

BENZYLIC FUNCTIONALITY IN COAL DERIVED ASPHALTENES:
A CALIFORNIUM-252 PLASMA DESORPTION MASS SPECTROMETRY APPROACH*

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INTRODUCTION

The hydroaromatic components embodied in coal molecules strongly influence the thermal behavior of coal in a variety of conversion processes. A body of indirect evidence suggests that effects due to facile bond breaking at benzylic carbon atoms are operative in coal liquefaction (1,2), mesophase development (3,4) and devolatilization behavior (5). In an ongoing study of the structure of coal derived molecules by the technique of Californium-252 Plasma Desorption Mass Spectrometry (CFPDMS), we have found (6) that asphaltenes display positive ion groups of semiregular periodicity in the mass region 150 to 400 amu, and that this pattern is strikingly similar to that of pure hydroaromatic compounds. Such ion groups are also observed (7,8) in Field Ionization Mass Spectrometry (FIMS) spectra of coal derived materials. We wish to present evidence that such ion groups are due to benzylic functionalities and not to families of compound group classes.

The CFPDMS technique involves the use of the nuclide ^{252}Cf , one of whose modes of decay is spontaneous fission. Each fission event ejects two fragments in opposite directions, each with speeds of $c/10$, and energies of 80 to 150 MeV. Interaction of one of these fission fragments with a thin film of organic substrate generates a highly localized hot spot which devolatilizes positive and negative ions. In the CFPDMS experiment (9,10) these ions are accelerated towards a charged grid and into a time of flight (TOF) mass spectrometer. The TOF clock is triggered by the second, simultaneously ejected fission fragment colliding with a start detector and stopped when an organic ion collides with the TOF detector. Acquisition of the TOF data over many events is managed under computer control. Accumulated data is assembled into a mass spectrum by calibration with known common ions.

Native coal asphaltenes can be isolated from low rank coals by dimethylsulfoxide (DMSO) extraction and solvent fractionation. DMSO extraction of the Wilcox seam lignite lithotype yields almost a quarter of the organic matter present. From this extract is isolated the tetrahydrofuran (THF)-soluble, hexane-insoluble fraction, formally a asphaltene-preasphaltene blend. The positive ion CFPDMS spectrum of this sample displays the ion

* Dedicated to Professor Peter Given, honorable recipient of the 1984 Henry H. Storch Award in coal research.

groups described. Such ions are also seen in the spectra of asphaltenes and preasphaltenes from coal liquefaction products, and in the spectra of hydroaromatic compounds. The CFPDMS fragmentation pattern of 1,2,3,6,7,8 hexahdropyrene (HHP) can be interpreted in rational structural terms and illustrates how the mass distribution and configuration of these ion groups is a function of the type of benzylic methylene functionalities present.

EXPERIMENTAL

Wilcox seam lignite (Martin Lake, Texas) is agitated with sonication in ten times its mass of DMSO for twenty four hours, filtered through a ceramic frit, and the solvent removed by evaporation in vacuo. The tar is digested in THF for twenty four hours and the DMSO-soluble, THF-insoluble solid is removed by filtration. Solvent-free THF-soluble matter is digested in excess hexane. Solids are filtered through a ceramic thimble and extracted with hexane in a Soxhlet apparatus for six hours, then with water for twenty four hours, to remove any DMSO. Upon drying, a five percent yield (DAF basis) of asphaltene-preasphaltene blend is obtained in the form of a fine brown powder.

Liquefaction of Herron seam bituminous coal (Illinois No. 6), Pittsburgh seam bituminous coal (West Virginia) and Wilcox seam lignite (Texas) is carried out in tetralin under hydrogen at 400° C. THF-soluble matter is digested in benzene and filtered to obtain preasphaltenes. Benzene-soluble matter is extracted with hexane to yield oil-free asphaltenes.

CFPDMS spectra are taken by methods described previously (9,10).

CFPDMS SPECTRAL RESULTS

The periodic positive ion groups in the mass range 150 to 400 amu are commonly seen in the CFPDMS spectra of coal derived asphaltenes and preasphaltenes. Representative examples are shown in Figure 1. The groups occur with a mass periodicity of from 12.1 to 14.1 amu, and are most apparent in the region from 200 to 350 amu. Mass centroids of these groups are very nearly the same in all samples examined, including the pure hydroaromatic compounds. Average masses of these centroids are listed in Table 2. These masses are very similar to those of analogous FIMS ions obtained from other coal products (7,8). It is significant that these ion groups usually appear at the top of a broad envelope of ions extending from 200 to 500 amu, the high mass downward slope of which is devoid of ion groups. An additional analogy with the FIMS coal spectra is the more intense ion groups below 200 amu. The composite ions could be interpreted as several families of compound group classes of the form $C_n H_{2n-2} O_y$, the populations of which result in apparent mass periodicities of less than fourteen. The CFPDMS spectra of pure hydroaromatic compounds suggests that an alternate explanation must be considered

Figure 2 shows the 150 to 500 amu range of the positive ion CFPDMS spectrum of HHP (MW 208). Fourteen ion groups appear between 152 and 340 amu. The first five groups are large, consisting of the parent ions and its fragments. Higher mass ions are smaller, and from expansions of the spectrum (Figure 2) it is apparent that the ion groups fall at approximately the same masses as the asphaltene ions (Table 2). The parent ion group (200-208 amu) consists of a benzyl cation type ion at 207 amu, its unsaturated analogs at 205 and 203 amu, and the pyrene cation radical at 202 amu. Most probable structures are shown in Table 1. The latter ions are derived by facile dehydrogenation, for which hydroaromatic compounds are well known (2). Ion groups at lower masses correspond to the extrusion of carbon and hydrogen from the skeleton, as methylene, methine or carbon chains. Fragment masses imply that the extrusions are accompanied by rearrangement, dehydrogenation and/or intramolecular recombination to produce ions isomeric with the most probable structures shown in Table 1. The apparent periodicity of these ion groups is nearly the same as that of the asphaltene ion groups. The smaller "postparent" ion groups - eight of them between 221 and 325 amu - appear to be recombinant ions, originating from the attack of fragment ions on the parent molecule, or on other fragments.

DISCUSSION

In a preliminary survey of the CFPDMS fragmentation behavior of coal-like compounds (6) we have screened polynuclear aromatic hydrocarbons, aromatic and aliphatic carboxylic acids, phenols, aryl ethers, monoalkylbenzenes and hydroaromatic compounds. Oxygen containing compounds invariably yield parent ions an order of magnitude more intense than their fragment ions. Hydrocarbons, such as phenyl pentadecane, dibenzanthracene and hexahydropyrene, do not fragment in this manner, but give rise to fragment ions typically half as intense as the parent ions. The periodicity of the fragment ions is rational, but quite different from that seen in electron impact ionization mass spectrometry. For example, the positive ion CFPDMS spectrum of behenic acid exhibits a series of ion groups of periodicity 14 amu (Figure 3), reflecting random cleavage along the alkyl chain (11). 1,2,5,6 Dibenzanthracene displays fragments of periodicity 13 amu (Figure 3) corresponding to successive expulsion of from one to eight methine groups from the parent structure. The fragment periodicity of alkylaromatics (including hydroaromatic compounds) is not so regular, and their intensities are of the same magnitude as the parent ions. This is a result of multiple fragmentation modes available to benzylic functionalities, and the formation of very stable benzyl cation structures, exemplified by the fragment ions of HHP shown in Table 1.

CFPDMS fragmentation resembles that of Pyrolysis-Field Desorption Mass Spectrometry (PFDMS). The PFDMS positive ion groups of German coals (8) fall at the same masses as those shown in Table 2. Schulten attributes some of the principal ions of these groups to several series of compositions C_nH_{2n-z} . An additional similarity between PFDMS and

CFPDMS is the appearance of high molecular weight ions of periodicity 74 amu. We find that monoalkylbenzene compounds, and some coal fractions, show positive CFPDMS ions at $m/z = 948 + 74n$, where n is 0 to 14. Such ions appear to be polymeric tris-fused triphenylene structures formed in the pyrolytic environment in which the ions are devolatilized (6). Ions of these same masses have also been seen in Schulten's study (8).

The coincidence of the masses of the asphaltene ions with those of HHP and other hydroaromatics leads us to conclude that the CFPDMS technique is detecting hydroaromatic and other benzylic functionalities among the disparate coal components. A supporting observation is the presence of smaller recombinant ions in the spectrum of HHP which appear at masses above that of the parent. This is a general feature of the CFPDMS spectra of hydroaromatic compounds. In the asphaltene spectra, individual recombinant ions are not seen. The variety of hydroaromatics in the sample gives rise to a broad envelope of ions, superimposed by the larger fragment ions. The feature is very obvious in the FIMS spectra (12) of coal liquids. The configuration of the individual ion groups contains information reflecting the population of extant hydroaromatic molecules.

Organic CFPDMS ions have been detected up to 1200 amu in many coal derived products, yet the ion groups described in this report do not appear at masses above 600 amu. These ion groups have not been detected in the CFPDMS spectra of hexane-soluble coal products, because many other intense ions interfere. They are definitely absent from the CFPDMS spectra of DMSO-soluble, THF-insoluble fractions. A working hypothesis is that as hydroaromatic components condense into high molecular weight crosslinked molecules during coalification metamorphosis, their benzylic character is lost.

ACKNOWLEDGEMENTS

Support from the Gas Research Institute, the Robert A. Welch Foundation, and the Center for Energy and Mineral Resources is gratefully acknowledged.

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Table 1: Most probable structures of the main positive CFPDMS fragment ions of 1,2,3,6,7,8 Hexahdropyrene, shown in Figure 2

MASS		MASS	
207		179	
205		178	 †
203	 †	176	 †
202	 †	165	 †
191		163	 †
189	 †	152	 †

Table 2: Mean mass centroids of CFPDMS positive ion groups exhibited by asphaltenes and hexahdropyrene in the mass range 150 to 370 amu.

151	224	299
167	237	311
179	250	323
191	263	337
201	275 (irregular)	349
212	284	361

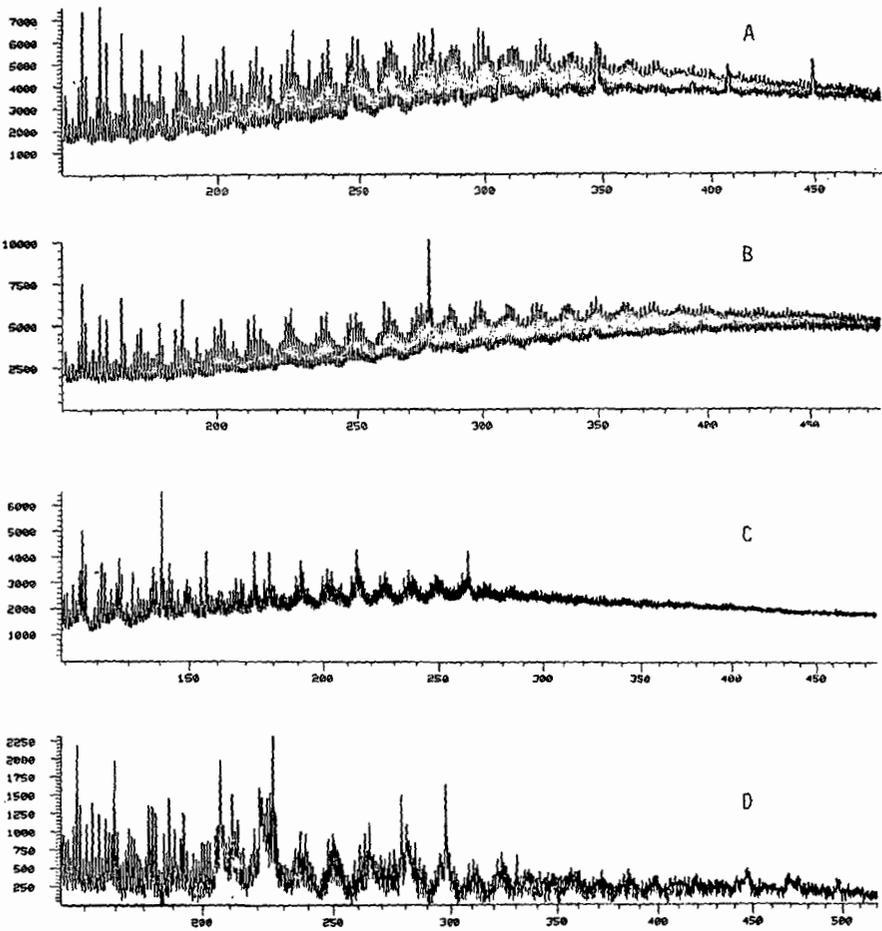


Figure 1: Positive CFPDMS ion groups of Coal derived Asphaltenes in the mass range 150 to 500 amu. A - Illinois No. 6 liquefaction asphaltene, B - Pittsburgh Seam Bituminous Coal liquefaction asphaltene, C - Wilcox Seam Lignite, native asphaltene-pre-asphaltene blend, D - Wilcox Seam Lignite liquefaction preasphaltene.

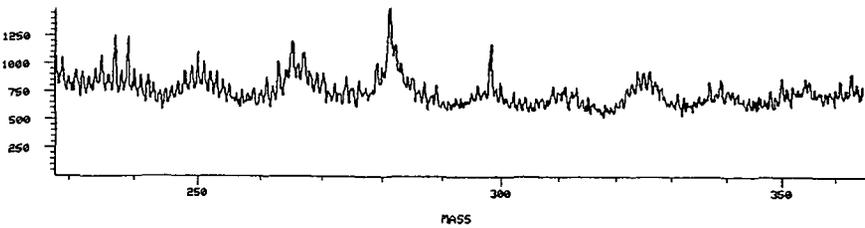
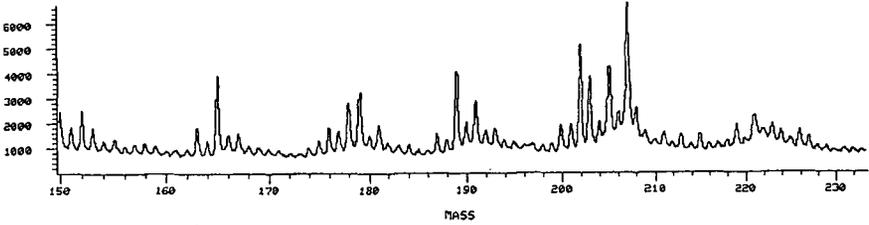
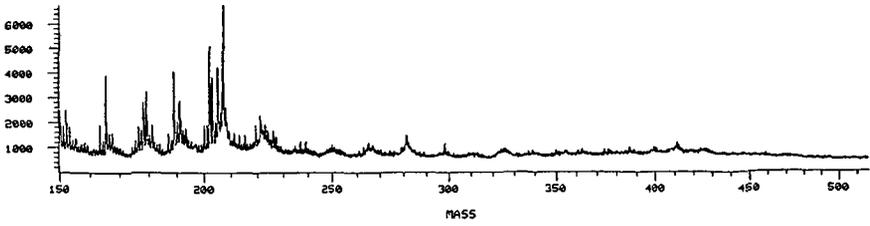


Figure 2: Positive ion CFPDMS spectrum of 1,2,3,6,7,8 Hexahydro-pyrene in the mass range 150 to 500 amu. Vignettes show detail of fragment ions (150 to 208 amu) and recombinant ions (220 to 340 amu).

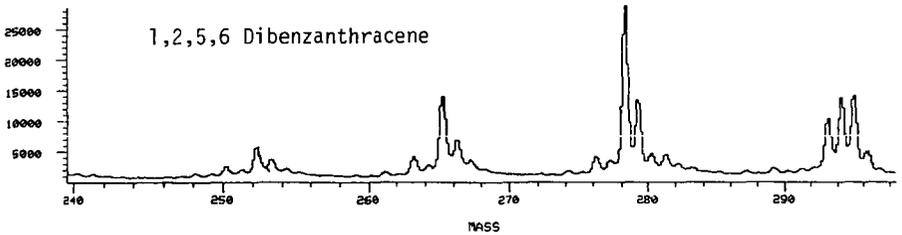
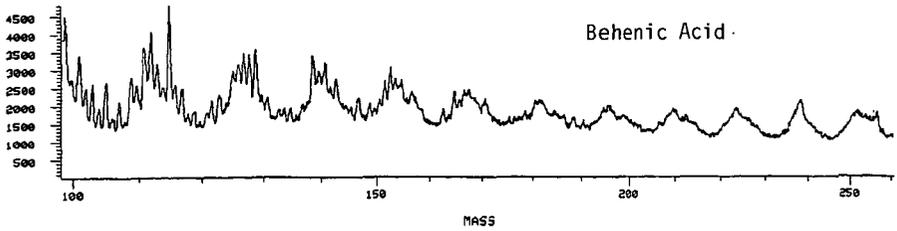


Figure 3: Periodic positive CFPDMS ion groups. Periodicity 14 amu fragments from cleavage of alkyl chain of Behenic acid (Top), and periodicity 13 amu methine extrusion fragments of Dibenanthracene (Bottom). The Dibenanthracene spectrum shows the parent ion at 278 amu and an oxygenated impurity at 294 amu.