1500 K and 2000 K, where the formation of corresponding isomers was favored. Therefore, it can be inferred that the analogous treatment of rate constants is acceptable in the larger PAH radical + C₄H₄ reaction system, as the reaction rate calculation error is nearly within a factor of three due to the energy accuracy (as shown in Table S6 and Fig. S5 in the supplementary material) and uncertainty in MultiWell.

Conclusions

This study systematically investigated the possibilities of the formation of phenanthrene and PAH with a C₄H₃ radical substitution, through the reaction of a naphthyl radical and vinylacetylene (C₄H₄). Potential energy

surfaces were obtained from the combination of DFT/B3LYP/6-311+G(d,p), CCSD/6-311+G(d,p), and CBS-QB3 methods. The reaction rate constants at 0.1-100 atm were evaluated by the RRKM theory with solving master equation in the temperature range of 800-2500 K. The yield distribution was investigated in a 0-D batch reactor. Finally, the reaction pathway analysis and analogous treatment of rate constants toward a larger PAH radical + C₄H₄ reaction system were discussed. The following conclusions can be made:

The potential energy surfaces show that the products including phenanthrene, anthracene, PAH with a five-membered ring structure, and PAH with a C₄H₃ radical substitution can be formed in A₂-1+C₄H₄ and A₂-2+C₄H₄ reaction systems. The PAH with a C₄H₃ radical substitution can be generated by one step H elimination reaction from the adduct intermediate. The formation of phenanthrene, anthracene, and PAH with five-membered rings is a multistep reaction process. The yield distribution in each sub-reaction system suggests that the PAH with a C₄H₃ radical substitution is more likely to form due to the relatively low energy barrier in the formation pathways, but the corresponding reversible reactions (H addition reaction) occur rapidly at flame temperature.

Kinetic results revealed that the rate constants of the bimolecular A₂-1(A₂-2)+C₄H₄→product+H reaction are pressure-independent. The yield distribution in a 0-D batch reactor indicated that phenanthrene and PAH with C₄H₃ radical substitution are the main products when the temperature is higher than 1000 K. The existence of abundant PAH with a C₄H₃ radical substitution at flame temperatures supports (to some extent), the chemical-coalescence nucleation pathway driven by PAHs with a radical substitution.

For the development of PAH mechanisms, sensitivity analysis was performed to reduce the reaction pathways. The results showed that the pathways linked to products CS11_P, CS35_P, CS54_P, CS55_P, CS56_P and CS63_P could be removed from the reaction network. Comparisons between the formation rate of A₂ from phenyl+C₄H₄ reactions and the formation rate of A₃ from naphthyl radical+C₄H₄ reactions were discussed. Their formation rates were similar, indicating that the analogous treatment of rate constants from A₂-1(A₂-2)+C₄H₄ reactions to larger PAH radical+C₄H₄ reaction is reasonable.

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Supplementary materials

The T1 diagnostic values, effect of collision energy transfer on the branching ratio of products, IRC analysis, sensitivity analysis of reaction pathways leading to A₃ formation, reaction rate parameters for one-step A₃ formation process and direct H abstraction reactions, rate uncertainty analysis, energies, vibrational frequencies (1-D hindered rotation), rotational constants, external symmetry number, optical isomers, electronic ground state, Lennard-Jones parameters for all optimized structures were provided in supplementary material.

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Fig. 1 Rate constants of C₄H₄ attaching to A₂-1 (a) and A₂-2 (b) reaction steps.

Fig. 2 Potential energy surface of reaction A₂-1+C₄H₄ (C1), energies calculated at CBS-QB3 level.

Fig. 3 Yield distribution of products in $A_2-1+C_4H_4$ (C1) reaction system at 1 atm.

Fig. 4 Potential energy surface of reaction $A_2-1+C_4H_4$ (C4), energies calculated at CBS-QB3 level.

Fig.5 Yield distribution of products in $A_2-1+C_4H_4$ (C_4) reaction system at 1 atm.

Fig. 6 Potential energy surface of reaction A_2-2 and C_4H_4 (C_1), energies calculated at CBS-QB3 level.

Fig. 7 Yield of products in $A_2-2+C_4H_4(C_1)$ reaction system.

Fig. 8 Potential energy surface of reaction A_2-2 and C_4H_4 (C_4), energies calculated at CBS-QB3 level.

Fig. 9 Yield distribution of products in the reaction of A_2-2 and C_4H_4 (C_4).

Fig. 10 Potential energy surface for anthracene formation in reaction $A_2-2 + C_4H_4$, energies calculated at CBS-QB3 level.

Fig. 11 Yield distribution of products in anthracene formation reaction system ($A_2-2 + C_4H_4$).

Fig. 12 Calculated rate coefficients. (a) total addition reaction rate at high-pressure limit, (b) rate coefficients for formation of individual products in $A_2-1 + C_4H_4$ reaction at pressure of 0.1, 1, 10, and 100 atm, respectively.

Fig. 13 Yield distribution of products for $A_2-H-C_4H_4$ reaction system in a 0-D reactor.

Fig.14 Sensitivity analysis of A_3 formation at zig-zag and free edge surface sites.

Fig.15 Formation of new benzene ring in A_1 -H- C_4H_4 (A_2) and A_2 -H- C_4H_4 (A_3) reaction systems, reaction time = 10 ms.

Table 1. Reaction rate parameters for A_1 -H- C_4H_4 system, in the form of $AT^n \exp(-E/RT)$, units are s^{-1} , $cm^3 mol^{-1} s^{-1}$ and kcal.

Reaction	A	n	E	Reference
$A_1 + H \rightarrow A_1 + H_2$	6.75×10^8	1.910	15.61	[16]
$A_1 + H_2 \rightarrow A_1 + H$	1.22×10^4	2.655	42.66	[16]
$A_1 + C_4H_4 \rightarrow P_3 + H$	3.80×10^{-10}	6.780	14.68	[25]
$P_3 + H \rightarrow A_1 + C_4H_4$	2.32×10^{-1}	4.840	23.21	[25]
$P_3 + H \rightarrow P_2 + H$	2.84×10^{16}	0.120	27.31	[25]
$P_2 + H \rightarrow P_3 + H$	3.13×10^{16}	0.150	26.58	[25]
$P_2 + H \rightarrow A_2 + H$	1.50×10^{18}	-0.950	15.43	[25]
$P_3 + H \rightarrow A_2 + H$	8.49×10^{31}	-4.660	29.38	[25]

P2 and P3 represent cis-1-phenyl-vinylacetylene and trans-1-phenyl-vinylacetylene, respectively.

Table 2. Reaction rate parameters in the form of $AT^n \exp(-E/RT)$, units are s^{-1} , $cm^3 mol^{-1} s^{-1}$ and Kcal.

Reaction	Entrance well	A	n	E	Valid T range (K)	P (atm)
$A_2 + 1 + C_4H_4 \rightarrow CS2$	CS2	2.59×10^{289}	-81.54	155.02	800-1600	0.1-100
$A_2 + 1 + C_4H_4 \rightarrow A_3 + H$	CS2	9.52×10^{18}	-1.862	25.08	800-2500	0.1-100
* $A_2 + 1 + C_4H_4 \rightarrow CS10_P + H$	CS2	7.05×10^{30}	-4.693	28.68	800-2500	0.1-100
$A_2 + 1 + C_4H_4 \rightarrow CS11_P + H$	CS2	2.17×10^{29}	-4.271	34.96	800-2500	0.1-100
$CS10_P + H \rightarrow CS2$	CS2+CS16	3.13×10^{293}	-82.31	155.32	800-1600	0.1-100
* $CS10_P + H \rightarrow CS7_P + H$	CS2+CS16	2.19×10^{34}	-5.869	33.62	800-2500	0.1-100
$CS10_P + H \rightarrow CS11_P + H$	CS2+CS16	1.94×10^{42}	-7.615	41.50	800-2500	0.1-100
* $CS10_P + H \rightarrow A_2 + 1 + C_4H_4$	CS2+CS16	2.51×10^{27}	-3.723	27.30	800-2500	0.1-100
$CS11_P + H \rightarrow CS2$	CS2	6.82×10^{302}	-85.12	160.92	800-1500	0.1-100
$CS11_P + H \rightarrow A_3 + H$	CS2	1.06×10^{21}	-2.094	24.08	800-2500	0.1-100
$CS11_P + H \rightarrow CS10_P + H$	CS2	4.40×10^{30}	-4.298	25.62	800-2500	0.1-100
$CS11_P + H \rightarrow A_2 + 1 + C_4H_4$	CS2	3.19×10^{27}	-3.616	29.56	800-2500	0.1-100
* $CS17_P + H \rightarrow CS7_P + H$	CS20+CS13	1.44×10^9	1.530	5.16	800-2500	0.1-100
* $CS17_P + H \rightarrow CS10_P + H$	CS13	9.92×10^6	2.338	35.12	1400-2500	0.1-100
$CS17_P + H \rightarrow CS11_P + H$	CS13	4.85×10^8	1.838	42.64	1400-2500	0.1-100
$A_2 + 1 + C_4H_4 \rightarrow CS20$	CS20	3.77×10^{260}	-74.06	128.74	800-1500	0.1-100

A ₂ -1+C ₄ H ₄ →CS7_P+H	CS20	2.14x10 ⁵³	-11.73	39.84	800-2500	0.1-100
A ₂ -1+C ₄ H ₄ →CS35_P+H	CS20	2.60x10 ¹⁰	0	21.90	800-2500	0.1-100
*A ₂ -1+C ₄ H ₄ →CS17_P+H	CS20	4.47x10 ³²	-5.286	33.82	800-2500	0.1-100
*A ₂ -1+C ₄ H ₄ →CS37_P+H	CS20	4.55x10 ³⁷	-7.207	26.74	800-2500	0.1-100
*A ₂ -1+C ₄ H ₄ →CS65_P+H	CS20	1.80x10 ³⁶	-6.346	34.58	800-2500	0.1-100
CS17_P+H→CS20	CS20	7.01x10 ²⁹¹	-82.52	149.78	800-1500	0.1-100
CS17_P+H→CS35_P+H	CS20	6.26x10 ⁶	1.304	16.85	800-2500	0.1-100
*CS17_P+H→A ₂ -1+C ₄ H ₄	CS20+CS13	1.28x10 ²⁸	-4.135	29.42	800-2500	0.1-100
*CS17_P+H→CS37_P+H	CS20	1.47x10 ⁴⁵	-8.934	31.82	800-2500	0.1-100
*CS17_P+H→CS65_P+H	CS20	2.67x10 ⁴²	-7.709	38.62	800-2500	0.1-100
CS37_P+H→CS20	CS20	3.68x10 ²⁷⁰	-76.38	136.22	800-1600	0.1-100
*CS37_P+H→CS7_P+H	CS20	9.22x10 ⁶⁹	-16.10	51.00	800-2500	0.1-100
CS37_P+H→CS35_P+H	CS20	9.86x10 ²⁰	-2.646	31.10	1200-2500	0.1-100
*CS37_P+H→CS17_P+H	CS20	4.33x10 ⁵²	-10.57	49.38	1200-2500	0.1-100
*CS37_P+H→A ₂ -1+C ₄ H ₄	CS20	4.62x10 ⁴²	-8.26	41.50	900-2500	0.1-100
*CS37_P+H→CS65_P+H	CS20	9.51x10 ⁵⁷	-12.10	51.42	800-2500	0.1-100
CS65_P+H→CS20	CS20	2.26x10 ²⁶⁵	-74.93	127.9	800-1500	0.1-100
*CS65_P+H→CS7_P+H	CS20	2.12x10 ⁵⁷	-12.48	37.02	800-2500	0.1-100
CS65_P+H→CS35_P+H	CS20	5.95x10 ¹⁴	-0.8253	20.44	800-2500	0.1-100
*CS65_P+H→CS17_P+H	CS20	3.10x10 ³⁴	-5.438	29.72	800-2500	0.1-100
*CS65_P+H→A ₂ -1+C ₄ H ₄	CS20	5.94x10 ³⁰	-4.848	27.14	800-2500	0.1-100
*CS65_P+H→CS37_P+H	CS20	8.83x10 ⁴⁷	-9.679	29.66	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS57	CS57	4.54x10 ²⁶⁶	-75.78	133.42	800-1600	0.1-100
*A ₂ -2+C ₄ H ₄ →CS60_P+H	CS57+CS66	2.81x10 ³⁷	-6.712	31.14	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS63_P+H	CS57	1.14x10 ²³	-3.522	30.26	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS7_P+H	CS57	1.99x10 ⁴⁴	-9.462	30.86	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS71_P+H	CS66+CS72	1.17x10 ⁵⁵	-12.41	36.68	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS66	CS66	5.79x10 ¹⁷²	-47.74	86.06	800-1800	0.1-100
A ₂ -2+C ₄ H ₄ →CS72	CS72	1.58x10 ²⁰⁹	-59.4	97.92	800-1600	0.1-100
CS60_P+H→CS58	CS58	6.91x10 ²⁵⁸	-74.6	110.96	800-1300	0.1-100
*CS60_P+H→CS7_P+H	CS58	1.19x10 ²⁹	-4.553	25.8	800-2500	0.1-100
CS60_P+H→CS56_P+H	CS58	3.49x10 ⁴	2.685	27.18	900-2500	0.1-100
*CS60_P+H→A ₂ -2+C ₄ H ₄	CS58+CS66	1.99x10 ⁴⁴	-8.269	36.46	800-2500	0.1-100
CS60_P+H→CS66	CS66	3.91x10 ¹⁶⁹	-46.38	83.62	800-2100	0.1-100
CS60_P+H→CS71_P+H	CS66	3.40x10 ⁶⁸	-16.01	42.22	800-2100	0.1-100
A ₂ -2+C ₄ H ₄ →CS40	CS40	2.51x10 ²⁷⁷	-77.53	155.38	800-1800	0.1-100
A ₂ -2+C ₄ H ₄ →CS7_P+H	CS40	1.01x10 ⁴⁸	-9.991	46.02	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS54_P+H	CS40+CS72	2.30x10 ³	2.705	3.03	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS55_P+H	CS40	5.07x10 ⁴³	-8.305	45.60	800-2500	0.1-100
A ₂ -2+C ₄ H ₄ →CS56_P+H	CS40	1.27x10 ¹⁰	0.9241	35.36	900-2500	0.1-100
CS54_P+H→CS40	CS40	1.75x10 ²⁸⁶	-79.52	161.1	800-1800	0.1-100
CS54_P+H→CS7_P+H	CS40	5.71x10 ⁶¹	-13.42	55.80	800-2500	0.1-100
CS54_P+H→CS55_P+H	CS40	4.26x10 ⁵⁸	-12.04	56.66	800-2500	0.1-100
CS54_P+H→CS56_P+H	CS40	2.33x10 ¹⁷	-0.7257	40.14	1200-2500	0.1-100
CS54_P+H→A ₂ -2+C ₄ H ₄	CS40+CS72	8.52x10 ⁶¹	-12.93	57.40	800-2500	0.1-100
CS54_P+H→CS72	CS72	5.86x10 ²⁰⁶	-57.93	98.6	800-1700	0.1-100
CS54_P+H→CS71_P+H	CS72	6.47x10 ⁹	0.4187	4.44	800-2500	0.1-100
CS55_P+H→CS40	CS40	9.84x10 ²⁷⁶	-77.12	152.78	800-1700	0.1-100
CS55_P+H→CS7_P+H	CS40	1.18x10 ⁵³	-11.15	46.74	800-2500	0.1-100
CS55_P+H→CS54_P+H	CS40	5.23x10 ⁵⁶	-11.74	47.58	800-2500	0.1-100

CS55_P+H $\rightarrow$ CS56_P+H	CS40	1.24x10 ²¹	-1.83	41.70	800-2500	0.1-100
CS55_P+H $\rightarrow$ A ₂ -2+C ₄ H ₄	CS40	7.87x10 ⁵³	-10.83	48.66	800-2500	0.1-100
CS56_P+H $\rightarrow$ CS7_P+H	CS46	7.31x10 ¹⁶	-0.8238	9.46	800-2500	0.1-100
CS56_P+H $\rightarrow$ CS54_P+H	CS46	1.35x10 ¹⁹	-1.29	40.06	1000-2500	0.1-100
CS56_P+H $\rightarrow$ CS55_P+H	CS46	3.57x10 ²⁶	-3.202	51.86	1200-2500	0.1-100
CS56_P+H $\rightarrow$ A ₂ -2+C ₄ H ₄	CS46	1.05x10 ²⁰	-1.409	43.86	1100-2500	0.1-100
A ₂ -1+C ₄ H ₄ $\rightarrow$ all products	CS2	8.10x10 ¹	3.206	1.641	800-2500	H-P ^a
A ₂ -1+C ₄ H ₄ $\rightarrow$ all products	CS20	4.73x10 ²	2.831	1.452	800-2500	H-P ^a
A ₂ -2+C ₄ H ₄ $\rightarrow$ all products	CS40+CS72	1.23x10 ²	3.053	1.834	800-2500	H-P ^a
A ₂ -2+C ₄ H ₄ $\rightarrow$ all products	CS57+CS66	4.26x10 ²	2.928	0.752	800-2500	H-P ^a
A ₂ -1+C ₄ H ₄ $\rightarrow$ A ₂ + i-C ₄ H ₃	-	2.91x10 ⁰	3.579	5.30	800-2500	H-P ^a
A ₂ + i-C ₄ H ₃ $\rightarrow$ A ₂ -1+C ₄ H ₄	-	4.25x10 ⁰	3.468	21.16	800-2500	H-P ^a
A ₂ -1+C ₄ H ₄ $\rightarrow$ A ₂ + n-C ₄ H ₃	-	9.00x10 ⁻¹	3.77	8.49	800-2500	H-P ^a
A ₂ + n-C ₄ H ₃ $\rightarrow$ A ₂ -1+C ₄ H ₄	-	3.71x10 ¹	3.468	9.58	800-2500	H-P ^a
A ₂ -2+C ₄ H ₄ $\rightarrow$ A ₂ + i-C ₄ H ₃	-	4.97x10 ⁰	3.525	5.24	800-2500	H-P ^a
A ₂ + i-C ₄ H ₃ $\rightarrow$ A ₂ -2+C ₄ H ₄	-	3.34x10 ⁰	3.512	20.92	800-2500	H-P ^a
A ₂ -2+C ₄ H ₄ $\rightarrow$ A ₂ + n-C ₄ H ₃	-	2.73x10 ⁰	3.615	8.78	800-2500	H-P ^a
A ₂ + n-C ₄ H ₃ $\rightarrow$ A ₂ -2+C ₄ H ₄	-	1.23x10 ¹	3.576	9.04	800-2500	H-P ^a

*Reactions filtered by pathway analysis.

^aHigh-pressure limit