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Reactions of the Toluene-Insoluble, Pyridine-Soluble Fraction of Illinois No. 6 Coal*

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Illinois No. 6 coal was extracted with pyridine at 100° and the toluene-insoluble, pyridine-soluble (TIPS) fraction of the extract was used as a model for the 84% of insoluble coal. Various TIPS fractions had number-average molecular weights ($\overline{M}_n$) in pyridine of 980 to 1380 but were insoluble or only partly soluble in most other solvents. Elemental and ^1H and ^{13}C NMR analyses indicate an H/C ratio of only 1.3 in the aliphatic portions of the TIPS molecules. The TIPS fraction was treated with a variety of reagents and their abilities to cleave ether and ester bonds were measured by decreases in $\overline{M}_n$: $ZnCl_2 > LiI{\cdot}H_2O > ZnBr_2 >$ pyridine•HI > methyl iodide > benzylamine > alcoholic KOH > toluene sulfonic acid. Evidence for ester groups comes from saponification equivalents and the effects of alcoholic KOH and amines on $\overline{M}_n$. HI appears to cleave all the bonds that Na cleaves and more, suggesting that there are few diaryl ether bonds and more phenyl alkyl and benzyl ether than dialkyl ether bonds.

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DISCLAIMER

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 only single bonds. The objective of this work is to determine the proportions of the various kinds of single bonds and how they can be broken, i.e., to determine the structure of coal in terms of breakable single bond crosslinks and the average structures of the condensed systems. This approach requires low reaction temperatures, preferably 100°C or below, to avoid the pyrolyses common in practical liquifactions reactions. Our plan is to extract as much coal as possible with an inert (pyridine) or mildly reactive solvent (aliphatic amine) at 100°, then to dissolve the insoluble portion by chemical reaction with minimum loss of carbon. The soluble products are then investigated by chemical reaction, molecular weight change, and NMR.

About one-third of the 16% coal extracted by pyridine is soluble in toluene. However, as shown in this paper, the remaining toluene-insoluble, pyridine-soluble (TIPS) fraction has nearly the same composition as the 84% of insoluble coal and thus serves as a model for the main mass of coal.[1] This paper is concerned mostly with the cleavage of this TIPS fraction. However, extractions of the pyridine-insoluble fraction with benzylamine ($BnNH_2$) or with ethylenediamine (EDA) in dimethyl sulfoxide (DMSO) have yielded about 15% and 35%, respectively, of additional extract,[2] formerly attached to the coal network, but presumably containing fewer ester and ether groups. Investigation of these extracts and residues is in progress.

2. EXPERIMENTAL

2.1. General Remarks

The coal used in this work was beneficiated Illinois No. 6 (PSOC-026) from the Penn State Coal Data Base, reported to be 82% vitrinite (mean reflectance 0.54) on a dry mineral-matter-free basis. For the preparation of toluene-insoluble, pyridine-soluble (TIPS) fraction 35-A, a 200-g sample of -400 mesh coal was ground under nitrogen and extracted repeatedly with pyridine, and the extracts fractionated by our published method.[1] The TIPS fractions are discussed in Section 3.1.

In general, reactions were carried out under nitrogen. Solid products were separated by centrifuging and washed with a solvent as necessary. The soluble products and washings were concentrated and/or drowned in water to precipitate the products. Products from experiments with KOH or amines were routinely washed with 1N HCl. Nearly all products were dried for 2 hours in a heated Abderhalden drier at a vacuum of < .02 Pa (~0.001 torr) with sulphuric acid at room temperature as the absorbent. For early samples 1-D, 6-D, 13-A, 16-B, 17-A, B, 21-C to F, 24-A, 35-A, 39-A, B, 43-A, B, and 46-A, C, the heating agent was boiling xylene (140°); for other samples, the heating agent was usually boiling CCl_4 (76°) although (as noted) xylene was used to remove nitrogen bases or pyridine from pyridinium salts. However, at least part of these bases was removed by repeated washing with 1N HCl and water before drying. When the material balance was near or below 100%, analyses for nitrogen permitted corrections for bound N, but for higher recoveries of substrate, heating to 140^0 was usually employed instead or in addition. All dried samples were stored under vacuum or nitrogen. A sample of TIPS stored in air for 18 months showed a decrease in molecular weight from 1214 to 690 and an increase in oxygen content.

Number-average molecular weights ($\bar{M}_n$) were determined on a Wescan Model 233 vapor pressure osmometer (VPO) using pyridine at 50°C as solvent and 0.005M to 0.1M phenanthrene (Aldrich Chemical Co.) as a calibration standard. Each molecular weight is based on measurements at three concentrations. In general, plots of voltage versus concentration were straight lines with a least squares correlation coefficient $r^2 > 0.98$. Solutions for VPO analysis passed a 0.45 μm millipore filter without significant back-pressure or residue.

Concentrations of phenolic (and alcoholic if any) hydroxyl groups were determined by acetylation/saponification[3] or trimethylsilylation.[4]

All analyses are collected and coded in Table 1. To keep this paper within a reasonable length, experimental details for only the more important experiments are given below. Several experiments were repeated with essentially the same results; these are designated "(duplicated)."

2.2. Cleavage by Na in NH_3 + $BuNH_2$

The method of Lazarov and Angelova[5] was modified as follows. The blue solution formed by dissolving 0.5g (21 mmole) of sodium in 60 mL of liquid ammonia plus 10 mL of n-butylamine was added over 3 hours to a well-stirred mixture of 1.5g (1.1 mmole) of TIPS 35-A suspended in 30 mL n-butylamine at -35°. After an additional 2.5 hours, 2.1g of NH_4Cl was added and the mixture allowed to warm to room temperature under a slow flow of nitrogen. Then 15 mL of diethyl ether and one mL of water were added and evaporated to dryness. Butylamine was removed by repeated washings with 1N HCl. The dried product was 1.40g (93%) of 24-A, whose analysis is in Table 1. (Duplicated)

Table 1

Analytical Data for Coal Fractions

Sample No.	Description	Section Reference	Derived from Fraction	Wt % Yield	% C	% H	% N	% Other	% Ash	H/C	VPO Mol.Wt.
1-D	TIPS	2.5,2.8,3.1	Whole coal	3.8	79.2	4.83	1.79	1.64S	0.62	0.744	1250
4-A	Ether-extracted	2.5,3.2	35-C	68.5	55.2	3.35	1.50			0.724	856
6-A	Pyr·HI cleavage	2.5	28-A	88.5	72.4	4.75	1.89	5.15I		0.787	430
6-D	$(CH_3)_3SiI$ Product	4	1-D	113	63.3	3.92	1.30	19.0I 1.03Si		0.738	760
7-A	$ZnBr_2$ cleavage	2.6	28-A	118.8	67.6	4.40	3.04	15.7Br		0.776	428
8-A	$ZnCl_2$ cleavage	2.6,3.2	28-A	108	67.1	4.50	3.54	7.76Cl		0.804	379
9-A	$LiI \cdot H_2O$ cleavage	2.5,3.2	28-A	102	74.7	4.79	2.06	2.21I		0.769	363
13-A	Acetylated 35-A	2.7	35-A	116	78.5	5.06	1.77			0.767	1390
14-C	TMS-Pyr·HI Product	2.5	15-A	206	64.8	5.02	3.12	3.3Si		0.924	517
15-A	Pyr·HI Product	2.5,3.2	1-D	102	70.0	4.38	1.74	9.15I		0.746	462
16-A	TIPS + $ZnCl_2$/THF	2.6	28-A	92.7	74.3	5.18	1.64			0.831	596
16-B	Pyr-sol. Me ether	2.7	35-A	90	79.3	5.75	2.50			0.864	1280
17-A	Insol. $BnNH_2 + Et_2O$	3.3	35-A	76	79.6	5.16	2.54			0.769	1130
17-B	Sol. $BnNH_2 + Et_2O$	3.3	35-A	21	74.2	6.72	1.35			1.079	377
17-G	TIPS	3.1	Whole coal		77.9	5.15	1.74	1.65S		0.787	980
18-A	Pyr-ext. coal	3.1	Whole coal		73.5	4.52	2.16	1.89S	1.95	0.733	
19-A	Pyr.HI Product	2.5,3.2	24-A	110	74.7	5.70	2.19	3.39I		0.909	548
20-A	MeI Product	2.5,3.2	1-D	95.3	77.8	5.02	1.74	0.10I		0.768	660
21-C	Insol. $BnNH_2$ + MeOH	3.2	35-A	85	75.8	5.16	2.58			0.812	540
21-D	Insol. $BnNH_2$ + MeOH	2.4,3.2	35-A	49	76.3	5.24	2.59			0.817	
21-E	Sol. $BnNH_2$ + MeOH	3.2	35-A	50	79.8	5.64	3.84			0.842	
21-F	Sol. $BnNH_2$ + MeOH	2.4,3.2	35-A	51	75.1	5.68	3.16			0.902	
23-A	Tosic acid cleavage	3.2	17-B	83.6	76.5	4.99	1.62	2.26S		0.777	524
24-A	Ether split	2.2,3.2	35-A	93	76.5	5.76	2.43	1.51S	0.84	0.897	790
24-G	Pyr·HBr cleavage	3.2	17-B	83.4	75.5	4.97	1.98			0.790	616
28-A	TIPS	2.3	17-B		76.7	5.00	1.68	1.65S	0.57	0.782	1090
35-A	TIPS	2.3	Whole coal	10.2	78.2	5.13	1.80	1.72S	0.78	0.781	1380
35-C	I_2/pyr treatment	2.5,3.2	28-A	125	50.0	3.09	1.96	34.1I		0.737	602
36-A	$NaNH_2$ + MeI	2.7	28-A	93.7	71.9	4.98	2.24			0.824	446
36-B	$LiClO_4$ product	3.2	28-A	82.8	75.9	4.80	2.01			0.754	650
38-A	Acetylated 28-A, insol. H_2O	2.7	28-A	98.8	73.6	4.88	1.89			0.790	
39-A	Insol. $BnNH_2 + Et_2O$	2.4,3.2	35-A	74	77.3	5.01	2.17			0.772	995
39-B	Sol. $BnNH_2 + Et_2O$	2.4,3.2	35-A	21	78.7	6.26	2.23			0.948	350
39-G	$BnMe_3NI$ product	2.5,3.2	28-A	83.0	74.8	4.93	2.42			0.785	540
42-A	$ZnBr_2$ cleavage	2.6	28-A	102	70.5	4.76	3.06	13.08Br		0.810	392
43-A	Insol. KOH/EtOH	3.3	1-D	81.9	77.5	4.84	1.51			0.744	940
43-B	Sol. KOH/EtOH	3.3	1-D	12.3	56.0	4.14	1.16			0.881	420
44-A	Insol. KOH/EtOH	2.3,3.2,3.3	28-A	31.3	73.8	4.60	1.34			0.743	1427
44-D	Sol. KOH/EtOH, sol. EtOH	2.3,3.2,3.3	28-A	3.9	73.7	5.61	1.44			0.980	347
44-G	Sol. KOH/EtOH, ppt. by acid	2.3,3.2,3.3	28-A	40.5	75.7	4.85	1.12			0.763	791
46-A	Insol. KOH/EtOH	2.4,3.2	39-A	80	76.7	4.64	1.92			0.721	
46-C	Sol. KOH/EtOH	2.4,3.2	39-A	19.5	63.4	4.47	1.84		1.24	0.840	

2.3. Cleavage with Alcoholic KOH

The experiments described show that treatment with alcoholic KOH of our TIPS fraction not only reduces the average $\overline{M}_n$ of this fraction but permits its separation into at least three fractions. 0.5463 g of TIPS 28-A was heated with 10 mL of 5% KOH in alcohol for 24 hours at 100°C with the results shown in Table 2. The dissolved material was acidified with HCl gas and separated into soluble (44-D) and insoluble (44-G) fractions. 44-G had to be redissolved in a minimum of alcoholic KOH and reprecipitated with HCl to remove salts. On the two larger fractions, carboxyl contents were determined by the method of Blom et al.[3] These products were recovered and used to determine hydroxyl contents by acetylation with pyridine-acetic anhydride at room temperature (with 4-dimethylaminopyridine as catalyst[6]).

Only 75.7% of the original TIPS was recovered. The remainder that disappeared without being noticed must have been nearly colorless and water-soluble or volatile products of lower molecular weight than 44-D. Hence substantial cleavage occurred, presumably by ester saponification. The substantial increase in carboxyl groups in Table 2 also indicates ester hydrolysis. The smaller increase in hydroxyl groups may be associated with loss of material.

Table 2

PRODUCTS FROM KOH/EtOH TREATMENT OF TIPS FRACTION 28-A

	Sample Number			
	28-A	44-A	44-G	44-D
Solubility	Sol. pyridine	Undissolved	Soluble KOH/EtOH Insol. HCl/EtOH	Sol. HCl/EtOH
Yield, % by weight	(original)	31.3	40.5	3.9
$\overline{M}_n$ in pyridine	1090	1427	791	347
$-CO_2H$, equivalent/kg fraction	0.12	0.81	0.62	--
$-CO_2H$/molecule	0.13	1.2	0.49	--
-OH, equivalent/kg fraction	3.2	2.3	4.4	--
-OH/molecule	3.5	3.3	3.5	--

To determine the suspected ester groups, 0.5015 g of TIPS 28-A was treated under nitrogen with 5% KOH, 6.15 mmoles in 8.0 mL EtOH. Consumption of base was followed by quenching an aliquot in water, centrifuging, and titrating to pH 7 with 0.1N HCl. A blank on the KOH/EtOH was determined in the same manner. Twenty-five percent of the available KOH was consumed in 30 minutes at room temperature, associated with the blank and free phenols. Another 5% was consumed in the first 16 hours at 95°, and another 0.3% after 178 hours. The additional KOH consumption corresponds to a saponification equivalent for 28-A of 1400, again indicating the presence of ester groups. Heating KOH/EtOH for 178 hours at 95° without any TIPS gave no significant change in titer.

2.4. Benzylamine

An important reaction of $BnNH_2$ with TIPS 35-A is summarized:

1.457 g TIPS (35-A), $\overline{M}_n$ = 1380 + 25 mL $BnNH_2$

45 h at 25°, pour into 300 mL Et_2O

74% insoluble (39-A), $\overline{M}_n$ = 995 ↙ ↘ 19% soluble (39-B), $\overline{M}_n$ = 350

5% KOH in EtOH, 3 days at 25°

20% soluble (46-C), $\overline{M}_n$ = 570 ↓ → 80% insol. (46-A), $\overline{M}_n$ = 1250

A 74/19 mixture of 39-A and 39-B, dissolved in pyridine that was then removed, had a $\overline{M}_n$ of 628 compared with calculated 718 for the mixture and 1380 for the initial 35-A. From nitrogen analyses, the low 628 value could be due to residual $BnNH_2$ in the reconstituted material, but it seems clear that the bonds broken by benzylamine are not reformed when the products stand in pyridine.

Treatment of the insoluble fraction (39-A) with 5% KOH in EtOH resulted in fractionation, not cleavage, of this fraction. The weighted average $\overline{M}_n$ for 46-A and 46-C is 1010, essentially that of the starting material, 39-A, 995. A direct treatment of TIPS 35-A with alcoholic KOH for 70 min. at 100° gave nearly the same yields of products, but a treatment of 35-A with n-butylamine with drowning in methanol gave less (49%) insoluble fraction, 21-D, and more (51%) soluble material 21-F, reflecting differences in ether and methanol as solvents. Analyses are in Table 1.

2.5. Hydrogen Iodide and Iodides

Most of the cleavages in this and the next two subsections were carried out in pyridine solution, initially because of its excellent solvent properties. It was then found that the products made with iodides usually contained iodine and pyridine that could not be washed out, but most could be removed by heating to 140°C at 0.133 Pa (0.001 torr). The following explanation is proposed:

$$\text{R-O-R}' + \text{HI} \longrightarrow \text{R-I} + \text{ROH}$$

$$\text{R-I} + \text{C}_5\text{H}_5\text{N} \underset{\text{heat}}{\rightleftarrows} \text{C}_5\text{H}_5\text{NR}^+ + \text{I}^-$$

However, efforts to replace pyridine with other solvents were unsuccessful; a single exception with ZnCl_2 in THF is in section 2.6. Perhaps the pyridine assists the first reaction by removing RI.

A cleavage with pyridine hydroiodide in pyridine is summarized:

0.523 g TIPS 1-D($\bar{M}_n$ = 1250) + excess HI in 50 mL pyridine

6 days at 25°

↓

102% 15-A($\bar{M}_n$ = 462), 9.15% I, 0.33 equiv./mole

Reflux 32 h with hexamethyldisilazane in pyridine

↓

Me_3Si ether, 14-C ($\bar{M}_n$ = 517, calc. 541)

3.3% Si corresponds to 1.1 equiv. OH in 462 g 15-A

15-A contained 2.8 times as many molecules as 1-D (Duplicated). By the same Me_3Si procedure, TIPS 1-D contained 1.2 equiv. of OH/mol; thus 15-A contains 2.5 times as many hydroxy groups as 1-D, in remarkable agreement with the equations above.

A 0.173-g portion of sodium-cleaved TIPS 24-A (Section 2.2) in 5 mL pyridine was treated with 5 mL of a concentrated solution of pyridine hydroiodide in pyridine under N_2 at room temperature for 3 days. After the usual workup, the product, 19-A, weighed 9.6% more than the starting material and had a molecular weight of 548. This material incorporated less iodine than 15-A (3.4% versus 9%) and did not show as large a reduction in molecular weight. The results are discussed in Section 3.2.

Trimethyliodosilane is reported[7] to cleave alkyl and aryl alkyl ethers to alkyl iodides. Accordingly, we treated TIPS 1-D, as a slurry in chloroform, with this reagent for 24 hours at room temperature and then for 42 hours at 50°C. After workup and drying, the major product (6-D) was insoluble in chloroform and weighed 12% more than the starting material. 6-D contained 18.99% I and 1.03% Si, and it accounted for 90% of the carbon, 92% of the hydrogen, and 82% of the nitrogen in the starting material. The apparent $\overline{M}_n$ was 760. An 8.8% yield of chloroform-soluble material was also obtained.

Since the above reaction produces HI and since HI in pyridine cleaved TIPS, the reaction to produce 6-D may involve HI as well as $(CH_3)_3SiI$. Jung and Lyster[7] report that cleavages of dialkyl ethers with trimethyliodosilane proceed in the presence of pyridine but at a reduced rate. They take this as evidence against the involvement of HI, which is dubious in view of our results with HI in pyridine.

TIPS 1-D (M_n = 1250) was treated with an excess of MeI, without pyridine, under nitrogen for 2 days at room temperature, to see if evidence of cleavage of sulfide bonds could be obtained. The washed and dried product, 20-A, weighed 95.3% as much as the starting material, contained 0.1% I, and had a $\overline{M}_n$ of 660. The original TIPS contained 1.64% S or 0.64 S/molecule. If all of these S atoms were sulfides split by MeI, the $\overline{M}_n$ of 1-D would have been reduced to 760. Because most of the S is probably aromatic and heterocyclic, the MeI is cleaving links other than aliphatic sulfide links (e.g., amines) and is unsuitable for estimating such links. (Duplicated.)

Harrison[8] reported that alkyl aryl ethers are cleaved by lithium iodide, and so we tested this reagent on our TIPS fraction. 0.3513 g of TIPS 28-A was treated with 0.2342 g of $LiI \cdot H_2O$ in 20 mL of pyridine under nitrogen for 140 hours at room temperature. The 0.3594 g of product, 9-A, was obtained in 102% yield by weight. The $\overline{M}_n$ of 28-A was reduced from 1090 to 363 but it was high (4%) and variable in nitrogen content. 9-A was therefore ground, rewashed with HCl and water and dried further at 76° and 0.001 torr. Here it lost weight slowly and persistently and approached the expected N analysis, apparently by decomposition of pyridinium salts.

To avoid difficulties with pyridine, a similar experiment was carried out with 28-A, $LiI \cdot H_2O$, and tetrahydrofuran, but there was no significant change in $\overline{M}_n$.

Similar experiments were carried out with 28-A in pyridine for 3 days at room temperature with benzyltrimethylammonium iodide or iodine. One employed 0.254 g of 28-A and 0.1827 g of quarternary iodide, the other, 0.4143 g of 28-A and 0.3052 g of I_2. The benzyltrimethylammonium iodide product (39-G) was obtained in 83% yield, contained a little excess nitrogen, and had a $\overline{M}_n$ of 640. The iodine product, even after washing with chloroform, ether, and 0.1M HCl, gave 125% yield of 35-G containing 34% iodine. Continuous extraction of 35-G with ether removed I_2 corresponding to 28% of 35-G; the resulting 4-A had a $\overline{M}_n$ of 866.

2.6. Zinc Salts

Two cleavage experiments were carried out with anhydrous $ZnBr_2$ and then it was found that $ZnCl_2$ was as good or better. All the cleavages were carried out under nitrogen and the first three products contained excess weight and nitrogen, as shown in Tables 1 and 3, and analyses were poorly reproducible.

Table 3

Cleavages of TIPS 28-A in Pyridine with Anhydrous Zinc Halides

28-A[a] mg	Zn Halide mg	Pyridine mL	Time h	Temp. °C	Product	$\overline{M}_n$
376	Cl 232	20	140	25	108% 8-A	379
367	Br 260	20	68	25	119% 7-A	428
227	Br 200	39	68	50	102% 42-A	392
477	Cl 477	20[b]	192	25	93% 16-A	596

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[a] $\overline{M}_n$ = 1090. [b] Tetrahydrofuran

The last experiment in Table 3 shows that $ZnCl_2$ cleaves TIPS in tetrahydrofuran solution, but not as well as in pyridine. Extensive washing with water and 1N HCl was required to remove the zinc, probably with some loss of product, but there was no gain in weight or nitrogen.

2.7. Derivatives of TIPS Fractions

Several derivatives of TIPS fractions were made in an effort to increase their solubilities for NMR investigations.

Acetylation--A 0.4 g sample of TIPS 35-A was heated to reflux under nitrogen in 7 mL of pyridine and 5 mL of acetic anhydride for 24 hours. The product was drowned in water and centrifuged. The purified product (13-A) weighed 116% of the theoretical yield based on two phenol residues for starting material of molecular weight 1380. This material was not significantly more soluble than the starting material in pyridine-d_5 or $CDCl_3$.

Another TIPS fraction, 28-A, 0.9467 g, in 15 mL of pyridine, was treated with 30 mL of equal volumes of pyridine and acetic anhydride, containing 60 mg of 4-dimethylaminopyridine as catalyst.[6] This mixture was stirred under nitrogen for 24 hours, then concentrated to 5 mL and drowned in water. By the method of Blom et al.,[3] the acetic ester content of the product, 38-A, corresponded to 2.69 meq/g or 3.50 meq OH/mmole 28-A.

Methylation--TIPS 35-A was methylated with a large excess of diazomethane in ether at 0° for several days but only 82% of the product (16-B) was soluble in pyridine (all of 35-A was soluble), with an apparent $\overline{M}_n$ of 1280.

Ignasiak and coworkers[9] reported that treatment of a bituminous coal (81% C d.a.f.) with sodamide in liquid ammonia followed by treatment with ethyl iodide resulted in alkylation but not in bond cleavage. We applied this method to our TIPS fraction of pyridine extract (28-A) with MeI and obtained our product, 36-A. The $\overline{M}_n$ of 36-A in pyridine by VPO is 446, a significant reduction from 1090 for the starting material. Another experiment with $NaNH_2/NH_3$, with NH_4Cl quenching instead of MeI treatment, showed only a slight reduction in $\overline{M}_n$ (850), indicating that most of the cleavage is due to iodide ion.

3. RESULTS AND DISCUSSION

3.1. Characterization of TIPS Fractions

Four TIPS fractions from pyridine extractions of Illinois No. 6 coal were used in this work: 1-D, $\overline{M}_n$ 1250; 17-G, $\overline{M}_n$ 980; 28-A, $\overline{M}_n$ 1090; and 35-A, $\overline{M}_n$ 1380. 35-A was prepared by extraction at room temperature, 1-D at reflux. 17-G was a later extraction at 100° of the same coal, and used very little; it was reprecipitated again from pyridine with toluene to give 28-A. These molecular weights are close to those found in a still earlier extraction and fractionation, 1214.[1] The yields of extract are not sensitive to particle size (60-250 or 400 mesh) or extraction temperature.

The C analyses in Table 1 suggest that some oxidation of coal was involved between preparations of 35-A and 28-A, even though the coal was protected from air. However, the C and O contents of the TIPS fractions also depend on the separations from the toluene-soluble, hexane-insoluble (35-B) and hexane-soluble fractions (35-C), which contain much more carbon and less oxygen.[1]

The TIPS fractions are only partially soluble in tetrahydrofuran, $CHCl_3$, and dimethyl sulfoxide and are insoluble in toluene, alcohols, and ethers. However, they are partly soluble in KOH/EtOH.

Table 4 gives ^1H NMR assignments for TIPS 35-A in solution and ^{13}C assignments for solid-state NMR of the same material (because it was not sufficiently soluble even in pyridine). The $\overline{M}_n$ of this fraction was 1380, corresponding to an average of 90.6 C atoms and 70.8 H atoms per molecule, but comparisons are made on a per 100 C and 78.1 H basis.

The aliphatic H/C ratio in Table 4, 1.31, has important implications for the carbon skeleton of the aliphatic portion of coal. Replacing carbonyl oxygen atoms by H_2 and ether oxygens by CH_2 and correcting for the methyl groups results in $H/C \gtrsim 1.4$ for the analogous parent hydrocarbon, maybe 1.5 if the ^{13}C measurements underestimate by 10% carbon atoms common to two aromatic rings. Aliphatic H/C ratios are 1.8 in decalin, 1.6 in adamantane, 1.89 in the Wiser structure[10] for coal and 1.125 for a highly-condensed, three-dimensional structure for a Wyodak SRC proposed by Farcasiu.[11]

Table 4

ALIPHATIC/AROMATIC RATIOS FOR TIPS 35-A

For 100[a] C Atoms	^{13}C Assignments	For 78.1 H Atoms
5.6	C=0 205-160 ppm	
62.8	Aromatic 160-100 ppm	36.7 including -OH
13.2	Ether and alcohol 100-45 ppm	
18.4	Aliphatic 45-0 ppm	14.1
	aliphatic Me	4.7
	benzyl	22.6

$$\frac{\text{Arom H}}{\text{Arom C}} = \frac{36.7}{62.8} = 0.584 \qquad \frac{\text{Aliph H}}{\text{Aliph C}} = \frac{14.1 + 22.6 + 4.7}{13.2 + 18.4} = 1.31$$

[a] Data supplied by Prof. Gary E. Maciel of Colorado State University, who used the magic angle, crossed polarization technique with modified JEOL FX-600 spectrometer at 15 MHz.

Thus, the aliphatic portion of Illinois No. 6 coal appears to have a condensed and crosslinked structure about half-way between the Wiser and Farcasiu structures. Investigation of its detailed structure may be too difficult to warrant the effort. However, we are trying to make the TIPS fractions sufficiently soluble in an NMR solvent so that we can obtain solution data with both ^1H and ^{13}C NMR. The heterogeneity of the TIPS fractions is discussed in Section 3.3.

Analysis of the extracted coal, 18-A, is close to that of the corresponding TIPS fraction, 28-A, which we think serves as a good model for the extracted coal. The extracted coal contains a little more ash, N, S, and O, and therefore less C. By NMR, the extracted coal contains 3.2% more carbonyl C, 2.2% less ether and alcohol C. Unpublished experiments show that total KOH consumption, by phenols plus esters, is nearly constant in several extracts and insoluble residues,[12] The principal difference between the soluble and insoluble fractions in probably that the soluble molecules are branched while the insoluble ones are crosslinked.

3.2. Cleavage Reactions

From the results of our cleavage reactions, we conclude that these reactions depend on the presence of ether and ester groups in our TIPS fractions: alcoholic KOH and benzylamine cleave the ester groups to similar extents; ethylenediamine on long reaction and the acidic reagents cleave both esters and ethers. In the latter reactions, halide ions produce alkyl halides that react with any pyridine present to give salts that are subsequently decomposed by heat. Cleavages by sodium metal will be discussed later.

Table 5 summarizes our experiments on cleavages of the four TIPS fractions described in Section 3.1. The TIPS fractions are cleaved by both strongly basic amines (benzyl, butyl, and ethylenediamine) and by alcoholic KOH. Both kinds of reagents effect fractionations of the products by salt formation, as shown by solubilities in alcohol, ether, and methanol in the presence of base but not in its absence. Section 2.3 and Table 2 show that cleavage as well as fractionation occurs with alcoholic KOH. The saponification equivalent of 1400 and $\overline{M}_n$ of 1090 for TIPS 28-A indicate that an additional 0.6 molecule should be formed from each TIPS molecule if each hydrolysis of an ester group results in formation of an additional molecule.

Section 2.4 showed that mixing the benzylamine cleavage products from TIPS 35-A gave a low average instead of the original molecular weight. Thus, the amine effects an irreversible cleavage of the TIPS as if it cleaved an ester to amide and alcohol:

$$\text{R-CO}_2\text{-R}' + \text{R}''\text{-NH}_2 \longrightarrow \text{RCONHR}'' + \text{R}'\text{OH}$$

One amine molecule should be incorporated for each cleavage. On this basis, recovery is less than the stated 95% and the gain in N content is less than expected, but the lost material may be richer in N. When the insoluble fraction, 39-A, from the BnNH_2 cleavage was treated further with alcoholic KOH, the resulting fractions correspond to a separation without significant cleavage. Although alcoholic KOH cleaved TIPS 1-D at room temperature, it cleaved no bonds in TIPS 35-A that had not already been cleaved by benzylamine.

In all the alcoholic KOH extractions, the soluble material is a black powder, whereas the low molecular weight material made soluble by

Table 5

Cleavages of TIPS Fractions

$\overline{M}_n$ Initial TIPS[a]	Reagent	Solvent	Reaction Time	Temp[b]	Products[c]	Yield, % on C	Yield, % by wt.	$\overline{M}_n$
Bases								
1090	KOH	5% in EtOH	24 h	100°	44-A insol		31	1427
Soluble frac.	HCl	Et_2O			44-G insol		41	791
					44-D sol		4	347
1250	KOH	5% in EtOH	8 10-min extractions		43-A insol	80	82	940
					43-B sol	9	12	420
1380	$BuNH_2$		1 h		21-F sol	49	51	
			then MeOH		21-D insol	48	49	
1380	$BnNH_2$		45 h		39-B sol	21	21	350
			then Et_2O		39-A insol	73	74	995
Insol. 39-A	KOH, 5% in EtOH		3d		46-C sol		20	570
					46-A insol	79	80	1250
1380	$BnNH_2$		1 h		21-E sol	51	50	
			then MeOH		21-C insol	82	85	540
Iodides								
1250	HI	pyridine	6d		15-A	90	102	462
1090	$LiI \cdot H_2O$	pyridine	6d		9-A	99	102	363
1090	$BnNMe_3I$	pyridine	3d		39-B		83	540
1250	I_2	pyridine	3d		35-G		125	602
1250	Me_3SiI	$CHCl_3$	42 h	50°	6-D	90	113	760
1250	MeI		2d					
			then 140°		20-A	94	95	660
Other Salts and Acids								
980	HBr	pyridine	3d	50°	24-G	81	83	616
980	$p\text{-}C_7H_7SO_3H \cdot H_2O$	pyridine	3d	50°	23-A	82	84	524
1090	$LiClO_4$	pyridine	3d		36-B		83	650
1090	$ZnBr_2$	pyridine	3d		7-A	105	119	428
1090	$ZnBr_2$	pyridine	3d	50°	42-A	96	102	392
1090	$ZnCl_2$	pyridine	6d		8-A	95	108	379
Sodium, then HI								
1380	Na	$NH_3 + BuNH_2$	5h	-35°	24-A	91	93	790
790(24-A)	HI	Pyridine	3d		19-A	97	110	548

[a] Code numbers and $\overline{M}_n$ values are related in Section 3.1.

[b] 20-25° except as indicated

[c] Analyses and code numbers are in Table 1.

amine treatment or trimethylsilylation is medium brown. For those fractions that have been checked, the aromatic proton contents of the soluble fractions are lower than those of the starting materials and the soluble fraction contains less C and more O than the insoluble fraction. Different C and O relations also appear in the amine separation products, 39-G and 39-A, 21-E and 21-C, and 21-F and 21-D.

Table 5 shows that either acids (toluene sulfonic, HI, HBr), sources of halide ions (MeI, I_2, Me_3SiX), or salts ($ZnCl_2$, $ZnBr_2$, $LiI \cdot H_2O$, benzyltrimethylammonium iodide) will effect cleavages. It is possible that the phenol groups in the TIPS supply the hydrogen ions required for ether cleavage:

$$R\text{-}O\text{-}R' + HX \longrightarrow R\text{-}OH + R'X$$

However, even $LiClO_4$ cleaves TIPS; perhaps the very small Li^+ ion can substitute for H^+ so that $LiClO_4$ behaves somewhat like an acid.

In terms of the number of molecules recovered per initial molecule of TIPS fraction of pyridine extract, the order of decreasing effectiveness of cleaving agents is: $ZnCl_2$, 3.1; $LiI \cdot H_2O$, 3.1; $ZnBr_2$, 3.0; pyridine hydroiodide, 2.3; methyl iodide, 2.0; benzylamine, 1.8; alcoholic KOH, 1.7; toluene sulfonic acid, 1.6; trimethylsilyl iodide, 1.5; $LiClO_4$, 1.4; and pyridine hydrobromide, 1.3. These are not quantitative values because some recoveries are more and some are less than 100%, and low molecular weight material was often lost, but they indicate a surprising effectiveness of some halide salts, presumably in cleaving ethers and esters.

From changes in molecular weight, neglecting small gains and losses in C content, the increase in the number of molecules with TIPS 35-A was 1.74 in the Na-NH_3-$BuNH_2$ cleavage and then 1.44 in the succeeding HI cleavage, for a total increase of 2.5. However, HI cleavage alone with 1-D increased the number of molecules by 2.7. These results strongly suggest (but hardly prove) that HI cleaves all the bonds that Na cleaves, and more. Therefore, there may be no diaryl ether bonds (which would be split by Na but not HI) in our TIPS fraction and there are more phenyl alkyl and benzyl ether bonds (split by both Na and HI) than dialkyl ether bonds (split by HI but not Na).

3.3. Heterogeneity of TIPS Fractions

^1H NMR measurements were made on several coal fractions on a Varian EM 360 Spectrometer, with pyridine-d_5 as solvent and 1% of tetramethylsilane as standard. Table 6 compares proton distributions for two pairs of fractions that were soluble or insoluble in excess ether containing a little $BnNH_2$ and for three fractions based on an initial extraction with alcoholic KOH. In general, the smaller, soluble portions have lower molecular weights, higher oxygen (lower carbon) contents, and lower aromatic hydrogen content.

We now use these and other data[2] and some semiquantitative observations to indicate the nature of coal extracts made at 100°C. The TIPS fraction of pyridine extracts ($\sim$ 10% of original coal, $M_n \sim 1300$) and the TIPS fraction of the $BnNH_2$ extract of pyridine-extracted coal

Table 6

PROTON DISTRIBUTION IN COAL FRACTIONS BY NMR

Fraction	Yield, wt. %	H/C	Arom.,% 6-10δ	Benzylic,% 3.5-2δ	Other Aliphatic,% 1.1-2δ	Aliphatic Me,%, 1.1-0.4δ
TIPS 35-A + $BnNH_2$, 70 min. at 110°, then excess Et_2O						
17-A Insoluble	76	0.769	49	31[b]	15	5
17-B Soluble[a]	21	1.079	26	26[b]	28	19
Alcoholic KOH extraction, Table 5						
43 A Insoluble	82	0.744	52	25	5	18
43 B Soluble	12	0.781	35	29	9	27
Alcoholic KOH extraction, Table 5						
44-A Insoluble	31	0.743	62	15	12	4
Soluble + HCl + Et_2O →	4	0.980	38	24	22	10
→	41	0.763	54	24	15	5

[a] NMR in $CDCl_3$ solution with added $BnNH_2$ + D_2O

[b] Range extends to 5δ

($\sim$ 13% of original coal, $M_n \sim 1700$) are of course wholly soluble in pyridine. The EDA-DMSO extract of $BnNH_2$-extracted coal ($\sim$ 20% of the original coal, $\overline{M}_n$ presumably ≥ 2000) is only about 20% soluble in pyridine but the EDA-DMSO extract of whole coal ($\sim$ 45%) is about 70% soluble in pyridine but 96% soluble in $BnNH_2$. Apparently, the part of the coal network that is insoluble in pyridine but brought into solution by $BnNH_2$ or EDA has a higher molecular weight and presumably more acidic and basic groups per molecule. We take these results to mean that lower molecular weight fractions increase the solubility of higher molecular weight fractions, at least partly through phenol-pyridine type interactions.[1] Further, bases (Table 5) dissolve some of the pyridine-soluble material, and small proportions of $BnNH_2$ substantially increase the solubility of the TIPS fraction in poorer solvents than pyridine. It has long been known that the toluene-soluble, hexane-insoluble fraction of coal liquefaction products can be separated into basic, acid, and neutral fractions[13] but these contain much less oxygen than our TIPS fractions.

Thus far, we have separated our TIPS fraction of pyridine extract into a low molecular weight, mostly phenolic fraction with a higher aliphatic content, and a higher molecular weight, less acidic, more aromatic fraction. If the basic groups are mostly heterocyclic aromatic, then the greater aromatic content of the higher molecular weight fraction is accounted for. By refinement of our fractionation procedures, both fractions can probably be resolved into several others, depending on H/C ratio, molecular weight, and acid-base balance. Similar experiments with additional material extracted by benzylamine or EDA-DMSO from pyridine-extracted coal should permit us to examine groups of molecules that were previously built into the insoluble coal network and have never been heated above 100°C. Such experiments may be a more quantitative and rewarding approach to determining breakable single bonds in the original coal network than degrading solvent-extracted coal by oxidation, and certainly much superior to work based on products heated to 400°C.

REFERENCES

1 F. R. Mayo and N. A. Kirshen, Fuel, 57, 405 (1978).

2 F. R. Mayo and L. A. Pavelka, ms. submitted to Fuel.

3 L. Blom, L. Edelhausen, and D. W. Van Krevelen, Fuel, 36, 135 (1957).

4 S. Friedman, M. L. Kaufman, W. A. Steiner and I. Wender, Fuel, 40, 33 (1961).

5 L. Lazarov and G. Angelova, Fuel, 47, 333 (1968).

6 G. Höfle and W. Steglich, Synthesis, 1972, 619.

7 M. E. Jung and M. A. Lyster, J. Org. Chem., 42, 3761 (1977).

8 I. T. Harrison, J. C. S. Chem. Comm., 1969, 616.

9 B. Ignasiak, D. Carson, and M. Gawlack, Fuel, 58, 833 (1979).

10 W. H. Wiser, Dept. of Energy Symposium Series, Proceedings of Conference on Scientific Problems Relevant to Coal Utilization, University of West Virginia (1977), see Preprints, Division of Fuel Chemistry, **20** (2), 122 (1975).

11 M. Farcasiu, Preprints, Division of Fuel Chemistry, **24** (1), 129 (1979).

12 Manuscript in preparation.

13 H. W. Sternberg, R. Raymond, and F. K. Schweighardt, *Science*, **188**, 149 (1975).