

OXIDATIONS OF ILLINOIS NO. 6 COAL AT AND BELOW 60°C

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INTRODUCTION.-- The objective of our research program is to determine the nature of the singly-bonded connecting links between the condensed aromatic and hydroaromatic ring systems in Illinois No. 6 coal. Our approach has evolved as the work has progressed. We started with separate investigations of (1) the toluene-insoluble, pyridine-soluble (TIPS) fraction (about 2/3) of the 16% of this coal that can be extracted by pyridine and (2) the 84% that is insoluble. We have used the TIPS fraction as a model for the insoluble fraction and have investigated several cleavage reactions by changes in molecular weight, all at temperatures at or below 50° to avoid changes in the carbon skeleton. (1) We conclude that the number-average molecular weights (M_n) can be reduced to about 1/3 of the initial values by cleavage of ether and ester groups. However, such reactions have succeeded in dissolving only about 10% of the pyridine-insoluble fraction and therefore much of the effort described in this paper was directed toward dissolving, by oxidation, the maximum proportion of the pyridine-insoluble fraction with a minimum loss of carbon, for further chemical and spectroscopic investigation.

In the course of this work, we found that extraction of the pyridine-extracted coal with benzylamine ($BnNH_2$) at 100° would dissolve an additional 14% of the coal (on the original unextracted coal) and then that ethylene diamine + dimethylsulfoxide would dissolve an additional 15%, to produce extracts that were largely or entirely soluble in pyridine, and insoluble fractions that would swell to increasing extents in pyridine. This progress report also includes some oxidations of $BnNH_2$ -extracted coal, carried out with the idea that the smaller and less tightly crosslinked insoluble fraction should lose less carbon on oxidation.

The principal products of all of our oxidations are black acids, sparingly but completely soluble in water at pH 7 or above to give dark solutions, and almost completely insoluble at pH 3 or below. Other products are light-colored acids that are so soluble that they are difficult to separate from sodium chloride, and undissolved coal. Yields are given on the basis of carbon recovery and the loss is mostly, and assumed to be wholly, carbon dioxide.

EXPERIMENTAL.-- To minimize further oxidation of dissolved material, reactions were carried out in steps, at the ends of which the undissolved material was extracted with dilute aqueous base, often at 60°, with separations by centrifuging, until the washings became light-colored. The insoluble material was then reoxidized, but only after drying in the K-O-t-Bu experiments. All the soluble material was combined, filtered through a very fine fritted filter, concentrated at about 20 torr, acidified, collected, washed with very dilute HCl, and dried. Oxidations with oxygen were followed by oxygen absorption. (2) Oxidations with aqueous NaOCl (household bleach) were carried out with gradual additions of reagent to the bottom of the reaction tube, where the coarsest material would collect. The reaction in a 30° bath was followed by the amount of 5N NaOH required to maintain the pH at 13 (about 0.5 NaOH/NaOCl consumed), or by the self-heating on addition of NaOCl containing this proportion of NaOH in addition to that required to bring the pH of the NaOCl solution to pH 13.0. The rate of oxidations decreased as the spent NaOCl solution accumulated. In the HNO_3 oxidations, the acid was removed by water washing of the insoluble coal after each step and the soluble material was then extracted with aqueous base. The water-soluble organic products were recovered from the HNO_3 washings.

In general, the water-soluble acids were determined from the carbon contents of the dried acid-NaCl washings but in an experiment similar to NaOCl oxidation 3, this residue was methylated and the proton NMR was determined in chloroform: 26% methoxy, 38% other aliphatic, 21% benzyl and 15% aromatic. When these results are recalculated, substituting H atoms for methyl in methoxy, these acids would contain 11% carboxyl and phenol hydrogen atoms, and a little more aliphatic than benzyl plus aromatic hydrogen atoms. Further, a few milligrams of nearly colorless oil was isolated from the esters by microdistillation; microanalysis gave 48.36% C, 5.23% H, 1.1% N, and H/C = 1.29.

This H/C ratio is surprisingly low for methyl esters of an acid containing mostly aliphatic and benzyl groups and is consistent with earlier suggestions that Illinois No. 6 coal (3) and Wyodak solvent-refined coal (4) contain condensed alicyclic rings.

Rates of Oxidation.-- Rates of oxidation depended on the state of subdivision of the extracted coal, -325 U.S. mesh with pyridine-extracted coal, -60 mesh with BnNH₂-extracted coal. However, the finest material would oxidize first and fastest and the coarser residue with BnNH₂-extracted coal was often dried and ground between steps. Rates are compared in Table 1.

The initial reaction of 0.7M NaOCl with wet pyridine-extracted coal at pH 13 and 30°C is obviously exothermic and too fast to measure conveniently. The next fastest oxidation is with oxygen and K-O-t-Bu in dimethyl sulfoxide (DMSO) at 30° but this rate depends on the amount of base present. The rates of oxidation decrease as the base is consumed and eventually reach a nearly constant rate, about 0.25 mmole O₂/hour in 21 g of DMSO solution, nearly independent of the amount of coal left in suspension between 0.1 and 1.0 g. The rate is restored to as high as 20 mmole O₂/hr by addition of more K-O-t-Bu. However, most of the black acids produced are insoluble in DMSO and must be washed out with water. Then the insoluble coal must be dried before the next step.

Oxidations with oxygen in suspension in water at pH 13 and with 34% nitric acid are next fastest. Slowest are oxidations 6 and 7 with oxygen in pyridine with azobis(2-methylpropanitrile) as initiator and t-BuO₂H as promoter. (2) These oxidations are self-retarding.

NaOCl No. 21 and oxygen No. 8 were run with different portions of the same dispersion of pyridine extract in water. The TIPS fraction was dissolved in pyridine and precipitated by water, then washed with water and collected by centrifuging. The NaOCl oxidation was fast. The oxygen oxidation was slow and became slower; after three steps, 52.3% of the C remained undissolved and 11.1% had been lost as CO₂. The recovered TIPS fraction was redispersed in water by way of a pyridine solution and then oxidized much faster and nearly completely, with little loss. The significance of these results is not clear.

Products of Oxidation.-- Products of oxidation are described in Table 1. In discussing the relations between the oxidizing agents and conditions and the products of oxidation, several factors should be considered.

(1) Substrate. With both NaOCl (20 and 23) and O₂ (2 and 9), BnNH₂-extracted coal gave less black acids and more losses than pyridine-extracted coal. The TIPS fraction of pyridine-soluble extract reacted more completely and gave higher yields of black acids than the extracted coal with either oxidizing agent.

(2) Basicity. NaOCl appears to react by two mechanisms (3), a selective high-pH reaction of acidic hydrogen whose rate increases with pH and toward which the black acids are relatively stable, and an unselective low-pH reaction that involves a large variety of organic substrates, including black acids, and ends with oxidation-stable carboxylic acids. The selective mechanism probably involves hypochlorite ion, the other, unionized HOCl, chlorine, or the intermediate in the NaOCl-NaClO₂ disproportionation. (3) The rate of oxidation of a water suspension of extracted coal with oxygen also increases with pH near pH 13 and becomes very fast in DMSO in the presence of K-O-t-Bu.

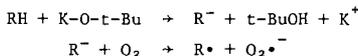
(3) Yields of Black Acids. Superficially, all the black acids are similar in color and solubility. The yields are limited by the amount of coal that oxidizes sufficiently to dissolve in weak base, the loss of carbon, presumably as CO₂, and their lower resistance to further oxidation by NaOCl below pH 12.

(4) Composition of Black Acids. As has been shown elsewhere (3), the extensive oxidation of pyridine-extracted coal by NaOCl at pH 10 (No. 3) results in a large increase in carbonyl, a preferential loss of aromatic carbon, and a large increase in H/C in the black acids formed. In black acids formed with less loss of carbon, changes in H/C ratios and in solid state ¹³C NMR spectra are smaller, but the product of HNO₃ oxidation 1 has the most aromatic and carbonyl carbon, the least ether and alcohol carbon, and by far the lowest H/C ratio, showing preferential destruction of aliphatic material. A NaOCl product like 20 and the DMSO product 11 are almost identical by NMR, but the latter product has the higher H/C ratio, indicating preferential loss of aromatic material. In oxidations of the pyridine-soluble extract, neither oxidation 8 or 21

resulted in much change in H/C, at least partly because of low loss of CO₂.

MECHANISMS.-- Oxidations in pyridine of both pyridine-extracted coal and the TIPS fraction of the extract with free-radical initiator and added t-BuO₂H (to restrict termination reactions to t-BuO₂• radicals) (2) is slow, incomplete, and inefficient in cleaving coal molecules or fragments. In the conventional free radical-chain mechanism, the -CH₂- and -CH₂O- links are much less reactive than the hydroaromatic and polynuclear structures (5).

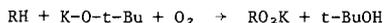
The mechanism proposed for the oxidation of coals in aqueous NaOH at 50 to 100°C by Kapo and Calvert (6) appears to be applicable to our oxidations in with K-O-t-Bu. The initiating steps are:



The two-step chain cycle is then:



but each cycle also requires an equivalent of base in the production of the required R⁻ by the first initiating step. The net result for the initial stage of the oxidation is:



However, for breakage of C-C bonds, further and more complicated steps are required.

We have proposed (3) that aromatic rings with phenol groups are most susceptible to attack by NaOCl at pH 13. Similar reactions may also be involved in oxygen oxidations with strong base.

SUMMARY.-- The Introduction showed that Illinois No. 6 coal can be largely converted to soluble material by cleavages at ether and ester bonds, without loss of carbon, at or below 50°C. For further breakdown of connecting links in both dissolved and undissolved fractions, several oxidation methods are effective at 30 to 50°C. Aqueous NaOCl gives the fastest and most complete reaction and some of the lowest losses as CO₂. 34% nitric acid is most selective in attacking aliphatic material (connecting links); the yield of black acids can probably be improved by use of more and shorter oxidation steps between separations of oxidation products. The highest selectivity in the removal of aromatic material was in NaOCl oxidation 3 at pH 10, but with high loss of carbon. Oxidation with K-O-t-Bu in DMSO also appears to remove aromatic material preferentially but the change in H/C ratio is limited by low formation of CO₂.

Selective oxidation at low temperatures appears to have great potential for making coal soluble at low temperatures for further investigation, with only 10 to 20% loss of carbon, either by preferential destruction of connecting links or of key rings in condensed systems (perhaps leaving most of the aliphatic connecting links intact). A combination of F₃C-CO₂H, H₂O₂, and H₂SO₄ is notable for removing aromatic material from coal (6), but its potential in making coal soluble with minimum loss of carbon is unknown to us.

ACKNOWLEDGEMENT.-- This research was supported by the U.S. Department of Energy through the Pittsburgh Energy Technology Center under Contracts No. ET-78-C-01-3293 and AC22-78ET11423. Discussions with the Contract Monitor, Dr. Sidney Friedman, have been helpful.

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TABLE 1

OXIDATIONS OF COAL FRACTIONS IN WATER SUSPENSION
(except as noted)

experiment No.	21	3 ^a	20	22 ^b	23	9	11 ^c	7 ^c	2	6 ^c	8	1
Coal fraction	Pyridine extract	Pyridine-extracted	Pyridine-extracted	Benzylamine-extracted	Benzylamine-extracted	DMSO	Pyridine	Pyridine-extracted	Pyridine-extracted	Pyridine-extract	Pyridine-extract	Pyridine-extracted
Oxid. agent	←	←	←	←	←	←	←	←	←	←	←	←
Solvent	←	←	←	←	←	←	←	←	←	←	←	←
Temperature, °C	←	←	←	←	←	←	←	←	←	←	←	←
Initial concn.	←	←	←	←	←	←	←	←	←	←	←	←
coal, g/ml	←	←	←	←	←	←	←	←	←	←	←	←
Steps	3	6	5	2	5	10	4	1	6	1	5	3
Average pH	12.9	10.1	12.9	11.0	13.1	12.9			13.2		12.9	
Reac. time, hr	3.2	2.3	5.3	30	>10	286	12	100	75	32	110	>6.5
Maximum rate	>2	>12	>5	>0.4	>8	0.8	7	0.14	1	0.1	0.3	>0.05
% of initial C in black acids	93.4	43.0	73.3	72.3	65.3	48.8	69.4	6.8 ^e	68.0		80.0	64
H ₂ O-sol. acids undissolved	5.8	7.6	7.9	8.3	3.9	3.1	4.9		5.2		3.1	11
lost	~0	42.1	11.5	19.4	23.6	23.4	10.4	1	11.1		2.3	1
Analyses of black acids									15.7		14.6	24
% C	59.4	46.3 ^f	65.1	54.4	58.8	65.5	62.1		67.8		73.6	55.9
% H	3.66	3.14	3.79	3.30	3.72	4.11	4.07		4.42		4.80	3.04
% N	1.47	1.35	1.61	0.60	1.85	1.58	1.61		1.40		1.60	4.96
% Cl	5.55	6.36	4.69	<0.05	7.03							
% ash	5.2	9	1.43	11.4	8.9						3.5	36.1
%(O+S) by diff.	20.7	>34	22.4	30.3	19.6	28.8	32.2		25.9		16.6	0.659
(H + Cl)/C	0.734	<0.95	0.718	0.723	0.794	0.748	0.772		0.777		0.777	
Oxidizing agent consumed												
mmole/g coal fractions used	15	30	21	11	20	5.63	9.83	3.4	4.44	2.0	3.38	
% C	74.9	72.5	75.5	65.1 ^b	76.0	76.0	73.8	75.6	79.5	74.9	73.5	
% H	4.73	4.44	4.44	3.79	4.76	4.76	4.52	4.46	5.41	4.73	4.52	
% N	1.90	2.10	1.58	1.61	2.36	2.36	2.19	1.72	2.36	1.90	2.16	
H/C	0.752	0.730	0.731	0.718	0.746	0.746	0.746	0.729	0.703	0.752	0.733	

^a Reference 3. ^b Started with black acids from oxidation 20. ^c Oxidations 6 and 7 in pyridine with 0.06M ABN and 2M or 1M t-BuO₂H, respectively; 11 in DMSO with K-O-t-Bu. In mmoles O₂ (or equivalent)/g coal/hr. ^d Mn = 991; neutral equivalent = 394.