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Polycyclic Aromatic Hydrocarbon Formation Mechanism in the “Particle Phase”. A Theoretical Study

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Running Title:  PAH Formation in the Particle Phase

Graphical contents entry:

A gas phase growing PAH-like radical prefers cyclization over chain elongation by ethyne addition, when both can take place, and adsorption on a soot platelet enhances this preference.
Summary: The synthesis of polycyclic aromatic hydrocarbons (PAHs) and the formation of soot platelets occur both during combustion at relatively low \([\text{O}_2]\), or under pyrolysis conditions. When the PAH size grows beyond the number of three-four condensed cycles, the partitioning of PAHs between the gas and particle phases favours the latter (i.e. adsorption). This study aims to assess which role can the soot particle play during PAH synthesis. In particular, if catalytic or template effects of some sort can be exerted by the soot platelet on the adsorbed growing PAH-like radical. Our theoretical calculations indicate that chain elongation by ethyne addition cannot compete with cyclization, when both can take place in the growing PAH-like radical, already in the gas phase. When it is adsorbed, cyclization is found to become easier than in the gas phase (more so, in terms of Gibbs free energy barriers, at higher temperatures), hinting to some sort of template effect, while chain elongation by ethyne addition becomes somewhat more difficult. The underlying soot platelet can assist (at lower temperatures) the formation of a larger aromatic hydrocarbon, by a final hydrogen abstraction from that endocyclic saturated carbon the newly formed cycle still bears. As an alternative (at higher temperature), a spontaneous hydrogen atom loss can take place. Finally, at rather low temperatures, the addition of the growing radical to the underlying soot platelet might occur and cause some reticulation, form more disordered structures, i.e. soot precursors instead of PAHs.

Keywords: 1) polycyclic aromatic hydrocarbons; 2) PAH growth; 3) adsorption; 4) soot; 5) density functional theory.

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Electronic Supplementary Information (ESI) for this article is available: it includes the geometries and energetics of all optimized structures (one pdf file).
Introduction

Soot aerosol contributes in a significant way to the total mass of atmospheric aerosol.\textsuperscript{1} Soot particles have an irregular agglomerate structure of graphenic layers, which can be curved and present defects; the layers gather as globular particles, which form, in turn, clusters of different shapes.\textsuperscript{ii} Polycyclic aromatic hydrocarbons (PAHs) are generated by the same combustion processes at relatively low O\textsubscript{2} concentrations which bring about the growth of soot platelets,\textsuperscript{iii,iv} or during pyrolysis.\textsuperscript{v} Moreover, both have been tentatively identified also in planetary atmospheres, in the envelopes of carbon-rich stars, or in the interstellar medium.\textsuperscript{vi} PAHs (and derivatives) not only share the same nature and origin of soot, but can also be found in association with it.\textsuperscript{vii,viii} While PAHs containing 4-5 rings are found partitioned between the gas phase and the particle phase (i.e. absorbed in, or adsorbed onto, solid particles), the heavier ones (more than 5 rings) are primarily found in the particle phase.\textsuperscript{ix} Since the aerosol can carry them into contact with, for example, the lung tissues, these species, adsorbed on fine particles, are of concern as regards human health. The interest in this class of compounds is also theoretical, as regards in particular the important concept of aromaticity.\textsuperscript{x} On the other hand, technological applications have been envisaged, and this has prompted the synthesis and study of very large systems.\textsuperscript{x}

The most commonly mentioned and discussed growth mechanism for PAHs and soot particles, under combustion conditions, is the \textit{HACA} mechanism (\textit{Hydrogen Abstraction–C\textsubscript{2}H\textsubscript{2} Addition}), independently proposed by Frenklach\textsuperscript{xi} and Bockhorn,\textsuperscript{xii} which involves alternate cyclization and ethyne addition steps. Other growth models have been considered as well, as possible or promising, and included in kinetic models.\textsuperscript{xiii,xiv,xv,xvi} \textit{HACA} variants, \textit{e.g.} that put forward by Bittner and Howard,\textsuperscript{xvii} have been discussed in more recent years.\textsuperscript{xviii,xix} Also some gas-phase quantum mechanical studies have dealt with growth mechanisms.\textsuperscript{xx,xxi,xxii,xxiii,xxiv}

Though PAHs are sometimes seen as precursors of soot, other opinions have appeared in the literature. Homann hypothesized\textsuperscript{iii} that the reactions leading to PAHs could also bring about the formation of more irregular structures, starting from association between PAHs and subsequent H\textsubscript{2} losses. These structures, called "aromers" (see ref. iii, pp 2448-2450), could grow as cages containing more or less hydrogens, become curved, and so be possible precursors of both fullerenes and soot, depending on temperature and relative abundance of small growth components, as ethyne. Thus, we can suppose that the synthesis of all these species could proceed also with some interaction among them. Indeed, PAHs have also been supposed to possibly originate on the surface of particulate matter, in view of the fact that they have been detected in diesel exhaust.\textsuperscript{xxv} Siegmann, Sattler, and Siegmann,\textsuperscript{xxvi} on the basis of their experimental results (relevant to atmospheric-pressure flames), put forward the hypothesis that soot synthesis can even precede PAH synthesis.
Scheme 1. Growth of a radical unsaturated system R by ethyne additions (pathway 3-8) and cyclization (pathways 3-4-7 and 3-5-6-7). The underlying model soot platelet P is not represented for clarity. Brackets hint to the focus of the paper, which is on the fate of the intermediate 3.

The present investigation aims to ascertain if, during PAH formation, when a growing unsaturated structure (R) is adsorbed on a soot platelet (P), particular effects can be present, which could be classified in a more or less appropriate way as “catalytic” or “template” effects. To this purpose, we will investigate the key step in PAH formation, cyclization, and assess if it can be contrasted by other processes. We do not aim to estimate if cyclization will, or will not, dominate over chain elongation on the whole, because we are not going to take into account all the possibilities. Therefore, we will attempt to assess:

(1) the geometrical traits and energetics of the “growing radical R – soot platelet P” system;

(2) if the interaction of R with underlying P models of different nature (vide infra) can affect the competition between chain elongation and cyclization, when both are possible because of the length of the growing open chain and its conformation with respect to the aromatic part (Ar) to which it is bound;
(3) if the soot platelet P can play some role different from being just a “base” which can hold together the reacting moieties, such as some sort of template or catalytic effect, causing the balance between simple further ethyne addition or ring closure to lean toward the latter;

(4) another possible effect of adsorption could be a direct addition reaction between the growing radical R and the platelet P, giving origin to some reticulation and more disordered structures, precursors of soot particles instead of PAHs.

To investigate these points computationally, we have limited the study to a single mechanism. Within the HACA mechanism, the Bockhorn-Frenklach and Bittner-Howard variants have been compared in theoretical studies of gas phase reactions and found to correspond to comparably viable channels. Indeed, in refs. xx and xxii, the latter was found slightly favored (further comments can be found in the ESI file, §1). Therefore, we have chosen the Bittner-Howard variant of HACA, which involves a growing PAH-like radical, Ph−CH=CH−CH=CH− (3 in Scheme 1), and ethyne.

Theoretical Method

All stationary points on the energy hypersurface, i.e. minima and first order saddle points, corresponding to transition structures (TS), were determined by gradient procedures within the Density Functional Theory (DFT), and making use of a modified B3LYP functional, B3LYP-D, which appears to describe the interaction of unsaturated systems in a rather reliable way. The B3LYP functional is of widespread use, and, even if prone to underestimate to some extent certain reaction barriers, has generally performed well as regards geometries and energetics. The B3LYP-D variant has been designed to allow the study of complexes of the van der Waals type, in which dispersion forces play a significant or dominant role. For this study in particular, it allows to define the energetics for the growing system R when it is in interaction with an unsaturated graphenic model for a soot platelet P. Such an approach has been found in recent investigations to provide quite satisfactory results.

The polarized 6-31G(d) basis set was used in the DFT(B3LYP-D) optimizations and subsequent vibrational analysis and thermochemistry assessment. The extension of the basis set was forcibly limited by the size of the R–P system studied. One particular optimization, aimed to explore the effects of size enlargement for the soot platelet model P, was even carried out with the smaller 3-21G(d) basis set as detailed in the Appendix.

When the nature of the 6-31G(d) critical points was checked by vibrational analysis, inspection of the normal mode related to the imaginary frequency was in all cases sufficient to confidently establish its
connection with the initial and final energy minima. The thermochemical corrections gave estimates of the zero point vibrational energy, by which the relative energies were corrected ($\Delta E_{ZPE}$), and allowed to estimate relative Gibbs free energies ($\Delta G$, reported in kcal mol$^{-1}$ throughout the paper). In all cases but one, 6-31G(d) energy data were associated with the 6-31G(d) thermochemistry. Only for the particularly large system mentioned above, the 3-21G(d) geometry was combined with a 6-31G(d) energy (single-point calculation), and with the 3-21G(d) thermochemistry (see the Appendix). The thermochemistry was assessed in all cases at temperatures ranging from room $T$ up to those typical of combustion ($T$ reported in the Tables in Kelvin degrees). Rate ratios were estimated by using Eyring’s formula and the computed Gibbs free energy differences.

The reacting system $R$ shown in Scheme 1 is considered in the calculations either by itself (“gas phase” results, reported in Table 1), or adsorbed onto the soot platelet model $P$ (dubbed “particle phase”, Tables 2-4). Whenever distinct moieties interact, the Basis Set Superposition Error (BSSE) relevant to their interaction is accounted for.$^{xxxix, xli}$

All calculations were carried out by using the GAUSSIAN 03 system of programs.$^{xli}$ The MOLDEN program was exploited for the graphics.$^{xlii}$

**Results and Discussion**

To address the points (1)–(4) declared in the Introduction, we will focus in the following (as hinted by the brackets in Scheme 1) only on the competition that can occur in the intermediate $3$, Ph–CH=CH–CH=CH·, taken as representative of $R$, between the cyclization channels, $3\text{-}4$ and $3\text{-}5\text{-}6$, and a further radical addition to ethyne, $3\text{-}8$, having all species either alone (subsection 1) or in interaction with a model PAH-like soot platelet $P$ (subsection 3A). Two different $R$–$P$ interaction modes are preliminarly discussed in subsection 2. Then, possible attacks by $3$ onto different underlying soot platelet models are also examined (subsection 3B). In the following, “gas phase” stands for: “computed in the absence of a model of soot platelet $P$”, as opposed to “particle phase”, in which case the computations are carried out for a growing system $R$ adsorbed onto $P$. So, $3$ will be in any case the reference (zero) for all energy and Gibb's free energy differences ($\Delta E$ and $\Delta G$) reported in the Tables ($\Delta G$ values discussed in the text). The intermediates $4$ and $6$ could add more ethyne molecules and these channels would bring about chain extension, ring closure, and a further system expansion. As an alternative to further growth, the final steps in Scheme 1 (4-7 or 6-7) exemplify, for any system size (Ar larger than Ph), the production of a PAH system (here 7) larger than the initial aromatic radical (here Ph·) by one aromatic ring.
1. “Gas phase” growth pathways for the system R

The "gas phase" pathways will provide an energetic reference (Table 1) for the subsequent discussion on the adsorbed system (Tables 2 and 3).

As regards the entropic contributions, only the $\Delta S$ value at $T = 300$ K is reported in all Tables, because its variation with $T$ is moderate; comprehensive data (Tables B-D) can be found in the ESI file, § 4-6. Ring closure 3-4 requires ca. 5-26 kcal mol$^{-1}$ (in the $T$ range 300-2300 K).$^{xl iii}$ This appears to indicate a rather easy monomolecular step. The competing H transfer 3-5 faces similar barriers (5-22 kcal mol$^{-1}$) and is favored to a limited extent by increasing temperatures. The subsequent ring closure 5-6 presents barriers of somewhat lower height (2-17 kcal mol$^{-1}$) with respect to either the preceding step 3-5, or the competing step 3-4. Finally, both radicals 4 and 6 can generate the larger aromatic system through H-loss processes, with barriers of ca. 15-18 kcal mol$^{-1}$, making reference to 4,$^{xl iii}$ or 33-34 kcal mol$^{-1}$, making reference to 6. These show a rather limited dependence on temperature.

Table 1. “Gas-phase” system. Energy and Free energy differences with respect to intermediate 3.$^{a}$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{ZPE}$</th>
<th>$\Delta S$</th>
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<td>T/K :</td>
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<td>cyclizations</td>
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<tr>
<td>3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
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<td>-0.1</td>
<td>-1.9</td>
<td>0.4</td>
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<tr>
<td>TS 5-6</td>
<td>0.5</td>
<td>-7.1</td>
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<tr>
<td>6</td>
<td>-57.4</td>
<td>-9.4</td>
<td>-55.4</td>
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aromatization

<table>
<thead>
<tr>
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<th>$\Delta E_{ZPE}$</th>
<th>$\Delta S$</th>
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<td>H loss TS 4-7</td>
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<td>H loss TS 6-7</td>
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<tr>
<td>7 + H</td>
<td>-25.8</td>
<td>10.5</td>
<td>-28.8</td>
</tr>
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</table>

chain extension
If chain elongation in 3 by HCCH addition is now considered (step 3-8), we see in Table 1 (ΔE_{ZPE} column) that the energy barrier is quite low, 0.2 kcal mol\(^{-1}\), to be compared with the 3.3-3.7 kcal mol\(^{-1}\) ΔE_{ZPE} barriers pertinent to the ring closure pathways. However, the entropic contribution is very different, as can be expected: -7 to -12 cal mole\(^{-1}\) K\(^{-1}\) for cyclization, vs. -34 to -33 for the ethyne addition step (see Table B in the ESI file, § 4). So, addition is severely penalized by the –TΔS term: its G barrier results already higher by ca. 5 kcal mol\(^{-1}\) at the lowest T, with respect to cyclization, and this difference rises to 51-54 kcal mol\(^{-1}\) at the highest T. The k_{cycl} / (k_{add}×[HCCH]) ratio can be assessed on the basis of reasonable hypotheses about the concentration of ethyne. However, even by using, for instance, a reported peak value for ethyne concentration in a diffusion flame\(^{xliv}\) as high as 12000 ppm, we can see that, in the gas phase, chain elongation has not even the chance of being a secondary pathway, when in direct competition with cyclization: k_{cycl} / (k_{add}×[HCCH]) = 10\(^7\), at typical combustion temperatures.

2. Mutual orientation of the R and P moieties

When the growing model system R is adsorbed onto the platelet model P, most of the steps shown in Scheme 1 are found to take place with two relative orientations. One arrangement is very close to be parallel (“∥”), while the other, which can be considered as perpendicular only in a very approximate way, is labeled nevertheless as “⊥” for convenience (see the ESI file, § 2, and the relevant structures, p 72 and ff.). Subsection 3 will deal only with the results obtained for the ∥ arrangement,\(^{xlv}\) because it is favored, as said, as soon as the system’s size grows beyond some limit (with consequent higher probability of being adsorbed).

To illustrate this point just by showing a trend, Figure 1 displays some DFT(B3LYP-D)/6-31G(d) complexation energy values.\(^{xlvi}\) These data indicate that a PAH-like system growing in size will begin to prefer a parallel arrangement, when increasing the system size from naphthalene to pyrene (point C in Figure 1). The inter-plane distance is 3.4-3.6 Å, larger, to some extent, than that found for graphite, 3.35 Å. Other relevant and consistent data on PAH dimers (naphthalene, anthracene, pyrene, coronene) can be found in two recent papers.\(^{xlvii,xlviii}\)
3. "Particle phase" growth pathways for the R–P system

Computations were carried out on the reacting system made by the intermediate 3, (Scheme 1), and by C2H2, taken as interacting with different PAH-like models (Pn) of an underlying soot platelet (Chart 1). The models explored were:

(P1) the planar PAH ovalene, C32H14;  
(P2) a larger and still planar PAH, tetrabenzo-ovalene, C42H16;  
(P3) a curved PAH containing a five-membered cycle, tribenzo-corannulene, C28H12;  
(P4) a modified ovalene system, in which the central carbon atom along the longer border is saturated by addition of one extra hydrogen: the resulting 7-H-ovalene, C32H15, is an "odd sp² carbon number/odd-π electron" system.\textsuperscript{xlix}

This forcibly limited series of platelet models encompasses a variety of structural and electronic situations that can be locally present in actual soot particles. We decided to carry out the complete exploration of the steps described in Scheme 1 by using only model P1, adsorption onto ovalene (subsection A here below), but we considered models P1, P3, and P4 to compare the key steps which could in principle compete (subsection B).
A. Complete survey of the possible reaction steps.

We consider now the complexation energies of the “reactant” 3 with P1, ovalene. In all structures having "parallel" orientation, the adsorbed growing system comes out to be positioned at ca. 3.5 Å with respect to the ovalene plane, a distance close to that mentioned for the structures shown in Figure 1. The BSSE-corrected energies are negative, thus describing stable associations (||: -11.4 kcal mol⁻¹; \(\bot\): -8.1 kcal mol⁻¹). However these values are significantly smaller than those expected for the association of larger systems. In fact, not only Pn but also R is to be considered here as a model. This means that also in 3 (+ ethyne, both interacting with Pn) Ph is to be intended as representative also of larger Ar groups. We can see that the -TΔS term heavily penalizes the complexes. Thus, we get estimates of the complexation constants which suggest, for this small model system, that only one molecule over \(10^{-3}-10^{3}\) would be adsorbed (T = 1100-2300 K).

This estimate stresses the point that the molecular system chosen for this study is to be intended just as a model used to ascertain the main points discussed in the text.

Cyclizations. In this case (Table 2), ring closure 3-4 (Figure 2) requires ca. 4-10 kcal mol⁻¹, which describes again a rather easy unimolecular step, actually becoming significantly easier than in the gas-phase case as temperature grows up. A similar trend is found for the competing H transfer 3-5 (Figure 3), whose
barrier heights also span the 4-10 range. But the subsequent ring closure 5-6 (Figure 4) requires overcoming barriers in the 1-15 range, therefore causing a preference for the 3-4 channel for a temperature higher than 700 K. The overall 3-5-6 channel could compete with the 3-4 channel only at the lowest temperatures.

**Chain extension.** When the adsorbed 3 system can undergo cyclization, it could also add ethyne instead, as an alternative. This could be either a free ethyne in the gas phase or an already adsorbed ethyne,
and we might assume that ethyne molecules are desorbed / adsorbed ceasessly on the soot platelet, and some can be available at any moment for addition. Therefore, if (adsorbed) 3 is the obvious energetic reference for the energetics of the unimolecular H transfer (3-5) and cyclization (3-4 and 5-6) processes, the references for the addition process could be two: either (A) “adsorbed 3 plus gas phase ethyne”, correponding to the Eley-Rideal mechanism,1 or (B) “the complex which has the ethyne and growing radical moieties still separate but both adsorbed onto ovalene” (labeled B-complex), correponding to the Langmuir-Hinshelwood mechanism.1 From Table 2, it can be seen that the energy barriers in the two cases are rather different: while $\Delta E_{ZPE}(A)$ is very small, $\Delta E_{ZPE}(B)$ is ca. 8 kcal mol$^{-1}$. Consistently (Figures 5 and 6), TS 3-8 (B) appears to be slightly later, in a geometrical sense, since the C−C distance of the forming bond is significantly shorter in the B case, and the ethyne HCC angle involving the carbon attacked by the radical center departs more significantly from its initial value of 180° (A: 171°; B: 158°). Besides, in TS 3-8 (B), the distance between the ethyne hydrogen pointing toward the platelet model and the platelet’s closest carbon is 2.66 Å, while in the B-complex it was 2.46 Å.

Table 2. “Particle-phase” system. Energy and Free energy differences with respect to intermediate 3.$^a$

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<thead>
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1
H loss TS 4'-7  -16.6  -10.6  -14.5  -9.8  -4.8  0.4  5.7  11.2
H abstr.TS 4-7  -18.2  -10.0  -16.4  -11.8  -6.7  -1.5  3.9  9.3
H loss TS 6-7  -24.7  -9.5  -21.8  -17.6  -13.1  -8.5  -3.7  1.3
7-H complex      -25.8  2.3  -26.4  -27.5  -28.9  -30.5  -32.2  -33.9
  7 + H           -15.2  52.7  -31.4  -51.9  -71.5  -90.5  -109.1  -127.4
H abstr.TS 6-7  -29.2  -13.6  -26.5  -20.4  -13.7  -6.8  0.2  7.4
7 + ovalene-H    -39.1  -4.4  -38.6  -36.4  -33.7  -31.1  -28.4  -25.7

a units: $\Delta E$ and $\Delta G$ in kcal mol$^{-1}$, $\Delta S$ in cal mol$^{-1}$ K$^{-1}$. Thermochemistry at 6-31G(d) (ZPE contribution, $\Delta H$, $\Delta S$) computed in correspondence of the 6-31G(d) optimized structures.

However, under hypothesis A, we find that the addition TS for chain lengthening is penalized severely by the $-T\Delta S$ term ($G$ barrier of 10-78 kcal mol$^{-1}$, with respect to adsorbed 3, close to the gas phase data: 10-76). Chain elongation again cannot compete, when in direct competition with cyclization:

$$k_{\text{cycl}}/(k_{\text{add}}*[\text{HCCH}]) = 10^8$$

at typical combustion temperatures (it was assessed $= 10^7$ in the gas phase). Assumption B could seem capable to put the chain elongation process on a better ground, by assigning to the soot element (ovalene) the task of possibly placing the to be-reactants in a convenient relative position. In other words, since hypothesis B relies on ethyne being already adsorbed on the platelet in the B-complex, it seems liable to reduce, at least partially, the unfavourable entropy change. In fact, the $G$ barrier spans the range 11-43 kcal mol$^{-1}$, and, from 700 K up to 2300, it is significantly lower that that assessed under hypothesis A (see in Table 2 the B-complex line and the following TS 3-8 line).

Figure 5. TS 3-8 for ethyne addition under hypothesis A.
Figure 6. TS 3-8 for ethyne addition under hypothesis B.

But, at this point, the obvious question is: how many ethyne molecules will be found adsorbed? Now, we can just estimate the ethyne complexation equilibrium constant $K$, based on the adsorption $\Delta G$’s. They are collected in Table 2 for the B-complex: all are positive and growing with $T$, thus indicating that the number of adsorbed ethynes will be negligible. Therefore, hypothesis A is more plausible. Chain extension remains described as not competitive with ring closure, in particular presenting higher $G$ barriers at higher temperatures.

Aromatization of the new cycle. As a possible last step in Scheme 1, we can consider that the $\pi$–delocalized free radical intermediates 4 and 6 can conduct further sequential additions to ethyne, leading to larger condensed systems, or produce an aromatic system having one ring more, 7, by C(sp$^3$)–H bond cleavage. The process discussed here for 4 and 6, and leading to naphthalene, is intended as representative of any conclusive step for PAH formation, also for larger systems generated by further HCCH additions. In Scheme 1, the ovalene interacting with the growing system is not represented, but can be imagined as underlying the various structures. The intermediate 4 can be adsorbed having its C(sp$^3$)–H bond preferentially pointing toward ovalene (H$_{\text{inner}}$), or in the opposite direction (H$_{\text{outer}}$). These structures are indicated as 4 and 4' in Table 2. The intermediate 6 carries both H$_{\text{inner}}$ and H$_{\text{outer}}$ on the sp$^3$ carbon. Dehydrogenation could simply take place, under combustion conditions, as a unimolecular H loss. Dissociation of H$_{\text{outer}}$ would require 15-17 kcal mol$^{-1}$ from 4', and 34-29 kcal mol$^{-1}$ from 6 ("H loss" entries in Table 2). However, it is interesting to notice that in both 4 and 6 the “soot platelet” can operate the abstraction of H$_{\text{inner}}$ (Figures 7 and 8 and "H abstr." entries in Table 2), though the underlying aromatic system becomes perturbed by the hybridization change. In the relevant transition structures, while H$_{\text{inner}}$ is transferred, the carbon (tertiary in 4 and still bearing H$_{\text{outer}}$ in 6) undergoes planarization (Figures 7 and 8). In the case of 4, the barrier for abstraction of this H$_{\text{inner}}$, to give 7 + ovalene-H, is 15-40 kcal mol$^{-1}$ high. The abstraction barrier 6-(7 + ovalene-H) is 29-35 kcal mol$^{-1}$ high. Consequently, H abstraction can be competitive with simple H loss at the lowest temperatures (up to ca. 1200 K for 6). At lower T the step from 6 is more endoergic (line: 7 + ovalene-H, +17 kcal mol$^{-1}$ at T=300 K, for instance), while at higher T it becomes close to isoergic (+2 kcal mol$^{-1}$). Since
at higher temperatures H abstraction can be less likely, one can imagine that, if sheer H loss cannot take place, the delocalized radical intermediates as 4 or 6 could undergo further additions (e.g. of ethyne molecules).

**Figure 7.** TS 4-7 for $H_{\text{inner}}$ transfer.

**Figure 8.** TS 6-7 for $H_{\text{inner}}$ transfer.
B. The key steps compared for adsorption on different soot platelet models.

In this phase, adsorption of the growing system also on the other models of Chart 1 is considered, and the free energy barriers are compared for the key steps. We begin by comparing (i) the step from 3 to 4, cyclization, and (ii) that from 3 to 8, chain elongation. Then, (i) will be compared with (iii), addition of the radical R to the platelet model P.

Table 3. Key reaction steps for the “particle-phase” system on different platelet models\(^a\) (Figure 9). Energy and Free energy differences with respect to the intermediate 3.\(^b\)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{ZPE}$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
<td>700</td>
<td>1100</td>
</tr>
<tr>
<td><strong>on P2</strong>(^c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-4</td>
<td>3.9</td>
<td>-0.6</td>
<td>4.0</td>
</tr>
<tr>
<td>TS 3-8</td>
<td>1.7</td>
<td>-34.2</td>
<td>11.5</td>
</tr>
<tr>
<td><strong>on P3</strong> (curved)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-4</td>
<td>3.9</td>
<td>-0.6</td>
<td>3.9</td>
</tr>
<tr>
<td>TS 3-8</td>
<td>1.7</td>
<td>-34.9</td>
<td>11.7</td>
</tr>
<tr>
<td><strong>on P4</strong> (odd)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-4</td>
<td>4.0</td>
<td>-2.5</td>
<td>4.3</td>
</tr>
<tr>
<td>TS 3-8</td>
<td>1.8</td>
<td>-37.0</td>
<td>12.3</td>
</tr>
</tbody>
</table>

\(^a\) data for model P1 reported in Table 2.

\(^b\) units: $\Delta E$ and $\Delta G$ in kcal mol\(^{-1}\), $\Delta S$ in cal mol\(^{-1}\) K\(^{-1}\). Thermochemistry at 6-31G(d) (ZPE contribution, $\Delta H$, $\Delta S$), computed in correspondence of the 6-31G(d) optimized structures, but for P2 (see footnote c).

\(^c\) Only for P2, 6-31G(d) energy (single-point calculation) on the 3-21G(d) geometry, combined with the 3-21G(d) thermochemistry.
Figure 9. Comparison of cyclization (TS 3-4) vs chain elongation (TS 3-8) free energy barriers for the platelet models of Chart 1. Data from Table 2 (P1) and Table 3 (P2-P4). ∆G in kcal mol⁻¹. Continuous lines: 6-31G(d)//6-31G(d) energy data (P1, P3, P4). Dashed line: 6-31G(d)//3-21G(d) energy data (P2). Diamonds: adsorption on P1, ovalene. Circles: adsorption on P3, tribenzo-corannulene. Triangles: adsorption on P4, 7-H-ovalene. Squares: gas phase data. Dashes: adsorption on P2, tetrabenzo-ovalene. The scale on the abscissa axis is enlarged with respect to the ordinates to stretch the plot horizontally.

Cyclization vs chain elongation. Table 3 reports the results (those for P1 are in Table 2). In Figure 9 continuous lines represent ∆G‡(TS 3-8) vs ∆G‡(TS 3-4) data at 6-31G(d)//6-31G(d) for the gas phase and models P1, P3, and P4; the dashed line refers to additional 6-31G(d)//3-21G(d) energy data for the largest system, model P2 (how the data change in going from one computational protocol to the other is briefly discussed in the Appendix).

Figure 9 allows a straightforward evaluation of the results obtained for the above processes (i) and (ii), when the growing system is adsorbed on the platelet models P1-P4. The main features are: (a) The balance between chain extension and cyclization is described much in the same way whichever soot platelet model is chosen. This confirms ovalene as an acceptable choice for the extended exploration of the reactions pathways. (b) It is also clear that this balance is sharply in favour of cyclization in all cases because of the rather “vertical” curves (take into account that the abscissa scale is expanded). (c) The set of grouped curves for the adsorbed growing radical (colors) departs significantly from the gas phase curve (black): they are closer to the ordinate axis, meaning that the preference for cyclization is more pronounced. (d) In all curves this preference increases with rising temperature. This is an apparent effect of the −T∆S term on the ∆G (the T dependence is obviously damped when the rate constant ratios are considered).
Cyclization vs radical addition to the platelet. During combustion or pyrolysis both PAH synthesis and formation of soot precursors can take place. When the growth proceeds, the adsorbed radical system R might operate an addition to the underlying soot platelet P (or to another PAH). This kind of addition could open the way to the formation of more disordered and complex structures (reticulation). Of course, a large variety of situations can be envisaged. To put to the test the viability of this possibly competitive channel, we have carried out four TS searches (Table 4).

Table 4. Radical additions of the growing “particle-phase” system to the underlying platelet models (Figure 10). Energy and Free energy differences with respect to the intermediate 3 (+ platelet).\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{\text{ZPE}}$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>on P1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-9</td>
<td>13.7</td>
<td>-8.2</td>
<td>15.4</td>
</tr>
<tr>
<td>9</td>
<td>-6.4</td>
<td>-4.6</td>
<td>-5.9</td>
</tr>
<tr>
<td>on P3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(curved)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-10</td>
<td>2.9</td>
<td>-7.3</td>
<td>4.5</td>
</tr>
<tr>
<td>10</td>
<td>-32.5</td>
<td>-6.3</td>
<td>-31.6</td>
</tr>
<tr>
<td>on P4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(odd)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 3-11</td>
<td>8.0</td>
<td>-12.6</td>
<td>10.9</td>
</tr>
<tr>
<td>11</td>
<td>-26.3</td>
<td>-15.1</td>
<td>-23.0</td>
</tr>
<tr>
<td>TS 3-12\textsuperscript{b}</td>
<td>-0.4\textsuperscript{c}</td>
<td>-7.5</td>
<td>1.4</td>
</tr>
<tr>
<td>12</td>
<td>-53.5</td>
<td>-5.1</td>
<td>-52.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a} units: $\Delta E$ and $\Delta G$ in kcal mol$^{-1}$, $\Delta S$ in cal mol$^{-1}$ K$^{-1}$. Thermochemistry at 6-31G(d) (ZPE contribution, $\Delta H$, $\Delta S$) computed in correspondence of the 6-31G(d) optimized structures.

\textsuperscript{b} Attack on a border position of P4 (Fig. 11b).

\textsuperscript{c} Given the composite origin of this energy difference (+ZPE, + CP), a small negative value, as any small positive value, is to be intended just as indicating an “easy step”.

The growing radical could perform this addition at any step of its growth, in particular if the intermediate carries a localized radical center (as in 2, 5, 8… see Scheme 1), therefore also not in direct competition with cyclization. But, as stated in the Introduction, the focus of this study is on cyclization (PAH growth) and on different reaction steps which can possibly compete with it. Therefore, 3 has been chosen as representative of
the growing radical \( R \), because this choice allows a direct comparison with the cyclization and ethyne addition steps. The three platelet models chosen are P1 (closed shell and planar), P3 (closed shell and curved), and P4 (a planar, odd-\( \pi \) electron system). The attack has been carried out on an internal position of them, then on one border position of P4, choosing those carbons that could appear as good candidates for such an attack, because of their relatively high electron or spin densities. For the internal positions, the resulting adducts are labeled 9, 10, or 11, while 12 is that originated by addition to the P4 border position.

The results for the internal positions (Table 4, TS 3-9, TS 3-10, TS 3-11) show that the two planar systems, P1 and P4, present relatively high \( E \) barriers: almost 14 and 8 kcal mol\(^{-1}\), respectively, both significantly higher than those for cyclization and ethyne addition; see Table 2 and Table 3). By contrast, the attack to the curved P3 model (Figure 10a) requires overcoming a smaller \( E \) barrier of 3 kcal mol\(^{-1}\). Even easier is the attack on the border position of P4 (Figure 10b), where the \( E \) barrier is close to zero.

![Figure 10](image.png)

**Figure 10.** (a) TS 3-10 for radical addition to the platelet model P3. (b) TS 3-12 for radical addition to a border position of the platelet model P4.

However, a serious penalization on the \( G \) barrier by the \(-T\Delta S\) term is expected in all cases. The temperature dependence of the barrier height is such that they cannot in general be competitive with cyclization. The preference is confirmed when looking at the rate ratios, though the estimated \( k(T) \) values vary less significantly at combustion temperatures. The \( G \) barrier for P3 is low enough to be comparable with that for ring closure only at the lowest temperatures, which are actually not of interest for pyrolysis or combustion. These trends can be seen in Figure 11: it shows that the balance between these two processes, described similarly whichever soot platelet model is chosen, is again generally in favour of cyclization. This preference increases with rising temperature. But, as regards the cyclization of 3 adsorbed on P4 vs its addition to a high-spin density P4 border position, a crossing occurs between the \( \Delta G \) curves of the two processes (Tables 3 and 4), so that ring closure prevails above ca. 900 K, while addition is easier at lower temperatures. To sum up, we can only draw a qualitative conclusion, based on the not-compelling
suggestions provided by this set of calculations: at lower temperatures, in some cases, reticulation might take place and give origin to soot nucleation, a pathway which is diverging from PAH formation.

Figure 11. Comparison of cyclization (TS 3-4) vs addition of the radical growing system to the platelet model (TS 3-9, TS 3-10, TS 3-11, TS 3-12). Data from Table 4. $\Delta G$ in kcal mol$^{-1}$. Same $T$ range as Figure 9. Attacks on selected internal positions of: P1 (diamonds), P3 (circles); P4 (triangles). Attack on a border position of P4 (squares). The scale on the abscissa axis is enlarged with respect to the ordinates to stretch the plos horizontally.
C. Final remarks on the results obtained.

We have already mentioned that, though PAHs are sometimes considered as precursors of soot, other views can be found in the literature (which can be compared with the results described above). Homann, for instance, conjectured that in addition to the growth pathways which bring about the formation of PAHs, different curved structures could grow, irregular to some extent. He dubbed them *aromers*, surmising that they could be precursors of both fullerenes and soot.iii The creation of all these species could thus proceed also with some interaction among them, and in some cases PAHs have been supposed to originate on the surface of carbonaceous particulate.iv Siegmann, Sattler, and Siegmann even suggested that soot synthesis can precede PAH synthesis.vi

Considering these different standpoints, we have addressed the points (1)-(4) listed in the Introduction by studying a growing aromatic radical \( R = \text{Ph} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{Ph} \), in an attempt to clarify if (and, in an affirmative case, how) an underlying soot platelet \( P \), on which it is supposedly adsorbed, can affect its growth. \( P \) has been represented simply by ovalene in an first extensive search, then also by three other models (still planar but larger; curved; radicalic) to re-investigate the key steps (ring closure, chain extension, reticulation). Adsorption cannot be important in the early phases of PAH growth, when the size of \( R \) is limited (Point 1). Therefore, growth must take place initially in the gas phase, where it is already inclined to privilege ring closures, when these compete with other processes (Point 2). Then, when \( R \) arrives to possess 3-5 rings, adsorption on \( P \) will gain importance, more so for a number of rings > 5.\textsuperscript{xxv} In the particle phase (\( R - P \) system), chain extension can of course take place, but, again, not when it competes with cyclization. Indeed, at any ethyne concentration, cyclization is easier, and is even relatively easier than in the gas phase (Point 2). This can hint to some sort of loosely intended “template” effect (Point 3). Cyclization produces an intermediate with one cycle more, but still having either a tertiary carbon bound to a hydrogen, or an endocyclic methylenic group. Simple H loss, or H abstraction, can both produce a more extended aromatic system. Thus, if H were abstracted by the underlying P to produce a larger aromatic system, soot would be described as playing an active, cooperative, role in a key step of PAH formation. H abstraction by P is found to be competitive with simple H loss only at the lowest temperatures. However, for the soot platelet to be regenerated, hence seen also as a real catalyst, it should subsequently lose that H, which is possible only at higher T (Point 3). We can conclude that a role of P as a real catalyst is hardly imaginable, though it can assist the final PAH formation. As a final aspect, another possible role of P could be a direct addition reaction between \( R \) and \( P \). Our results suggest that at lower temperatures, in some cases, reticulation might take place and give origin to soot nucleation instead of PAH synthesis (Point 4).
Conclusions

This study is, to the best of our knowledge, the first attempt to investigate theoretically the combustive/pyrolytic process of PAH formation when the growing aromatic radical can be in interaction with a soot platelet. Though the overall system’s size needs to be kept within reasonable dimensions, we have found clearcut indications on the features of three competing processes: (1) cyclization, leading to a larger PAH, (2) chain extension by ethyne addition, and (3) reticulation, due to addition of the growing radical to the underlying soot platelet. These key steps were investigated on four platelet models, planar and curved, closed or open shell as regards their π systems. The free energy barriers are found to privilege cyclization, when it is in competition with the other processes. This is true already in the gas phase, but adsorption on soot significantly reinforces this preference (which is found not to depend on the soot platelet model). This could be interpreted, in a rather loose way, as a sort of “template” effect. Then, since the larger aromatic system forms upon H loss subsequent to cyclization, the soot platelet can be seen as exerting a cooperative effect, because it is able to abstract the extra hydrogen. However, since it can operate this way at lower temperatures, while its regeneration can occur only at higher temperatures, its role can hardly be classified as catalytic. Finally, the platelet does not alter the mechanistic features qualitatively, unless the addition of R to P is considered. In that case, reticulation (starting the formation of more disordered structures, possible soot precursors instead of PAHs) is found to be possible only at lower temperatures, consistently with experimental findings.
Appendix

This part illustrates briefly the validation of the procedure adopted for the rather large “growing radical on tetrabenzoovalene” system, described in the Method section (results in Table 3). The chain elongation (TS 3-8) vs cyclization (TS 3-4) free energy barrier differences are compared for a series of temperatures. In this procedure, the relevant optimizations were carried out with the rather small 3-21G(d) basis set. Then, a 6-31G(d) single-point energy calculation was done on the 3-21G(d) geometry and subsequently combined with the 3-21G(d) thermochemistry (dashed lines). The same procedure was adopted for R either in the gas phase or adsorbed on ovalene. For both systems the computation of G fully executed at the 6-31G(d) level (optimization and thermochemistry) is also available (continuous lines). The continuous and dashed lines are close (see Figure 12), and these results appear to validate the computations carried out on the largest system, R adsorbed tetrabenzo-ovalene (Figure 9).

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Settore *Sviluppo Sostenibile*. We thank professor Vincenzo Barone for kindly providing a development version of the GAUSSIAN program.
References


iv  B. J. Finlayson-Pitts, J. N. Pitts, Jr., *Chemistry of the Upper and Lower Atmosphere*; Academic Press, New York, 2000, ch. 10. See, in particular, Figures 10.2 and 10.3.


We could make reference to ref. xxiii, namely to their Figure 1 (p 913) and Table S2 in the Supplementary Material, from which a plot of branching free energy profiles could be drawn [G3(MP2,CC) data]. In ref. xxiii, the process A3-A3 a-A4b-A5-N1 corresponds to the Bittner-Howard variant, while the sequence A3-A10-A11-A12-A13-N1 corresponds to the original proposal by Frenklach & coworkers (ref. xi). A branching occurs right from the beginning along the Bittner-Howard pathway, corresponding to simple H loss (upper curve) or to a +H/-H\textsubscript{2} process. A similar branching occurs at the end of the Frenklach pathway. The first barrier is 4.5 kcal mol\textsuperscript{-1} high for the former, while it is 6.2 kcal mol\textsuperscript{-1} for the latter.
A. Giordana, A. Indarto, G. Tonachini, V. Barone, M. Causà, M. Pavone “An attempt to define a computational level suitable to investigate large van der Waals complexes: Theoretical study of the associations of benzene with CH$_2$=CH, HC≡CH, and H$_2$C=CH$_2$, and the naphthalene dimer”, to be submitted for publication.


A special issue of *PCCP* dedicated to the subject *Stacking Interactions* has appeared recently: *Phys. Chem. Chem. Phys.* 2008, **10**, 2581-2865.


J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939-947. The sp basis set 3-21G was enriched with d functions on all carbons (with gaussian exponent = 1.0), and is referred to as 3-21G(d) in this work.


This means in general to consider, in the gas phase, the BSSE correction for a bimolecular step (TS 3-8 for ethyne addition). In the particle phase, we have at any time two interacting moieties (R and P), unless also an ethyne molecule is adsorbed on P, in which case we have three. For the bimolecular addition process from the B-complex through the related TS 3-8 (see Tables 2 and 3) the BSSE was corrected by taking into account the basis set superposition involving three moieties: (1) R and ethyne; (2) R and P; (3) ethyne and P. In the case of the additions reported in Table 4, the BSSE correction for two interacting moieties is assessed for the adsorbed “reactant” 3 and the subsequent TS for its addition to P. In all cases, the geometries determined without correction are used.


Our gas phase data for the step 3-4, as those of the step 4-7, can be compared with G3(MP2,CC) data of ref. xxiii (compare their Figure 1). The overall comparison is rather satisfactory.

xlv “Perpendicular” adsorption is dealt with briefly in the ESI file, since for larger growing systems the \( \perp \) adsorption mode is more stable. The critical points and barriers for channel 3-5-6 come out to be the very same already defined for the \( \perp \perp \) arrangement, since the growing species slips sideways and abandons the \( \perp \perp \perp \perp \) orientation. The \( \perp \perp \perp \perp \) ring closure 3-4 presents barriers of 9-23 kcal mol\(^{-1}\), higher (to different extents) than those assessed for the gas-phase (5-22 kcal mol\(^{-1}\)) and \( \perp \perp \) (5-12 kcal mol\(^{-1}\)) cases.


li The ethyne-benzene (\( \perp \)) BSSE corrected complexation energy is estimated here as \( \Delta E_{ZPE} = -2.9 \text{ kcal mol}^{-1} \), at DFT(B3LYP-D)/6-31G(d). These values can be compared with an experimental estimate: \( -2.7 \pm 0.2 \text{ kcal mol}^{-1} \), reported in: K. Shibasaki, A. Fujii, N. Mikami, S. Tsuzuki, *J. Phys. Chem. A* 2007, **111**, 753-758. In that paper, also a CCSD(T) interaction energy is reported: -2.8 kcal mol\(^{-1}\).