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LOW TEMPERATURE CHEMICAL FRAGMENTATION OF COAL

MASTER

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ABSTRACT

Trifluoroperoxyacetic acid chemically fragments coals at 25-80°. The reagent is so selective for oxidizing aromatic rings and is so inert towards benzylic hydrogen that isopropylbenzene, tetralin, indan, and dihydrophenanthrene have their benzene ring(s) totally destroyed without any evidence of oxidation at the benzylic hydrogen. The fragments contain more and different structural information relative to conventional oxidations with Mn VII, Cr VI, HNO₃, and O₂. These latter selectively oxidize benzylic hydrogen.

Products from 37 selected coals show that 9,10-dihydroanthracene and 9,10-dihydrophenanthrene units are prominent features in most bituminous coals in accord with Given's structure of coal. Their frequency accounts for the fact that no continuous fused ring structure or graphite structure exists. The only simple alkyl substituent is methyl.

Liquefaction (solvent refining) sharply increases the amount of arylmethyl and aromatic structure and causes the appearance of unsubstituted phenyl groups.

Nitric acid degradations have been reinvestigated and are developed into a premier method for analyzing the amounts and lengths of linear alkane chains in coals. Generally the amounts of such chains represents 0-2% of the carbon in coal, but in one Utah coal they account for about 42% of the carbons.

INTRODUCTION

If a chemical reaction could be developed which would cleave coals to identifiable fragments without loss of carbon or loss of structural information, the problem of the chemical structure of coal would be largely solved. Such an achievement would also provide a basis for producing marketable organic chemicals without loss of carbon. Although present methods of cleavage fall far short of the above ideal, much has been learned, and it is timely to review two low temperature degradative methods which have been recently developed.

OXIDATIONS WITH TRIFLUOROPEROXYACETIC ACID (CF₃CO₃H)

This oxidizing agent has the unusual property of oxidizing alkylaromatics to form alkyl carboxylic acids instead of aromatic acids.¹⁻⁴ For example, propylbenzene forms butanoic acid and cyclohexylbenzene forms cyclohexanecarboxylic acid in 70-80% yields. With isopropylbenzene, the combined yields of isobutyric acid and

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isopropylmaleic acid are 70-80% so again the alkyl group is preserved in high yield. Hydroaromatic structures and alkane bridges are oxidized to aliphatic diacids, again with preservation of aliphatic structure and destruction of aromatic structure. Examples are the formation of succinic acid from 1,2-diphenylethane and 9,10-dihydro-phenanthrene, succinic and glutaric acids from indan, and glutaric and adipic acids from tetralin. Yields are in the 50-80% range.^{2,3}

The above results suggest that coals will dissolve in $\text{CF}_3\text{CO}_3\text{H}$, and the products will reveal the aliphatic structures. In fact lignites and bituminous coals (but not graphite) dissolve to give colorless or near colorless solutions. However, the interpretations proved to be more subtle than first envisioned. This was due to complexities of the reaction and particularly complexities associated with dihydrobenzene components of the coal structure. These will be discussed before turning to the results with coals.

The first complexity involves lower homologous products. With propylbenzene, although the main product is butanoic acid, it is accompanied by lesser amounts of propanoic and acetic acids. This formation of lower homologs is not due to degradation of the butanoic acid, but arises from multiple pathways in the oxidation of intermediates. The formation of minor amounts of lower homologs is also found in the oxidation of cyclic aliphatic structures fused to aromatic rings.

A second complexity is the formation of acetic acid from structures in which no methyl group is present. For example, indan and dihydrophenanthrene produce acetic acid as a major product when oxidized by $\text{CF}_3\text{CO}_3\text{H}$ alone. Fortunately, in the standard procedure³ with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$, this spurious acetic acid is not produced.

A third complexity is a consequence of the need for added H_2SO_4 . With $\text{CF}_3\text{CO}_3\text{H}$ alone, small secondary alcohols are stable. Even large secondary alcohols simply hydroxylate at remote positions until all carbons are brought within about four carbons of an alcohol group.⁵ With the addition of H_2SO_4 and reaction temperatures of 70° , secondary alcohols undergo oxidation and cleavage of the carbon chain. Primary alcohols are still stable, and 1-butanol was inert to $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$ for 3 hours at 70° . Primary alcohols with longer alkyl chains can be expected to hydroxylate to secondary alcohols which will cleave to diols and hydroxy acids.

A fourth complexity was the formation of alkylmaleic acids. With isopropylbenzene the yield of isopropylmaleic acid was comparable to the yield of isobutyric acid.² This ratio did not change on addition of H_2SO_4 . In contrast, the yield of cyclohexene-1,2-dicarboxylic acid from tetralin dropped from 36% to below 10% on addition of H_2SO_4 .³ Hydroxy substituents in the ring favor the production of alkylmaleic acids and this phenomenon needs more study.

A fifth complexity was the decarboxylation of benzenepoly-carboxylic acids. Fortunately, the added H_2SO_4 strongly inhibits these decarboxylations so that they are not significant in the usual $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$ procedure.³ In the absence of H_2SO_4 , the decarboxylations are much faster and benzenepentacarboxylic acid degrades to benzene-1,2,3,4-tetracarboxylic acid and on to benzene-1,3,5-tricarboxylic acid.

A sixth complexity arose in connection with methylene (CH_2) groups attached to two aryl rings as in diphenylmethane or dihydroanthracene. While some malonic acid was produced, yields were low and erratic. To compound the problem, malonic acid was produced from many polyaromatic compounds. The formation in this latter case is undoubtedly via hydroxylation, ketonization to the cyclohexadienone, and excising out the methylene unit as malonic acid.³ The result was to render malonic acid yields of doubtful value in determining coal structure.

With the above background, the products from coals can be interpreted. Acetic acid is always produced. Its amount is determined from NMR (nuclear magnetic resonance) spectra of the reaction mixture. Providing H_2SO_4 is used in the oxidation, the yield of acetic acid is a good measure of the amount of arylmethyl groups in the coal. In general, about 1% of the carbon in the coals were present as arylmethyl. The yield of acetic acid increases to 2-4% of the carbon in solvent refined (liquified) coals (Table I).^{4,6} This increase in arylmethyl is a result of thermal cleavage to benzyl radicals and hydrogen abstraction by these benzyl radicals to form arylmethyl.

Propionic, butyric, and other simple aliphatic monoacids were not observed. This question is being further investigated by trying to reduce the lower homolog problem and by developing better isolation of products. However, despite an early misinterpretation, the best data show no evidence for these acids from which it is concluded that arylmethyl is the only small arylalkyl group in coals.

Arylalkyl groups larger than propyl are also absent. These would form linear acids longer than butanoic. Such acids would undergo remote hydroxylation⁵ and oxidative cleavage to form diacids and ω -hydroxy acids. The latter would be distinctive, but they largely polymerize to non-volatile polyesters under the present isolation procedures. Fortunately the 40% HNO_3 method, described in the next section, clearly shows the absence of simple arylalkyl groups where the alkyl contains four or more carbons.

Closely related to the existence of arylmethyl groups is the formation of minor amounts of methylmalonic, methylmaleic, and methylsuccinic acids. The first two are attributed to arylmethyl and the last to 9-methyl-9,10-dihydrophenanthrene units. The formation of these and the absence of other alkyl substituents reinforces the view that arylmethyl is the only arylalkyl in coals.

Succinic acid is a significant product from all coals. In Illinois no. 6 Monterey coal the four carbons of succinic acid account for 19.6% of the carbon of the coal.³ At present there is no simple basis for deciding whether the succinic acid comes from dihydrophenanthrene or from 1,2-diarylethane components of coal structure.

The most intriguing product is benzene-1,2,4,5-tetracarboxylic acid (I). Although this is a major product from treatment of polyaromatics and polyalkyl aromatics with HNO_3 , Mn VII, Cr VI, and O_2 , it is not a product from these substrates when $\text{CF}_3\text{CO}_3\text{H}$ or $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$ is the oxidant. Specifically it is not formed from a wide

Table I Yields of acetic acid from oxidative degradations with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$

Name	Penn State coal base number ^a				
	372 Kentucky Imboden	330 Penn. Middle Kittanning	256 Penn. Lower Freeport	312 Arizona Red	405 Oklahoma Lower Hartshorne
% liquified ^a (3 min)	79	70	65	51	25
% C (maf)	85.9	83.5	88.2	78.4	89.8
rank	IIVA	HVB	med. vol.	HVC	low vol.
Yield of acetic acid (meq. per g of maf) ^b					
parent coal	0.44	0.33	0.31	0.42	0.31
SRC (3 min)	0.77	0.74	1.05	1.46	1.51
SRC (90 min)	1.45	1.15	1.06	1.60	1.69
residue (3 min)	0.33	0.41	0.27	0.27	0.24

^a Samples and liquefaction data were supplied by D. D. Whitehurst, Mobil Research and Development Corp.

^b The percentages of moisture (m) and ash (a) are available from the Penn State Coal Base computer printouts. The SRC samples had negligible moisture or ash. In calculating the yields of acetic acid from the residue, it was assumed that all of the ash in the coal was retained in the residue in correcting to a maf (moisture and ash free) basis.

variety of polyaromatics including anthracene and benzantracenes nor is it formed from 9,10-dihydroanthracene or tetraalkylbenzenes. The key to this mystery was that naphthalene-2,3-dicarboxylic acid (II) produced I as the major product and 9,10-dihydroanthracene produced phthalic acid. This suggested that if an additional benzene ring were fused onto dihydroanthracene, the dihydroanthracene would degrade to II which would form I. Not only was this realized, but oxidation of 5,12-dihydronaphthacene also gave many of the minor products observed from coals such as oxiranetricarboxylic acid,

oxiranetetracarboxylic acid, ethanetricarboxylic acid, and benzene-1,2,4-tricarboxylic acid. Table II illustrates these parallels.

Methanol is a product from lignites. Its amount is an accurate determination of the amount of arylmethoxy groups. In North Dakota lignite, 16% of the hydrogen of the dry lignite was present in arylmethoxy groups,² and this is comparable to the amounts in lignin as determined either by $\text{CF}_3\text{CO}_3\text{H}$ oxidative degradations or by the Zeisel method. With lignin and lignites, the high volatility of methanol and methyl trifluoroacetate are not a problem because the oxidations are complete at 25° . With bituminous coals where temperatures of $60\text{--}100^\circ$ are required, special precautions would be required to trap these volatile products. Such precautions have not been taken because Zeisel determinations had indicated the absence of arylmethoxy in bituminous coals. Finally, the $\text{CF}_3\text{CO}_3\text{H}$ oxidations of lignite and lignin showed the absence of any higher homologs of methanol.

Polyaromatic clusters of three or more rings are rare or absent. Model studies (reported in part³) have shown that these produce predominantly phthalic (benzene-1,2-diCOOH) acid and minor amounts of certain lactones. In oxidation of coals, phthalic acid was absent or minor product and the distinctive lactones were not observed. These results support the many lines of evidence which indicate that polyaromatic clusters are largely limited to 2-4 fused rings. After liquefaction (solvent refining), phthalic acid becomes a significant product (Table III) indicating the formation of polyaromatic clusters and the appearance of the lactones (Table III) provides added evidence.

A phenyl substituent attached to a more oxidizable aromatic system reveals itself by formation of benzoic acid. Benzoic acid was not a product from the original coals, but it was a product from the liquified coals (Table III). This generation of unsubstituted phenyl in the process of liquefaction is interpreted as a result of removal of the heteroatom in benzfurans, benzthiophenes, and possibly benzpyrroles. It shows that at least some of these benz rings are unsubstituted in the heterocycle.

Anthraquinone was a product from a few coals. The structures responsible for its formation have not been fully defined. It does not form from anthracene or anthrone and is only a minor product from dihydroanthracene. It is the major product from 9-formylanthracene. We also have data indicating that the yield of anthraquinone increases after exposure of the coal to air. In one coal sample (PSOC-155), 22% of the carbon of the coal was accounted for by anthraquinone. Although the structural precursors are not yet completely defined, production of anthraquinone shows the presence of some kind of anthracene structure with the A or C ring unsubstituted.

The $\text{CF}_3\text{CO}_3\text{H}$ oxidative degradations of coals provide evidence for arylmethyl as the only arylalkyl and an analytical method for its estimation.³ They provide direct evidence for dihydroanthracene and dihydrophenanthrene units as the principal aliphatic components as proposed by Given in his famous structure for coal.⁸ A remarkable

Table II A comparison of products from per TFA oxidation of 5,12-dihydronaphthacene (I) and Monterey coal

Product	Relative area of g.c. peak of methyl ester			
	I ^b	I ^c	I ^d	coal
malonic acid	23	7	8	45
benzoic acid	48	22	12	9
ethanetriCOOH	3	2	0	3
oxiranetriCOOH	11	13	15	16
propane-1,2,3-triCOOH	6	6	18	11
benzene-1,2-diCOOH ^a	60	60	60	60
benzene-1,4-diCOOH	18	8	11	16
oxiranetetraCOOH	13	9	3	12
benzene-1,2,4-triCOOH	41	34	35	60
benzene-1,2,4,5-tetraCOOH	25	22	61	54

^a Arbitrarily set at 60.

^b Peak heights from a capillary column.

^c Areas from a 0.25 inch packed column.

^d In this experiment, the initial CH₂Cl₂ extraction was aided by saturating the aqueous layer with NaCl. The relative increase in the tetramethyl ester of benzene-1,2,4,5-tetracarboxylic acid is evident. Areas were obtained on a 0.25 inch packed column.

Table III Absolute yields (mg per g maf) of products^a from oxidative degradations with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$

MW of methyl ester	132	146	136	204	218a	218b	194a	194b	194c	276	252a	252b	310a	310b
PSOC-372														
coal	17.7	4.9	---	1.2	0.7	4.3	---	---	---	1.3	3.3	---	2.1	---
SRC (3 m)	10.5	3.7	2.3	0.5	0.7	5.6	---	0.9	0.7	2.0	2.0	0.8	0.9	0.1
SRC (90 m)	13.7	6.8	3.5	0.6	0.5	7.2	---	2.4	1.3	2.0	6.7	2.4	2.4	0.4
res (3 m)	7.6	0.7	0.6	0.3	0.7	1.6	1.0	0.4	0.4	0.2	2.8	---	1.7	0.3
PSOC-330														
coal	21.0	6.1	---	1.2	0.9	2.3	---	0.2	0.2	1.5	1.5	---	1.6	---
SRC (3 m)	18.4	6.8	6.1	1.0	0.4	10.0	---	2.4	---	2.6	6.0	---	1.7	0.2
SRC (90 m)	2.5	7.1	7.1	0.1	0.7	2.8	7.7	4.9	3.2	3.0	9.3	0.1	4.4	1.0
res (3 m)	5.1	4.2	1.5	0.1	0.3	0.6	0.5	0.4	0.4	0.6	2.2	---	1.9	0.7
PSOC-256														
coal	18.7	3.9	---	1.1	0.6	1.6	0.2	0.5	0.4	0.9	3.2	---	2.2	---
SRC (3 m)	6.8	5.2	5.9	0.1	0.8	0.7	2.0	1.9	1.9	2.7	9.3	0.2	5.3	0.7
SRC (90 m)	5.8	3.4	6.6	0.4	1.0	10.2	3.2	3.3	2.3	3.5	12.0	0.1	0.5	1.1
res (3 m)	12.5	3.1	2.3	1.0	0.2	2.4	1.7	0.8	0.6	1.6	7.1	---	2.9	0.5
PSOC-312														
coal	13.8	4.9	---	2.0	1.8	10.7	---	---	0.5	2.8	2.5	0.2	1.1	0.2
SRC (3 m)	6.7	12.8	5.9	1.6	0.8	10.4	---	3.3	---	2.8	3.9	1.3	0.9	0.2
SRC (90 m)	11.7	14.3	4.8	0.3	1.8	6.7	---	2.6	3.1	3.3	8.2	0.1	2.8	0.4
res (3 m)	14.8	3.4	1.6	1.2	0.6	4.9	0.7	0.5	0.7	1.6	3.3	0.2	2.3	0.5
PSOC-405														
coal	7.9	2.4	---	0.6	0.1	2.5	1.3	0.9	0.5	0.8	2.5	0.2	1.0	0.3
SRC (3 m)	3.5	10.7	5.8	0.2	1.4	5.2	2.8	3.6	2.7	2.6	7.2	0.2	4.5	0.6
SRC (90 m)	0.9	9.1	5.3	0.3	1.8	1.3	4.0	6.9	---	3.6	9.1	0.2	2.9	0.4
res (3 m)	10.9	3.9	2.4	0.2	0.5	2.8	2.5	1.6	1.8	3.6	10.0	---	6.1	1.1

^aIdentified in Table IV.

Table IV Identification of products in Table III

MW of methyl ester	Relative GC ret. time	Name of corresponding acid (X is COOH)
132	3.20	malonic acid (XCH_2X)
146	4.60	succinic acid (XCH_2CH_2X)
136	5.15	benzoic acid
204	9.23	1,1,2-ethanetricarboxylic acid
218a	10.54	1,2,3-propanetricarboxylic acid
218b	10.97	oxiranetricarboxylic acid
194a	11.10	benzene-1,2-dicarboxylic acid
194b	11.33	benzene-1,4-dicarboxylic acid
194c	11.58	benzene-1,3-dicarboxylic acid
276	14.33	oxiranetetracarboxylic acid
252a	15.79	benzene-1,2,4-tricarboxylic acid
252b	16.14	benzene-1,3,5-tricarboxylic acid
310a	19.18	benzene-1,2,4,5-tetracarboxylic acid
310b	19.50	benzene-1,2,3,5-tetracarboxylic acid

observation is that of some 37 coals studied, generally over 90% of the peak areas in the gas chromatograms are due to the same 10-15 compounds. In contrast, many pure substrates such as anthracene, chrysene, and adamantane produce more complex mixtures of products. Perhaps coals are simpler and more regular than their black, amorphous, heterogeneous nature would suggest.

Many minor products have been identified. A few of these are shown in Table V.

The CF_3CO_3H technique is recently discovered¹⁻⁴ and is not fully developed. Esterifications have been conducted with BF_3-CH_3OH rather than CH_2N_2 because of the desire to avoid the hazardous and toxic CH_2N_2 and because of the large amounts of CH_2N_2 that would be required to destroy all the H_2SO_4 . The BF_3-CH_3OH procedure may give incomplete esterification with certain polyacids. There are also problems in quantitatively isolating the methyl

Table V (continued)

^aThe following identifications (somewhat speculative) are based on MW from chemical ionization mass spectra, the number of carbonyls from the MW of the CD₃OH ester, and fragmentation in electron impact mass spectra. The MW's in the Table are of the methyl esters and the following names are of the corresponding carboxylic acids: 209, 3-carboxypyridine-2-acetic acid; 239, pyridine-2,x,y-tricarboxylic acid (the 2-COOH does not esterify); 253, pyridine-3,4,5-tricarboxylic acid; 297, pyridine-2,3,4,5-tetracarboxylic acid (the 2-COOH does not esterify); 311, a pyridinetetracarboxylic acid.

The lactones (named as the corresponding hydroxy acid) were as follows: 192, 2'-carboxyphenyl-2-hydroxyacetic acid (a major product from naphthalene); 250b-e, analogs of 192 with an additional carboxyl on the benzene ring (one at each of the four positions); 264, 2'-carboxyphenyl-3-hydroxypropanoic acid; 308a and b, analogs of 192 with two carboxyl groups on the benzene ring; 322, the analog of 264 with an additional carboxyl group on the benzene ring.

esters, and the data in Table II show the beneficial effect of salting out.

The five nitrogen containing products in Table V appear to be pyridinepolycarboxylic acids. Their formation is direct evidence for aromatic clusters containing a pyridine ring and a measure of the amount of pyridine rings in the coal. Pyridine is inert towards CF₃CO₃H-H₂SO₄ whereas benzene is rapidly oxidized.^{2,3} Thus, oxidation of an aromatic cluster containing pyridine can be expected to give pyridine polyacids in high yield. The absence of pyrrole polyacids may simply reflect the reactivity of pyrroles. For example, carbozole reacted but did not produce pyrrole polyacids.

OXIDATIONS WITH NITRIC ACID

Nitric acid acts on alkylaromatic systems in two distinct ways. First is to nitrate aromatic rings. This is favored by high acidities which generate the active agent (NO₂⁺).⁹⁻¹¹ Second is the oxidizing action of nitric acid. Oxidation is favored by lower acidities which inhibit the competing nitration, addition of nitrites to generate the active agent (NO₂), and higher temperatures.¹² Addition of urea and other agents that scavenge NO₂ block oxidation.¹²

It has been found that 40% aqueous nitric acid at 60° oxidatively cleaves alcohols, ketones, and alkylbenzenes to form carboxylic acids. The aliphatic and aromatic carboxylic acids do not react further in general, and specifically, alkane chains do not react appreciably below 80°. The reaction is an excellent method for determining the amounts and lengths of saturated linear alkane chains in coals.¹² Table VI summarized data on six coals. To illustrate the interpretations, a 1,8-diphenyloctane would produce

Table V Absolute yields (mg per g maf) of selected minor products from oxidative degradations with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$

	MW of products containing N					MW of lactones								
	209	239	253	297	311	192	250b	250c	250d	250e	264	308a	308b	322
PSOC-372														
coal	---	---	0.4	0.4	0.4	---	---	---	---	0.1	---	0.4	0.3	---
SRC (3 m)	0.2	---	---	0.4	---	0.2	---	0.2	0.2	---	---	0.3	tr	---
SRC (90 m)	0.3	---	---	---	---	0.8	0.5	0.5	0.7	0.1	---	0.6	0.3	---
res (3 m)	0.1	0.5	---	0.4	---	---	---	0.1	---	---	---	---	---	---
PSOC-330														
coal	---	0.1	0.2	0.4	0.5	---	---	---	---	---	---	0.3	0.4	---
SRC (3 m)	---	---	---	---	---	0.2	0.2	0.2	0.2	---	---	0.5	0.3	---
SRC (90 m)	0.3	0.3	---	0.7	---	0.2	0.5	0.5	0.3	0.7	0.3	0.7	1.0	0.4
res (3 m)	---	0.2	---	---	---	---	---	---	0.2	0.5	---	---	0.7	---
PSOC-256														
coal	---	0.1	0.3	0.6	0.2	---	---	---	---	0.2	---	0.1	0.3	---
SRC (3 m)	---	0.4	---	1.1	---	---	0.7	0.3	0.1	0.6	---	0.2	0.7	---
SRC (90 m)	0.2	---	---	---	---	0.3	0.5	0.4	0.5	0.3	---	1.3	1.0	---
res (3 m)	---	0.2	---	0.3	---	---	---	---	---	---	---	0.3	---	---
PSOC-312														
coal	---	---	---	0.3	---	---	---	---	---	0.1	---	0.4	0.4	---
SRC (3 m)	---	---	---	---	---	0.4	0.5	0.8	0.3	0.2	---	0.3	---	---
SRC (90 m)	0.3	---	---	---	---	0.3	0.4	0.2	0.4	0.2	0.2	0.6	0.4	0.2
res (3 m)	0.2	0.1	---	0.7	---	---	---	0.1	---	---	---	---	0.4	---
PSOC-405														
coal	---	---	---	0.1	---	---	tr	tr	---	tr	---	0.1	tr	---
SRC (3 m)	---	0.6	---	1.8	---	0.2	0.4	0.2	---	0.6	0.2	0.4	0.2	0.2
SRC (90 m)	0.6	0.5	---	3.4	---	0.8	0.9	0.2	0.3	1.1	---	0.2	0.2	0.4
res (3 m)	0.4	0.9	---	3.1	---	---	---	0.9	---	---	---	---	0.4	---

Table VI GC peak areas of $(CH_2)_n(COOCH_3)_2$ products as percentage of total peak areas

n =	Coal ^a					
	Monterey	Wyodak	PSOC-110	PSOC-405	PSOC-124	PSOC-155
2	10.9	9.2	8.8	1.8	8.3	10.5
3	7.1	5.8	7.5	1.6	15.6	14.9
4	5.1	5.3	6.9	1.7	17.4	17.3
5	4.5	4.6	4.7	1.5	15.9	18.0
6	4.5	4.7	3.7	2.0	13.0	13.5
7	5.1	3.7	0.9	0	9.4	9.9
8	4.5	2.9	0	0	6.2	5.2
9	1.7	1.3	0	0	2.9	2.0
10-	0	0	0	0	7.7 ^b	5.7 ^b
total	43.4	37.5	32.5	8.6	96.4	97.0
% C (dry)	69.7	71.8	79.5	81.49	75.78	56.87
% H (dry)	4.93	5.20	5.20	4.29	6.33	5.36
% moisture			1.46		0.58	9.36
wt. of coal sample	0.201	0.203	0.216	0.211	0.522	0.524
wt. of methyl esters	0.0121	0.0104	0.0093	0.0072	0.017	0.208
fraction of carbon ^c	1.86 (2.14)	1.34 (1.50)	1.51 (1.63)	0.39 (0.42)	2.33 (2.34)	38.3 (42.2)

^aThe Monterey and Wyodak coals are the Illinois no. 6 Monterey mine coals and the Belle Ayre mine (Amax Co.) of the Wyodak-Anderson seam in Wyoming that were used before.^{1,2} The PSOC numbers refer to the

Table VI (continued)

Penn State/DOE Coal Base collection of coals. These coals can be further characterized as follows: PSOC-110 is Pittsburgh seam, PSOC-405 is Oklahoma Lower Hartshorne, PSOC-124 is West Virginia Lower Kittanning, and PSOC-155 is Utah Cannel coal. The PSOC 110, 124, and 155 coals were used as received. The other three were used as dried samples.

^bThe homologous series continued in a declining manner. With PSOC-155, members of the series could be detected out to $(CH_2)_{38}(COOCH_3)_2$.

^cThis is the fraction of carbon in the coal which appeared in the diacids of four or more carbons. The number in parentheses is an estimate of the fraction of carbon in alkane chains assuming that each chain contained two more carbons that appeared in each diacid as discussed in the text.

adipic acid so that the yield of the six-carbon adipic acid measures the amount of eight-carbon alkane chains in coals.

The fraction of carbon in such chains varied from 0.4-2.3% in five of the six coals. In the sixth coal, it accounted for 42% of the carbon, and diacids out to C_{40} were observed. The yields of diacids formed a smooth continuous curve. The question is whether this reflects a smooth distribution of amounts and lengths of such chains or whether the chains are of a single length or a few selected lengths with an oxidizable and cleavable group (such as $C=C$) randomly distributed.

The absence of linear monoacids shows the absence of aryl-alkyl groups larger than propyl.

OTHER OXIDANTS

A superb review (Molecular Structure of Coal)⁷ has appeared which summarizes other methods of chemically fragmenting coal at low temperature. The results are all in reasonable accord with our work on $CF_3CO_3H-H_2SO_4$ and 40% HNO_3 oxidative degradations.

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