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The interior of a flame generates small and large particles.

Fullerenes and Soot Formation—New Pathways to Large Particles in Flames**

Klaus-Heinrich Homann*

In memory of Wilhelm Jost

It is only rarely mentioned in the fullerene literature that there is a natural source for fullerenes, namely the combustion of certain hydrocarbons within rich mixtures with O_2. Under most combustion conditions, however, soot is the nearly exclusive high-molecular-weight product formed. This is probably the reason why fullerenes were not found earlier, even though soot extraction studies have been performed frequently in the past. As the first experimental conditions that led to the discovery of fullerenes—laser evaporation of graphite—were very different from conditions found in flames, combustion researchers did not expect to find fullerenes among the products of combustion. As is so often the case, serendipity led to the discovery of fullerenes, even though the flames under investigation were studied for completely different reasons: namely to look for very large polycyclic aromatic hydrocarbons (PAHs) that were the assumed precursors of soot particles. These species could not be worked up after precipitation, so they were sampled with a molecular beam of a flame burning at low pressure. PAHs also have low ionization potentials; hence it was decided to study the natural flame ions of PAHs, as these are more readily detected. As it was also known that the flames of aromatic compounds contain many PAHs, benzene was used as the fuel. These three conditions (low pressure, flame ions, and benzene as the fuel) turned out to be favorable for the detection of a large variety of fullerenes in flames. Even though it has not yet been possible to obtain larger quantities of fullerenes by combustion, it has been possible to get closer to answering the question as to how these uniquely built carbon molecules are formed together with the much less orderly structured soot particles.

Keywords: combustion · flames · fullerenes · polycycles · soot

1. Introduction

Soot is the best known high-molecular-weight product of combustion. The presence of fullerenes in flames was discovered in 1987,[1] two years after their initial discovery.[2a] During normal or industrial combustion the formation of fullerenes relative to soot is so low that they can only be detected with the most sensitive analytical techniques. By the use of special fuels and certain combustion conditions, however, flames can be created in the laboratory in which fullerenes and soot are formed in approximately equal proportions. This article will only deal with such laboratory flames. From this vantage point, fullerenes are certainly the most spectacular high-molecular-weight products of incomplete combustion. After all, they have been on the front page of the New York Times, and the 1996 Nobel Prize was awarded for their discovery during the condensation of carbon vapor after laser bombardment of graphite.[2b] Soot does not command the same degree of scientific respect. With respect to their economic importance, however, the relationship between these two substances is reversed.

At high temperatures, the thermodynamic driving forces in a C/H/O system that does not contain enough oxygen to oxidize all the carbon to CO favor edifices that are rich in carbon. Which mechanisms, however, can explain why large fullerene molecules, having a well-defined molecular formula and exhibiting very high symmetry such as the structure of buckminsterfullerene, are formed under the same conditions and at approximately the same time scales as comparatively huge soot particles, which have neither a molecular formula nor a defined structure? Could fullerenes be a product stemming from soot? Or could the situation be reversed, namely that a fullerene molecule, or something similar, is the

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starting point for the growth of a soot particle? Or are there parallel reaction steps that lead to soot particles and fullerenes?

The chemistry of combustion begins with the fuel, a pure, low-molecular-weight hydrocarbon such as methane, ethylene, acetylene, or an aromatic species such as benzene. It is necessary, therefore, to search from these beginnings for intermediates in the formation of large carbon-rich species. The formation of fullerenes by laser evaporation of graphite[2b] or in the fullerene generator by Krätschmer,[3] both of which are pure carbon/helium systems, will not be considered in this article.

2. Classification of Large Particles in Flames

There are five classes of large particles in rich hydrocarbon flames, including soot and fullerenes. Four of them have been known for some time. These four classes, which are depicted in Figure 1, do not only differ in their range of molecular masses, but also in the dimensionality of the arrangement of their C atoms. The fifth class was only found through the application of new analytical methods and is considered to be very important for soot and fullerene formation and will be discussed later.

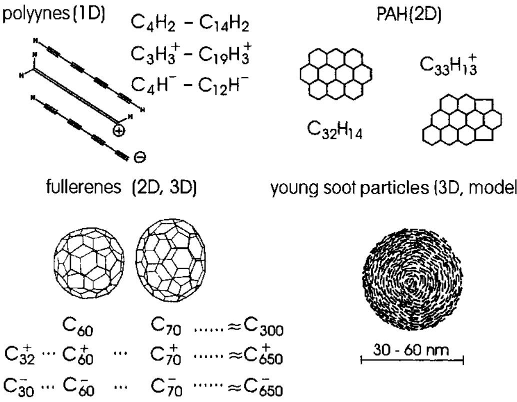


Figure 1. In rich hydrocarbon flames there are carbon-rich particles with one, two, and three-dimensional C backbones that also occur as intrinsic ions in the flame. The residual double bonds of the polycyclic compounds in the diagram are not shown.

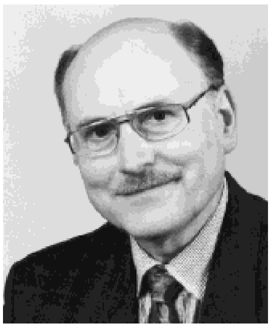
2.1. Polyacetylenes

The first class is the extended polyynes or polyacetylenes. They posses a one-dimensional linear arrangement of carbon atoms and in the electrically neutral (normal) state they carry one hydrogen atom on each end of the chain; their generic formula is $C_{2n}H_2$. They have been detected with formulas up to $C_{14}H_2$. In flames they also exist as radicals, mainly with one additional H atom on one end;[4] and formulas up to $C_8H_3^{\bullet}$ have been detected. As all polyacetylenes have a high proton affinity and the longer ones also possess relatively low ionization potentials,[5] they exist in flames in the protonated form and, with increasing chain length, also as simple positively charged ions, albeit in very low concentrations (e.g., $x_{\max}$ $(C_6H_3^+) \approx 4 \times 10^{-11}$ or $[C_6H_3^+]/[C_6H_2] \approx 10^{-8}$). They can also exist as negatively charged ions, for example, $C_{2n}H^-$.[6]

The most remarkable property of polyacetylenes in flames is that in the region of maximum temperature within the flame they are all in partial chemical equilibrium with each other and with acetylene and hydrogen. This is also true for their radicals and ions and their equilibria with the normal polyacetylenes.[4, 7] These equilibria limit the growth of the polyacetylenes, as the large chains tend to degrade. This keeps their range of molecular masses far from that of fullerenes and soot particles, which means that polyacetylenes can be ruled out as potential precursors. There are, however, additional arguments for this assumption; for example, the polyacetylene concentration in rich acetylene flames is particularly high, while the fullerene formation is relatively low.[8]

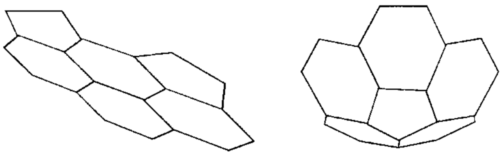
2.2. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are two-dimensional carbon-rich molecules. Naphthalene can be looked on as the smallest PAH, while the largest PAHs have molecular formulas of around $C_{320}H_{50}$.[9] By the use of authenticated materials, about 30 unsubstituted PAHs have been identified up to the molecular mass of coronene (300 u).[10] Beyond this range only very little is known about their structures. As a consequence of the two-dimensional arrangement of their C atoms the multitude of structures is much larger than of one-dimensional species. The most common structural element of



Klaus-Heinrich Homann was born in Göttingen (Germany) in 1935. He studied Chemistry at the Universities of Freiburg/Breisgau and Göttingen from 1955 to 1961. He was awarded his doctorate at the University of Göttingen in 1964 and in 1969 finished his Habilitation in Physical Chemistry. He was a Fellow of the National Science Foundation, Washington, D.C. at Boston College 1969–70 before becoming a Lecturer (Universitätsdozent) at the Universität Göttingen. Since 1971 he has been Professor at the Technische Hochschule Darmstadt. In 1994 he received the Bernard Lewis Gold Medal and the Silver Medal of the International Combustion Institute. In 1995 he gave the Hottel Lecture at MIT, in Cambridge, MA (USA) and the Wilhelm Jost Memorial Lecture. His research interests include chemical kinetics and the chemistry of combustion.

PAHs is the hexagon of benzene. The structural variety is increased by the addition of pentagons. The existence of five-membered rings in PAHs is of particular interest with respect to fullerene formation. When five-membered rings are bordered by hexagons on not more than two adjacent edges, the molecule is still nearly planar as seen in dicyclopenta[*cd*,*fg*]pyrene. The bowl-shaped structure of corannulene is markedly different; here a five-membered ring is bordered on all sides by hexagons (Figure 2).



dicyclopentapyrene $C_{20}H_{10}$ corannulene $C_{20}H_{10}$

Figure 2. Five-membered rings only cause strong molecular distortions when they are bordered by condensed six-membered rings on more than two adjacent edges.

In flames, PAHs also exist as both σ and π radicals.[11] In the former species, the unpaired electron is located in a σ orbital, while in the latter it is found in a π orbital. PAHs also exist in protonated or ionized form.[7, 12] At 10^{-4} to 10^{-3}, their degree of ionization or protonation is markedly larger than for the polyyne C_6H_2.[9] PAHs apparently only exist as negatively charged ions if they contain one or more five-membered rings and/or one oxygen atom.[13]

Even though the density of the large ions in flames is very low they can be readily detected by mass spectrometry. All large molecules occur as ions, whether as anions, cations, or in both forms. Hence, much information about their occurrence and growth stems from studies of these species that naturally occur in flames. This does not imply that reactions, which will later be discussed with measurements on ions, only apply to ion–molecule reactions. For the large particles under study these reactions also pertain to the corresponding neutral reactants.

2.3. Fullerenes

Fullerenes exhibit a three-dimensional closed-cage structure. In flames the neutral species have been detected on-line from C_{60} up to about C_{300}. From C_{70} onward, all even-numbered species have been found.[11] The most prominent are always C_{60} and C_{70}. Which of these two species is more common depends upon the combustion conditions and the fuel. Ordinarily, however, C_{60} predominates. Regardless of form and size, all fullerenes must contain twelve pentagons in order to create a closed cage. Fullerene ions are much more readily detected in a flame than the neutral molecules. This can be gleaned from the fact that the ions are found in a mass range that is broader by a factor of about two relative to the neutral species (C_{32}^{+} up to approximately C_{650}^{+}, C_{30}^{-} up to about C_{600}^{-}). The ionized species C_{62} to C_{68} are found as well.[14] It is not unambiguously clear whether the upper limit of about C_{650} arises because of limitations of the measurement technique or stems from specific conditions within the flame. A mechanism of formation that will be discussed later indicates that the latter is true.

One could consider fullerenes to be two-dimensional species, as the C atoms only form a molecular surface. The upper mass limit, which is only about twice as high as that found for the planar PAHs, is relatively low for three-dimensional particles. This also supports the view that fullerenes are two-dimensional. The absolute lowest boundary appears to be C_{32}^{+} or C_{30}^{-}; this has been observed during the photolytic degradation of fullerenes as well.[15] The so-called nanotubes are related to fullerenes. These are elongated, fullerene-like cylindrical tubes which are closed at the rounded ends. They contain *several* layers of carbon atoms, possess much greater molecular masses, and have also been detected in flames.[16]

2.4. Soot Particles

Soot particles are definitely three-dimensional. The smallest ones exhibit a mass of about 2×10^3 u, while the largest ones get as big as 10^8 u.[17] This effectively unlimited growth, especially relative to one and two-dimensional particles, is characteristic of three-dimensional species. For some time, it has been known that the C/H ratio for very young soot particles is about 3.[18] Relative to the largest PAHs (about $C_{320}H_{50}$), this corresponds to a rather high hydrogen content. Even if it were possible to assign a definite molecular formula C_xH_y to a given soot particle, this would be rather useless as it must be assumed that no two soot particles are alike. All soot particles, even the smallest ones, occur in flames as negatively and positively charged species.[19, 20]

As is well known, fullerene molecules are hollow. Soot particles have filled interiors. A limited similarity can be found in the forms of the two species. One must, however, consider some special cases, both for fullerenes and for soot particles. There are soot particles that exhibit a nearly perfect spherical shape.[21] While the closed, highly symmetrical shape of C_{60} is intrinsic and a consequence of the particular arrangement of twelve pentagons and twenty hexagons, the spherical shape for soot particles is the result of a certain growth mechanism. These quite round particles were able to grow by the surface degradation of small hydrocarbon molecules. During growth, no coagulation with other soot particles occurred (quite accidentally). These turbostratically arranged layer segments exhibit an interlayer distance slightly larger than that found for graphite.[22] During growth at flame temperatures, it is assumed that they can shift with respect to each other at the surface and thereby briefly form, in effect, a two-dimensional liquid. Hence, the eventually spherical shape arises from a dynamic process, which leads to other shapes when particles coagulate during growth.

The depiction of a soot particle in Figure 1 should not be taken literally. It is meant to indicate the (usually only approximate) spherical shape of the particle as well as the layer fragments that are visible under an electron microscope. These layers are oriented in a more or less parallel fashion with respect to the surface and in exceptional cases are grouped around a common center. The considerations (see below) about the origins of soot and the appearance of the first soot particles are not really related to the structure of the finished particle. This structure is, in fact, created during the particle growth by the attachment and heterogeneous degradation of small unsaturated hydrocarbons (e.g., acetylene) at the surface, tempering processes in the interior accompanied by the loss of hydrogen, and coagulation with other soot particles. For this reason, the detailed knowledge about the morphology of some "finished" soot particles will not be taken into account for the following considerations. An extensive discussion of soot formation and its various aspects can be found in the review article by Haynes and Wagner.[23]

3. The Flame as a Chemical Reactor

Premixed flames have proven successful for the detailed study of flame chemistry. These flames burn at low pressures (about 30 mbar) on a circular, cooled, porous metal plate (diameter 75 mm). Figure 3 shows a schematic representation of such a burner with a flame. The flame burns in a stationary fashion, which means that the spatial distribution of temperatures and concentrations remains unchanged. In the interior of the flame, these variables change primarily only with the distance from the burner. Therefore, such flames are also referred to as quasi one-dimensional. Further outward towards the edge of the flame, the temperature is not as high as in the center. These different temperature profiles (at the edge and at the axis) for the combustion of the same hydrocarbon/oxygen mixture is of importance for the study of fullerene and soot formation, which will be discussed in Section 8.

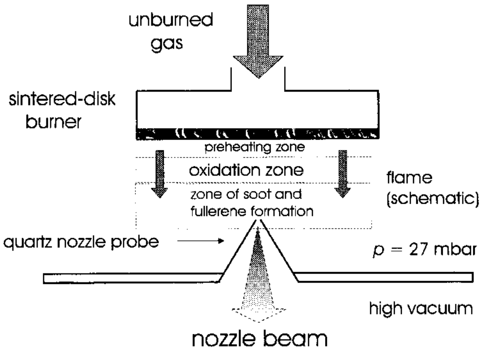


Figure 3. Schematic representation of a burner with a flat low-pressure flame and a nozzle beam probe.

The fuels employed were acetylene, 1,3-butadiene, benzene, and naphthalene. The flames were continuously sampled using a cone-shaped probe with an opening of about 0.7 mm in diameter, behind which a strong vacuum was applied. The sample was initially in the form of an expanding nozzle beam. From this (continuous) nozzle beam, a molecular beam was separated by a skimmer (see Figure 4) and a second vacuum pump. The various components of this molecular beam were then analyzed with several different apparatus. The probe that extended into the flame is indicated schematically in Figure 3. Even though the probe is not cooled and made of thin quartz glass, the flame is perturbed. The extent of this perturbation has been studied and consists mainly of a temperature drop of about 150–250 K at the probe tip, relative to the unperturbed flame, with the amount depending on the position in the flame.[24, 25]

A discussion of the chemistry of the reactions that constitute the bulk of the combustion is beyond the scope of this article. However, the most important conditions with respect to temperature and concentrations of critical reactants will be discussed in a qualitative manner, as the precursors for soot particles or fullerenes are exposed to these conditions on their path through the flame into the exhaust gas. A larger distance from the burner corresponds to a longer total reaction time.

3.1. Temperature

The temperature increases steadily from slightly above room temperature up to the end of the oxidation zone, at a distance of about 11–13 mm from the burner surface, where the supply of added molecular oxygen is exhausted. (A typical temperature profile is shown in Figure 13.) The maximum temperature at the flame axis at the end of the oxidation zone is dependent on the fuel, the fuel/oxygen mixture, and its unburned gas velocity (throughput). For the experiments described herein, mainly acetylene and benzene were used in a mixture with pure oxygen, which lead to a maximum temperature of 2050 to 2200 K. Hence, the temperature increases steadily in the flame zone, in which the higher molecular weight hydrocarbons are formed alongside the oxidation reactions.

The larger the activation energy, the more rapidly the rate constants of elementary reactions increase with temperature. For competition to occur between bimolecular association reactions (growth reactions) and rearrangement and degradation reactions, which exhibit higher activation energies, the following is implied: At the relatively low temperatures at the beginning of the oxidation zone, the molecules grow but rearrangement and degradation reactions do not play a significant role. With increasing temperature, the growth reactions become faster, but the rates of the degradation and rearrangement reactions increase even more rapidly. Since the concentration of the oxidizing radicals (mainly OH) also increases with temperature, the effect of degradation reactions increase with temperature in any case. This means that, depending on the combustion conditions, the growth of the molecules or particles can be limited and soot formation can be inhibited. How the formation of fullerenes is affected under these conditions will be described. After the maximum temperature is reached, it drops by about 70 K for every 10 mm. In this region growth reactions can catch up again, provided that enough reactants remain available in the exhaust gas.

3.2. Smaller Molecules and Radicals

The addition of acetylene to hydrocarbon radicals is a known type of growth reaction.[26] Under the conditions that prevail when soot and fullerene formation sets in within C_2H_2/O_2 flames the concentration of C_2H_2 drops by a factor of about 50 from the burner to the end of the oxidation zone.[24] This loss of a growth component is more than compensated for by the increase in the rate constants of the growth reactions, which grow by several orders of magnitude. Hence, growth reactions remain important throughout the entire flame.

During the combustion of benzene, the benzene molecule itself is an important reactant for the formation of higher molecular weight PAHs. In contrast to acetylene, benzene is completely consumed, even before the end of the oxidation zone. In the vicinity of the temperature maximum benzene is, therefore, no longer available as a building block for larger molecules or particles. Within a benzene flame, however, acetylene is formed with increasing temperature. At the end of the oxidation zone, acetylene is present in nearly the same concentrations as those found in acetylene flames.[27]

The most important small radicals found in fuel-rich hydrocarbon flames are H, CH_3, and OH,[28] with OH being the most important oxidizing agent in flames. The maximum concentration of the three radicals is reached just before the end of the oxidation zone. As the OH concentration drops sharply outside the oxidation zone of fuel-rich flames, the rate of formation of the large particles in the oxidation zone determines how greatly they will be affected by oxidative degradation. If they are formed rapidly they effectively only represent a transformation of the fuel and most of them will undergo combustion. If formation is slower and still continues when the OH concentration is decreasing, the large particles can reach the exhaust gas and are emitted together with it from the flame. As the growth of the large molecules starts in any case inside the oxidation zone, all possible precursors of soot and fullerenes are more or less exposed to oxidative degradation.

The primary role of the free H atoms is the propagation of the driving force of flame chemistry, the chain branching reaction $H + O_2 \rightarrow OH + O$. They thereby indirectly influence the formation and combustion of large molecules. It is much more difficult to discern a potential direct effect of free H atoms on the formation reactions of large molecules. This is because until now very few experiments have been performed to study the fundamental reactions of H with, for example, large PAHs or even soot particles at temperatures comparable to those found in flames. Attempts to accelerate the growth of PAHs and soot particles by the addition of free H atoms to a flame have mostly had the opposite effect.[29] Methyl radicals do not contribute to the formation of large molecules. This is apparent from the study of methane flames where methyl radicals reach a relatively high intermediate concentration, but do not lead to a significant formation of larger particles.

4. Apparatus and Experimental Methods

Our experimental methods are specially tailored to the online analysis of the just described medium-sized to large particles. Analytically speaking, trace analyses are performed. A further aspect was the ability to apply as many analytical methods as possible to the same flame. The main problem was the separation and, if possible, identification of the single components, which numbered in the thousands. This goal was realized by examining the nozzle beam or the molecular beam of the flame with various methods. This will be briefly discussed by use of the schematic diagram shown in Figure 4.

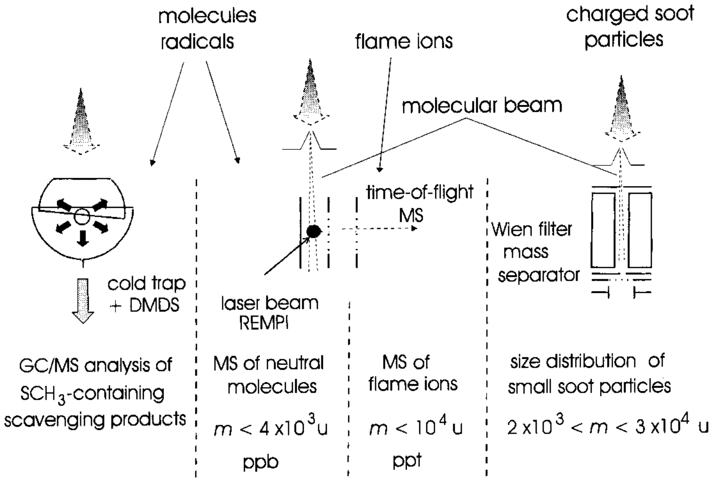


Figure 4. Methods for the analysis of molecular or nozzle beams from flames. From left to right: cold trap to trap radicals in frozen dimethyl disulfide (DMDS); time-of-flight mass spectrometry after resonance-enhanced laser photoionization (REMPI); time-of-flight mass spectrometry of flame ions; separation of very small electrically charged soot particles with a Wien filter mass separator.

The mass and sensitivity ranges of the methods employed are given in the figure. In the particle beam, indicated by an expanding arrow (nozzle beam) or dashed lines (molecular beam), we analyzed:[30]

- *Free hydrocarbon radicals, PAHs as well as oxygen-containing PAHs*, by condensing them together with excess dimethyl disulfide in a special cold trap at the temperature of liquid nitrogen. The radicals are trapped according to the reaction $R^{\bullet} + CH_3SSCH_3 \rightarrow RSCH_3 + SCH_3^{\bullet}$. After the contents of the cold trap are allowed to melt, the trapped radicals are identified and quantified by GC/MS analyses of the stable products $RSCH_3$. The largest thus found radical was pyrenyl. The nonradical condensable components were also determined quantitatively. In this case, the upper mass boundary was found to be coronene.
- *PAHs, PAH radicals, and fullerenes* by resonant (REMPI) and nonresonant multiphoton ionization with a frequency-doubled, pulsed dye laser and separation with a time-of-flight mass spectrometer, equipped with an ion reflector, which was specially designed for large ions. Photoionization is particularly effective for PAHs, and minimal fragmentation enables the detection of PAH radicals.
- *Positive and negative flame ions*, also with a reflectron time-of-flight mass spectrometer. As these species are already present in the molecular beam of the flame, a pulsed deflection voltage was used instead of the laser.

- *Very small positively and negatively charged soot particles* by employing a specially designed Wien filter mass separator (Wien filter + electrical deceleration field). This instrument does not yield single mass peaks but a (continuous) mass distribution, which is quite appropriate for small soot particles.

The procedure for all experiments was to take samples from the flames at various distances from the burner and to interpret the concentration profiles or mass distributions in terms of the combustion chemistry of the large particles.

5. Properties and Behavior of Large PAHs in Flames

As the mass range of large PAHs overlaps with that of the fullerenes as well as with that observed for small soot particles, it is an obvious choice to study the type of PAHs, their radicals and ions, as well as their development.

PAHs occur with any number of C atoms. The largest ones that have been detected in flames contained about 320 C atoms. Figure 5 shows the same segment of a mass spectrum of neutral PAHs (top) and PAH flame ions in a fashion that falsely suggests equal intensities, in reality the concentration of the neutral species is much higher. The mass spectrum of the flame ions is completely free of fragments and the spectrum of the neutral species nearly so. Both mass spectra show groups of PAHs with the same number of C atoms, ranging from 27 to 36. It is apparent, that in the range $C_{27}H_x$ to $C_{33}H_x$ the signals of ions containing odd numbers of C atoms are more intensive, while for the neutral species the even-numbered PAHs stand out. This difference in intensity becomes smaller with increasing mass of the PAHs, until it is only marginal for species with more than 50 C atoms. It is useful for other reasons as well (see below) to note whether PAHs contain an even or odd number of C atoms.

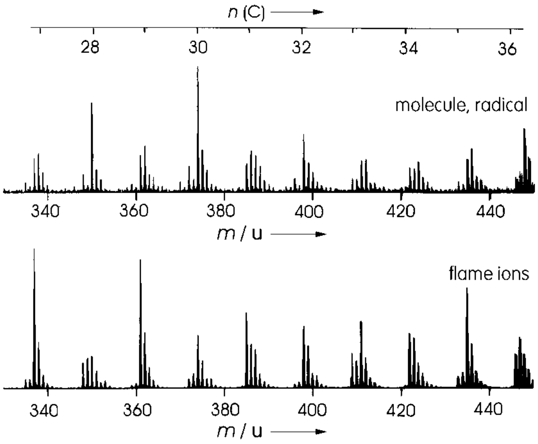


Figure 5. The mass spectra of a group of uncharged PAHs and their radicals show many similarities with those of corresponding positively charged flame ions. The upper abscissa shows the number *n* of C atoms per group of PAHs.

The different signals within a group stem primarily from molecules or ions with a different number of H atoms. In such a group, there are relatively H-rich and H-poor PAHs. The true ratio of H-rich to H-poor PAHs is obtained once the ^{13}C isotope distribution in the groups has been evaluated and usually shows PAHs that clearly dominate a group together with PAHs of lower intensity. The PAHs with the highest intensity within a group are termed the main PAHs.

5.1. The Molecular Formulas

The mass spectra yield initially only the molecular formulas of the PAHs. It is known from other studies of flame PAHs that one molecular formula usually encompasses several isomers.[31] The molecular formulas of the PAHs belonging to the isotope-corrected signals in the mass spectrum can be plotted in a C/H diagram, where each point corresponds to a certain formula C_xH_y. This is shown in Figure 6 for the PAHs from the flames of three different fuels. The PAHs of a group in the mass spectrum are listed in a vertical column in the C/H diagram. The most intensive ones within a group are denoted by the filled squares, weaker ones by the unfilled squares of decreasing size. In this diagram, the molecular formulas of the PAHs form a band that widens towards larger PAHs. This observation indicates that with an increase in the number of C atoms, the bandwidth for the H content becomes larger. This behavior becomes more pronounced when the fuel is changed from acetylene to benzene and finally to naphthalene. It is useful to provide an orientation aid in this diagram. Therefore, the solid line connects molecular formulas of PAHs or their ions that possess a highly condensed system of six-membered rings. These species are shown in Figure 7 up to a maximum of 59 C atoms. The odd-numbered ones also contain an odd number of H atoms. In the neutral state, these particles are π radicals. In ions with this structure the charge is delocalized, which contributes to their stability. These structures are the most C-rich or most H-poor PAHs formed solely from six-membered rings.

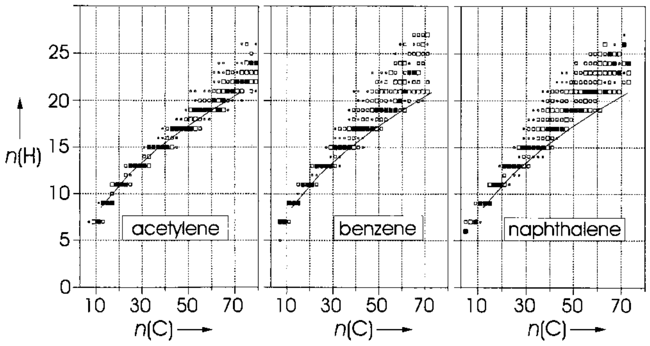


Figure 6. C/H diagram of the molecular formulas of positive PAH ions in the flames of three fuels. Black squares: PAH^+ ions at relatively high maximum concentrations; unfilled squares (according to size): PAH^+ ions at lower concentrations. PAHs exhibiting a structure having the maximum number of condensed six-membered rings fall on the solid line.

It is noteworthy that the dominant PAHs in acetylene flames, up to about $C_{70}H_x$, are densely grouped around this line. Hence, all PAHs above this line are richer in hydrogen

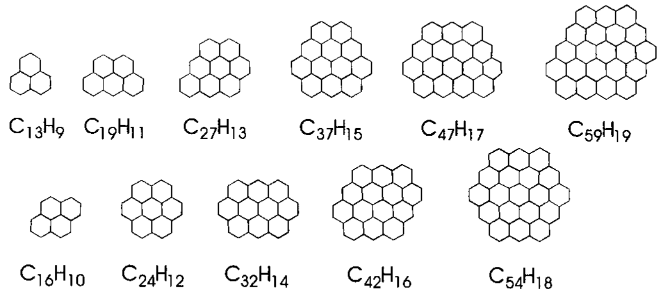


Figure 7. Odd- and even-numbered PAHs with a maximally condensed six-membered ring structure. In electrically neutral molecules the odd numbered species are π radicals.

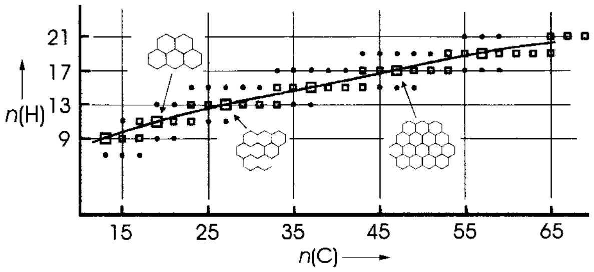


Figure 8. Segment of the C/H diagram of the PAH molecular formulas from an acetylene flame. The main PAHs (unfilled squares) form steps; the species exhibiting the maximally condensed six-membered ring structure lie in the center of these steps.

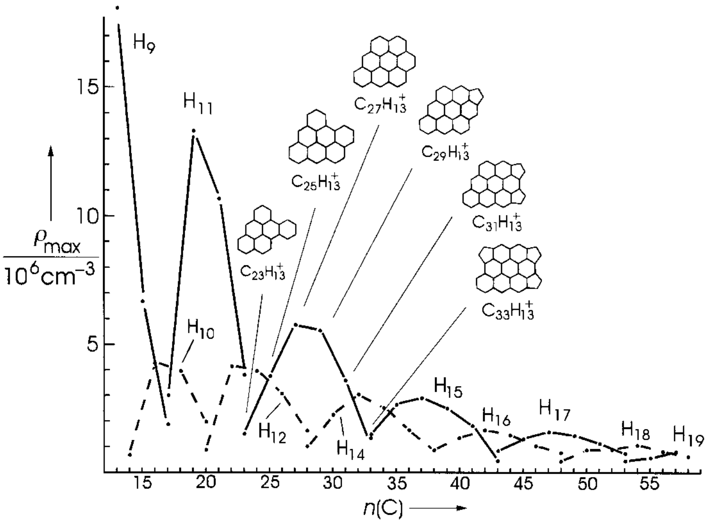


Figure 9. Maximum densities ρ of odd-numbered (solid line) and even-numbered (dashed line) PAH^+ ions in a C_2H_2/O_2 flame as a function of the number of C atoms per molecule. For PAH^+ ions with the same number of H atoms, there are maxima at the maximally condensed six-membered ring structures.

than the highly condensed structures shown in Figure 7, for which there are no other isomers built solely from six-membered rings. Thus, there are some very hydrogen-rich large PAHs, particularly in flames of aromatic fuels.

The diagrams in Figure 6 have only been constructed from the formulas of odd-numbered PAHs and they refer to ions, which can be gleaned from the odd number of H atoms. It should be noted that a plot of even-numbered PAHs, either as neutral species or positively charged ions, is on this scale essentially indistinguishable from the one shown.

5.2. Probable Structures of Large PAHs

The molecular masses corresponding to the peaks in the mass spectra yield molecular formulas, but only knowledge of the structures leads to further progress with respect to the question about the precursors of soot and fullerenes. For this, it is necessary to use all available knowledge about the high-temperature reactions of known PAHs and their identified PAH products—not only from flames—as well as calculations of the thermodynamic stability of PAHs and the dependency on structure and temperature. Knowledge of proton affinities and ionization potentials is equally useful.

It becomes possible to draw reasonable conclusions about the structural types of flame PAHs from the mass spectrometric intensities and their repeat patterns with dependence on the molecular formulas, which can be correlated with similar repeat patterns for certain structural types. For this purpose, a section from the lower segment of the C/H diagram of the acetylene flame (which is the simplest one) and the intensities of the corresponding main PAH^+ ions will be considered more closely (Figure 8). The *unfilled* squares, which represent the main PAH^+ ions, form steps (in Figure 6, these species are denoted by filled squares for better clarity). At the beginning of a step, the intensities of two signals in a group are comparable, so that two main PAH^+ ions can be registered. The PAH^+ ions in Figure 7 that posses formulas corresponding to highly condensed structures are found roughly in the middle of the steps. The steps become broader with an increase in the number of C atoms.

Interesting correlations are obtained when the maximum densities of these main PAH^+ ions in a flame are plotted separately for odd and even-numbered main PAH^+ ions against the number of C atoms (Figure 9). Those points that belong to PAH^+ ions with the same number of H atoms are connected by the line to improve clarity. These curves exhibit maxima always for those PAH^+ ions with molecular formulas corresponding to the structures shown in Figure 7. This is observed for odd and even-numbered PAH^+ ions and include $C_{13}H_9^+$, $C_{19}H_{11}^+$, $C_{27}H_{13}^+$, etc., and $C_{16}H_{10}^+$, $C_{24}H_{12}^+$, $C_{32}H_{14}^+$, etc. Relatively high concentrations of particles at high temperatures indicate thermal stability. For this reason, it is likely that the PAH ions marked among the main PAH^+ ions posses just these structures. It is, therefore, better to use the terms H-rich and H-poor PAHs and PAH^+ ions with respect to these structural standards, that is, the line drawn in the C/H diagram, instead of solely using the main PAH in the groups as orientation. The points on the curves left of the maxima thus correspond to H-rich PAHs, those on the right to H-poor PAHs.

There are many different reasons for a change in the relative H content. A PAH becomes more H-rich, for example, by substituting a H by a methyl group, by hydrogenation with retention of the C arrangement, by a more open carbon backbone that exhibits coves, by a more oblong arrangement of hexagons without cove formation, or by the formation of biaryl species. More H-poor structures can be generated by replacing an H with an ethynyl group and by incorporating one or more five-membered rings into the structure. All these structural characteristics have been found in PAHs from flames, however, some such as substituted or hydrogenated PAHs only in very small quantities. In the zones of the flame where these main PAHs reach their maximum concentration, the temperature is so high that changes in the relative H content (along one of the lines in Figure 9) must not affect the stability of the corresponding structures in an overly negative way. Taking this fact into account, of the possibilities just mentioned only the more open, cove-containing or more oblong arrangement of hexagons (→H-rich) and the incorporation of pentagons (→H-poor) remain viable. This has also been confirmed by theoretical studies.[32] Possible structures are shown next to the line for 13 H atoms in Figure 9. While $C_{27}H_{13}^+$ has only one isomer, there are three for $C_{25}H_{13}^+$ and four for $C_{23}H_{13}^+$. For the more H-poor species $C_{29}H_{13}^+$, $C_{31}H_{13}^+$, and $C_{33}H_{13}^+$ there are also several possibilities for the peripheral arrangement of the pentagons.

Based on these arguments is becomes clear that PAHs from the same mass spectrometric groups, that is, with the same number of C atoms, but different numbers of H atoms, have very little in common in terms of structure and mechanisms of formation, even though they occasionally have a similar maximum concentration. For example, $C_{33}H_{13}^+$ probably contains three five-membered rings in a highly condensed structure, while $C_{33}H_{15}^+$ exhibits a structure containing only six-membered rings and probably two four-carbon coves. A rule of thumb can be formulated as: *Flame PAHs with the same number of C atoms but different numbers of H atoms have different C backbones.*

Up to now, only main PAHs stemming from acetylene flames and lying along the "steps" have been considered. The same considerations apply also to H-rich large PAHs from the flames of aromatic fuels. Many of these PAHs, however, are so H rich that they can only be viewed as biaryls or oligoaryls (mainly with phenyl and naphthyl groups). Smaller biaryls have been detected and identified in large numbers in naphthalene flames.[31] They are not very thermally stable, which agrees with the observation that these components reach their maximum concentration at the beginning of the oxidation zone, where the temperature is not yet very high.

5.3. The Occurrence of Extremely Large PAHs

The largest PAHs and their ions are found, somewhat surprisingly, in acetylene flames and not in those of aromatic fuels. A slightly modified depiction of their H content with increasing number of C atoms in the molecule or ion is shown in Figure 10; Instead of the number of H atoms, the C/H ratio is employed. The reason for this lies in the better comparison with very young soot particles, for which this ratio has also been determined. Only main PAHs have been used in the plot, but both odd (unfilled dots) and even-numbered (filled dots) species are included in the diagram. As before, the curve drawn connects the maximally condensed species according to Figure 7. Some structures of large odd-numbered species are included as well. In this diagram, the H-rich PAHs lie below the line and the H-poor ones above it.

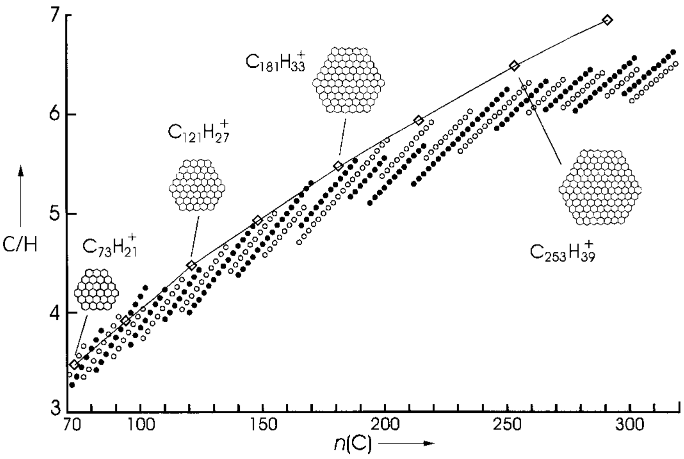


Figure 10. The atomic C/H ratio of the very large main PAH⁺ ions in a C_2H_2/O_2 flame, as a function of the number *n* of C atoms. Filled dots: even-numbered PAH⁺ ions; unfilled dots: odd-numbered PAH⁺ ions. For comparison, the structures and C/H ratios of some odd-numbered PAH⁺ ions with the maximally condensed six-membered ring structure are shown as well.

It is apparent, that for very large PAHs as well, there is no principal difference between odd and even-numbered species with respect to H content. In acetylene flames, the "band" of growth follows the line of maximally condensed hexagons fairly well up to about C_{100} PAHs. When the number of C atoms increases further, the PAHs become slightly more rich in hydrogen. The diamond at the upper end of the solid line represents $C_{294}H_{42}$. The main PAH for this C content is $C_{294}H_{46}$. This is only a small difference in H content. While $C_{294}H_{42}$ has an unambiguous structure (Figure 11), there are many possible structural isomers for $C_{294}H_{46}$, one of which is also depicted in Figure 11. This demonstrates the kind of structural change that a slightly larger H content can cause for very large PAHs. The course of the "band" shows that very large H-poor PAHs and, hence, the incorporation of five-membered rings into the structure must be quite rare. Otherwise, the "band" would cross the line, as is observed for PAHs with $C_{100}H_x$ or lower. This means that large PAHs are essentially planar molecules. The existence of these very

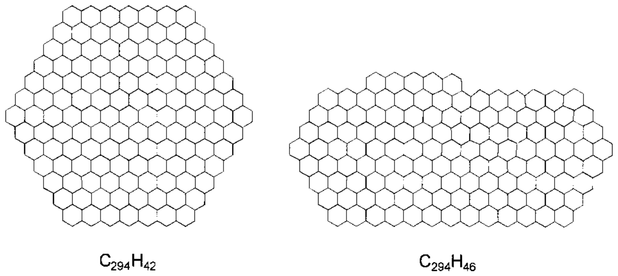


Figure 11. While the PAH $C_{294}H_{42}$ possesses only one unique, highly symmetrical structure, which is made up only of hexagons, the slightly more H-rich main PAH $C_{294}H_{46}$ exhibits numerous isomeric structures in a flame, which are most probably oblong and/or contain four C coves. One isomer is shown here.

large PAHs indicates that PAH growth does not stop with the onset of soot formation, as it clearly goes beyond the mass of the smallest soot particles ($\approx 2 \times 10^3$ u).

A detailed discussion of the relationship between PAH growth and structure is beyond the scope of this article. It suffices to note the relevant literature.[9] Important characteristics of the growing PAHs in the different flames with respect to soot and fullerene formation should, however, be summarized. Hydrogen-poor PAHs are formed primarily in acetylene flames up to about $C_{100}H_x$. Only those structures, however, that contain at most three five-membered rings are observed in significant concentrations. The growth by continuing reactions with C_2H_2 can be represented by a "band" that consists of probably thousands of individual PAHs. There is, however, no such "band" in the C/H diagram that leads to fullerenes (located on the n(C) axis).

In the flames of aromatic fuels, the situation is different. Fewer H-poor PAHs are formed, that is, those containing five-membered rings in their structure. In contrast, there is quite a number of H-rich PAHs, in particular in species with 30 or more C atoms. These have structures that must consist nearly exclusively of six-membered rings with four-carbon coves. In addition, one finds large biaryls. In benzene and naphthalene flames, relatively strong fullerene formation is observed, but no "band" in the C/H diagram that leads to fullerenes.[33]

5.4. Profiles of PAHs and PAH Radicals

For some time now, PAH radicals have played a dominant role in the discussion of the growth reactions of PAHs and in the formation of soot and fullerenes. Only recently, however, has it been possible to determine the concentration profiles of such radicals in flames. In some cases, this was done quantitatively. The following surprising results were obtained. Figure 12 shows the concentration profiles of ethynylbenzene and PAHs as well as of the corresponding radicals with one H atom less.[11, 31] All PAHs and their radicals are intermediates in the oxidation zone. The maximum concentration for ethynylphenyl reaches only 0.3 % of that of ethynylbenzene and the maximum is found at a larger distance to the burner, that is, at a higher temperature. For the larger indenyl radical, the maximum concentration is already 1.6 % and for the even larger pyrenyl radical about 20 % of the corresponding closed-shell PAH. The maxima also move closer together. For very large odd-numbered PAHs, the radical concentrations are surprisingly *larger* than those of the corresponding nonradical species. The maxima are reached at the same distance from the burner. In all probability, the latter species are π radicals like indenyl. For large even-numbered σ radicals, the radical concentrations also reach a high percentage, but they do not become larger than the concentrations of the closed-shell PAHs.[11, 31]

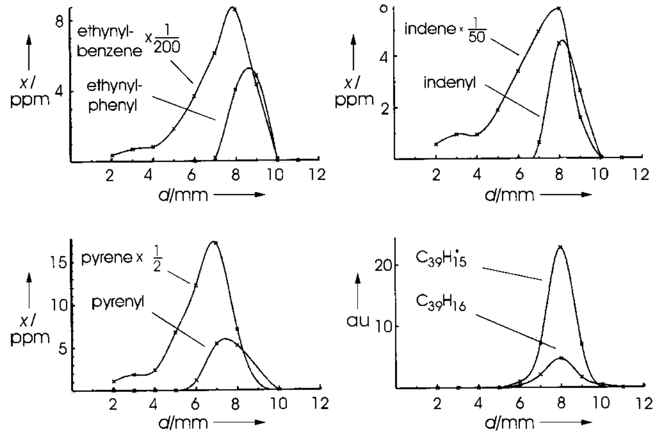


Figure 12. Profiles of the mole fractions x of PAHs and corresponding radicals (−1H) plotted against the distance d from the burner in a naphthalene/O_2/Ar flame. The relative concentration of the radicals increases strongly with the number of C atoms. For large odd-numbered PAHs, the radicals even become the more common species.

As the reactivity of radicals is greater than that of the corresponding valence-saturated (by H) molecules, their concentration generally remains small. As a consequence of their higher enthalpies of formation, their maximum concentrations are expected to occur at higher temperatures. This is certainly also true for radicals of smaller PAHs. For very large PAHs and, assumably, for other large molecules with many internal degrees of freedom this well-known picture appears to change. The difference between the reactivity of radicals and their corresponding molecules vanishes with increasing size and increasing number of internal degrees of freedom. It is quite possible that the remaining differences in the reactivity between species having the same or very similar molecular formulas—whether molecule or radical—stem from other criteria, for instance the structure itself or some bonds weakened by steric effects. Very little is known about the elementary reactions of large molecules or clusters at high temperatures. It is unreasonable to expect, for example, that the rate constant of the reaction between naphthyl and acetylene is similar to that of the reaction between acetylene and a young soot particle, which also possesses one or more unpaired electrons. Research is still only just beginning in this area.

5.5. The Role of Oxidation Reactions in PAH Growth

The growth of PAHs occurs primarily in the oxidation zone of the flames. Therefore, all participating reactants, intermediates, products, and their ionized forms are more or less exposed, directly and indirectly, to the influence of oxidation reactions. The indirect influence stems from the change in the temperature profile of the flame by the more intense and more rapid (or slower) combustion of all oxidizable components. This leads to a change in the concentration profiles of the small radicals (H, OH, O, CH_3, etc.) that participate in the chain-branching reactions. In contrast, the direct influence lies in the reactions of PAHs and their radicals or of fullerenes and their precursors with oxidizing reactants such as OH, O, or O_2.

The oxidation of aromatic- and alkyl-substituted aromatic species in flames and under flamelike conditions, for example, in flow reactors at temperatures up to about 1200 K, as well as behind shock waves has been studied frequently.[27, 34, 35, 36] Hydrocarbons with relatively small aromatic cores were employed for these studies, with phenanthrene being the largest one used.[37] The reactions of O and OH with benzene and substituted benzenes have also been studied.[38] The presence of partially oxidized higher aromatic species in fuel-rich flames has also led to knowledge of the first intermediates of oxidative attack.[31] This leads to the following general picture, in particular with respect to the effects on the growth reactions. Hydroxyl arenes (phenol, naphthols, hydroxyphenanthrenes, hydroxypyrenes) are the very early and dominant, if not primary, products of oxidation. This leads to the conclusion that corresponding compounds can also be formed from higher aromatic species.

In addition, oxygen is found in ketogroups (e.g., indene-1-one), aldehydes (e.g., benzaldehyde), or as a heteroatom in rings (e.g., benzofuran). Usually only one O atom is found in partially oxidized arenes, very rarely two O atoms are observed (quinones). On the other hand, carbon monoxide is found very early in the oxidation of arenes at temperatures around 1200 K. This gas results from cleavage of an hydroxyarene or of the respective radical (e.g., the phenoxy radical). Concurrently, a PAH with a condensed five-membered ring is formed. This indicates that thermal degradation quickly follows the oxidative attack on a C atom, which leaves no time for the further attachment of another O atom. Such a degradation step, however, does not significantly perturb the growth reactions because, at temperatures that are not too high, a PAH containing a five-membered ring is formed, which just possesses one less C atom. It is also possible, that in the course of this oxidation/CO release reaction sequence a PAH σ radical is formed that could even favor further growth. Partially oxidized PAHs or their ions have only been detected up to a mass of about 400 u.[13]

At higher temperatures, and primarily at the maximum temperature in a flame, no binding of OH or O to form hydroxyarenes takes place. Instead, an abstraction of H from the arene occurs, thus forming an aryl radical and H_2O or OH, respectively. This does not mean, however, that the C skeleton of the PAH is not further affected. Under these conditions, unimolecular degradation reactions are faster than bimolecular association reactions with small unsaturated hydrocarbons. In addition, the C–C bonds in radicals are much more readily broken than in intact molecules.[39] Hence, there is not only the release of one C atom in a single step (as CO), but, after the cleavage of the six-membered ring, up to four C atoms are cleaved off simultaneously, as is known from the oxidation of alkylarenes. This leads to the formation of another aryl radical, and so on. A single oxidative attack (or the reaction with H; indirect influence) can therefore initiate a rapid succession of degradation reactions. The end products of such a degradation are acetylene and polyacetylenes.

In the flame zone, where relatively many PAHs are formed, their growth is not significantly hindered by oxidation; no O-containing PAHs accumulate since they rapidly decompose. For appropriately hot flames, the oxidative attack also acts as the initiator for rapid PAH degradation, which happens anyway at high temperatures. Under these conditions no soot is formed. Hence, the steep drop in the PAH profiles in Figure 12 at 8–10 mm is not only caused by consumption through growth but also by decomposition.

6. The Controversy Over Soot and Fullerenes in Flames

Already in 1986, one year after the discovery of fullerenes, Smalley, Kroto, and co-workers suggested that fullerene-like structures could be the "nuclei" for roughly spherical soot particles.[40] These species would not be closed cages like C_{60}, C_{70}, or their larger analogues, but would have failed to achieve closure of the cage in *one* carbon layer during their growth. Growth would continue in a second layer, which places itself over the first one, and in several more layers, all of which would be curved by the incorporation of five-membered rings. In this way, only incompletely closed fullerene shells would be formed, which all in all would exhibit a roughly spherical shape. Kroto expanded these ideas in 1988 and proposed a so-called icospiral nucleation process.[41] According to this mechanism, the first stages of soot particles resemble the shell of a nautilus. Free valences, which are unavoidable because of the nonclosure of the cage in an all-carbon system, would be saturated (primarily around the opening of the nautilus shell) by hydrogen atoms during soot formation in combustion processes. Only along the edge (along the opening of the nautilus shell) would growth proceed along a spatial spiral, thus increasing the volume of the particle and its otherwise fullerene-like surface.

In the meantime, in 1987, fullerenes were discovered in sooting hydrocarbon flames, initially in the form of positively and negatively charged ions.[1] The fact that these ions were still also present in the soot-containing exhaust gas, lead to the conclusion that fullerenes in flames represented stable final products—albeit in small concentrations—and not just short-lived intermediates. Accordingly, in 1991, C_{60} and C_{70}, were, for the first time, extracted from a premixed low-pressure flame and separated by HPLC.[42]

In the past, there have been many hypotheses about the structure of the very first soot particles. These varied from tiny stacked graphite layers to droplets of high-boiling oil.[43, 44] In 1941, Rummel and Veh had already proposed that soot formation is preceded by PAH formation.[45] All these proposals were more or less well founded on experimental evidence. But none of these hypotheses caused such a controversy among some flame and soot researchers as Kroto's icospiral mechanism, which placed initial soot particles close to fullerenes.[46, 47] The counter arguments were mainly: The growth of PAH molecules in flames, proven many times by experiments, which has also been subjected to model calculations, was completely ignored, as well as the fact that soot, with respect to its chemical reactions, is much more similar to arenes than to graphite. In addition, it had been shown that during the initial stages of soot formation, when the particles are small and particle number density relatively high, coagulation of particles played an important role. According to Kroto's model, however, even the larger particles grow only in a very specific manner, by the binding of smaller carbon clusters, so that more and more layers with a fullerene structure are formed. According to this mechanism, even the initial soot particles should be very H-poor. It was found, however, that young soot exhibits a C/H ratio of about three.[18] Baum has presented an impartial summary of this controversy.[48]

The fact that fullerenes (or fullerene-like structures) had been predicted to occur in flames, as well as the reasonable idea that during the formation of fullerenes "errors" could occur that might prevent closure of the cage but not further growth, in addition to the general fascination associated with fullerenes, did lend some credibility to Kroto's hypothesis. One of the major causes of the controversy, however, was that the chemical environments in hot, cluster-containing carbon vapor and in a sooting flame are very different, a fact that was probably not appropriately appreciated. The unfortunate term "fullerene soot" for the amorphous carbon formed during the Krätschmer process for fullerene synthesis later added more confusion to this matter, as this material has nothing in common with soot from flames.

Thus, at the end of the 1980s, there were roughly four models for the relationship between fullerenes and soot: soot particles are formed by the faulty growth of fullerenes; fullerenes are formed from soot particles; soot particles and fullerenes are formed simultaneously, side-by-side; both species are formed in the flame, but are not interconnected in any way. This situation could only be remedied by well-designed experiments.

7. Fullerenes in Flames

7.1. Properties and Behavior of Fullerenes in Flames

While the maxima of all PAHs are found within the oxidation zone—they are shifted to larger distances from the burner with increasing molecular mass because the larger ones are formed from the smaller ones—fullerenes are formed later. They reach their maximum concentrations at the end of the oxidation zone or just behind it. The exact location depends on the fuel and the combustion conditions. Figure 13 shows an example of one PAH and one fullerene profile to demonstrate the characteristic concentration profile of the two classes of large molecules. A typical temperature profile is shown as well. While large PAHs show only very small concentrations in the exhaust gas, fullerenes reach a nearly constant level after a small drop behind the maximum. The partial consumption of fullerenes after the maximum is caused by oxidation. The remaining constant concentration indicates that there is no further degradation of the thermally stable fullerenes in the range of 2100–1800 K.

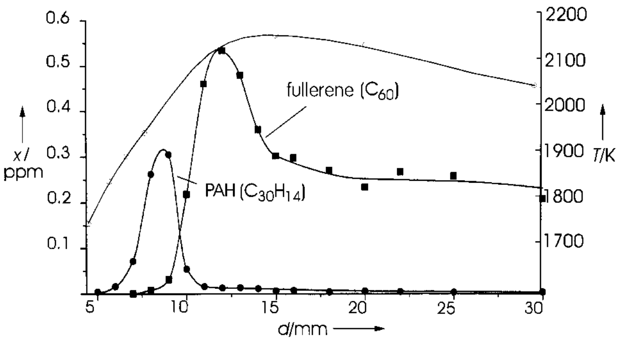


Figure 13. Temperature profile ○ and mole fractions ●, ■ of a PAH ($C_{30}H_{14}$) and a fullerene (C_{60}) in a benzene/O_2 flame.

Roth and co-workers have studied the thermal decay of C_{60} and its reaction with O_2 behind shock waves.[49] This study leads to the conclusion that the oxidation of C_{60} with the remaining oxygen in the flame at temperatures of greater than 2000 K occurs on a time scale comparable to the other flame processes. Thermal degradation becomes significant only at temperatures above 2400 K.

The multitude of formed fullerenes can be gleaned from a mass spectrum of the positively charged fullerene flame ions from an acetylene flame (Figure 14). Above C_{100}^+, the mass spectrum is quasi-continuous. Signals up to C_{650}^+ can be distinguished, albeit at decreasing intensity. The steady intensity development for very large fullerenes indicates that they are empty cages as well, not multiple-layer molecules (onion structure). If this were the case, one would expect discontinuities in the intensity development, for example, at the beginning of a new layer.

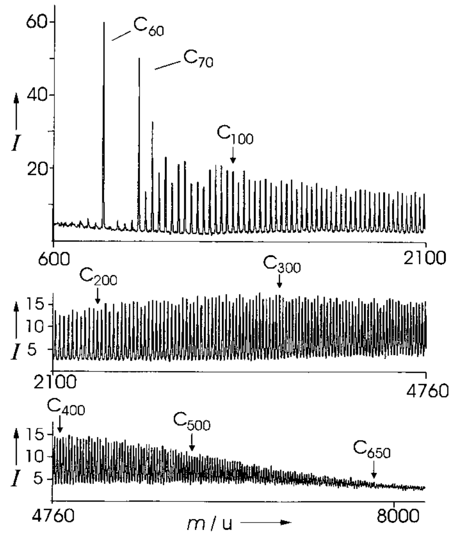


Figure 14. Mass spectrum of positive fullerene flame ions in a sooting acetylene/O_2-flame.

Recently, larger fullerenes up to C_{96} have been extracted from the soot of low-pressure benzene flames, separated by HPLC, and isolated.[50] The obtained amounts of C_{60}:C_{70}:C_{76}:C_{78}:C_{84} corresponded to 100:100:4:3:6, while those of C_{84}:C_{86}:C_{90}:C_{92}:C_{94}:C_{96} followed a ratio of 100:0.5:5:0.5:1.25:1.

Fullerenes smaller than C_{60} are a peculiarity. They occur primarily in flames of aromatic fuels, but also during the combustion of butadiene. Figure 15 shows a mass spectrum of the positively charged ions of these particles in a benzene flame. It has thus far not been possible to isolate fullerenes smaller than C_{60} from flames or to detect them on line as neutral species with multiphoton ionization mass spectrometry. This method, however, is not very sensitive to fullerenes.

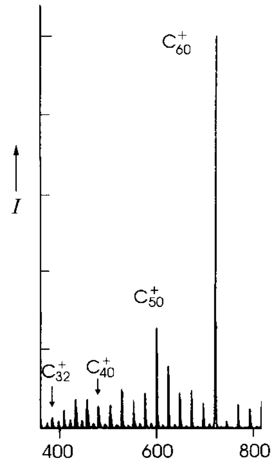


Figure 15. Mass spectrum of fullerene flame ions C_{32}^{+} up to C_{66}^{+} in a benzene/O_2 flame. The very small signals between those of the fullerenes stem from residues of large PAH^+ ions.

The small fullerenes can be found as positively and negatively charged flame ions.

From all that is known about the relationship between charged and their corresponding neutral species in flames, it must be assumed that fullerenes smaller than C_{60} do actually exist in flames as neutral species. Apparently the sensitivity and separation capabilities of the currently employed on-line techniques are insufficient to detect these species. Their occurrence in ionized form indicates that they possess exceptionally high electron affinities and low ionization potentials. This makes them detectable, in contrast to their uncharged counterparts, which probably only exist in very small concentrations relative to C_{60} and C_{70}. All these small fullerene ions must exhibit adjacent five-membered rings, those smaller than C_{50} even triples of five-membered rings. The reason that they have not been found during the extraction of soot could be their very low concentrations or their instability in the condensed phase. It is also possible that ionized and neutral small fullerenes exhibit different structures. It has only recently been observed that, in flames, very large odd-numbered PAHs preferable occur as radicals.

In flames, small fullerenes readily add one or more H atoms even at high temperatures. This reduces the stress on the cage.[8] They are not precursors of C_{60}, C_{70}, and the larger fullerenes. In general, it has been found that fullerenes—in contrast to PAHs—do not grow by adding smaller hydrocarbons. The delayed formation of very large fullerenes, relative to C_{60} and C_{70}, has different reasons, which will be discussed together with their mechanism of formation.

A further peculiarity is the formation of "odd-numbered" fullerenes, which occur in low concentrations together with normal fullerenes.[30c] They always carry at least one, sometimes two H atoms. Their structure is unknown, as it has thus far been impossible to isolate them. They have only been detected on-line in their ionized form. It is likely that the additional C atom is not integrated into the cage structure but exists as a CH or CH_2 bridge on the outside of the cage, where it is particularly sensitive to oxidative attack. Odd-numbered fullerenes are highly unstable and are quickly consumed in a zone where the concentration of even-numbered fullerenes decreases only partially.

7.2. Fullerene Precursors

The discovery of fullerene precursors was enabled by the fortunate fact that their detection in the form of negatively charged ions is very sensitive, while the large majority of PAHs in the corresponding mass range does not form negatively charged ions at all. Therefore, there are no overlaps in the mass spectrum stemming from PAHs that occur in the corresponding flame zone with much higher concentrations. These overlaps do occur, however, in the mass spectra of positively charged flame ions and neutral molecules.

Figure 16 depicts a mass spectrum of negatively charged flame ions from a flame zone in which fullerenes are formed. The mass range spans from about C_{44} to C_{60}.[51] Based on their intensity, the groups of mass signals arise from $C_{60}H_x^- \approx C_{50}H_x^- > C_{2n}H_x^- > C_{2n+1}H_x^-$, where x varies from 0 to about 7 for the even-numbered species and from 1 to about 7 for the odd-numbered ones. The upper part of Figure 16 shows the development of the group $C_{50}H_x^-$ over 2 mm in the flame. At 6 mm the mass spectrum consists of weak signals at all masses, which do not differ much in intensity. From these, signal groupings grow, in which the signals belonging to hydrogen-containing ions decrease again and finally disappear completely (with the exception of the odd-numbered $C_{2n+1}H^-$). The formation and consumption of H-containing species occurs in distinct intervals. The most H-rich species can be detected first. Corresponding profiles of the signal intensities of the $C_{50}H_x^-$ group, after ^{13}C deconvulution, are shown as an example in Figure 17. Finally, only the hydrogen-free even-numbered fullerenes remain. Other fullerenes show the same

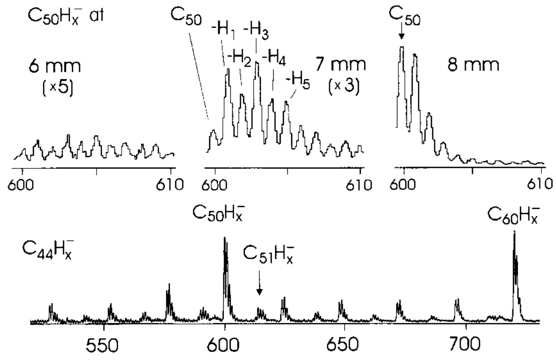


Figure 16. Section of a mass spectrum of negative ions of even-numbered ($C_{2n}H_x$) and odd-numbered ($C_{2n+1}H_x$) fullerene precursors. Top: mass spectrum of $C_{50}H_x$ upon increasing distance from the burner; bottom: $C_{44}H_x^-$ to $C_{60}H_x^-$ at a burner distance of 7 mm.

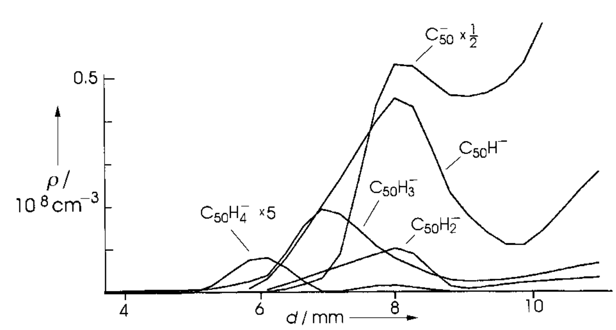


Figure 17. Profiles of the number density ρ of negative ions of hydrogen-containing fullerene precursors in a benzene/O_2 flame, plotted against the distance d from the burner.

behavior. The signal groupings that first appear above the background of weak peaks in the mass spectrum belong to $C_{60}H_x^-$ and $C_{70}H_x^-$.

Another important observation with respect to fullerene precursors is the presence in the mass spectrum of a continuous background of negative ions in the mass range of less than 500 to far beyond 2×10^3 u. This can be seen clearly in the fullerene mass spectrum in Figure 18.[51] This is a previously unknown observation during on-line analysis of flames with molecular beam mass spectrometry. Whenever fullerenes and/or soot are formed, the continuous mass spectrum is observed as an intermediate.

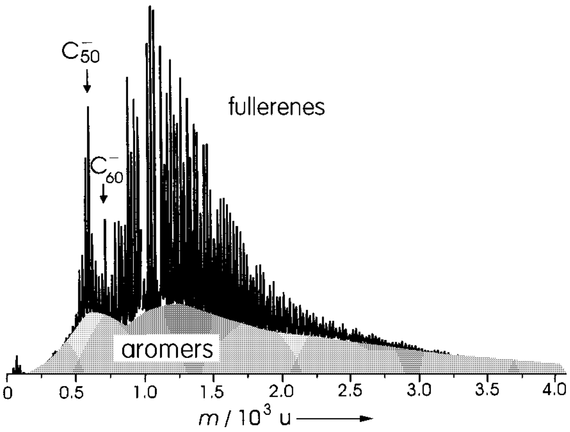


Figure 18. Mass spectrum of negative fullerene flame ions showing a continuous background of the negatively charged aromers (=*aro*matic oligo*mers*) in a benzene/O_2 flame.

A plot of, for example, the integrated signal intensity over the mass range 720–750 u in the form of an intensity profile together with that of a PAH ion and C_{60}^+ (Figure 19) shows that the components that cause the background are very likely the precursors of fullerenes. We have termed this thus far unknown class of large particles in fuel-rich flames "aromers" (=*aro*matic oligo*mers*). This is the fifth of the classes that were discussed in Section 2.

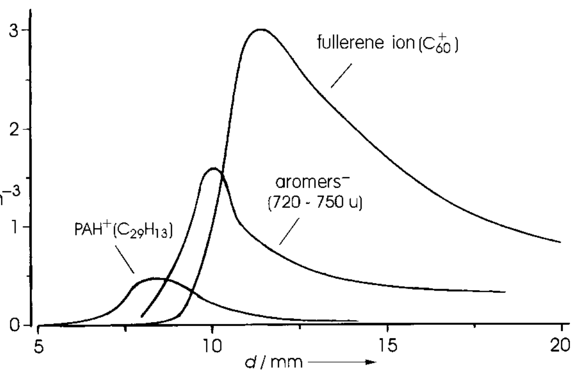


Figure 19. The intensity profile of the aromers in the range 720–750 u (intensity arbitrarily scaled) fits between the number density ρ profiles for large PAHs and C_{60}.

7.3. Probable Properties of Aromers

Aromers are characterized by the following properties:

- They form negatively charged ions particularly well in the flame, but can be photoionized externally to yield positively charged ions.
- They yield a continuous mass spectrum.
- Their mass distribution changes within a flame as well as with different fuels and combustion conditions.
- One can deduce their properties also from the type of molecules and ions, which show a discrete mass spectrum in the same mass range.

Aromers, or at least a substantial fraction of them, are very reactive particles, which behave in the mass spectrometer like 'metastable ions', long known from electron impact ionization.[52] In contrast to these ions, which gain their internal energy from the ionization process, the big flame ions obtain their energy from simple internal thermal excitations in the flame.

When they no longer undergo collisions (molecular beam, ionic beam in MS), only intramolecular processes can occur, which are, at least in part, degradation reactions that change the mass of the particle. This exactly corresponds to the unimolecular degradation after thermal activation according to the Lindemann mechanism, the only difference being that it is possible to observe the effects of the *isolated* degradation step, namely the continuous mass spectrum. From the fact that, relative to the other large molecules (fullerenes, large PAHs), this mass spectrum is barely shifted in its mass range, it can be concluded that during unimolecular decay only small neutral particles are cleaved off (e.g., H_2), but that the aromer as a whole does not break up into two roughly equal halves. The observation that aromers are best detected as negatively charged ions indicates that they possess many five-membered rings and probably also adjacent five-membered rings in their structures. This increases their electron affinity. The well-known, very stable cyclopentadienyl anion is a good example for this effect.

The aromers occur initially together with stable particles, which yield a negatively charged flame ion mass spectrum in which every mass is observed at approximately equal intensities. This indicates the presence of C–H compounds that are quite hydrogen rich relative to the PAHs discussed so far. It is, therefore, assumed that the same is true for the aromers. The H-rich PAH ions discussed in section 5.1, on the other hand, yield discrete mass peaks, which means that they do not lose hydrogen in the mass spectrometer, even though among them there are some very large specimens with many internal degrees of freedom. This implies that aromers cannot be planar like PAHs, but must possess structures that facilitate the loss of H_2. This leads to their role as precursors for fullerenes.

7.4. Reactions of Aromers

These observations fit best to particles that are initially formed by the agglomeration of two large arenes. This agglomeration must occur in such a fashion that the arene parts are not in the same plane, but can approach each other over a large range of their peripheries. A primary formation of the C–C single bond as in biaryls would be conceivable. An attractive interaction without localized bonding is also possible, such as between a large aromatic π radical and a large PAH molecule to give a type of radical π complex. Van-der-Waals forces have also been suggested for the agglomeration of two large PAH molecules.[53] In any case, the intermediate would be relatively H rich, as it would exhibit a noncondensed structure, in contrast to the planar PAHs. These edifices are envisioned to be flexible enough so that the aromatic parts can get sufficiently close to each other to lose their hydrogen in the form of H_2—not from two adjacent, but from two facing H atoms. Thus the original parts can be rapidly linked by C–C single bonds in a zipperlike fashion. The term "aromers" encompasses all possible structures from the initial edifice of two agglomerated PAHs (whether of the biaryl or the π complex type) to the nearly closed, but still H-containing cages. It is very possible that large radicals are among these species. Considering that PAH radicals have been detected in relatively large concentrations, this is actually quite likely.

It would now be possible to consider topological models of a large number of possibilities for the multiple peripheral linkages of two PAHs stemming from the large mass range that occurs in flames. Instead, however, only a few readily visualizable results as well as one surprising finding will be discussed. In terms of fullerene formation, the complete closure of the structure using only five and six-membered rings must be the goal. The simplest, but rare case, is that of two PAHs with the same number of H-carrying peripheral C atoms, but without four-carbon coves. Figure 20 depicts this situation using two ovalene molecules ($C_{32}H_{14}$) as the example. Only the peripheries of both PAHs are shown with their outer C atoms (solid lines, H atoms omitted). They are shown in a geometrically distorted fashion, but topologically correct, so that upon bond formation (dashed lines) between two facing C atoms, one can readily envision which types of polygons are formed.

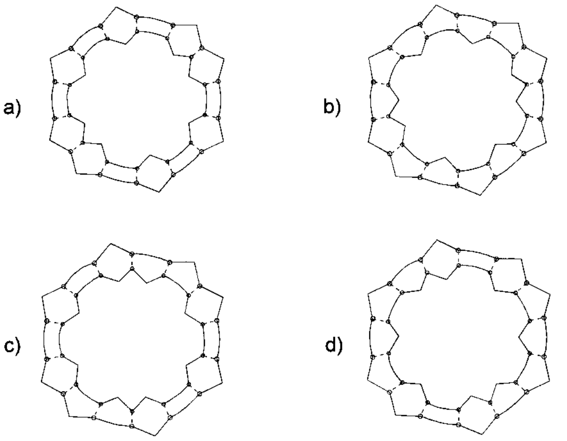


Figure 20. Topological considerations: connecting the peripheral H-carrying C atoms of two PAHs, in this example ovalene $C_{32}H_{14}$, results in several different polygons. In case (b), the twelve pentagons necessary for the closure of the fullerene cage are formed. (See text for explanation.)

In the first case (Figure 20a), six four-membered and eight six-membered rings are obtained. If one periphery is twisted with respect to the other until the next linkage situation is reached, two six-membered rings and twelve five-membered rings are formed (b). Further twisting leads, after link-up, to four four-membered, four five-membered, and six six-membered rings (c). The combination of two four-membered, eight five-membered, and four six-membered rings exists as well (d). Further rotations of either one PAH part leads to a repetition of these combinations. Case (b) would result in a fullerene, albeit a distorted one. This happens here in four out of fourteen situations (29%). As hydrocarbons incorporating four-membered rings have so far never been observed in flames, these cases can be excluded, unless one considers intramolecular rearrangements of a four-membered and an adjacent six-membered ring to form two five-membered rings.

This simple example demonstrates that not all linkages lead to twelve five-membered rings. The probability, however, increases with the size of two thus structured PAHs (PAHs on the solid lines in Figures 8 and 10). For two $C_{54}H_{18}$ molecules, it is 66%. The surprising result (less so for mathematicians familiar with Euler's work) is: If only five and six-membered rings are formed during a complete link-up, there will always be twelve five-membered rings, regardless of the size of the PAHs, that is, their number of peripheral C atoms.

7.5. Fullerene Formation

The initially unimolecular loss of hydrogen from the aromers occurs so rapidly that the concentration of the intermediates involved remain too small for detection. Therefore the C–H diagram shows no "band" in the direction of the fullerenes. Considering the multitude of different PAHs, the probability is not particularly large that just the right pair of aromers meet to have an exact fit after closure of the "zipper". It is much more common that two PAHs combine that have different numbers of H-carrying peripheral C atoms. Even when this number is the same in both molecules, but one (or both) of the PAHs contains coves, the "zipper" does not close smoothly. This implies that before the final formation of actual fullerenes, there ought to be particles with a few remaining H atoms that are lost more slowly, so that the lifetime of these species is long enough to enable detection. These are now the direct precursors, $C_{50}H_x$, $C_{60}H_x$, $C_{70}H_x$, and many more, which can be analyzed as negatively charged ions. Their loss of the remaining hydrogen atoms can also be studied. According to this model, the final closure of the cage usually also requires the "removal" of excess C atoms, either pyrolytically or by oxidative means. If the number of peripheral C atoms in the two original PAHs is too different, a closure of the cage in this manner becomes unlikely.

This hypothesis of fullerene formation also raises the question of how five-membered rings within a system of six-membered rings can be rapidly shifted intramolecularly so that five-membered rings that initially were connected are finally isolated from each other ("isolated pentagon rule" of fullerenes). They cannot remain at the site of the zipper, as the strain in the closing structure would become too high. Scott, Zimmermann, and co-workers have performed insightful experiments to resolve this question.[54, 55]

This mechanism in itself is not limited to any number of C atoms, odd or even, in the finally formed fullerene molecule. This is in agreement with the initial observation of all fullerene groups (see Figure 16). Calculations with H-containing fullerenes indicate that it is likely that at least the even-numbered detectable fullerene precursors already exhibit the closed cage structure and that the H atoms are not located on adjacent C atoms.[56] Otherwise, the H atoms would be lost too rapidly and the species could not be detected in the mass spectrometer. Without already closed cage structures, it would also be difficult to explain why it is that $C_{60}H_x$ and $C_{70}H_x$ appear as the first detectable fullerene precursors.

There are aromers formed from smaller and from larger PAHs; larger ones can lead to fullerenes containing more C atoms. This mechanism explains why there are large fullerenes that are formed somewhat later. The PAHs that subsequently form the aromers grow with time, while complete fullerenes do not. It is noteworthy, that the largest detectable fullerenes ($\approx C_{650}$) contain about twice as many C atoms as the largest PAHs that can be distinguished ($\approx C_{320}H_x$). This supports the model of their formation from aromers.

There are still many questions regarding the formation as well as the detection of smaller fullerenes, C_{30} to C_{58}. Because of the large ring strains involved, a zipper mechanism is difficult to conceive for smaller aromers. As the fullerenes that are smaller or equal to C_{50}, in particular, are formed *after* C_{60} and C_{70} and are favored by an increase in flame temperature, one working hypothesis has them formed by oxidative degradation of larger fullerenes. The effect of O_2 on solid or dissolved C_{60} and C_{70} in the range of 200 to 500 °C has been the subject of several studies,[57, 58, 59] but the results (intercalation of oxygen, possible linkage of fullerene molecules by oxygen, formation of carbon-rich C–O polymers, degradation to the point of complete destruction of the fullerene structure) cannot be applied to oxidation reactions in flames. Low quantities of epoxides such as $C_{60}O$ and $C_{70}O$ can be detected together with fullerenes isolated from soot as well,[60] while they are not found in situ analyses in flames. Anderson and co-workers have shown that the ion–molecule reaction $O^+ + C_{60}$ leads to smaller fullerene fragments and to species like $C_{59}O^+$,[61] but the impact energies used in these studies were significantly larger than the thermal energy available in flames. It is, therefore, necessary to await the results of studies of thermal elementary reactions, such as $C_{60} + O_2$, O, and OH, at high temperatures before it can be determined whether, apart from possibly CO, smaller fullerenes are formed as well. The very exothermic oxidative degradation reactions of the larger fullerenes could overcome the energy barriers stemming from the cage strain. The absolute lower limit for this type of degradation should be around C_{32} to C_{30}.

As the entire process occurs in a flame zone in which every particle is still exposed to some extent to oxidative or thermal degradation, the principal "survival of the fittest" also plays a role. This certainly includes the even-numbered fullerenes and in particular C_{60} and C_{70}.

7.6. The Acetylene Mechanism of Fullerene Formation

The formation of fullerenes in flames via aromers is not the only mechanism under discussion. Howard and co-workers have proposed a different pathway and have tested it with model calculations.[62] It also considers PAHs to be precursors of fullerenes, but it particularly stresses the importance of those PAHs that are derived from corannulene ($C_{20}H_{10}$). Parallel to the formation of large planar PAHs others are formed as well, also by acetylene binding, which not only contain a few five-membered rings along their periphery, but also in the interior, in between the six-membered rings. The continued incorporation of five-membered rings while simultaneously more and more H-poor hydrocarbons are formed leads to a bending of the forming PAHs that increases until the cage is closed with the formation of the twelfth five-membered ring. Intermediates in this mechanism are $C_{20}H_{10}$, $C_{30}H_{10}$, $C_{40}H_{10}$, and $C_{50}H_{10}$ on the way to C_{60} and additionally $C_{60}H_{10}$ on the way to C_{70}. A further crucial difference to the aromer mechanism is that the successive growth leading to C_{60} and C_{70} is primarily assumed to occur through *bimolecular* reactions, namely the binding of acetylene with essentially concomitant loss of H_2. Even though model calculations show that fullerene formation is possible this way in the short time intervals available in flames, it has so far not been possible to detect the H-poor intermediates. This mechanism predicts a particularly strong formation of C_{60} and C_{70} in rich acetylene flames. This has also not been confirmed by observations.

8. Soot Formation versus Fullerene Formation

The same continuous mass spectra that are found in benzene flames during fullerene formation are observed in acetylene flames shortly before soot formation. It is, therefore, reasonable to assume that aromers do not only participate in fullerene formation, but also act as precursors to soot particles. Indeed, why should every half-closed aromer form a closed cage structure under all circumstances? From the growth of PAHs it is known that all particles with open edges can grow by binding acetylene, for example. An experiment is noteworthy in which large particles in the interior and at the edge of a flat benzene/oxygen flame were examined. The result is shown in Figure 21. In the relatively hot interior there are fullerenes, but no soot. Soot forms only in the less-hot edge zone, where only very few fullerenes are found.[63]

In combination with the observation that acetylene-rich flames contain few fullerenes, but a lot of soot, as long as the temperature is not too high, this temperature effect, together with the model of aromers as precursors for both types of large particles, yields the following overall picture that is summarized in Figure 22. High temperature environments containing relatively low concentrations of small unsaturated hydrocarbons, favor *unimolecular* reactions of aromers. This includes the "zipper reactions" leading to fullerenes, but also general degradation reactions, so that it is conceivable that very large particles are not formed at all. If the temperature is lower and small growth components (such as acetylene) are

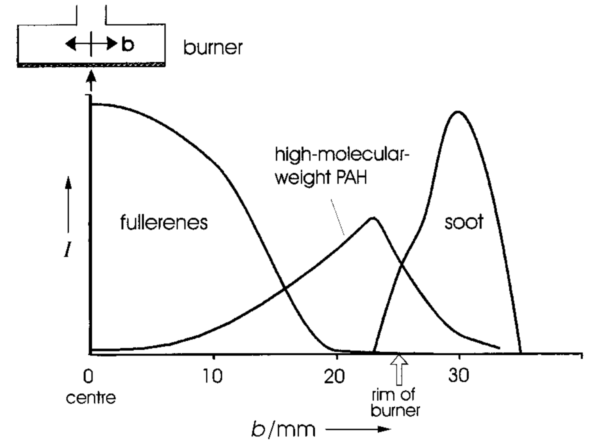


Figure 21. Cross section profile of large particles in a sooting benzene/O_2 flame at a burner distance of $d = 20$ mm plotted against the distance b from the middle of the flame. Within this flame, fullerenes are formed in the hot interior, while soot forms at the less hot edges. (Intensity I in arbitrary units.)

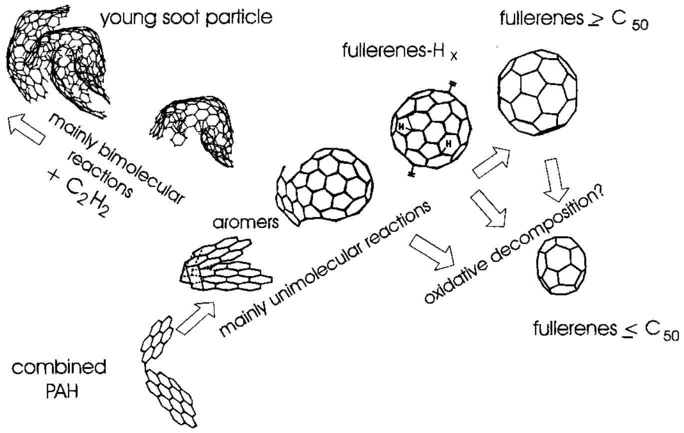


Figure 22. Paths to fullerenes and soot via aromers. While the formation of fullerenes from aromers occurs mainly through unimolecular reactions at high temperatures, soot particles are formed in bimolecular addition reactions of small unsaturated hydrocarbons (e.g., C_2H_2) at lower temperatures. Small fullerenes could possibly be formed in very small quantities by the oxidative degradation of larger fullerenes.

present in higher concentrations, *bimolecular* reactions of aromers dominate, which do not provide enough time for cage closure but instead rapidly lead to small soot particles. It is important to note that these reactions occur with particles that contain aromatic partial structures, but are no longer overall planar. In the case of normal PAHs, these alternatives would either lead only to degradation or to growth up to the stability limit for planar particles.

In the case of soot formation, continuous mass spectra are found somewhat below about 2×10^3 u, and then develop into the mass distribution of larger particles.[30d] If the formation of the corresponding aromers requires that two large PAHs must first combine, this leads to an average PAH mass of nearly 1×10^3 u, corresponding to about 70 to 90 C atoms. According to Figure 10, these have a C/H ratio between 3.2 and 3.8, not very different from the C/H ratio found for very young soot, which was about 3. The formation of the first soot particles is, therefore, not a simple continuation of PAH growth, as the mass of the largest PAHs, about 4.5×10^3 u, is significantly larger than that of the smallest soot particles. The C/H ratio of the largest PAHs, about 6.5, is also significantly larger.

9. Conclusion

The controversy, whether initial soot particles in flames are formed by a fullerene mechanism or vice versa, can be resolved by the currently available experimental studies that indicate that both species have common precursors. We have termed these precursor particles aromers. It has thus far only been possible to draw indirect conclusions with respect to their properties. They possess aromatic partial structures and are rich in hydrogen. Hence, they cannot resemble the intermediates in the Kroto icospiral mechanism. Once these aromers have formed, the conditions in the flame determine the further course of the reaction. Fuel-rich combustion under normal pressures (relatively high density of small unsaturated hydrocarbons) but with air instead of pure oxygen (lower temperature) favors the formation of soot. Special flames, however, allow the adjustment of conditions (low pressure, a specific temperature range, aromatic fuel) in such a manner that the large particles formed in small amounts are exclusively fullerenes, formed by essentially unimolecular reactions from aromer precursors, while no soot is formed.

As there are, however, other models of fullerene formation in flames as well, further specific experiments will be necessary before the mechanisms of formation and degradation of fullerenes can be finally clarified. It does, however, appear to be certain that reactions as well as intermediates are different in flames from those in the fullerene generator and the laser evaporation of graphite.[64, 65] The species found under those conditions, medium-sized chains, rings, and (assumably) multiple-ring systems made of pure carbon, could not be detected in flames.[66] While C_2 is found in fuel-rich flames, its concentration is not sufficient to model fullerene formation.[67] The concentration of negative ions C_{2n+1}^-, $n = 1-5$, is also much too low, just several 10^6 cm^{-3}, in order for these species to initiate fullerene formation.[6, 14]

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[1] P. Gerhardt, S. Löffler, K.-H. Homann, *Chem. Phys. Lett.* **1987**, *137*, 306.

[2] a) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162; b) R. F. Curl, *Angew. Chem.* **1997**, *109*, 1636;

Angew. Chem. Int. Ed. Engl. **1997**, *36*, 1566; H. W. Kroto, *Angew. Chem.* **1997**, *109*, 1648; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1578; R. E. Smalley, Angew. *Chem*. **1997**, *109*, 1666; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1594.
[3] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354.
[4] M. Hausmann, K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 651.
[5] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.
[6] P. Gerhardt, K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1086, 1521.
[7] P. Gerhardt, K.-H. Homann, *J. Phys. Chem.* **1990**, *94*, 5381.
[8] J. Ahrens, M. Bachmann, T. Baum, R. Kovacs, P. Weilmünster, K.-H. Homann, *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 133.
[9] P. Weilmünster, A. Keller, K.-H. Homann, *Combust. Flame* **1998**, in press.
[10] a) H. Bockhorn, F. Fetting, H. W. Wenz, *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1067; b) T. G. Benish, A. L. Lafleur, K. Taghizadeh, J. B. Howard, *Symp. Int. Combust. Proc.* **1996**, *26*, 2319.
[11] R. Kovacs, *Dissertation*, Technische Hochschule Darmstadt, **1996**.
[12] D. B. Olson, H. F. Calcote, *Symp. Int. Combust. Proc.* **1981**, *18*, 453.
[13] S. Löffler, K.-H. Homann, *Symp. Int. Combust. Proc.* **1990**, *23*, 355.
[14] T. Baum, S. Löffler, P. Löffler, P. Weilmünster, K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 841.
[15] S. C. O'Brien, J. R. Heath, R. F. Curl, R. E. Smalley, *J. Chem. Phys.* **1988**, *88*, 220.
[16] J. B. Howard, K. Das Chowdhury, *Nature* **1994**, *370*, 603.
[17] "Soot Formation in Combustion": K.-H. Homann in *Nachr. Akad. Wissensch. Göttingen*, *II. Math.-Phsik. Klasse*, *No. 3* (Eds.: H. Jander, H. G. Wagner), Vandenhoeck & Ruprecht, Göttingen, **1989**, pp. 101–107.
[18] K.-H. Homann, H. Gg. Wagner, *Symp. Int. Combust. Proc.* **1967**, *11*, 371.
[19] K. G. Payne, F. J. Weinberg, *Proc. R. Soc. London A* **1959**, *250*, 316.
[20] K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 738.
[21] a) J. Lahaye, G. Prado in *Particulate Carbon Formation During Combustion* (Eds.: D. C. Siegla, G. W. Smith), Plenum, New York, **1981**, pp. 33–55; b) L. L. Ban, P. C. Vegvari, W. M. Hess, *Norelco Reporter* **1973**, *20*, 1.
[22] J. Lahaye, G. Prado, *Chemistry and Physics of Carbon*, *Vol. XIV* (Eds.: P. L. Walker, P. A. Thrower), Dekker, **1978**, pp. 167–294.
[23] B. S. Haynes, H. G. Wagner, *Prog. Energy Combust. Sci.* **1982**, *7*, 229.
[24] K.-H. Homann, H. G. Wagner, *Ber. Bunsen-Ges. Phys. Chem.* **1965**, *69*, 20.
[25] J. C. Biordi, C. P. Lazzara, J. F. Papp, *Combust. Flame* **1974**, *23*, 73.
[26] K. Guthier, P. Hebgen, K.-H. Homann, J. Hofmann, G. Zimmermann, *Liebigs Ann.* **1995**, 637.
[27] J. D. Bittner, J. B. Howard, *Symp. Int. Combust. Proc.* **1981**, *18*, 1105.
[28] see for example P. R. Westmoreland, J. B. Howard, J. P. Longwell, *Symp. Int. Combust. Proc.* **1986**, *21*, 773.
[29] M. Bachmann, W. Wiese, K.-H. Homann, *Symp. Int. Combust. Proc.* **1994**, *25*, 635.
[30] a) M. Hausmann, K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 853; b) J. Ahrens, R. Kovacs, E. A. Shafranovsky, K.-H. Homann, *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 265; c) P. Gerhardt, S. Löffler, K.-H. Homann, *Symp. Int. Combust. Proc.* **1988**, *22*, 395; d) Ref. [6]; e) R. Wegert, W. Wiese, K.-H. Homann, *Combust. Flame* **1993**, *95*, 61.
[31] J. Griesheimer, *Dissertation*, Technische Hochschule Darmstadt, **1997**.
[32] S. E. Stein, A. Fahr, *J. Phys. Chem.* **1985**, *89*, 3714.
[33] M. Bachmann, J. Griesheimer, K.-H. Homann, *Chem. Phys. Lett.* **1994**, *223*, 506.
[34] K. Brezinsky, G. T. Linters, T. A. Litzinger, I. Glassman, *Symp. Int. Combust. Proc.* **1986**, *21*, 833.
[35] C. R. Shaddix, K. Brezinsky, I. Glassman, *Symp. Int. Combust. Proc.* **1992**, *24*, 683.
[36] P. Frank, J. Herzler, T. Just, C. Wahl, *Symp. Int. Combust. Proc.* **1994**, *25*, 833.
[37] H. Frerichs, M. Tappe, H. G. Wagner, *Symp. Int. Combust. Proc.* **1990**, *23*, 21.
[38] K. Lorenz, R. Zellner, *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 629.
[39] W. Müller-Markgraf, J. Troe, *Symp. Int. Combust. Proc.* **1986**, *21*, 815.
[40] Q. L. Zhang, S. C. O'Brien, J. R. Heath, Y. Lin, C. F. Curl, H. W. Kroto, R. E. Smalley, *J. Phys. Chem.* **1986**, *90*, 525.
[41] H. W. Kroto, *Science* **1988**, *242*, 1139.
[42] J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur, M. E. Johnson, *Nature* **1991**, *352*, 139.
[43] U. Hofmann, D. Wilm, *Z. Elektrochem.* **1936**, *42*, 504.
[44] a) S. C. Graham, J. B. Homer, J. L. J. Rosenfeld, *Proc. R. Soc. London A* **1975**, *344*, 259; b) H. Jinno, S. Fukutani, A. Takaya, *Symp. Int. Combust. Proc.* **1976**, *16*, 709.
[45] K. Rummel, P. O. Veh, *Arch. Eisenhüttenwes.* **1941**, *14*, 489.
[46] L. B. Ebert, *Science* **1990**, *247*, 1468.
[47] M. Frenklach, L. B. Ebert, *J. Phys. Chem.* **1988**, *92*, 561.
[48] R. M. Baum, *Chem. Eng. News* **1990**, *February 5*, 30.
[49] S. von Gersum, P. Roth, *Symp. Int. Combust. Proc.* **1994**, *25*, 661.
[50] H. Richter, K. Taghizadeh, W. J. Grieco, A. L. Lafleur, J. B. Howard, *J. Phys. Chem. B* **1997**, *101*, 1556.
[51] M. Bachmann, *Dissertation*, Technische Hochschule Darmstadt, **1997**.
[52] J. A. Hipple, E. U. Condon, *Phys. Rev.* **1945**, *68*, 54.
[53] J. H. Miller, K. C. Smyth, W. G. Mallard, *Symp. Int. Combust. Proc.* **1984**, *20*, 1139.
[54] a) L. T. Scott, N. H. Roelofs, *J. Am. Chem. Soc.* **1987**, *109*, 5461; b) L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291; c) L. T. Scott, A. Necula, *Tetrahedron Lett.* **1997**, *38*, 1877.
[55] a) S. Hagen, U. Nuechter, M. Nuechter, G. Zimmermann, *Polycyclic Aromat. Compd.* **1995**, *4*, 209; b) S. Hagen, H. Christoph, G. Zimmermann, *Tetrahedron* **1995**, *51*, 6961.
[56] C. J. Pope, J. B. Howard, Massachusetts Institute of Technology, personal communication.
[57] R. Assink, J. E. Schirber, D. A. Loy, B. Morosin, G. A. Carlson, *J. Mater. Res.* **1992**, *7*, 2136.
[58] J. A. Nisha, V. Sridharan, J. Janaki, Y. Hariharan, V. S. Sastry, C. S. Sundar, T. S. Radhakrishnan, *J. Phys. Chem.* **1996**, *100*, 4503.
[59] M. Wohlers, H. Werner, D. Herein, T. Schedel-Niedrig, A. Bauer, R. Schlögl, *Synth. Met.* **1996**, *77*, 299.
[60] J. B. Howard, *Symp. Int. Combust. Proc.* **1992**, *24*, 933.
[61] J. F. Christian, Z. Wan, S. L. Anderson, *Chem. Phys. Lett.* **1992**, *199*, 373.
[62] C. J. Pope, J. A. Marr, J. B. Howard, *J. Phys. Chem.* **1993**, *97*, 11001.
[63] M. Bachmann, W. Wiese, K.-H. Homann, *Combust. Flame* **1995**, *101*, 548.
[64] R. F. Curl, *Philos. Trans. R. Soc. London A* **1993**, *343*, 19.
[65] H. Schwarz, *Angew. Chem.* **1993**, *105*, 1475; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1412.
[66] G. von Helden, M.-T. Hsu, N. Gotts, M. T. Bowers, *J. Phys. Chem.* **1993**, *97*, 8182.
[67] M. Hausmann, P. Hebgen, K.-H. Homann, *Symp. Int. Combust. Proc.* **1992**, *24*, 793.