

RUTHENIUM TETROXIDE OXIDATION OF LIGNITE

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The objective of these studies was to develop new methods for the elucidation of the organic structure of low-rank coals, especially with regard to the nature of the hydroaromatic groups, the substituent groups on aromatic moieties and bridging groups between aromatic moieties. Isolation of the nonaromatic groups in coal could be achieved if the aromatic rings in the structure could be oxidized without degrading the alkyl substituents on the aromatic rings. Selective oxidation of the benzene ring has been observed in reactions with trifluoroperacetic acid (1); however the severe conditions required with this reagent result in extensive degradation of the alkyl groups (2). Thus tetralin gave succinic, glutaric, and adipic acids in the ratio 1:4:4(3). Confusion also resulted from the isolation of different products when different acid concentrations were used in the oxidation, e.g. cyclohexene-1,2-dicarboxylic anhydride was reported as the product from tetralin (1).

Ruthenium tetroxide is a useful reagent for the oxidation of alcohols, ethers, aldehydes, amides, alkenes and aromatic compounds (4). In the case of alkylbenzenes, the benzene ring is preferentially attacked, preserving any alkyl substituents as aliphatic carboxylic acids. Stock has reported the oxidation of Illinois No. 6 coal (5) using ruthenium tetroxide in a coordinating cosolvent, acetonitrile, which enabled the oxidation to proceed with much higher conversions (6).

We have reported the use of the ruthenium tetroxide with a phase transfer catalyst, a quaternary ammonium salt, in a carbon tetrachloride-aqueous system for the analysis of alkylnaphthalenes and a North Dakota lignite sample (3). The phase transfer catalyst transports the primary oxidant (periodate) into the organic phase as well as removes the carboxylate products from the organic phase. Improvement of the yield is believed to result from the avoidance of an inactive complex formed by the acid products with the ruthenium tetroxide. This method was used previously for the synthesis of fatty acids from 1-alkenes (7).

A number of model compounds were oxidized with ruthenium tetroxide in the two-phase system so that the method could be evaluated and compared with ruthenium tetroxide oxidation in acetonitrile. Reactions were carried out as reported earlier (3). Methods which did not require derivatization were devised for the analysis of the reaction products. The aqueous layer was analyzed on an ion moderated reverse phase HPLC column (Aminex HPX-87H) using 0.008 N H_2SO_4 as the eluent (1 ml/min) (refractive index detection). 3-Methyladipic acid was added as an internal standard and the system was calibrated for malonic, succinic, glutaric, adipic, and phthalic acids (single level calibration). The aqueous layer was also analyzed by GC with an AT-1000 phase fused silica capillary column. This column was calibrated for benzoic, phenylacetic and hydrocinnamic acids using 2-methylbutyric acid as the internal standard (multilevel calibration). The carbon tetrachloride layer was analyzed on an SE54 fused silica column calibrated for the aromatics, hydroaromatics and ketones and on the AT1000 column for the same acids as above. Diphenic acid was extracted from the carbon tetrachloride layer with NaOH and analyzed by weighing the crystals obtained after acidification of the extract.

High conversions were observed for the model compounds oxidized with RuO_4 in the two-phase system with a phase transfer catalyst (Table I). The conversions for diphenylmethane and bibenzyl were a little higher than when acetonitrile was used as the solvent. Another indication of higher reactivity for ruthenium tetroxide in the

Table I. Oxidation of Model Compounds With Ruthenium Tetroxide and Phase Transfer Catalyst (PT cat.)

Compound	Conversion	Product	Product Distribution	
			PT Cat.	Acetonitrile ^a
Indan	100%	1-Indanone	31	16
		Glutaric Acid	64	77
		Succinic Acid	5	7
Tetralin	100%	1-Tetralone	26	8
		Adipic Acid	50	75
		Glutaric Acid	24	17
Diphenylmethane	80%	Benzophenone	18	32
		Phenylacetic Acid	70	41
		Benzoic Acid	12	4
Bibenzyl	90%	Benzil	1	Trace
		Succinic Acid	43	35
		Hydrocinnamic Acid	45	63
		Phenylacetic Acid	2	--
		Benzoic Acid	10	--
Phenanthrene	100%	Phenanthrenequinone	2	4
		Diphenic Acid	92	91
		Phthalic Acid	6	5

^a = Data from reference 5.

two-phase system over the acetonitrile system is the greater yield of succinic acid as compared with hydrocinnamic acid in the oxidation of bibenzyl.

Oxidation of the alkyl substituent groups at the α -carbon to give the aryl ketone occurred in all model compounds. This was observed to a greater extent with indan and tetralin and to a lesser extent with diphenylmethane, as compared to the oxidation carried out with acetonitrile cosolvent. The ratio of glutaric to succinic acids resulting from the oxidation of indan was greater than 10 to 1 for both oxidation conditions. The ratio of adipic to glutaric acids from the oxidation of tetralin was higher when acetonitrile was used. The selectivity of the ruthenium tetroxide reagent for aryl versus alkyl attack thus varies in the two methods with the type of substrate being oxidized. Oxidation of the PAH, phenanthrene, showed no difference in product distribution between the two systems.

The oxidation of lignite (Beulah mine) with ruthenium tetroxide proceeded rapidly at room temperature. The products from the oxidation in the aqueous layer could not be analyzed directly by the HPLC method because the solution was too dilute. Diazomethane in ether was stirred with the aqueous layer for two hours to convert the acids to ether soluble esters, which were analyzed by GC (DB1701 capillary column) (see Figure 1). Table II lists major components and the relative GC peak area percentages.

The major components were aliphatic dicarboxylic acids and benzene polycarboxylic acids. Very low concentrations of aliphatic monocarboxylic acids were formed. Since succinic acid is present in the largest concentrations of the diacids, we may infer that a major structural feature of the lignite is a

TABLE II
 CARBOXYLIC ACIDS FROM RuO₄ OXIDATION OF BEULAH LIGNITE (See Figure 1)

Peak No.	Compound (as methyl ester)	Area, %
1	siccinic	10.7
2	methylsuccinic	1.1
3	glutaric	7.6
4	methyl glutaric	1.0
5	adipic	2.7
6	unknown	7.7
7	phthalic	0.7
8	terephthalic	0.4
9	isophthalic	0.2
10	unknown	3.2
11	benzene-1,2,4-tricarboxylic	3.4
12	benzene-1,2,3-tricarboxylic	4.2
13	benzene-1,3,5-tricarboxylic	0.7
14	benzene-1,2,4,5-tetracarboxylic	5.7
15	benzene-1,2,3,4-tetracarboxylic	4.5
16	benzene-1,2,3,5-tetracarboxylic	5.7
17	benzene pentacarboxylic	7.3

dimethylene bridge occurring between aromatic moieties or present in a hydroaromatic such as 4,5-dihdropyrene. The model compound studies with diphenylmethane show that this method is limited in its applicability to the determination of single methylene bridges. Since malonic acid was produced in only trace amounts from oxidation of diphenylmethane, the absence of malonic acid in the lignite oxidation products does not rule out methylene bridges between aromatics in the coal.

The greater amounts of benzenepolycarboxylic acids relative to the benzenedicarboxylic acids which would be expected from naphthalene oxidation may seem surprising, however some of the acid groups were undoubtedly present in the coal before the oxidation. This aspect is being studied by labeling the original acid groups.

In order to fully interpret the results of the lignite oxidation with this reagent, the oxidation of several more model compounds will be studied. Quantitation of the methyl esters of the products from the lignite oxidation is also in progress.

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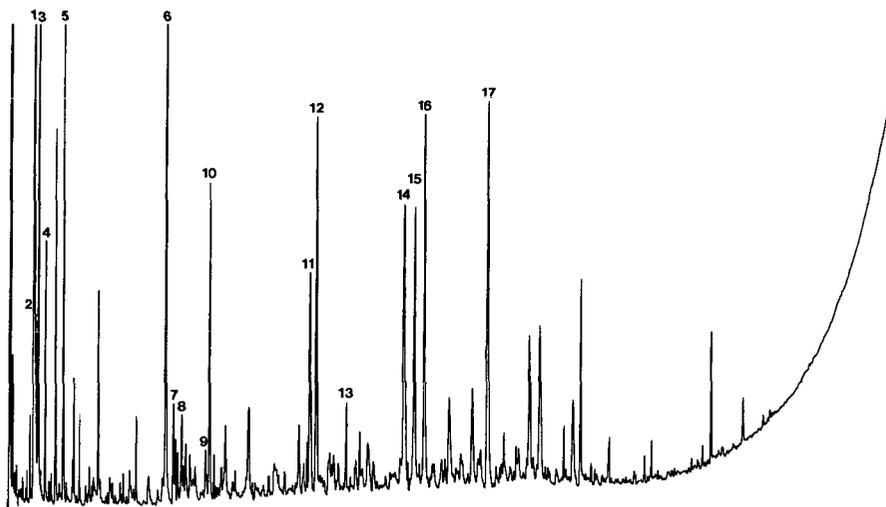


Figure 1. Methyl esters of products of ruthenium tetroxide oxidation of Beulah 3 lignite. DB1701 (0.25 μ) FSOT 15m x 0.32 mm. On-column injection. FID. H₂ carrier (41 cm/sec at 240°C).