

MOLECULAR CHARACTERIZATION OF HYDROCARBONS FROM SOOTS IN LOW TEMPERATURE FLAMES OF BIPHENYL AND ILLINOIS NO 6 COAL

Jerry E. Hunt¹, R. E. Winans¹, N. A. Tomczyk¹, and R. Pugmire²

¹Argonne National Laboratory, Chemistry Division,
9700 S. Cass Ave., Argonne, IL 60439

²Department of Chemical and Fuels Engineering,
University of Utah

Abstract

Soot hydrocarbons were collected from regions in low temperature flames of atmospheric biphenyl and Illinois No. 6 coal. High resolution and API mass spectrometry were used to analyze the solvated soot particles. PAH's were detected in the soot up to a mass of 500 amu. These high mass PAH's varied with the temperature region from which the soots were collected. In particular, liquid chromatography/mass spectrometry highlighted differences between the biphenyl soot and the Illinois No. 6 coal soot. The data show the first molecular steps in soot formation prior to carbonization and large particle formation.

Introduction

One of the environmental hazards of fuel combustion is polycyclic aromatic hydrocarbon and eventually soot emission. Combustion is a very complex, but poorly understood physiochemical process. This is especially true of the (PAH) and soot particle formation mechanisms. Emissions of PAH's from incomplete combustion are of special environmental concern because of the potential carcinogenicity for some of these compounds. A better understanding of the formation mechanisms that are responsible for PAH and soot emissions will lead to better methods to control and, potentially reduce the formation of these compounds and soot in combustion systems. Our goal for this paper is to select model compounds that will provide molecular information on PAH growth including ring size prior to formation of pure carbonaceous soot. In this study the soluble fractions of the soot and soot precursors from temperature specific regions of a fuel rich flame were investigated by liquid chromatography and mass spectrometry.

Experimental

Soot hydrocarbons were collected from regions in low temperature atmospheric flames of biphenyl and Illinois No. 6 coal as the fuels. Fuel rich flat flame burner has been previously described.² The CO hydrogen flame was operated under fuel rich pyrolysis and combustion conditions. This produced a stable flame with temperatures as low as 1100K. This is much lower than can be achieved with a methane flame (1600K). Soot samples were collected on a probe with residence times of 15 to 180 msec. The temperature regions of the biphenyl flame were 1365K through 1470K. The Illinois No. 6 coal encompassed a similar temperature region. The soots were extracted into methylene chloride for analysis.

Mass spectrometry. Gas chromatography/mass spectrometry was a HP 5890 with a DB-35MS column of 0.25 mm i.d. x 30 m length. The products were identified by matching with a mass spectra library and comparison with known retention indices. Ideally every compound should be identified individually using a known standard of that compound, however this is impractical due to the large number of PAH species observed in the combustion.

LC/MS. A HP 1100 HPLC was used in conjunction with a Finnigan LCQ ion trap mass spectrometer in API ionization mode. The column used was a C18 reversed phase with methylene chloride as the mobile phase.

Laser Desorption Mass Spectrometry. A Kratos MALDI III time of flight mass spectrometer was used to measure the mass spectra of the soot extracts. A 337 nm N2 laser was the volatilization and ionization source.

Results and Discussion

We have characterized the extractable soot molecules by mass spectrometry. In Table 1 the characteristic PAH identities from the low temperature (1365K) biphenyl soot are presented. These are the basic molecular precursors to soot formation. It is interesting to note that even at 1365K there is an appreciable amount of unreacted biphenyl. The GC/MS identities were very similar for the higher temperature biphenyl soot. As the temperature increases there is more soot, but less low ring PAH's, such as biphenyl, terphenyl, and so on. At higher temperatures ring opening reactions may occur which result leading to decomposing products observed in the mass spectra, such as C₂H₂ and C₄H₂.

Table 1. PAH identities from GC/MS of biphenyl 1365K soot

Compound	Mass	Formula
biphenyl	154	C ₁₂ H ₁₀
pyrene	202	C ₁₆ H ₁₀
fluoranthene	206	C ₁₆ H ₁₀
methyl-pyrene ?	216	C ₁₇ H ₁₂
methyl-fluoranthene?	216	C ₁₇ H ₁₂
Benzo[ghi]fluoranthene	226	C ₁₈ H ₁₀
benz[a]anthracene	228	C ₁₈ H ₁₂
chrysene	228	C ₁₈ H ₁₂
Triphenylene	228	C ₁₈ H ₁₂
Benzo[c]phenanthrene	228	C ₁₈ H ₁₂
Perylene	252	C ₂₀ H ₁₂
Benzo[a]pyrene	252	C ₂₀ H ₁₂
Benzo[e]acephenanthrylene	252	C ₂₀ H ₁₂
Benzo[ghi]perylene	276	C ₂₂ H ₁₂
Indeno[1,2,3-cd]pyrene	276	C ₂₂ H ₁₂
Dibenzo[def,mno]chrysene	276	C ₂₂ H ₁₂
Quaterphenyl	306	C ₂₄ H ₁₈

The high resolution mass spectral data also shows ion intensity of a number of larger species, which we can assign to C₂₄H₁₄, C₂₄H₁₆, C₂₆H₁₄, C₂₈H₁₆, and C₃₀H₁₈. The latter two species correspond to 7 and 8 condensed ring species. The laser desorption mass spectra show a series of mass peaks from 200 to about 600 amu for the 1365K biphenyl soot. The 1470K biphenyl soot shows a similar mass spectral pattern, but with more high mass species present above 300 amu.

The soot extracts from Illinois No. 6 coal are more complex with many more molecular species than the biphenyl soot at these low temperatures. Most of the soot samples are pre-carbonaceous particles containing abundant PAH species. At higher temperatures the mass range of the PAH species is broadened and aliphatic fragments are found in the mass spectra. Questions remain about the solubility of the soot precursors, particularly, the larger hydrocarbons that may form the beginning of carbonaceous non-PAH containing particles.

The comparison of biphenyl soots at two temperatures is shown in Figure 1. The data from the high resolution mass spectra were simplified by reducing to approximate ring sizes using the exact mass of the ions. The ring size of the 1365K

species peaks near 5 rings, while the higher temperature soot peaks near 6 rings.

The API mass spectrum of the 1365K soot was characterized by an envelope that encompasses a mass range of the 200 to more than 650.

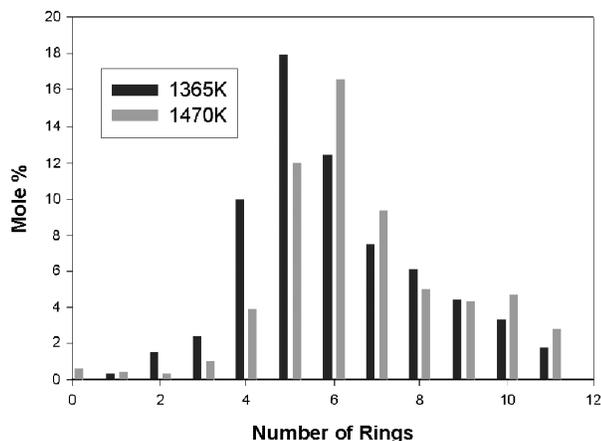


Figure 1. The ring size profile of biphenyl soot from two different temperature regions by HRMS.

Figure 2 shows the UV chromatogram of the soot extract. Several peaks in the UV spectrum can be correlated with species such as pyrene, fluoranthene and larger ring systems. There is also an indication of short aliphatic side groups on these ring systems, especially from the higher temperature species. Overall the LC/MS of the 1365K-biphenyl soot was dominated by an ion series that were separated by 14 amu from 200 to in excess of 600 amu.

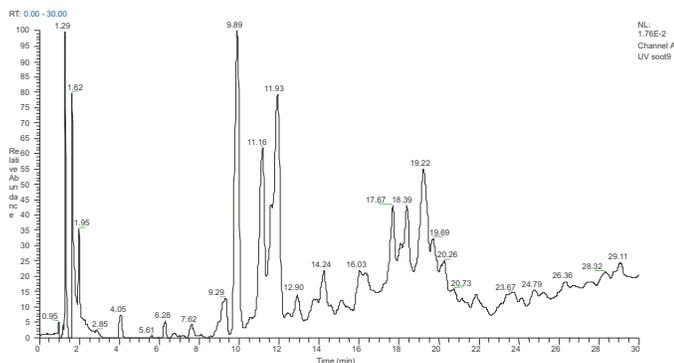


Figure 2. The liquid chromatogram of the methylene chloride extract of the 1365K biphenyl soot. (UV trace at 254 nm)

Conclusions

Our experiments represent the first steps in the soot formation process, that of PAH-containing soots. As the process continues, carbon cluster soots develops. All of the soots show PAH signal intensity above m/z 300. The profiles of the compounds identified changes in accordance with the chemical structure of the original sample. Experiments designed to define gas phase PAH-soot and carbonaceous agglomeration are underway.

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References

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