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IDENTIFICATION AND CLEAVAGE OF BREAKABLE SINGLE BONDS BY SELECTIVE OXIDATION, REDUCTION, AND HYDROLYSIS

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1. INTRODUCTION

We assume that bituminous coal consists mostly of an aggregate of condensed aromatic and aliphatic rings, connected and made insoluble (but swellable) by crosslinks containing single bonds. The objective of this project is to determine the proportions of the various kinds of connecting links and how they can best be broken--in other words, to determine the structure of bituminous coal, with emphasis on the crosslinks and breakable single bonds.

The program began with an investigation of the structure of the TIPS fraction of Illinois No. 6 coal, that is, the two-thirds of the 16% extracted by pyridine that is <u>t</u>oluene-<u>i</u>nsoluble, <u>p</u>yridine-<u>s</u>oluble, mostly through changes in molecular weight during cleavage reactions in pyridine solution. This work is described in an accompanying manuscript accepted for publication in *Fuel*. The most promising of these cleavage reactions are now being applied to the 84% of coal that is insoluble in pyridine and presents the main problem in coal liquefaction, following the progress of the reactions by formation of soluble material and swelling of the insoluble portion.

Near the end of the first year, we found that benzylamine ($BnNH_2$) would extract an additional 14% (of the original weight of coal) of material from pyridine-extracted coal, and later that an ethylenediamine/dimethyl sulfoxide (EDA/DMSO) mixture would dissolve another 21% of the original coal. The $BnNH_2$ extracted is soluble in pyridine. Our best present guess is that the $BnNH_2$ extract cleaves most of the ester groups in coal and that EDA/DMSO cleaves the remaining ester and most of the ether groups.

Our investigations of solvent extractions of Illinois No. 6 coal are summarized in a note to *Fuel*, which also accompanies this report. (This manuscript was submitted in February, but no response except a notice of receipt has been received.) A manuscript comparing the properties of the pyridine, $BnNH_2$, and EDA/DMSO extracts and extracted coals is nearly complete; preparation of another, comparing the oxidations of these fractions, has begun. Our immediate objective is to complete preparation of these last two manuscripts for publication and to present our conclusions on the proportions of the various kinds of connecting links in Illinois No. 6 coal.

2. SUMMARY

This section summarizes the results obtained during the past quarter and serves as an index to the details in the rest of the report.

Section 3 and Table 1 list the code numbers, origins, and analyses of the starting materials and products discussed in this report.

Section 4 describes: (1) a new pyridine extraction of whole Illinois No. 6 coal; (2) the fractionation of the pyridine-soluble fraction, both to provide working material; (3) an exhaustive extraction of the whole coal with EDA; and (4) the swelling of EDA/DMSO-extracted coal by mixtures of solvents. Item (3) shows that, when air is excluded carefully during the extractions, EDA extracts 3% less soluble material and the extract contains less oxygen. Item (4) shows that the EDA/DMSO combinations show the largest effect of supplemental solvent.

Section 5 brings together several small efforts directed toward cleaning up the breakable single bond problem. Some model ethers are not cleaved by EDA under extraction conditions. A few others will be tried. Oxidation of diaryl ketones with m-chloroperbenzoic acid and saponification of the resulting esters is promising for identifying diaryl ketones. Treatment of a black acid with pyridine hydroiodide reduced the acid's molecular weight and increased considerably its solubility in pyridine, but treatment with ZnI_2 was relatively ineffective.

Section 6 shows that, in comparison with 0.1 M $K_2S_2O_8$, 0.01 M persulfate is relatively ineffective in accelerating oxidation of $BnNH_2$-extracted coal in water suspension.

Section 7 describes the work planned for the next quarter.

Section 8 is a revised index to this and the previous 11 reports.

3. CODE KEY AND SUMMARY OF ANALYSES

Table 1 lists the elemental analyses of the substrates and products referred to in this report. Designations are by notebook and page numbers.

Several $\bar{M}_n$ determinations were made using vapor pressure osmometry (VPO) and are noted in the table with a superscript c to distinguish them from previous results in pyridine. N-Dimethylformamide was used as the solvent at 88°C. The solvent change was made because DMF is a better solvent than pyridine for black acids.

4. EXTRACTIONS AND FRACTIONATIONS OF COAL PRODUCTS

4.1. Pyridine Extraction

To obtain more coal fractions, especially more toluene-soluble material, whole coal was extracted and fractionated as summarized in Figure 1, where weights are in grams of carbon. After treatment with pyridine, each fraction was washed with aqueous 3 M HCl, aqueous 3 M NH_3,

TABLE 1

ANALYTICAL DATA FOR COAL FRACTIONS

Code Number	Description		Section Reference	Derived from Fraction	Yield Wt.%	% C^a	% H^a	% N^a	% Other	H/C	$\bar{M}_n$ VPO
4093-79-D	EDA/DMSO insoluble		4.3	11689-18-B	53.5	67.2	5.08	4.09		0.901	
90-A	EDA-insoluble		4.3	4336-26	49.7	69.7	5.03	5.22		0.860	
90-B	EDA-soluble		4.3	26	47.4	61.0	5.48	9.19		1.090	
91-A	EDA-insoluble		4.3	26	53.3	73.5	5.37	4.47		0.870	
4336-25-A-2	Pyr-insoluble, HCl and NH_3-treated		4.1	26	77.8	73.8	4.47	1.99		0.721	
26	Whole coal, 60-325 mesh		4.1	——	——	75.0	4.71	1.47^b	1.90S	0.730	
35-A-1	First TIPS, dry 25°		4.1	26	12.0	77.1	4.79	2.32		0.745	
35-A-2	First TIPS, dry 76°		4.1	26	10.6	77.5	4.74	2.25		0.734	
36-B	Sol.KOH/EOH		4.2	11689-28-A	34.7	75.5	4.51	0.76		0.717	
37-A	Insol. KOH/EOH		4.2	28-A	48.1	75.8	4.41	0.93		0.698	
39-B	Sol. aq. NH_3		4.2	28-A	0.5	10.25	3.71	11.64		4.34	
44-A-1	Second TIPS		4.1	4336-26	1.5	77.3	5.00	2.06		0.776	
44-A-2	After Soxhlet		4.1	26	1.0	76.0	4.75	1.46		0.750	
45-B	Toluene-soluble		4.1	26	4.8	69.5	6.90	1.07		1.19	
45-D	THF-soluble		4.1	26	1.4	50.1	6.30	2.14		1.39	
53-B	PhMe/TIPS extract		4.1	44-A-1	27.2	70.5	6.06	0.92		1.03	
53-C	THF-insoluble		4.2	11689-28-A	65.1	75.0	4.41	1.20		0.706	
53-D	THF-soluble		4.2	11689-28-A	28.2	70.2	5.85	1.40		0.992	
61-A	$(CH_3)_3SiI$-treated		5.2	4336-25-A-2	——	70.7	4.31	2.82	0.24·I	0.732	
64-B	Soluble in base, acid		4.2	11689-28-A	31.6	19.9	2.2	0.45		1.33	
69-C	Base-sol., acid-insoluble		4.2	28-A	13.4	70.7	4.72	2.14		0.802	
70-A	Base-insoluble		4.2	28-A	50.5	73.9	4.39	2.15		0.713	
4354-1-A	Insoluble	O_2 Oxidn. 16	6.2	11676-11-C	3.5^b	43.3	3.29	0.70		0.905	
1-B	Black acids		6.2	11-C	65.0^b	33.0	2.66	1.83		0.960	
1-C	H_2O-soluble acids		6.2	11-C	29.1^b	1.72	0.37	0.76		——	
4-B	Black Acids	O_2 Oxidn. 17	7.2	11-C	12.9^b	58.9	4.66	1.24		0.943	608^c
6-A	Insoluble	NaOCl Oxidn. 26	6.1	11744-30-E	5.8^b	5.97	0.47	0.14	1.34Cl	0.939	
6-B	Black acids		6.1	30-E	54.0^b	47.0	3.57	1.67	8.40Cl	0.904	359^c
6-C	H_2O-soluble acids		6.1	30-E	40.0^b	1.58	0.65	1.95			
7-A	Insoluble	NaOCl Oxidn. 27	6.1	11851-6-A	10.2^b	56.1	4.61	0.69		0.980	
7-B	Black acids		6.1	6-A	42.0^b	55.0	3.80	1.28		0.823	400^c
7-C	H_2O-soluble acids		6.1	6-A	19.8^b	0.75	0.03	0.15		0.456	
10-A	Insoluble	O_2 Oxidn. 18	6.2	11676-11-C	7.9^b	55.9	4.21	0.98		0.897	
10-B	Black acids		6.2	11-C	68.0^b	60.3	3.89	1.57		0.769	672^c
10-C	H_2O-soluble acids		6.2	11-C	4.5^b	0.30	0.52	1.82			
14-A	Pyr·HI, pyr-insoluble		5.6	11676-28-D	42.2	55.9	3.35	2.83		0.714	
14-B	Pyr·HI, pyr-soluble		5.6	28-D	55.9	50.8	3.02	0.81		0.707	345^c
15-A	$ZnCl_2$, pyr-insol.		5.6	28-D	81.9	58.0	3.48	2.59		0.714	
15-B	$ZnCl_2$, pyr-sol		5.6	28-D	12.7	60.5	4.61	3.36		0.908	
16-D	Methylation, Me_2SO_4		7.1	29-F	——	63.0	3.76	1.00		0.710	958^c
17-A	Methylation, Me_2SO_4		7.1	29-F	——	45.3	3.94	2.52		1.036	
17-B	H_2O extraction		7.1	4354-17-A	——	65.3	3.93	1.52		0.717	
19-A	Insoluble	NaOCl Oxidn. 29	6.1	11851-6-A	42.4^b	64.7	5.13	1.25		0.943	
19-B	Black acids		6.1	6-A	26.3^b	41.8	2.84	0.81		0.810	224^c
19-C	H_2O-soluble acids		6.1	6-A	8.8^b	0.48	3.24	11.05		——	
20-A	Pyridine-insoluble		5.6	11676-28-D	77.5	57.5	3.31	2.36		0.686	
20-B	Pyridine-soluble		5.6	28-D	14.9	61.1	4.28	2.83		0.835	632^c
25-A	ZnI_2 in pyridine		5.5	11689-28-A	99.3	72.3	4.52	2.18		0.744	
25-B	ZnI_2 in DMSO		5.5	28-A	100.0	70.4	4.61	1.70		0.780	775^c
31-A	Insoluble	NaOCl Oxidn. 30	6.1	11744-30-E	3.6^b	15.75	1.20	0.20		0.896	
31-B	Black acids		6.1	30-F	34.3^b	50.8	3.41	1.81		0.799	
31-C	H_2O-soluble acids		6.1	30-E	13.6^b	0.23				——	
11676-11-C	$BnNH_2$-extracted		6.2	11689-18-A	79.5	76.0	4.76	2.36		0.746	
28-D	pH 4.98	Precipitated Black Acids	5.6	Combined black acids	22.4	61.2	4.08	1.54		0.795	
29-F	pH 4.01		7.1		16.7	63.9	4.14	1.54		0.772	1004^c
11689-18-A	Pyridine extracted-coal		6.1	Whole coal	——	73.5	4.52	2.86	1.89 S^b	0.733	
28-A	Pyridine TIPS		5.5	Whole coal	——	76.7	5.00	1.68	1.65 S^c	0.782	1090
11744-30-E	Butylated 18-A		6.1	11689-18-A	——	58.9	4.57	3.69		0.925	
11851-6-A	Methylated 18-A		6.1	18-A	116.8	72.4	5.58	1.44		0.919	

[a] Mean of two determinations.

[b] Based on C content; other yields by weight.

[c] $\bar{M}_n$ determinations done in DMF at 88°C, all others in pyridine at 50°C.

and water, and dried at 76°C at <0.1 torr, except as noted.

Whole coal, 4336-26, was extracted with pyridine in a Soxhlet extractor until the extract was light in color. The extracts were concentrated, and TIPS Fraction No. 1 was precipitated with toluene. The oily solid was centrifuged, washed, and dried at 25°C to yield 2.15 g of the first TIPS fraction, 4336-35-A-1. An aliquot was dried further under vacuum at 76°C to give 35-A-2.

The 1:10 pyridine/toluene solution was concentrated to 25 mL. Toluene, 150 mL, was added to give more oily residue, which is the second TIPS fraction. This fraction was washed as before and dried at 25°C to give solid 4336-44-A, which was then Soxhlet-extracted with toluene to give solid 44-A-2 and an oil, 53-B.

The toluene solution from the second precipitation was concentrated to give 0.924 g of an oily residue, which was taken up in toluene, treated with aqueous HCl and washed with aqueous 3 M NH_3. The remainder was concentrated to ~10 mL and filtered through a medium glass frit to give, after drying, an oily residue, 45-B, 0.96 g. The solid on the frit was dissolved in THF and dried to give 0.345 g of 45-D.

Further fractionation of these fractions is described in the next section.

4.2. Fractionation of TIPS Fractions

TIPS 11689-28-A has been divided into subfractions by three methods, as indicated in Figure 2. One method (Minimum Saponification) involved extracting the TIPS fraction under mild conditions with dilute alcoholic base. This extraction should remove the more acidic groups from the rest of the TIPS fraction, with minimum saponification of esters,

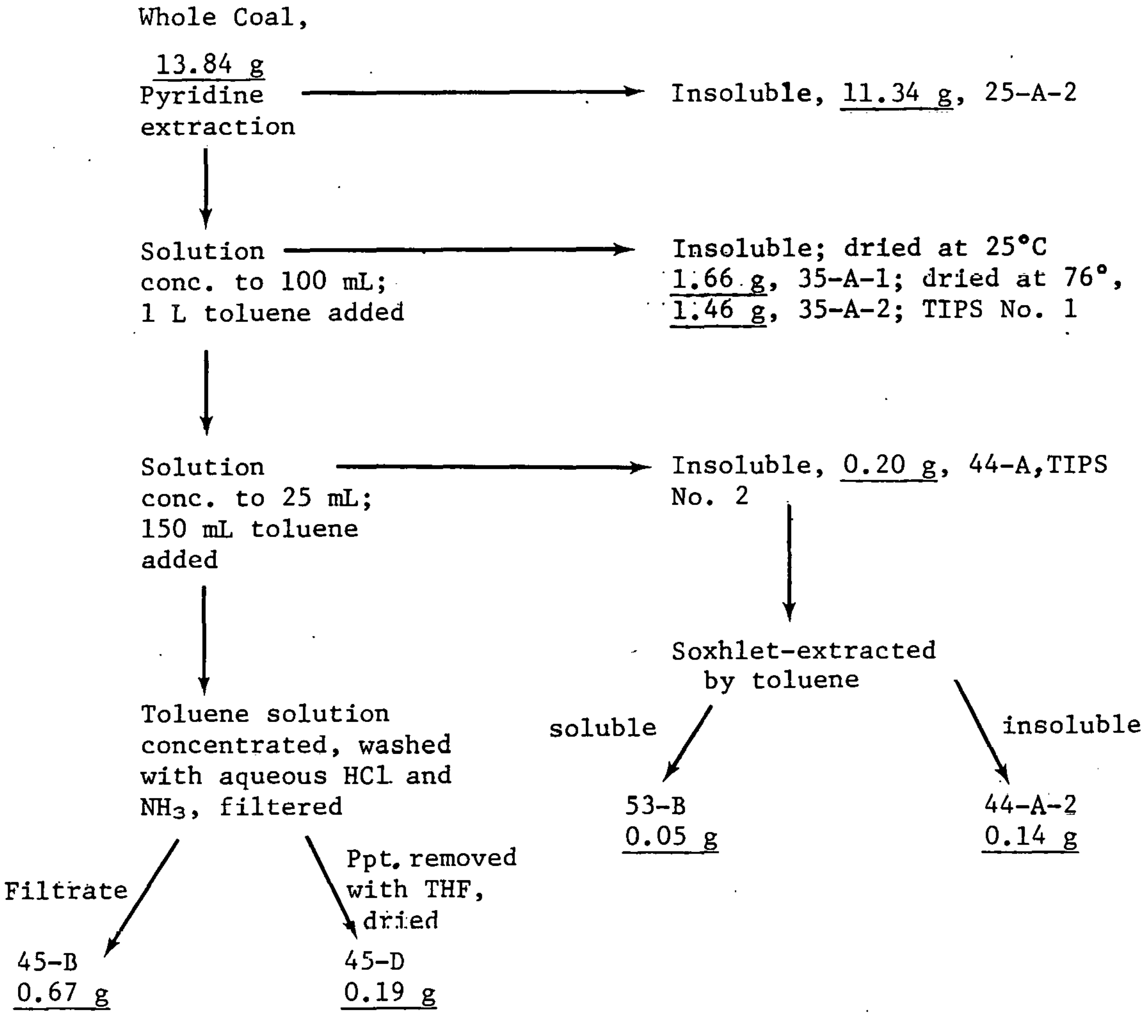

FIGURE 1. PYRIDINE EXTRACTION OF WHOLE COAL. All weights are in grams carbon. 13.84 g C in coal gave 2.51 g dissolved C + 11.34 g undissolved C.

and reduce the acid-base interactions in the coal fraction. Analysis of the products gave 34.7% of the carbon soluble and 48.1% insoluble in base, and 0.5% of the carbon was found in the salts.

In the second procedure (saponification),TIPS was treated with alcoholic base for 48 hours at 70 to 80°C. Under these conditions all of the ester and amide groups should be cleaved. The cleavage products were then divided into base-soluble and base-insoluble fractions. Analysis showed that approximately the same amount of base-insoluble material remained as in the previous experiment (50.5%). The base-soluble material contained 13.4% of the carbon and the salts contained 31.6%. The salts are presently being refractionated. Details follow.

A third fractionation separated TIPS into 34% THF-soluble and 66% THF-insoluble portions. The THF-soluble portion is convenient for separations by liquid chromotography.

Minimum Saponification Method. TIPS 28-A was subjected to five consecutive 5-minute extractions with 20 mL portions of 0.1 M KOH in ethanol. The extracts, all darkly colored, were neutralized immediately with 3 M HCl and combined. The solid residue was extracted three times with 10 mL portions of EtOH. Each of these extracts was colored. The extracts were added to the acidified EtOH solution

The acidifed extraction solution was evaporated to dryness under vacuum and treated with 3 M aqueous NH_3 to give a light orange solution and 0.47 g of a black residue, 36-B.

The solid residue from the basic extractions was acidified with glacial acetic acid, washed, and dried to give 37-A. All samples were dried at 76°C at <0.1 torr.

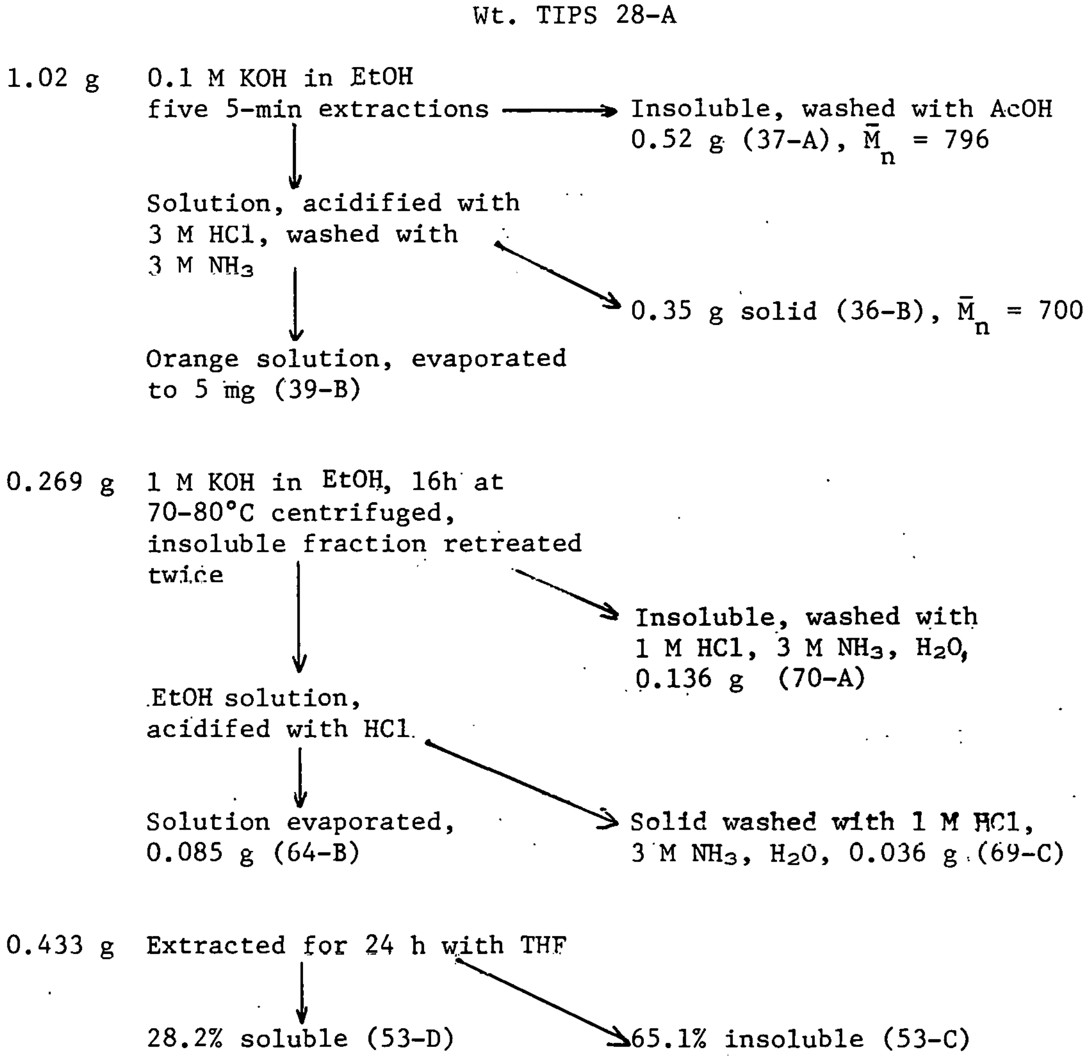

FIGURE 2. FRACTIONATIONS OF TIPS 28-A. All weights are in grams carbon.

Saponification Method. TIPS 28-A, 0.342 g, was treated with 25 mL of 0.1 M KOH in ethanol at 70-80°C for a total of 48 hours. The reaction mixture was centrifuged for 16 hours and separated into soluble and insoluble fractions. The proceedure was repeated two more times, until the base extraction solution was no longer strongly colored. Further work-up is summarized in Figure 2. The net result is recovery of 95.5% of carbon.

4.3. Extraction of Illinois No. 6 Coal with EDA

A previous extraction of Illinois No. 6 coal, 4336-26, by EDA, resulted in the incorporation of substantial amounts of oxygen (Report 9, p. 11). In a new extraction of whole coal, great care was taken to exclude oxygen from the reaction vessel and resulting solutions. The elemental analyses of the products, 4093-91-A and -B, show no oxygen incorporation (Table 1). However, less coal was dissolved in this extraction and fewer steps were needed to complete it (Table 2). Thus, slow oxidation brings more coal into solution, as has been noted previously with coal and pyrrolidine.*

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* F.R. Mayo, L.A. Pavelka, and John S. Zevely, manuscript submitted to *Fuel*.

Table 2

EXTRACTIONS OF ILLINOIS NO. 6 COAL (100°C)

Solvent	Solvent[a] (mL)	Time (hr)	Steps	Soluble	Insoluble	Total	Swelling Ratio[c]
EDA (Report 9)	360	203	7	90-B: 55.1 47.4[b]	90-A: 61.3 49.7[b]	116.4 97.1[b]	5.01
EDA (no O_2)	310	147	6	91-B: 51.5 44.5[b]	91-A: 57.3 53.3[b]	108.6 97.8[b]	4.63

[a] For an initial 1.0015 g of coal, 50 mL of solvent was used in each step and 10 mL for final transfer and wash.

[b] Corrected for bound EDA from excess N content.

[c] Weight of swollen centrifuged precipitate per dry weight of the insoluble fraction.

4.4. Swelling Ratios of Coal Samples

Before undertaking extractions of other coals, a standard extraction procedure is needed. To determine whether a mixed solvent would be advantageous by increasing swelling of extracted coals, samples of EDA/DMSO-extracted coal, 4093-79-D, were swollen with pyridine, EDA, and various proportions of solvent mixtures. The results are shown in Table 3. Each swelling ratio in Table 3 is the ratio is the weight of the wet centrifuged precipitate to the dry weight of the coal.

The largest effect of a second solvent is with the EDA/DMSO combination. A few other combinations will be tried.

5. EXPERIMENTS ON BREAKABLE SINGLE BONDS

5.1. Reactions of Ethylenediamine and Model Ethers

We have assumed that ethylenediamine extractions of coal result in cleavage of ethers, but recent experiments with EDA and model ethers have given no evidence of ether cleavages.

Benzyl phenyl ether, 0.56 g, 3.0 mmol, and 5 mL EDA were mixed in a vial under nitrogen and heated at 100°C for one week. A mixture of 1-methoxy-naphthalene, 0.5 mL, 3.4 mmol, and EDA was treated similarly. The reactions were monitored by observing the benzylic or methoxy protons in the NMR spectra of the mixtures, but no changes in these resonances were detected. To see whether phenol would accelerate the cleavages, 0.30 and 0.34 mmol, respectively, were then added to the benzyl phenyl and naphthyl methyl ether vials, which were then heated for another week at 100°C. No evidence of ether cleavage was detected.

The experiments were repeated, using equal portions of whole coal and ether in the ethylenediamine reaction vials. Again, the ether was recovered unchanged. An experiment is now underway to determine if EDA can cleave an aliphatic ether, n-butyl ether.

Table 3

SWELLING RATIOS OF EDA/DMSO EXTRACTED COAL

		Volume % of Cosolvent							
Solvent	Cosolvent	0	20	33	50	60	70	80	0%[a]
Pyridine	DMSO	4.45	4.87	5.32	5.09	5.32	5.10	5.26	4.43
EDA	DMSO	6.38	6.98	8.02	8.53	9.00	9.33	9.72	6.00
Pyridine	MeOH[b]	4.43	4.29	4.01	3.95	3.72			
Pyridine	Phenol[c]	4.52	5.40	5.56[d]	5.45	5.41			

[a] In original solvent after washing out cosolvent.

[b] Concentrations are subject to possible loss of MeOH during degassing.

[c] Proportions are by weight.

[d] 40% phenol.

5.2. Reaction of Pyridine-Extracted Coal with Me_3SiI

This experiment was undertaken to determine if the pyridine-insoluble fraction could be made more soluble by treatment with Me_3SiI, which should cleave both ester and ether linkages. Pyridine-extracted coal, 4336-25-A, 1.53 g, and 10 mmol NaI were suspended in 25 mL of MeCN under N_2. Me_3SiCl, 10.2 mmol, was slowly added to the reaction mixture, which was then refluxed for one week under N_2. the mixture was then quenched by addition of 25 mL of water, evaporated to dryness, washed with aqueous **thiosulfate** and then with water, and dried. Preliminary testing showed no increase in solubility in pyridine. The reaction was then repeated, using 9.4 mmol of ZnI_2 and 23.5 mmol of $(CH_3)_3SiCl$ in a mixture of 15 mL of pyridine and 10 mL of MeCN. This mixture was relfuxed for one week and worked up as before. The product was then treated with 1 M HCl, 3 M NH_3, and dried at 76°C to yield ~1.4 g of 4336-16-A. A Soxhlet extraction with pyridine is presently underway on a portion of 61-A, but the extract is only lightly colored.

5.3. Baeyer-Villiger Oxidations

An investiation has begun to find a convenient method of converting diaryl ketones to esters. This method should be useful in coal studies, since any esters thus formed could be hydrolyzed, breaking the coal network into smaller fragments. Aryl groups joined by two or more methylene groups are assumed to be cleaved more easily than diarylmethanes, probably to two separate arylcarboxylic acids, not susceptible to further cleavage. Treatment of benzophenone with m-chloroperoxybenzoic acid in dichlormethane converted the ketone to phenyl benzoate in >85% yield. Treatment of phenyl benzoate with 1 M KOH in EOH for

24 hours at 50°C resulted in saponification of ester. Thus, m-chloroperoxybenzoic acid appears to be a promising reagent to cleave carbon-carbon bonds in the coal network. It has been used to treat two coal fractions, 4354-10-B, an O_2 oxidation product, and 4336-7-B, a nitric acid oxidation product. Preliminary results in each experiment indicate an increased solubility of the coal fractions.

5.4. Reaction to Diphenylmethane with 15% HNO_3

To determine whether nitric acid might oxidize diphenylmethane to benzophenone, 1 mL of diphenylmethane was treated with 20 mL of 15% aqueous HNO_3 and stirred for 5 hours at 50°C. The organic material was extracted with ether to yield only diphenylmethane. Thus, it appears mild oxidations with nitric acid do not oxidize diaryl methanes to ketones.

5.5. Cleavage of TIPS with ZnI_2

TIPS fraction 11689-28-A, $\bar{M}_n$ 1090, was treated with ZnI_2 in pyridine and also in DMSO, to determine whether either if these combinations would be useful in cleaving ether bonds. The product from the reaction in DMSO, 4354-25-B, had a $\bar{M}_n$ of 775 in DMF. The $\bar{M}_n$ of the product from the reaction in pyridine, 3454-25-A, has not yet been determined. Both products will have $\bar{M}_n$ determinations done in pyridine so that they can be compared with products from other cleavage reactions.

5.6. Cleavage of Black Acids

Black acid samples 11676-28-D was treated with pyridine•HI and with $ZnCl_2$, both treatments in pyridine at room temperature, in efforts to improve solubility. Results are summarized in Table 4. With no cleaving agent, pyridine dissolved only 15% of the black acid, but after treatment with pyridine•HI, 56% of the black acid was soluble. $ZnCl_2$ has little or no effect (Table 4). The losses were associated with the water washes. The $\bar{M}_n$ of the pyridine-soluble portion from the pyridine•HI cleavage reaction, 4354-14-B, was 345, whereas the $\bar{M}_n$ from the pyridine extract, 4354-20-B, was 632. Thus, pyridine•HI effectively cleaves the black acids. The insoluble product from the pyridine•HI cleavage will be retreated with pyridine•HI in an attempt to increase solubility.

Table 4

CLEAVAGES OF BLACK ACIDS 28-D IN 30 mL PYRIDINE

Reagent	Pyridine	Pyridine•HI	$ZnCl_2$
Starting wt, g	0.5002	1.0096	0.5006
Reagent wt, g	none	0.5486	0.5129
Time, days	10	11	10
Soluble C, %	14.9 (20-B)	55.9 (14-B)	12.7 (15-B)
$\bar{M}_n$	632	345	
Insoluble C, %	77.5 (20-A)	42.2 (14-A)	81.9 (15-A)
Lost C, %	7.6	1.9	5.4

6. OXYGEN OXIDATION NO. 18

In oxygen Oxidation No. 16 of $BnNH_2$-extracted coal (11676-11-C) the rate of oxygen uptake was accelerated over that of other oxidations and less carbon was lost. ABN was used in the second step of the reaction to test its effect on the oxidation, and subsequent steps contained 0.1 M $K_2S_2O_8$ (Report 11, p. 13). Oxidation No. 18 was run with 0.01 M $K_2K_2O_8$ in all steps to determine whether this concentration of persulfate would accelerate the reaction sufficiently. No ABN was used, because it was incorporated into the products of the earlier oxidation. Both reactions were run with 100 mL of water at pH 13 and 50°C. Oxidation No. 18 was much slower than No. 16 and resulted in a much higher C loss (Table 5).

Table 5

OXYGEN OXIDATIONS OF $BnNH_2$-EXTRACTED COAL

	OXYGEN 16	OXYGEN 18
Sample wt, g	1.0056	0.9427
Reaction temp, C°	50	50
Reaction time, hour	63.75	120.70
Initiator	ABN 0.1 M $K_2S_2O_8$	0.01 M $K_2S_2O_8$
O_2 consumed, mmol	5.40	4.80
Number of steps	4	6
Carbon balance		
In initial coal, g	0.76	0.72
In black acids, %	65.0 (1-B)	68.0 (10-B)
In H_2O-soluble acids, %	29.1 (1-C)	4.5 (10-C)
Undissilved, %	3.5 (1-A)	7.9 (10-A)
Lost, %	2.4[a]	19.6

[a] Low loss due to ABN incorporation in soluble acids.

7. WORK PLANNED FOR AUTUMN QUARTER

To complete our manuscript (Section 1) on the distribution of breakable single bonds in coal, we assign high priority to the three main problems listed below along with our proposed approaches to them.

1. What does EDA do to coal if it isn't breaking ether links?
   a. determine the effect of EDA on TIPS at 25°C and 100°C*.
   b. Treat pyridine-extracted coal with HI; then see if EDA will extract more material than pyridine does at 25°C*.
   c. Hydrolyze TIPS with KOH/EOH to remove esters, then determine effects of HI, $ZnCl_2$, and EDA, separately.*
   d. Test some additional ethers for cleavage by EDA: Bn_2O, Bu_2O, HOC_6H_4OR.*

2. Obtain ^{13}C NMRs in solution on coal fractions to ascertain at least the aliphatic and benzyl H/C ratios. Oxidize soluble fractions, if necessary, to to make them more soluble.

3. Degrade coal fractions and black acids to increase their solubilities for ^{13}C NMR.

   a. Treat black acids further with peracids to remove more aromatic material and facilitate investigation of aliphetic portion.

   c. Oxidize the products of the EDA extraction of pyridine-extracted coal.*

In addition, we need to choose a reactive solvent for extractions of other representative coals. Candidates are ethanolamine, THF + $BuNH_2$, $BnNH_2$ + DMSO.

Fractionation of the pyridine extract of Illinois No. 6 coal (Section 4.2) will continue.*

Asterisks indicate work in progress.

8. INDEX TO REPORTS, OCTOBER 1978 to SEPTEMBER 1981. (References are to report numbers and page numbers)

EXTRACTIONS OF COAL	
Pyridine	1, 2; 3, 2; 4, 3, 6; 12, 3
$BnNH_2$	4, 4; 7, 14, 21
Pyrrolidinone	7, 20
N-Methylpyrrolidinone	8, 10
+EDA	9, 13
DMSO	7, 20; 11, 4
DMSO/$BuNH_2$	7, 20
Ethylenediamine (EDA)	8, 10; 11, 4; 12, 9
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NMR	11, 9
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with $BnNH_2$	2, 16
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