

## REACTION OF COAL WITH NITRONIUM TETRAFLUOROBORATE

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If, as is generally supposed, coal is comprised of predominantly aromatic carbon configurations, it should be open to attack by electrophilic agents. However, while sulphonation, halogenation and nitration of coal have been reported (1), interaction of coal with a selective electrophile - for example, interaction with the nitronium ion - have not yet been explored in detail. Some investigations of this reaction have been published by Brown (2) who employed cupric nitrate in acetic anhydride and by Lahiri et al (3) who used mixtures of nitric and sulphuric acids; and in these cases, it was presumed that the active agent was the nitronium ion which formed as an intermediate in the solvent system. With crystalline salts which contain the nitronium ion, e.g.  $\text{NO}_2^+\text{BF}_4^-$ ,  $\text{NO}_2^+\text{ClO}_3^-$  now readily available, it should, in principle, now be possible to achieve selective nitration more cleanly in non-aqueous, acid-free systems; and we have in fact used nitronium tetrafluoroborate for "activating" bituminous coal before subjecting it to hypochlorite oxidation (4). But recent studies, notably by Olah et al (5), indicate that such salts can also promote reactions other than nitration. They will, for example, oxidize benzyl alcohols to ketones, induce nitrolysis of alkanes, and cleave ethers. In the case of reactions between nitronium tetrafluoroborate and coal, it must therefore be expected that various oxygen-bearing functions as well as nitro-groups could be established in the coal. The work reported in this paper was undertaken in efforts to determine the validity of these expectations.

### EXPERIMENTAL

#### Reaction with nitronium salt

A mixture of 5 to 90 mmoles of the salt and 25 ml acetonitrile or methylene chloride was stirred at ice-bath temperature to produce a homogeneous suspension, and 1 g of dry coal was added. Reaction was allowed to continue for 16 hours at ice-bath temperature under a blanket of helium. The solvent was then evaporated under reduced pressure, the residue quenched with ice-water, and the product isolated by filtration and washed free of acid.

Similar reactions were performed with model compounds, e.g. polystyrene, adamantane, tetrahydronaphthalene and decahydronaphthalene.

For comparison, one coal sample was nitrated with 1:1 v/v concentrated with nitric-sulphuric acid at ice-bath temperature for 16 hours. The mixture was then poured into crushed ice, diluted to a large volume, the nitro-coal filtered off and finally washed free of acid.

#### Functional group analysis

The number of nitro groups introduced was estimated by titration with stannous chloride or titanous chloride, using a standard procedure (6).

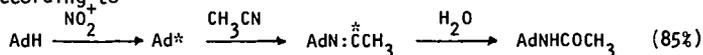
The carboxylic acidity was estimated by ion-exchange with sodium acetate and distilling off the acetic acid, and the hydroxyl-content was determined by acetylation with acetic anhydride in pyridine, following the procedure developed by L. Blom (7).

### RESULTS AND DISCUSSION

Tetramethylene sulfone, acetonitrile and various other solvents have been used for nitration with nitronium salts. Initially, acetonitrile was used in this study. The nitration of polystyrene in this system introduced one nitro group per chain-length of four monomer units. The yield of mono-nitrotetralin was 78%. In con-

rust, adamantane and octahydronaphthalene could not be nitrated but varying yields (up to 85%) of some other nitrogen-containing product was obtained. The product derived from adamantane was identified as N-(1-adamantyl)acetamide by comparing melting point, infra-red and <sup>1</sup>H-n.m.r. spectra of the sample with authentic compound. The spectral data indicated the formation of a similar product (in 3% yield) from octahydronaphthalene, whilst tetrahydronaphthalene only furnished the mono-nitro product.

It may be presumed that the nitronium ion, being an oxidant, oxidizes adamantane to the adamantyl radical or ion which, in turn, reacts with the solvent according to



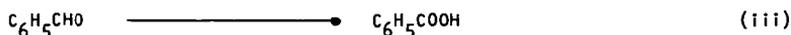
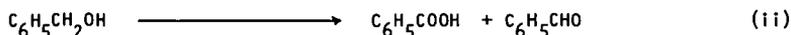
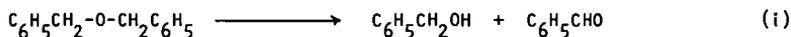
It is interesting to note that of the four model compounds studied, adamantane has the most easily oxidizable C-H bonds. From hypochlorite oxidation (4), it was demonstrated that coal has similar types of C-H bonds, and it is possible that reaction with nitronium salt in acetonitrile may produce an acetamide derivative of coal.

Nitro-coal prepared with nitric-sulfuric acid mixtures gave a titration profile which accounts for all added nitrogen in nitro groups, and similar results were obtained when coal was treated with nitronium salt in methylene chloride. However, in acetonitrile solvent, depending on the amount of nitronium salt used in each reaction, only 48-67% of the added nitrogen could be found in nitro groups (Table 1).

Material balances indicate that little, if any, carbon is lost when the coal is treated with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture or with a nitronium salt in methylene chloride. However, the reaction of coal with nitronium salt in acetonitrile yields products with more carbon and nitrogen content. Since the only extraneous source of carbon was the solvent, the added carbon must come from the reaction of acetonitrile with coal. Moreover, it was also found that for every nitrogen atom added other than as N in nitro groups two carbon atoms were added. And hydrolysis of the products in 1N phosphoric acid gave acetic acid. From these observations it is surmised that a nitronium salt in acetonitrile introduces acetamido as well as nitro groups. The results of reaction between nitronium salts and coal, based on material balances and titration data, are presented in Table 2.

Mazumdar et al (8) have reported that the major reactions during nitration of coal with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> involve introduction of nitro groups and, even under very mild conditions, simultaneous oxidation of the carbon-structure. The oxidation creates carboxyl, hydroxyl and ketonic functions, with formation of carboxyl being the dominant process. But since no loss of carbon was observed, it was concluded that oxidation is limited to methyl groups. Reaction of coal with nitronium salt also induces some oxidation and 7-15% weight increase could be ascribed to newly created oxygen functions. The concentration of oxygen-bearing groups in variously treated coal samples are shown in Table 3.

It is interesting to note that whatever the nitrating system, almost identical oxygen-bearing groups are generated. Since nitronium salts can cleave ethers, the oxidation can be related to such cleavage reactions followed by further degradation depending on the oxidation potentials of the nitrating systems, e.g.



From the nitration studies, some inferences about coal structure can be drawn. Thus, reaction with nitronium salt introduces 3-7 nitro groups per 100 carbon atoms while HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixtures permit addition of 8-10 nitro groups. If it is assumed that isomerizations of condensed polycyclic aliphatic structures to aromatic structures does not occur during nitration at 0°C, the number of nitro groups per 100

carbon atoms may provide information about aromatic ring size. In Table 4, the average composition of coal sub-units with nitro group are calculated from published data (8). These sub-groups vary from  $C_{12}H_9$  to  $C_{10}H_6$  and consequently suggest that only benzene or naphthalene nuclei are present in them.

Some support for this deduction is afforded by data relating to reduction of coal with lithium in ethylene diamine. Reduction of aromatic compounds in such or similar systems yields dihydro- or tetrahydro-derivatives, and assuming benzene or naphthalene as the only aromatic structure in the unknown molecule, the hydrogen uptake by the sample can be calculated from the number of such ring per 100 carbon atoms of the samples (Table 5). A comparison of these data with experimental results indicates that the abundance of naphthalene rings increases with rank. It is hardly expected that the reduction of single benzene ring would stop at the tetrahydro-stage. From this discussion we conclude that the smallest hydrocarbon skeletal structure in coal may be in units of  $C_{12}H_9$  to  $C_{10}H_6$ , and that, depending on rank and geographical location, the nucleus of such unit is a benzene or naphthalene ring.

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Table 1. Nitro-groups in Reacted Coal and Model Compounds

Sample	N <sub>total</sub> mmole/g	N <sub>NO<sub>2</sub></sub> , mmole/g		N <sub>NO<sub>2</sub></sub> /N <sub>total</sub> (added) %
		SnCl <sub>2</sub>	TiCl <sub>3</sub>	
a. 1 g coal reacted with				
(i) HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> (10°C)	5.1	4.14	4.28	100
(ii) 90 mmole NO <sub>2</sub> BF <sub>4</sub> /MeCN	5.6	2.36	2.50	48
(iii) 45 " " " "	3.0	1.28	1.35	57
(iv) 5 " " " "	1.5	0.00	0.49	67
(v) 90 " " CH <sub>2</sub> Cl <sub>2</sub>	2.9	2.32	2.35	100
b. Model compounds/NO <sub>2</sub> BF <sub>4</sub> /MeCN				
(i) Polystyrene	2.0	2.26	2.40	
(ii) Adamantane	7.2	0.00	0.00	
(iii) Aniline	14.5	7.28	6.98	
(iv) Benzoic acid	6.0	6.0	5.98	

Table 2. Reactions with Nitronium-Tetrafluoroborate

Substrate	% Weight Increase	Product	Analysis			
			%C	%H	%N	NO <sub>2</sub> meq/g
<b>Acetonitrile Solvent</b>						
1. Polystyrene (C <sub>8</sub> H <sub>8</sub> ) FW n x n <sup>104</sup>	10	(C <sub>8</sub> H <sub>8</sub> ) <sub>3.35</sub> C <sub>8</sub> H <sub>7</sub> NO <sub>2</sub> FW 498	a. 83.39 b. 84.2	6.8 7.0	2.8 2.8	2.0 2.4
2. Coal %C = 85.7	36	C <sub>100</sub> H <sub>68</sub> N <sub>0.93</sub> (NO <sub>2</sub> ) <sub>6.4</sub> (NHCOMe) <sub>3.9</sub> FW 1904	a. 68.0 b. 69.0	4.4 4.1	8.2 7.9	3.4 3.2
		C <sub>100</sub> H <sub>78.3</sub> N <sub>0.93</sub> O <sub>6.76</sub> FW 1401				
3. Coal %C = 88.8	35	C <sub>100</sub> H <sub>59.1</sub> N(NO <sub>2</sub> ) <sub>5</sub> (NHCOMe) <sub>1.8</sub> FW 1822	a. 68.2 b. 69.0	3.6 3.3	6.0 6.2	2.7 2.6
		C <sub>100</sub> H <sub>65.9</sub> NO <sub>4.3</sub> FW 1350				
<b>Methylene Chloride Solvent</b>						
4. Coal %C = 88.8	21	C <sub>100</sub> H <sub>55.1</sub> N(NO <sub>2</sub> ) <sub>3.7</sub> FW 1623	a. 74.0 b. 74.0	3.4 3.4	4.1 4.0	2.3 2.3
a. calculated b. found						

Table 3. Oxygen-Bearing Functional Groups in Treated Coal

Sample	-OH meq/g	-COOH, meq/g
1. Coal %C = 88.8	0.9	nil
2. Sample 1/NO <sub>2</sub> BF <sub>4</sub> /CH <sub>3</sub> CN	2.3	3.0
3. Sample 1/NO <sub>2</sub> BF <sub>4</sub> /CH <sub>2</sub> Cl <sub>2</sub>	1.5	0.8
4. Sample 1/HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	2.2	2.8
5. NO <sub>2</sub> -Coal* from Coal %C = 89.8	2.8	3.5

\*See Reference (8)

Table 4. Nitration of Bituminous Coals\*

Coal %C	Nitro gr per 100 C-atoms	Average composition of subunit/NO <sub>2</sub> gr Number of atoms			
		C	H	N	O
80.8	8.6	11.6	8.9	0.24	1.24
83.6	8.2	12.2	9.6	0.29	0.90
85.5	9.2	10.9	7.9	0.22	0.65
87.1	9.9	10.1	7.7	0.24	0.38
89.8	8.6	11.6	7.3	0.23	0.27
90.2**	9.3	10.8	6.6	0.15	0.31

\*Data recalculated from B. K. Mazumdar et al, Fuel 46, 380, 1967.

\*\*From the study by the author.

Table 5. Reduction of Coals by Alkali Metals in Basic Solvent  
H-uptake per 100 Carbon Atoms

Coal % C	Calculated value from nitration of Gondwana coal		Experimental value (10)	American coal
	dihydro	tetrahydro	%C	H-uptake
80.8	17.2	34.4		
83.6	16.4	32.8	83.1	17
85.5	18.4	36.8	85.1	19
87.1	19.8	39.6	88.7	27
89.8	17.2	34.4	89.3	29
90.2*	18.6	37.2	90.1	45

\*Canadian coal