

The Chemistry of Precursor Soot and Its Ramifications

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Abstract

Precursor soot was generated in a flow tube reactor by acetylene pyrolysis. The reactor effluent was diluted by a factor of 100 with nitrogen immediately upon exiting the reactor. The particle and gas phase species were analyzed in real time with an ion trap mass spectrometer. Comparison of the particle and gas phase ion distributions reveal great differences and demonstrate the richness of the chemistry of precursor soot. The precursor soot particles show clear evidence of high-mass (>1000 Da) polymeric species when they are examined in real time. The effluent was collected on a filter and extracted with methylene chloride. The extracted material was then loaded on 5- μm particles that are used as packing material in LC columns. Upon evaporation of the solvent, the particles were sampled into our aerosol mass spectrometer to provide an off-line comparison to our real-time work. The off-line mass spectra reveal a chemical alteration of the polymeric structure in the greater than 1000 Da mass distribution indicating that the polymeric species are metastable. Ramifications of these observations will be discussed.

Introduction

For the past fifty years and more, theories of soot formation have been based on the chemistry of the gas phase. The most probable reason for this approach is that most hydrocarbon precursors are gases at the temperatures where soot is formed. However, there is a form of hydrocarbon that does exist in the condensed phase under these high temperature conditions called precursor soot. Unfortunately, the very existence of this material has been shrouded in controversy and has resulted in many curious ideas for the process of soot formation.

The controversy stems from the composition of precursor soot. In general, free polycyclic aromatic hydrocarbons (PAHs) as defined by chromatographic and mass spectrometric analysis make up a large percentage of the mass of collected precursor soot samples. The controversy arises from the physical properties of the free PAHs; their boiling points are much lower than the temperatures where precursor soot is formed. Consequently, it has been concluded by many that these species must be condensing during the sampling process when they are removed from the high temperature environment.

Evidence of precursor soot in flames was observed and reported by Parker and Wolfhard [1] in 1950. Definitive evidence for the existence of precursor soot was demonstrated by the carbon black industry in 1956 [2]. They observed a white mist (micron-sized particles) develop in their furnace. Sampling and chemical analysis of the white mist showed it to be an oil of PAHs. Further heating of the white mist produced soot. Their work proved that a high-temperature stable form of liquid hydrocarbon (precursor soot) could be produced by fuel pyrolysis.

More recently, our group showed that micron-sized droplets of precursor soot are formed in atmospheric pressure diffusion flames of pure acetylene [3]. In a companion study, we showed that fullerenes are produced directly in the particle phase during the carbonization of the precursor soot in the same flame [4]. During the publication of this work, we noticed that the PAH distributions observed in our real-time mass spectra were truncated ending at approximately 400 Da.

Remarkably, the PAH distributions found in the gas phase of flames were quite different. The PAH distribution from a relatively low sooting methane diffusion flame truncated at approximately 500 Da [5], whereas the PAH distribution from highly sooting flames, such as acetylene [6], benzene [7], and ethylene-naphthalene [8] do not truncate. They keep going well past 1000 Da. The vast difference in the PAH distributions of the gas and particle phases suggested that a great deal of chemistry was occurring in the precursor soot particle in the flame.

It was subsequently recognized that none of the studies to date provides simultaneous real-time measurements of both gas phase and particle phase species. Moreover, it was clear that these experiments had to be carried out under very well defined conditions. For these reasons, pyrolysis of pure acetylene in a flow tube reactor was the chosen method for producing precursor soot for simultaneous measurement of the gas and particle phase species. These real-time experiments were undertaken with the expressed mission of trying to understand and observe the chemistry occurring in and producing precursor soot.

Experimental

The experimental data shown here are only a part of a larger program for understanding the chemistry of precursor soot. Experiments have also been performed at higher temperatures and by a variety of techniques.

Pure acetylene at atmospheric pressure was passed through a 3.85-mm ID 45-cm long quartz tube reactor at a constant temperature of 700 and 800 °C in two separate experiments. The flow through the reactor was laminar at a 40-ml/min flow rate. Immediately, upon exiting the reactor, the effluent was rapidly diluted one hundred fold with a 4-l/min flow of pure room temperature N₂. The diluted effluent was sampled directly into our ion trap based aerosol mass spectrometer. The configuration of this instrument has been described in detail elsewhere [3].

Particle mass spectra were obtained by ablating each individual particle in real time as it passed through the ion trap with a focused pulse from a 308 nm excimer laser (~1 J/cm²). Gas phase mass spectra of the diluted effluent were obtained with the 308-nm laser whenever the laser "missed" the particle. The composition of the gas phase was checked by deliberately mistiming the laser to miss the particles as they passed through the trap. The composition of the gas phase was also examined by electron impact (EI) ionization with an ion collection time of 500 ms. The laser and electron impact mass spectra were comparable with the EI spectra showing subtle differences primarily in the degree of hydrogenation.

The diluted effluent was collected on hydrophobic polyvinylidene fluoride membrane filters (Millipore, 0.22 μm pore size) for further off-line analysis. The effluent was extracted from the filter with methylene chloride. The extractant was analyzed by several techniques. GCMS was used to identify the low mass components (< 300 Da). Laser desorption/ionization mass spectrometry (LDMS) was used to evaluate the high mass components (> 300 Da). The extracted effluent was also deposited on C18 coated 5- μm silica beads by solvent evaporation. These beads are standard packing for liquid chromatography columns. The beads were analyzed individually with our aerosol mass spectrometer by sprinkling them over the inlet thus yielding a direct comparison between real-time and off-line particle analysis.

Results

The pyrolysis of acetylene at 700 $^{\circ}\text{C}$ yielded no black particulate matter in the effluent. After extraction with methylene chloride, the filter returned to its original white color. No solid matter was suspended in the extractant. Black particulate matter was found in the extract and on the filter of the effluent collected from pyrolysis at 800 $^{\circ}\text{C}$.

The average of 494 individual particle mass spectra sampled from the one hundred fold diluted effluent of the 700 $^{\circ}\text{C}$ pyrolysis of acetylene is shown in Figure 1 (a). This average contains both hits and misses; therefore, it is an average of both the gas and particle phase spectra. In another experiment, the laser was deliberately mistimed to miss the incoming particles so that only gas phase species were ionized. Figure 1 (b) shows the average gas phase spectrum from 501 laser shots.

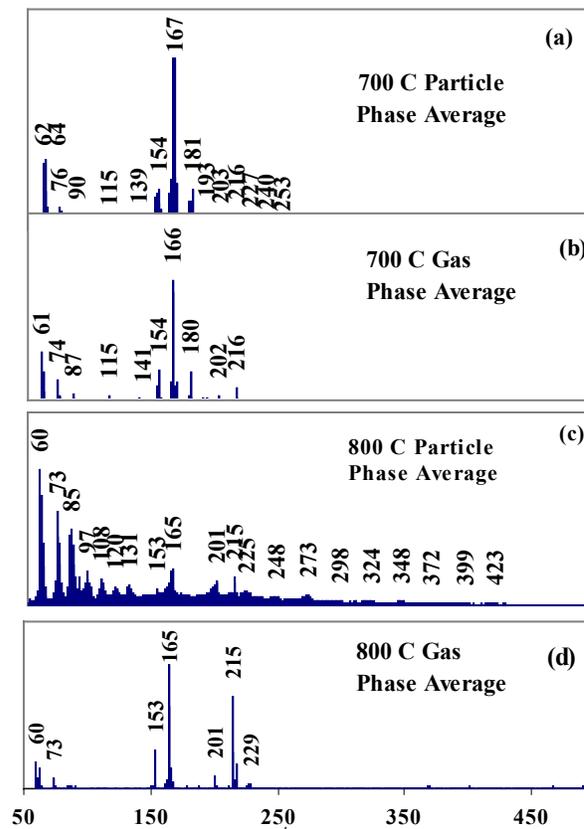


Figure 1. Low mass gas and particle spectra

Comparison of the gas phase spectra with the particle spectral average in Figure 1 (a) reveals remarkable similarity in the overall shape of the distribution; however, there are two understated differences. There is a noticeable local broadening of the PAH mass lines. This broadening was observed before [3] and was attributed to hydrogen exchange between the PAHs. It is a condensed phase phenomenon. There is also a one mass unit shift in the PAH distribution

between the gas and particle phases. In order for the sampling- or dilution-induced condensation to produce the our observed particle phase spectra, there would have to be a mechanism to provide the extra hydrogen that causes the mass shift to maintain the conservation of mass. Since, we could think of no reasonable mechanism based on physical condensation, we maintain the mass shift is proof that the particles were created in the reactor not during dilution.

Further and more obvious proof that the precursor soot particles that we see with our technique are forming in the reactor as opposed to the dilution step is revealed in our 800 °C data. Figure 1 (c) shows the average of 550 particle mass spectra at the 800 °C temperature. Figure 1 (d) shows the average of 329 spectra from gas phase laser ionization at this same temperature. The distributions from the gas and particle phases are completely different. Since the particle phase species originated in the gas phase, a tremendous amount of chemical rearrangement must occur to convert the gas phase distribution into the particle phase distribution. This condensed phase chemistry could only occur under the high temperature conditions of the reactor and not during a sampling induced condensation process..

Because ion traps inherently have a limited dynamic range, the high mass species were investigated in a separate experiment. (The y-axis intensity scales have been removed in all the figures so that inappropriate intensity comparisons are not made for this reason as well.) Figure 2 (a) shows the average of 357 individual particle spectra scanned from 350 to 1750 Da. On the left hand side of the spectrum, the tail end of the individual PAH distribution is observed. As the PAH distribution fades, a distribution of peaks evenly spaced by 24 Da appear. The most intense peak in this distribution

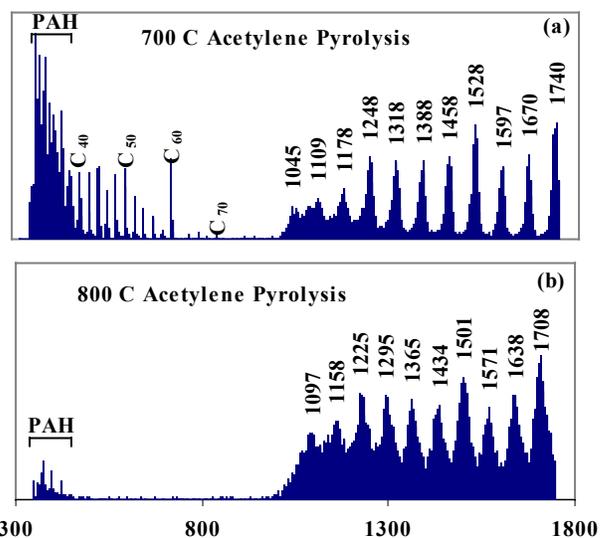


Figure 2. High mass particle spectra

appears at 720 Da. This is indicative of fullerene formation. No ions were observed in this mass range when the laser missed the particles or when employing electron impact ionization. This evidence suggests that fullerenes are formed in or on the surface of the precursor soot particles. More importantly, these fullerenes are formed without the production of carbonaceous soot.

Above 1000 Da in this spectrum, a polymer-like ion distribution was observed with a regular spacing of approximately C_5H_n , where n is near 10. The average local distribution about each of the "polymer-like" ion units is Gaussian and broad indicating rapid hydrogen exchange.

The average of the 800 °C high mass spectra is shown in Figure 2(b). Here we note that the fullerene distribution has disappeared suggesting fullerene production is in competition with mature soot production. The distribution of the polymer-like high mass ions has changed as well with the increase in pyrolysis temperature. The C_5H_n peak separation has not changed yet the distribution has shifted and the polymer-like peaks have a broader hydrogen distribution. At either temperature, no high mass species were found to exist in the gas phase using laser and electron impact ionization.

These polymer-like high mass distributions have never been reported for any pyrolytic or combustion process by any off-line technique (ours included) because these ionic species are apparently metastable. Laser desorption ionization (LDI) of the effluent extracted from the filter and deposited on a stainless steel probe yields no high mass ion intensity (<1000 Da). (The LDI spectra will be presented in a future publication.) When that same extractant is deposited on 5- μ m silica beads with a C-18 coating and the solvent evaporated, the mass spectra taken from these beads yields ion intensity above

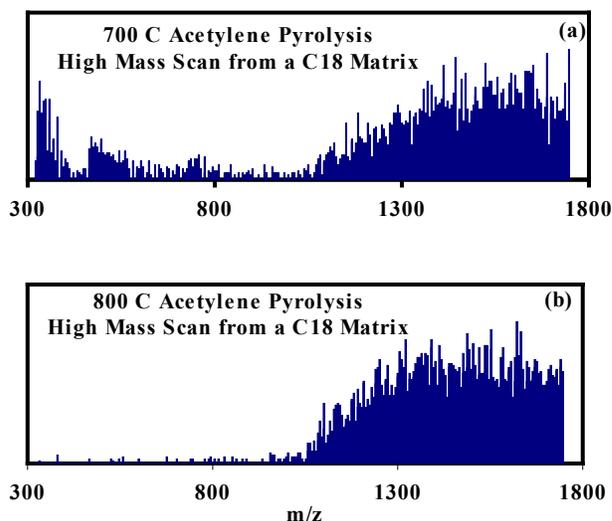


Figure 3. Averaged off-line particle spectra of the filter extract deposited on C-18 coated silica beads

550 Da but the polymer-like peak distribution becomes scrambled (see Figure 3 (a) and (b)). This technique permits a direct comparison between off-line and real time experiments using the same particle mass spectrometer. The validation of this off-line technique will be presented in a future publication.

Discussion

Comparison of the gas and particle phase mass spectra (Figure 1) yields unequivocal proof that the particles that we observe are not produced by rampant physical condensation of the PAHs and other hydrocarbons during the dilution and sampling processes. Particle production by rampant physical condensation would yield the same overall ion distributions in the gas and particle phases without a mass shift. Because the particles must condense from of the gas phase species, an enormous amount of chemistry must occur to convert the 800 °C gas phase distribution into the particle phase distribution. The only place that this chemistry could occur is in the particle phase inside the reactor. The same conclusion can be reach for the 700 °C data.

This result leaves us with a dilemma. All of the species observed in the particle phase mass spectral data have significant vapor pressures at their respective reactor temperatures. The boiling points of the vast majority of chemical species observed in the extractant (the composition was checked by GCMS) have boiling points hundreds of degrees below the reactor temperatures. There is no evidence of chemical bonds in between the species according to our particle mass spectral data and our GCMS data. How can these species condense at high temperatures without showing evidence of chemical bond formation?

To answer this question, one must first accept that particles containing some form of hydrocarbon can form during high temperature pyrolysis. This has been definitively proven by members of the carbon black industry who observed through a window with their eyes a white mist formed inside their furnace prior to the formation of carbon black [2]. Subsequent sampling and analysis of the mist showed it to be composed of the same types of hydrocarbons that are typically found in precursor soot. The fact that the mist was white means that the particles are in the micron size range and suggests a phenomenal mass growth rate.

Now consider the state of a condensed phase of hydrocarbons at 700-800 °C. At these temperatures, the condensed phase hydrocarbons rapidly exchange hydrogen in a concerted reaction that forms two free radicals for each H atom exchanged. We have seen evidence of the hydrogen exchange in our real-time particle mass spectra while off-line mass spectrometric techniques do not. Moreover, free radicals are extremely reactive. This is especially true in the condensed phase. This means that the hydrocarbon radicals are continuously reacting with their neighbors and rearranging their own chemical structures. Under high temperature conditions a condensed phase of hydrocarbons (i.e., precursor soot particles) should not be thought of as an agglomeration of individual molecules, rather the precursor particle should be thought of as a giant macromolecule or "radical plasma" whose internal structure is in a state of constant flux.

The growth rate of precursor particles depends on the concentration of free radicals. TEM evidence suggests that the remarkable growth rate of soot particles can be attributed to the precursor particles. This suggests that the concentration of free radicals in precursor soot is relatively large. Any hydrocarbon that collides with the particle would have a high probability of forming a chemical bond with the particle. The hydrocarbon would instantaneously be absorbed into the macromolecular structure by the continuous rearrangement. This means that the chemical species found in the cooled precursor soot are products of the decomposition of the "macromolecular" hot precursor soot particles that results when the thermally induced hydrogen exchange ceases.

Let us now consider the cooling process that occurs when the hydrocarbon particles are suddenly removed from the high temperature environment. First the hydrogen exchange process ceases and the radicals are eliminated by radical-radical recombination. Radical elimination is fast and occurs without regard for overall thermodynamic stability. Standard rules for preserving stability, such as aromaticity, yield to the expedience of removing the radicals from the matrix. This is the origin of the high mass polymer-like species observed in Figure 2. It is also the reason for the metastable nature of these high mass species. With time and interaction with the environment, the metastable species convert into their most thermodynamically stable configuration, an oil of PAHs and other hydrocarbons.

Another demonstration of the chemistry occurring in precursor soot is the presence of the "polymeric" species that only exists above 1000 Da. The large mass gap between the PAHs and the polymeric species suggests that the stability of the polymer-like species is size related. Observation of the polymeric distribution shows the width of the polymer peaks decreases with increasing size. We suggest that the size related threshold results from the formation of a three-dimensional structure. In other words, below 1000 Da there is a tendency for forming planar structures that are not as stable.

Because PAHs and fullerenes are the only other species present in the mass spectra, it is logical to conclude that the products of the decomposition of the polymeric species are primarily PAHs. This suggestion is supported by LDI experiments on the same filter extract that shows a laser power dependence on the PAH distribution. These data will also be presented in a future publication.

Why is the condensed species PAH distribution measured from sooting flames different from the gas phase distribution? The precursor matrix has a lot of excess hydrogen in it. A medium that can rapidly exchange hydrogen can also store it. Preservation of the hydrogen means smaller PAHs in the measured particle phase distribution than in the gas phase distribution. It is also the reason that the observed composition of the tar fraction in soot is composed of alkyl and aromatic species and not just big aromatic molecules, as one would expect since alkyl species are not nearly as stable as aromatic molecules at high temperatures. The alkyl species are created with the excess hydrogen during the temperature-induced transformation of precursor soot. Reducing the hydrogen concentration in the precursor matrix increases the size of the PAHs in the particle phase distribution. When the hydrogen concentration becomes too small, carbonization occurs. When the hydrogen is lost so are the radicals and the soot mass growth process decreases dramatically. This is precisely what was observed in our real-time measurements of the carbonization process [3] and in the TEM data.

The final evidence of the wealth of chemistry occurring in the precursor soot is the presence of the fullerenes. No fullerenes are observed in the gas phase by either laser or electron impact ionization. A large number of reactions are required to convert the hot hydrogen-rich precursor material into fullerenes. Both mature soot and fullerenes are produced from the same process, namely carbon skeletal rearrangement with concurrent dehydrogenation. Fullerenes are more stable and ordered than mature soot. The presence of the hydrogen facilitates the carbon rearrangement process—fewer dangling bonds. If the hydrogen is removed too rapidly, the carbon skeletal structure does not have sufficient time to rearrange itself into the most thermodynamically stable structure (fullerenes). The consequence of rapid removal of hydrogen from the precursor soot medium is the production of mature soot. This is the reason that the fullerenes are not observed in the 800 °C pyrolysis particle spectra.

Our findings lead to sweeping ramifications with regard to soot formation theory. First, rampant physical condensation of PAHs and other hydrocarbons in the flame or during the dilution and sampling process is not supported by the experimental results. High temperatures and radicals are required for rapid mass growth.

The presence of the metastable high mass species is strong evidence of the macromolecular nature of precursor soot. This macromolecular nature is the reason for the high temperature stability of the precursor soot. Upon cooling it transforms into the oil of PAHs and other hydrocarbons that we observe. This means that there are two completely different mechanisms for the production of the PAHs whereas only the gas phase production mechanism has previously been considered. Consequently, the lack of predictability of the current soot models is not surprising. Better experiments and theories including precursor soot formation are needed for comprehensive combustion models.

The low mass PAHs that manifest during the transition to lower temperatures make up a considerable amount of the precursor soot mass. These PAHs will evaporate if they are left at elevated temperatures (too low for efficient hydrogen exchange) for too long. They also evaporate in vacuum during TEM and mass spectrometric measurements. Future experiments on precursor soot need to be carefully considered. Consequently, all vacuum-based measurements on soot and condensed species need to be redone with cryogenic samples. Another reason that the TEM measurements need to be redone is that the precursor soot material is a viscous oil of PAHs and other hydrocarbons. Diffusion of nanometer spherules in viscous oil is significant on the time scale of the TEM experiments. Diffusion causes the images of the mature soot particles in the precursor soot matrix to appear non-spherical. It also causes the surrounding precursor soot medium to appear more optically dense as the nascent mature soot particles grow. Finally, assuming that sampling-

induced condensation is the reason for the PAH-containing material surrounding the mature soot particles is not correct.

Conclusions

Simultaneous measurements of gas and particle phase species have been made in real-time for the pyrolysis of acetylene. The gas and particle phase PAH distributions are very different. They indicate that a tremendous amount of chemistry is occurring in the condensed phase that has previously been ignored. The concept of rapid mass growth by physical condensation of gas phase species has been refuted. Polymer-like high mass species have been observed and were determined to be metastable by comparison with off-line techniques. Their presence and the high temperature stability of the precursor soot was explained to result from radical reactions that occur in the condense phase due to thermally induced hydrogen exchange. Precursor soot provides a second mechanism for the production of PAHs that needs to be taken into account for any realistic soot formation model. The sweeping ramifications of these measurements were discussed.

Acknowledgement

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