The growth of PAHs and soot in the post-flame region

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Abstract

The PAHs- C_2H_2 pathway ($PAHs + C_2H_2 \rightarrow intermediate \rightarrow product + H_2$) has been shown, in theory, to be the important contributor to the growth of polycyclic aromatic hydrocarbons (PAHs) and soot in the post-flame region where H atoms are rare. Calculations of the potential energy surface (PES) using the DFT B3LYP 6-311 + G(d,p) method, and the reaction rate coefficients using the RRKM theory, reveal that arm-chair and bridge surface sites share similar kinetic characteristics, and are more likely to be the targets of C_2H_2 molecules in flames compared to zig-zag and 5-membered ring surface sites. Results show that the energy barrier of a 2-H elimination reaction (14–23.8 kcal/mol) is much lower than that of a 1-H elimination (typically 30–40 kcal/mol) for some molecules. The formation of pyrene from phenanthrene via HACA ($PAHs + H \rightarrow PAHs\ radical + C_2H_2 \rightarrow intermediate \rightarrow product + H$) and PAHs- C_2H_2 pathways is investigated using a closed homogeneous zero-dimensional reactor with combustion parameters abstracted from the premixed stagnation $C_2H_4/O_2/Ar$ sooting flame. Results show that the HACA pathway is the dominant pathway for the formation of PAHs and soot surface growth in the main-flame region where H atoms are abundant, but that the PAHs- C_2H_2 pathway is the preferred pathway in the post-flame region. Our study also suggests that the soot nucleation involving a chemical coalescence of moderate-sized PAHs into a crosslinked three-dimensional structure via the addition reactions of PAHs and PAH radicals in the main-flame region should be considered for inclusion in any soot modeling.

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1. Introduction

Driven by the need to continually improve the design and performance of clean combustion engines, our understanding of polycyclic aromatic hydrocarbons (PAHs) and soot formation has evolved

from phenomenological observation to quantitative description over the last two decades, especially in C_2H_4 flames [1–4]. It is well accepted that benzene plays an important role in the formation of PAHs and soot, and that it is formed mainly by the addition reaction $C_2H_x + C_4H_x$, the recombination reaction of two C_3H_3 radicals, and the cyclization reaction of C_6H_x [5–8]. The formation of PAHs starting from benzene has been modeled by the widely used hydrogen-abstraction—carbon-addition (HACA) pathway, which was originally

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proposed by Frenklach and co-workers [7, 9]. However, the HACA pathway is not strong enough to explain the fact that the formation of PAHs and soot still occurs in the post-flame region where the concentration of H atoms is very low [3].

The electronic, photonic, transport, spin and chemical reactivity properties of PAHs have sparked intense interest in materials science [10,11]. This is because PAHs can be used as model molecules for nanographenes [12], which are promising candidates for key applications of non-linear optics [13]. The theoretical study by Nagai et al. [14] and You et al. [15] showed that the PAHs have significant di-radical or multi-radical characteristics, and that the edge of PAHs is the main active moiety via analysis of molecular orbital theory. Therefore, the addition of active small molecules to the edge of PAHs may happen in flames. Among active small molecules, C_2H_2 molecule should be the priority object due to the triple bond and relative high concentration in the whole flame region. Additionally, a study by Kislov et al. showed that the addition of C_2H_2 to biphenyl led to the formation of phenanthrene without the presence of H atoms [16], and suggested that the growth of PAHs and soot without the assistance from H atoms at high temperature is possible. This provides a potential pathway accounting for PAHs and soot growth in the post-flame region where the temperature is higher than 1500 K. However, the probability for C_2H_2 addition to different surface site of PAHs (or soot) needs further investigation, as the oxidation rate of PAHs is very sensitive to the type of surface site targeted by oxygen atoms [17,18]. Additionally, the competitiveness of the PAHs- C_2H_2 pathway ($PAHs + C_2H_2 \rightarrow intermediate \rightarrow product + H_2$) in sooting flame needs further discussion.

Here, the sensitivity of the PAHs + C_2H_2 pathway towards the type of surface site exhibited by PAHs is closely examined. Particular attention is paid to the zig-zag (naphthalene), armchair (phenanthrene), 5-membered ring (acenaphthylene), and bridge (biphenyl) surface sites. The bridge surface sites have received less attention in previous studies, yet they may be very abundant in transportation fuel flames. Indeed, mass spectrometric data reveal that the phenyl radical addition reaction (like phenyl + phenyl $\rightarrow$ biphenyl) should be the main growth pathway of PAHs instead of the acetylene addition reaction in benzene pyrolysis [19]. To extend the kinetic parameter of the PAHs + C_2H_2 pathway from PAHs to soot, the size effect of PAHs on the PAHs + C_2H_2 pathway is also examined.

The PES and reaction rate coefficients of the PAH + C_2H_2 pathway using both the density functional theory (DFT) and the Rice – Ramsperger – Kassel – Marcus (RRKM) theory are investigated. Subsequently, the forma-

tion of pyrene with the PAH + C_2H_2 pathway first and then with the HACA pathway, both under C_2H_4 sooting flame conditions, is discussed. Finally, we evaluate the potential of a mechanism for soot nucleation and surface growth considering the PAHs + C_2H_2 pathway.

2. Calculation details

In this study, the optimization of molecule structures and vibrational frequency calculations were carried out using the DFT B3LYP 6-311 + G(d,p) method [20,21]. A factor of 0.967 is applied to correct the vibrational frequencies. We further refine the PES of naphthalene + C_2H_2 and biphenyl + C_2H_2 reactions at the CBS-QB3 level, in order to estimate the precision of the energy value obtained with the DFT method. The application of the CBS-QB3 method to other PAHs is limited by its memory requirement; for example, 300 GB memory is not enough to store the integrals file of phenanthrene. Intrinsic reaction coordinate (IRC) calculations are performed to ensure that the transition state is connected to the corresponding reactant and product. The Gaussian 09 program package is selected for all quantum chemistry calculations [22].

We evaluate the rate coefficients of unimolecular thermal decomposition reactions based on the RRKM theory by solving the master equation using the MultiWell suite of codes (MultiWell-2016.2) [23–25]. The rate coefficients of biomolecular reactions are derived from the corresponding unimolecular reaction rates and equilibrium constants. Brevity, the pressure is set as 1 atm in MultiWell suite and the exponential-down model with $\langle \Delta E_{down} \rangle = 260 \text{ cm}^{-1}$ was selected to describe the collisional energy transfer. The argon was used as the bath gas collider with Lennard-Jones parameters σ and ε/kB equaling to 3.47 Å and 114 K, respectively. More details on how we evaluate the rate coefficients can be found in our previous studies [5,17].

3. Results and discussion

3.1. Potential energy surface

The chemical species are named according to the type of surface site C_2H_2 molecule targets. S1, S2, S3 and S4 represent the PAHs- C_2H_2 pathway occurred on the armchair (Fig. 1a and b), bridge (Fig. 1c and d), zig-zag (Fig.S1 e and f) and 5-membered ring (Fig.S1 g and h) surface sites of PAHs, respectively. The PAHs- C_2H_2 pathway comprises two elementary reaction steps: one is the addition of C_2H_2 , and the other is the release of H_2 , as presented in Fig. 1. The addition of C_2H_2 of the PAHs- C_2H_2 pathway is highly sensitive to the

Fig. 1. The potential energy surface for PAH- C_2H_2 pathway; the energies are calculated at B3LYP 6-311 + G(d,p) level.

type of surface site. It was found that the energy barrier of C_2H_2 addition to the zig-zag (naphthalene) and 5-membered ring (acenaphthylene) is 72.0 and 68.6 kcal/mol, which is higher than that to the armchair (phenanthrene, 48.6 kcal/mol) and bridge (biphenyl, 48.8 kcal/mol) by at least 20 kcal/mol, as shown in Fig.S1. This suggests that the armchair and bridge surface site are the priority target for the C_2H_2 molecule, compared with the zig-zag surface site and 5-membered ring surface site. For brevity, the detail of PAHs- C_2H_2 pathway occurred on zig-zag and 5-membered ring surface site is moved to the Fig.S1 of the supplementary material. The energy barrier of the 2-H elimination reaction ($S1-CS2 \rightarrow S1-CS3 + H_2$) is as low as 14.8 kcal/mol, which is much lower than the value (92.3 kcal/mol) in our previous study [8] for a similar 2-H elimination reaction, and even lower than that of 1-H elimination reaction (typically 30–40 kcal/mol) [5]. The elementary reaction features of the PAHs- C_2H_2 pathway are almost insensitive to the size of PAHs, but the energy barrier for the addition of C_2H_2 slightly decreases for larger PAHs. For example, the energy barriers for the reactions $S1-CS4 + C_2H_2 \rightarrow S1-CS5$ is lower than that of $S1-CS1 + C_2H_2 \rightarrow S1-CS2$ by 8.7 kcal/mol. This

may be due to the enhanced reactivity at the edge of larger PAHs [14]. The corresponding IRC results are presented in Fig. S2 in the supplementary material.

Generally, characteristics of the bridge reaction system (S2) and the armchair reaction system (S1) are similar. The PES results indicate that the structures with the benzene ring in a staggered arrangement (S2-CS6) are more likely to be formed than those in a partially linear arrangement (S2-CS8), due to the lower energy barrier of the C_2H_2 addition reaction. This makes it easier for the PAHs- C_2H_2 pathway to occur, as the vanishing of the bridge surface site gives more accessibility to the armchair surface site.

In order to more accurately estimate the energy barriers associated with the various reactions, the PES of naphthalene + C_2H_2 and $S2-CS1 + C_2H_2$ reactions are refined at the CBS-QB3 level. Results show that the DFT method overestimates the energy barrier of the addition reaction of C_2H_2 to naphthalene by 6.9 and to $S2-CS1$ by 7.1 kcal/mol respectively, as illustrated in Figs.S3–S4. In the following kinetic analysis, the gaps in energy barriers calculated by DFT and CBS-QB3 methods for other C_2H_2 addition reactions are assumed to

Table 1
Reaction Rate Coefficients in the Form of $AT^n \exp(-E/RT)^a$.

Reaction	<i>A</i>	<i>n</i>	<i>E</i>
Armchair			
S1-CS1 + C ₂ H ₂ → S1-CS2	2.1×10^2	2.585	39.92
S1-CS2 → S1-CS1 + C ₂ H ₂	8.7×10^{32}	−5.5	44.06
S1-CS2 → S1-CS3 + H ₂	1.3×10^{10}	0.7003	14.00
S1-CS3 + H ₂ → S1-CS2	2.8×10^{-3}	4.27	70.36
S1-CS4 + C ₂ H ₂ → S1-CS5	4.6×10^1	2.603	31.18
S1-CS5 → S1-CS4 + C ₂ H ₂	4.9×10^{31}	−4.881	54.28
S1-CS5 → S1-CS6 + H ₂	3.4×10^{12}	0	22.26
S1-CS6 + H ₂ → S1-CS5	6.4×10^2	2.363	66.14
Bridge			
S2-CS1 + C ₂ H ₂ → S2-CS2	2.0×10^2	2.646	40.04
S2-CS2 → S2-CS1 + C ₂ H ₂	3.9×10^{-4}	4.903	25.96
S2-CS2 → S2-CS3 + H ₂	1.2×10^{12}	0.1182	17.06
S2-CS3 + H ₂ → S2-CS2	2.2×10^2	2.818	70.34
S2-CS4 + C ₂ H ₂ → S2-CS5	5.3×10^1	2.628	35.86
S2-CS5 → S2-CS4 + C ₂ H ₂	3.5×10^6	2.174	33.74
S2-CS5 → S2-CS6 + H ₂	5.3×10^{10}	0.5964	19.20
S2-CS6 + H ₂ → S2-CS5	5.8×10^1	2.826	64.80

^a The energy barrier of C₂H₂ addition reaction are estimated at CBS-QB3 level, and units are kcal/mol, K, cm³mol^{−1}s^{−1}, and/s. The effective temperature ranges from 800 to 2500 K, and the pressure is 1 atm.

be the same as for the S2-CS1 + C₂H₂ (naphthalene + C₂H₂) reaction; this is because the C₂H₂ addition reactions on larger PAHs present almost similar reaction features, including the vibration mode of transition state and the energy barrier at B3LYP 6-311 + G(d,p) level.

3.2. Kinetic analysis

The rate coefficients are evaluated at 1 atm and for a temperature range of 800–2500 K. To examine the accuracy of our rate coefficients, the theoretical rate coefficients of phenoxy decomposition and C₆H₅ + C₂H₂ → C₆H₅C₂H + H addition reactions were compared with corresponding experimental values in previous studies [5,17], and the uncertainty is within a factor of 3. Additionally, our rate coefficient calculation results for the reaction of S2-CS1 + C₂H₂ → S2-CS2 are compared with those reported by Kislov et al. [16]. The values reported here are slower by a factor of 1.27 at 1500 K. The details and deviation analyses are provided in Tables S1–S2. The formation of S2-CS8 species with partial benzene rings in a linear arrangement in the S2 reaction system is not considered here due to their higher energy barriers compared with the energy barriers for the formation of S2-CS6. The kinetic parameters of the PAHs-C₂H₂ reactions are presented in Table 1.

As shown in Fig. 2(a), the values of the rate coefficients for the C₂H₂ addition reaction on zig-zag (S3-CS1) and 5-membered ring surface sites (S4-

CS1) are quite close, but much lower than those for the armchair (S1-CS1) and bridge surface sites (S2-CS1). This means that the new carbon ring is more likely to be formed on the armchair or bridge surface site of PAHs and soot surface. We also observed that the rate coefficients of C₂H₂ additions to PAHs are at least 5 orders of magnitude lower than those for C₂H₂ additions to PAHs radical even at 1500 K due the higher energy barrier. The comparisons between the reaction rate coefficients of 1-H and 2-H elimination reactions indicate that more attention should be given to 2-H elimination reactions, as shown in Fig. 2(b). The energy barrier of 2-H elimination reaction varies from 14.0 to 85.0 kcal/mol in this study, its correlation with PAHs structure is shown in Fig. 3. It seems that the structure symmetry along the two C atoms where the redundant H atom locates is the main factor determining the energy barrier of 2-H elimination reaction. If the molecule structure is symmetrical like (a) and (b) in Fig. 3, the 2-H elimination is easy to happen with a lower energy barrier (14.8 and 14.2 kcal/mol). The energy barrier increases to 20.4 kcal/mol if the whole structure like (c) in Fig. 3 is asymmetrical along the purple dash line, but the local structure is symmetrical (both C atoms connect to two benzene rings). If the local structure is asymmetrical like (d) in Fig. 3, where one C atom connects two 5-membered rings and the other C atom connects 5-membered ring and benzene ring, the 2-H elimination reaction is unlikely to happen due to the relative high energy barrier (85.0 kcal/mol).

3.3. Simulation for pyrene formation

Here, we discuss the competitiveness of the proposed PAHs-C₂H₂ (PAHs + C₂H₂ → intermediate → product + H₂) pathway relative to the HACA (PAHs + H → PAHs radical (+ C₂H₂) → intermediate → product + H) pathway. To this end, the formation of pyrene starting from phenanthrene in a closed homogeneous zero-dimensional reactor is simulated, using the Chemkin Pro software. For convenience, phenanthrene is also considered as a part of the soot (C_nH_m) surface and pyrene as the addition product (C_{n+2}H_m) in the rate discussion of soot surface growth. These assumptions are reasonable as the reaction type and reaction rate constant of the soot surface growth are considered to be equal to that of PAHs surface growth along the HACA pathway in current soot models [7,27]. The rate constants of soot surface growth on an armchair surface site via the PAHs-C₂H₂ pathway are assumed to be equal to that of S1-CS4-C₂H₂ due to its size. To make the comparison more rigorous, H abstraction from every C atom on phenanthrene surface is considered as shown in Fig. S5 [28]. The addition reactions of H and O₂ with PAH radicals (soot radicals) are also considered for

Fig. 2. Comparisons of reaction rates for the PAHs + C_2H_2 pathway, the rate coefficients of $A_1 + C_2H_2 \rightarrow A_1C_2H_2$ and $A_1C_2H_2 \rightarrow A_1C_2H + H$ come from [26].

Fig. 3. The correlation of PAHs structure with the energy barrier of 2-H elimination reaction.

the HACA pathway, as the active site on PAHs (soot) is available for H and O_2 before being targeted by C_2H_2 [28,29]. The specific reactions and corresponding reaction rate coefficients used in the simulation of PAHs and soot surface growth along HACA pathway are listed in Table S4 and Table S5 respectively. The species considered in the simplified combustion atmosphere include phenanthrene, C_2H_2 , O_2 , H_2 , H, and N_2 . The mole fractions of phenanthrene, C_2H_2 , O_2 , and H_2 are fixed at 0.0001, 0.04, 0.15, 0.1, in accordance with the experimental results [30–32]. Temperature and mole fraction of H (mole fraction of $N_2 = 1 - \text{others}$) are abstracted at different heights above burner surface (HABs) in the premixed stagnation flame at $C_2H_4/O_2/Ar = 16.15/23.44/60.41$ with a inlet gas velocity of 20 cm/s, using the ABF mechanism [7]. The simulation is carried out at 1 atm with a residence time of 0.02 s.

The formation of pyrene was investigated at different HABs where the peak concentration of H atom (A, $T = 1575$ K, $H = 7.17 \times 10^{-4}$),

the peak flame temperature (B, $T = 1839$ K, $H = 2.10 \times 10^{-4}$), and the turning point of temperature profile (C, $T = 1672$ K, $H = 4.89 \times 10^{-5}$) are located and shown in Fig. 4(a). During the growth of PAHs, pyrene is predominantly formed with the HACA pathway in the main reaction zone (A), mainly formed through the S1-CS1- C_2H_2 pathway at position B and C, as shown in Fig. 4(b). Comparative results also indicate that the pyrene formation is mainly constrained by the H mole fraction for HACA pathway, and by the flame temperature for the PAHs- C_2H_2 pathway.

Observations show that soot surface growth on armchair surface sites by PAHs- C_2H_2 pathway is competitive with that of HACA pathway in the past-flame region (Fig. 4(b)). We also investigate the formation of acenaphthylene (S3-CS3) starting from naphthalene (S3-CS1), either with a HACA or a naphthalene + $C_2H_2 \rightarrow$ acenaphthylene + H_2 pathway. Results show that the latter pathway is unable to compete with the HACA pathway, even in the post-flame region of high-temperature flame.

Fig. 4. The mole fractions of H, temperature in premixed stagnation flames at $C_2H_4/O_2/Ar = 16.15/23.44/60.41$, $V_{cold-gas} = 20$ cm/s (a), and mole fraction of pyrene in 0-D chamber at $t = 0.02$ s (b).

Fig. 5. Conceptual mechanism of soot nucleation and surface growth, with structures optimized at pm6 level.

3.4. Implications for soot nucleation and surface growth

Currently, there are three conceptual pathways leading to soot nucleation [3,33–36]: 1) the dimerization of two pyrene molecules [36], 2) the formation of fullerene-like structures from large PAHs via a HACA pathway [33], 3) the chemical coalescence of moderate-sized PAHs into crosslinked three-dimensional structures via the addition reaction of PAHs and PAH radicals [37,38] as shown

in Fig. 5(a)–(c). However, each pathway has a concern. In the first pathway, the dimer is likely to be dissociated at flame temperatures due to the weak binding energy [39] and the non-reactive collisions with gas molecules [3]. The rate of the second pathway is too low to capture the experimentally determined soot nucleation rates in flames [40]. The third pathway is limited to the generation of PAH radicals via H-abstraction reaction and possible further growth in the post-flame region where H atoms are rare. By investigating PAHs-C₂H₂ pathway, we

hope to dispel this doubt. One can easily speculate that C_2H_2 will bond to two PAH fragments connected by the bridge surface site on the crosslinked three-dimensional structure, similarly to the process (a) $\rightarrow$ (d), (b) $\rightarrow$ (e), and (c) $\rightarrow$ (f) shown in Fig. 5. The termination of one bridge site gives birth to two or three armchair sites, which is illustrated by the processes (a) $\rightarrow$ (d) and (b) $\rightarrow$ (e). Furthermore, a new armchair site can also be formed when the existing armchair site is occupied, which is evidenced by the processes (d) $\rightarrow$ (g) and (e) $\rightarrow$ (h). In this way, the thermal stability of the curved three-dimensional structure is enhanced by bridging two PAH fragments, and the formed structure then rapidly grows up in the main-flame and post-flame region via the addition of C_2H_2 on the newly formed armchair site, as shown in Fig. 5.

4. Conclusion

In this study, the PAHs- C_2H_2 reaction mechanism is investigated by applying both DFT B3LYP 6-311 + G(d,p) and RRKM theories. Also, the formation of pyrene under sooting conditions for both the HACA and the PAHs- C_2H_2 pathways is studied using a zero-D reactor. Additionally, the nucleation and surface growth of soot with the PAHs- C_2H_2 pathway are discussed.

Apart from HACA pathway, our results show that the growth of PAHs and soot can be achieved by a C_2H_2 addition followed by an H_2 releasing reaction. In some reactions, the energy barrier of a simultaneous elimination of 2-H (14–23.8 kcal/mol) is much lower than that of 1-H elimination reaction (typically 30–40 kcal/mol).

Potential energy surface and kinetic analysis indicate that the armchair and bridge surface sites are inclined to be occupied by C_2H_2 molecules compared with the zig-zag and 5-membered ring.

The simulation of pyrene formation suggest that the HACA pathway is dominant in the main-flame region where H atoms are abundant, and the PAHs- C_2H_2 pathway occurring on armchair and bridge surface sites is more competitive in the post-flame region where H atoms are rare, especially in high-temperature flames.

The soot nucleation is likely initiated by the chemical coalescence of moderate-sized PAHs into crosslinked three-dimensional structures via the addition reaction of PAH and PAH radicals in the main-flame region, followed by the addition of C_2H_2 on the bridge and armchair sites of soot surface in the post-flame region.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2018.05.047.

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