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THE ORIGIN OF CERTAIN HETEROCYCLIC COMPOUNDS FROM THE DEPOLYMERIZATION OF COAL (Title used at Gordon Conference)
ACID-CATALYZED PHENOLIC DEPOLYMERIZATION OF COAL - INFERENCES ON COAL STRUCTURE (Title used in Journal Publication)

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THE ORIGIN OF CERTAIN HETEROCYCLIC COMPOUNDS FROM THE DEPOLYMERIZATION OF COAL

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In a previous account[1] of ^{13}C nmr and ir studies of the phenol-acid-catalyzed depolymerization[2] of a lignite, we reported the detection of diaryl- and triarylmethane functional groups and a pattern of reactivity similar to that reported by Heredy[3-5] and Ouchi.[6, 7] Ouchi has twice reported[6,7] the detection of xanthene and 9-arylxanthene derivatives and other compounds from the depolymerization of coals from diverse sources. We report results from a study of structural and kinetic relationships between functional groups and coal depolymerization characteristics which confirms the presence of certain specific aliphatic methylene and methine structures in depolymerized lignite, and demonstrates that aromatic structure in xanthene and 9-arylxanthene derivatives is derived from phenol. Possible alternate precursors and pathways to the observed alkyl functional groups are discussed.

Samples of Knife River coal (ASTM lignite, ultimate daf analysis C, 61.8, H, 4.1; N, 0.5; S, 0.7; O, 29.3) were depolymerized in a manner similar to that of Ouchi[6] by refluxing coal for 6 or 12 hr with phenol or 1-^{14}C-phenol and p-toluenesulfonic acid. The depolymerized coal exhibited a 25% net weight increase and contained 39% chemically bonded phenol by ^{14}C analysis. The portion of depolymerized coal which was soluble in methanol (37%) exhibited an average molecular weight of 350 by vapor pressure osmometry. The methanol-soluble fraction was methylated by refluxing with methyliodide and sodium-methoxide, and then extracted with benzene (50-60% dissolved). The benzene soluble fractions were analyzed by ^{1}H and ^{13}C nmr (Figure 1), gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS) (Figure 2) with electron impact (EI) and chemical ionization (CI) techniques. Table 1 presents yields of major compounds determined for two different reaction times from GC and GCMS studies.

The methylated fractions (unlabeled and ^{14}C-labeled) were further fractionated by liquid chromatography using silica gel columns. Samples of unlabeled and ^{14}C-labeled 9-(4-methoxyphenyl)-xanthene and 2-(4-methoxyphenyl)-benzofuran were thus isolated from 6-hr depolymerizations and ^{14}C-labeled samples of 9-(4-methoxyphenyl)-xanthene and xanthene contained 2.9 and 2.0 equivalents of ^{14}C-phenol per mole, respectively, by ^{14}C analysis. These figures indicate that at least 97 and 100% of aromatic structure in the two compounds is formed from phenol during depolymerization. This shows that aromatic ether formation occurs during depolymerization, and proves that the xanthenes were not liberated from the high oxygen-containing lignite.

The ^{13}C nmr spectrum (Figure 1) of the methylated, benzene-soluble fraction of depolymerized Knife River coal indicates the presence of diaryl- and triarylmethanes (∿30 ppm downfield shift from tetramethylsilane) determined by off-resonance decoupling techniques, as well as a complex aromatic pattern (110-160 ppm) and methoxyl absorptions (∿57 ppm). The nmr data indicate the absence of significant concentrations of normal paraffinic carbons as well as the absence of cycloaliphatic and naphthenic carbons. A small contribution from internal (ε) carbons of long chain ($\gtrsim C_{20}$) normal paraffins to the absorption of 29.5 ppm, however, cannot be ruled out.[8] The aliphatic structure is dominated by the presence of 9-(4-methoxyphenyl)-xanthene and 9-(2-methoxyphenyl)-xanthene present to the extent of 8-12% by weight of the methylated, benzene-soluble depolymerized coal. The absence of aromatic methyl groups (19-21 ppm) is consistent with the predominance of solvent-derived aromatic structure in this fraction.[5]

GC and GCMS analysis of this fraction permitted identification of aliphatic structures detected by ^{13}C nmr and detected in other lignites and brown coals.[6,7] Numerous components were detected and identified by GCMS. More detailed description of ^{13}C nmr, GCMS, and kinetic studies of the depolymerization products will be presented in a full paper elsewhere.[9] As indicated by Table 1, the yield of 9-arylxanthenes decreases slightly from the 6-hr to the 12-hr reaction time. The yield of xanthene increases dramatically while total concentrations of dianisylmethanes and ethanes remain approximately constant. These data, when taken with the ^{14}C results, are consistent with a mechanism (Scheme 1) in which an equilibrating mixture of di- and tri(hydroxyphenyl) methanes (presumably derived from labile methylene or methine carbons in the coal structure) undergoes gradual cyclodehydration to xanthene and 9-(2-hydroxyphenyl) or 9-(4-hydroxyphenyl)-xanthenes. Consistent with this view, xanthene has been synthesized in 85% yield by digestion of a phenol-formaldehyde resin with phenol and H_3PO_4.[10] The depletion of some of the 9-(hydroxyphenyl)-xanthenes to form xanthene by acidic cleavage of the 9-aryl group (a facile reaction[11]) and reaction of the resulting 9-xanthyl carbonium ion with a hydride donor (e.g., 9-xanthhydrol[12]) as depicted in steps c, d, and e, Scheme I, cannot be ruled out from our data. This is a much more probable explanation[12] for the detection of xanthone than that provided by Ouchi.[6] Xanthene is also formed from the reaction of o-cresol and phenol in the presence of $AlCl_3$.[13] Thus, aromatic methyl, methylene, and methine carbons may all contribute to structures previously assigned[6,7] to aromatic methylene groups. A further complication in the interpretation of depolymerization products arises from the condensation of phenol with ketones to form 9-diaryl- or 9-aryl-9-alkyl-xanthenes.[14-16] The further reaction of 9-disubstituted xanthenes by acidic cleavage and reduction would provide 9-arylxanthene or xanthene itself (as in steps c, d, and e, Scheme I). Thus, the potential for interconversion of methyl, methylene, methine, and carbonyl carbons makes their relationship with and assignment to similar functional groups in coal ambiguous. However, if the interconversion of the various functional groups is shown to be insignificant by competitive reactions of model compounds containing potentially interfering functional groups, then the concentration of alkyl groups in coal into a few easily detected compounds can provide convenient molecular parameters with which coal dissolution behavior can be correlated. The work by Heredy, et al.[5], in functional group characterization by nmr of depolymerized coals suffers from the complications described above, and further work necessary to develop reliable measures of coal functional groups from the depolymerization of coal is underway in these laboratories.

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CAPTIONS TO FIGURES AND SCHEME

Figure 1. ^{13}C nmr spectrum of the benzene-soluble, methylated fraction of depolymerized coal in $CDCl_3$. A Varian XL-100-15 Spectrometer was used with interactive disc data system operating at 25.1604 MHz. Chemical shifts are in parts per million from internal tetramethylsilane (δ_c=0). Dioxane (δ_c=67.4 ppm) was added as a secondary standard (∿5% V/V) for consistency with other spectra run in our laboratory.

Figure 2. GCMS trace of a subfraction of the benzene-soluble methylated depolymerized coal. GCMS data were collected using a Finnigan 1015 GCMS system connected to a Systems Industry 250 Data System, using both electron and chemical (methane) ionization. Gas chromatography was carried out on a 1.8 m x 0.32 cm 3% OV-1 on 60/80 mesh chromosorb W (AW/DMCS) column, temperature program 5°/min, starting temperature 140°, final temperature 250°. Major peaks are as follows: A_1, A_2 = dianisylmethane isomers; B_1, B_2, B_3 = 1, 2-dianisylethane isomers; C_1=2-(2-methoxyphenyl)benzofuran, C_2=2-(4-methoxyphenyl)-benzofuran; D_1=9-2-methoxyphenyl)-xanthene, D_2 = 9-(4-methoxyphenyl)-xanthene.

Scheme 1. Genesis of Xanthene Compounds. Xanthene (1) and 9-(4-hydroxyphenyl)-xanthene (2) are formed by transarylalkylation and cyclodehydration. The possible formation of xanthene and xanthone (3) by acidic cleavage and disproportionation from 2 is depicted in pathways c, d, and e.

TABLE 1. COMPOUNDS FROM THE DEPOLYMERIZATION OF KNIFE RIVER COAL

Compound	Yield[a]	
	6 Hr[b]	12 Hr[b]
Xanthene	0.01	0.8
9-(4-Methoxyphenyl)-xanthene	1.0	0.72
9-(2-Methoxyphenyl)-xanthene	0.3	0.22
2-(2-Methoxyphenyl)-benzofuran	0.1	0.05
2-(4-Methoxyphenyl)-benzofuran	0.2	0.1
Dianisylmethane[c]	0.2	0.2
1,2-Dianisylethane[d]	0.1	0.1

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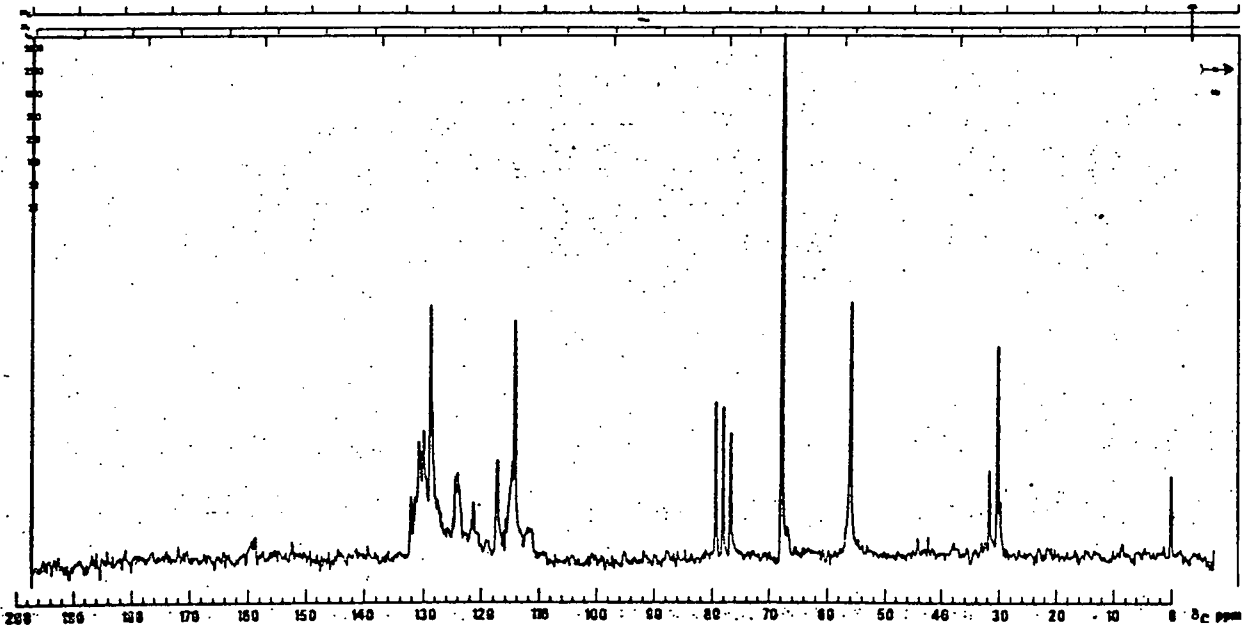
a. Weight percent of total depolymerized coal. Yield by quantitative GC analysis of chromatography fractions, est. error <15%. b. Reaction time. c. Isomer not determined (see Figure 2), but is not 4,4'-Dianisylmethane. Yield is based on peak A_1, Figure 2. d. Isomer not determined. Yield is based on peak B_1, Figure 2. All isolated compounds were characterized by nmr, ir, mp, mass spectrometry, and GC mixed retention times.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190
180
170
160
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110
100
90
80
70
60
50
40
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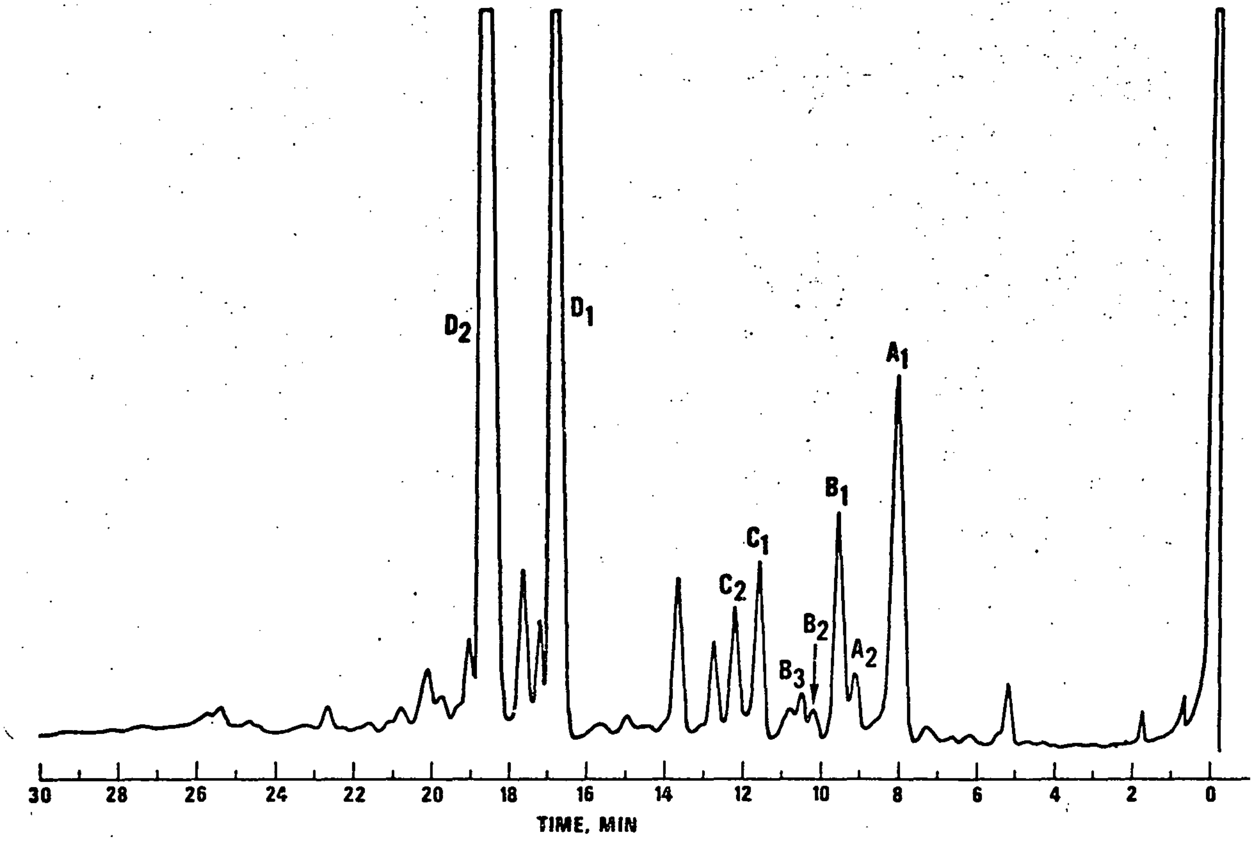
0
δC ppm

Figure 1.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D1
A1
B1
C1
C2
B2
A2
B3
30
28
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24
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14
12
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8
6
4
2
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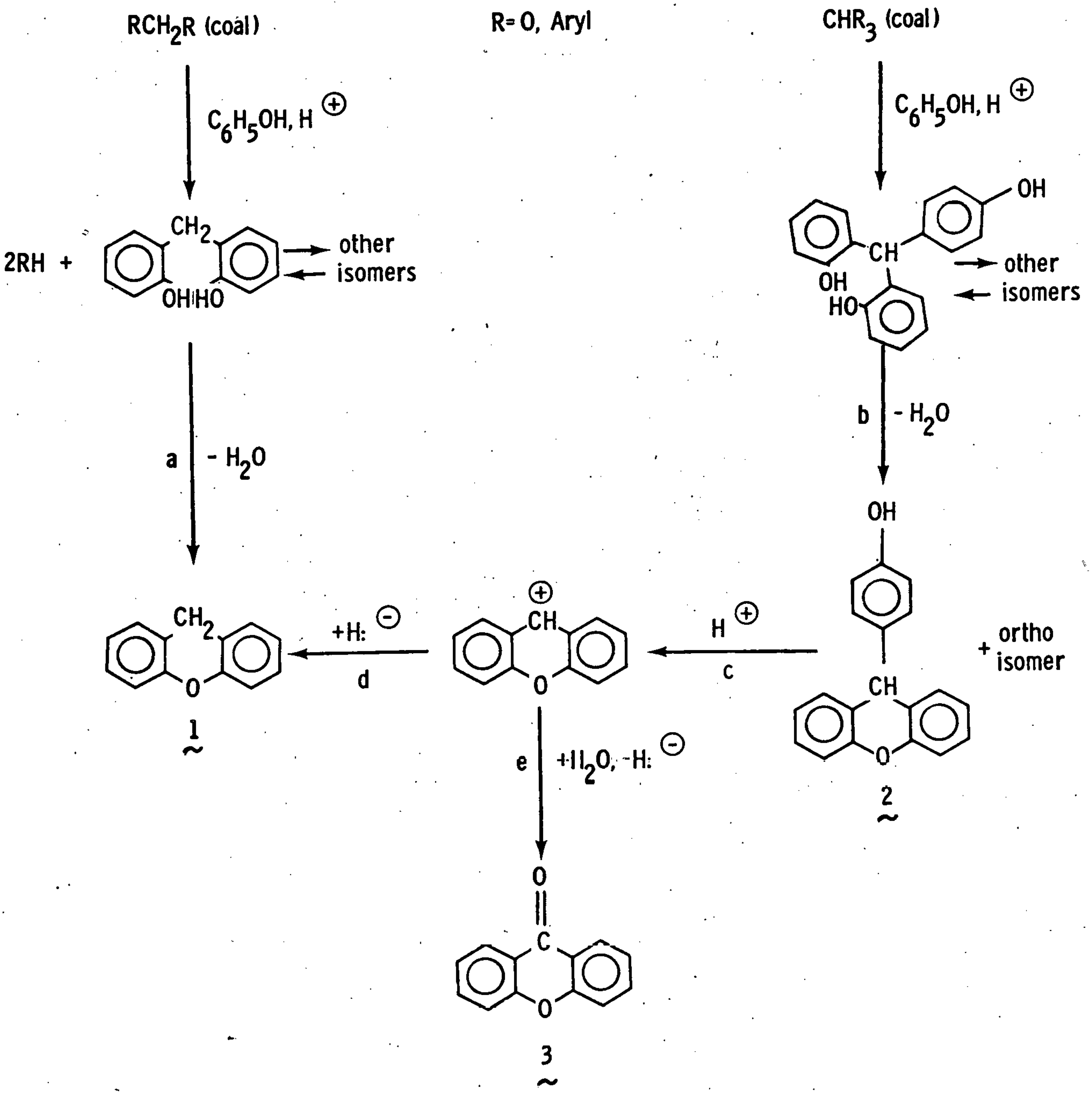
TIME, MIN

Figure 2.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R= O, Aryl
CHR3 (coal)
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C6H5OH, H ⊕
2RH +
CH2
OH HO
other isomers
OH
CH
OH
HO
other isomers
a
- H2O
b
- H2O
OH
CH2
O
1
+H: ⊖
d
⊕
CH
O
H ⊕
c
+ ortho isomer
CH
O
2
e
+H2O, -H: ⊖
O
C
O
3