

LOW-RANK COAL STRUCTURE ELUCIDATION WITH RUTHENIUM TETROXIDE

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The goal of these studies was to elucidate the structural features of coals which are believed to be important in conversion processes. Of special interest are the nature of the hydroaromatic groups and the bridging groups between aromatic moieties, because of their roles in thermal cleavage and depolymerization processes and the hydrogen shuttling which occurs during the depolymerization and stabilization of cleavage products. The first objective was the development of new methods for the isolation or solubilization of the aliphatic groups in the coal, which may then be related to these hydroaromatic systems and bridging groups. We have successfully used ruthenium tetroxide in a two phase solvent system with a phase transfer catalyst to selectively oxidize the aromatic groups (1). Stock has used ruthenium tetroxide in the presence of acetonitrile to oxidize a Texas lignite and Illinois No. 6 coal (2,3). These procedures are a more viable alternative than the use of trifluoroperacetic acid which was used in earlier studies by Deno (4) and whose difficulties have been pointed out (1,2).

The oxidation of a North Dakota lignite with ruthenium tetroxide with the phase transfer catalyst proceeded rapidly at ambient temperature giving carbon dioxide and carboxylic acid products which were converted to methyl esters by diazomethane for qualitative analysis using GC and GC/MS. A very complex mixture of aliphatic mono and polycarboxylic acids and aromatic polycarboxylic acids was formed in the reaction. In contrast to the trifluoroperacetic acid studies, no oxiranepolycarboxylic acids were found. Keto acids were also found to be absent. An ion trap mass spectrometer was found to be useful in these analyses since an M+1 peak was found for many of the esters which normally do not exhibit any molecular ion.

A major effort was expended to find a reliable and accurate method for the quantitative analysis of carboxylic acid products. Loss of dicarboxylic acids and esters during extraction and conversion to methyl esters was a major problem. Analysis of the low molecular weight monoacids was carried out on a calibrated capillary GC using direct on-column injection of the distilled reaction products. High pressure liquid chromatography of the diacids directly on an Aminex HPB7H resin was unsuccessful due to interferences between aliphatic and aromatic acids, even though satisfactory resolution of the aliphatic diacids was obtained using two columns in series (5). Ion exchange chromatography both as a cleanup for the Aminex resin and analytical separations by itself was also unsuccessful. A calibrated GC method using an internal standard added to the acid mixture before cleanup and methylation also failed to give reproducible results, especially for the aromatic polycarboxylic acids. Finally, several deuterated acid standards were prepared or purchased so that isotope dilution methods using quadrupole GC/MS analysis of the methyl esters could be carried out. Calibration curves were highly linear ($r^2 = 0.99$) over a wide range. A series of repetitive oxidations on the same Beulah lignite sample gave highly consistent results, especially for the adipic and phthalic acids which were labeled with four deuteriums. The average deviations were in the second decimal place and thus are no more limiting than the proximate analysis data.

In order to interpret the data, a number of model compounds have been oxidized using the ruthenium tetroxide with a phase-transfer catalyst. Some of these data were reported previously (1). Basically alkyl substituents are converted in very high yield to the monocarboxylic acids. Hydroaromatics give a mixture of products consisting of the α -ketone, the diacid which maintains the same number of methylene

carbons as in the hydroaromatic ring, and smaller amounts of the diacid corresponding to loss of one methylene group. Stock obtained less of the ketone and more of the larger diacid. One-carbon methylene bridges are oxidized to ketones or carboxylic acid groups, but the arylacetic acid may be isolated in good yield. Malonic acid which would have resulted from oxidation of the second benzene ring is not found. Unfortunately it is not stable in the oxidizing system, in contrast to other carboxylic acids. Dimethylmalonic acid was isolated as a product from 2,2-diphenylpropane. Thus it probably not possible to determine one-carbon bridges in the structure using this reagent, unless they are quaternary. Two carbon methylene bridges gave succinic acid and hydrocinnamic acid. 9,10-Dihydrophenanthrene, however, gave succinic and diphenic acid, the major product from phenanthrene. Phthalic and other aromatic polycarboxylic acids are products from various polynuclear aromatic systems.

The effect that oxygens in the structure of hydroaromatics exert on the product yield was studied because of the prevalence of hydroxyl-substituted hydroaromatics in the devolatilization products of lignites. Oxidation of 6-hydroxytetralin with RuO_4 gave no ketone and more degradation to glutaric and succinic than that which occurred in the oxidation of tetralin. 6-Methoxytetralin behaved similarly. 5,6,7,8-Tetrahydronaphthoquinone gave a considerable amount of succinic acid in addition to the adipic. 1-Tetralone gave no reaction, however 2-tetralone was oxidized to succinic acid.

A comparison of three oxidation methods, the ruthenium tetroxide with phase transfer catalyst, the ruthenium tetroxide with acetonitrile and the trifluoroacetic acid, was carried out on the same sample of Beulah lignite. There was no significant difference in the amounts of acid products between the two ruthenium tetroxide methods (Table 1). Thus whatever differences exist between these reagents in their reactions with model compounds, no differences are apparent in the products from lignite oxidation. This may be a reflection of the more complete oxidation expected for hydroxyaromatics at the ends of the aliphatic bridging groups and for hydroxyhydroaromatic groups or perhaps the absence of tetralin groups in the coal structure. No evidence for a tetralone type of structure in the products of oxidation has been found. The lower yields of aliphatic acids found when the Deno oxidation with trifluoroacetic acid was used reflect the same problems encountered with model compound oxidations with this reagent.

Table 1. Comparison of Oxidation Methods on Same Beulah Lignite Sample

Method	SU	GL	AD	PT	PH	BT
RuO_4/PTC	3.04	0.49	0.14	0.55	0.05	0.67
RuO_4/CH_3CN	2.93	0.57	0.14	0.49	0.08	1.01
CF_3CO_3H	0.93	0.30	0.09	0.14	0.02	2.25

A number of low-rank coals were oxidized for comparison purposes. Values for the amounts of six carboxylic acid products which were determined using the isotope dilution method are reported in Table 2. The amounts of the six acids in the oxidation products generally increase with coal rank or % C. There is a little variation in the three North Dakota lignites (Beulah, Gascoyne and Velva), which have about 71% C. There is a greater variation in acids from the Texas lignites (San Miguel - 67% C and Martin Lake - 73% C) and the subbituminous coals (Wyodak - 73% C and Decker - 76% C). This trend is consistent with the hypothesis that the western subbituminous coals have a higher algal lipid-derived aliphatic component than the lignites. A Pittsburgh bituminous coal was also oxidized and found to have

a much lower aliphatic acid content, but higher aromatic acid content, consistent with the hypothesis that it has been aromatized to a greater extent than the subbituminous coals. It was not possible to find a correlation between these data in Table 2 and corresponding published tubing bomb liquefaction data for these coals (6).

Table 2. Results of Coal Oxidations with RuO₄ (% maf Basis)

<u>COAL</u>	<u>SUC</u>	<u>GLU</u>	<u>AD</u>	<u>PT</u>	<u>PH</u>	<u>BT</u>
Beulah	2.38	0.59	0.11	0.70	0.07	1.53
Gascoyne	2.58	0.56	0.13	0.62	0.07	1.60
Velva	2.71	0.56	0.16	0.73	0.05	1.37
Martin Lake	2.50	0.96	0.27	0.76	0.09	1.55
San Miguel	2.94	0.61	0.12	0.62	0.04	0.73
Wyodak	3.74	0.89	0.23	0.82	0.08	1.64
Decker	4.17	1.69	0.30	0.75	0.09	1.66

A comparison of all the major acid products for two coals, Beulah lignite and Wyodak subbituminous is given in Table 3 and 4. Amounts of those acids not determined by isotope dilution were obtained by a calibrated FID method.

Table 3. Oxidation of Beulah Lignite and Wyodak Coal (% of maf Coal)

<u>Aliphatic Acids</u>	<u>Beulah</u>	<u>Wyodak</u>
Succinic*	2.38	3.74
2-Methylsuccinic	0.41	0.11
Glutaric*	0.59	0.89
2-Methylglutaric	0.26	0.14
Adipic*	0.11	0.23
2-Methyladipic	0.07	0.15
Pimelic	0.04	0.11
Suberic	0.12	0.10
Azeleic	0.04	0.12
Sebacic	0.01	0.05
Octanoic	0.02	0.04
Nonanoic	0.00	0.00
Lauric	<0.01	0.00
Myristic	0.01	0.02
Palmitic	<0.01	0.02
1,2,3-Propanetricarboxylic*	0.70	0.82
1,2,4-Butanetricarboxylic	0.31	0.40

*determined by isotope dilution, the others by fid calibration

Table 4. Oxidation of Beulah Lignite and Wyodak Coal (% of maf Coal)

<u>Aromatic Acids</u>	<u>Beulah</u>	<u>Wyodak</u>
Phthalic*	0.07	0.08
1,2,3-Benzenetricarboxylic	0.23	0.32
1,2,4-Benzenetricarboxylic	0.30	0.32
1,3,5-Benzenetricarboxylic	0.01	0.01
1,2,3,4-Benzenetetracarboxylic	1.5	1.7
1,2,4,5-Benzenetetracarboxylic*	1.53	1.64
1,2,3,5-Benzenetetracarboxylic	1.5	1.7
Benzenepentacarboxylic	1.5	1.4
Benzenhexacarboxylic	0.01	0.37

Three lithotypes have been separated from Beulah lignite on the basis of physical properties and have been extensively studied at the University of North Dakota Energy Research Center (7). Oxidation of the vitrain, durain and fusain lithotypes gave a wider variation in the amounts of the six carboxylic acids (Table 5) than did oxidation of many of the samples from different mines (Table 2). The durain and fusain appear to be more aromatized than the vitrain. The main point is that a great variability is likely to be found in the samples obtained from one mine, depending on the lithotype composition, and consequently one should not attempt to correlate any data from different experiments unless they are all done with the same sample.

Table 5. Oxidation of Beulah Lignite Lithotypes with RuO₄

<u>Lithotype</u>	<u>SU</u>	<u>GL</u>	<u>AD</u>	<u>PT</u>	<u>PH</u>	<u>BT</u>
Vitrain	2.41	0.60	0.08	0.58	0.02	0.71
Durain	2.10	0.50	0.12	0.52	0.08	1.38
Fusain	1.38	0.33	0.10	0.27	0.15	1.40

Since the aliphatic diacids which are found in the products from ruthenium tetroxide oxidation may have been derived from either a hydroaromatic or a bridging group, a number of experiments have been attempted to try to distinguish the amount of diacids which are derived from each type of precursor. One of these experiments was a dehydrogenation of the lignite prior to oxidation with ruthenium tetroxide. Water was removed from Beulah lignite by Dean-Stark distillation with xylene under nitrogen and the lignite suspension in xylene was then refluxed with dichlorodicyanoquinone. The dehydrogenated coal was then oxidized with ruthenium tetroxide. The resulting acids were analyzed (Table 6). The amount of succinic acid decreased substantially, however the amount of adipic decreased very little. This result implies that about half of the succinic may be derived from the hydrophenanthrene or dihydropyrene type of hydroaromatics, whereas about 10% of the adipic acid may have been derived from the tetralin type of hydroaromatics. The increase in the amount of phthalic acid resulting from oxidation of the dehydrogenated lignite may also be noteworthy. Dehydrogenation of dihydrophenanthrene or dihydroanthracene structures to the polynuclear aromatics may explain this increase in phthalic acid.

Table 6. Effect of Dehydrogenation on Beulah Lignite

<u>SU</u>	<u>GL</u>	<u>AD</u>	<u>PH</u>
1.42	0.38	0.12	0.22

An experiment was carried out to determine the extent to which the original carboxylic acid groups of the coal make up the acid groups found in the products obtained after oxidation with the ruthenium tetroxide. In order to label the original carboxylic acid groups, a sample of Beulah lignite was methylated with methyl-d₃ iodide using Liotta's procedure (8). This sample containing the methyl-d₃ labelled ester groups was subsequently oxidized with ruthenium tetroxide and the ratio of labelled to unlabelled ester groups determined using mass spectrometry. The ratio of M+1 to M+4 was determined under CI conditions, since the molecular ions are not usually present. For the aliphatic acids, about 10% of the esters were labelled, indicating that 10% of the aliphatic diacid products resulted from oxidation of arylalkanoic acids, such as succinic from 3-arylpropanoic acid.

References:

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