

DISSOLVING COAL AT MODERATE TEMPERATURES AND PRESSURES

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Introduction

The objective of the research reported here was to determine the kinds and proportions of breakable C-C and C-O bonds in the connecting links between the condensed systems in coal. Such information should tell us about the possibility of coal liquefaction under mild conditions. The kinds and proportions of C-O and C-C bonds were investigated by cleavage reactions. Cleavages of C-O bonds in esters and ethers by strongly basic amines, iodides, and acids are discussed first and then our results on the distribution of oxygen in coal are compared with the results of other workers. We then discuss the cleavage of C-C bonds in connecting links by oxidations of coal fractions and some differences among the oxidation products. In terms of C-C bonds to be broken by oxidation, the principal problem is determining whether the condensed aromatic systems are joined by single or multiple methylene groups. Our conclusions are compared with some in the literature. This paper is an expansion of a previous presentation.(1)

The above findings and conclusions are the foundation for a new program to prepare a coal product on a laboratory scale at a moderate temperature and pressure that will melt or dissolve in a cheap solvent at or below 100°C. Ash can then be removed and the product can be used as a clean fuel or processed more easily than coal to a liquid fuel. A progress report will be made.

Coal Preparation: Extraction of Coal With Pyridine

All of the work reported here was done with a beneficiated Illinois No. 6 coal, obtained from Pennsylvania State University as PSOC 25. This dried coal contained 76.0% C, 4.88% H, 1.46% N, 2.17% S, 1.71% ash, and 13.8% O by difference. Much of the work reported in this section was carried out with soluble coal fractions so that changes could be followed by number-average molecular weights (\bar{M}_n). Some of these fractions were prepared by extracting our coal exhaustively with pyridine at 100°C. About 16% dissolved, apparently without chemical reaction. About one-third of the pyridine-soluble material was soluble in toluene; it contained more hydrogen and less oxygen than the toluene-insoluble, pyridine-soluble (TIPS) fraction, which is a useful model for coal and was used in much of our work. The TIPS fraction is heterogeneous in molecular weight and chemical composition. One TIPS fraction of \bar{M}_n 1100 (by vapor-phase osmometry) was fractionated by GPC; 76% of the total had \bar{M}_n in the range 550-1550. After hydrolysis of a TIPS fraction by alcoholic KOH, the products were easily separated into fractions of \bar{M}_n 350 to 1430, H/C ratios (a measure of aromaticity) of 0.98-0.74, and with different proportions of aromatic hydrogen.

Reactions of Coal Fractions With Amines

Strongly basic amines have long been known to dissolve more coal than pyridine.(2,3) We now attribute the high solubilities of coals in these solvents to chemical cleavage of C-O bonds in ester and ether groups. This conclusion comes from reactions of both TIPS and pyridine-extracted coal with BnNH_2 . After these reactions, most of the free BnNH_2 was removed by vacuum distillation and the rest by washing with dilute aqueous HCl; the latter was then extracted by aqueous ammonia. Table 1 shows that close to one molecule of BnNH_2 becomes bound to the TIPS for each cleavage reaction or additional molecule formed. With both TIPS and pyridine-extracted coals, the extents of reaction increase with the severity of treatment. For the pyridine-extracted coal, we do not know how much BnNH_2 is incorporated per cleavage, but if the ratio is 1, there is about 350 in molecular weight units associated with each bound BnNH_2 .

The amine extracts from long reactions of coal at 100° are apparently true solutions, but they become partly insoluble on drying. Thus, one EDA extract was

centrifuged and dried at 76° and 1 torr, but then only 90.5% was soluble in EDA and only 24% was soluble in pyridine on repeated extractions. In a BnNH_2 extraction, considered to be equivalent, the extract was centrifuged in an ordinary centrifuge. Another 1.5 hours at 30,000 g then produced no additional precipitate. Nearly all the solvent was then removed from the solution and 200 mL of pyridine was added to a 1-g sample. The total solubility in Table 2 is consistent with other extractions but the high solubility in pyridine was unprecedented. We think that this high solubility is due to the omission of the first drying, but the presence of a few tenths of 1% of BnNH_2 in the pyridine may also have had some effect. The drying may partly reverse the cleavage or cause condensation in other ways.

Other Cleavage of TIPS

Several other reagents, mostly halides or sources of halogen, but also acids and sodium, also cleave TIPS, presumably at C-O bonds as reported at the Houston meeting.(4) Table 3 gives the average numbers of molecules recovered from an original TIPS molecule, as measured by \bar{M}_n . After allowance for bound halogens, the carbon recoveries were usually 90-95%. We assume that the missing material was low molecular weight water-soluble or volatile material lost in the workup and therefore that the numbers in Table 2 are minimum values. However, to the extent that the products contain salts or other impurities (for which we have no evidence), the numbers in Table 2 are too large.

A TIPS fraction of \bar{M}_n 1283 was treated for 7-15 days at 90°C with hydrogen iodide in solution in pyridine, toluene, or water. By GPC, the high-molecular weight peak in the TIPS disappeared almost completely and was replaced by low molecular weight peaks. Similar but incomplete changes occurred in toluene and water. The reaction of HI in pyridine resulted in recovery of 4.4 moles of product per 1283 g of TIPS and incorporation of 3.03 g-atoms of iodine per initial mole of TIPS. From the iodine content of the product, we would expect 4.03 molecules of product, in good agreement with the \bar{M}_n data considering that there was 6% loss of carbon and that the iodide hydrolyses at room temperature.

Distribution of Oxygen in a TIPS Fraction

A TIPS fraction of \bar{M}_n 1090, by reaction with alcoholic KOH, contains ~ 0.8 ester group per average molecule and reaction with HI or ZnCl_2 gives ~ 1.2 additional cleavages per TIPS molecule. The phenol content corresponds to 3.5 oxygen atoms per average molecule. The net result is that these three functional groups account for 64% of the 14.4% oxygen in our coal. These results are compared with results of others in Table 4. The principal difference is that we report as esters what others report as carboxyl groups.

Although there is little doubt about the cleavage of ethers by hydrogen iodide, or of esters by amines, the cleavage of ethers by EDA and BnNH_2 has no precedent in the literature. We have treated model ethers with these amines for long periods at 100°C, sometimes in the presence of an equal weight of coal, but we have found no evidence of reaction with benzyl phenyl ether, dihexyl ether, 4-hexyloxyphenol, or trimethylene oxide. However, since the amines and the halides produce similar effects, we see no alternative to ether cleavage by amines. Perhaps the involvement of condensed aromatic nuclei or the uneven concentration of phenol groups(9) makes the coal ethers more reactive.

Oxidations of Coal Fractions

We reported most of our work on coal fractions at the Atlanta Meeting.(10) We aimed at maximum recovery of "black acids", slightly soluble in weak aqueous base, with minimum loss of carbon. We expected investigations of these black acids, made with different oxidizing agents, to give us information on breakable C-C bonds in coal. For oxidations, we used mostly extracted coals in suspension, and aqueous NaOCl or oxygen in water at pH 13, adding sodium hydroxide to maintain the pH, or a suspension in 15-35% nitric acid. We obtained 65-80% yields on carbon of black acids with the reagents named, with \bar{M}_n about 1000, and 12-20% loss of carbon. Five to 10% yields of water-soluble acids were also obtained. Although the nitric acid

oxidation products had the lowest H/C ratios (0.65 from 0.73 in pyridine-extracted coal) other differences among the black acids were not obvious.

Because the yields of black acids with the three main oxidizing agents were similar, we have compared the black acids with respect to molecular weight distributions and water solubility. We used both gel permeation chromatography (GPC) in dimethylformamide and high performance liquid chromatography (HPLC), starting the elution with 10 mL of 25% *n*-propanol in water, followed by neat DMF. GPC was done in a Waters column with 500 Å pores, packed in DMF. HPLC separations were done on a Hamilton PRP-1 column. With each column, the flow rate was 1 mL/min and a UV detector at 313 nm was used. Several known compounds were tested on the HPLC column: 2-naphthoic acid, trimellitic acid, pyromellitic acid, and phenyl benzoate eluted at 8-12 mL but everything else tested (mostly aromatic hydrocarbons, some with one oxygen atom) eluted at 24 mL or more. Thus the HPLC column is mostly a test for water solubility. The plots of UV absorption against retention time consist mostly of fairly sharp peaks with little absorption between well-separated peaks.

Results on 11 black acids are summarized in Table 5 arranged according to their origins. Several black acids from NaOCl oxidations of pyridine-extracted coal were combined, dissolved in dilute base, and fractionally precipitated by addition of hydrochloric acid. Sample F28D precipitated between pH 5.5 and 5.0, F29E between 5.0 and 4.66. As expected, by GPC 28-D contained more of the highest molecular weight (lowest retention volume) component at 5 mL and less of the lower molecular weight materials. Sample F29E suggests that the 5.0 mL GPC peak corresponds to the 4.3 mL HPLC peak, but the correspondence is poor with Sample F29D. We suspect that the 5.0 mL GPC peak is not as homogeneous as it appears and that the water-soluble components are polycarboxylic acids that are associated in DMF.

The 5.0 mL GPC component is the major GPC component in most of the black acids in Table 5. Exceptions are black acids T74B, U60B, and U85A, which show that degradations by sodium hypochlorite, 50% nitric acid, and Ce^{4+} are relatively severe. The most 5.0 mL component came from an oxidation with oxygen in water suspension at pH 13 and 50°C; this reagent is apparently the mildest and most selective of those that we have used. However, 35% nitric acid gave more lower molecular weight and water-soluble material without much sacrifice of carbon recovery.

By HPLC, five of the eleven black acids gave at least 46% of the 4.3 mL component and seven of the eleven have a 27.8 mL component that is either the largest or second largest component. Six of the black acids in Table 3 contain more than 70% of one component by either GPC or HPLC (underlined in the Table); two of them show more than 70% of one component on both columns. One of the latter black acids, T10B, represents 68% recovery of carbon in the coal fraction. Because of our high recoveries of soluble carbon and the different effects of oxidizing agents on the aliphatic and aromatic portions of coal, these chromatographic methods offer considerable potential for determining some average structures in unprocessed coal.

Oxidations with *m*-Chloroperbenzoic Acid (MCPA)

The objective of this work was to determine the proportion of single methylene groups as connecting links between condensed systems in coal. This problem evolved into a search for diaryl ketones in the black acid oxidation products of coal fractions. The diaryl ketones were expected to react with MCPA to convert them to esters, which were then saponified. The critical measurement is a decrease in \bar{M}_n on saponification of the esters. However, we could measure the \bar{M}_n only on the water-insoluble products that we recovered from the saponification; the water-soluble products were presumably the lowest molecular weight material. In three out of four experiments deserving consideration, there was a 2-9% increase in \bar{M}_n of the recovered acids. In one experiment, there was a decrease in \bar{M}_n from 410 to $^{n}391$, but these black acids represent only 18% of the carbon in a TIPS fraction that was oxidized with 50% nitric acid. We propose that this oxidation concentrated diaryl ketones in the black acids, but even then, their proportions were barely measurable by our MCPA method.

These results indicate that there are no important proportions of bridging methylene groups in our coal, but our method is insensitive. However, the next section shows that this conclusion is consistent with most of the evidence from the literature.

Cleavages in Diphenylalkanes

Literature data on breakdown of α,ω -diphenylalkanes are summarized in Table 6. These hydrocarbons are designated by the number of methylene groups that they contain. The first reference shows that with AlCl_3 and H_2 at 325°C , 1,3-diphenylpropane is most reactive, followed by diphenylmethane and diphenylethane. All the hydrocarbons with 0 to 4 methylene groups were cracked; the extents of reaction ranged only from 32 to 83%. The second reference indicates that 1 has the most reactive bond in coal because a very small yield of dihydroxydiphenylmethane, in which both aryl- CH_2 -aryl bonds were broken, was obtained. However, all the other references in Table 5 indicate that in the absence of AlCl_3 or BF_3 1 is the least reactive of these hydrocarbons and that there may not be much of this kind of bond present in coal anyway. Two references indicate that ether links break more easily than C-C bonds. In terms of bond energies, the phenyl-C bonds are strongest. In terms of our project objective, the C-C bonds that are breakable in conventional coal liquefaction appear to be mostly, perhaps entirely, in sequences of two or more methylene groups.

Summary and Conclusions

We have shown that 44% of the carbon in our beneficiated Illinois No. 6 coal can be dissolved by cleavage of ester and ether links by amines, acids, or iodides at 100°C and atmospheric pressure. Up to 80% of the remaining carbon can then be made soluble in weak aqueous base by oxidation at 60°C or below. One practical problem in coal liquefaction is now to try the use of cheaper reagents to break ester and ether links, and to determine what temperatures and pressures are required. Other practical problems are to reduce the consumption of base in oxidations with oxygen (pH 13 has been required) and to see if oxygen can replace part of the sodium hypochlorite or nitric acid used for oxidations. Some remarks on our progress are expected to be made at the meeting.

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Table 1

REACTIONS OF ILLINOIS NO. 6 COAL WITH EXCESS BnNH₂

Pyridine extraction → 18.1% sol. + 81.9% insol.

TIPS (toluene-insol., pyr.-sol.), yields corrected.

	% N	\bar{M}_n	Moles/1090g TIPS	TIPS BnNH ₂
No extraction	1.68	1090	1.0	0
24 h at 23°	2.79	534	2.0	1.1
9 d at 100°	3.31	379	2.9	1.7

Pyridine-insoluble, yields corrected (%N)

4 h at 23° → 1.3% sol.(4.36) + 97% insol.(3.49)

16 d at 23° → 7.3% sol.(4.12)

11 d at 100° → 45.7% sol.(5.11)+ 52% insol.(5.13)

Table 2

EXHAUSTIVE EXTRACTION OF ILL. 6 COAL
BY BnNH₂

	Carbon recoveries after correction for bound amine
Soluble in pyridine	42.7%
Soluble in BnNH ₂ , not in pyridine	1.5
Undissolved	54.2
Unaccounted for	1.6

Table 3

MOLECULES FORMED BY CLEAVAGE OF ONE MOLECULE TIPS
(mostly in pyridine solution)

Reagent	Molecules	Reagent	Molecules
ZnCl ₂	3.1	p-C ₇ H ₇ SO ₃ H	1.6
LiI·H ₂ O	3.1	Na in NH ₃ + BuNH ₂	1.6
ZnBr ₂	3.0	Me ₃ SiI	1.5
Pyridine·HI	2.7	LiClO ₄	1.4
MeI neat	2.0	HBr	1.3
Benzylamine	1.8	I ₂	1.1
BnMe ₃ N ⁺ I ⁻	1.7		

Table 4

OXYGEN DISTRIBUTIONS IN COALS

Coal	%C	daf	%O	Distribution of O, %					Ref.
				OH	C=O	CO ₂ H	Ether	Inert	
A	79.4		12.5	48	13	6	18	14	Blaumik HI 1962, 5
B	83.0		8.4	50	6	2	26	16	
C	88.0		4.0	30	5	0	40	25	
K-I	78.2		15.1	16	4	5	8	67	Wachowska OH change 1977, 6
K-II	81.1		11.7	11	4	4	5	76	
K-III	87.0		6.0		4	6	25	65	
K-N	87.9		4.5		8	8	61	23	
A	92.6		4.2			5	28	67	
Canadian	89.4		3.9	24		8	48	20	Wachowska 1979, 7
Ill. 6	82.5		6.7	36	6	10	42	6	Ruberto, 8 1978
Subbit.	77.3		16.2	35	6	27	6	26	
Ill.	76.0		14.4	36	ester	16	12	36	This paper

Table 5

FRACTIONATIONS OF BLACK ACIDS BY GPC AND HPLC

Black Acid No.	Origin		Yield ^a	Retention Times, min. ^b					
				GPC			HPLC		
T74B	TIPS	NaOCl	74	10.0 45	12.1 28	5.0 27	27.7 54	3.5 18	4.5 14
T57B	EDA extract		43	5.1 37	7.7 20	8.1 16	23.7 81	4.8 3	4.3 2
F28D	Pyr-extd. ^c			5.0 88	10.4 10	6.4 2	4.3 46	25.0 28	5.6 7
F29E	Pyr-extd. ^d			5.0 74	6.8 9	7.0 8	4.3 71	27.9 25	31.1 3
T33B	EDA-extd.		62	5.0 56	9.5 41	12.3 3	25.6 53	4.0 27	28.2 6
R56B	O ₂ in H ₂ O			5.0 90	7.1 5	9.9 3	24.9 33	3.8 22	4.1 22
T10B	EnNH ₂ -extd.		68	5.0 76	11.0 13	8.2 8	4.3 75	27.6 19	31.0 2
L23B	Pyr-extd.	15% HNO ₃	68	4.8 77	7.9 18	9.7 3	27.8 51	3.9 23	29.0 18
K23A		35% HNO ₃	64	5.0 53	7.7 32	10.0 15	4.3 62	27.9 36	31.0 2
U60B	EDA-extd.	50% HNO ₃	18	8.1 61	10.5 25	9.7 7	4.6 58	28.0 38	31.1 3
U85A	TIPS	Ce ⁴⁺	54	8.2 58	5.2 20	10.7 17	25.7 40	4.3 34	6.0 9

^a Yield of black acid from indicated substrate, on carbon.

^b The numbers on the second lines for each retention times are the percentages of the total products, as measured by an ultraviolet detector.

^{c, d} Combined black acids from NaOCl oxidations precipitated between pH 5.5-5.0^c or 5.0 to 4.66^d.

Table 6

CLEAVAGES OF Ph-(CH₂)_n-Ph

Reagent	Temp., °C	Order of reactivity for n values	Reference
AlCl ₃ + H ₂ in C ₆ H ₆ , 90 m	325	3 > 1 > 2 > 4 > 0	Taylor, ¹¹ 1980
PhOH + BF ₃	100	1	Heredy, ¹² 1981
Tetralin, 18 h	400	3 > 2, 4	Benjamin, ¹³ 1978
Tetralin + H ₂ 30 m	450	2 > 1	Vernon, ¹⁴ 1930
Excess tetralin	450	2 > 4 >> 1	Gronauer, ¹⁵ 1979
Decalin + H ₂ ± Ph ₃ SnCl, 1 h	<400 450	mostly ether splits 2, 3	Kuhlmann, ¹⁶ 1981
¹ H NMR		No significant amount of 1 in THF-soluble products	Liotta, ¹⁷ 1981
CO + H ₂ O, 1 h	400	3 > 2 > 1 Ethers split more easily	Takemura, ¹⁸ 1981