Proof of the Transient Nature of Precursor Soot

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Introduction

For more than fifty years, scientists and engineers have attempted to model and understand the chemistry of mature soot formation through the chemistry of the gas phase without success as evidenced by the lack of any model with predictive capabilities. Until now, the chemistry of the condensed phase has been essentially ignored.

Yet the existence of a condensed phase other than mature soot has been know to exist in flames and other pyrolytic environments since 1950 when Parker and Wolfhard[1] observed the presence of precursor soot in flames. In 1956, the existence of precursor soot (a high temperature stable form of hydrocarbon) was conclusively proven by the observance of a white mist that formed in huge furnaces used for the industrial production of carbon black.[2] When the temperature of the furnace was raised, the mist became carbon black (mature soot).

Though this evidence was conclusive, the presence of precursor soot in combustion environments has been ignored and even denied by experts with the suggestion that sampling-induced condensation or dilution is the reason for observations of precursor soot. We have searched the literature for refutation of the existence of precursor soot but nothing was found. However, our search of the literature showed that the existence of precursor soot has resurfaced on a fairly regular basis over the last thirty years, first by the shock tube work of Graham and coworkers in the 1970's,[3] then in the 1980's by Miki et al.[4] during flow tube pyrolysis of fuels. Later Dobbins and others[5] demonstrated its presence in flames by TEM and thermophoretic sampling in the late 80s and early 90s. Subsequently, D'Alessio et al.[6] rediscovered precursor soot in flames using absorption, fluorescence and scattering measurements and finally our group directly observed the carbonization process using real-time aerosol mass spectrometry from an acetylene flame.[7]

Given the nature of the pyrolysis experiments performed by Swietzer and Heller in 1956 and the vehemence of the experts that suggest precursor soot is the result of sampling and dilution artifacts or only exists in minute amounts, we thought that it would be a good idea to establish hard physical evidence of the existence of precursor soot as well as develop a theory for its presence in combustion environments.

Furthermore, we noticed that there is a big difference between the mass spectra of the gas phase[8] and condensed species[9] of rich flames. We also realized that there have been no simultaneous measurements of the gas and condensed phases for an accurate comparison. Consequently, we decided to perform these measurements on fuel pyrolyzed in a flow tube reactor to maintain simplicity and reproducibility. For further comparison, we also decided to perform direct comparisons of our real-time measurements with off-line techniques.

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 preformed at higher temperatures and by a variety of techniques, including electron impact ionization mass spectrometry, GCMS and laser desorption ionization mass spectrometry (LDMS).

Acetylene at atmospheric pressure with a small impurity of acetone 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. Miki et al.[4] obtained similar results during flow tube pyrolysis of a variety of hydrocarbons; therefore we suggest that the small acetone impurity did not significantly perturb our results. 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 N_2. 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.[7]

Briefly, the diluted aerosol was sampled through a differentially pumped inlet that creates a collimated particle beam that passes through the center of the ion trap. On the way to the ion trap the particles were aerodynamically sized by light scattering based time-of-flight. When the detected particles reached the center of the ion trap, a focused pulse from an excimer laser (~ 1 J/cm^2) ablated and ionized the individual particles. The ablated ions were then mass analyzed by standard ion trap techniques. For each detected particle, we obtained the aerodynamic size and a mass spectrum.

Particle mass spectra were obtained by ablating each individual particle in real time as it passed through the ion trap. 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 and Discussion

Figure 1 shows the averaged mass spectra of the gas phase, the particle phase, and the filter collected effluent deposited on 5-µm C-18 coated silica beads to give a direct comparison of the gas phase species with the real-time and off-line analysis of the condensed species. Comparison of the gas (a) and real-time particle phase (b) averaged spectra reveal similar ion intensity patterns yet there are subtle and profound differences. There is an obvious broadening of the local mass distributions that is due to hydrogen exchange.[7] This is a condensed phase phenomenon. There is also a positive mass shift between the gas and condensed phases. Since atomic or molecular hydrogen does not condense at room temperature, the particles that we are observing have to be created in the reactor and not during the dilution step. The differences in the gas and particle phase compositions become more pronounced at higher temperatures.

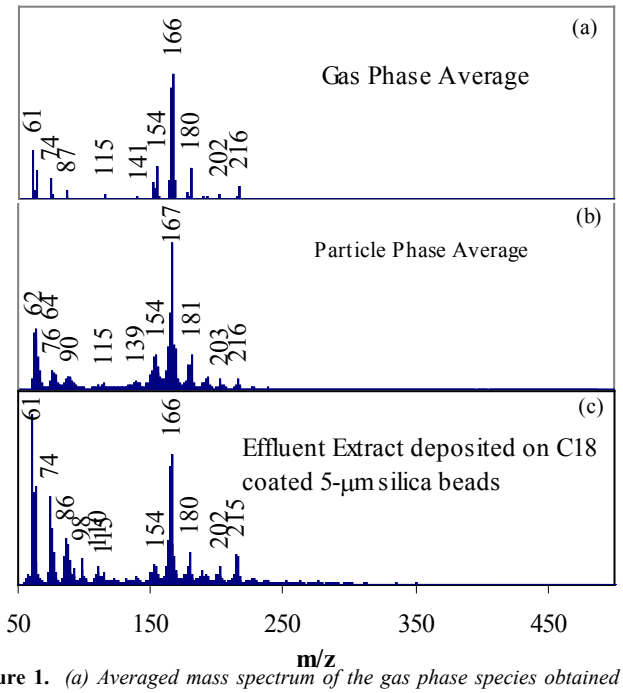

Figure 1. *(a) Averaged mass spectrum of the gas phase species obtained by mistiming the laser. (b) Averaged particle mass spectrum. (c) Averaged mass spectrum of the filter collected effluent deposited on 5-µm C18-coated silica beads and dropped into the particle mass spectrometer inlet for direct comparison of real-time and off-line measurements.*

Comparison of the real-time and off-line mass spectra shows that the particles that we sample in real-time have the same composition as the filter collected effluent with excess hydrogen. This means that we have a valid method for comparing real-time and off-line measurements. To demonstrate the volatility of the PAHs in the precursor soot at room temperature, we performed standard LDMS on the extractant deposited on a stainless steel probe. The solvent was allowed to evaporate and the before the probe was placed in vacuum. Figure 2 shows the averaged mass spectrum of the extractant. Comparison of Figures 1 (c) and 2 reveal that large quantities of the condensed species evaporate in vacuum before the measurements are made. This comparison clearly demonstrates the need for freezing the precursor soot samples before they are exposed to vacuum. This is particularly relevant to those people that do TEM and LMMS measurements on precursor soot.

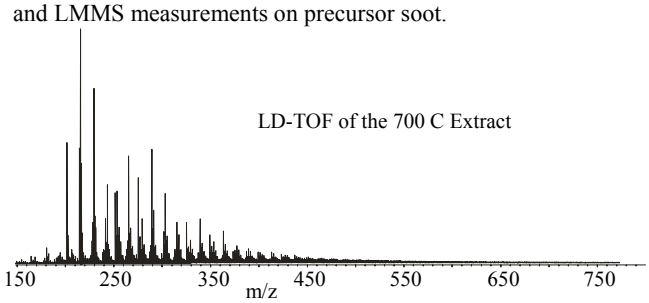

Figure 2. *Averaged laser desorption time-of-flight mass spectrum of the filter-collected extract deposited on a stainless steel probe.*

Ion traps are known to have a limited dynamic range. Consequently, high mass species have to be measured in separate experiments. Figure 3 (a) presents the averaged real-time mass spectrum of the high mass of the high mass species in the particles and Figure 3 (b) presents the averaged off-line mass spectrum of the high mass species from the filter extract deposited on the C-18 coated

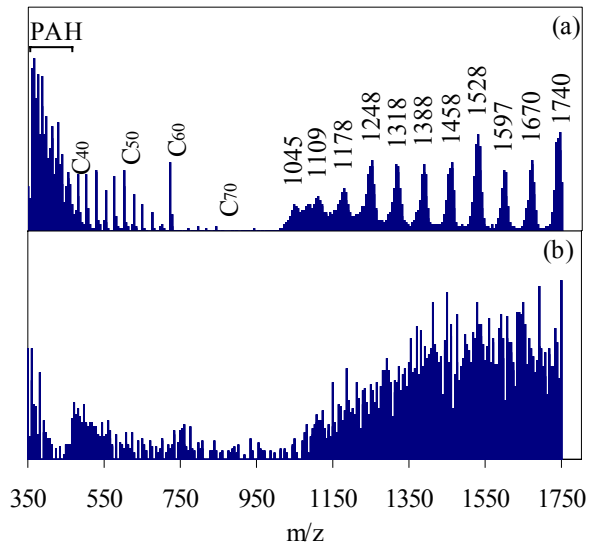

Figure 3. *(a) Averaged real-time high mass spectrum of the particle phase. (b) Averaged off-line high mass spectrum of the extract.*

particles. In the real-time mass spectrum (a), we observe the tail end of the PAH distribution on the left. Out of that distribution, we see a distribution of fullerenes emerge marked by a 24 u peak separation and the highest intensity at 720 u (C_{60}). At higher mass, we see an ion distribution that looks similar to that seen in the mass spectra of polymers. This distribution is marked by a peak separation of approximately 70 u (C_5H_{10}). This distribution has never been seen before. Comparison to the off-line mass spectra reveals scrambling of the high mass species and loss of the fullerene masses (fullerenes are not soluble in the C-18 matrix). The off-line LDMS spectrum from the same extract in Figure 2 was taken weeks later and reveals only digitizer noise above 1000 u. Species in the high mass region of the spectrum do not evaporate in vacuum. Consequently, our observed high mass species must be metastable. Since the only other species in the mass spectra are low mass PAHs and other small hydrocarbons, it seems likely that these high mass species have decomposed into the species observed in the low mass region of the spectrum. Our data proves the transient nature of precursor soot and suggests that the theory and experiments on soot formation need to be completely reexamined.

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