

**THE OXIDATION OF THE KEROGEN OF CHATTANOOGA SHALE
WITH ALKALINE PERMANGANATE AND CHROMIC ACID**

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INTRODUCTION

The majority of the organic material in oil shales is present in the form of kerogen. Kerogen is a high molecular weight heteropolymer which is insoluble in common organic solvents. Due to the interferences inherent in the analysis of such material, data obtained from raw kerogen concentrates is somewhat limited and valid only on a statistical basis. One method used to more thoroughly characterize the kerogen structure is to break down the polymeric matrix by controlled oxidation followed by analysis of the oxidation products.

Several methods have previously been used to oxidize Chattanooga Shale and kerogen concentrates derived from the shale. Leonard (1) used 3.5 percent ozone to oxidize shale samples and a kerogen concentrate. Water and ether soluble acids were extracted from the oxidized material. Products consisted primarily of aliphatic hydroxy acids. A later study by Kinney and Leonard (2) produced highly oxygenated ether and water soluble acids. Kinney and Schwartz (3) oxidized Chattanooga Shale with air at 200°C for 200 hours in order to maximize the production of humic acids. The acids obtained were quinoid in nature and similar to those obtained from coal. Stanton and co-workers (4,5,6) utilized a stepwise oxidation with perchloric acid to oxidize Chattanooga Shale. The primary products were highly polar, unsaturated carboxylic acids. A model for the structure of the kerogen in Chattanooga Shale was proposed by Stanton et al. (6). The model consisted of highly condensed aromatic material with alkyl side chains. Ether oxygen was a major crosslink in the kerogen matrix.

This paper describes the characterization of two kerogen samples derived from Chattanooga Shale by oxidative degradation with alkaline potassium permanganate and chromic acid. The oxidation products were separated into acidic and basic fractions. Samples were analyzed by fourier transform infrared spectrophotometry (FTIR) and gas chromatography (GC). Selected samples were analyzed by gas chromatography coupled to mass spectrometry (GC-MS).

EXPERIMENTAL

A sample of the Gassaway member of the Chattanooga Shale was obtained from the Eastern Highland Rim area of Tennessee. The sample was ground to minus 60 mesh in preparation for demineralization and bitumen extraction. A 1000-g sample was demineralized using a combination of hydrochloric and hydrofluoric acids (5). Bitumens were removed by soxhlet extractions with benzene and methanol. The kerogen concentrate obtained had a mass of 235.1 g. A kerogen concentrate previously prepared by Stanton (4,5) was also used in this study.

Both kerogen samples were oxidized with alkaline permanganate solution. Samples having a mass of approximately two grams were oxidized in a stepwise manner using 100-mL aliquots of a 0.06 molar potassium permanganate solution in 1.6 percent potassium hydroxide. The solution was heated to 90°C until complete permanganate consumption was indicated by the loss of purple and green colors in the reaction flask. The mixture was filtered at the end of each reaction step and the residue washed with 1.6 percent potassium hydroxide to insure complete product removal. Neutral and basic molecules were separated from the aqueous product mixture by ether extractions. The remaining aqueous phase was then acidified and extracted with ether to remove the ether soluble acids. Precipitated acids which formed at this stage were also collected. All extractions were performed in three steps with one hour allowed for partitioning between the phases in each step. The remaining aqueous solution was essentially colorless, indicating a low concentration of water soluble acids. No effort was made to recover these compounds. The residue from alkaline permanganate oxidation contained large amounts of manganese dioxide, which was removed by treatment with oxalic acid in order to determine the mass of the remaining organic material. The residue from one sample dissolved completely, indicating that the kerogen sample had been entirely converted to soluble species.

A 14-g sample of the kerogen concentrate was also oxidized in a stepwise manner using 3.0 M chromic acid solution and successively longer oxidation steps. The time periods of the oxidation steps were 3, 6, 12, 24, and 48 hours. The oxidation products were separated at the end of each step by a series of extractions. Heptane and ether extractions removed the oxidation products from the aqueous solution. These extracts were then extracted with 6.0 M sodium hydroxide in order to separate the basic fraction of the products. The sodium hydroxide solutions were then back-extracted with heptane or ether to isolate the basic products.

The raw kerogen concentrate was analyzed by X-ray diffraction (XRD) and scanning electron microscopy using energy dispersive X-rays (SEM-EDX) in order to determine the identity of any resistant mineral material. Oxidation products obtained from alkaline permanganate and chromic acid oxidations were analyzed using FTIR, GC, and GC-MS. Infrared spectra were obtained by

using thin films and potassium bromide pellets with a Nicolet 20 DXB FTIR Spectrometer. Gas chromatograms of the neutral and basic fractions, and of the methyl esters of the ether and heptane soluble acids were obtained on a Perkin-Elmer 8500 Gas Chromatograph with an SGE SPB-5 capillary column. Selected samples were analyzed by GC-MS using a Hewlett Packard 5987 gas chromatograph/mass spectrometer with a similar column.

RESULTS AND DISCUSSION

The kerogen concentrate was 17.1 percent ash. The ash was brick red in color. After dissolution, iron was determined spectrophotometrically with 1,10-phenanthroline (7). The ash was found to be 55.4 percent iron(III) oxide. Scanning electron microscopy of the kerogen concentrate indicated the presence of iron and sulfur. X-ray diffraction confirmed these findings and indicated that the mineral material consisted almost exclusively of pyrite. This was expected as pyrite is not removed by the demineralization procedure. By comparison, inorganic ash made up 33.8 percent of the kerogen concentrate prepared by Stanton. The difference is due mainly to the somewhat irregular distribution of pyrite in the Chattanooga Shale.

The oxidation products obtained from both alkaline permanganate and chromic acid oxidations were separated into basic and acidic fractions. Chromic acid oxidation products were further separated into heptane and ether soluble fractions. Alkaline permanganate oxidation also produced considerable high molecular weight acids which precipitated from solution. These precipitated acids remained complex enough to make analysis difficult. Therefore, 50-mg samples of precipitated acids from several steps were further oxidized with 10-mL portions of 0.06 alkaline permanganate. These reactions were carried out using microscale apparatus. Products were separated in a manner similar to the original permanganate oxidations, the exception being that any precipitated acids formed were returned to the reaction flask.

Product mass data for the alkaline permanganate oxidations reveal some interesting differences between the two samples. While the recovery of basic material and soluble acids is very similar, that of precipitated acids and residual material is quite distinct. The kerogen concentrate with 33.8 percent ash (Table 1) produced only moderate amounts of precipitated material and left no residue. Slightly less than 30 percent of the original sample weight was recovered as oxidation products. This suggests that large amounts of the structure were oxidized to carbon dioxide and other light molecules which would be lost. The kerogen concentrate with 17.1 percent ash (Table 2) produced large amounts of precipitated acids as well as considerable residual material. One hundred thirty percent of the initial sample weight was recovered as oxidation products and residual material. This represents not only the retention of much of the initial structure but also the incorporation of large amounts of oxygen. This data appears to indicate some significant

heterogeneities in the kerogen of the Chattanooga Shale, although no definite conclusions may be drawn on the basis of two samples. Chromic acid oxidation of the 17.1 percent ash sample (Table 3) produced generally low product recovery. This is consistent with oxidation of only the more reactive sites of this resistant material.

Infrared spectra were obtained for all fractions. Spectra for both acidic and basic fractions indicated the presence of both aromatic and aliphatic material. Basic fractions were found to contain hydroxyl and amide groups, as well as various substituted benzenes. The presence of ether functionalities and both aromatic and aliphatic ester groups was indicated, as were quinone structures. Spectra of acidic fractions were dominated by peaks attributable to carboxylic acid groups. Aromatic ethers, alcohols, phenols, and thiols were also present. The spectra of precipitated acids were similar to those of soluble acids. The major difference between the two was that oxygen containing functional groups were more dominant in the precipitated acid fraction and aliphatic material was greatly reduced.

Gas chromatograms were obtained for all basic fractions. The acidic fractions were converted to methyl esters using boron trifluoride in methanol (8). Gas chromatograms were then recorded for the methyl esters of all acidic fractions with the exception of the precipitated acids produced by alkaline permanganate oxidation. Chromatograms were obtained for the degradation products of the precipitated acids. Gas chromatography data indicated a broad diversity of products.

Selected samples from each product type were analyzed by gas chromatography-mass spectrometry. Preliminary analysis of the mass spectra obtained has confirmed the presence of both aromatic and aliphatic material. Both acidic and basic fractions contained multisubstituted benzenes, saturated and unsaturated cyclic structural units, and long alkyl chains. n-Alkane chains containing up to thirty carbons have been identified. The basic fractions were found to contain amines, alcohols, thiols, and esters. Hydrocarbons and alcohol functionalities were dominant. Carbon skeletons consist primarily of disubstituted benzenes, multisubstituted cyclohexanes, and n-alkyl chains. Molecular sizes range from sixteen to twenty-seven carbons. The acidic fractions were esterified prior to analysis, and the spectra of these samples were characterized by peaks attributable to the ester functionality. The compounds were interpreted as originally being mono- and poly-carboxylic acids. Carbon skeletons consisted of mono-, di-, and tri-substituted benzenes, phenols, cyclic groups, and n-alkyl chains. Molecular sizes range from ten to thirty carbons.

CONCLUSIONS

A kerogen concentrate derived from the Chattanooga Shale was oxidized in a stepwise manner with alkaline potassium permanganate and chromic acid. Infrared analysis of the oxidation products indicated the presence of aromatic and aliphatic material. Functionalities included alcohols, thiols, phenols, ethers, esters, quinones, and carboxylic acid groups. Gas chromatography-mass spectrometry analysis of selected oxidation products confirmed that both aromatic and aliphatic material was present in the oxidation products. Carbon skeletons of the products were found to consist of substituted benzenes, saturated and unsaturated cyclic structures, and n-alkyl chains. Molecular sizes ranged from ten to thirty carbons. The largest molecules were interpreted as n-alkanes and n-saturated monocarboxylic acids. Aromatic material was typically multifunctional, and was probably responsible for most of the cross-linking within the kerogen. This data will be used to suggest modifications to the structure of Chattanooga Shale kerogen proposed by Stanton (6). Several basic modifications to the structure are in order. Sulfur and nitrogen containing compounds are confirmed in the oxidation products and amine, amide, and thiol groups should be introduced into the model. Alkyl chains of up to thirty carbons should also be included, essentially doubling the length of those in the present model. Other groups which should be accommodated include carbon chains with multiple double bonds, phenols, quinones, and disubstituted benzene rings.

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REFERENCES

1. Leonard, J.T., "Ozonolysis of the Organic Matter of Chattanooga Black Shale," Univ. Microfilms (Ann Harbor), L.C. Card No: Mic 59-2987, 1288 (1959).
2. Kinney, C.R. and J.T. Leonard, "Ozonization of Chattanooga Uraniferous Black Shale," J. Chem. Eng. Data, **6**, 474 (1961).
3. Kinney, C.R. and D. Schwartz, "Partial air Oxidation of Chattanooga Uraniferous Shale," Ind. Eng. Chem., **49**, 1125 (1957).

4. Stanton, B.J. and C.W. McGowan, " The Analysis of the Organic Matter in Chattanooga Shale by Oxidation with Perchloric Acid," Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., **33**, 449 (1988).
5. Stanton, B.J., R.M. Morris and C.W. McGowan, "The Characterization of the Kerogen of Chattanooga Shale, Part I - the Oxidation of the Chattanooga Shale with Boiling Perchloric Acid," Fuel Process. Technol., **29**, 85 (1991).
6. Stanton, B.J., D.J. Davidson and C.W. McGowan, "The Characterization of the Kerogen of Chattanooga Shale, Part II - Analysis of Oxidation Products and Proposal of a Model of the Structure of Kerogen in Chattanooga Shale," Fuel Process. Technol., **29**, 97 (1991).
7. Diehl, H. and G.F. Smith, Quantitative Analysis, John Wiley and Sons, Inc., New York, 368 (1952).
8. McGowan, C.W. and H. Diehl, "The Oxidation of Green River Oil Shale with Perchloric Acid. Part II - The Analysis of Oxidation Products," Fuel Process. Technol., **10**, 181 (1985).

TABLES

TABLE 1. Product masses (in mg) resulting from the alkaline permanganate oxidation of the kerogen concentrate with 33.8 percent ash

	Basic Fraction	Soluble Acids	Precipitated Acids	Total Product
Step 1	10.2	12.6	8.6	31.4
Step 2	7.0	14.9	69.3	91.2
Step 3	5.0	19.0	33.9	57.9
Step 4	4.0	19.1	43.5	66.6
Step 5	10.6	31.6	55.1	97.3
Step 6	13.5	23.5	61.4	98.4
Step 7	3.7	32.3	48.5	84.5
Step 8	3.3	25.3	35.4	64.0
Step 9	3.4	24.1	19.7	47.2
Step 10	4.4	11.1	0	15.5
Residue				0
Total	65.1mg	213.5mg	375.4mg	654.0mg
Initial sample: 2.2106g				

TABLE 2. Product masses (in mg) resulting from the alkaline permanganate oxidation of the kerogen concentrate with 17.1 percent ash

	Basic Fraction	Soluble Acids	Precipitated Acids	Total Product
Step 1	7.5	22.0	27.1	56.6
Step 2	12.1	21.0	185.2	218.3
Step 3	6.9	21.1	78.9	106.9
Step 4	5.9	32.0	555.7	593.6
Step 5	3.9	32.6	30.8	67.3
Step 6	10.5	29.9	37.2	77.6
Step 7	11.9	29.1	54.5	95.5
Step 8	3.2	31.0	32.4	66.6
Step 9	3.6	14.0	0	17.6
Step 10	8.8	6.0	0	14.8
Residue				1380.3mg
Total	66.8mg	216.7mg	974.7	2638.5mg

Initial sample: 2.0164g

TABLE 3. Product masses (in mg) resulting from the chromic acid oxidation of the kerogen concentrate with 17.1 percent ash

Oxidation Step	Water Soluble Bases	Ether Soluble Bases	Heptane Soluble Bases	Ether Soluble Acids	Heptane Soluble Acids
3 hour	1.0	2.5	0.4	2.3	4.3
6 hour	2.0	41.1	1.1	5.8	3.5
12 hour	43.2	43.3	40.5	6.2	35.2
24 hour	8.4	11.6	7.7	10.4	10.1
48 hour	9.1	8.9	6.9	14.5	6.0
Total	63.7mg	107.4mg	56.6mg	39.2mg	59.1mg

Total product: 326.0mg Residue: 14.1458g
Initial sample: 14.4139g