OXIDATIVE DEGRADATION STUDIES OF COAL AND SOLVENT REFINED COAL

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INTRODUCTION

The bulk of the organic matter in coals consists of a macromolecular material of complex and variable composition. Many workers have attempted to degrade coals to smaller molecules which could be identified and interpreted in terms of coal structure. Oxidation has been one of the more important degradation methods. To date a number of oxidizing agents have been used. Among these were HNO_3, HNO_3-$K_2Cr_2O_7$, $KMnO_4$, O_2, H_2O_2-O_3 and NaOCl, all drastic oxidants. Because these reagents in general result in extensive ring degradations, with benzene carboxylic acids the only aromatic compounds identified, they have been of limited usefulness. Our approach has been to compare the products from drastic oxidants with more selective ones designed to break up the macromolecules into identifiable units with a minimum of chemical change so that units indigenous to coals can be identified. We have found aqueous $Na_2Cr_2O_7$ to be selective and have reported a number of polynuclear aromatic units which resulted from the dichromate oxidation of a bituminous coal and which we believe to be indigenous to the coal (1). We have explored a number of oxidizing agents using the samples listed in Table 1.

Table 1

Elemental Analyses of Samples (maf %)

No.	Sample	C	H	N	S	O (by diff)
1	Lignite (Sheridan Wyoming)	64.4	5.3	1.1	1.1	28.1
2	Bituminous (Illinois Seam #2)	77.8	5.4	1.4	2.1	13.3
3	Bituminous (Pittsburgh Seam #8)	82.7	5.5	1.3	2.8	7.7
4	Anthracite (Pennsylvania PSOC #85)	91.3	3.9	0.6	1.1	3.1
5	SRC (from Pittsburgh Seam #8)	87.2	5.5	1.8	1.2	4.3
6	SRC benzene-methanol ext.*	86.2	5.6	1.8	0.7	5.7
7	Char	84.9	1.7	---	---	---
8	Synthetic Polymer (from Fischer-Tropsch) (2)	80.0	5.1	1.3	0.0	13.6
9	Polymeric Material (from Murchison Meteorite (2))	76.1	4.6	2.8	1.3	15.2

*The SRC was fractionated into 3 fractions on the basis of solubility: hexane (4.5%), benzene-methanol mixture (82.3%), pyridine (11.8%) and a small residue (1.4%).

In addition to four coals, a solvent refined coal (SRC) and two completely abiotic samples, the synthetic Fischer-Tropsch polymer, and the polymer from the Murchison meteorite, were used for comparison and to test the oxidation methods.

RESULTS AND DISCUSSION

Identification of products: In general the products of oxidation were chiefly carboxylic acids which were esterified with diazomethane to increase their volatility for easier analysis by time-of-flight mass spectrometry (TOFMS), a variable temperature solid inlet, GC-TOFMS and high resolution mass spectrometer (HRMS).

Nitric Acid Oxidation: All samples of Table 1 except #6 were refluxed with 70% HNO_3 for 16-24 hours yielding a clear orange colored solution. The acid solutions were evaporated to dryness under reduced pressure and the residue weighed. The methylated acids were analyzed by GC-MS, HRMS and the solid probe. Fragmentation patterns and precise mass determination of both molecular ions and fragments, in particular $(M-OCH_3)^+$, were used for identification. In Figure 1 are summarized the data for benzene carboxylic acids (as their methyl ester). The synthetic sample had been prepared by heating CO, H_2 and NH_3 with an Fe-Ni catalyst at 200°C for six months (2). It was a macromolecular material insoluble in organic solvents, HCl, HF and KOH. Despite the drastic nature of the nitric acid oxidation it appears that useful information can be obtained by the procedure. For example the yield of total acids and the number of carboxylic acid groups per benzene ring seem correlated with the degree of condensation of the original material. The spectra from the synthetic sample from the Fischer-Tropsch reaction, and from char are relatively simple consisting primarily of the benzene carboxylic acid esters with from two to six ester groups. The coal samples and coal derived products (except for char) are more complex and contained nitro substituted esters and pyridine derivatives. Note the similarity between the synthetic sample and the char prepared from Illinois bituminous coal by heating under vacuum to 800°C. The abundance of the benzene hexacarboxylic acids for these two suggest a high degree of condensation in the original samples. The similarity in distribution of the oxidation products from the two bituminous coals (the Illinois and Pittsburgh) is striking. The solvent refined coal derived from the Pittsburgh #8 coal is shown later (Figure 3, Table 2) to have a higher degree of aromatic ring condensation than its feed coal. Thus it is surprising to see the shift to fewer acid groups for SRC. This may mean that many aliphatic crosslinks were destroyed in the SRC process and evolved as light hydrocarbons.

The results from the meteoritic polymer (not shown in Figure 1) were very similar to those of the synthetic polymer.

Sodium dichromate oxidation: In general 1-3 g of sample was heated at 250°C for 36-40 hours with excess $Na_2Cr_2O_7$ (60-120 ml of 0.4 M - 0.6 M) with stirring. This procedure oxidizes side chains and alicylic appendages to polynuclear aromatic systems with a minimum of degradation of aromatic rings (3). We have found that model compounds are oxidized in high yields (78-95%) to their corresponding carboxylic acids. Samples 1, 2, 3, 4, 6, and 9 were oxidized with $Na_2Cr_2O_7$ with a high degree of conversion to soluble or

volatile compounds (70-100%). The yields of soluble compounds were 50-70% of the weight of the original samples. The anthracite also yielded 17% of a humic acid type material of high molecular weight soluble in alkaline solution. In Figure 2 are shown graphically the relative abundances of aromatic and heteroaromatic units produced by the dichromate oxidation of three coals (samples 1, 2 and 4). It is obvious that the degree of aromatic condensation increases with rank of coal from lignite to bituminous to anthracite. The $Na_2Cr_2O_7$-aq oxidation procedure has been questioned because of the possibility that major structural rearrangement with pyrolytic formation of polynuclear aromatic compounds might occur during the reaction at 250°C (4). The fact that no polynuclear aromatic compounds with more than two fused rings were detected in the oxidation products of lignite (sample 1) and that the degree of condensation increases with rank of coal is internally consistent and suggests that condensation during oxidation with $Na_2Cr_2O_7$ is minimal. In a blank experiment bituminous coal (sample #2) which had been extracted with an organic solvent to remove trapped compounds was heated at 250°C for 40 hours with water. An insoluble residue 96.2% and inorganic salts 2.9% were obtained. Mass analysis of the residue was indistinguishable from that of the original coal and the H/C ratio was unchanged. Furthermore, detailed pyrolysis studies of the coal showed no evidence of significant thermal decomposition until heated above 250°C.

The gas chromatograms of the oxidation products (as methyl esters) from the Pittsburgh coal (sample 3) and its SRC (benzene methanol extract-sample 6) are shown in Figure 3. The numbered peaks are identified in Table 2. A greater degree of aromatic condensation of the SRC extract over that of its feed coal is observed. For example, naphthalene and phenanthrene rings are much more abundant in the SRC. The dibenzofuran ring is the most abundant heterocyclic to have survived the SRC process.

Fifteen aromatic ring systems were identified in the $Na_2Cr_2O_7$ oxidation product of the meteorite polymer: benzene, biphenyl, naphthalene, phenanthrene, fluoranthene (or pyrene), chrysene, fluorenone, benzophenone, anthraquinone, dibenzofuran, benzothiophene, dibenzothiophene, pyridine, quinoline or isoquinoline and carbazole (2). These data support the generally accepted idea that the polymeric material in meteorites has a highly condensed aromatic structure (2, 5, 6) and gives us confidence in the dichromate oxidation procedure.

Photochemical oxidations: Oxidation by air bubbling through an aqueous HCl solution while irradiating with ultraviolet light from a high pressure mercury lamp was investigated. In Table 3 are shown the results obtained with model compounds. From the results with the model compounds it appears that aromatic hydrocarbons are readily oxidized to benzene carboxylic acids. On the other hand N-heterocyclics resist oxidation. In Table 4 are listed the aromatic carboxylic acids isolated from a bituminous coal (sample 2) after photochemical oxidation. The products from lignite (sample #1) were primarily benzene carboxylic acids with only traces of pyridine tricarboxylic acids and xanthone di- and tricarboxylic acids. Several aliphatic carboxylic acids were identified (after methylation) in the photo-oxidation product of bituminous by TOF variable temperature solid inlet and HRMS. They are methyl esters of malonic acid, succinic acid, glutamic acid and saturated monocarboxylic acids (CH_3-$(CH_2)_n$-$COOCH_3$ n = 1-7). The fragments for 3-methyl

Table 2

Aromatic Acids Found in the Oxidation of SRC and Its Feed Coals[a] Identified as Methyl Esters

C Peak Number		Number of $-COOCH_3$	Relative Abundance (± 15%)[b]	
			SRC Extract	Coal
1	Benzene	2	100	100
5		3	58	29
10		4	9	10
4	Biphenyl	1	3	9
2	Naphthalene	1	47	30
8		2	82	29
16		3	24	8
		4	*7*	*3*
13	Phenanthrene	1	82	28
20		2	8,*15*	*8*
		3	*5*	*7*
		4	*1*(T)	---
19	Pyrene/Fluoranthene	1	7	*3*
		2	*4*	*2*
11	Fluorenone	1	4	8
		2	*3*	*2*
		3	*3*	---
14	Anthraquinone	1	26	4
		2	*3*	---
7	Dibenzofuran	1	32	21
17		2	9	4
		3	*10*	*4*
15	Xanthone	1	4	9
		2	*6*	*7*
		3	*2*(T)	*3*
3	Benzothiophene	1	---	4
12	Dibenzothiophene	1	*2*	8
		2	---	*5*
	Pyridine	3	---	*5*(T)
	Carbazole	1	*4*	*3*
		2	*3*	*4*
18	Benzoquinoline/Acridine	1	3	7
		2	*5*	*4*
		3	*2*	*2*
6[c]				11
9[d]				22

Table 2 (Footnotes)

[a]92% of the extract was oxidized and the yield of total acidic and non-acidic less volatile compounds was ≈59%. For the feed coal, 84% of the coal was oxidized; Yield of totals was ≈58%.

[b]Benzene dicarboxylic acid methyl ester is normalized to 100.

[c]Peak no. 6 is tentatively identified as trimethoxyxanthone.

[d]Peak no. 9 shows prominent mass ions at 216 and 215. HRMS shows their elemental composition corresponding to $C_{12}H_{10}O_3N$, $C_{12}H_9O_3N$ or $C_9H_{12}O_6$, $C_9H_{11}O_6$. Identification has not been made at this present time.

T = identification tentative; --- = not detected; x = peak consists of more than one component which are difficult to identify by GC-MS.

Italics indicate that identification and estimation of relative abundances were made by TOF variable temperature solid inlet and HRMS, because of difficulty of identification by GC-MS.

Table 3

Photochemical Oxidation of Model Compounds*

Compound	Unreacted† (%)	Major Oxidation Products§
p-cresol	0	unident. small species, polymer
anisole	0	unident. small species, polymer
naphthalene	8	phthalic acid
1,4-diMe-naphthalene	5	phthalic acid
2,6-diMe-naphthalene	7	benzene-1,2,4-tricarboxylic acid
indane	3	phthalic acid
fluorene	8	fluorenone
acenaphthene	10	phthalic, naphthalene-1,8-dicarboxylic acids
phenanthrene	24	phthalic acid, phenanthrene-9,10-diketone
pyrene	12	benzene tri- and tetracarboxylic acids
dibenzofuran	32	styrene, salicyclic acid
xanthone	78	unidentified chloro compounds
dibenzothiophene	43	styrene, thiophenol
carbazole	78	polymer
N-Et-carbazole	83	polymer
poly(2-vinylpyridine) -polystyrene polymer	8	pyridine-2-carboxylic, pyridine-2-aldehyde, benzoic, malonic, and succinic acids

*The oxidation was carried out in 10% aq. HCl solution for 6-10 days.
†Values are accurate to ±10%.
§After preliminary separation into acidic, neutral, and basic fractions, products were identified by TOFMS with variable temperature solid inlet. Except for the first two samples and the two carbazoles, all identifications were checked by high-resolution MS. For the italicized samples, GC-MS was used as well, after esterification of the product.

All major products were accompanied by lesser amounts of their monochloro derivatives.

Table 4

Aromatic Acids Found in the Photochemical Oxidation of Bituminous Coal: Identified as Methyl Esters[a,g,h]

Nucleus	Number of $-COOCH_3$	Precise mass $(M-OCH_3)^+$ elemental composition	observed	Dev. x 10^3	Relative Abundance[b] ± 15-20%
Benzene	2	$C_9H_7O_3$	163.0388	-0.7	42
	3	$C_{11}H_9O_5$	221.0457	0.8	100
	4	$C_{13}H_{11}O_7$	279.0510	0.6	97
	5	$C_{15}H_{13}O_9$	337.0555	-0.3	29
	6	$C_{17}H_{15}O_{11}$	395.0593	-2.0	4
Cl-benzene[c]	2	$C_9H_6O_3Cl$	196.9990	-1.5	24
	3	$C_{11}H_8O_5Cl$	255.0066	0.6	31
	4	$C_{13}H_{10}O_7Cl$	313.0125	1.1	26
	5	$C_{15}H_{12}O_9Cl$	371.0124	-4.4	2
Fluorenone	2	$C_{16}H_9O_4$	265.0494	-0.6	9
Anthraquinone	2	$C_{17}H_9O_5$	293.0451	0.2	3
	3	$C_{19}H_{11}O_7$	351.0520	1.6	1
Phthalan	2 (T)	$C_{11}H_9O_4$	205.0478	-2.2	2
	3 (T)	$C_{13}H_{11}O_6$	263.0572	1.8	1
Xanthone	2	$C_{16}H_9O_5$	281.0461	1.2	9
	3	$C_{18}H_{11}O_7$	339.0510	0.6	7
Dibenzofuran[d] and/or naphthofuran	2	$C_{15}H_9O_4$	253.0477	-2.3	3
	3	$C_{17}H_{11}O_6$	311.0560	0.6	2
Pyridine	2	$C_8H_5O_3NCl$[e]	197.9974	1.6	3
	3	$C_{10}H_8O_5N$	222.0408	0.5	3
	4	$C_{12}H_{10}O_7N$	280.0488	3.2	3.5
Quinoline and/or isoquinoline	1	$C_{10}H_6ON$	156.0412	-3.7	0.5
	2	$C_{12}H_8O_3N$	214.0468	-3.5	2
Carbazole[f]	1	$C_{13}H_8ON$	194.0598	-0.7	4
	2	$C_{15}H_{10}O_3N$	252.0660	-0.0	2
	3	$C_{17}H_{12}O_5N$	310.0708	-0.6	2
Acridone	1	$C_{14}H_8O_2N$	222.0525	-2.9	5
	2	$C_{16}H_{10}O_4N$	280.0592	-1.8	2
	3	$C_{18}H_{12}O_6N$	338.0635	-2.8	1

Table 4. Footnotes

[a]Some preliminary results were reported earlier (1). Identification based on TOF variable temperature solid inlet, GC (Carbowax 20 M)-TOFMS and high resolution MS.

[b]Benzene tricarboxylic acid methyl ester is normalized to 100. Relative abundances were estimated from the GC and an integration of the base peak of each compound during the time that the sample was completely volatilized in the MS.

[c]Monochlorobenzene carboxylic acids were always obtained when coal or model compounds were oxidized in 10% HCl aq. solution. Chlorocarboxylic acids of other aromatics were also observed in very low yield.

[d]Relatively large amounts of dibenzofurans were found to be produced by $Na_2Cr_2O_7$-oxidation (1), while photo-oxidation produced dibenzofuran carboxylic acids in low yield. Perhaps this shows the photochemical procedure destroyed most of the dibenzofuran ring.

[e]For pyridine dicarboxylic acid, only chloroderivatives were found.

[f]The previous estimates of relative abundances (1) were somewhat high.

[g]The products of lignite photo-oxidation in 5% KOH aq. solution were very similar to those shown in this Table. In addition some mono- and dimethylbenzene carboxylic acids were identified.

[h]Polynuclear aromatic carboxylic acids such as naphthalene and phenanthrene found in the $Na_2Cr_2O_7$ oxidation product (see Fig. 2) are not observed in this product. From our model experiments, we have found that these aromatic compounds are oxidized by the present procedure.

T = identification tentative.

and 3,3-dimethyl aliphatic carboxylic acid methyl esters were also seen in the mass spectra. A similar observation was made for the oxidation product of lignite.

Hydrogen Peroxide-Acetic Acid: It is probable that in the oxidation experiments described above aromatic units with phenolic groups would have been destroyed. Schnitzer et al. (7) have shown that an acetic acid-H_2O_2 mixture under mild conditions oxidizes humic acids while preserving phenols. Using this procedure we have oxidized lignite (sample #1) and bituminous coal (sample #2) with over 80% conversion to methanol soluble acids and have methylated the acids produced.

The gas chromatogram of the aromatic portion of the methylated product from lignite is shown in Figure 4. The identification of individual compounds was made by coincident MS and HRMS of the mixture. The methyl esters identified gave the following approximate distribution: 36.1% benzene, 7.6% methyl-benzene, 22.1% methoxy-benzene, 15.9% furan and 18.2% dibasic aliphatic. For the bituminous coal the methoxy derivatives were half as abundant. These results suggest that the lignite has twice the phenolic content of the bituminous coal. It is interesting to note that methyl furan

tetracarboxylate has been identified and other furan derivatives have been tentatively identified.

It appears that the coals are acting as catalysts for this oxidation. If 2,6-dimethylnaphthalene is reacted with H_2O_2 under the same conditions as used for the coals, only 2,6-dimethylnaphthaquinone is isolated in essentially quantitative yield. With the addition of a small amount of lignite to the reaction, 5-methyl phthalic acid is obtained as the major product. Also no hydroxylated benzene carboxylic acids were isolated which indicates that this procedure does not hydroxylate aromatic rings. Transition metals are known to catalyze reactions of hydrogen peroxide. Part of the catalytic effect may be due to the mineral matter in the coal.

No polyhydroxyl benzene carboxylic acids have been observed in the products from either coal. It is expected that these species would undergo ring oxidation and subsequent degradation. However, the concentration in coal of these species is probably small. These compounds are expected to be very reactive and probably would not survive the coalification process. We have examined aqueous NaOH extract of the Wyoming lignite. Numerous hydroxylated aromatic hydrocarbons and aromatic acids were identified, but no polyhydroxylated species were detected.

Sodium Hypochlorite Oxidation: On the basis of results of oxidation of coal with NaOCl, Chakrabartty et al. have suggested that coal has a non-aromatic "tricycloalkane or polyamantane" structure (8). They pointed out that no evidence for aromatic compounds other than benzene derivatives was found in their oxidation product. The specificity of NaOCl as an oxidant has been questioned (9) and is still in dispute (10). We are attempting to resolve the question and have oxidized samples 6, 9, and 2,6-dimethyl naphthalene under conditions described by Chakrabartty et al. (8, 10, 11). Of particular interest is the oxidation of the polymeric material from the Murchison meteorite (sample 9). Numerous studies have shown this material to be a highly condensed aromatic structure. All samples were nitrated according to the method of Chakrabartty et al. When nitration was followed by NaOCl oxidation at 60°C for 3-4 hours almost no oxidation was observed for nitrated samples 6 (SRC) or 9 (meteorite) while 26% of nitrated dimethyl naphthalene was converted to benzene carboxylic acids and their nitro and/or methyl derivatives. No naphthalene acids were detected. When the reaction was continued for 15 hours, at 65-70°C 57% of sample 9 and 42% of sample 6 were oxidized to water soluble acids. Polynuclear aromatic and heterocyclic acids were not detected in the oxidation products of either sample although both are highly aromatic. Benzene carboxylic acids were the major products (nitro and/or methyl derivatives and a methyl chloro dicarboxylic acid). Apparently polynuclear aromatic systems were destroyed and the product distribution closely resembled that from a nitric acid oxidation. Obviously more work is needed to clarify the role of NaOCl in the oxidation of coal.

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REFERENCES

(1) R. Hayatsu, R. G. Scott, L. P. Moore and M. H. Studier, Nature 257, 378 (1975); Nature 261, 77 (1976).

(2) E. Anders, R. Hayatsu, and M. H. Studier, Science 182, 781 (1973); R. Hayatsu, S. Matsuoka, R. G. Scott, M. H. Studier, and E. Anders, to appear in Geochim. Cosmochim. Acta (1977).

(3) K. B. Wiberg (ed.), Oxidation in Organic Chemistry, Part A, page 90, (Academic Press, New York, 1965).

(4) S. K. Chakrabartty and N. Berkowitz, Nature 261, 76 (1976).

(5) B. Nagy, Carbonaceous Meteorite (Elsevier, Amsterdam, 1975).

(6) E. L. Bandurski and B. Nagy, Geochim. Cosmochim. Acta 40, 1397 (1976).

(7) M. Schnitzer and S. I. M. Skinner, Can. J. Chem. 52, 1072 (1974).

(8) S. K. Chakrabartty, et al. Fuel 51, 160 (1972); Fuel 53, 132 & 240 (1974).

(9) F. R. Mayo, Fuel 54, 273 (1975); G. Ghosh, A. Banerjee, and B. K. Mazumder, Fuel 54, 294 (1975); R. G. Landelt, Fuel 54, 299 (1975).

(10) S. K. Chakrabartty and N. Berkowitz, Fuel 55, 362 (1976).

(11) S. K. Chakrabartty and H. O. Kretschmer, J. Chem. Soc. Perkin 1, 222 (1974).

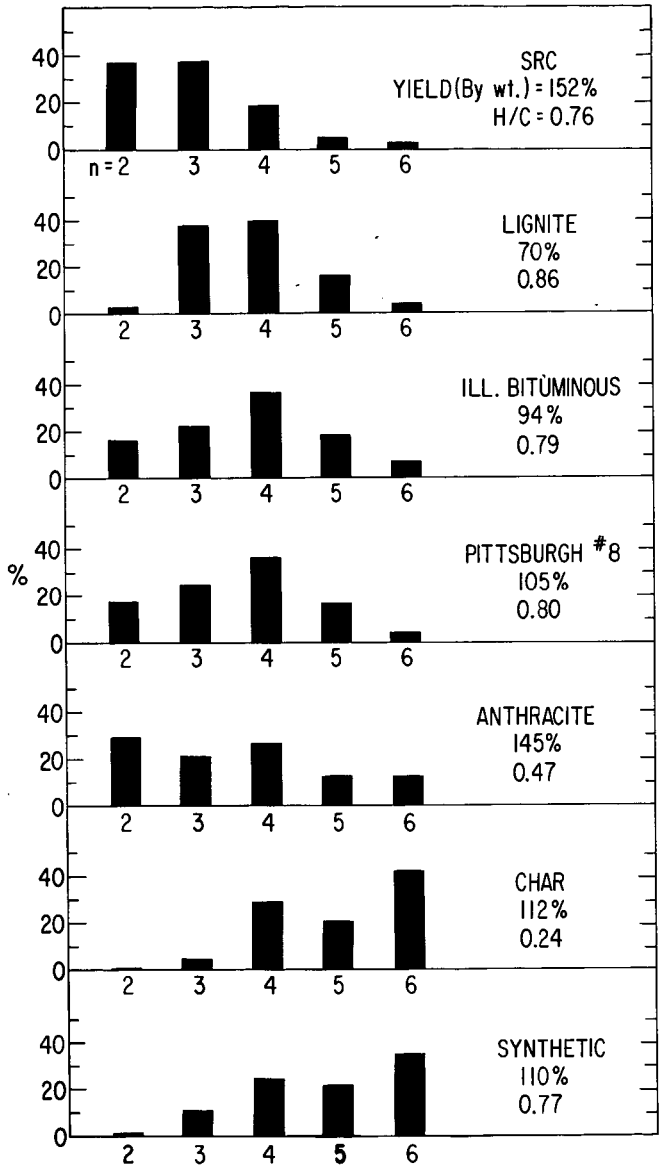

Figure 1. Abundances (%) of benzene carboxylic acids, determined as their methyl esters, produced by nitric acid oxidation. n = number of ($COOCH_3$) groups per benzene ring.

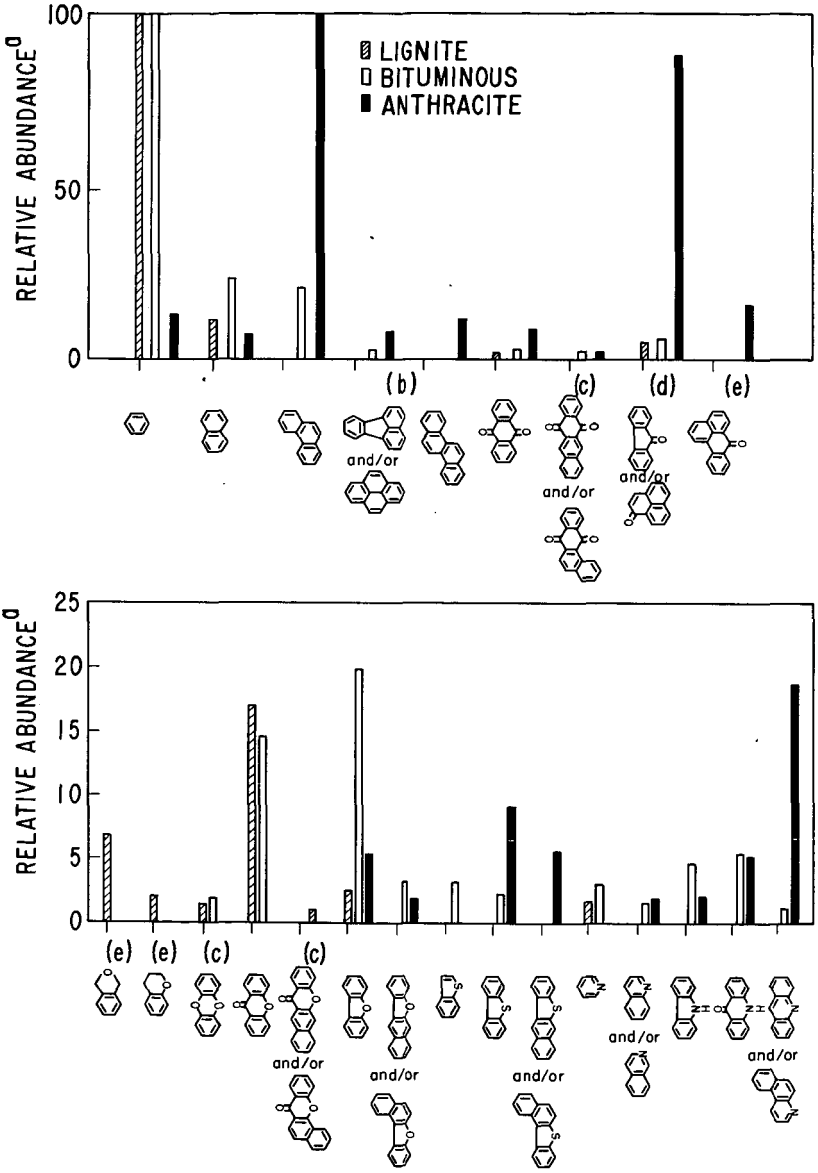

Figure 2. Relative abundances of aromatic and heteroaromatic units produced by sodium dichromate oxidation of lignite, bituminous and anthracite coals.

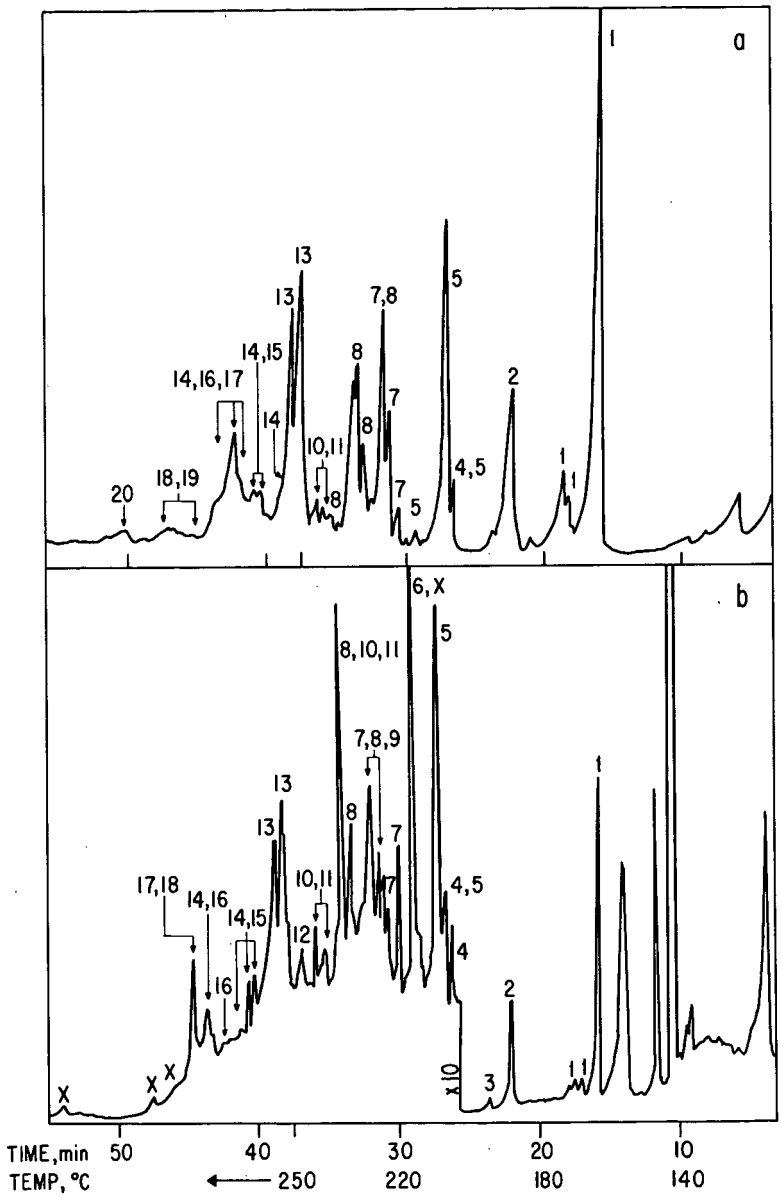

Figure 3. Gas chromatograms of methylated $Na_2Cr_2O_7$ oxidation products of SRC benzene-methanol extract (a) and its feed coal, Pittsburgh #8 (b). Separations were made on an OV-101 SCOT column.

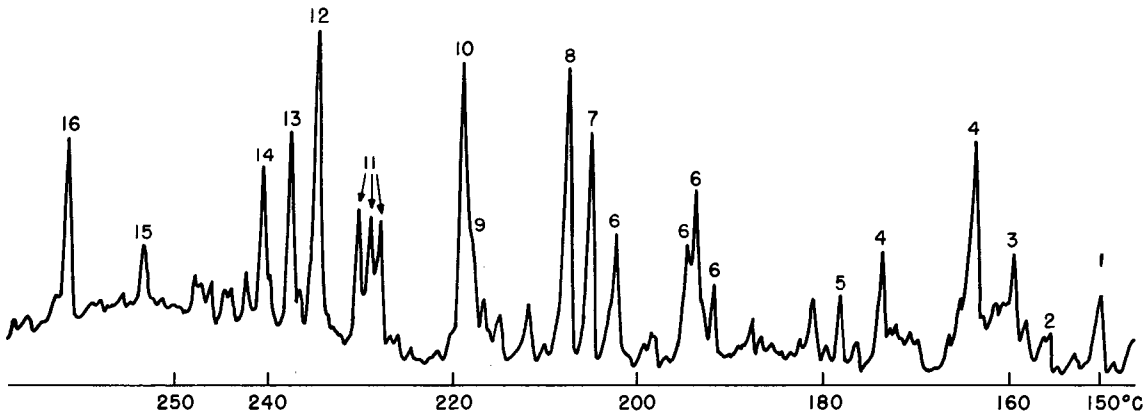

Figure 4. Methyl esters from hydrogen peroxide-acetic acid oxidation of lignite separated on an OV-101 SCOT column. Numbered compounds: 1. methyl o-methoxybenzoate; 2. methyl m- or p-methoxybenzoate; 3. methyl methylfurandicarboxylate; 4. methyl benzenedicarboxylate; 5. methyl carbomethoxyphenylacetate; 6. methyl methoxybenzenedicarboxylate; 7. methyl 1,2,3-benzenetricarboxylate; 8. methyl 1,2,4-benzenetricarboxylate; 9. methyl methoxybenzenetricarboxylate; 10. methyl furantetracarboxylate; 11. methyl methoxybenzenetricarboxylate; 12. methyl 1,2,3,4-benzenetetracarboxylate; 13. methyl 1,2,4,5-benzenetetracarboxylate; 14. methyl 1,3,4,5-benzenetetracarboxylate; 15. methyl methoxybenzenetetracarboxylate; and 16. methyl benzenepentacarboxylate.