

THE RUTHENIUM(VIII) CATALYZED OXIDATION OF TEXAS LIGNITE AND ILLINOIS NO. 6  
BITUMINOUS COAL. THE ALIPHATIC AND AROMATIC CARBOXYLIC ACIDS.

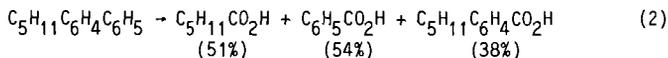
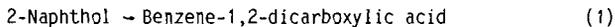
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INTRODUCTION

The structural elements in coals have been under study by modern methods in several laboratories over the past decade. Demo and his associates pointed out the need for specific reagents for the elaboration of the aliphatic network in these materials and have exploited the acid-catalyzed reactions of peroxyacids for the selective decomposition of the aromatic structural elements (1-5). Unfortunately, the initial reaction products are often unstable under the reaction conditions and it is difficult to relate the structures of the observed products to the original structural elements of the coals (5). Considerations of this kind and other objectives led us to consider the use of ruthenium(VIII) as an oxidant for coal. Sharpless and his associates recently pointed out that oxidation reactions with ruthenium(VIII) could be carried out very effectively in the presence of acetonitrile (6). Their suggestion led to the discovery that ruthenium(VIII) in a nitrile-rich solvent was an excellent oxidant for coal (7).

The oxidation reactions of representative hydrocarbons such as the alkyl-benzenes, alkylnaphthalenes, phenanthrenes and anthracenes have been investigated (7). The selectivity of the reaction is illustrated by the results for the oxidation of 2-naphthol and 4-pentylbiphenyl, equations (1) and (2).



The reagent has also been used successfully for the oxidation of Illinois No. 6 coal (7). Further, the volatile monocarboxylic acids have been determined quantitatively using the oxidation reaction in conjunction with isotope dilution techniques (10). Mallya and Zingaro investigated the oxidation of Texas lignite using ruthenium(VIII); they pointed out that ester groups were produced during the reaction (8). Olson and his coworkers employed the reagent and a phase transfer catalyst for the oxidation of North Dakota lignite; they identified 16 principal products (9).

This report concerns the similarities and differences we observed in the product distribution obtained in the oxidation of Texas lignite and Illinois No. 6 coal.

## EXPERIMENTAL PART

Materials.--Ruthenium(III) chloride trihydrate, carbon tetrachloride, acetonitrile, and ether were obtained from commercial sources. Authentic samples of the carboxylic acids or esters were obtained from commercial sources and from R. Hayatsu and R.E. Winans of the Argonne National Laboratory. Diazomethane was prepared from Diazald.

Illinois No. 6 coal [77.2%C, 5.6%H, 0.68%N, 0.15%Cl, 2.95% organic S, 0.89% pyritic S, 0.00% sulfate, and 12.5% O (by difference)] was obtained from the Peabody mine in Pawnee, Illinois. Texas lignite [70.0% C, 5.0% H, 1.5% N, 2.0% S, 19.6% O (by difference)] was obtained from the Wilcox formation near Rockdale, Texas and was supplied by N. Mallya. Each sample was extracted before oxidation with aqueous hydrochloric acid, aqueous sodium hydroxide, benzene-methanol, and chloroform as described by Hayatsu and coworkers (11).

Oxidation Procedure.--The oxidation reactions were carried out as described previously (7) using coal (400 mg), ruthenium(III) chloride trihydrate (12 mg), and sodium periodate (4 g) in a mixture of carbon tetrachloride (8 ml), acetonitrile (8 ml) and water (12 ml). The mixture was stirred for about 24 hours at room temperature. The solids were collected by filtration and the organic and the aqueous phases were retained. The mildly acidic aqueous layer was washed with four portions of ether (15 ml). The solid was also washed with ether. All the organic extracts were combined and dried with sodium sulfate. The solvents were removed with a rotary evaporator at 40°C. The acids in the concentrated solution were methylated using 0.35M diazomethane in ether (10 ml). The ether was carefully removed using a rotary evaporator at room temperature. This procedure was repeated three times and the final solution was examined by gas chromatography/mass spectrometry.

Gas Chromatography Mass Spectrometry.--The GC/MS results were obtained using an HP Model 5790A gas chromatograph with VG Model 70-250 mass spectrometer. The chromatograph was equipped with a 50 meter, OV-1701 (0.25 $\mu$ ) capillary column supplied by Quadrex Corporation for the analysis of the oxidation products of the Illinois No. 6 coal. The conditions for the analysis are noted: injection port, 250°C; the oven temperature was programmed to hold at 50°C for one minute then to heat to 270°C at the rate of 7°C/min and then to hold at 270°C. The entire oxidation procedure and analysis was repeated. The gas chromatograms of the products are shown in Figures 1a and 1b.

In the analysis of Texas lignite, a 60 meter Durabond 1701 (0.25 $\mu$ ) capillary column supplied by J & W Scientific Inc. was used. The conditions for the analysis are noted: injection port, 250°C, the oven temperature was programmed to hold at 50°C for one minute, and to heat to 270°C at the rate of 8°C/min and then to hold at 270°C. The gas chromatogram of the oxidation product of Texas lignite is shown in Figure 2.

One scan per second was used in low resolution electron impact (EI) and chemical ionization (CI) mass spectral analyses. Isobutane was used as the reagent gas in the chemical ionization work.

## RESULTS

The oxidation reactions of Texas lignite and Illinois No. 6 bituminous

coal proceeded smoothly with the ruthenium ion catalyst and the carboxylic acids were isolated without difficulty. The esterification reactions were carried out exhaustively to insure that substances such as benzenetetracarboxylic acid were completely converted to the corresponding methyl esters. Capillary gas chromatography as described in the Experimental Part provided an excellent separation of the esters. In many cases, the structures of the products were established by comparison with authentic samples. When authentic samples were not available, electron impact and chemical ionization mass spectrometry were used to assign their structures in conjunction with libraries of mass spectral data. These procedures enabled the identification of about 100 compounds including virtually every compound formed in greater than 5% yield relative to dimethyl butane-1,4-dioate. It is notable that neither nitrogen- nor sulfur-containing compounds have been detected among the reaction products of these coals. Accordingly, we are continuing our study of the less abundant substances and of the substances that are not fully resolved by capillary chromatography.

The results for the more prominent benzene and aliphatic carboxylic acids are summarized in Tables 1 and 2.

#### DISCUSSION

**Benzenecarboxylic Acids.**--Ruthenium(VIII) is a selective electrophilic oxidant. Phenolic compounds and activated polycyclic aromatic compounds are oxidized to benzenecarboxylic acids by the reagent (7). Neither phenolic compounds nor ethers, for example 4-hydroxy- or 4-methoxybenzenecarboxylic acid, nor reactive aromatic compounds, for example naphthalene-2-carboxylic acid, are observed among the oxidation products. Rather, the reaction provides a broad array of benzenecarboxylic acids, some of which have methyl, methylene-carboxyl ( $\text{CH}_2\text{CO}_2\text{H}$ ) or oxocarboxyl ( $\text{COCO}_2\text{H}$ ) groups bonded to the benzene ring. The absence of hydroxyl and methoxyl derivatives in the products coupled with a knowledge of the carbon atom balance strongly suggests that the benzenecarboxylic acids observed in this reaction account virtually quantitatively for the oxygen-free carbocyclic structures in these coals.

Five important features are apparent in the results for Texas lignite. Only 10-15 mole % of the products are benzenecarboxylic acids. Among these acids, benzene-1,2-dicarboxylic acid is the most abundant product. Neither benzene-1,3-, benzene-1,4-dicarboxylic acid, nor benzene-1,3,5-tricarboxylic acid are formed in the reaction. Benzene-1,2-dicarboxylic acid, benzene-1,2,3-, benzene-1,2,4-tricarboxylic acid, and benzene-1,2,4,5-tetracarboxylic acid are produced in a 20:20:10:1 ratio. A variety of methylbenzenecarboxylic acids are also obtained.

These results provide cogent evidence for the view that ortho substitution patterns are predominant in the carbocyclic structures of this material and that biphenyl structures are insignificant. The more abundant benzenedi- and tricarboxylic acids presumably arise from naphthalenes, naphthols, and oxygen-containing heterocyclic compounds. The low abundances of the tetracarboxylic acids indicate that the carbocyclic structures are not condensed to a significant degree. Thus, the results are incompatible with an important role for phenanthrenes or anthracenes.

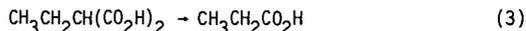
\* For convenience, the products are described as carboxylic acids rather than methyl esters in this discussion.

The Illinois No. 6 coal undergoes ruthenium(VIII) oxidation to yield a very different array of benzenecarboxylic acids. In this instance, benzenecarboxylic acids constitute about 25-30 mole % of the product. Benzene-1,2-dicarboxylic acid, benzene-1,2,3- and 1,2,4-tricarboxylic acids and benzene-1,2,4,5-tetracarboxylic acid are the most prominent products. Only very small quantities of benzene-1,3- and 1,4-dicarboxylic acid and benzene-1,3,5-tricarboxylic acid are formed. Benzene-1,2-dicarboxylic acid, benzene-1,2,3-, benzene-1,2,4-tricarboxylic acid, and benzene-1,2,4,5-tetracarboxylic acid are formed in a 0.8:0.9:1.2:1 ratio. This oxidation product also contains a variety of methylbenzenecarboxylic acids.

The product distribution for Illinois No. 6 coal contrasts sharply with that for Texas lignite. The most prominent differences appear in the large increase in the yields of the tri- and tetracarboxylic acids which indicate that the carbocyclic network of the Illinois coal is significantly more condensed than that of the lignite.

The oxidation reactions of these coals also yield aliphatic monocarboxylic acids (10). Acetic acid is the predominant product of this kind. Quantitative analyses indicate that the Illinois No. 6 coal used in this study yields 1.7 moles of acetic acid/100 carbon atoms. This acid arises principally from the oxidation of methylated aromatic fragments. The results presented in Table 1 indicate that a variety of other methylated compounds are also formed. Several lines of evidence now suggest that Illinois No. 6 coals contain between 4 and 6 methyl groups per 100 carbon atoms (10,12).

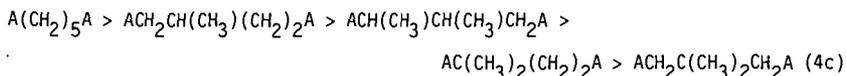
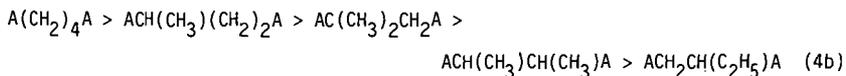
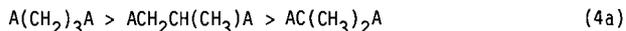
Aliphatic Carboxylic Acids.--Ruthenium(VIII) reacts selectively with activated aromatic structures. Most aliphatic structures are stable. Thus, alkylaromatic compounds provide the corresponding alkylcarboxylic acids (RAR - RCO<sub>2</sub>H), hydroaromatic compounds provide dicarboxylic acids (indan - pentane-1,5-dioic acid) and bridging alkyl fragments yield dibasic acids (bibenzyl - butane-1,4-dioic acid). Most aliphatic acids are stable under the reaction conditions. Unfortunately, the propane-1,3-dioic acids decompose as illustrated for the ethyl derivative in equation (3).



In spite of this limitation, the ruthenium(VIII) oxidation provides both a better yield of aliphatic acids and a more diverse array of products than other oxidants such as the peracids (2,3).

The aliphatic reaction products obtained from Texas lignite and Illinois No. 6 coal are summarized in Table 2.

The oxidation of Texas lignite provides about 60 aliphatic acids. Virtually all of the acids produced in greater than 5% abundance relative to butane-1,4-dioic acid have been identified. All the  $\alpha,\omega$ -diacids from butane-1,4-dioic acid to undecane-1,11-dioic acid are present. Many other diacids are also produced including almost every isomer of the 5,6, and 7 carbon atom derivatives as illustrated in equation (4). An interesting array of tri- and tetracarboxylic acids are also formed.



The interpretation of these results is complicated by the fact that several of the products can be formed in different ways. To illustrate, pentane-1,5-dioic acid can be formed from four different structures:  $Ar(CH_2)_3Ar$ ,  $Ar(CH_2)_3CH(Ar)_2$ , indan, and 1-aryltetralin. Nevertheless, the results provide a basis for the discussion of the complex aliphatic network in this coal.

The product mixture obtained from Illinois No. 6 coal is much less complex. About 40 compounds have been identified. In contrast to the lignite, only 5  $\alpha,\omega$ -dicarboxylic acids are obtained and there are correspondingly fewer di- and tricarboxylic acids. There is a considerable decrease in the quantities of the higher molecular weight aliphatic acids.

The product distribution observed in this study is considerably more diverse than that obtained in previous studies of the aliphatic network of this coal. Many of the aliphatic acids produced in the reaction of the lignite are also formed from this coal during oxidation, but the yields are uniformly lower. Thus, the structures of the two materials appear to be closely related.

#### CONCLUSION

Ruthenium(VIII) is a selective oxidant for activated aromatic compounds and, therefore, provides definite information concerning the less readily oxidized carbocyclic and aliphatic structural elements in these coals. There are significant differences in the benzenecarboxylic acid product distributions for Texas lignite and Illinois No. 6 bituminous coal. While it is clear that ortho structures are dominant in the two coals, the degree of condensation differs appreciably for these 70 and 77% C (daf) materials. Hayatsu and co-workers have commented on this difference previously (13). Ruthenium(VIII) oxidation provides the aliphatic mono-, di-, tri- and tetracarboxylic acids in greater quantity and structural diversity than other techniques, such as peracid oxidation (2,3), designed to elaborate this structural element. Both Texas lignite and Illinois No. 6 coal yield many of the same low molecular weight di- and tri-carboxylic acid. While it is evident that the aliphatic structure of the lignite is more diverse, the structures of the two coals appear to be correlated inasmuch as many of the products have similar three and four carbon fragments. Broadly, our results are compatible with the viewpoint that the carbocyclic aromatic network becomes more diverse and the aliphatic network less diverse as coalification proceeds.

#### ACKNOWLEDGEMENT

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Table 1. The Benzenecarboxylic Acids Formed in the Oxidation of Texas Lignite and Illinois No. 6 Coal.

| Compound                               | Texas Lignite<br>Number Abundance <sup>a</sup> |       | Illinois No. 6<br>Number Abundance <sup>a</sup> |        |
|--|--|-------|---|--------|
| Benzenemonoacid                        | W  |       | W   |        |
| Benzene-1,2-diacid                     | VS   |       | S   |        |
| Benzene-1,3-diacid                     | Not detected                                   |       | VW  |        |
| Benzene-1,4-diacid                     | Not detected                                   |       | Not detected                                    |        |
| Methylbenzenediacyds <sup>b</sup>      | 4  | 2M,2W | 2   | W,M    |
| Dimethylbenzenediacyds <sup>b</sup>    | 1  | VW    | 1   | VW     |
| Benzene-1,2,3-triacid                  | S  |       | VS  |        |
| Benzene-1,2,4-triacid                  | VS   |       | VS  |        |
| Benzene-1,3,5-triacid                  | VW   |       | VW  |        |
| Methylbenzenetriacyds <sup>b</sup>     | 5  | VW    | 5   | 4W,1VW |
| Dimethylbenzenetriacyds <sup>b</sup>   | 2  | VW    | 2   | VW     |
| Trimethylbenzenetriacyds <sup>b</sup>  | Not detected                                   |       | 4   | 3W,1M  |
| Benzene-1,2,3,4-tetraacid              | W  |       | M   |        |
| Benzene-1,2,3,5-tetraacid              | W  |       | VW  |        |
| Benzene-1,2,4,5-tetraacyds             | W  |       | VS  |        |
| Methylbenzenetetraacyds <sup>b</sup>   | 1  | VW    | 2   | 1M,1VW |
| Dimethylbenzenetetraacyds <sup>b</sup> | Not detected                                   |       | 1   | W      |
| Benzenepentaacid                       | Not detected                                   |       | VW  |        |

<sup>a</sup>The relative abundances are based upon the relative ion currents with di-methyl butane-1,4-dioate adopted as 100%. The notation is VS > 30%; S 15-30%; M 5-15%; W 2-5% and VW < 2%.

<sup>b</sup>Certain of the methyl-containing molecules have CH<sub>2</sub>CO<sub>2</sub>H fragments rather than simple methyl groups.

Table 2. The Relatively Abundant Aliphatic Carboxylic Acids Formed in the Oxidation of Texas Lignite and Illinois No. 6 Coal.

| Compound <sup>a</sup> | Texas Lignite |                        | Illinois No. 6 |                        |
|-----------------------|---------------|------------------------|----------------|------------------------|
|                       | Number        | Abundance <sup>a</sup> | Number         | Abundance <sup>a</sup> |
| 2C2A                  | 1             | VS                     | 1              | VS                     |
| 3C2A                  | 3             | 2VS, 1W                | 3              | 2VS, 1W                |
| 4C2A                  | 5             | 2VS, 1M, 1W, 1VW       | 3              | 2S, 1VW                |
| 5C2A                  | 7             | 1VS, 4M, 2W            | 6              | 2M, 2W, 2VW            |
| 6C2A                  | 7             | 1VS, 3W, 3VW           | 2              | 1W, 1VW                |
| 7C2A                  | 4             | 1VS, 1S, 1W, 1VW       | -              | -                      |
| 8C2A                  | 1             | VW                     | -              | -                      |
| 9C2A                  | 1             | M                      | -              | -                      |
| 10C2A                 | 2             | 1M, 1VW                | -              | -                      |
| 11C2A                 | 1             | W                      | -              | -                      |
| 3C3A                  | 1             | VS                     | 1              | S                      |
| 4C3A                  | 5             | 1S, 4M                 | 5              | 1M, 3W, 1VW            |
| 5C3A                  | 5             | 4M, 1W                 | 4              | 4W                     |
| 6C3A                  | 6             | 2M, 4VW                | 1              | W                      |
| 7C3A                  | 3             | 1M, 2VW                | -              | -                      |
| 4C4A                  | 1             | VW                     | -              | -                      |

<sup>a</sup>The numbers of unoxidized aliphatic carbon atoms in the structure are indicated first, followed by the number of acid groups. Thus, 2C2A could be 1,4-butanedioic acid or 2-methyl-1,3-propanedioic acid.

<sup>b</sup>The abundance is defined in footnote b of Table 1.

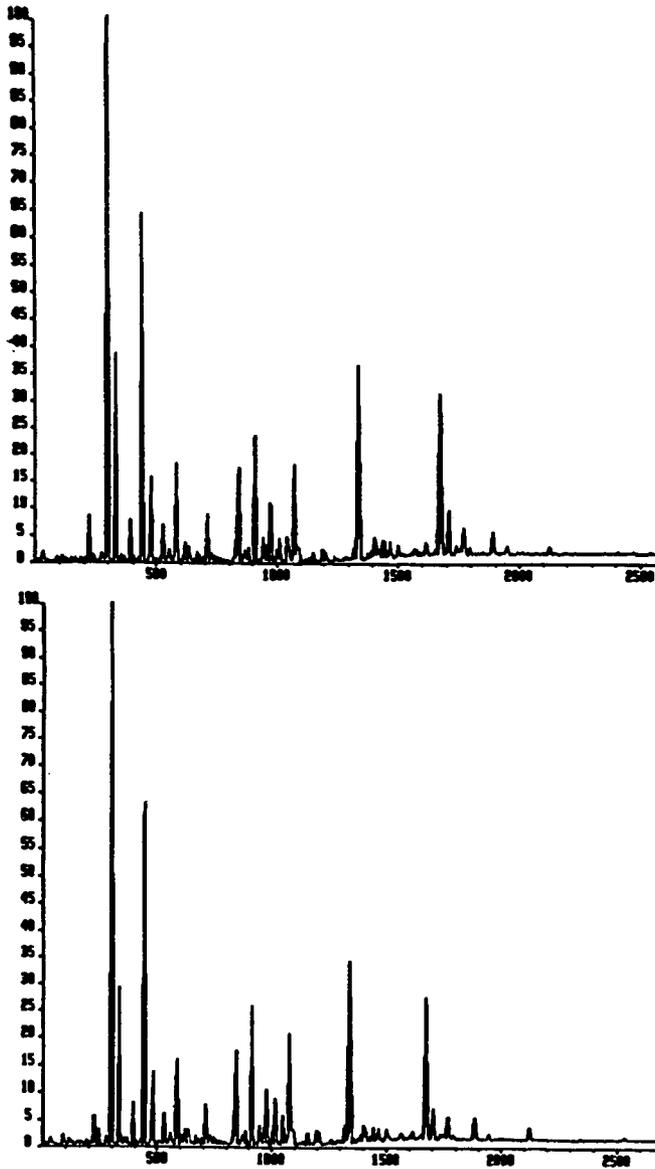


Figure 1. Chromatograms (GCMS) of the oxidation products of Illinois No. 6 coal obtained in fully independent experiments.

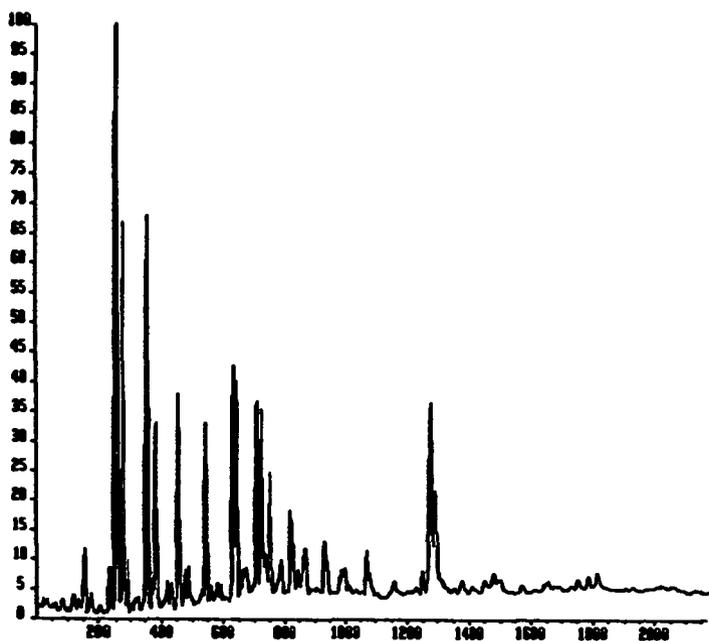


Figure 2. Chromatogram (GCMS) of the oxidation product of Texas lignite.