[CONTRIBUTION NO. 46 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Aromatization of Cellulose by Heat

BY R. C. SMITH AND H. C. HOWARD

Graphite is one of the ultimate products of thermal decomposition of all organic substances and thermodynamically can logically be considered the limiting member of the series of aromatic hydrocarbons.[1] Little information is available as to the temperature at which this C_6 ring structure begins to appear when a non-aromatic substance, such as cellulose, is subjected to increasingly severe thermal treatment although the subject is of great theoretical interest in connection with coalification and carbonization processes. Fischer and Schrader[2] regarded the fact that the bituminous coals yield significant amounts of aromatic acids on oxidation as evidence for the point of view that such coals are derived from lignin, since in parallel oxidation experiments on lignin and cellulose, aromatic acids were recovered from the former and not from the latter. Bone[3] confirmed the results of the German workers and reported that in quantitative oxidations with alkaline permanganate, 39–46% of the carbon of three British bituminous coals could be accounted for as benzene carboxylic acids; with cellulose 96.8% of the carbon was found in the simple acids carbonic, oxalic and acetic.[4] Obviously the recovery of aromatic acids by oxidation of coal does not prove that coal is derived exclusively from lignin if it is found that by heating cellulose to temperatures which may conceivably have been reached during coalification, substances are formed which yield aromatic compounds on oxidation.

In the present investigation samples of pure cotton cellulose were heated in a nitrogen atmosphere at temperatures ranging from 190 to 400°. The ultimate composition of the residues from the pyrolyses, with the theoretical composition of cellulose for comparison, are shown in Table I. The high carbon content of the product obtained at 250°, as compared with that at 190°, is very striking. A strong exothermic reaction was observed in this temperature range. The residues from pyrolysis at 190° were light brown in color and fibrous; all the others were black friable chars, but still retained some fiber structure. The gaseous products from a 250° pyrolysis, after correction for nitrogen, consisted of 74.6% carbon dioxide, 11.6% hydrogen, 12.1% carbon monoxide and 1.6% hydrocarbons.

TABLE I

ULTIMATE COMPOSITIONS

	C	H	O (diff.)	Ash[b]
Cellulose, %	44.44	6.17	49.39	. .
190° Char[a]	45.34	6.21	47.81	0.64
250° Char	71.54	4.79	22.48	1.19
400° Char	85.58	4.51	9.42	0.49

[a] All chars dried at 100° in vacuum. [b] From corrosion of the bomb.

The residues from the pyrolyses were completely converted to water soluble acidic oxidation products by exhaustive oxidation with alkaline permanganate. The amounts of carbonic, oxalic and volatile acids, the latter calculated as acetic, formed were determined and the percentage distribution of the carbon among the various oxidation products calculated. The results are shown in Table II and data on the oxidation of the original cellulose are included for comparison. The column designated "aromatic carbon" was obtained by difference and gives the percentage of the total carbon in the soluble products unaccounted for by the simple acids, carbonic, acetic, and oxalic. Even in the case of the 250° char, significant amounts of the carbon are not so accounted for. The essentially aromatic character of the carbon assigned to aromatic acids was established by decarboxylation of the mixed acids. Benzene and diphenyl were the only condensable hydrocarbons recovered. With the 250° char the carbon appearing as aromatic acids is less than that found in similar oxidation experiments with a Pittsburgh seam bituminous coal for which an average figure of 30% has been obtained.[5] In the case of the 300° char, however, the aromatic carbon is of the same order as that from the Pittsburgh coal. The 2% "aromatic carbon" reported in the oxidation products of the original cellulose indicates the probable experi-

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(1) Jacobs and Parks, THIS JOURNAL, **56**, 1516 (1934).

(2) F. Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 208, 551 (1920); F. Fischer, *ibid.*, **8**, 373 (1925–1927).

(3) Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935). The method of determining the carbon reported as "benzene carboxylic acids" was not disclosed.

(4) Bone, Parsons, Sapiro and Groocock, *ibid.*, **A148**, 507 (1935).

(5) Unpublished data.

TABLE II

DISTRIBUTION OF CARBON IN OXIDATION PRODUCTS AND RESULTS OF DECARBOXYLATION

			Carbon					Steam volatile hydrocarbons	
		KMnO4 g./g. char	Total, g.	Carbonic, %	Oxalic %	Acetic %	Aromatic %	Yield, g.	% to 90°
Original cellulose[a]		6.7	46.9	63.9	32.3	1.7	2.1	..	..
Chars Temp., °C.	Chars Yield, %								
190	89	8.4	43.7	93.7	1.1	0.5	4.7	Trace	..
250[b]	50	12.0	38.6	73.8	11.1	1.5	13.7	1.38	48.9
275	45	11.1	36.2	59.0	14.1	1.8	25.1	2.25	66.8
300	44	10.8	35.4	51.6	18.5	1.6	28.4	2.50	67.5
350	43	10.5	32.7	52.0	12.0	1.8	34.0	1.79	59.3
400[c]	38	10.8	34.3	53.3	12.9	1.0	32.8	4.95[d]	82[e]

[a] 75 g. used, computed on the basis of 100 g. [b] Average of two experiments. [c] Average of three experiments. [d] Three samples decarboxylated together, yield computed for 38 g. of char. [e] To 79.5°.

mental error of the method. The higher recovery of total carbon for cellulose as well as the products of pyrolysis, than calculated, is due to carbonate in the alkali and absorption of carbon dioxide from the air.

The actual recovery of steam volatile hydrocarbons by decarboxylation of the acids from oxidation of the 400° char is somewhat higher than that obtained by decarboxylation of acids from a Pittsburgh seam coal[6] and corresponds to 13 g. per 100 g. of cellulose char. This is equivalent to 5 g. per 100 g. of original cellulose linters.

Densities, d^{25}_4, and refractive indices, n^{20}_D of the hydrocarbons recovered from the 250, 275, 300, 350° chars were 0.92, 0.90, 0.91, 0.89, and 1.529, 1.538, 1.522, 1.526, respectively (benzene, d^{25}_4 0.873; n^{20}_D 1.501). Fractionation of the hydrocarbons from the 400° char yielded 82%, boiling 78–79.5°, n^{20}_D 1.500; 5% crude diphenyl and 13% of tarry residue. Densities and refractive indices prove the hydrocarbons to be aromatic and boiling points indicate a large proportion of benzene.

It is evident that during the thermal decomposition of cellulose, C_6 ring structures are formed rapidly above 200°. While there is wide disagreement as to the temperatures reached in the coalification process,[7] 200–300° appears possible, especially in view of the fact that strong exothermic reactions, such as cellulose exhibits at 150–200°, may have taken place. Hence it follows that the establishment of the presence of aromatic structures in bituminous coals does not necessarily exclude cellulose as a progenitor of such coals.

Experimental

Thermal Decomposition of the Cellulose.—One hundred-gram samples of cellulose linters[8] were packed into a one-liter bomb and flushed with nitrogen. The bomb was electrically heated at a rate of 2° per minute. Temperatures were measured by two thermocouples, one in the center of the bomb and the other between the furnace and the outer wall of the bomb; a temperature gradient of approximately 50° was found, and the temperatures reported correspond to the minimum values observed.

Oxidation and Determination of Carbon Balances.—The dried residue from pyrolysis of 100 g. of cellulose, after vacuum drying at 100°, was suspended in about 2500 cc. of potassium hydroxide solution (140 g. per liter of water) in an iron vessel provided with agitator, cover and reflux condenser. Potassium permanganate was added in small portions over several hours until an excess was present. The vessel was then closed and kept at the boiling point for the period required for discharge of the permanganate, usually several days. The manganese dioxide formed in the reaction was filtered off by suction and thoroughly washed. The combined filtrate and washings, golden yellow in color, were concentrated to less than 2000 cc., cooled, transferred to a 2000-cc. volumetric flask, made up to volume, thoroughly mixed and aliquots withdrawn for determination of the distribution of the carbon. Total carbon was determined in a 5-cc. aliquot by wet oxidation with a chromic–sulfuric acid mixture; carbonic acid in a 10-cc. aliquot by evolution with dilute hydrochloric acid. To determine volatile acids a large aliquot, 100 cc., was diluted to 500 cc., acidified with dilute sulfuric acid and distilled to a small volume. The distillate was titrated with 0.1 *N* alkali using phenolphthalein. To determine oxalic acid a 25-cc. aliquot was made acid with dilute hydrochloric acid, alkaline with potassium hydroxide and finally acid with acetic acid. Calcium acetate was added in excess and the precipitated calcium oxalate, after digestion, was filtered off, washed thoroughly, dissolved in dilute sulfuric acid and the oxalic acid titrated with 0.1 *N* permanganate. Contamination of the calcium oxalate precipitate with the calcium salts of benzene carboxylic acids could have little effect on the oxalate determinations since work on known

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(6) *Cf.* Juettner, Smith and Howard, THIS JOURNAL, **57**, 2324 (1935).

(7) *Cf.* Lewis, *J. Inst. Fuel*, **9**, 235 (1936).

(8) Obtained through the courtesy of Dr. Charles Carpenter Carnegie Institute of Technology.

mixtures of oxalic and benzene carboxylic acids had shown that the former can be titrated quantitatively in the presence of the latter.

Decarboxylation.—Previous work with the oxidation products of coal had indicated the difficulty of recovering in good yields the individual pure aromatic acids present, so recourse was had to decarboxylation as a method of establishing aromatic character.[6] In some cases the solutions remaining, after the aliquots had been removed for analytical work, were concentrated until salts began to separate and placed in the middle compartment of a three-compartment cell, subjected to electrolysis, and the free acids recovered by vacuum evaporation of the anode liquors on the water-bath. The required amount of alkali was added and the decarboxylation carried out as previously described.[9] In other cases the alkali salts were evaporated to a small volume and decarboxylated directly.

Summary

The presence of C_6 ring structures in products obtained by pyrolyzing cellulose at temperatures up to 400° has been established by oxidation followed by decarboxylation and recovery of benzene and diphenyl. The yield of aromatic hydrocarbons, based on the pyrolyzed cellulose, is of the same order as that obtained by similar attack on a Pittsburgh seam bituminous coal. It has been pointed out that the presence of C_6 ring structure in bituminous coal does not exclude the possibility of such coals having been derived from cellulose.

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[9] Ref. 6, page 2326.

[CONTRIBUTION NO. 47 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Oxidation of a Pittsburgh Seam Bituminous Coal and Low Temperature Coke by Alkaline Permanganate

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The present generally accepted picture of the structure of bituminous coal as a system containing condensed rings is based largely on evidence from oxidation experiments.[1] Certain bituminous coals have been reported to yield as much as 46% of their carbon as benzene carboxylic acids on oxidation with alkaline permanganate.[2] Obviously such high yields of one type of compound are of great theoretical interest, and are of possible technical importance.

A study has been made of the nature of the products obtained by exhaustive alkaline permanganate oxidation of a Pittsburgh seam coal[3] and a 500° coke prepared from this coal. It has been found that 90–95% of the carbon of these materials can be recovered after oxidation as a solution of water soluble, non-colloidal acidic products, which vary in color from pale yellow to deep reddish-brown, depending upon the amount of permanganate employed and the oxidation period. Typical data showing the distribution of the carbon[4] among the chief oxidation products are given in Table I. The assumption that the carbon not found as carbonic, oxalic and acetic acids is in aromatic acids, is based upon the fact that the only condensable hydrocarbons recovered by decarboxylation were aromatic and consisted chiefly of benzene and diphenyl. On this basis it is evident that a significant fraction of the carbon in the Pittsburgh coal is in cyclic structures and that coking increases the proportion of cyclic carbon present. However, we have found no evidence that would justify a statement that any considerable fraction of the acids produced by the action of alkaline permanganate on this coal consists of benzene carboxylic acids.

TABLE I

CARBON DISTRIBUTION IN POTASSIUM SALTS

Material		Edenborn coal	500° Edenborn coke
Carbon as	Carbonic acid, %	45.0	40.7
	Acetic acid, %	2.2	1.6
	Oxalic acid, %	15.0	11.6
	Arom. acids (diff.), %	30.8	37.1
Total C recov. as K salts, %		93.0	91.0

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[1] For a review of the work of F. Fischer and co-workers, see Horn, *Brennstoff-Chem.*, **10**, 362 (1929); Bone and co-workers, *Proc. Roy. Soc.* (London), **A110**, 537–542 (1926); **A127**, 480–510 (1930); **A148**, 492–522 (1935). Recent hydrogenation work by Biggs, THIS JOURNAL, **58**, 1020 (1936), constitutes even more convincing evidence.

[2] Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935).

[3] Described in detail in Bur. Mines Tech. Paper 525, 1932.

[4] The general procedure described in ref. 2 has been used. These authors do not reveal the method employed to determine the carbon reported as oxalic and benzene carboxylic acids in their carbon balances.