

**THE ANALYSIS OF THE ORGANIC MATTER IN CHATTANOOGA SHALE BY
OXIDATION WITH PERCHLORIC ACID**

Bobby J. Stanton and Chris W. McGowan

Department of Chemistry
Tennessee Technological University
Cookeville, Tennessee 38505 (USA)

ABSTRACT

A kerogen concentrate was prepared from a raw Chattanooga shale sample. The kerogen concentrate was oxidized in a stepwise fashion by varying the boiling point, and subsequent concentration and oxidizing strength of perchloric acid. The progress of the reaction was monitored with respect to the amount of undissolved material, the color of the aqueous phase, and the conversion of carbon to carbon dioxide. The dissolution of kerogen occurred between 150-180°C. The color intensity of the aqueous phase rose to a maximum, then faded to clear at 203°C. The maximum color corresponded to the dissolution of kerogen. The percentage of carbon converted to carbon dioxide was negligible when the boiling point of perchloric acid was below 150°C. Above 150°C, the carbon converted to carbon dioxide rose almost linearly. Polar unsaturated carboxylic acids were indicated as the major oxidation products.

INTRODUCTION

For some time workers have attempted to characterize the kerogen present in oil shales. Kerogen is a high molecular weight, polymeric material which is said to be insoluble in common organic solvents. In order to characterize the kerogen in oil shale, it has been necessary to destroy the kerogen by oxidative degradation of the kerogen matrix with subsequent analysis of the oxidation products. Analysis of the soluble lower molecular weight oxidation products has yielded insight into the nature of the structure of kerogen in oil shale.

Leonard (1) used 3.5 percent ozone to oxidize Chattanooga shale. Similar ether and water soluble acids were extracted from the raw shale and a kerogen concentrate prepared from the raw shale sample. The ozonization products were primarily aliphatic hydroxy acids. Ozonolysis of the kerogen of Chattanooga oil shale by Kinney and Leonard (2) yielded highly oxygenated ether and water soluble acids. Kinney and Schwartz (3) oxidized Chattanooga shale with air at 200°C for 200 hours to produce the maximum amounts of humic acids. The acids were similar to those obtained from coal, and were quinoid in nature.

This paper describes the characterization of the kerogen of Chattanooga oil shale by oxidative degradation with perchloric acid of varying boiling point. Smith (4) demonstrated that the

apparent reduction potential of perchloric acid increases sharply as the boiling point rises above 150°C and the concentration increases. A stepwise oxidation of the kerogen can be effected by increasing the boiling point and subsequent oxidizing ability of perchloric acid. This study was analogous to the work completed by McGowan and Diehl (5,6,7) on Green River Shale.

EXPERIMENTAL

A Gassaway member of the Chattanooga shale from the Eastern Highland Rim area of Tennessee was ground to -60 mesh. A kerogen concentrate was prepared from the raw shale sample by demineralization using a combination of hydrochloric and hydrofluoric acids. Samples of the kerogen concentrate were oxidized with boiling perchloric acid within a modified Bethge apparatus as described by McGowan and Diehl (5). Perchloric acid solution was added to the reaction flask of the Bethge apparatus, and the boiling point was adjusted to the desired temperature by positioning the teflon stopcock to remove reflux condensate, or by addition of water through the top of the water condenser. The boiling point was kept constant by returning the reflux condensate to the reaction vessel. The amount of perchloric acid added was varied such that approximately 50 ml of solution remained after the temperature adjustment was completed. After cooling to room temperature, three 1.00 ml aliquots were taken and titrated with 0.25 N sodium hydroxide. A 1-g sample of kerogen concentrate was added to the reaction vessel, and the system was purged for 30 minutes with nitrogen. A weighed Turner absorption bulb containing ascarite and anhydrous magnesium perchlorate was added to the reaction system. The reaction flask was heated for 1.5 hours. The stable reaction temperature was recorded. The system was repurged with nitrogen for 30 minutes at the termination of the reaction. The absorption bulb was reweighed and the percentage of carbon converted to carbon dioxide was calculated. The undissolved material was filtered and washed with 300 ml of distilled water. Upon dilution as a result of filtration, the perchloric acid solution became more aqueous, and a precipitate formed in the aqueous layer upon standing. The precipitate was filtered. The undissolved material, the aqueous layer, and the precipitate filtered from the aqueous layer were retained for the analysis of oxidation products.

The reaction time was reduced for samples KC-160 and KC-165 due to excessive foaming. Reaction KC-190 was violent. Flaming occurred on the surface of the reaction mixture. The reaction was contained in the reaction flask of the Bethge apparatus with no apparent damage to the reaction system. The sample size was reduced to 0.1 gram for KC-200 as a safety precaution. The reaction proceeded smoothly.

Each reaction was performed in a perchloric acid fume hood behind an explosion shield. The authors recommend that extreme caution be exercised when perchloric acid alone is used to oxidize organic material.

The undissolved material was designated as KC-^oC-U, and the precipitate filtered from the aqueous layer was designated as KC-^oC-A. The undissolved material and the aqueous layer precipitate were washed free of perchloric acid with distilled water. The samples were dried and weighed.

Samples KC-110-U through KC-190-U of the undissolved material were washed with 0.25 N sodium hydroxide. The sodium hydroxide washings were acidified with 12 M hydrochloric acid. A brown precipitate formed and was filtered. The precipitate was washed with heptane into a weighed 50 ml flask. The heptane washings (KC-^oC-U1) were evaporated to dryness and weighed. The precipitate was then washed with benzene into a weighed 50 ml flask. The benzene washings (KC-^oC-U2) were evaporated to dryness and weighed. The undissolved material was washed with methanol into a weighed 50 ml flask. The methanol washings (KC-^oC-U3) were evaporated to dryness and weighed. The remaining precipitate (KC-^oC-U4) was sodium hydroxide soluble, and was retained for analysis.

Samples KC-150-A through KC-180-A of the precipitate filtered from the original aqueous layer were washed with heptane into weighed 50 ml flasks. The heptane washings (KC-^oC-A1) were evaporated to dryness and weighed. The precipitate was washed with benzene into a weighed 50 ml flask. The benzene washings (KC-^oC-A2) were evaporated to dryness and weighed. The precipitate was washed with methanol into a weighed 50 ml flask, the washings (KC-^oC-A3) were evaporated to dryness and weighed. Only a trace of precipitate remained after the washing of the precipitate with methanol which was sodium hydroxide soluble.

Ultraviolet spectra were recorded for all U3 and A3 samples. A portion of each sample was dissolved in methanol. A background spectrum of methanol was recorded. The spectra were recorded on a Perkin Elmer Lambda 4B UV/VIS spectrometer. Infrared spectra were obtained via a diffuse reflectance technique with a Nicolet 20 DXB FTIR spectrometer. All U3, U4, and A3 samples were esterified with methyl-8 methylating reagent. One milliliter of methyl-8 was added to 5-10 milligrams of sample. The mixture was heated for 20 minutes at 60°C. The methyl esters produced from the acid oxidation products were to be analyzed by gas chromatography and gas chromatography/mass spectrometry, however, analysis was not completed at the time of the writing of this paper.

RESULTS AND DISCUSSION

The kerogen concentrate produced from the raw Chattanooga shale sample was dark brown. The kerogen concentrate was 46.53 percent carbon, 4.34 percent hydrogen, 1.37 percent nitrogen, and 19.73 percent sulfur. The atomic hydrogen to carbon ratio was 1.1 to 1.0 indicating a high degree of unsaturation for the kerogen concentrate. Scanning Electron Microscope/X-Ray Diffraction analysis of the kerogen concentrate indicated the presence of iron, sulfur, and titanium. Iron constituted 18 percent of the mineral content present in the kerogen

concentrate, determined with a Perkin Elmer Inductively Coupled Plasma Spectrometer. The kerogen concentrate was approximately 34 percent ash. The mineral content was predominantly pyrite based on the analysis of the kerogen concentrate and the percentages of iron and sulfur present.

The extent of oxidation of the organic material in Chattanooga oil shale was determined by monitoring the percentage of undissolved material, noting color changes in the aqueous phase, and calculating the percentage of carbon converted to carbon dioxide. Results from the oxidation of the kerogen concentrate are presented in Table 1.

The results presented in Table 1 for the percentage of undissolved material indicated the kerogen dissolved between 150°C and 180°C. The percentage of undissolved material decreased approximately 27 percent between 140-155°C. This was probably due to the dissolution of pyrite, which was approximately 30 percent of the kerogen concentrate. The dissolution of pyrite in boiling perchloric acid at 140-155°C has been demonstrated (8). Aromatic material was suspected to have dissolved between 170-180°C. It has been demonstrated by ¹³C-NMR (9) that approximately half of the organic carbon present in Chattanooga shale is aromatic.

The color intensity of the aqueous phase rose to a maximum then faded to clear. The color changes ranged from colorless to pale yellow below 150°C, dark orange-brown between 150-180°C, dark yellow at 190°C, and clear at 203°C. The maximum color intensity corresponded to the dissolution of kerogen.

The data for the percentage of carbon converted to carbon dioxide presented in Table 1 for the kerogen concentrate indicated no significant amounts of carbon were converted to carbon dioxide when the boiling point of perchloric acid was below 150°C. The percentage of carbon converted to carbon dioxide rose in a linear fashion above 150°C. The results for the total carbon present in the kerogen concentrate at 203°C are not useful. It has been demonstrated that chlorine gas is produced by perchloric acid at 203°C (4). Thus, the calculated percentage of carbon converted to carbon dioxide at 203°C was elevated due to the absorption of chlorine onto ascarite.

The oxidation products were separated into fractions. The first type of oxidation product fractionated was the acidic fraction isolated from the undissolved material. The solid acids were separated into heptane, benzene, and methanol soluble fractions. There was no evidence that any material was extracted by heptane or benzene. Polar acids were extracted with methanol (KC-⁰C-U3). The remaining acids (KC-⁰C-U4) were sodium hydroxide soluble. The acid products KC-150-U3 through KC-170-U3 were brown in color and flaky in texture. Sample KC-180-U3 was brownish-yellow. Samples KC-150-U4 through KC-180-U4 were black. The second type of oxidation product was the precipitate which settled out of the aqueous layer. These acids were separated into heptane, benzene, and methanol soluble fractions. No acid

material was extracted with heptane or benzene. A trace of acid material remained after the methanol extraction was completed which was sodium hydroxide soluble (KC-⁰C-A4). The methanol soluble acids (KC-⁰C-A3) were identical in color and texture to the methanol soluble acids extracted from the undissolved material.

The infrared spectra recorded for selected U3, U4, and A3 samples were characteristic of unsaturated carboxylic acids. The spectra exhibited a broad band between 3500-3000 cm^{-1} indicative of the hydroxyl stretch of a carboxylic acid. A band between 1750-1700 cm^{-1} was typical for a carbonyl stretch of a carboxylic acid. The presence of aldehydes and ketones can not be ruled out. A peak from 1610 cm^{-1} to 1590 cm^{-1} was the typical region for carbon-carbon double bonds. The bands between 1200-1300 cm^{-1} and 1400-1440 cm^{-1} were typical for the C-O stretching and O-H bending of a carboxylic acid.

The ultraviolet spectra were recorded for all U3 and A3 samples. Each spectra contained one broad peak which was essentially identical for each sample. The maximum absorbance occurred between 206-211 nm. This was the characteristic region for unsaturated carboxylic acids which were also indicated by infrared analysis. Each peak exhibited a shoulder peak in the 230 nm to 255 nm region which was suspected to have arisen from the presence of aromatic material in the oxidation products.

CONCLUSION

A stepwise oxidation of the kerogen of Chattanooga oil shale was effected by oxidative degradation with perchloric acid. The dissolution of the kerogen occurred between 150-180°C. The atomic hydrogen to carbon ratio indicated a high degree of unsaturation. Highly polar unsaturated carboxylic acids were indicated as the primary oxidation products. Gas chromatography and gas chromatography/mass spectrometry analysis of the oxidation products were not completed at the time of the writing of this paper. No suitable technique has been developed to separate organic oxidation products from perchloric acid solution. Work will be continued in this area utilizing XAD resins. The GC/MS data and the data obtained from the oxidation of model compounds will be used to propose a model for the structure of the kerogen of Chattanooga oil shale.

ACKNOWLEDGEMENTS

This work was funded through an American Chemical Society - Petroleum Research Fund grant-in-aid # 19461-B2, and a Faculty Research Grant from Tennessee Technological University. The authors would like to thank Dr. Wayne Leimer of the Geology Department at Tennessee Technological University, Glenn Norton from the Ames Laboratory at Iowa State University, and Karen R. Merkle from Fleetguard Inc. for technical assistance.

REFERENCES

1. Leonard, J.T., Univ. Microfilms (Ann Harbor), L.C. Card No: Mic 59-2987: 1288, (1959).
2. Kinney, C.R. and Leonard, J.T., J. Chem. Eng. Data, 6: 474 (1961).
3. Kinney, C.R. and Schwartz, D., Ind. Eng. Chem., 49: 1125 (1957).
4. Smith, G.F., Analyst, 80: 16, (1955).
5. McGowan, C.W. and Diehl, H., Fuel Process. Technol., 10: 169, (1985).
6. McGowan, C.W. and Diehl, H., Fuel Process. Technol., 10: 181, (1985).
7. McGowan, C.W. and Diehl, H., Fuel Process. Technol., 10: 195, (1985).
8. McGowan, C.W. and Markuszewski, R., Fuel. Process. Technol., 17: 29, (1987).
9. Minkis, P.P. and Smith, J.W., Org. Geochem., 5: 193, (1984).

TABLE 1

Results obtained from the oxidation of the Kerogen Concentrate

Sample	Normal- ity HClO ₄	Boil- ing point HClO ₄ (°C) ⁴	Reaction temp (°C)	Reaction time (hour)	Total Carbon (per- cent of sample)	Undis- solved material (percent of sample)
KC-111	2.07	111	106	1.5	0.63	97.80
KC-120	4.26	120	112	1.5	0.49	98.11
KC-132	6.30	132	123-4	1.5	0.47	96.62
KC-141	6.77	141	129-30	1.5	0.17	89.91
KC-151	8.02	151	139-40	1.5	3.08	72.27
KC-156	8.42	156	145-48	1.5	10.96	62.37
KC-162	8.52	162	149-52	1.2	12.00	56.37
KC-166	8.63	166	152-60	1.3	14.70	47.65
KC-171	9.26	171	163-68	1.5	16.26	38.74
KC-181	9.73	181	169-74	1.5	27.45	13.53
KC-190	10.46	190	175-83	1.5	54.06	0.27
KC-203	11.67	203	202	1.5	119.04	0.00