Masters Theses & Specialist Projects   Graduate School

5-1984

H2O2-TFA-H2SO4 Oxidation of Coal & Coal Model Compounds

Darrell Pierce
Western Kentucky University

Follow this and additional works at: https://digitalcommons.wku.edu/theses

Part of the Chemistry Commons

Pierce,

Darrell K.

1984

H_2O_2-TFA-H_2SO_4 Oxidation of Coal

and

Coal Model Compounds

A Thesis

Presented to

The Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

by

Darrell K. Pierce

May 1984

AUTHORIZATION FOR USE OF THESIS

Permission is hereby

☒ granted to the Western Kentucky University Library to make, or allow to be made photocopies, microfilm or other copies of this thesis for appropriate research or scholarly purposes.

☐ reserved to the author for the making of any copies of this thesis except for brief sections for research or scholarly purposes.

Signed *Darrell K. Pierce*

Date *April 19, 1984*

Please place an "X" in the appropriate box.

This form will be filed with the original of the thesis and will control future use of the thesis.

H_2O_2-TFA-H_2SO_4 Oxidation of Coal

and

Coal Model Compounds

Recommended _27 March 1984_
(Date)

John W Reason
Director of Thesis

John T. Riley

Curtis C. Wilkins

Approved _April 19, 1984_
(Date)

Elmer Gray
Dean of Graduate College

ACKNOWLEDGEMENTS

I would like to express my appreciation to the faculty of the Chemistry Department of Western Kentucky University. I especially would like to thank Dr. John W. Reasoner for his direction during the course of this research project.

I would also like to express my appreciation to my wife, Mrs. Lindy Pierce, for her support during this time and for typing this thesis.

TABLE OF CONTENTS

INDEX OF TABLES

H_2O_2-TFA-H_2SO_4 OXIDATION OF COAL
AND
COAL MODEL COMPOUNDS

Darrell Keith Pierce   May 1984   60 Pages

Directed by: John W. Reasoner

Department of Chemistry   Western Kentucky University

The Deno coal oxidation technique was investigated as a tool for the characterization of the aliphatic components of coal. This technique was applied to three high sulfur Kentucky coals:(1) No. 789673, (2) KCER 4002-Elkhorn No. 2, (3) KCER 7122-Ky. No. 12 and a low sulfur coal from Alpha Resources, Inc. Model compound investigations on toluene, ethyl benzene, propyl benzene, bibenzyl, indan and tetralin were also conducted. Different addition modes were investigated using ethyl benzene and diphenylmethane. The stability of the expected aliphatic acid products in the oxidation reagent were also investigated.

The data indicated the following:

1. Pyrite present in high sulfur coals catalyzes the decomposition of the oxidizing reagent.

2. Complete oxidation of both coals and model compounds to CO_2 and H_2O was occuring.

3. The expected aliphatic acid products were not stable in the oxidizing reagent.

I. INTRODUCTION

Coals are varying and complex in their chemical structures. Structural studies of materials of this type have classically been accomplished by degradative procedures which reduce the complex components of coal to simpler component parts that are more easily analyzed. Several useful coal degradation procedures have emerged providing us with much information on coal structure. These methods are (1) destructive distillation of coal to benzene and pyridine derivatives, (2) depolymerization and alkylation, (3) liquifaction or solvent extraction to produce components with molecular weights around 600, and (4) oxidation with the usual oxidizing agents HNO_3, O_2, Mn(VII), Cr(VI) to produce benzenecarboxylic acids.

Deno and co-workers reported that a mixture of 30% H_2O_2, trifluoroacetic acid, and H_2SO_4 dissolves coals, giving colorless or near colorless solutions with preservation of most of the aliphatic structure of the coal. It was suggested that this oxidation technique be adopted as a general method for characterizing the aliphatic structures in coals.[32]

In this study, seven model compounds and four coals were oxidized, the products analyzed, and their yields determined. The Deno method was followed in both model compound and coal oxidations. The effects of pyrite on the oxidizing agent and

-1-

the stability of the reported acid products in the oxidizing agent were also studied.

II. HISTORICAL

Destructive distillation or pyrolysis of coal is one
of the oldest techniques used to study coal structure.
This technique involves thermal cracking of the complex
coal polymers to more easily analyzed molecules.

Low temperature pyrolysis ($<400^{o}C$) of coal yields
three classes of compounds: (1) acidic class, (2) neutral
class, and (3) basic class. The acidic fraction contains
predominately phenolic compounds. The neutral fraction
contains paraffins, olefins, alicyclics, hydroaromatics,
aromatics, and various neutral ether and heterocyclic
derivatives. The basic fraction contains anilines,
pyridines, and other heterocyclic amine derivatives.
The product distribution among these fractions is highly
dependant on the nature of the coal being pyrolyzed. Over
800 different compounds have been isolated and characterized,
with the majority of these having been obtained in yields of
less that 1%.[1]

Model compound studies suggest that the C-O bond of
benzylic ethers and ethylene bridges connecting aryl groups
are cleaved by low temperature pyrolysis.

$$\text{C}_6\text{H}_5\text{—CH}_2\text{-CH}_2\text{—C}_6\text{H}_5 \quad \xrightarrow{\text{(H)}} \quad 2\ \text{C}_6\text{H}_5\text{—CH}_3$$
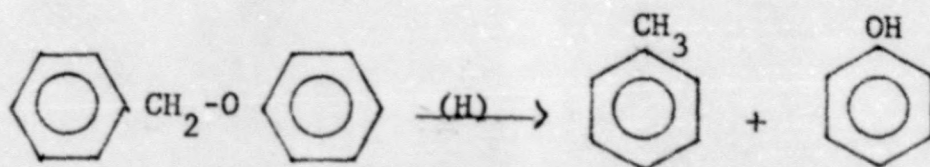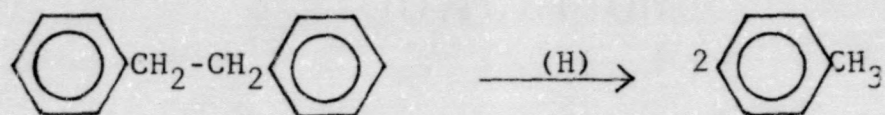
It was also found that methylene and ethylene bridges are more easily cleaved when one or more of the aryl rings contains a hydroxyl substituent.[2]

$$\text{C}_6\text{H}_5\text{—CH}_2\text{-CH}_2\text{—C}_6\text{H}_4\text{—OH} \quad \xrightarrow{\text{(H)}} \quad \text{C}_6\text{H}_5\text{—CH}_3 + \text{CH}_3\text{—C}_6\text{H}_4\text{—OH}$$
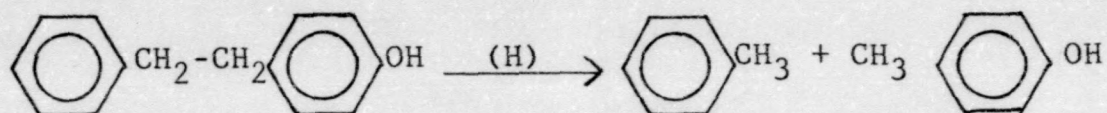
In mass spectrometric studies of the vacuum pyrolysis of coal extracts, it was observed that between 90 and 150°C only the lowest rank coals give appreciable spectra. The products evolved from the low rank coals were largely aliphatic in nature. Between 200 and 370°C aliphatic hydrocarbons of a wide molecular range were evolved. The yield of aliphatic materials was found, however, to decrease rapidly with increasing coal rank. Alkylbenzenes and alkylnaphthalenes were also found among the products at this temperature range. Because of the long duration of the observed spectra the simple aromatics were thought to be diffusing out of the pore structure of the coal. At higher temperatures (>400°C) there was an increase in the quantity of materials in the 450 to 640 molecular weight range. Among the products alkylphenols and naphthols were identified. The phenols were postulated to have come from the cleavage of $\text{Ar-CH}_2\text{-O-Ar}$ type bonds to form alkylbenzenes and phenols, suggesting that the coal matrix is starting to decompose at temperatures greater than 400°C.[3]

A number of techniques have been developed to study the structure of coal by depolymerization and alkylation.

Friedel-Crafts alkylation of coals appears to occur readily. It has been shown that bituminous coal can be alkylated by 2-chloropropane in the presence of aluminum chloride under very mild conditions.[4] Table 2.1 shows the results of alkylation studies at 0-5°C and at 150°C.

Table 2.1

Friedel-Crafts Alkylation with

2-Chloropropane/AlCl$_3$

Coal	% Solubility		H/C
	Benzene	Pyridine	
Raw Coal$_a$	2	11	0.82
Alkylated Coal (5°C)	11	30	0.94
Alkylated Coal (150°C)	15	39	0.98
a) 77.66% C, 5,36% H, 4.75% S, 1.36% N, 10.88% O			

Increased solubility is most likely brought about by the partial structural decomposition of the coal matrix caused by alkylation.

It has also been shown that hydrofluoric acid can be used as a catalyst for the alkylation of bituminous coals using either an alkene or an alcohol as the alkylating agent. Table 2.2 shows the results of HF catalyzed alkylation.[5]

Table 2.2

Alkylation of Coal with

Alcohol/HF

Coal	Tetrahydrofuran Solubility (Wt%)	Pyridine Solubility (Wt%)
Pittsburgh Seam$_a$	8	20
Pittsburgh Seam (HF only)	20	30
Pittsburgh Seam (HF + Butyl Alc.)	59	83
Illinois No. 6$_b$	8	15
Illinois No. 6 (HF only)	10	20
Illinois No. 6 (HF + sec-Butyl Alc.)	61	99

a) 78.5% C, 5.1% H, 1.5% N, 2.1% S, 11.1% O, 1.7% Ash

b) 73.4% C, 4.9% H, 1.5% N, 3.2% S, 6.6% O, 10.4% Ash

Acid catalyzed cleavage of certain ether linkages is the probable cause of the increased solubility upon treatment with HF alone. One problem arising from the use of HF alkylation is the tendency of the alcohol to undergo condensation and polymerization.

Coal matrix depolymerization also occurs when coal is placed in a phenol/BF_3 solution. BF_3 functions as a Lewis acid catalyst. The function of phenol may be attributed to several factors. First, phenol can be alkylated by the coal fragments produced by the acid catalyzed depolymerization of the coal matrix. Second, phenol can promote swelling and subsequent extraction of materials by penetration into the

micropores of the coal particles. Third, the scission of ether

linkages is promoted by phenol. Table 2.3 shows the results

of phenol/BF_3 depolymerization.[6]

Table 2.3

Depolymerization of Coal with

Phenol/BF_3

Coal	Coal Type	Chloroform Solubility (%)	
		Initial	Final
MacFarlane[a]	HVB	2	96
Ohio No. 8[b]	HVB	4	95
Clarion[c]	HVB	3	84
Mary Lee[d]	HVB	0.9	7
W. Virginia[e]	LVB	1	14

a) 67.3% C, 4.9% H, 1.29% N, 6.89% S, 19.6% O, 21.8% Ash

b) 80.9% C, 5.65% H, 1.41% N, 4.12% S, 7.9% O, 7.7% Ash

c) 60.5% C, 4.1% H, 0.78% N, 16.75% S, 18.3% O, 20.6% Ash

d) 77.8% C, 4.9% H, 1.59% N, 1.43% S, 14.3% O, 8.9% Ash

e) 90.65% C, 4.75% H, 1.38% N, o.72% S, 2.5% O, 5.9% Ash

All the depolymerized coals were at least 75% soluble in alkali

with the exception of the West Virginia coal. It has been

reported that low-volatile bituminous coals are not as sus-

ceptible to depolymerization as high-volatile bituminous

coals.[7] After acetylation all the high sulfur coals were

found to become 84 to 96% soluble in chloroform. The solu-

bility of the Mary Lee and West Virginia were only slightly

improved over the raw coals.

The Sternberg reductive alkylation procedure[8] is another technique used to study coal structure. The treatment of coals with alkali metals in the presence of naphthalene yields polyanions or "coal anions" which may be alkylated to give soluble products. In this case, naphthalene functions as an electron transfer agent making possible the formation of the "coal anion."

$$\text{Coal} + nC_{10}H_8^{\cdot -} \longrightarrow \text{Coal}^{n-} + nC_{10}H_8$$
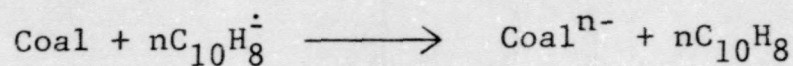
The naphthalene radical will cleave ether linkages and methylene bridges between aromatic rings.

$$\text{Ar-O-R} + C_{10}H_8^{\cdot -} \longrightarrow \text{Ar-O}^- + R^{\cdot} + C_{10}H_8$$
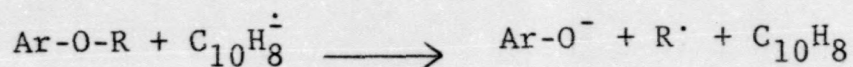
The coal anion may then be alkylated causing depolymerization of the coal matrix. The actual solubility of reductively alkylated coals depends upon the rank of coal used. The number-average molecular weights for benzene extracts of low rank coals range from 500 to 800. Higher rank coals give benzene extracts with number-average molecular weights from 1300 to 2000. This would be expected due to the increase in the degree of condensation of the aromatic system with increasing rank.[9]

Reduction of a bituminous coal followed by alkylation with butyliodide gave an approximately 90% conversion into soluble products. There was evidence that both carbon and oxygen alkylation had occured. The majority of the oxygen alkylation appears to have occured on aryl oxygen suggesting that ether linkages were being cleaved during depolymerization.[10]

Solvent extraction is another technique that has been widely used to study the structure of coal. In discussing solvent extraction, some of the terms that are commonly used to classify the extraction products need to be defined. There are three major classifications of the extraction products: (1) oils-hexane soluble, (2) asphaltenes-benzene soluble, hexane insoluble, and (3) preasphaltenes-pyridine soluble, benzene insoluble.

Four basic types of extraction procedures have been used to study coal structure: (1) non-specific extraction, (2) specific extraction, (3) extractive pyrolysis, and (4) reductive extraction.

Non-specific extraction is carried out in solvents such as benzene, chloroform, or ethanol at temperatures less than 100°C. At these low temperatures there is little or no degradation of the coal matrix. Most likely the substances extracted by this method are contained within the pore structure of the coal. Normal products obtained by non-specific extraction are alkenes, alkanes, cycloalkanes, hydroaromatics, and alkylnaphthalenes. Low rank coals tend to produce relatively large amounts of paraffinic materials,whereas higher rank coals tend to produce less aliphatic and more aromatic and hydroaromatic material.

Use of non-specific solvents above the critical temperature of the solvent has proven useful in the study of the structure of coal. The use of solvents above their critical temperature supposedly leads to unusual solvent properties. For example, it has been shown that the solubility of

p-iodochlorobenzene in ethylene can be increased a thousand times by this technique.[11]

For coal studies using "supercritical" solvents, one technique uses toluene (critical temperature $318^{\circ}C$) at approximately $350^{\circ}C$ to extract approximately 17% of the dry ash-free weight of a low rank coal.[12] Since this extraction takes place at temperatures below those at which extensive decomposition of the coal matrix is known to occur, the extract should be representative of the lower molecular weight materials found in coal. The extraction of this coal was found to contain 0.4% paraffinic materials plus a small amount of cycloalkanes. The major paraffinic components were straight chain alkanes of odd carbon numbers, a feature of biogenic residues. Also identified were 2-methyl and 3-methyl alkanes, cyclo-alkanes, and some isoprenoidal hydrocarbons. The remainder of the extract was aromatic in nature consisting of deriva-tives of benzene, naphthalene, biphenyl, phenanthrene, pyrene, benzanthrene, and fluoroanthrene.

The chemical nature of the coal extract from non-specific extraction is consistent with the view that this material separated from the parent coal with little or no alteration. It also suggests that the extracted material actually arose from plant coalification and not from pyro-lytic decomposition during extraction.

Specific extraction is carried out in nucleophilic solvents such as pyridine at temperatures below $200^{\circ}C$. Approximately 20 to 40% of the coal is extracted by this method.

Studies of pyridine extracts of coal have yielded
valuable information about the aromatic character of
coal. Aromaticity (f_a) is defined as that fraction of
the total carbon that is part of an aromatic system.
As the carbon content of the parent coal increased
from about 61 to 86% the aromaticity (f_a) of the pyridine
extract increased from about 0.4 to 0.7. In even higher
rank coals the aromaticity increased to a value of
approximately 0.88. The number of condensed aromatic rings
in a given structural unit is often expressed by the symbol
R_n. This number was found to be approximately 1 for peat
and lignite, 2 to 4 for coals with 73 to 86% carbon content,
and about 5 to 7 for coals with 87 to 91% carbon content.
The degree of alkyl substitution was observed to decrease
with increasing rank.[13]

Extractive pyrolysis is basically a pyrolysis reaction,
as discussed earlier, carried out in the presence of a
solvent. This technique can lead to reasonably high
yields of extracted products. Actual yields depend on
the nature of the solvent, the rank of the coal being
extracted, and the temperature at which the experiment
is being performed.

Reductive extraction is carried out at temperatures
greater than 400°C in solvents that are good hydrogen
donors. Under these conditions the coal matrix is
undergoing decomposition to smaller fragments. At these
reaction temperatures the solvent can enter the pore
structure of the coal causing it to enlarge. Exposed
C-C, C-O, and C-S bonds can undergo thermal cleavage

followed by hydrogen transfer from the solvent resulting
in the formation of smaller, more soluble units.

Tetralin is an example of a good hydrogen donating
solvent that has been widely used to study the structure
of coal. In one study, for example, a subbituminous
coal was converted into approximately 80% tetrahydrofuran
soluble products within two hours by reaction with
tetralin at 427°C.[14] The number-average molecular weight
dropped from approximately 1200 at 10 minutes reaction
time to approximately 500 at 30 minutes and longer
reaction time. This suggests a rapid cleavage of relatively
few "active" bonds to form preasphaltenes followed by
a slower conversion of the preasphaltenes into the lower
molecular weight asphaltenes and oils.

Extraction studies have shown a preferred sequence
for the evolution of hydrocarbons from coal. Cycloalkanes
and branched alkanes are favored over the simpler straight
chain alkanes. Also, the more complex aromatic hydrocarbons
tend to predominate over the less complex ones. This
selectivity can be explained on the basis of a "molecular
sieve effect."[15] That is, hydrocarbons with larger critical
dimensions show greater ease of evolution from the capil-
lary structure of coal.

Oxidation has been one of the more widely used techniques
for the degradation of coal into smaller molecules
which can be identified and applied to the interpretation
of the structure of coal. Many oxidizing agents have been

tried, most of them being strong oxidants which convert
most of the aromatic material present in coal to a
mixture of benzenecarboxylic acids.
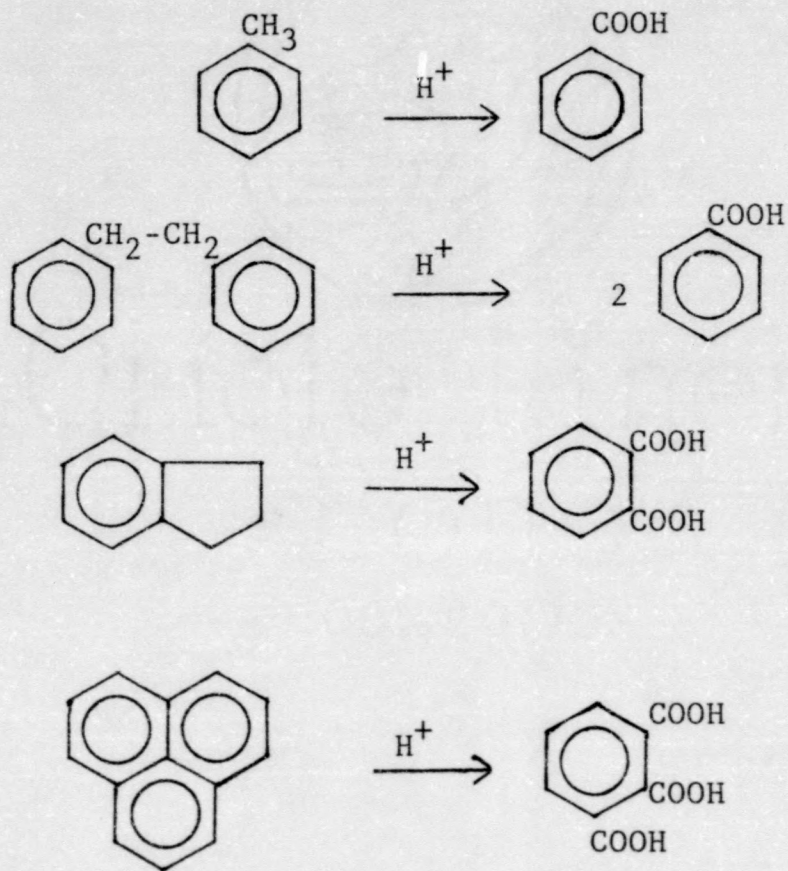
This type of oxidation is of limited usefulness, but
can at least give some information about the aromaticity
and degree of substitution of the aromatics in coal.

Nitric acid (HNO_3) is one of several oxidants used
in the degradation of coal. It has been shown that nitric

acid oxidation of coal produces mostly benzenecarboxylic acids.[16,17] Among those isolated include phthalic, isophthalic, terephthalic, 1,2,3-benzenetricarboxylic, 1,2,4-benzenetricarboxylic, 1,3,5-benzenetricarboxylic, 1,2,3,4-benzenetetracarboxylic, 1,2,4,5-benzenetetracarboxylic, benzenepentacarboxylic and benzenehexacarboxylic acids. The yields of benzenehexacarboxylic acid have been shown to increase with the metamorphosis of coal.[17] This suggests that as coal proceeds through metamorphosis, the degree of condensation of the aromatic system increases.

Table 2.4 shows the results of different rank coals oxidized with 70% nitric acid for 16 to 24 hours.[18]

Table 2.4

Oxidation of Coal with

70% Nitric Acid

Coal	Abundances (%) Benzenecarboxylic Acids n=No. COOH				
	n= 2	3	4	5	6
Lignite Sheridan, Wyo.$_a$	3	38	39	15	4
Illinois No. 2 Bituminous$_b$	15	20	35	16	6
Pittsburgh No. 2 Bituminous$_c$	16	25	35	15	4
Penn. PSOC-85 Anthracite$_d$	28	20	15	12	12

a) 64.4% C, 5.3% H, 1.1% N, 1.1% S, 28.1% O

b) 77.8% C, 5.4% H, 1.4% N, 2.1% S, 13.3% O

c) 82.7% C, 5.5% H, 1.3% N, 2.8% S, 7.7% O

d) 91.3% C, 3.9% H, 0.6% N, 1.1% S, 3.1% O

The oxidation products also contained nitrosubstituted esters and pyridine derivatives. The yield of total acids and the number of carboxylic acid groups per benzene ring seem correlated with the degree of condensation of the aromatic system of the original material.

A recent study has shown that oxidation of coal using 40% aqueous nitric acid at 60°C produces linear aliphatic diacids starting with succinic acid (C_4).[19] Before any coal oxidations were performed, model compound studies were conducted to find the optimum conditions for the production of the diacids. These studies revealed that under these conditions, linear diacids would be produced from alcohols, ketones, and other oxidizable groups without harm to the diacids. Table 2.5 shows the results of the oxidation of six coals under these conditions.

Other products observed were oxalic, methyl succinic, methyl glutaric, benzoic, benzenedicarboxylic, benzenetri-carboxylic, benzenecarboxylic, propane tricarboxylic, and butane tricarboxylic acids. The yields of benzene-polycarboxylic acids was lower due to the milder conditions used. The absence of monoacids and nitro products along with conditions that are too mild to attack linear alkanes show that the diacids produced do not arise from linear alkanes in the coal.

The data also show that the yields of linear diacids decrease as the carbon content of the coals increases. This would be expected in terms of the increase in the degree of condensation of the aromatic system with increasing coal rank.

Table 2.5

Oxidation of Coal with

40% HNO_3 at 60°C

G.C. Peak Areas of $(CH_2)_n(COOH_3)$ Products

as % of Total Peak Areas

Coal	n=2	3	4	5	6	7	8	9	10	Tot.
Illinois No. 6 Monteray[a]	10.9	7.1	5.1	4.5	4.5	5.1	4.5	1.7	0	43.4
Wyodak Anderson, Wyo.[b]	9.2	5.8	5.3	4.6	4.7	3.7	2.9	1.3	0	37.5
Pittsburgh Seam[c]	8.8	7.5	6.9	4.7	3.7	0.9	0	0	0	32.5
Lower Hartshorne Oklahoma[d]	1.8	1.6	1.7	1.5	2.0	0	0	0	0	8.6
Lower Kittaning W. Virginia[e]	8.3	15.6	17.4	15.9	13.0	9.4	6.2	2.9	7.7[g]	96.4
Utah "Cannel"[f]	10.5	14.9	17.3	18.0	13.5	9.9	5.2	2.0	5.7[g]	97.0

a) 69.7% C, 4.98% H

b) 71.8% C, 5.2% H

c) 79.5% C, 5.2% H

d) 81.49% C, 4.29% H

e) 75.78% C, 6.33% H

f) 56.87% C, 5.36% H

g) The homologous series continued in a declining manner.

Oxidation of coal with alkalin potassium permangenate ($KMnO_4$) also yields a variety of benenecarboxylic acids.[20] Among those isolated are benzoic, phthalic, isophthalic, 1,3,5-benzenetricarboxylic, 1,2,4-benzenetricarboxylic, 1,2,3-benzenetricarboxylic, 1,2,3,5-benzenetetracarboxylic, 1,2,4,5-benzenetetracarboxylic, 1,2,3,4-benzenetetracarboxylic, benzenepentacarboxylic, and benzenehexacarboxylic acids.

Four macerals, namely—exinite, vitrinite, micrinite, and fusinite, as well as the original coal, carbon black and graphite, were oxidized with aqueous alkaline $KMnO_4$. After 30 hours the unoxidized coal particles were separated and treated again in the same way.[21] The yields of aliphatic acids, oxalic acid and aromatic acids were determined. The aromatic acids were further separated and quantified. The results are shown in Table 2.6.

Table 2.6

Oxidation of Coal, Coal Macerals, Carbon Black

and Graphite by $KMnO_4$

Sample	Wt % Total Aromatic Acid Content n=No. COOH				
	n=2	3	4	5	6
Exinite	7.75	10.67	20.36	18.71	27.13
Vitrinite	5.23	13.63	23.79	16.92	23.96
Micrinite	1.51	4.90	18.85	23.42	32.55
Fusinite	0.89	2.11	12.07	24.23	43.22
Coal	6.24	13.95	21.91	13.47	17.82
Carbon Black	0.53	1.67	5.16	12.92	61.15
Graphite	-	-	-	-	95.55

It should be noted from Table 2.6 that the yields
of benzenedicarboxylic, benzenetricarboxylic, and benzene-
tetracarboxylic acids decrease while the yields of ben-
zenepentacarboxylic and benzenehexacarboxylic acids increase
as one goes from exinite to fusinite. This indicates that
the degree of substitution or condensation of the aromatic
system of the coal macerals increases as one proceeds
from exinite to fusinite. This agrees with the results of
an earlier study[22] which revealed that the aromaticity (f_a)
of the organic matter in the macerals increased as one goes
from lower carbon content exinite to higher carbon content
fusinite. Likewise, as one proceeds from coal to graphite
(graphite being almost 100% aromatic in character) the yields
of benzenehexacarboxylic acid increase dramatically while the
yields of the other acids decrease.

Aqueous sodium dichromate ($Na_2Cr_2O_7$) is also used
to study the structure of coal. The main virtue of this
oxidant is that it results in the oxidation of side-chains
on polynuclear aromatic rings to their corresponding
carboxylic acids with minimum degradation of the ring systems.[23]
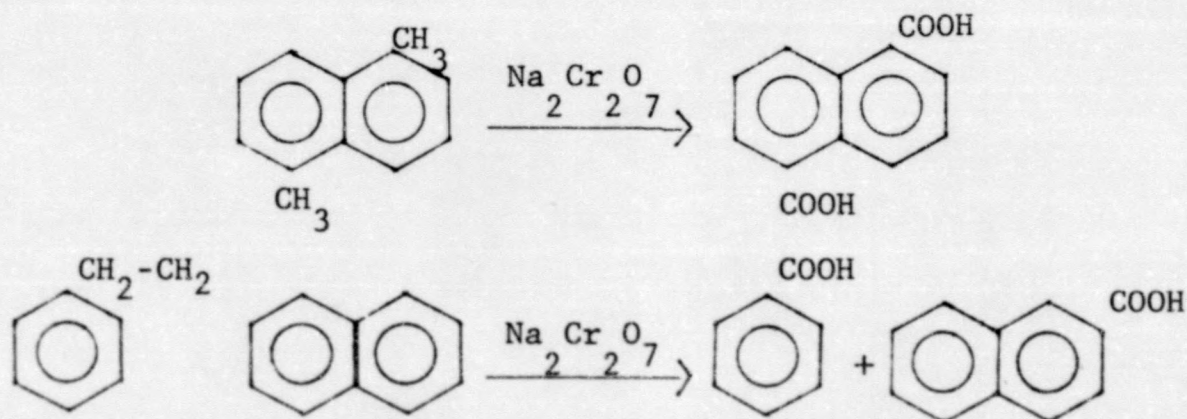
Table 2.7

Oxidation of Coal with

Aqueous Sodium Dichromate

Acid	Number of -COOCH$_3$	North Dakota Zap Lignite	Pittsburgh No. 8
Benzene	2	100[a]	100[a]
	3	133	29
	4	49	10
Biphenyl	1	6	9
Naphthalene	1	4	30
	2	5	29
	3	3	8
	4	–	3
Phenanthrene	1	–	28
	2	–	8
	3	–	7
	4	–	–
Pyrene/Fluoranthene	1	–	3
	2	–	2
Fluorenone	1	7	8
	2	2	2
	3	–	–
Anthraquinone	1	3	4
	2	1	–
Dibenzofuran	1	4	21
	2	3	4
	3	–	4
Xanthone	1	12	9
	2	4	7
	3	–	3
Benzothiophene	1	–	4
Dibenzothiophene	1	–	8
	2	–	5
Pyridine	3	5	5
Carbazole	1	–	3
	2	–	4
Benzoquinoline/ Acridine	1	–	7
	2	–	4
	3	–	2

a) Benzenedicarboxylic acid methyl ester is normalized to 100 (± 10-15%).

Table 2.7 shows the results of the oxidation of North Dakota, Zap Lignite[24] and Pittsburgh No. 8 bituminous[18] coals with aqueous sodium dichromate. The lignite coal was

oxidized at 250°C for 72 hours with excess dichromate.
The bitumonous coal was oxidized at 250°C for 36 to 40
hours with excess dichromate.

From Table 2.7 one can see that no polynuclear aromatic
compounds with more than two fused rings were identified
among the oxidation products of the lignite coal --
further evidence that few, if any, highly condensed structures
are present in the lower rank lignite coal. Among the oxida-
tion products of the bituminous coal, polynuclear aromatic
compounds consisting of three or more fused rings were
identified. This shows that there is a higher degree of
condensation of the aromatic system in the higher rank
bituminous coal.

Aqueous sodium hypochlorite (NaOCl) may also be used
as an oxidant in the study of coal structure. Caution must
be used, however, in the interpretation of data generated
by this technique. The type of oxidation products ob-
tained is dependent upon the conditions of the reaction
mixture. For example, it has been shown that oxidations of
Illinois No. 6 coal by aqueous NaOCl have yielded several
products.[25] They range from black, bicarbonate-soluble acids
of molecular weight as high as 1000 to nearly colorless,
water-soluble acids with molecular weights near 300. The
product mix depends mostly on the pH during oxidation
and on the mesh size of the coal. At pH 13, 96% of the coal
is dissolved and 80% of the carbon dissolving is found
as the higher molecular weight acids. At lower pH, more of
the coal structure is destroyed. Simple oxidation-resistant

benzene and aliphatic carboxylic acids and carbon dioxide then become the principal products.
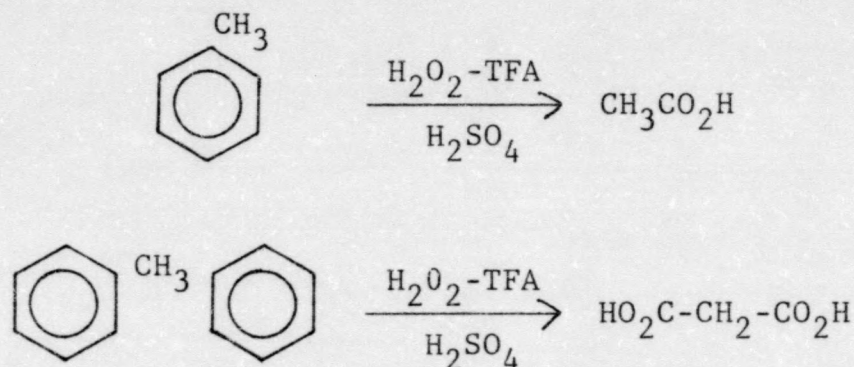
Coal and coal model compound oxidation had also been studied using molecular oxygen (O_2) as the oxidant. In this technique the solvent extract of a coal or a model compound is place in the reaction vessel under 1.1 to 1.5 atm of O_2 with 2.2-azobis (2-methylpropionitrile) used as the initiator. It was discovered that the final rate of oxidation of the coal and some of the models was considerably slower than the initial rate. Refluxing with alcoholic KOH, however, reduced this retardation effect. It was suggested that the oxidation rates were being retarded by the phenols and quinones already present in the coal and also new phenols and quinones being produced during the oxidation. The KOH pretreatment apparently destroys these inhibitors allowing the oxidation to proceed at a steady rate. [26,27]

Oxygen in the form of ozone (O_3) has been used in the study of coal structure also. For example, one technique exposes coal to room temperature for 8 hours followed by addition of H_2O_2 to complete the oxidation of the products to acids.[28] The products from the oxidation of a bituminous coal were identified as hydroxyadipic and hydroxypimelic acids together with phthalic, a propyl-substituted phthalic, as well as tri and tetrabenzenecarboxylic acids. These compounds could be reasonably expected from the oxidation of structures such as those proposed for bituminous coals.

In April of 1977 Deno and co-workers reported that a mixture of 30% H_2O_2 and trifluoroacetic acid (TFA) caused

the disappearance of the NMR singlet of benzene without the appearance of any new CH absorptions.[29] Since earlier reports stated that polymethylbenzenes were converted to cyclohexadienones[30] and phenols,[30,31] the concept arose that H_2O_2-TFA might completely oxidize the benzene ring in alkylbenzenes and leave the aliphatic component untouched.

$$\text{(toluene)} \quad \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_2\text{O}_2\text{-TFA}} \quad CH_3CO_2H$$

$$\text{(bibenzyl)} \quad \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_2\text{O}_2\text{-TFA}} \quad HO_2C\text{-}CH_2\text{-}CO_2H$$

Preliminary studies were conducted on toluene, ethyl-benzene, propylbenzene and isopropylbenzene.[29] With toluene, acetic acid was the only product. With ethylbenzene, 81% of the NMR absorption was due to propionic acid and 19% was due to acetic acid. With propylbenzene, 6% of the NMR absorptions was due to acetic acid, 74% due to butyric acid, 8% due to propionic acid,and 13% was unidentified background. Even isopropylbenzene gave isobutyric acid which accounted for 32% of the NMR absorptions.

These discoveries prompted Deno and co-workers to study a larger number of model compounds and the applica-tion of this technique to the study of the aliphatic structure of coal.

For the following model compound and coal studies the oxidation reagent was prepared by mixing 10ml of 30% aqueous H_2O_2 and 8ml of 96% H_2SO_4 slowly with cooling. For coal

studies 0.8g of 20 U.S. mesh coal is added to the oxidation reagent. The reaction is exothermic. After 1 to 4 h the solutions become colorless or near colorless. Model compounds were added to the reagent over a period of 20 min in the belief that slow addition more closely approached the conditions of dissolving coals. Faster addition was noted to give somewhat different products.[32]

Model compounds that produce mostly succinic acid on oxidation with H_2O_2-TFA-H_2SO_4 are shown in Table 2.8.[32,33]

Table 2.8

Model Compound Oxidation with

$\underline{H}_2\underline{O}_2$-TFA-$H_2\underline{SO}_4$
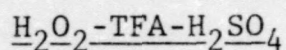
Model Compound	Yield[a] (%)			
	Succinic Acid	Acetic Acid	Glutaric Acid	Malonic Acid
1,2-Diphenylethane	73	0	0	9
1.5-Dihydrophenanthrene	71	0	0	11
Acenaphthrene	64	0	0	0
Indan	27	0	27	0
1-Indanol	30	0	36	0
4,7-Dimethylindan	42	60[a]	50	0
1-Indanone	41	0	0	17
4-Oxo-4-phenylbutyric acid	62	0	0	0

a) Calculated on the basis that one mol of model compound produces one mol of product except for 4,7-Dimethylindan. In this case the basis was that 2 mols of acetic acid form from one mol of model compound.

Table 2.9 shows model compounds that produce acetic acid on oxidation with H_2O_2-TFA-H_2SO_4.[32,33]

Table 2.9

Model Compound Oxidation with

$$\underline{H_2O_2}\text{-TFA-}\underline{H_2SO_4}$$

Model Compound	Yield of Acetic Acid (%)
Toluene	68
1,2-Dimethylbenzene	46[a]
1,3-Dimethylbenzene	66[a]
1,4-Dimethylbenzene	66[a]
Acetophenone	72
Pyruvic Acid	100

a) On the basis that one mol of model compound forms 2 mols of acetic acid.

Table 2.10 shows model compounds that produce products other than acetic or succinic acids on oxidation with H_2O_2-TFA-H_2SO_4.[32,33]

The generalization was made that H_2O_2-TFA-H_2SO_4 oxidation of alkylbenzenes leads to degradation of the benzene ring to a carboxyl group with over 70% preservation of the aliphatic structure. This generalization was found to be true for alkyl bridges as well as alkyl substituents.[32]

Table 2.11 lists the coals that were studied using this oxidation technique.[32,33]

Table 2.10

Model Compound Oxidation with

H_2O_2-TFA-H_2SO_4

Model Compound	Identification	Yield[a] (%)
Ethylbenzene	Propionic Acid	71
	Acetic Acid	19
Propylbenzene	Butyric Acid	73
	Propionic Acid	8
	Acetic Acid	10
Isopropylbenzene	Isobutyric Acid	37
	Acetic Acid	48
4-Propylphenol	Butyric Acid	70
	Propionic Acid	10
	Acetic Acid	12
Benzyl Acetate	Acetic Acid	60
1-Phenylethanol	Acetic Acid	60
3-Phenyl-1-propanol	Butyrolactone	100
Methoxybenzene	Methanol	90
Diphenylmethane	Malonic Acid	9
Tetralin	Hexahydrophthalic Acid	71
9,10-Dihydroanthracene	Malonic Acid	36
2-Propylthiophene	Butyric Acid	84
	Propionic Acid	13
2-Propylfuran	Butyric Acid	61
	Propionic Acid	30
1-Hydroxytetralin	Glutaric Acid	74
1-Tetralone	Glutaric Acid	43
	Malonic Acid	13
	Succinic Acid	6
2-Methyl-1-tetralone	4-Hydroxypentanoic Acid	52
	Succinic Acid	18
	Acetic Acid	15
	Malonic Acid	8

Table 2.10 (continued)

Model Compound	Identification	Yield[a] (%)
1-Methylindan	2-Methylglutaric Acid	60
	Acetic Acid	24
	Malonic Acid	16

a) On the basis that one mol of model compound gave one mol of product.

Table 2.11

Coals Used in H_2O_2-TFA-H_2SO_4

Oxidation Studies

Coal	%C[a]	%H[a]	%Ash[a]
Lignite, North Dakota	65.3	4.4	8.4
Illinois No. 6 Monteray	69.7	4.4	10.8
Illinois No. 6	70.8	4.3	8.4
Wyodak Subbituminous	71.9	5.2	4.6
PSOC-330	78.4	5.1	6.1
Pittsburgh Seam	79.6	5.2	6.1
PSOC-372	81.2	5.2	5.5
PSOC-405	82.4	4.3	8.2
PSOC-256	82.9	4.6	6.0

a) Wt % dry basis.

Table 2.12 shows the results of the oxidations of the above coals.[32,33]

It is likely that acetic acid arises largely from methyl groups attached to benzene rings since the yield of acetic acid from methylbenzenes was 46-68%. Some acetic acid may also arise from structures like α-methylbenzyl alcohols

27

as shown by the model compound 1-phenylethanol. Structures similar to acetophenone also may produce acetic acid.

Table 2.12

Aliphatic Acid Yields[a] from Coal Oxidations

Coal	Methanol	Acetic Acid	Propionic Acid
Lignite, North Dakota	16.2	4.2	nd
Illinois No. 6, Monteray	0	3.2	nd
Illinois No. 6	0	6.1	0.7
Wyodak, Subbituminous	-	0	-
PSOC-330	-	2.4	-
Pittsburgh Seam	0	0.9	0.4
PSOC-372	-	4.0	-
PSOC-405	-	2.0	-
PSOC-256	-	3.2	-

Coal	Malonic Acid	Succinic Acid	Glutaric Acid
Lignite, North Dakota	-	6.0	nd
Illinois No. 6, Monteray	-	10.2	nd
Illinois No. 6	-	13.4	2.2
Wyodak, Subbituminous	0	2.6	-
PSOC-330	10.3	5.7	-
Pittsburgh Seam	-	4.4	0.5
PSOC-372	6.9	7.3	-
PSOC-405	10.5	5.3	-
PSOC-256	3.6	20.9	-

a) Percent of original hydrogen of dry coals which appears as carbon-bound hydrogen in identified products.

Propionic acid arises mainly from arylethyl structures. Model compound studies showed that ethylbenzene yielded 71% propionic acid.

The appearance of glutaric acid arises from either 1,3-diarylpropane or indan structures.

Malonic and succinic acids are the major products of coal oxidation. Malonic acid arises from diarylmethane structures. Succinic acid arises from diarylethane or indan type structures. It was shown that alkyl, alkoxy, or hydroxyl substituents on the aryl ring attached to the indan components of coal would not significantly affect the production of succinic acid.[32]

None of the bituminous coals contained arylmethoxy as shown by the complete absence of methanol in the oxidation products. Lignite, however, showed the presence of arylmethoxy by a 16.2% yield of methanol in the oxidation products. This type of substituent is lost in the early stages of coalification.

In later per TFA oxidation studies[34,35] of Illinois No. 6 Monteray and Wyodak coals, Deno and co-workers identified benzene di, tri, tetra, and pentacarboxylic acids and two compounds provisionally identified as the epoxides of ethylene tri and tetracarboxylic acids as well as the aliphatic diacids as reported earlier. The benzenecarboxylic acids were uncommon products from per TFA oxidations. Since it had already been shown that they were not produced from polyalkylbenzenes,[30,32] an interior unit had to be discovered that would degrade to

an aromatic dicarboxylic acid. Anthracene and phenanthrene units in which an end ring is activated were considered; however, the failure of 2-methoxyphenanthrene and 1,4-chrysoquinone to form benzene tri and tetra acids (Table 2.13) dismissed that possibility. Although the formation of 1,2,3-benzenetricarboxylic and 1,2,4-benzenetricarboxylic acids from 1 and 2 naphthoic acids, and the formation of 1,2,4-benzenetricarboxylic and 1,2,4,5-benzenetetracarboxylic acids from naphthalene-2,3-dicarboxylic acid was shown (Table 2.13), these structures were also dismissed because they cannot be interior units in a polymer and because of the small amount of carboxyl groups in bituminous coal.

The behavior of 9,10-dihydroanthracene was found to be the key to the formation of the polycarboxylic acids. This formed 1,2-benzenedicarboxylic acid and benzoic acid as the dominant products (Table 2.13). A dihydroanthracene unit in the interior of a polymer would cleave, leaving an aromatic diacid. Further oxidation would destroy all but the carboxyl substituted ring as with the naphthalene carboxylic acids and the anthracene carboxylic acid (Table 2.13). The benzenetricarboxylic and benzenetetracarboxylic acids were believed to arise from dihydroanthracene units in which the fourth ring is an α-fusion as in compound I rather than the β-fusion of compound II.[34]
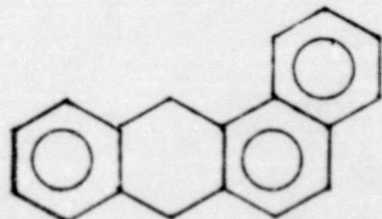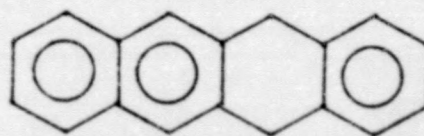
I   II

Table 2.13

Oxidation of Model Compounds

with H_2O_2-TFA-H_2SO_4

Model	Product (Yield-Relative g.c. peak areas)
2-Methoxyphenanthrene	1,2-Benzenedicarboxylic acid (75) Malonic (4) Succinic (4) Maleic (2) Others (15)
1,4 Chrysoquinone	Maleic (50) 1,2-Benzenedicarboxylic acid (34) Phthalide-α-COOH (5) Others (11)
1-Naphthoic acid	1,2,3-Benzenetricarboxylic acid (31) 1,2-Benzenedicarboxylic acid (11) Others (58)
2-Naphthoic acid	1,2,4-Benzenetricarboxylic acid (59) 1,2-Benzenedicarboxylic acid (18) Others (23)
Naphthalene-2,3-dicarboxylic acid	1,2,4,5-Benzenetetracarboxylic acid (35) 1,2-Benzenedicarboxylic acid (25) 1,2,4-Benzenetricarboxylic acid (20) Phthalide (20)
9,10-Dihydroanthracene	1,2-Benzenedicarboxylic acid (70) Maleic and Succinic (14) Benzoic (5) Others (11)
2-Anthroic acid	1,2,4-Benzenetricarboxylic acid (38) 1,2-Benzenedicarboxylic acid (25) Others (37)

Further studies on the use of trifluoroperacetic
acid as an oxidizing agent were conducted to determine
the stability of the reaction mixture and to determine the
behavior of aromatic amines and sulfur compounds, which are
known to be present in coal, in the reaction mixture. Partial

oxidation studies were also conducted to determine the mechanistic details of the reaction.[36]

These studies revealed that more carbon dioxide was produced in certain reactions than was possible from the amount of organic model present. It was hypothesized that the oxidizing reagent was decarboxylating according to the following equation:

$$CF_3CO_2H \xrightarrow{H_2O_2} CHF_3 + CO_2$$
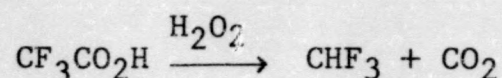
To test this hypothesis an experiment was run on a blank containing no organic substrate; CO_2 was observed to slowly evolve. It was also discovered that the evolution of CO_2 was enhanced by certain materials. It was shown that cuprous chloride added to the standard reaction mixture produced 13.0 mmol of CO_2 in 3 h. Mass spectral analysis of the gas which was passed through a barium hydroxide trap to collect the CO_2 revealed the presence of fluoroform.[36]

It was shown that certain heterocyclic structures react rapidly and exothermically with H_2O_2/TFA but not in the same manner as hydrocarbons. Pyridine and quinoline reacted rapidly to form the corresponding N-oxide (Eq. 1 and 2) which is resistant to further attack even upon heating several hours under reflux.


(1)

(2)
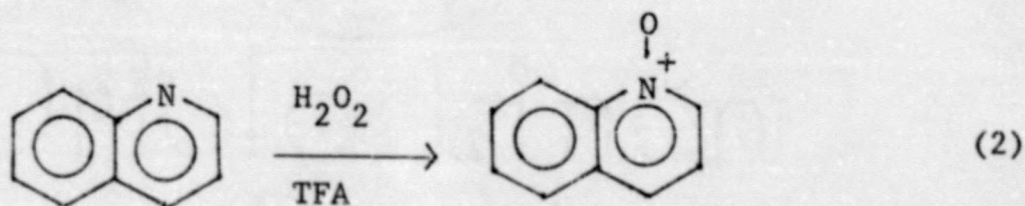
Aromatic sulfur-containing compounds such as dibenzothiophene are converted to the corresponding sulfone (Eq. 3).


$$\text{(3)}$$
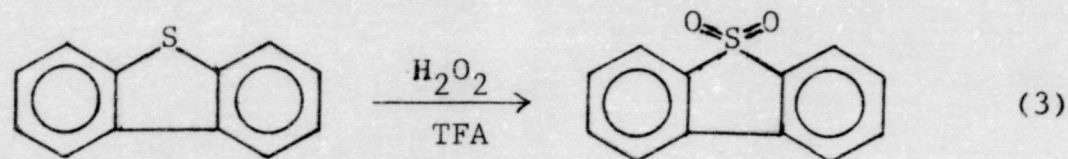
The production of the sulfone or N-oxides appeared to be quantitative for the models studied. It was suggested that this technique be used to quantify aromatic heterocyclic structures in coal. It was also suggested that due to the variability of the yields of aliphatic acids this technique would not be efficient enough to quantify aliphatic substituents in coal.[36]

Partial oxidation studies were done on toluene n-pentylbenzene and acenaphthene. The major product from the partial oxidation of toluene was acetic acid which arises from complete oxidation of the aromatic ring (Eq. 4).

$$PhCH_3 \xrightarrow{\frac{H_2O_2}{TFA}} CH_3CO_2H + CH_3CH=CHCH=CHCO_2H \qquad (4)$$
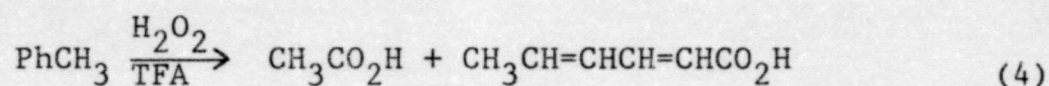
One other partial oxidation product was identified as n-2,4-hexadienoic acid. This product may arise from hydroxylation of the aromatic ring ortho to the methyl substituent producing o-cresol which would react much faster than toluene (Eq. 5).

$$\text{(5)}$$
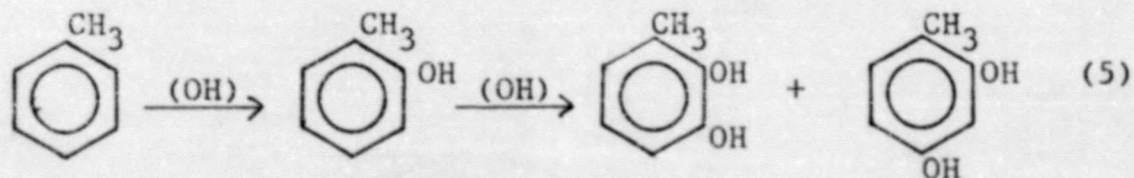
2,3-Dihydroxytoluene would then undergo oxidative cleavage (Eq. 6).

$$(6)$$
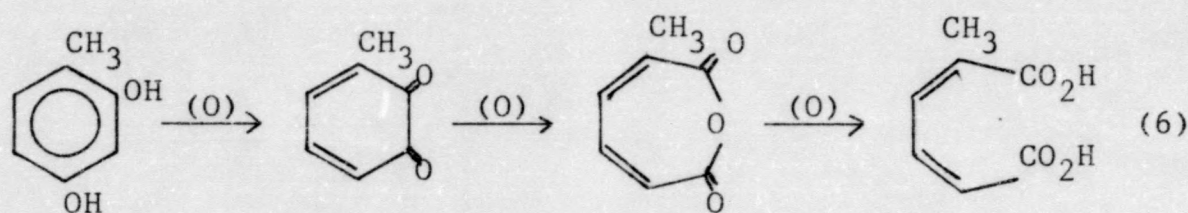
The unsaturated diacid may then decarboxylate to produce n-2,4-hexadienoic acid (Eq. 7).[36]
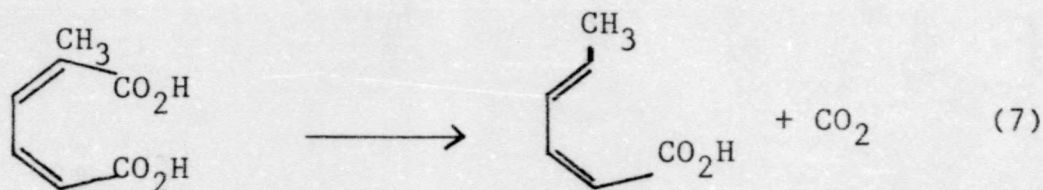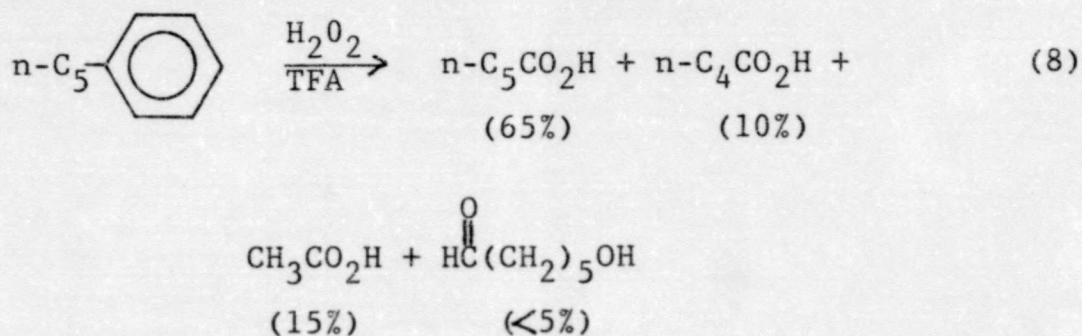

$$+ CO_2 \qquad (7)$$

The major product of the partial oxidation of n-pentyl-benzene was hexanoic acid. Minor products were pentanoic and acetic acids and 6-hydroxyhexaldehyde (Eq. 8).

$$\xrightarrow{\frac{H_2O_2}{TFA}} \quad n\text{-}C_5CO_2H + n\text{-}C_4CO_2H + \qquad (8)$$

$$(65\%) \qquad\qquad (10\%)$$

$$CH_3CO_2H + H\overset{O}{\overset{\|}{C}}(CH_2)_5OH$$

$$(15\%) \qquad (<5\%)$$

Propionic and butyric acids were not observed, indicating that the acetic acid did not come from higher acid homologues. Benzene was then treated in an analogous manner as pentyl-benzene; acetic acid was observed as a minor product. This suggested that the ring carbons are the source of its formation.[36]

The major product of acenaphthene was succinic acid.

Acetic acid, 3-hydroxycyclopentene and tricarboxylic acid were also found (Eq. 9).

$$CO_2H \qquad CO_2H \; + \; CH_3CO_2H \; +$$

$$OH \; + \; HO_2C \qquad CO_2H$$
$$CO_2H$$

(9)
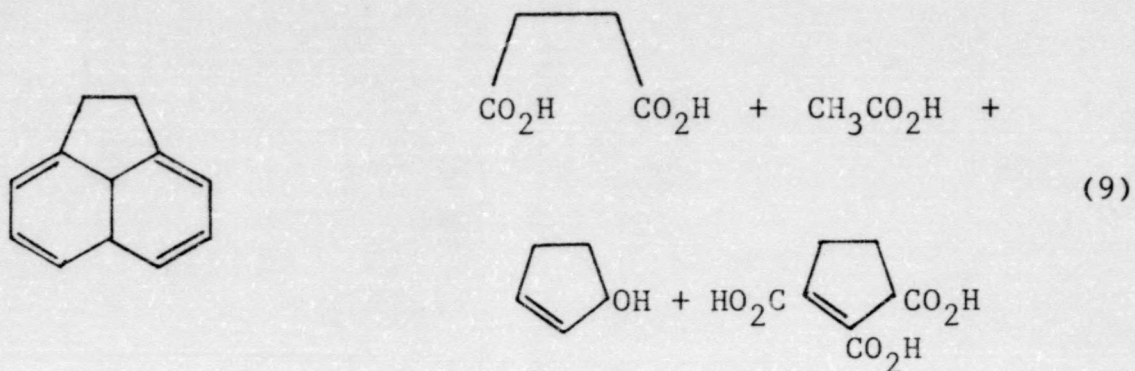
The existance of succinic acid and the cyclopentene deriva-tives demonstrates that the attack of the reagent is directed at the aromatic carbons.[36]

The results of another study on Wyodak coal[37] proved to be essentially the same as the results of Deno and co-workers, indicating the reliability of the method. The oxidation of phenol, ethylbenzene and some aromatic com-pounds with long aliphatic side chains and ring aliphatic structures were also studied.

The oxidation products of ethylbenzene contained not only propionic and acetic acids as reported by Deno, but also contained succinic, malonic and fumaric acids as well as some unidentified components.[37]

The oxidation products of phenol showed several promi-nent signals similar to those observed for Wyodak coal. This oxidation was repeated several times. The product distribution remained the same, but the total product yields varied from 10 to 38% by weight of the starting phenol.[37]

Two aromatic compounds with long-chain aliphatic

substituents, nonylphenol and 4-n-dodecyl resorcinol
were treated with per TFA. Both compounds yielded an oily
material upon oxidation. The [1]Hn.m.r. spectra of the oily
material from nonylphenol showed high field signals identi-
cal to those observed in the starting material. The methyl
ester of the oily material and the methyl ester of decanoic
acid were shown to be identical.[37]

The [1]Hn.m.r. spectra of the oily material from 4-n-
dodecyl resorcinol showed the presence of an aliphatic com-
ponent and acidic protons. After esterification of the
soluble products in the filtrate,only the methoxy protons
present in the parent compound were detected.[37]

Ring aliphatic compounds hexahydropyrene and octa-
hydroanthracene were also subjected to per TFA oxidation.
Large quantities of the starting material did not dissolve
during the reaction period. The [1]Hn.m.r. spectra of the re-
covered solids showed that the solids were starting material.
The [1]Hn.m.r. spectra of the esters of the oxidation products
of hexahydropyrene showed the presence of dimethyl glutarate
and dimethyl succinate. Oxidation product esters of octohydro-
anthracene were not identified.

These studies show that long-chained aliphatic compounds
are highly resistant to oxidation by per TFA and can escape
detection in the analysis of the oxidation products. It
was suggested that the interpretation of the results of per
TFA oxidation of coal may not be straightforward. However, it
is a valuable technique for investigating coal structure.

III. EXPERIMENTAL

I. Gas Chromatography

Toluene oxidation products were analyzed on a Varian Model 1700 dual column gas chromatograph with an Omniscribe Model 5310-14 chart recorder and a thermal conductivity detector. The remaining oxidation products were analyzed on a Varian Model 3700 dual column gas chromatograph with a flame ionization detector and a Varian Model 20 recorder equipped with a Disc Institute Model 244-R disc integrator.

Benzophenone was chosen as the internal standard because its retention time was much longer than any of the expected oxidation products. For model compounds, a 1:1 molar ratio of compound to standard was used based upon complete conversion to one product. For coals, a 1:1 molar ratio was used based upon complete conversion to succinic acid, the major product found by Deno and co-workers.[32] For the acid stability tests, a 1:1 molar ratio of acid to standard was used. The ratio of product peak area to internal standard peak area was calculated to give a relative response factor. Yield determinations were made by the ratio of product peak area to internal standard peak area.

For the toluene oxidation analysis, a five foot, 20% SE-30 column (Methyl silicone gum rubber) was used. For the remaining analyses, a five foot OV-17 (50% Phenyl

-36-

silicone) was used. The analysis conditions were as follows: for toluene, detector temperature 300°C; injection port temperature 300°C; oven temperature 45°C for two minutes programmed to 250°C final temperature at a rate of 20°C/minute; filament current 150 milliamps. For the remaining analysis detector temperature 270°C; injection port temperature 270°C; oven temperature 45°C for two minutes programmed to 250°C final temperature at a rate of 20°C/minute. For the acid stability tests the above conditions were also used.

II. Oxidation Reagent

The oxidation reagent was prepared by mixing 15ml of aqueous 30% H_2O_2 (Fisher ΔH-325), 8ml of TFA (Fisher O-4901), and slowly adding 8ml of 96% H_2SO_4 (Fisher ΔA-300) with cooling. This gives approximately a 16:1 peroxide to model compound ratio. The coals were oxidized with 10ml of 30% H_2O_2, 8ml of TFA and 8ml of 96% H_2SO_4. Additional 10ml aliquots of H_2O_2 were added if the KI test for peroxide was negative after the initial reaction time.

III. Compound Addition and Apparatus

The reaction vessel consisted of a 100ml round bottom flask fitted with a reflux condensor. Eight-tenths gram samples of model compound, coal, or acid were added through the top of the flask over a 20 minute period. Additional trials were conducted on some model compounds with addition of the model all at once. The reflux condensor was attached and the reaction allowed to proceed as a slow reflux for one hour. After one hour the reaction had subsided. The mixture was allowed to stand an additional two hours to com-

plete the reaction. The reaction mixture was concentrated

on a rotary evaporator at reduced pressure. To prevent

explosion hazards,excess peroxide was destroyed by addition

of MnO_2 until O_2 evolution ceased and the KI Test was

negative. Excess methanol was added to the concentrated

reaction mixture and refluxed for two hours to form the

methyl esters of the acid products. The internal standard

was added during the last ten minutes of the reflux period.

IV. Oxidations

Toluene

Toluene (.8g, 8.68mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and had subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of one product with a retention time of 2.5 min. This product was identified as methyl acetate by matching retention times and by spiking the reaction mixture with methyl acetate. The relative peak area for the product was 0.62.

Ethyl Benzene-First Trial

Ethyl benzene (.8g, 7.55mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and had subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3, 6.25, 9.75, 12.5 and 21.5 min. Retention times for the methyl esters of acetic and propionic acids are 1.75 and 3.75 min, respectively. The expected products were not found.

Ethyl Benzene-Second Trial

Ethyl benzene (.8g, 7.55mmol) was added to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture

was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3, 6.25, 9.75, 12.5 and 21.5 min. Retention times for the methyl esters of acetic and propionic acids are 1.75 and 3.75 min, respectively. The expected products were not found. To determine if partial oxidation had occurred the reaction mixture was spiked with 1-phenyl-2-ethanol ($PhCH_2CH_2OH$) and acetophenone ($PhCOCH_3$). Upon spiking with 1-phenyl-2-ethanol three addition peaks with retention times at 11.9, 13.5 and 17 min appeared in the gas chromatogram. Spiking with acetophenone produced one additional peak with a retention time of 16.1 min. These experiments indicated that partial oxidation had not occurred.

Diphenyl Methane-First Trial

Diphenyl methane (.8g, 5.0mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed for 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3, 6.0, 9.75, 12.5 and 21.5 min. The retention time of the dimethyl ester of malonic acid is 13.25 min. The expected product was not found.

Diphenyl Methane-Second Trial

Diphenyl methane (.8g, 5.0mmol) was added to a solution

of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed for 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3, 6.25, 10.0, 12.5 and 21.5 min. The retention time of the dimethyl ester of malonic acid is 13.25 min. The expected product was not found. To determine if partial oxidation had occurred the reaction mixture was spiked with benzhydrol ($PhCH_2OHPh$). This resulted in the appearance of an additional peak with a retention time of 22.8 min indicating that partial oxidation had not occurred.

Propyl Benzene

Propyl benzene (.8g, 7.0mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed for 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3, 6, 9.75, 12.5 and 21.25 min. The retention times of the methyl esters of acetic and butyric acids are 1.75 and 6.0, respectively. The expected products were not found.

Bibenzyl

Bibenzyl (.8g, 4.39mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4.

The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 6.25, 10, 12.5 and 21.5 min. The retention time for the dimethyl ester of succinic acid is 15.5 min. The expected product was not found.

Indan

Indan (.8g, 6.77mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed for 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3.5, 6.25, 10, 12.5, 20.5 and 21.5 min. The retention time of the dimethyl ester of glutaric acid is 16.75 min. The expected product was not found.

Tetralin

Tetralin (.8g, 6.05mmol) was added over a 20 min period to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction was exothermic and subsided after 1 h. The reaction mixture was allowed to stand an additional 2 h. Excess methanol was added and the solution refluxed for 2 h to esterify the expected acid products. Gas chromatographic analysis indicated the presence of products with retention times of 3.5, 6.25, 10, 12.5, 17.25, 19 and 21.5 min. The retention time for the dimethyl ester of adipic acid is

18.5 min. The expected product was not found.

Coal Oxidations

KCER 7122-First Trial

KCER 7122 (IMMR sample, 57.2%C, 4.1% H, 0.76% N, 4.56% S)
was added to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and
8ml 96% H_2SO_4. The reaction was highly exothermic resulting
in a small part of the reaction mixture being lost out the
top of the reaction vessel. After 1 h the solution was
light brown in color,and all the peroxide had been consumed.
An additional 10ml of H_2O_2 was added and the reaction mixture
allowed to stand an additional 2 h. After the additional
sitting time the solution color was pale yellow. Again,
all the peroxide was consumed. Excess methanol was added
and the solution refluxed for 2 h to esterify the expected
acid products. Gas chromatographic analysis indicated
the presence of products with retention times of 10.5, 13.25,
15.25 and 21.5 min. The reaction mixture was spiked with the
methyl esters of acetic, propionic, succinic and glutaric
acids resulting in four new peaks with retention times of
1.75, 3.75, 15.5 and 16.75 min,respectively. This indicates
the expected acid products were not present. After two days
sitting another gas chromatographic analysis was conducted
resulting in peaks with retention times of 10.5, 13.75, 15.25
and 21.5 min which were almost identical to the results of
the first analysis.

KCER 7122-Second Trial

KCER 7122 (IMMR sample, 57.2% C, 4.1% H, 0.76% N, 4.56% S)
was added to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and

8ml 96% H_2SO_4 with cooling in an ice bath. The reaction
subsided after 1 h resulting in a pale yellow solution.
After 2 h additional sitting time, there was no color change.
All the peroxide had been consumed. Excess methanol was
added and the solution refluxed for 2 h to esterify the
expected acid products. Gas chromatographic analysis
indicated the presence of products with retention times of
10.25, 13.25 and 21.5 min. The analysis from this trial
was nearly identical to the first trial.

No. 789673

Coal No. 789673 (IMMR sample, 73.28% C, 4.8% H, 0.72% N,
2.82% S) was added to a solution of 15ml aq. 30% H_2O_2, 8ml
TFA and 8ml 96% H_2SO_4 with cooling. The reaction subsided
after 1 h. After sitting an additional 2 h the solution
color was pale yellow. All the peroxide had been consumed.
Excess methanol was added and the solution was refluxed for
2 h to esterify the expected acid products. Gas chromato-
graphic analysis indicated the presence of two products
with retention times of 10.1 and 19.25 min respectively.
Spiking with the methyl esters of acetic, propionic,
succinic and glutaric acids resulted in four additional
peaks with retention times of 1.75, 3.75, 15.5 and 16.75
min, respectively. This indicated the expected acid products
were not present in the reaction mixture.

KCER 4002 (Elkhorn No. 2)

KCER 4002 (IMMR sample, 74.6% C, 4.96% H, 1.32% N,
1.94% S, 8.78% O) was added to a solution of 15ml aq. 30%
H_2O_2, 8ml TFA and 8ml 96% H_2SO_4 with cooling. The reaction

subsided after 1 h. After sitting an additional 2 h the
solution color was pale yellow. All the peroxide had been
consumed. Excess methanol was added and the solution re-
fluxed for 2 h to esterify the expected acid products.
Gas chromatographic analysis indicated the presence of
products with retention times of 10.25, 12.5 and 21.5 min.
No spiking was conducted on this trial.

Alpha Resources Coal Standard

The coal standard (Alpha Resources, Inc., 70.79% C,
5.16% H, 1.06% N, 0.30% S, 16.95% O) was added to a solution
of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4 with cooling.
The behavior of this coal in the reaction mixture was milder
than that of the other three coals studied. After 1 h
the reaction had subsided. After 2 h additional sitting
time the solution was clear in color. Excess methanol
was added and the solution refluxed for 2 h to esterify the
expected acid products. Gas chromatographic analysis
indicated the presence of products with retention times of
3, 6, 10, 12.5, 15.1 and 21.5 min. No spiking was conducted
on this trial.

Blank

Due to the similarities of the gas chromatograms of
both the model compounds and coals, a blank using 15ml aq.
30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4 was prepared, the per-
oxide destroyed and methanol added. Gas chromatographic
analysis indicated the presence of products with retention
times of 6.25, 10, 12.5 and 21.5 min. These products were
not identified.

Pyrite Study

It was postulated that the pyrite in high sulfur coals would catalyze the decomposition of the reaction mixture since all the peroxide was consumed in the oxidation of the three high sulfur coals. Addition of iron sulfide (FeS_2) to the reaction mixture resulted in violent gas evolution. All the peroxide was consumed by the iron pyrite.

Stability of Acids in Reaction Mixture

Since the expected acid products were not being found in the model compound oxidations, the following experiments were conducted to determine the stability of those acids in the oxidizing reagent. The acids and esters were analyzed on a new OV-17 column. Studies were conducted on propionic, butyric, malonic and succinic acids. The retention times of the methyl esters of these acids was 9.25, 11.5, 17.5 and 19.5 min, respectively.

Propionic Acid

Propionic acid (.8g, 10.8mmol) was added to a solution of 15m. aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction mixture was refluxed for 3.5 h. Excess methanol was added and the solution refluxed for 2 h. Gas chromatographic analysis showed peaks with retention times of 11.5 and 14.5 min. The methyl ester of propionic acid was not observed.

Butyric Acid

Butyric acid (.8g, 9.1mmol) was added to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction mixture was refluxed for 3.5 h. Excess methanol was added and the solution refluxed for 2 h. Gas chromatographic

analysis showed peaks with retention times of 11.5 and 14.5 min. A small peak at 11.5 min retention time appeared in all acid stability tests and in this case cannot be attributed to butyric acid. The methyl ester of butyric acid was not observed.

Malonic Acid

Malonic acid (.8g, 7.7mmol) was added to solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction mixture was refluxed for 3.5 h. Excess methanol was added and the solution refluxed for 2 h. Gas chromatographic analysis showed peaks with retention times of 11.5 and 14.5 min. The dimethyl ester of malonic acid was not observed.

Succinic Acid

Succinic acid (.8g, 6.8mmol) was added to a solution of 15ml aq. 30% H_2O_2, 8ml TFA and 8ml 96% H_2SO_4. The reaction mixture was refluxed for 3.5 h. Excess methanol was added and the solution refluxed for 2 h. Gas chromatographic analysis showed peaks with retention times of 11.5, 14.5 and 19.5 min. The peak at 19.5 min matched the retention time of succinic acid methyl ester.

IV. RESULTS AND DISCUSSION

Deno and co-workers reported that a solution of H_2O_2-TFA-H_2SO_4 dissolved coals over a 1 to 4 hour period resulting in colorless or near colorless solutions. It was reported that the aromatic portions of the coal were oxidized leaving the majority of the aliphatic components untouched. It was proposed that this technique be adopted as a method of characterizing the aliphatic components of coal.[32]

This technique was applied to three Kentucky (Table 4.1) coals to characterize their aliphatic components. Upon oxidation the coals yielded pale yellow solutions. The peroxide initially in the oxidizing reagent was totally consumed after 1 h. Additional peroxide was added to KCER 7122 (Kentucky No. 12). After 2 h the solution was pale yellow in color, and the additional peroxide had been consumed. Gas chromatographic analysis showed minute traces of the same materials for all the coals. The aliphatic acids were not observed (Table 4.2).

Since it had been reported that certain materials such as cuperous chloride enhanced the decomposition of the oxidation reagent,[36] it was theorized that iron pyrite present in high sulfur coals would catalyze the decomposition of the oxidation reagent. This theory was tested by addition of iron sulfide (FeS_2) to the oxidation reagent. Rapid gas

-48-

Table 4.1

Ultimate Analysis of Coals Used

in Per TFA Oxidation Studies

Coal	%C	%H	%N	%S	%O	%Ash
No. 789673[a]	73.28	4.80	0.72	2.82	-	9.76
KCER 7122[a] Ky. No. 12	57.2	4.10	0.76	4.56	-	21.6
KCER 4002[a] Elkhorn No. 2	74.6	4.96	1.32	1.94	8.78	-
Alpha Resources[b] Coal Standard	70.79	5.16	1.06	0.39	16.95	-

a) Samples supplied by the Institute for Mining and Minerals

Research.

b) Supplied by Alpha Resources, Inc.

Table 4.2

Aliphatic Acid Yields from Per TFA

Oxidation from Coals

Coal	% Yield			
	Acetic	Propionic	Succinic	Glutaric
No. 789673	0	0	0	0
KCER 7122 KY. No. 12	0	0	0	0
KCER 4002 Elkhorn No. 2	0	0	0	0
Alpha Resources Coal Standard	0	0	0	0

Table 4.3

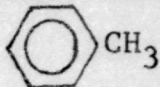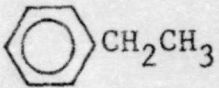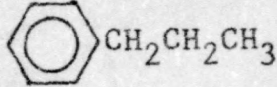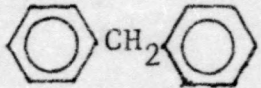Model Compounds Used in

Per TFA Oxidation Studies
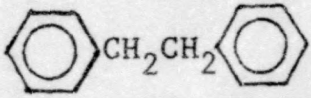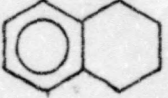
Compound	Structure
Toluene	
Ethyl Benzene	
n-Propyl Benzene	
Diphenylmethane	
Bibenzyl	
Tetralin	
Indan	

Table 4.4

Aliphatic Acid Yields from Per TFA
Oxidation of Model Compounds

Compound	Expected Product	Retention Time of Methyl Esters(min)	Response Factor	Relative Peak Area	% Yield
Toluene	Acetic Acid	2.5	.61	37	77.8
Ethyl Benzene First Trial	Acetic Acid Propionic Acid	1.75 3.75	1.18 1.15	0 0	0 0
Ethyl Benzene Second Trial	Acetic Acid Propionic Acid	1.75 3.75	1.18 1.15	0 0	0 0
Diphenylmethane First Trial	Malonic Acid	13.25	.52	0	0
Diphenylmethane Second Trial	Malonic Acid	13.25	.52	0	0
Propyl Benzene	Acetic Acid Butyric Acid	1.75 6.25	1.18 1.11	0 0	0 0
Bibenzyl	Succinic Acid	15.5	.76	0	0
Indan	Glutaric Acid	16.75	.69	0	0
Tetralin	Adipic Acid	18.5	.55	0	0

Table 4.5

Acids Used in Stability Tests

Acid	Structure
Propionic	CH_3CH_2COOH
Butyric	$CH_3CH_2CH_2COOH$
Malonic	$HOOC-CH_2-COOH$
Succinic	$HOOC-CH_2CH_2-COOH$

Table 4.6

Acid Stability Tests

Acid (Methyl Ester)	Retention Time (min)	Response Factor	Relative Area	% Yield
Propionic	9.25	1.15	0	0
Butyric	11.5	1.11	0	0
Malonic	17.5	.52	0	0
Succinic	19.5	.76	41	7.28

evolution was observed and the peroxide was totally consumed. Further experiments were conducted on a low sulfur coal from Alpha Resources, Inc. (Table 4.1). Peroxide was present at the end of the reaction period, suggesting that difficulties may arise in the study of high sulfur coals due to reagent degradation by pyrite.

Because the coal oxidations were not favorable, model compound studies were conducted. Table 4.3 lists the compounds studied. The oxidation of toluene yielded 77% acetic acid and was in agreement with what had been reported.[32] The other models upon oxidation yielded minute traces of several products. The aliphatic acids were not observed in the gas chromatographic analyses.

To determine if intermediate products were present, spiking studies with a variety of possible oxidation products of ethyl benzene and diphenylmethane were conducted. The ethyl benzene oxidation products were spiked with 1-phenyl-2-ethanol and acetophenone. Diphenylmethane products were spiked with benzhydrol. The retention times of these compounds did not match the retention times of any of the oxidation products. This showed that intermediate oxidation products were not present.

Due to similarities in the chromatograms of the model compound oxidation products a blank experiment was conducted. The conditions were the same but the model compound was omitted. The gas chromatogram of the blank yielded essentially the same products that were appearing in the chromatograms of the model compounds and coals.

Since the data were showing that the bulk of the models was not present in the reaction mixture, the stability of the expected acid products in the oxidation reagent was examined. Propionic, butyric, malonic, and succinic acids were examined. After a 3.5 h reaction period the remaining acid was esterified with methanol. Gas chromatographic analysis revealed that propionic, butyric, and malonic acids were not present in the oxidation products. The succinic acid trial yielded only 7.28% of the original product, suggesting that under the conditions used in this study complete oxidation to CO_2 and H_2O may have occured.

The results of this study were not in agreement with the earlier reports published by Deno and co-workers. These differing results may have been caused by variations in reaction temperatures and variations in the oxidizing reagents themselves. Since low temperature oxidations of model compounds have been shown to produce partial oxidation products,[36] high temperature oxidation may cause conplete oxidation to CO_2 and H_2O. It is also possible that the oxidizing agent used in this investigation had a greater oxidizing strength, thus causing complete oxidation also.

There are problems associated with this technique, and they must be considered when using it to study coal structure. Quantitative measurements of the amounts of aliphatic materials in coals cannot be made. The acids produced from model studies are far from being quantitative and in some cases are very low. Decomposition of the oxidizing reagent may be catalyzed by the presence of certain minerals in the coal. Among the

oxidation products various other components other than the simple aliphatic acids are found. Some of the higher molecular weight aliphatics may also escape detection in the analysis of the oxidation products.

V. SUMMARY

The scope of this study was to investigate the Deno oxidation technique as a tool for characterizing the aliphatic components in coal and to apply this technique to determine the aliphatic characteristics of several Kentucky coals.

Oxidation of the high sulfur Kentucky coals yielded none of the aliphatic acids reported. Decomposition of the oxidation reagent by pyrite was noted when high sulfur coals were oxidized. This was confirmed by decomposition of the oxidizing reagent by iron sulfide.

Model compound investigations, with the exception of toluene, yielded none of the aliphatic acids reported. The bulk of the model compounds was not showing up in the gas chromatograms of the reaction mixtures. Studies on the stability of the expected acid products in the oxidation reagent indicated that the models were being completely oxidized to CO_2 and H_2O.

This technique may be a valuable tool for investigating the aliphatic structure of coal. However, difficulties do arise and must be considered in applying this technique.

BIBLIOGRAPHY

1. J. W. Reasoner, Department of Chemistry, Western Kentucky University, Personal Communication.

2. B. M. Benjamin, V. F. Rosen, P. H. Maupin, L. L. Brown and C. J. Collins, Fuel, 57, 269(1978).

3. H. W. Holden and J. C. Robb, Fuel, 39, 485(1960).

4. R. H. Schlosberg, M. L. Gorbaty and T. Aczel, J. Amer. Chem. Soc., 100, 4188(1978).

5. R. A. Flores, M. A. Geigel and F. R. Mayo, Fuel, 57, 697(1978).

6. L. J. Darlage, J. P. Weidner and S. S. Block, Fuel, 53, 54(1974).

7. L. A. Heredy, A. E. Kostyo and M. B. Neuworth, Fuel Lond., 44, 125(1965).

8. H. W. Sternberg and C. L. Delle Donne, Am. Chem. Soc. Div. Fuel Chem. Preprints, 12, 13(1968).

9. H. Wachowska, Fuel, 58, 99(1979).

10. L. B. Alemany, S. R. King and L. M. Stock, Fuel, 57, 738(1978).

11. J. C. Whitehead and D. F. Williams, J. Inst. Fuel, 48, 182(1975).

12. K. D. Bartle, T. G. Martin and D. F. Williams, Fuel, 54, 226(1975).

13. J. W. Reasoner, Department of Chemistry, Western Kentucky University, Personal Communication.

14. J. A. Franz, Fuel, 58, 405(1979).

15. M. Vahrman, Chemistry in Britain, 8, 16(1972).

16. K. P. Medveder, Sb. Nauchem. Tr., Ukr. Nauchem-Issled. Uglekhim Inst., 13, 38(1962):From Chem. Abstr., 61, 4111h(1958).

17. B. Juettner and H. Bertling, Brennstaff Chem., 46, 277(1965).

18. R. Hayatsu, R. E. Winnins, R. G. Scott, L. P. Moore and M. H. Studier, (Argonne National Labs, Argonne, IL.) Report, 1977, CONF-770814-8:From Energy Res. Abstr., 3, 5(1978). Abstr. No. 10742.

19. N. C. Deno, K. W. Curry, A. D. Jones, K. R. Keegan, W. G. Rakitsky, C. A. Richter and R. D. Minnard, Fuel, 60, 212(1981).

20. P. D. Salbut and A. Wielopolsky, Rocz. Chem., 44, 585(1970): From Chem. Abstr., 73, 122220Z(1970).

21. P. D. Salbut and A. Wielopolsky, Koks. Smola. Gaz., 4, 351(1969):From Chem. Abstr., 73, 37222g(1970).

22. H. Tschamler and E. deRuiter, "Coal Science," R. F. Gould, Ed., Amer. Chem. Soc., Washington, D. C., 333(1966).

23. L. Friedman, D. L. Fishel and H. Shechter, J. Org. Chem., 30, 1453(1965).

24. R. C. Duty, R. Hayatsu, R. G. Scott, L. D. Moore, R. E. Winnins and M. H. Studier, Fuel, 59, 97(1980).

25. F. R. Mayo and N. A. Kirshen, Fuel, 58, 698(1979).

26. J. G. Huntington, F. R. Mayo and N. A. Kirshen, Fuel, 58, 24(1979).

27. J. G. Huntington, F. R. Mayo and N. A. Kirshen, Fuel, 58, 31(1979).

28. M. C. Bitz and B. Nagy, Anal. Chem., 39, 1310(1967).

29. N. C. Deno, B. A. Greigger, L. A. Messer, M. D. Meyer and S. G. Stroud, Tet. Lett., 20, 1703(1977).

30. H. Hart, Accounts Chem. Res., 4, 337(1971).

31. T. Suzuki and S. Naito, Ger. Patent 2,404,114: Chem. Abstr., 81, 151796(1974).

32. N. C. Deno, B. A. Greigger, S. G. Stroud, Fuel, 57, 455(1978).

33. N. C. Deno, B. A. Greigger, S. G. Stroud, A. D. Jones, W. G. Rakitsky, AT-960 "EPRI Research Project Report," 779-16(1979).

34. N. C. Deno, K. W. Curry, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith and R. D. Minard, Fuel, 59, 694(1980).

35. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith and R. D. Minard, Fuel, 59, 699(1980).

36. R. Liotta and W. S. Hoff, J. Org. Chem., 45, 2887(1980).

37. R. K. Hessley, B. M. Benjamin, J. W. Larsen, Fuel, 61, 1085(1982).

B2. F3