

The Aliphatic Structures in Coal

N. C. Deno, Barbara A. Greigger, and Stephen G. Stroud

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Coals are varying and complex in their chemical structures. This type of situation is classically studied by degradative procedures which reduce the complexity to simpler component parts. This has been done with coal and four degradative methods have emerged to which we owe much of our concepts of coal structure. These are (a) destructive distillation of coal to benzene and pyridine derivatives, (b) alkyl transfer to phenol and determination of the alkylphenols, (c) liquifaction or solvent refining which reduces MW from the 5000 to 600 range, and (d) oxidation with the usual oxidizing agents (HNO_3 , O_2 , Mn VII, Cr VI) to produce benzene carboxylic acids.

We now introduce a 5th degradation procedure. This is oxidation with H_2O_2 in TFA (trifluoroacetic acid) with or without addition of H_2SO_4 . This system has the capability of completely dissolving coal to form colorless or pale brown solutions in which all aromatic structures have been destroyed and most of the aliphatic structures preserved (1,2). The nature of its action is illustrated by three examples. Treatment of propylbenzene, isopropylbenzene, and 1,2-diphenylethane by the usual oxidizing agents (HNO_3 , O_2 , Mn VII, Cr VI) leads to attack at the benzylic positions, oxidative cleavage, and formation of benzoic acid. In contrast, the H_2O_2 -TFA- H_2SO_4 oxidations attack the aromatic rings leaving the benzylic positions virtually untouched even when tertiary as in isopropyl and cyclohexyl benzenes. The products from the three examples are respectively butyric acid, isobutyric acid, and succinic acid (2). It is immediately evident that this new degradation procedure is particularly suited to cataloging and categorizing the aliphatic structures in coals.

The products from the H_2O_2 -TFA- H_2SO_4 oxidations have been examined in two ways. The nmr (nuclear magnetic resonance) spectra of the reaction mixture provides an inventory of the hydrogen present in the products. Acetic acid, succinic acid, and methanol (as the trifluoroacetate) can be easily recognized because they generate sharp singlets and because they are dominant products. The absolute yields were determined using malonic acid as an internal standard. The non-volatile products can be isolated by evaporation in vacuo, conversion to methyl esters, and examination by nmr and gc (gas chromatography).

It must be emphasized that there has not been sufficient time or funding to optimize and standardize procedures. However, it has been found that acetic acid is produced from a wider variety of models in H_2O_2 -TFA oxidations than in H_2O_2 -TFA- H_2SO_4 oxidations. In the latter, acetic acid formation is mainly limited to arylmethyl groups. The current procedure is to add 0.8 g of <20 mesh coal to a mixture of 12 ml of TFA, 15 ml of 96% H_2SO_4 , and 15 ml of 30% aq. H_2O_2 . Addition is exothermic, but not enough to require any precautions with the above amounts. The mixture is heated for five hours at 60°. After cooling, it is important to destroy excess peroxide with 10% Pt on asbestos until O_2 evolution ceases and a KI test for peroxide is negative.

Table I summarizes data on products from oxidations of coal. Table II summarizes data on model compounds. The data has been submitted for publication in greater detail (2).

Despite the preliminary nature of the data, several conclusions are possible. No propionic acid, butyric acid, or isobutyric acid were observed in the products from any of the coals. This eliminates structures involving ethyl, propyl, and

Table I. NMR Spectra of Solutions of Coals in H₂O₂-TFA-H₂SO₄

Coal	H Obsvd. x 100/Total H in Coal			Other bands
	Acetic acid (2.18 δ)	Succinic acid (2.78 δ)	alkyl other than α or β (0-2.0 δ)	
Pittsburgh Seam 79.5% C 5.2% H	1.0	3.3	0	3.5
Illinois #6 70.5% C 5.1% H	5.7	8.9	0.5	2.6
Illinois #6 Monterey 69.7% C 4.98% H	2.8	8.9	2.2	4.1
Illinois #6 Monterey solvent refined	4.4	2.4	1.0	2.8
Wyodak solvent refined 87.0% C 6.6% H	2.3	1.0	8.1	5.9
Lignite North Dakota 65.3% C 4.4% H	0	10.6	50.6	20.4 ^a

^a This was entirely methanol as its trifluoroacetate.

Table II. H₂O₂-TFA-H₂SO₄ Oxidations of Model Compounds

Compound	Predominant Product(s)	% Yield ^a
1,2-diphenylethane	succinic acid	73
9,10-dihydrophenanthrene	succinic acid	71
acenaphthene	succinic acid	64
indan	succinic acid	27
5-hydroxyindan	succinic acid	38
4,7-dimethylindan	succinic acid ^b acetic acid ^b	
toluene	acetic acid	68
1,4-dimethylbenzene	acetic acid	66
1,3-dimethylbenzene	acetic acid	66
1,2-dimethylbenzene	acetic acid	46
ethylbenzene	propionic acid	71
propylbenzene	butyric acid	73
isopropylbenzene	isobutyric acid	32
t-butylbenzene	(CH ₃) ₃ CCOOH	
cyclohexylbenzene	c-C ₆ H ₁₁ COOH	
methoxybenzene	methanol	79
3-phenyl-1-propanol	butyrolactone	75
tetralin and 6-hydroxytetralin	cyclohexene-1,2-(COOH) ₂	69
1,3-diphenylpropane	glutaric acid	

^a Computed on the basis of one mol of substrate yields one mol of product except for the three dimethylbenzenes where the basis was 2 mols of acetic acid from one mol of substrate.

^b Acetic acid : succinic acid = 1.1.

isopropyl attached to an aryl ring. These structures have been reported previously (3,4). While our results will be more reliable if confirmed by gc studies, they seem reasonably firm now. Furthermore, the past reports are in some doubt because they depended on Friedel-Crafts type of degradations (3) or tenuous analysis of broad absorption bands in nmr spectra of coal extracts (4).

None of the bituminous coals contained arylmethoxy as shown by the complete absence of methanol in the oxidation products. This agrees with results of Zeisel determinations which also showed no methoxyl (5). This is particularly interesting because lignite and lignin are well-known to contain arylmethoxy groups. In fact an H_2O_2 -TFA- H_2SO_4 oxidation of lignin at 25° showed 14.0% by weight arylmethoxy which is typical for lignins (6-8). A sample of North Dakota lignite showed 9.6% arylmethoxy. Both yields were computed on the basis that each arylmethoxy went quantitatively to methanol. Neither lignin nor lignite produced acetic acid confirming the well-established absence of aryl methyl groups (6-8). Both produced succinic acid indicating unsubstituted $ArCH_2CH_2-C$ components in the structure.

All coals produced acetic acid, but in widely varying amounts. The model studies indicate that this acetic acid comes from arylmethyl groups and the amount of arylmethyl can be estimated from the data in Table I. In making this estimate, it should probably be assumed that the yield of acetic acid from each arylmethyl is ~70% based on the models in Table II.

The succinic acid originates from diarylethane or indan structures. Since any indan components in coal would likely have alkyl, alkoxy, or hydroxy groups on the aryl ring, it was of particular concern to us to show that such substituents did not significantly alter the production of succinic acid. For this purpose both 4,7-dimethylindan and 5-hydroxyindan were studied and both gave succinic acid as the dominant product the same as indan itself.

The question remains as to whether the succinic acid arises from indan or diarylethane structures or from some other type of structure which has not been studied. One bit of evidence is suggestive that indans are predominantly responsible for succinic acid formation. Oxidation of indan with H_2O_2 -TFA- H_2SO_4 gave no acetic acid whereas the amounts of acetic and succinic acids were comparable when H_2O_2 -TFA was the oxidizing agent. Pittsburgh Seam and Illinois #6 coals showed similar effects. Leaving out the H_2SO_4 in H_2O_2 -TFA oxidations caused the yield of acetic acid to more than double (2).

No aryl hydrogen appeared in the oxidation products despite the fact that benzoic acid is inert. This eliminates benzoate esters as components of coal structure.

The absence of cyclohexene-1,2-dicarboxylic anhydride shows that no tetralin structure can be present of the type which are unsubstituted on the aliphatic ring.

The solvent refining (liquifaction) of coal is thought to involve thermal cleavage of benzyl ethers and conversion of the benzyl radicals to arylmethyl by hydrogen abstraction (9-11). The data on Monterey Coal in Table I is in accord with this view in that the yield of acetic acid (reflecting arylmethyl) increased. The yield of succinic acid decreased presumably reflecting the aromatization or desaturation of indan, diarylethane, and partially reduced aromatic structures.

There is much to do in this field in the direction of varying the oxidation technique to make it more selective and to increase yields. Furthermore, no start has been made in identifying the other products of H_2O_2 -TFA- H_2SO_4 oxidations although their aliphatic nature, small size, and simple nmr spectra suggests that their identification is facile.

The total %H observed can be calculated by adding the columns in Table I. The highest was 81.9% for North Dakota Lignite and the lowest was 7.8% for Pittsburgh Seam Coal. This largely reflects the aromaticity of the coal. The aromatic hydrogens are completely lost while the aliphatic are largely preserved. However, even in model compounds loss of 30% of the aliphatic H was typical and the loss is even greater in certain aliphatic structures such as those on benzyl derivatives. Thus, while the %H observed in a typical bituminous coal such as Illinois #6 is a respectable 17.7%, this represents no more than about half of the total aliphatic hydrogen.

We are deeply indebted to Dr. Malvina Farcasiu and Dr. Duayne Whitehurst for the last 4 substrates in Table 1, for a sample of lignin, and for stimulating discussions. They will be coauthors with us in future papers on solvent refined coal and on lignin. We are also deeply indebted to Mr. Philip Dolsen and the Coal Research Station at The Pennsylvania State University for the first two substrates in Table I. Complete analyses of these coals are available (2). We also wish to acknowledge stimulating discussions with Dr. Ron Liotta of Exxon Corp., Linden, New Jersey.

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