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\textsubscript{4}H\textsubscript{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\textsubscript{4}H\textsubscript{3} radical substitution, can be formed in A\textsubscript{2}-1 (1-naphthyl)+C\textsubscript{4}H\textsubscript{4} and A\textsubscript{2}-2 (2-naphthyl) +C\textsubscript{4}H\textsubscript{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 A\textsubscript{2}-1 (A\textsubscript{2}-2)+C\textsubscript{4}H\textsubscript{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\textsubscript{4}H\textsubscript{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\textsubscript{4}H\textsubscript{3} radical substitution with the assistance of H atom. Reaction pathway sensitivity analysis for the PAH radical+C\textsubscript{4}H\textsubscript{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\textsubscript{4}H\textsubscript{4} reaction system are discussed. The formation rate of naphthalene from the reaction of phenyl+C\textsubscript{4}H\textsubscript{4} was found to be very close to that of phenanthrene from the reaction of naphthyl+C\textsubscript{4}H\textsubscript{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 (A₁) 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 (A₂) 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 C₂H₂ addition reactions on the ortho-position (relative to the existing C₂H 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-C₂H₂ pathway, in which C₂H₂ attacks the close-shell PAH molecule followed by an H₂ 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 (C₃H₃) addition onto naphthalene and the naphthyl radical, and concluded that the new benzene ring may form if C₃H₃ attacks the zig-zag site of PAH. However, the low concentration of C₃H₃ 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 (C₄H₄) and PAH radicals, since a second addition of other carbon species is not required during the cyclization process. C₄H₄ is abundant in combustion environments, including premixed ethylene, benzene, toluene, and gasoline flames [19-22]. The measured mole fraction of C₄H₄ is up to 2×10⁻³, comparable to C₂H₂ [19-22]. Correlations between C₄H₄ 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 C₄H₄ with a mole fraction of 3×10⁻¹.

Among the addition reactions of C₄H₄ with aromatic species, the phenyl+C₄H₄ reaction has received special attention [24-29]. The phenyl+C₄H₄ reaction was first considered in the PAHs mechanism by Appel et al. [27], and modelling results showed that phenyl+C₄H₄ reaction is the main route of naphthalene formation in ethylene flames. Subsequently, the addition reactions of C₄H₄ with PAHs radical have been merged into PAH mechanisms, assuming reaction rate coefficients to be equal to that of phenyl+C₄H₄ → naphthalene+H [28, 30-33]. The rate coefficients of the reaction phenyl+C₄H₄ → naphthalene+H come primarily from two sources. One was suggested by Appel et al. [27] with the expression of 2.5×10⁻²⁹×T⁻⁴⁴⁺×exp(-26400/RT) cm³mol⁻¹s⁻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 1.6×10⁻¹⁶ cm³mol⁻¹s⁻¹, which is beyond the physical collision limit (-10¹⁴ cm³mol⁻¹s⁻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 C₄H₄ + phenyl → naphthalene + H were assumed to be equal to that of the entrance elementary reaction step (C₄H₄ molecule attaches to the phenyl radical). Such treatment may exaggerate the role of C₄H₄ in PAHs growth, as the formation of other isomers and the H loss from the C₅H₅C₄H₄ 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+C₄H₄. 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 + C₄H₄ 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\textsubscript{4}H\textsubscript{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\textsubscript{2}1 + C\textsubscript{4}H\textsubscript{4}→ 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\textsubscript{2}1 (or A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{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 Intermediate\textsubscript{1} → A\textsubscript{2}1 (or A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{4} reaction was determined by initiating the Intermediate\textsubscript{1} with thermal energy distribution. Subsequently, the rate coefficients of recombination reaction A\textsubscript{2}1 (or A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{4} → Intermediate\textsubscript{1} were calculated via the combination of its reverse reaction rate coefficients and equilibrium constants. Finally, the global reaction rate coefficients of A\textsubscript{2}1 (or A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{4}→ Product A + H were evaluated by multiplying the yield of Product A and the rate coefficients of A\textsubscript{2}1 (or A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{4}→ Intermediate\textsubscript{1}. The yield of Product A was obtained by initiating the Intermediate\textsubscript{1} 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.

\[ \text{Product B + H} \]
\[ A\textsubscript{2}1(A\textsubscript{2}-2) + C\textsubscript{4}H\textsubscript{4} \rightarrow \text{Intermediate}1 \rightarrow \cdots \rightarrow \text{Product A + H} \]  

(1)
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 \(A_2-1 + C_4H_4\) (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 \(\sigma\) and \(\varepsilon/\text{k_B}\) 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 (A\(_3\)), 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 \(1 \times 10^6\) to \(1 \times 10^7\) 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 \(A_2-H-C_4H_4-H_2-N_2\) (A\(_1\)-H-C\(_4\)H\(_4\)-H\(_2\)-N\(_2\)) reaction system, with \(A_2\) (A\(_1\)), H, C\(_4\)H\(_4\), H\(_2\) and N\(_2\) as the initial reactants. The mole fractions of \(A_2\) (A\(_1\)) and C\(_4\)H\(_4\) were set as \(6.18 \times 10^{-5}\) and \(4.0 \times 10^{-4}\) respectively, as measured in a premixed sooting ethylene flame by Castaldi et al. [17]. The mole fractions of H, H\(_2\) and N\(_2\) were assumed to equal \(1.0 \times 10^{-4}\), \(1 \times 10^{-2}\), and \(0.9894382\) (\(N_2 = 1 - A_2 - C_4H_4 - H - H_2\), respectively. The reaction network and corresponding kinetics considered in \(A_1\)-H-C\(_4\)H\(_4\)-H\(_2\)-N\(_2\) reaction system are listed in Table 1. The kinetic information for \(A_2-H-C_4H_4-H_2-N_2\) reaction system comes from this study, as shown in Table 2. It should be noted that A\(_2\)-1 and A\(_2\)-2 are generated via the H abstraction reactions (\(A_2+H \rightarrow A_2-1+H_2\) and \(A_2+H \rightarrow A_2-2+H_2\)) in the \(A_2-H-C_4H_4-H_2-N_2\) 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

A\(_2\)-1 and A\(_2\)-2 exist simultaneously in the flame, and their concentrations are determined by the H abstraction reactions of A\(_2\) with H, OH, CH\(_3\) and other active radicals. In this study, both A\(_2\)-1+C\(_4\)H\(_4\) and A\(_2\)-2+C\(_4\)H\(_4\) 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 C3H3 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 C3H2 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 larger 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.
In this case, the yields of CS7_P and CS56_P are 0.8 % and 0.02 % at 1500 K, indicating that the reactions A2-2+C4H4 (C1) → CS7_P+H and A2-2+C4H4 (C1) → CS56_P+H are too slow to compete with reactions A2-2+C4H4 (C1) → CS54_P+H and A2-2+C4H4 (C1) → CS55_P+H. The entrance well in reactions A2-2+C4H4 (C1) → products, CS54_P+H → products, and CS55_P+H → 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 A2-2+C4H4 (C1) → CS54_P+H and A2-2+C4H4 (C1) → CS55_P+H are highly reversible, evidenced by the high yield of A2-2+C4H4 in the reaction of CS54_P+H → products and CS55_P+H → products. Although the yield of CS56_P is kinetically unsupported, it is still helpful to explore the yield distribution in reaction CS56_P+H → 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 → products in the temperature range studied, resulting from the low energy barrier in the channel of CS56_P+H→CS46→CS47→CS7_P+H.

3.1.4 A2-2+C4H4 (C4) reaction system

Generally speaking, the reaction network for the A2-2+C4H4 (C4) system shown in Fig.8 is similar to that for A2-1+C4H4 (C4) (Fig.4) and A2-2+C4H4 (C1) (Fig.6) systems. The adduct intermediate CS57 can lead to the formation of CS7_P via the channels of CS57→CS58→CS45→…→CS7_P+H, CS57→CS59→CS58→CS45→…→CS7_P+H, and CS57→CS64→CS44→CS9→…→CS7_P+H, where the H transfer reactions (CS57→CS58, 66.7 kcal/mol, CS62→CS43, 45.5 kcal/mol, and CS9→CS14, 46.2 kcal/mol) and rotation of C-C double bond (CS58→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→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 A2-2+C4H4 (C4) systems is more concise, as shown in Fig.9 (a)-(b). At flame temperature (T > 1200 K), the reaction A2-2+C4H4→products mainly produces CS60_P, as shown in Fig.9 (a). In turn, A2-2+C4H4 is the dominant product in reaction CS60_P+H→products, as
shown in Fig. 9 (b). The yield of CS63_P is lower than 0.01%, meaning that the pathway CS61→CS63_P+H→steady product is not as competitive as the pathway CS61→intermediate→steady product + H.

The formation of anthracene (CS71_P) is also possible in A2-2 + C4H4 reaction system if the C4H4 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 A2-2 + C4H4 → CS66 → CS67 → CS68 → CS69 → CS70 → CS71_P + H and A2-2 + C4H4 → CS72 → CS73 → CS74 → CS75 → CS76 → CS70 → CS71_P + H. In the former pathway, the highest energy barrier exists in the H transfer reaction (CS69 → CS70) with the value of 41.6 kcal/mol, which is lower than the energy barrier of corresponding competing reaction (CS69 → CS68, 45.7 kcal/mol). This means that anthracene is likely to form from the A2-2 + C4H4 → CS66 → CS67 → CS68 → CS69 → CS70 → CS71_P + 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 (CS73 → CS74, 31.2 kcal/mol) and the dissociation of the existing C-C bond (CS74 → CS75, 39.9 kcal/mol), are much higher than that of the corresponding competing reactions (CS73 → CS72, 19.5 kcal/mol, CS74 → 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 A2-2 + C4H4 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 CS72 → A2-2+C4H4 and CS72→CS73 → CS74 → CS75 → CS76 → CS70 → CS71_P + 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 CS54_P+H → CS40, as shown in Fig. 6-7.

Apart from the above reaction networks, direct H abstraction reactions including A2-1+C4H4 → A2 + i-C4H3, A2-1+C4H4 → A2 + n-C4H3, A2-2+C4H4 → A2 + i-C4H3, and A2-2+C4H4 → A2 + n-C4H3 were considered as shown in Table S3-S5 in the supplementary materials. Furthermore, a comparison of rate constants for phenyl+C4H4 → benzene+n-C4H3 [25] and A2-2+C4H4 → A2+n-C4H3 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 + C4H4 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 A2-1(A2-2) + C4H4. Comparisons between A2-1 (A2-2) + C4H4 and A1- (phenyl) + C4H4 were carried out to check the kinetic similarity. The theoretical high-pressure limit rate constant for A1- + C4H4 reaction was evaluated by Mebel et al. [25] at the G3(MP2,CC) level. As shown in Fig. 12 (a), the reaction rates of A2-1 + C4H4 were very close to that of A2-2 + C4H4, the deviation was within 3 % at 1500 K. This means that the C4H4 addition to PAH radical was insensitive to the type of surface site at least for free and zig-zag edges. The rate constants for A2-1 (A2-2) + C4H4 were also lower than that the A1- + C4H4 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 A2-2 + C4H4 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 A2-1 + C4H4 (C1) → CS10_P + H, A2-1 + C4H4 (C1) → CS11_P + H, and A2-1 + C4H4 (C1) → CS7_P + H, respectively. Similar pressure behavior was also observed in A2-1 + C4H4 (C4), A2-2 + C4H4 (C1), and A2-2 + C4H4 (C4) reaction systems. Therefore, it can be concluded that the rate constants of PAH radical + C4H4 → 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 A2-H-C4H4-H2-N2 (A2, H, C4H4, H2, N2 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 A3 indicated that A3 formation was unlikely to occur in the A2-H-C4H4-H2-N2 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 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.

Acknowledgments

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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.

Reference


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$_4$H$_4$ (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$_2$-I+C$_4$H$_4$ (C4) reaction system at 1 atm.

Fig. 6 Potential energy surface of reaction A$_2$-2 and C$_4$H$_4$ (C$_1$), energies calculated at CBS-QB3 level.
Fig. 7 Yield of products in $\text{A}_2\text{-2+C}_4\text{H}_4$ (C1) reaction system.
Fig. 8 Potential energy surface of reaction $\text{A}_2\text{-}2$ and $\text{C}_4\text{H}_4$ ($\text{C}_4$), energies calculated at CBS-QB3 level.

Fig. 9 Yield distribution of products in the reaction of $\text{A}_2\text{-}2$ and $\text{C}_4\text{H}_4$ ($\text{C}_4$).

Fig. 10 Potential energy surface for anthracene formation in reaction $\text{A}_2\text{-}2 + \text{C}_4\text{H}_4$, 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 $A_2$-$I + C_4H_4$ 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 A1-H-C4H4 (A2) and A2-H-C4H4 (A3) reaction systems, reaction time = 10 ms.

Table 1. Reaction rate parameters for A1-H-C4H4 system, in the form of AT^nexp(-E/RT), units are s⁻¹, cm³mol⁻¹s⁻¹ and kcal.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>E</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1+H → A1+H₂</td>
<td>6.75x10⁸</td>
<td>1.910</td>
<td>15.61</td>
<td>[16]</td>
</tr>
<tr>
<td>A1+H₂ → A1+H</td>
<td>1.22x10⁴</td>
<td>2.655</td>
<td>42.66</td>
<td>[16]</td>
</tr>
<tr>
<td>P₃+H → A₁+H+C₄H₄</td>
<td>2.32x10⁻¹</td>
<td>4.840</td>
<td>23.21</td>
<td>[25]</td>
</tr>
<tr>
<td>P₃+H → P₂+H</td>
<td>2.84x10⁻¹⁰</td>
<td>0.120</td>
<td>27.31</td>
<td>[25]</td>
</tr>
<tr>
<td>P₂+H → P₃+H</td>
<td>3.13x10⁻¹⁰</td>
<td>0.150</td>
<td>26.58</td>
<td>[25]</td>
</tr>
<tr>
<td>P₂+H → A₂+H</td>
<td>1.50x10⁻¹⁸</td>
<td>-0.950</td>
<td>15.43</td>
<td>[25]</td>
</tr>
<tr>
<td>P₃+H → A₂+H</td>
<td>8.49x10⁻³¹</td>
<td>-4.660</td>
<td>29.38</td>
<td>[25]</td>
</tr>
</tbody>
</table>

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

Table 2. Reaction rate parameters in the form of AT^nexp(-E/RT), units are s⁻¹, cm³mol⁻¹s⁻¹ and Kcal.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Entrance well</th>
<th>A</th>
<th>n</th>
<th>E</th>
<th>Valid T range (K)</th>
<th>P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₂-1+C₄H₄→CS₂</td>
<td>CS₂</td>
<td>2.59x10⁻⁸⁹</td>
<td>-81.54</td>
<td>155.02</td>
<td>800-1600</td>
<td>0.1-100</td>
</tr>
<tr>
<td>A₂-1+C₄H₄→A₃+H</td>
<td>CS₂</td>
<td>9.52x10⁻¹⁸</td>
<td>-1.862</td>
<td>25.08</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*A₂-1+C₄H₄→CS₁₀_P+H</td>
<td>CS₂</td>
<td>7.05x10⁻³⁰</td>
<td>-4.693</td>
<td>28.68</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*A₂-1+C₄H₄→CS₁₁_P+H</td>
<td>CS₂</td>
<td>2.17x10⁻²⁹</td>
<td>-4.271</td>
<td>34.96</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₀_P+H→CS₂</td>
<td>CS₂+CS₁₆</td>
<td>3.13x10⁻⁹³</td>
<td>-82.31</td>
<td>155.32</td>
<td>800-1600</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*CS₁₀_P+H→CS₇_P+H</td>
<td>CS₂+CS₁₆</td>
<td>2.19x10⁻³⁴</td>
<td>-5.869</td>
<td>33.62</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₀_P+H→CS₁₁_P+H</td>
<td>CS₂+CS₁₆</td>
<td>1.94x10⁻⁴²</td>
<td>-7.615</td>
<td>41.50</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*CS₁₀_P+H→A₂-1+C₄H₄</td>
<td>CS₂+CS₁₆</td>
<td>2.51x10⁻²⁷</td>
<td>-3.723</td>
<td>27.30</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₁_P+H→CS₂</td>
<td>CS₂</td>
<td>6.82x10⁻³⁰²</td>
<td>-85.12</td>
<td>160.92</td>
<td>800-1500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₁_P+H→CS₁₃_P+H</td>
<td>CS₂</td>
<td>1.06x10⁻²¹</td>
<td>-2.094</td>
<td>24.08</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₁_P+H→CS₁₀_P+H</td>
<td>CS₂</td>
<td>4.40x10⁻³⁰</td>
<td>-4.298</td>
<td>25.62</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>CS₁₁_P+H→A₂-1+C₄H₄</td>
<td>CS₂</td>
<td>3.19x10⁻²⁷</td>
<td>-3.616</td>
<td>29.56</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*CS₁₇_P+H→CS₇_P+H</td>
<td>CS₂₀+CS₁₃</td>
<td>1.44x10⁹</td>
<td>1.530</td>
<td>5.16</td>
<td>800-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*CS₁₇_P+H→CS₁₀_P+H</td>
<td>CS₁₃</td>
<td>9.92x10⁶</td>
<td>2.338</td>
<td>35.12</td>
<td>1400-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>*CS₁₇_P+H→CS₁₁_P+H</td>
<td>CS₁₃</td>
<td>4.85x10⁸</td>
<td>1.838</td>
<td>42.64</td>
<td>1400-2500</td>
<td>0.1-100</td>
</tr>
<tr>
<td>A₂-1+C₄H₄→CS₂₀</td>
<td>CS₂₀</td>
<td>3.77x10⁻²⁶⁰</td>
<td>-74.06</td>
<td>128.74</td>
<td>800-1500</td>
<td>0.1-100</td>
</tr>
</tbody>
</table>
A_{2}+C_{4}H_{4} \rightarrow CS_{7}P+H

\begin{align*}
A_{2}+C_{4}H_{4} & \rightarrow CS_{35}P+H & CS20 & 2.14 \times 10^{53} & -11.73 & 39.84 & 800-2500 & 0.1-100
A_{2}+C_{4}H_{4} & \rightarrow CS_{35}P+H & CS20 & 2.60 \times 10^{10} & 0 & 21.90 & 800-2500 & 0.1-100
\end{align*}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetic Parameter</th>
<th>Rate Constant</th>
<th>Reaction Constant</th>
<th>Temperature Limit</th>
<th>High-pressure Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS55_P+H → CS56_P+H</td>
<td>CS40</td>
<td>1.24x10^{21}</td>
<td>-1.83</td>
<td>41.70</td>
<td>800-2500</td>
</tr>
<tr>
<td>CS55_P+H → A2-2+C4H4</td>
<td>CS40</td>
<td>7.87x10^{53}</td>
<td>-10.83</td>
<td>48.66</td>
<td>800-2500</td>
</tr>
<tr>
<td>CS56_P+H → CS7_P+H</td>
<td>CS46</td>
<td>7.31x10^{16}</td>
<td>-0.8238</td>
<td>9.46</td>
<td>800-2500</td>
</tr>
<tr>
<td>CS56_P+H → CS54_P+H</td>
<td>CS46</td>
<td>1.35x10^{19}</td>
<td>-1.29</td>
<td>40.06</td>
<td>1000-2500</td>
</tr>
<tr>
<td>CS56_P+H → CS55_P+H</td>
<td>CS46</td>
<td>3.57x10^{26}</td>
<td>-3.202</td>
<td>51.86</td>
<td>1200-2500</td>
</tr>
<tr>
<td>CS56_P+H → A2-2+C4H4</td>
<td>CS46</td>
<td>1.05x10^{20}</td>
<td>-1.409</td>
<td>43.86</td>
<td>1100-2500</td>
</tr>
<tr>
<td>A2-1+C4H4 → all products</td>
<td>CS2</td>
<td>8.10x10^{1}</td>
<td>3.206</td>
<td>1.641</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-1+C4H4 → all products</td>
<td>CS20</td>
<td>4.73x10^{2}</td>
<td>2.831</td>
<td>1.452</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-2+C4H4 → all products</td>
<td>CS40+CS72</td>
<td>1.23x10^{2}</td>
<td>3.053</td>
<td>1.834</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-1+C4H4 → all products</td>
<td>CS57+CS66</td>
<td>4.26x10^{2}</td>
<td>2.928</td>
<td>0.752</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-1+C4H4 → A2 + i-C4H3</td>
<td>-</td>
<td>2.91x10^{0}</td>
<td>3.579</td>
<td>5.30</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2 + i-C4H3 → A2-1+C4H4</td>
<td>-</td>
<td>4.25x10^{0}</td>
<td>3.468</td>
<td>21.16</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-1+C4H4 → A2 + n-C4H3</td>
<td>-</td>
<td>9.00x10^{-1}</td>
<td>3.77</td>
<td>8.49</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2 + n-C4H3 → A2-1+C4H4</td>
<td>-</td>
<td>3.71x10^{1}</td>
<td>3.468</td>
<td>9.58</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-2+C4H4 → A2 + i-C4H3</td>
<td>-</td>
<td>4.97x10^{0}</td>
<td>3.525</td>
<td>5.24</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2 + i-C4H3 → A2-2+C4H4</td>
<td>-</td>
<td>3.34x10^{0}</td>
<td>3.512</td>
<td>20.92</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2-2+C4H4 → A2 + n-C4H3</td>
<td>-</td>
<td>2.73x10^{0}</td>
<td>3.615</td>
<td>8.78</td>
<td>800-2500</td>
</tr>
<tr>
<td>A2 + n-C4H3 → A2-2+C4H4</td>
<td>-</td>
<td>1.23x10^{1}</td>
<td>3.576</td>
<td>9.04</td>
<td>800-2500</td>
</tr>
</tbody>
</table>

*Reactions filtered by pathway analysis.

*aHigh-pressure limit