

THE ROLE OF ETHER OXYGEN AND CARBON DOUBLE BONDS AS LINKAGES DURING THE DISSOLUTION OF KEROGENS WITH PERCHLORIC ACID

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INTRODUCTION

In 1966, Fester and Robinson (1) reported that 53.5 percent of the oxygen in the kerogen of Green River oil shale was present in ether functional groups. Fester and Robinson had measured the amount of carboxyl, ester, amide, carbonyl and hydroxyl oxygen with a series of chemical analyses. Ether oxygen was determined by measuring the difference between the sum of the amounts of each of the above functional groups and the total oxygen present. The idea that ether oxygen was a "linkage" between kerogen units was further supported by McGowan et. al. (2) in 1985. In that work, a kerogen concentrate of Green River oil shale was oxidized with solutions of perchloric acid having various concentrations and subsequent boiling points. The kerogen concentrate dissolved at boiling points between 160°C and 170°C. The dissolution range of the kerogen concentrate was compared to the dissolution ranges for a series of model compounds. The compounds (and linkages tested) were polyethylene (carbon-carbon single bonds), graphite (aromatic carbon bonds), nylon (amide bonds) and polyethylene oxide (ether bonds). Polyesters, which readily hydrolyze and dissolve in cold perchloric, were not tested. Polyethylene required a boiling point of 202°C before dissolution occurred (the polymer caught on fire inside the reaction vessel). Boiling, concentrated perchloric at 202°C did not dissolve graphite to any appreciable extent. Nylon also resisted dissolution but a portion was dissolved at 202°C. Both the dissolution ranges and infrared spectra supported the conclusion that ether oxygen was being attacked during the dissolution of the kerogen concentrate from Green River oil shale.

Several additional kerogens have also been reacted with perchloric acid. These include a kerogen concentrate from Chattanooga Shale (3); and two bituminous coals, an Illinois #6 coal and a Charming Creek coal from New Zealand (4). The kerogen concentrate from Chattanooga Shale and the Illinois #6 coal dissolved in boiling point ranges similar to the kerogen of Green River oil shale. However the Charming Creek coal dissolved between 180°C and 190°C. Since the dissolution range for the Charming Creek coal fell outside the range of that for ether oxygen, several additional model compounds were tested. In this paper, the results for the dissolution of three new model compounds and two new kerogens is reported. The new model compounds are poly-m-phenoxyene (aromatic ether bonds), polybutadiene and a polybutadiene with 20 percent styrene copolymer (carbon double bonds). The new kerogens were a Mequinenza lignite from Spain and an Elizabethtown anthracite from Pennsylvania.

When cold or dilute, perchloric acid is a non-oxidizing acid. When hot and concentrated, perchloric acid is powerful oxidizing agent. The apparent reduction potential rises slowly as the concentration and subsequent boiling point increases. The apparent potential rises from 0.8 V at a boiling point of 130°C to 2.0 V at 203°C, the boiling point of the concentrated acid (5).

EXPERIMENTAL

The poly-m-phenoxyene and the polybutadiene-styrene copolymer were obtained from Dr. Vernon Allen of the Department of Chemistry at Tennessee Technological University. The polybutadiene was a Taktene 220 sample obtained from Ms. Pat Kolda at the Bayer Plant in Orange, TX. The Mequinenza coal was obtained by the Ames Laboratory at Iowa State University and was originally supplied by Dr. Sabino Moinelo at the Instituto Nacional del Carbon in Spain. The Elizabethtown coal was supplied by Dr. John Riley of the Department of Chemistry at Western Kentucky University. The ultimate analysis of the Mequinenza coal was determined by Analytical Services at Ames Lab and that of the Elizabethtown coal by the Materials Characterization Center at Western Kentucky. The results appear in Table 1. For comparison purposes, the ultimate analyses for the Illinois #6 and Charming Creek coals as determined at Ames Lab also appear in Table 1.

Table 1. Ultimate Analysis of Coal Samples (on a dry basis)

coal (rank)	carbon	hydrogen	nitrogen	oxygen	sulfur
Elizabethville (anthracite)	83.7	2.30	1.10	0.57	0.74
Charming Creek (bitum.)	79.0	5.32	0.95	9.26	5.44
Illinois#6 (bituminous)	62.2	4.13	1.60	15.5	3.45
Mequinenza (lignite)	53.7	3.94	0.85	9.55	9.93

Safety Note

All reactions were performed under total reflux, in a perchloric acid hood and behind an explosion shield. Generally 1-g samples were reacted at low boiling points and 0.1-g samples at 203°C. An explosion occurred when a 0.2 g sample of the polybutadiene was reacted with concentrated perchloric acid having a boiling point of 203°C. A stopper in the side-arm of the reaction flask was shattered and glass was embedded in the plastic explosion shield. When the sample size was reduced to 0.1 g, no explosion occurred.

Procedure

All reactions were performed in a modified Bethge Apparatus designed to maintain a constant boiling solution. The apparatus has been described by McGowan and Diehl (6). A perchloric acid solution was added to the Bethge Apparatus and the boiling point was adjusted to the desired value. Approximately 50 mL of solution remained. After cooling, a weighed 1.0-g or 0.1-g sample of the model compound or coal was added. The reaction vessel was heated for 1.5 hrs. After cooling, the reaction mixture was filtered. The residue was dried and weighed, and the amount of undissolved material was determined.

RESULTS AND DISCUSSION

The results for the dissolution of the Mequinenza lignite and the Elizabethville anthracite appear in Fig. 1. The lignite sample dissolved between 160°C and 170°C. This dissolution was almost identical to that of the kerogen of Green River oil shale and Illinois #6 coal. The hypothesis that ether linkages were being attacked in this coal was consistent with the high oxygen content and low rank of this coal. The anthracite sample appeared to have two dissolution ranges. One from 170°C to 180°C and a second from 190°C to 203°C. The first range was similar to the dissolution of the kerogen of Chattanooga Shale and was within the range of the dissolution of ethers. The second range was consistent with the dissolution polyethylene and, as presented below, with polybutadiene. The results for the dissolution of poly-m-phenoxyethylene, polybutadiene and the polybutadiene-styrene copolymer appear in Fig. 2. Poly-m-phenoxyethylene gained weight at all boiling points up to 190°C. The infrared spectra of the undissolved material indicated that the polymer had been extensively chlorinated. This chlorination process had been previously observed for other aromatic compounds (7). The polymer was almost completely dissolved at 203°C. The polybutadiene-styrene copolymer displayed a spike in the percent undissolved material at a boiling point of 185°C before dissolving at 190°C. The infrared spectra of the residue from the 185°C reaction also indicated extensive chlorination of the polymer. Although the polybutadiene-styrene copolymer may be a better model compound to represent the kerogen of a coal, it was decided that a polymer containing a double bond without aromatic rings should also be investigated. Polybutadiene displayed a smaller spike in the amount of undissolved material at a boiling point of 190°C. The sample was partially dissolved at 195°C and completely dissolved at 203°C. There was a kinetic problem with the dissolution of the polybutadiene. Even though the polymer was cut up into small particles, they would coalesce into large particles when heated with the perchloric acid solutions; thereby decreasing the surface area of the polymer. When a 1.0-g sample of the polymer was reacted at 195°C, the percent undissolved material was 125 percent. When a 0.1-g sample was reacted at 196°C, the percent undissolved material was 68 percent. Even with this problem, the dissolution of polybutadiene was similar to the dissolution of polyethylene and the second dissolution range of the Elizabethville coal. These results showed that the presence of aromatic rings in a polybutadiene polymer resulted in the double bonds being more susceptible to oxidation by perchloric acid. This could result from just the presence of the rings or could be enhanced by the chlorination of the rings. Since the presence of aromatic rings in the kerogens of coals is highly probable and if double bonds in the kerogen were being attacked, then the dissolution of the kerogen should be similar to the dissolution of the polybutadiene-styrene copolymer.

As the molar ratio of oxygen to carbon decreased, the range of boiling points of perchloric acid solutions, over which dissolution occurred, increased. This is shown in Table 2. The obvious implication would be that as the oxygen content dropped, the available ether linkages that could be attacked would also drop. Each increase in the dissolution range was accompanied by an order of magnitude decrease in the oxygen to carbon ratio.

Table 2. Molar O/C Ratios and Dissolution Ranges for Coal Samples

coal	molar O/C	Dissolution Range (b.p HClO ₄)
Elizabethville	0.0051	190°C to 203°C (2nd)
Charming Creek	0.088	180°C to 190°C
Illinois #6	0.19	160°C to 170°C
Mequinzenza	0.14	160°C to 170°C

CONCLUSIONS

The results of this study indicated that kerogens which contain a large amount of oxygen were dissolved by boiling perchloric acid solutions when ether oxygen was attacked. However, as the oxygen content of the kerogens decreased other bonds had to be attacked in order to dissolve the kerogen. For the kerogens in this study, the Illinois #6 coal, the Mequinzenza coal and the Green River oil shale were dissolved when aliphatic ether oxygen was attacked. The Charming Creek coal dissolved when carbon double bonds were attacked. The Chattanooga Shale and the first dissolution range for the Elizabethville coal were probably the result of the attack on aliphatic ethers, although the possibility of an aromatic-aliphatic ether has not been eliminated. The second dissolution range for the Elizabethville coal was probably due to the oxidation of carbon single bonds although the oxidation of carbon double bonds was a possibility.

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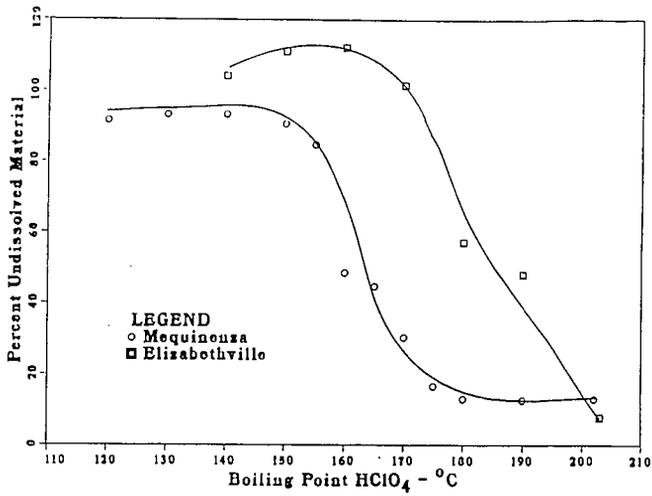


Figure 1. Dissolution Curves for the Mequinensa and Elizabethtown Coals

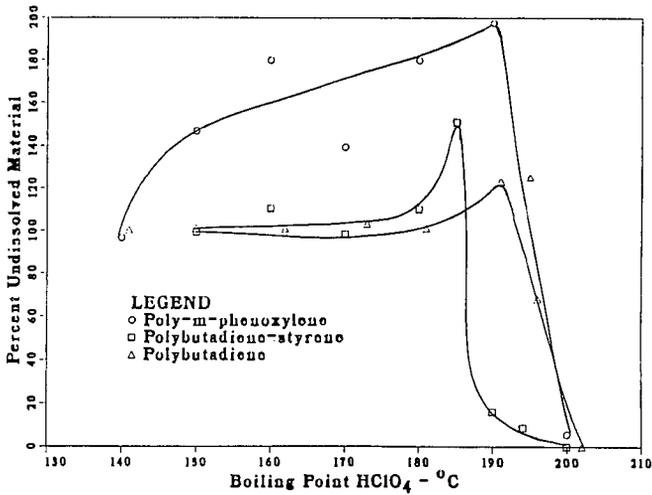


Figure 2. Dissolution Curves for the Model Polymers