

Oxidative Degradation of Coals

N. C. Deno, Kenneth W. Curry, A. Daniel Jones, Robert D. Minard, Thomas Potter, Walter G. Rakitsky, and Karen Wagner

Department of Chemistry, Pennsylvania State University, University Park, PA 16802

The methods for oxidatively fragmenting coals to identifiable structures divide themselves into two types. In the more traditional type as exemplified by oxygen, permanganate, chromate, and nitric acid; benzylic hydrogen are selectively attacked. Since about half of the aliphatic hydrogens in coals are benzylic, the result of this selectivity is to destroy the aliphatic structure. In the newly discovered RO^+ type of reagent as exemplified by trifluoroperoxyacetic acid (TFPA), the aromatic rings are selectively attacked and the reagent shows great reluctance to react with benzylic hydrogen, although such hydrogen may be ultimately lost in part due to subsequent hydrogen shifts. The two types of oxidants compliment each other and provide two of the most effective methods for investigating the chemical structure of coal. Although the TFPA method is still under development, early results on 27 coals can now be presented.

Products. Aliphatic diacids and triacids of 3-8 carbons generally account for 50-90% of the observed products. Extensive model studies show that these arise from hydroaromatic-aromatic polycyclic systems. A minor fraction of these products contain OH or C=C groups. Acetic acid is the only aliphatic monoacid. It arises from arylmethyl groups in 70-80% yields and the amount of acetic acid provides the best current method for determining the %C present as arylmethyl. This value is around 1% in most coals and increases to about 3% on liquefaction of the coal. Higher monoacids such as propanoic and butanoic are not observed from which it is concluded that arylethyl and arylpropyl groups are not present in the coals.

The formation of methanol and methyl trifluoroacetate, is a measure of the amount of arylmethoxy but special precautions must be taken to trap these volatile products. These precautions were taken with a lignin and a North Dakota lignite, and 15% of the carbon was found to be present in arylmethoxy groups.

Benzene triacids and tetraacids arise from most coals. These products do not arise from TFPA oxidations of polyaromatics of 1-5 rings, polyalkyl-benzenes, or any hydroaromatic-aromatic of 2-3 rings. They do form from TFPA oxidation of 5,12-dihydronaphthacene and their formation from coals presumably reflect structures of this type in the coals.

Phthalic acid is the dominant product from TFPA oxidation of polyaromatics. It is rare or absent from the products from most coals, but becomes a major product from liquefied coals and certain aromatic coals such as PSOC-349.

Oxirane tricarboxylic and tetracarboxylic acids are major products from virtually every coal. Model studies indicate that these arise from hydro-aromatic-aromatic structures.

Pyridine polyacids are minor products and are the only products which contain nitrogen. Pyridine-3,5-dicarboxylic acid, one pyridine tricarboxylic acid, and one pyridine tetracarboxylic acid were observed. The two remaining pyridine acids are more complex and contain a carboxyl which does not esterify. Model studies indicate that these two products are polycarboxypyridine-2-acetic acids.

Divergent Coals. Six of the 27 coals give products which diverge markedly from those of the remaining 21 coals. A Texas lignite (PSOC-623) gave two unusual products which accounted for 77% of GC peak areas. These two products appear to be a carboxybiphenyl with a lactone bridge across the 2,2' positions and a product of MW 286 which could be an acenaphthenetri-carboxylic acid.

A Utah cannel coal (PSOC-155) gave anthraquinone as 82% of the GC peak areas and this one product accounted for 23% of the carbon in the coal. This coal was also unusual in that 42% of the carbon was in unbranched aliphatic chains of six or more carbons. A Kentucky Imboden coal (PSOC-372) gave anthraquinone as 43% of GC peak areas and is another divergent coal.

One coal, PSOC-349 Pennsylvania Lower Clarion, contains polycyclic aromatic structures as evidenced by phthalic acid as a major product and certain phthalides as minor products. This coal resembled liquefied coals and perhaps has been subjected to times and temperatures equivalent to liquefaction conditions.

Two Utah coals (Blind Canyon PSOC-453 and Lower Sunnyside PSOC-459) had 15% and 28% of the GC peak areas due to a product of MW 268. This product appears to contain linear aliphatic chains and is either absent or a trace product in other coals.

The above examples show that certain coals have arisen from unusual and special circumstances. This could be an unusual bioorigin or an unusual biodegradation. Only the case of PSOC-349 does the divergent nature of the products appear to arise from the effect of elevated temperature on the coal.

Conclusions. It is accepted that coal, petroleum, oil shale, and tar sands have different biological origins. The data herein indicate that some coals can have radically different biological origins relative to other coals. Generally 80% or more of the GC peak areas were due to only 10-15 products. These products had unusual, specific, and non-trivial structures. This indicates that coals still retain much of the structural specificity of their bioorigins and are fossils in the sense of chemical structure. It is suggested that for many coals most of chemical changes occurred within a few years after deposition and were the result of bacterial and fungal action. However, there are exceptions such as PSOC-349 where the aromatic nature could be a consequence of times and temperatures equivalent to the conditions of coal liquefaction.

The catalysis of chemical changes by clays and other minerals is dismissed as being ineffective in a material as non-fluid as coal. The effects of geological pressure is dismissed on the basis that the known thermal reactions of coal (liquefaction) involve bond dissociations to benzyl and other radicals. Such reactions have positive volumes of activation and will be slowed by pressure, not accelerated. In summary, the nature of the products from TFPA oxidations and their paucity along with other arguments suggest that most coals have undergone relatively little chemical change over geological time after the early changes due to decay process.