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ELUCIDATION OF THE NATURE OF ORGANIC NITROGEN IN THE ARGONNE PREMIUM COALS*

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Elucidation of the Nature of Organic Nitrogen in the Argonne Premium Coals

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ABSTRACT

The objective of this study is to provide detailed information on the types of nitrogen compounds in coals as a function of rank and age. Desorption high resolution mass spectrometry is being used to examine both whole coals and their pyridine extracts. We have shown that nitrogen compounds tend to have larger ring numbers compared to all other aromatic clusters. Now we have found that in low rank coals, such as the subbituminous Wyodak-Anderson, the majority of nitrogen containing compounds have one or more oxygens. The most abundant group of molecules have a nitrogen plus two oxygens and an average ring size of four to five. We have evidence that many of these molecules may be derived from alkaloids. In the higher rank coals, the average ring size increases to seven for the medium volatile Upper Freeport coal. These multiple ring nitrogen compounds play an important role in coal processing and in NO_x production and elimination in combustion.

Keywords: mass spectrometry, coal products, nitrogen, coal structure.

INTRODUCTION

The organic nitrogen functionality found in coal are important in processing and in combustion. There have been a number of studies of nitrogen in coals especially on coal liquids and tars. The Argonne coals have been studied directly using XPS.[1] They found that the amount of pyrrolic nitrogen was essentially rank independent at approximately 60%. The remaining nitrogen is either quaternary or pyridinic with the quaternary disappearing in the higher rank coals. A N-aromatic fraction of extract of the Argonne coals have been examined by GCMS.[2] They observed alkylated azanaphthalenes and azaphenanthrenes and carbazoles. Structures with greater than 5-rings were not observed which may be due to the low volatility of the larger compounds. In desorption high resolution mass spectrometric analysis of the pyridine extracts, we found that the ring size for nitrogen compounds were consistently larger than any of the other classes of aromatic compounds.[3] We now feel we have a possible

explanation for this observation at least for the low rank coals.

EXPERIMENTAL

A complete description of the Argonne Premium Coal Samples is available via the internet at: *http://www.anl.gov/PCS/pcshome.html* and has been published.[4] Analytical data on the coals and pyridine extracts have been reported.[3] Nitrogen values are fairly constant between 1.3-1.7 N/100 carbons. Desorption electron impact high resolution mass spectra (DEIHRMS) are taken on a 3-sector MS-50. Samples are heated from 200 to 700 °C at 200 °C/min on a probe directly in the source. Precise mass measurements are averaged from scans over the entire temperature range. Formulae are assigned and the data sorted via a procedure developed in this program. High resolution mass spectrometry data is sorted by both heteroatom content and by hydrogen deficiency which is also termed double bond equivalents (dbe). From hydrogen deficiency, the size of aromatic clusters can be estimated.

RESULTS AND DISCUSSIONS

For this set of coals, the nitrogen content is quite constant while the oxygen content decreases with rank. We have looked at possible combinations of nitrogen and oxygen in the same molecule, which statistically one would expect to find, especially in the low rank coals. In the Wyodak subbituminous coal (APCS 2), we observed a large number of species that contained both, which is shown in Table 1. Also note the relatively large ring number. Alkaloids are a class of natural compounds produced by plants that contain nitrogen and oxygen and are multi-ring. Flowering trees, which produce alkaloids, were very abundant during the Tertiary Period when the organic sediment was laid down for this coal.

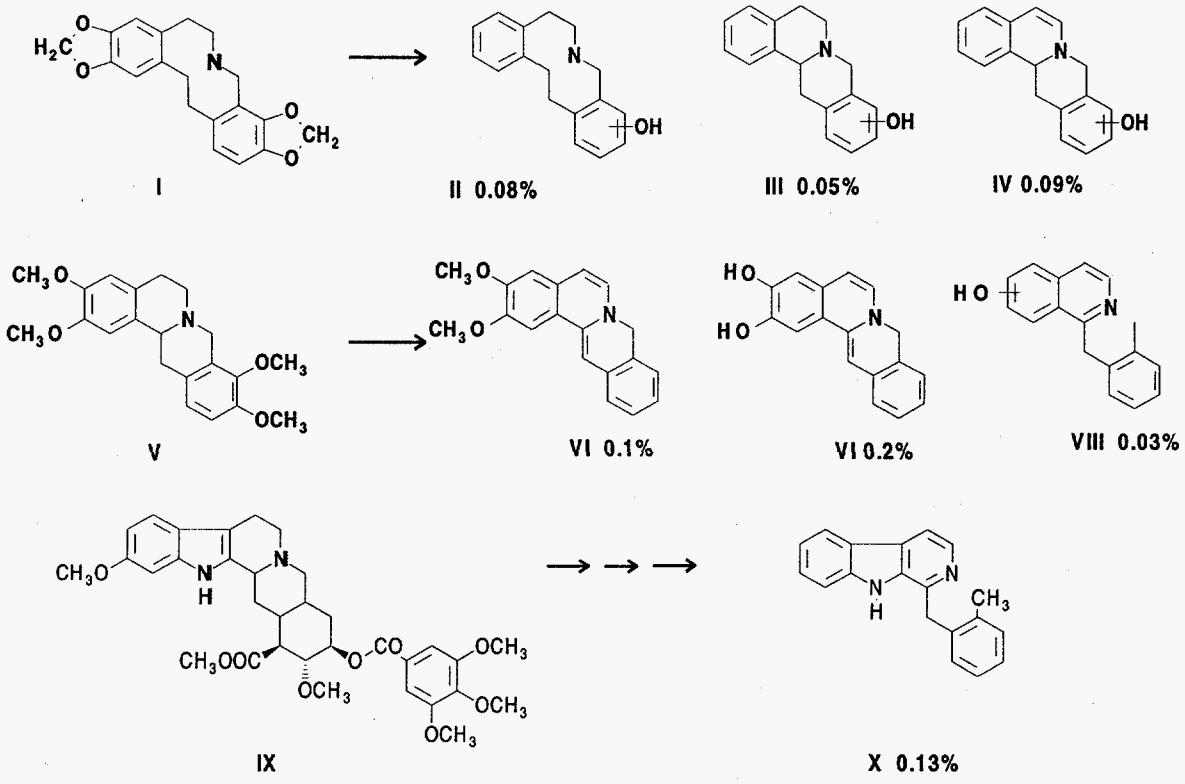
An example shown in Scheme 1 (the percentages indicate the amount observed in the analysis of APCS 2) is a fern derived alkaloid(I) which through the loss of oxygen functionality would produce compounds (II-IV) whose formulae fit ions observed in DEIHRMS of APCS 2. A similar alkaloid (V) has a common arrangement of rings found in many plants including magnolia trees and coalification could lead to compounds such as VI-VIII. These are the same transformations that are thought to occur to lignin during coalification.[5] Another generic ring system is IX which could be transformed to X.

If the molecules observed in coal are being derived from only a limited number of precursor structures, you would expect to find only limited number of species in each classification such as double band equivalent, which is what we observe. As the coals increase in rank, both the oxygen associated with nitrogen is reduced and the number of members in each class increases. An example is shown in Figure 1.

Table 1: Distribution of nitrogen compounds from DEIHRMS analysis of APCS 2 extract.

Nitrogen	Oxygen	Mole. %	Most Abundant Ring Number
1	0	2.5	5
2	0	4.0	4
1	1	6.3	5
1	2	9.2	4,5,7
1	3	5.5	2-4,7
1	4	5.8	3-5
2	1	3.5	3-5
2	2	4.6	2,5
2	3	4.8	2-4

Scheme 1



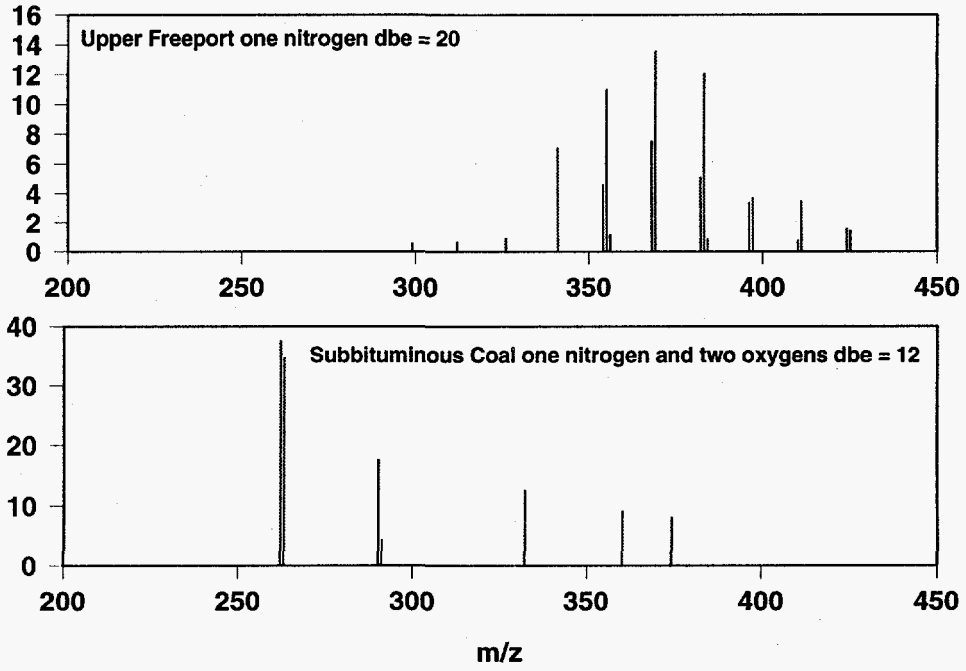


Figure 1. Selected ion mass spectra.

CONCLUSIONS

Alkaloids are a potential source of multi-ring nitrogen containing aromatic compounds in coals and could be a new class of biomarkers.

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