

## OXIDATION OF COAL: A MECHANISTIC PUZZLE

Sujit Kumar Chakrabartty

Alberta Research Council  
11315 - 87th Avenue  
Edmonton, Alberta, Canada  
T6G 2C2

### INTRODUCTION

All coals, other than anthracites, tend to be very sensitive to oxidation. Even exposure to air at ambient temperature causes deterioration to the extent that properties such as solubility, caking, fluidity, tar-yield, etc., are adversely affected. Although the loss of heating value and decrease in tar-yield due to oxidation can be explained in terms of loss in hydrogen contents, details of the chemical changes and the mechanism of oxidation are uncertain. There is agreement among coal chemists that the initial stages of air-oxidation involve chemisorption of oxygen at readily accessible surface sites, but further definition of the mechanistic path at the molecular level is still controversial.

Air-oxidation renders coal increasingly soluble in alkali as 'humic acid' with ultimate loss of 20-30% carbon as carbon-oxides and 40-50% hydrogen as water. The solubilized coal, named as 'humic acid', is spectroscopically similar to the parent coal except for oxygen functional groups identified as phenolic -OH, -COOH, and =CO (ketone and/or quinone) respectively. The peripheral molecular changes associated with the formation of oxygen-functions are explained (1) by a scheme resembling the gas-phase oxidation of naphthalene to phthalic acid and maleic anhydride in sequential steps. The limiting elemental compositions of the humic acids depend on the temperature of oxidation, and tend to vary slightly with coal rank. Higher temperature and/or higher oxygen partial pressure accelerates the rate of the reaction. At temperatures beyond 250°C, a virtual low-temperature combustion process sets in.

It could be argued that production of phthalic anhydride by gas-phase oxidation of naphthalene is a catalytic process, and requires temperature-pressure conditions far more severe than coal-oxidation. Coals, in contrast, weather away under ambient conditions, leaving chemically identical 'humic acid' that can be generated by air-oxidation at 150-200°C. The reactivity of coal for electrophilic attack by oxonium ions is therefore hardly comparable to that of naphthalene, and it is unlikely that the mineral matter in coal is a more effective oxidation catalyst than vanadium pentoxide.

The formation of transient ketones or quinones during air-oxidation is indirectly demonstrated by 'ammoxidation' of coal. If the reaction is conducted in an atmosphere of gaseous ammonia (2), the rate of reaction falls rapidly with progressive incorporation of nitrogen (as high as 20%), and the reacted solid resists further oxidation. In the postulated mechanism for this reaction, the transformation of transient ketonic functions to nitrogen functions in the form of amide or imide, and further stabilization of imido functions by oxidative ring-closure, are

put forward to explain the refractory nature of the "amoxidation" product (2b). The ketones may be generated by oxidation of hydroxyl groups, insertion of oxygen in C-H bonds, or by oxidation of carbanion species.

The presence of alkali, e.g. sodium hydroxide, on the other hand, accelerates rate of reaction. When coal is slurried with aqueous sodium hydroxide and reacted with oxygen under pressure (and temperature as high as 200°C), a complete break-down of structural components lead to aromatic carboxylic acids (3). Thirty to 45 per cent of the total carbon is recovered as carboxylic acids, and the remainder is lost to carbon dioxide. No attempt was made to demonstrate a mechanistic route for this process. However, reactions of coal with sodium dichromate at 250°C in an autoclave under autogenic pressure (4), or with sodium hypochlorite in an open flask at 60-65°C (5), also destroy the structural components to yield low-molecular weight carboxylic acids. In all these reactions, the oxidation paths appear to be substantially identical, (if one considers the generation of the products only), and the carbon distributions in the products at the completion of the reactions are quite similar. While the reactivity for oxidation decreases with increasing rank, such dependence is eliminated if the sample is partially air-oxidized or 'weathered'. This can be rationalized from the generation of ketones in the hydrocarbon skeleton of coal, which, in turn, would activate adjacent carbon atoms for further oxidation. The step-wise oxidative degradation of hydrocarbon chains (6) is supposed to follow this course. However, coal is not an agglomeration of hydrocarbon chains and a better mechanism (based on a strictly physical model) can be developed from the concept of a 'shrinking core'. The oxidant is chemisorbed and reacts on the surface. With air, the predominant process is rapid generation of humic acid followed by secondary decomposition of carboxyl functions as envisaged by Jensen et al (7) and elaborated by Berkowitz (1). In wet oxidation, the 'humic acid' formed at the outer layer of the particle is extracted, and further oxidized in a homogeneous solution phase; and a fresh reactive surface is created on the shrinking particle for continuing 'primary' oxidation.

But such a phenomenological description does not in itself offer clues to a mechanistic path at the molecular level. It merely defines questions that need to be answered, specifically,

- a. what are the active surface sites (and their chemical properties) at which initial oxidation occurs?
- b. does the reaction involve radical or ionic species, or does it proceed by simple insertion of the electrophilic agent?
- c. which bonds are cleaved to generate low molecular-weight compounds? and
- d. why is the reactivity of the oxidant insignificant in relation to the reactivity of the coal?

#### SEARCH FOR A PROBE

In coal-constitution studies, oxidants, thought to be selective, were used to explore the mechanistic maze of coal-oxidation. However, in the classical work of Bone and Wheeler (8) which was based on alkaline potassium permanganate, the oxidant cleaved aromatic as well as aliphatic C-C bonds. Later work was devoted to study the effect of milder oxidants. For example, aqueous performic acid (9) readily converts coal into humic acid (which was quite helpful because the humic acid on reduction with sodium amalgam yielded distinctive phenolic products in which propyl-benzene structure of lignin could be identified). Sodium dichromate (4), and sodium hypochlorite (5), intended for reactions with aliphatic structures, readily cleaved some coals to products much less complex than humic acid and yielded benzene polycarboxylic acids as major products. The study with dichromate was restric-

ted to hvb-coals, whereas, with hypochlorite from lignite to lvb-coal (C=90%) were reacted. Partial oxidation of aromatic structures by dichromate ions was suspected along with the intended cleavage of aliphatic C-C bonds. The mechanism of hypochlorite oxidation is not fully understood. The reactivity of coals toward hypochlorite oxidant is rank-dependent. Reaction with coal containing more than 82% C is limited to surface degradation; loses 5-12% carbon presumably as CO<sub>2</sub>; and the resulted solid residue has higher oxygen content than the parent coal. Yet, if the high-rank coals are pretreated with nitronium tetrafluoroborate (a nitrating agent), or are partially oxidized with air at 150°C, complete dissolution of coal can be achieved.

Pretreatment with a nitrating agent should yield conventional nitrobenzene derivatives. The nitro-group generally deactivates aromatic rings for electrophilic attack, and activates the side chain for oxidation. Derivatization might therefore be expected to confine oxidation to aliphatic structures and to preserve aromatic rings. But only 3-6% of the nitrogen of the nitro-coal could be recovered after hypochlorite oxidation, and the product-mixtures contained quite insignificant amounts of nitro-benzene structures (10).

The puzzle was unscrambled when it was observed that high rank coals could be more extensively oxidized when the hypochlorite was used in a two-phase (methylene chloride-water) system, and tetrabutylammonium fluoroborate was added as a phase-transfer catalyst. Table 1 shows the results of this study.

Table 1. Two-Phase Hypochlorite Oxidation: Recovery of Carbon in Products (per cent carbon)

Products	hvb-coal (C 86, H 5.5)	lvb-coal (C 88.1, H 4.9)
Carbon dioxide	13.2	22.04
Volatile acids (a)	1.8	3.0
Hexane soluble (Me-ester)	10.0 (b)	11.0 (c)
Hexane insoluble (Me-ester)	1.3	2.5
MeOH-soluble (acid)	9.0	14.1
Unaccounted	10.0	10.0
Oxidized insoluble residue	44.7	27.3

(a) acetic, chloroacetic, propionic and malonic acids; (b) phthalic acid, 94%; (c) phthalic acid 62%, tricarboxylbenzene 32% and tetracarboxylbenzene 5%.

It is noteworthy that in this system lvb-coal is oxidized to a greater extent (giving high yield of carbon dioxide and methanol-soluble acids), than hvb-coal. Structural differences between these two coals are also revealed in the respective product distributions. From the hvb coal, phthalic acid is a major product (in addition to carbon dioxide), and a substantial fraction (44.7% C) resists further oxidation by this reagent. From the lvb-coal, major products are di-, tri- and tetracarboxylbenzene; carbon dioxide yield is 50% greater and only 27% carbon resist further degradation.

In a parallel study of oxidation under the same conditions, a polymer, ethyl-polyvinylbenzene, was found to be unreactive in an uncatalyzed as well as in a catalyzed two-phase system. Even after nitration with nitronium tetrafluoroborate, it did not, like coal, break down to carbon dioxide or chloropicrin. Only discoloration and partial chlorination were observed. The reactivity of coal toward this oxidant was found to be very much greater than the reactivity of benzylic methylene or methine groups in ethyl-polyvinylbenzene polymer.

The catalyzed oxidation with hypochlorite ions of coal may not be restricted

to aliphatic structures only. Permanganate ions in the form of alkylammonium salts in pyridine solution have been used to oxidize aliphatic side-chains (11). Three coals, subbituminous, hvb and lvb, were treated with an excess of tetrabutylammonium permanganate in pyridine at 50°C and yielded results summarized in Table 2.

Table 2. Oxidation with Tetrabutylammonium Permanganate

Oxidation Data	Coal		
	subbit (C 78%)	hvb (C 86%)	lvb (C 88%)
% Carbon recovered as soluble product	9.5	6.2	11.3
Products, mole %			
Acetic acid	12.4	11.4	11.5
Propanoic acid	3.3	4.9	2.3
Butanoic acid	-	3.9	-
Pentanoic acid	yes	4.5	yes
Succinic acid	-	17.4	yes
Glutaric acid	-	0.7	-
Adipic acid	-	3.0	-
Octanedioic acid	86.1	50.5	84.2
Phthalic acid	-	3.5	-
Unknown peak	yes	yes	yes

The mole percent compositions were calculated from the major identified peaks in the gas chromatograms of the methyl esters. The unknown peak in the chromatogram was assigned as 1,1,2-ethanetricarboxyl acid from mass-spectral data and retention time. The yield of this acid from hvb coal was greater than from the other two; and, if the structural assignment is correct, the isolation of this product indicates the presence of bridged aliphatic configurations in the parent coals. In contrast, the large-component in the acid mixture was octanedioic acid (which must have derived from ring structures larger than cyclohexane) and is present in lesser quantity (50% as compared to 84-86%) in hvb coal. Moreover, only the hvb coal yielded succinic, glutaric and adipic acids, presumably by degradation of cyclohexane rings. The straight chain components, derived from oxidation, are almost identical in all three coals. Though the total conversion yields are in the order of 10% only, the data are very significant to indicate the structural differences between coals. The concept of systematic evolution of rank by increasing aromatization of hydroaromatic structures is too empirical to accommodate the results of this study. The presence of bridged alicyclic and large alicyclic rings in the hvb coal is demonstrated by these results; further attention would focus to establish whether these structural features are unique from some coals or belong to a set pattern of coal-constitution.

#### CONCLUSION

The above discussion justifies the theme of the presentation. Coal-oxidation is unique in a mechanistic sense, but much more complicated than would be expected from oxidations of standard organic compounds. It is reasonable to assume that aliphatic structures, particularly benzylic methyl, methylene or methine groups, or carbon adjacent to hetero-atoms are the most reactive, and are oxidized to ketones or carboxylic acids. In order to degrade coal to CO<sub>2</sub> and water-soluble low-molecular-weight compounds by mild oxidants, an abundance of these functional groups must be assumed. However, the stability of ethyl-polyvinylbenzene polymer towards hypochlorite oxidant indicates that activation of coal-carbon for

oxidation results from features other than electronegativity of aromatic rings. The uniqueness of the coal-oxidation has to rest on a destabilizing factor which makes even aromatic sites vulnerable.

One may speculate that mineral matter in coal is coordinated with aromatic structures, and that the resultant complexes are destabilized by electrophilic attack. If a coal is an entangled interpenetrating macromolecular mixture (12), the destabilizing effect would decrease with increasing compactness of the physical structure which accompanies increase in rank; higher rank coals would therefore be less reactive. However, if the oxidant can also, like mineral matter, intercalate, it would open the structure up, and produce destabilization. The success of wet oxidation would then depend less on the oxidation potential than on the ability of the oxidant to intercalate. The oxidation of lvb coal with assistance from phase-transfer catalysts in a two-phase system is consistent with this view.

## EXPERIMENTAL

The subbituminous and lvb coals are from Alberta, Canada (Cretaceous), and hvb coal is from Virginia, U.S.A. (Carboniferous). All coals are cleaned by gravity separation.

Commercial bleach (0.8 molar solution) was used for hypochlorite oxidation. Tetrabutylammonium fluoroborate was of electrometric grade supplied by Southwestern Analytical Chemicals Inc., Austin, Texas.

Tetrabutylammonium permanganate was prepared by exchange reaction between tetrabutylammonium bromide and analytical grade potassium permanganate.

### Two-phase Oxidation

5.0 g air-dried coal and 5.0 g tetrabutylammonium fluoroborate were placed in a 50 ml dichloromethane, and the suspension agitated in an Erlenmeyer flask at 30°C while hypochlorite solution was added at intervals until consumption of the oxidant ceased. The reaction required three days from completion. The reaction mixture was then further diluted with dichloromethane, and separated into layers. The organic layer contained the ammonium salt and was removed. The aqueous layer, after acidification, was extracted with ethyl ether. Solid products filtered from the aqueous layer were extracted with methanol. The ether-soluble fraction was methylated with diazomethane, and the esters were separated into hexane-soluble and -insoluble fractions. The composition of the hexane-soluble fraction was determined by G.C.-mass spectrometry.

### Oxidation with Tetrabutylammonium Permanganate

5.0 g dried coal, 20.0 g oxidant, and 75 ml pyridine were heated in a two-necked flask under helium atmosphere at 50°C, and mechanically stirred for 24 hours. The solvent was then distilled off under reduced pressure, and the residue diluted with water. Excess permanganate was neutralized with sodium bisulfite; the mixture acidified with hydrochloric acid, and finally filtered. The water-extract was washed with dichloromethane to separate tetrabutylammonium salt, and thereafter continuously extracted with ethyl ether. The ether-extract was methylated with diazomethane and analyzed by G.C.-mass spectrometry.

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