

Reaction mechanism of soot formation in flames

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Chemical reactions and physical processes responsible for the formation of polycyclic aromatic hydrocarbons and soot in hydrocarbon flames are reviewed. The discussion is focused on major elements in the present understanding of the phenomena, clarification of concepts central to the present state of the art, and a summary of new results.

1 Introduction

The formation of polycyclic aromatic hydrocarbons (PAH) and soot has become one of the central themes of research activities in the area of combustion and pyrolysis of hydrocarbon fuels. The interest in the subject stems mostly from environmental concerns on pollutant emission from combustion devices. The research activities span experimental, theoretical, and computational efforts and cover a diverse spectrum of the physics and chemistry of the process. The increasing amount of information prevents an exhaustive review in an article like this. Instead, the objective here is to focus on major elements in the present understanding of the phenomena, to clarify some key concepts (and especially those perceived as points of controversy), and present new results.

In term of the underlying science, soot formation may be viewed as being comprised of four major processes:^{1–7} homogeneous nucleation of soot particles, particle coagulation, particle surface reactions (growth and oxidation), and particle agglomeration. We discuss each below.

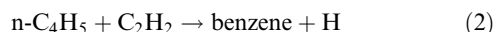
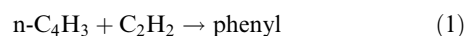
2 Soot particle precursor

There have been several principal proposals made regarding the general nature of soot particle inception; these involve polyacetylenes,⁸ ionic species,³ or polycyclic aromatic hydrocarbons² as the key gaseous precursors to soot. The majority opinion at present, supported by numerous experimental and modeling studies, is that soot particles form *via* PAHs. The PAH hypothesis also embraces the recent proposals on particle inception through formation of aromatic-aliphatic-linked hydrocarbons which later graphitize.^{9,10}

2.1 Formation of aromatics

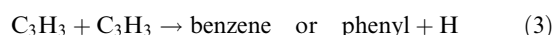
The formation and growth of aromatic species bridges the main combustion zone chemistry and soot formation. In addition, aromatic molecules are themselves toxic and subject to environmental regulations. The chemistry of aromatics at combustion temperatures has only recently received detailed attention. The primary focus is on the formation of the first aromatic ring from small aliphatics, because this step is perceived by many to be the rate-limiting step in the reaction sequence to larger aromatics. Arguments revolve between several possibilities.^{11–19}

Among these are the even-carbon-atom pathways that involve the addition of acetylene to $n\text{-C}_4\text{H}_3$ and $n\text{-C}_4\text{H}_5$,

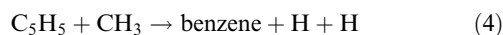


Reaction (1) was suggested to play a key role in the formation of the first aromatic ring on the basis of detailed kinetic simulations of shock-tube acetylene pyrolysis,¹¹ the result being reiterated in subsequent kinetic studies.^{20–23} These numerical simulations also identified reaction (2), suggested by Bittner and Howard,²⁴ as playing a role at lower temperatures.²²

Reactions (1) and (2) were dismissed by Miller and Melius,²⁵ who suggested that $n\text{-C}_4\text{H}_3$ and $n\text{-C}_4\text{H}_5$ could not be present in sufficiently high concentrations because they transform rapidly to their corresponding resonantly stabilized isomers, $\text{iso-C}_4\text{H}_3$ and $\text{iso-C}_4\text{H}_5$. Instead, they propose, along with others,^{14,15,26} an odd-carbon-atom pathway *via* combination of propargyl radicals



Indeed, the propargyl radical is an exceptionally stable hydrocarbon radical, and its implication in the formation of aromatics and soot has long been assumed.^{23,27} Quantum chemical calculations indicated that the chemical activation of the adduct might be sufficient to surmount the numerous potential energy barriers to its cyclization to an aromatic ring.¹⁶ Other odd-carbon-atom pathways have been suggested,^{17,28–30}

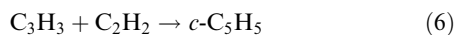


Past numerical analysis^{12,13} revealed that Miller and Melius' conclusion on the C_4H_3 and C_4H_5 abundances originated primarily from the much lower stabilities predicted by BAC-MP4 for the *n*- forms relative to the corresponding *iso*- forms of these radicals, which is especially pronounced in the case of the C_4H_3 isomers. The BAC-MP4 predictions for standard enthalpy differences, $\Delta_f H_{298}^0$, between the *n*- and *iso*- forms are 12 kcal mol⁻¹ for the C_4H_5 isomers and 19 kcal mol⁻¹ for the C_4H_3 isomers.²⁵ In contrast, the enthalpy differences in the initial kinetics studies of Frenklach *et al.*¹¹ were assumed to be about 8 kcal mol⁻¹, based on estimates provided by Benson (see ref. 27). The 8 kcal mol⁻¹ difference was incorporated into the group-additivity scheme of Stein, which served as a consistent thermodynamic set for the initial kinetic modeling.¹¹

Recent quantum-mechanical studies report differences in the range 7–14 kcal mol⁻¹ for the n-C₄H₅ isomers,^{31,32} and raise the standard enthalpy of formation of the n-C₄H₃ radical to 134 kcal mol⁻¹,³³ as compared to the previous estimates of 127³⁴ and 130²⁵ kcal mol⁻¹. A most recent theoretical study,³⁵ employing the diffusion Monte Carlo (DMC) method, reports 126.0, 119.4, 83.4, and 76.2 kcal mol⁻¹ for the n-C₄H₃, iso-C₄H₃, n-C₄H₅, and iso-C₄H₅, respectively, all with one standard deviation of 0.6 kcal mol⁻¹. These results translate into enthalpy differences of 6.6 ± 1.2 kcal mol⁻¹ for C₄H₃ and 7.2 ± 1.2 kcal mol⁻¹ for C₄H₅ radicals, substantially lower than the prior theoretical predictions. The DMC results suggest higher stability for the n-radicals, bringing the difference between the n- and iso-isomers essentially back to the Benson estimates. The higher stability of n-C₄H₃ and n-C₄H₅ predicted by DMC “restores” the importance of reactions (1) and (2). At the same time, results of a time-dependent solution of the energy master equations³² revealed a significantly lower rate for reaction pathway (3) as compared to the initial estimate²⁵ of 1 × 10¹³ cm³ mol⁻¹ s⁻¹; yet, the new theoretical values are consistent with those deduced by consistent modeling^{13,36} of experiment. Support for the even-carbon-atom channels comes also from recent experimental studies.^{37,38}

It is important to realize that focusing on the competition between reactions (1) and (3) confines one’s scientific quest to a narrow point of view. It is shown, for instance, that with increase in pressure, formation of the first aromatic ring *via* linear C₆H_x species³⁹ begins to play a significant if not a dominant role,⁴⁰ as do ring-ring reactions.⁴¹ In this regard, it is pertinent to mention that formation of single-aromatic-ring compounds, while probably most common, may not necessarily be the rate-limiting step,⁴² and the growth of PAHs can be initiated by the direct formation of multi-ring PAHs, bypassing the formation of the benzene ring. Such proposals include formation of aromatics from “condensation” of poly-acetylenes,² combination of C₄H_x species,⁴³ as well as combination of larger radicals.

Another possibility for the initial ring formation is the reaction between propargyl and acetylene to form a cyclopentadienyl radical,



This pathway combines the benefits of the two reactant types discussed above: highly stable radical, propargyl, and the most abundant “building block”, acetylene. Once formed, cyclopentadienyl reacts rapidly to form benzene.^{17,28,30} The possibility of a propargyl–acetylene reaction initiating the formation and growth of aromatics was brought up in the past, as a possible explanation for an experimentally observed enhancement in the production of soot in shock-heated mixtures of benzene and allene.²³ Recent quantum Monte Carlo calculations along with time-dependent solution of the energy-transfer master equations demonstrated the feasibility of this proposal.⁴⁴ Indeed, the equilibrium of reaction (6) at typical flame conditions is shifted to the right above 1700 K, implying the formation direction within the temperature window of aromatics formation. The predicted rate coefficient for these conditions (1 atm and 1500 K) is about 1 × 10¹¹ cm³ mol⁻¹ s⁻¹. Let us compare then the rate of reaction (6), $k_6[\text{C}_3\text{H}_3][\text{C}_2\text{H}_2]$, with that of reaction (3), $k_3[\text{C}_3\text{H}_3][\text{C}_3\text{H}_3]$. Noting that $[\text{C}_3\text{H}_3]$ is canceled out and using the value^{32,36,45} of $k_3 = (1 \text{ to } 5) \times 10^{12}$ cm³ mol⁻¹ s⁻¹, we obtain

$$\frac{k_6[\text{C}_3\text{H}_3][\text{C}_2\text{H}_2]}{k_3[\text{C}_3\text{H}_3][\text{C}_3\text{H}_3]} \sim (0.02 \text{ to } 0.1) \frac{[\text{C}_2\text{H}_2]}{[\text{C}_3\text{H}_3]} \quad (7)$$

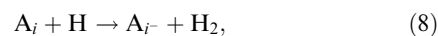
The concentration ratio $[\text{C}_2\text{H}_2]/[\text{C}_3\text{H}_3]$ is of the order of 10²–10⁴ as reported in numerous experimental flame studies (*e.g.*, ref. 43,46–48) and hence reaction (6) is expected to be faster than reaction (3) by a factor of 2 to 10³. This implies that

reaction (6) is not only fast enough to make a difference, but also should probably play a dominant role in the formation of the first aromatic ring.

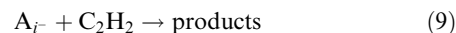
2.2 Growth of aromatics

We will begin the discussion of aromatics growth toward soot with HACA, to delineate what it stands for and through this to clarify the differences from and similarities to other ideas. Reference to HACA in PAH and soot literature has now become rather frequent. Perhaps due to this “popularity”, there are attempts to “widen” its meaning and, in doing so, some of these generalizations destroy the very essence of HACA.

2.2.1 HACA. The term “HACA” was introduced in Frenklach and Wang’s paper,⁴⁹ as a response to the word limit imposed on Combustion Symposium papers, to be used as an acronym for “H-abstraction-C₂H₂-addition.” The latter, in turn, implied a *repetitive* reaction sequence of two principal steps: (i) abstraction of a hydrogen atom from the reacting hydrocarbon by a gaseous hydrogen atom,

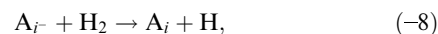


followed by (ii) addition of a gaseous acetylene molecule to the radical site formed,



Here we use our usual notation for aromatics:^{21,23} A_{*i*} is an aromatic molecule with *i* peri-condensed rings, and A_{*i*}⁻ is its radical. The significance of this (8)–(9) reaction-path feature was identified in the very first attempt at numerical modeling of detailed reaction kinetics of the growth of aromatics.¹¹

The essence of the two-step feature is as follows. The first step activates a molecule to further growth by converting it to a radical. Of course, this can be accomplished in many different ways, and many such possibilities have indeed been tested. It turns out that, under the conditions of typical shock-tube and flame experiments, which provide the majority of the present training experimental data, it is the H abstraction by a gaseous H which typically dominates.^{11,13,22} Obviously, if other reactions are to contribute to the process of converting an aromatic molecule to a radical, either as a result of different reactor conditions or by discovery of new chemistry, they should be included. The key feature of the first step of HACA, however, is its *reversibility*. The reverse steps can be the reverse direction of the H abstraction itself,

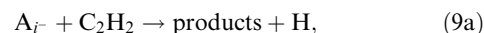


or other reactions, such as the combination with a gaseous H,

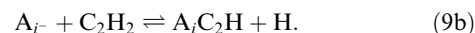


The contribution of reaction (10) as compared to the reverse of (-8) increases with pressure and molecular size, *i.e.*, as the rate coefficient of (10) approaches its high-pressure limit.

The reversibility of the acetylene addition step, reaction (9), or, more precisely, the degree of its reversibility, is what determines whether this step will contribute to molecular growth. For a simple addition, due to the entropy loss, the reaction is highly reversible, and often runs in reverse. Forming a hydrogen atom as a product,



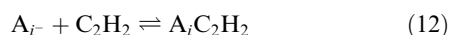
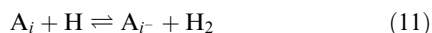
recovers some of the entropy but still, in many cases, the reaction is still highly reversible, like in the case of reaction



Only when, in addition to the recovery in entropy, the decrease in energy is large enough, does the reaction become more irreversible, and in the formation of particularly stable aromatics, referred to as islands of stability¹¹ or stabilomers,⁵⁰ the reaction becomes practically irreversible.

This coupling, between the “thermodynamic resistance” of the reaction reversibility and the kinetic driving force, is the defining feature of the “HACA model”. In this sense, the HACA meaning can be expanded to encompass other carbon growth species, as long as the thermodynamic-kinetic underpinning is preserved. The critical role of this coupling for aromatic growth became apparent from the very beginning of the kinetic simulations.¹¹ It turns out that among numerous possible reaction pathways the one that emerges as dominant is not necessarily the shortest one or the one that does not require costly reactivation, defining principles underlying the explorations of Homann and Wagner,⁸ Bittner and Howard,²⁴ and Bockhorn *et al.*,⁴³ but the one with the largest reaction affinity,⁵¹ *i.e.*, with the smallest thermodynamic resistance. The latter is attained most effectively, in the case of PAH growth, by a repetitive reactivation by hydrogen atoms while hopping from one island of stability to another. This thermodynamics-kinetics coupling explains¹¹ the reason for overcoming the energy barrier⁵⁰ to PAH growth and the appearance of stabilomer sequences^{43,50} during the growth. Furthermore, it appears to be a critical element, and hence a unifying feature,⁵² for other forms of carbon growth, such as fullerenes,⁵³ interstellar dust,⁵⁴ and synthetic diamond.⁵⁵

2.2.2 Kinetic regimes of HACA. The thermodynamic-kinetic coupling can be exemplified by a simplified, yet realistic model of PAH growth,⁵⁶



Assuming a steady state for the radicals, A_{i-} and $A_i C_2H_2$, the rate of aromatic growth can be expressed as

$$\frac{K_{11} \frac{[H]}{[H_2]}}{\frac{1}{K_{12}k_{13}[C_2H_2]^2} + \frac{1}{k_{12}[C_2H_2]} + \frac{1}{k_{-11}[H_2]}} \quad (14)$$

where the K s are the equilibrium constants and the k s the reaction rate coefficients. The main features are revealed by considering the limits of eqn. (14).

The first term in the denominator of eqn. (14) becomes dominant under the condition

$$\frac{K_{12}[C_2H_2]^2}{[H_2]} \ll 1 \quad (15)$$

and eqn. (14) becomes

$$\left(K_{11} \frac{[H]}{[H_2]} \right) (K_{12}[C_2H_2]) (k_{13}[C_2H_2]) \quad (16)$$

In this regime the PAH growth is controlled by the thermodynamic resistance of the first and second steps, reversible H abstraction and acetylene additions, respectively, and the kinetics of the third step, irreversible addition of acetylene to form a stabilomer. This regime was observed under conditions of high-temperature shock-tube experiments^{11,20–23} and in the post-flame zone of laminar premixed flames.^{22,42} The PAH growth in this regime is promoted by the superequilibrium concentration of hydrogen atoms and the formation of stabilomers.

At low temperatures inequality (15) is reversed and the second and third terms in the denominator of eqn. (14) determine the overall value of the growth rate. If $[C_2H_2] \gg [H_2]$, which characterizes, for instance, the preheat zone of a premixed acetylene flame,²² then eqn. (14) takes the form

$$k_{11}[H] \quad (17)$$

and the growth rate is determined by the rate of H abstraction. If, on the other hand, $[C_2H_2] \ll [H_2]$, which characterizes the outflow from red giant stars,⁵⁴ we obtain

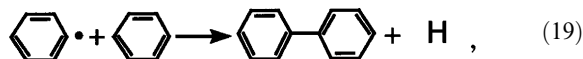
$$K_{11} \frac{[H]}{[H_2]} k_{12}[C_2H_2] \quad (18)$$

Under these conditions the PAH growth rate is controlled by the thermodynamic resistance of the first step, H abstraction, and the kinetics of the second step.

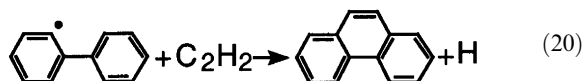
This simple analysis illustrates an important point: the observed characteristics of the growth of the aromatics should depend on the specific local regime which, in turn, is characterized by several experimental factors such as the temperature and the concentrations of hydrogen and acetylene. The list of influential parameters is further extended to include the concentrations of oxygen molecules and hydroxyl radicals under oxidative conditions.⁵⁶ Often, the PAH growth passes, in time and space, from one regime to another. For instance, a switch from a thermodynamically-shut flux close to a star, eqn. (16), to a kinetically-open one at around 1000 K, eqn. (17), marks the appearance of dust in the circumstellar of C-rich red giants.⁵⁴ One should consider all these factors, in their mutual localized realization, when attempting an explanation of experimental phenomena even in qualitative terms.

2.2.3 Growth by other species. Acetylene is obviously not the only species that can be envisioned to propagate the growth of aromatic rings. Several such proposals have appeared, including those involving methyl, propargyl, and cyclopentadienyl.^{17,48,57–63} The focus of these proposals is on the resonantly stabilized structure of the reacting radicals, which, in a general sense, follows the suggestion of Glassman⁶⁴ that hydrocarbons with conjugated structures and their derivatives are critical intermediates to soot nucleation.²⁷ While, indeed, the initiation of aromatics formation may proceed through different reactions, specific to the fuel used and conditions applied, numerical simulations indicate that such initial pathways quickly relax to the acetylene-addition path.^{20,23}

For instance, in the pyrolysis of benzene,²⁰ the aromatics growth is initiated by the formation of biphenyl,

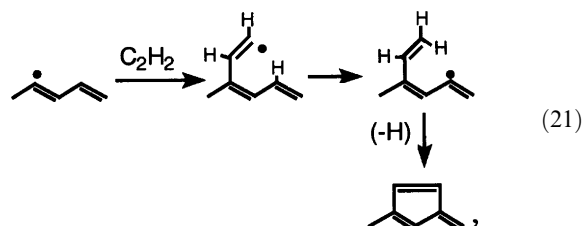


but the following growth proceeds *via* acetylene addition

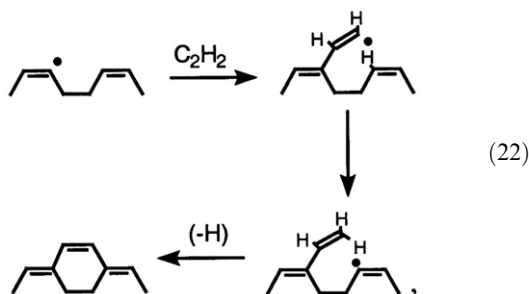


The same pattern appears at different conditions and fuels,^{20,23} as well as in flames with increased stoichiometry and pressure.⁴⁰

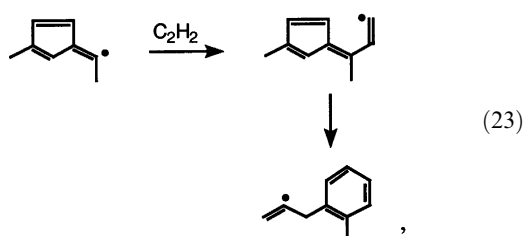
2.2.4 Migration reactions. Recent theoretical investigations have revealed new reaction pathways for aromatic ring growth,⁶⁵ such as enhanced formation of five-member aromatic rings



enhanced formation of six-member aromatic rings



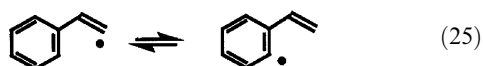
interconversion of five- and six-member rings



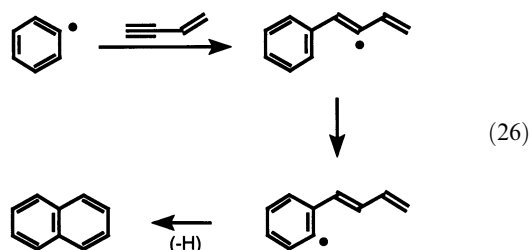
and migration of the cyclopenta ring along zigzag aromatic edges



All of these pathways have one critical mechanistic feature in common: the reaction pathway is induced or assisted by hydrogen atom migration. The kinetics and thermodynamics of such migration were investigated for the reaction



at several levels of quantum *ab initio* theory.⁶⁶ The most reliable level of theory results in reaction rates sufficiently fast for these reactions to play a role in high-temperature aromatic chemistry. For large aromatic structures, like condensed multi-ring soot precursors or those developed at the edges of the soot particle surface, the **H** migration step opens an additional and somewhat faster channel for reaction pathways (21) and (22), with the result of at least doubling the rate of cyclization. For some aromatics, the **H** migration may be ineffective, as in the case of reaction²⁴



due to excessive barriers to rotation,⁶⁷ or even may run in reverse, towards ring fragmentation, since the equilibrium con-

stant of reaction (25) is significantly lower than unity (~ 0.2 at 1500 K).⁶⁶

Reaction pathways like (23) and (24) open substantially new possibilities for surface growth, as will be discussed in section 4.4.

2.3 Oxidation of aromatics

Parallel to aromatics growth is aromatics oxidation. The primary mechanism seems to be the oxidation of aromatic radicals by O_2 , and oxidation by OH is rather unimportant, at least as deduced from numerical simulations of laminar premixed flames.²² The largest effect in the oxidation of aromatics occurs at the very beginning of the aromatics growth, at the phenyl stage. This is due to the rapidly decreasing concentration of O_2 in fuel-rich environments sustaining aromatics growth. Indeed, according to HACA, the growth is governed by the **H** atom production, but **H** atoms also destroy O_2 ; hence, as the aromatics growth progresses, it should be accompanied by the depletion of O_2 . The latter observation may also explain why soot inception usually appears in the vicinity (in time or space) of the main combustion zone, in an environment rich in **H** atoms and poor in O_2 molecules. The minor role of OH in the oxidation of gaseous aromatics contrasts with OH being considered the primary oxidizing agent of soot particles.^{2,68,69} The mechanism of soot oxidation by OH is still poorly understood.

Oxidation of aromatics removes carbon mass from further growth. However, even more important is the removal of mass at earlier stages, those preceding the aromatics formation. Numerical simulations identify oxidation of C_2H_3 as the key point of branching between carbon growth and carbon oxidation.^{21,22} The effect of oxidation at this small-molecule level is twofold. On the one hand, it diverts carbon mass from further growth. On the other hand, added in relatively small quantities in high-temperature pyrolytic environments, molecular oxygen actually promotes formation of soot by building up the radical pool, and specifically **H** atoms. The latter phenomenon, identified in experimental shock-tube studies⁷⁰ and parallel computational analysis,²¹ recurs repeatedly in analyses of diffusion flames.⁷¹

2.4 Importance of flame environment

A detailed kinetic model of soot formation, from the perspective of flame modeling, can be viewed as comprised of two principal components: gas-phase chemistry, which determines the flame structure, and soot particle dynamics, which describes the evolution of the particle ensemble. The correctness of the particle dynamics submodel relies, first of all, on the accuracy of the species profiles supplied by the gas-phase submodel, those that define the soot particle nucleation and surface growth rates. Therefore, if one is interested in a predictive description of soot evolution, the authenticity of the model for the flame structure must be confirmed first. While the latter is self-evident, unfortunately, this is not always the case.

As an example, Marinov and co-workers made a claim that the HACA mechanism is not able to predict the formation of aromatics in a series of laminar premixed flames. One of such cases⁷² was examined by us in detail: an atmospheric-pressure, laminar premixed flame of ethane studied experimentally by Castaldi and Senkan.⁷³ It turns out that the main problem was not in the aromatic chemistry but in the simulation of the main flame zone. The kinetic model was not able to predict correctly the profiles of the major species, fuel and oxygen. An exhaustive analysis concluded with the need to adjust the flame temperature.³⁶ After the maximum flame temperature was increased by 200 K, to match the reactant profiles, the PAH profiles predicted by the HACA model all fell into place. This experience shows that correct prediction of the flame environ-

ment must be a necessary requirement to satisfy before one enters kinetic modeling of aromatics.

3 Particle nucleation

The transition of gas-phase species to solid particles is probably the least understood part of the soot formation process. The vagueness of the initial discussions² came under criticism by Calcote,³ who argued that reactions of neutral species are not fast enough and hence proposed an ionic mechanism. Detailed kinetic simulations¹¹ disproved Calcote's arguments that neutral-species reactions are not sufficiently rapid and identified the factors (*i.e.*, the HACA thermodynamic-kinetic coupling) responsible for the growth of molecular mass on the scale seen in experiment. Also, it was shown that the presence of thermodynamic and kinetic barriers affecting the growth of neutral species apply equally well to reactions of ionic species.⁷⁴

In the initial reaction model¹¹ "soot" was defined as the mass accumulated in PAH species above a certain size; in other words, the transition from gaseous species to solid particles was assumed to take place as the result of a purely *chemical* growth. While using this definition could basically account for the amount of soot mass, it greatly underpredicted the particle size. In the follow-up work,^{12,49} the model of nucleation was expanded as follows. At some size PAH species begin to stick to each other during collision, thus forming PAH dimers. PAH dimers collide with PAH molecules forming PAH trimers or with other dimers forming PAH tetramers, and so on, all while individual PAH species keep increasing in size *via* molecular chemical growth reactions. In this manner the PAH clusters evolve into solid particles. As a practical measure, the formation of dimers was assumed to mark the emergence of the "solid" particle phase.

The essence of the above model is the accumulation of particle mass *via* chemical reactions with gaseous precursors *simultaneously* with the growth of particle size by collisions among PAH molecular species and clusters. As will be seen in the following section, such a model provides a consistent transition from gas-phase aromatics chemistry to particle surface reaction and aggregation dynamics. Here it is pertinent to mention that chemical growth alone is not sufficient to explain the time scale of the soot inception phenomena, and this result served as an argument⁵³ against the proposal of the purely fullerene growth model advanced by Kroto and co-workers.⁷⁵

To test the idea of PAH dimerization, Miller *et al.*⁷⁶ calculated concentrations of dimers that would be in equilibrium with benzene, coronene and circumcoronene and found that the estimated values are significantly below the number densities observed for small soot particles in flames. Based on this analysis, they ruled out the possibility that soot nucleation can begin with PAH dimerization. In a follow-up study, Miller⁷⁷ calculated size-dependent lifetimes of PAH dimers and found that they approach chemical-reaction times of aromatic growth at a PAH monomer mass four times that of pyrene. In his analysis, Miller⁷⁷ relied on the equilibrium results of the prior study⁷⁶ but derived PAH collision rates using trajectory calculations assuming PAH molecules are structureless balls attracted to each other through the Lennard-Jones potential. He made an interesting observation that some of the translational energy of the colliding molecular pair may be trapped in the angular momentum of an incoming molecule orbiting the other.

Recently, we have begun investigation of the collision of pyrene molecules using a technique of molecular dynamics with on-the-fly quantum forces.⁷⁸ This method allows us to examine in a physically realistic way the dynamics of energy transfer between external and internal degrees of freedom of colliding moieties. The immediate finding from the performed

numerical simulations is the internal rotation of PAH monomers, which translates into a substantially increased dimer lifetime.⁷⁹

A model of purely chemical growth for the soot nuclei formation has been pursued in a series of recent studies.^{9,10,58,80–84} As mentioned above, the evolution of gaseous species in this approach is presumed to occur by virtue of the increasing size of the growing molecular species which eventually acquires the property of a condensed phase. The proposals referenced above invoke the formation of ring-ring aromatics, possibly interconnected by aliphatic chains, that graphitize later.

The purely-chemical model of nucleation, nonetheless (despite its usual qualification as "different"), is entirely consistent with the nucleation model described earlier in this section. Indeed, let us consider PAH species growing chemically at the edges while forming clusters when colliding. One can envision two regimes. The first is realized when the chemical growth is limited by a high degree of reaction reversibility. Under these conditions the reaction pathways of aromatic growth are switched quickly to an acetylene-based HACA and the growing PAH species are dominated by "compact" stabilomers, as only those can survive such "harsh" environments while other species, with weaker bonding, decompose. The stabilomers then, when they collide, form physically-bound clusters. This regime seems to be able to describe soot formation in higher-temperature combustion.^{36,40–42,49,85–89} The other regime is realized when the formation of chemical bonds is not counterbalanced heavily by fragmentation and hence there is no thermodynamic limitation on the structural form the growing molecular moiety assumes. This leads to the formation of a variety of chemical structures as a result of collisions with different gaseous partners. Having a diverse molecular base may well lead to a network of aromatic-aliphatic-linked structures. Such a regime, for instance, was advocated for the conditions of kerogen-like material formation in the solar nebula, ascribed to the large propensity to chemical "condensation" in those environments.⁹⁰

It is important that the two, possibly extreme, regimes were obtained using the same reaction model. On this basis, we must conclude that the two models of nucleation should not be considered as different but rather as different realizations of fundamentally the same underlying mechanism. It also follows that one should anticipate various patterns of behavior, exhibiting different regimes under different conditions, spanning between the two extremes.

4 Surface reactions

4.1 Empirical approach

While the nucleation kinetics control the number of nascent particles and coagulation controls the evolution of the particle number density, the carbon mass accumulated in soot is determined primarily by surface reactions, growth and oxidation.⁶⁸ It was established in experimental studies of laminar premixed flames that acetylene is the principal gaseous species that reacts at the particle surface, and that this carbon deposition process follows first-order kinetics.^{91–93} Although some of the quantitative and qualitative aspects of these studies have been questioned,^{94–96} this empirical first-order rate law and the experimentally-determined rate-constant value are often used in simplified models of soot formation. Surface growth determined in laminar diffusion flames was found⁹⁷ to be generally consistent with the assumption of acetylene being the main growth species but with the rate constant different by a factor of 4 from that determined in laminar premixed flames.^{91,92} Species other than acetylene have been invoked as possible surface growth precursors, and among them, most often, aro-

metics.^{24,68,95,98–100} However, the evidence⁹⁹ for the latter has been questioned.¹⁰¹

Counterbalancing the surface growth is the oxidation of soot particles, which occurs predominantly by O₂ molecules and OH radicals. For the oxidation by O₂, an expression derived by Nagle and Strickland-Constable¹⁰² found widespread use. For the oxidation by OH the temperature-independent reaction probability was determined in laminar premixed flames⁶⁹ and shock-tubes.¹⁰³

4.2 Active sites and chemical similarity

Another direction regarding surface reactions was initiated by introduction of the hypothesis of chemical similarity,^{49,52,104} which postulates that chemical reactions taking place on a soot particle surface are analogous to those of large PAHs. This assumption has two immediate implications. First, it defines the specific physical nature of surface active sites discussed continuously in the carbon and soot literature but in generic terms,^{102,105–108} and second, provides a way of describing the rate of surface growth and oxidation in terms of elementary chemical reactions. In other words, the surface of soot particles is assumed to look like the edge of a large PAH molecule, covered with C–H bonds. Abstraction of these H atoms activates the sites, forming surface radicals. The latter react with incoming gaseous species, both hydrocarbons that propagate the growth and oxidizing agents that remove the carbon from the surface. In other words, the surface growth is assumed to be governed by the HACA mechanism.

4.3 Surface HACA

Under most conditions examined thus far with detailed kinetic models, the surface growth occurs in environments of acetylene abundance and hence only acetylene has been invoked as a growth species. The acetylene-driven HACA model is consistent with the analysis of Harris and Weiner,⁹² who concluded, on the basis of flame species abundances, that acetylene should dominate surface growth in their flames. Recent re-examination of surface growth by Faeth and co-workers fully supports not just the initial conclusion of Harris and Weiner,⁹² but also the validity of HACA in explaining their observations of soot surface growth rates in a series of laminar premixed^{109–111} and diffusion¹¹² flames.

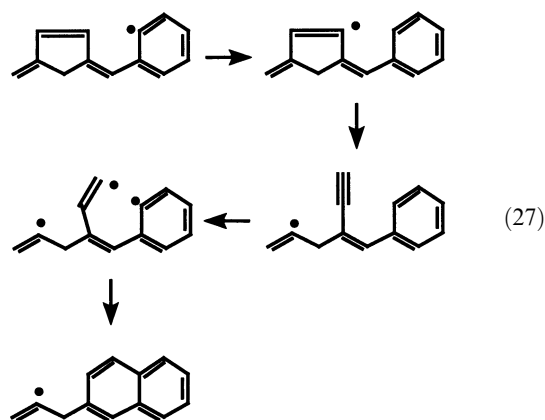
The original formulation of surface HACA included only irreversible addition of acetylene.^{12,49} The conclusion on a single-step irreversible addition of an acetylene molecule to a surface radical, leaving out the reversible addition step as compared to the analogous gas-phase HACA, was reached on the basis of numerical analysis of the temperature dependence of surface growth.⁴⁹ Inclusion of the reversible step led to an overprediction of thermal decomposition of surface intermediates with temperature. At the same time, exclusion of the reversible step caused insufficient dependence on temperature. Hence, the HACA growth was assumed to take place *via* a single irreversible step, but with the introduction of a temperature-dependent multiplier, α . This parameter α was rationalized as quantifying the changing morphology of the soot particle surface. In a subsequent study,³⁶ α was assumed to be dependent on both temperature and particle size.

Colket and Hall¹⁸ kept the reversible addition of acetylene in their modification of the original surface HACA. These authors¹⁸ and others^{86,113} have argued that such reversibility is necessary to reproduce surface deactivation, a phenomenon observed experimentally.^{2,68} However, sterically-resolved Monte Carlo simulations showed that the decreasing stability of surface intermediates is unlikely to be responsible for the decline in surface reactivity of soot particles.¹¹⁴ The mechanistic interpretation of the surface deactivation phenomenon is discussed in section 4.5.

4.4 Surface migration

The postulate of chemical similarity provides a natural extension of the gas-phase chemistry of aromatics, which in turn enables a seamless coupling of the gas-phase reaction model with that of surface growth and oxidation.¹² At the same time one must realize that the postulate of chemical similarity is only an assumption. In reality, one should anticipate differences between gaseous and surface reactions, even in cases of seemingly analogous molecular interactions. The primary cause of the possible dissimilarity is the difference in steric confinements of reactive sites. In other words, the reaction of a gaseous species with a surface radical may have the “sticking probability” and equilibrium constant varying with the nature of the neighboring sites and their occupancy. Furthermore, while the localized steric factors may affect the surface kinetics in its own right, sometimes, like in the case of surface migration discussed below, it leads to substantially different global kinetic patterns.

We now turn again to reactions discussed in section 2.2.4. The newly identified migration of the five-membered ring, reaction (24), is similar, in a general mechanistic sense, to migration of CH₂ bridges on diamond (100)-(2 × 1) surfaces.¹¹⁵ By analogy with diamond film growth, the five-membered-ring migration has important implications for the surface growth of soot particles. The migrating five-membered rings will propagate the zipper filling of the zigzag surface, *via* the reaction pathway



ensuring that the growth proceeds *via* a continuous front. A “collision” of these propagating fronts may create a site that cannot be filled by cyclization and thus cannot support further growth, again reminiscent of the diamond case. Formation of such surface defects may be responsible for the loss of reactivity of the soot particle surface to growth.^{65,114} In addition, the cyclopenta ring migration to an open edge provides a mechanism, *via* reaction (23), for the formation of a six-membered nucleus of the next aromatic layer. Another possibility for this may be the “collision” of two migrating cyclopenta groups.

4.5 Surface aging

Experimental observations on soot formation in flames indicate that the surface growth rate of soot particles declines with the extent of particle growth,^{2,68,91,92} a phenomenon termed soot surface aging. Based on the results of detailed numerical simulations, a mechanistic interpretation of the aging phenomenon can be attributed to two factors:^{12,49,65,114} decrease in the H atom concentration or a degree of H superequilibrium in the gas phase, and decrease in the number of active sites on the soot particle surface capable of sustaining growth. The former factor reduces the kinetic driving force of the HACA sequence as the system moves toward equilibrium. The second factor reduces the particle surface activity due to the formation of surface defects. If we assume that the appearance of unreactive

sites is caused by surface migration, then smaller, nascent particles, having largely the character of gaseous PAHs, will not be able to develop many such unreactive sites. As particles grow in size and their edges elongate, the surface migration described in section 4.4 leaves behind surface voids. Interestingly, formation of such voids, in addition to rationalizing the surface aging, may also explain the radical character of aging soot particles detected in magnetic resonance studies.²

5 Particle coagulation

Once soot particles are formed they collide with each other forming larger particles. Experimental studies observed that initially the particles look spherical and later acquire a fractal shape.² Hence, particle coagulation is usually classified as coalescent growth and agglomeration into fractal aggregates.

5.1 Coalescent growth

In this regime particles are usually assumed to be spherical. They collide and coalesce completely, forming new spherical particles. The phenomenology and mathematical treatment of this regime is borrowed from the field of aerosol dynamics.^{116–118} The process is described by the Smoluchowski master equations,¹¹⁹ with the collision coefficients dependent on the sizes of colliding particles. The functional form of this dependence is in itself dependent on the value of the Knudsen number¹¹⁶ which is the ratio of the mean free path to the particle radius, and hence is a function of pressure. At low pressures the coagulation is said to be in the *free-molecular* regime, and at high pressures in the *continuum* regime. Both of these limiting cases are well understood.^{117,118} The in-between regime, the *transition* regime, takes a much more complex form.^{116,117} For the free-molecular and continuum regimes, it has been established¹¹⁸ that the Smoluchowski master equations have asymptotic solutions resulting in *self-preserving* distributions of particle sizes. It is these asymptotic results that are usually used in simplified models of soot formation and in the interpretation of experimental data collected with optical methods. The experimental evidence¹⁰ and computational results¹² both show that there is a substantial deviation of the particle size distribution function from the self-preserving form in the soot particle inception zone.

5.2 Particle agglomeration

At some point in the flame, soot particles are observed to agglomerate, *i.e.*, stick to each other forming chain-like structures. The experimental data suggest that this process does not happen early in the flame where particle inception takes place, but occurs later when soot particles “mature” (or “age”). The chain-like structure has been analyzed in terms of fractal geometry.^{97,120–124} The fractal dimension determined in numerous flames seems to be confined to a rather narrow range, 1.7–1.8.^{123,125,126}

5.3 Transition from coalescent to fractal growth

It is usually presumed that formation of spherical soot particles precedes that of aggregates,² but the transition from spherical to fractal growth is not well understood. According to one school of thought, the particles are composed of viscous matter (liquid droplets) that coalesce completely at small sizes but do not have sufficient time for fusion as the particle size increases.^{127,128} Another point of view is that the nearly spherical shape of the primary particles is the product of simultaneously occurring coagulation and surface growth^{2,129,130} and that the transition to the fractal aggregates is caused by cessation of surface growth.¹³¹

Recent numerical simulations paint a different picture.¹³² Soot particle growth was modeled using time-dependent Monte Carlo simulations, *via* ensemble-averaged collisions between small, geometrically perfect spheres. Simultaneously with the collisions, the particle sphere surfaces grew at a prescribed rate. The simulations identified two factors affecting the level of particle sphericity. The first is a sufficiently fast surface growth rate. In the absence of surface growth, there is no smoothing necessary to construct spheroidal particles. However, for the geometry to become spheroidal, the rate of surface growth must be capable of burying colliding particles stuck to the surface of larger particles. If the colliding particles are too large, the surface growth may not be able to bury them quickly enough. Thus, the second factor is the size of the colliding particles. Smaller particles are more easily covered. Therefore, an ensemble replete with smaller (primary) particles is optimal for generating spheroidal particles.

These results show that particle aggregation is not separated in time from particle nucleation, as often presumed. Instead, aggregation begins with the onset of nucleation. At this point, collisions between the growing particles and PAH moieties ensue. The collisions may cause the incoming PAH clusters to deform and lose their individual characteristics. This contributes further to an overall spheroidal shape. Coupled with the two factors discussed above, the spheroidal shape of the emerging particles should be attributed to rapid surface growth, intense particle nucleation, and rearrangements of the internal structure of the colliding clusters.¹³²

6 Numerical modeling approaches

Soot formation models can be classified, based on their nature, as *empirical* and *physical*. Empirical models offer mathematical simplicity but suffer from unreliable predictability. Physical models, on the other hand, once established, can be applied with larger confidence over a wide range of conditions. The large size that such physical models take, the obvious problem for implementation with fluid-dynamics codes, can be overcome by applying various mathematical methods which reduce the size of the mathematical formulation without however distorting the physical nature of the initial detailed model.

6.1 Empirical models

Recent models in this class^{133–137} have usually been constructed assuming arbitrary nucleation, asymptotic regime of coagulation (*i.e.*, assuming a self-preserving particle size distribution function), and empirical growth and oxidation. Having some success with predicting qualitative trends, such models often miss quantitatively and require reparametrization for different combustion environments. This class of models was recently reviewed by Kennedy.¹³⁸

6.2 Physical models

Detailed kinetic modeling of soot formation and growth is an upcoming area of research. There are an increasing number of detailed chemical kinetics studies of the formation and growth of PAHs.^{13,36,58–60,139–146} Most simulations are carried out up to a specified aromatic size, one to four rings, while some treat the aromatic growth up to infinity^{12,113} with a linear lumping technique.¹⁴⁷

Several groups have extended the detailed description to soot particle dynamics.^{12,18,36,40,49,86–89,113,148–150} In these latter efforts, the transition from the gas phase to soot particles is described assuming the nucleation to take place at the collision of pyrene and larger aromatics^{12,36,40,49,86–89,113,148,150} or at the collision of benzene molecules.^{18,149} The surface growth is treated either empirically^{18,150} or based on chemical analogy to

aromatics chemistry.^{12,36,40,49,86–89,113,148} The coagulation of soot particles is modeled by using either a discrete-sectional method^{18,150} or the method of moments.^{12,36,40,49,86–89,113,148}

In the discrete-sectional method,¹⁵¹ the entire particle ensemble is divided into several dozens of sections and the particle properties are averaged within each section. In the method of moments,^{12,152} the detailed description of particle dynamics is reformulated in terms of moments of the particle size distribution function (PSDF). Knowledge of the infinite set of these moments is equivalent to knowledge of PSDF itself, in the same way as a given function is defined by the complete set of its derivatives. We know, however, that determination of just the first few derivatives is sufficient for most practical applications. In the same way, the first few PSDF moments are sufficient for determination of essentially all practical properties of a particle cloud, such as soot volume fraction, specific surface area, light absorption, light scattering, *etc.* The unique feature of our method of moments^{12,152} is that the mathematical closure of the differential equations is accomplished by interpolation, without prescription of a functional form for PSDF as typical of other variations of the method of moments. The method of moments was recently extended to include agglomeration of soot particles into fractal aggregates.¹⁴⁸

7 Concluding remarks

The general message that emerges from the present state of the art is that soot formation in flames can be understood from “first principles”. The discussion has shifted from phenomenological possibilities to specifics of reaction pathways. In many ways, this accomplishment is due to computer modeling as a scientific tool.

In the field of PAH and soot formation, as in other areas of combustion science, there is a multitude of different opinions. However some of them might be closer to consensus than is often proclaimed. Much is still unknown but to make progress it is extremely important to have a *consistent* effort. Being true everywhere, the consistency among different types of data—kinetics and thermodynamics, experimental and theoretical, gas-phase and surface—is even more critical for unraveling details of the PAH chemistry because of the complex kinetic-thermodynamic coupling of the underlying reaction network.

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