[CONTRIBUTION NO. 58 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Nature of Carbonaceous Materials as Revealed by the Yield of Mellitic Acid Obtained on Oxidation

BY BERNARD JUETTNER

In a previous paper[1] it was shown that, compared with other oxidation methods, the action of nitric acid followed by alkaline permanganate gave the highest yields of mellitic acid from a Pittsburgh seam coal, from cokes prepared from this coal, and from natural and artificial graphites. In the present paper the same method has been applied to coals of varying rank, to their 1000° cokes, to several carbonaceous materials of other origin than coal, and to two known compounds.

The following coals, listed in order of increasing carbon and decreasing oxygen content, on a moisture and ash-free basis, were studied.

Seam	Mine	County and state
Illinois no. 6	Orient no. 1	Franklin, Ill.[2a]
Pittsburgh	Edenborn	Fayette, Pa.[2b]
High Splint	Clo-Splint	Harlan, Kentucky[2c]
Pocahontas no. 3	Pinnacle	McDowell, W. Va.[2d]
Anthracite	Loomis	Luzerne, Pa.

Cokes were prepared by heating these coals to 1000° in a stream of nitrogen for one hour. The cellulose char was prepared in the same manner. The domestic coke,[3] the metallurgical coke,[4] the activated carbon,[5] the carbon black,[6] and the pitches from low[7] and high temperature tars[4] were commercial products. The carbonized pitch was prepared by heating the pitch from a low temperature tar to 700° for one hour. All the coals and the carbonization products were ground to −200 mesh. The pitches were crushed to −20 mesh. It was found useless to prepare a finer size since the particles caked together at the temperature of the boiling nitric acid.

The amounts of permanganate required to maintain an excess varied greatly with the different materials and ranged from 0.5 to 1.0 g. per gram for the 1000° cokes, the commercial cokes, the charcoals, and carbon black, to 8.0 g. for the petroleum coke. The coals required 2–4 g. per g., the pitch from low temperature tar 4.2 g. per g., and that from high temperature tar 8.5 g. per g.; 7.6 g. per g. was required to oxidize the triphenylene.

It is evident from the table that, in general, the higher rank coals, *i. e.*, those of a higher stage of coalification, give on oxidation greater yields of mellitic acid, indicating a more complete condensation to carbocyclic structures. It has been shown[1] (p. 211) that if a given coal is carbonized at increasing temperatures, there is a rapid rise in the yield of mellitic acid obtained by oxidation of the cokes, up to about 700°, and relatively little change at temperatures above this, indicating a rapid formation of condensed aromatic structures in the temperature range below 700°. The yield of mellitic acid obtained from a high rank coal, *e. g.*, anthracite, indicates a degree of condensation of the same order as a coke prepared by heating a bituminous coal to at least 700°. Judged by this criterion the anthracites have been formed at elevated temperatures. The relatively small increase in yield of mellitic acid obtained by oxidation of anthracite which had been heated to 1000°, as compared with the unheated coal, also indicates that a very complete degree of condensation to carbocyclic structures has been reached in the anthracite.

The Illinois, Pittsburgh and High Splint coals, although differing in ultimate composition, microscopic structure and resistance to thermal and chemical change, nevertheless yield, on the basis of carbon present, approximately the same amount of mellitic acid. It is possible that thermal conditions during the formation of these three coals did not differ greatly. The low yields of mellitic acid from the lower rank bituminous coals may be due not only to the presence of aliphatic and heterocyclic structures, but also to hydroaromatic rings. The latter would readily be converted to aromatics by the action of heat.

The yields of mellitic acid obtained from all carbonaceous materials which have been heated to 1000° are of the same order as from the graphites, thus affording further evidence of the essen-

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(1) Juettner, THIS JOURNAL, 59, 208 (1937).

(2) (a) *Bur. Mines Tech. Paper* 524; (b) *ibid.*, 525; (c) *ibid.*, 308; (d) *ibid.*, 405.

(3) Fairmont coke, purchased in Pittsburgh, Pa.

(4) Through the courtesy of the Carnegie-Illinois Steel Corporation from the Clairton plant.

(5) A commercial decolorizing carbon from a local supply house.

(6) Cabot spheronized carbon black, obtained through the courtesy of F. W. Amon.

(7) Through the courtesy of the Pittsburgh Coal Company from their low temperature carbonization plant.

DATA ON OXIDATIONS

Material[a]	Carbon per 100 g., g.	Residue after nitric acid oxidation, g.	Total acids after permanganate oxidation, g.	Mellitic acid recovered, g.	Mellitic acid formed per 100 g. carbon,[b] g.
	Coals and graphite				
Illinois no. 6	69.50	68.0	19.3	4.3	11.9
Pittsburgh	78.27	70.1	28.1	5.5	12.1
High Splint	78.70	53.2	14.4	5.0	11.4
Pocahontas no. 3	85.10	92.4	25.8	10.9	17.5
Anthracite	82.87	77.2	32.6	17.7	26.2
Natural graphite	97.40	78.5	26.9	21.7[c]	28.2
	1000° Cokes				
Illinois no. 6	83.78	52.3	26.2	19.4	27.9
Pittsburgh	88.74	50.9	29.4	22.5	30.5
High Splint	89.96	48.1	28.3	20.8	27.6
Pocahontas no. 3	88.68	49.5	30.5	22.1	29.4
Anthracite	87.73	48.6	26.1	19.8	27.1
	Other cokes and chars				
Pittsburgh—500°	80.17	95.5	29.7	11.9	19.8
Pittsburgh—700°	79.80	79.4	39.7	24.1	35.2
Domestic	84.23	46.6	27.5	19.8	28.2
Metallurgical	80.28	48.3	27.2	17.9	27.3
Cellulose char—1000°	91.59	39.5	30.0	24.8	31.5
Active carbon	83.10	39.0	33.1	19.7	28.5
Carbon black	93.91	56.5	42.9	32.2	38.6
Petroleum coke	92.31	139.6	49.9	20.7	26.8
Coke from low temperature pitch—700°[d]	88.05	99.2	47.3	22.9	30.5
	Pitches and known compounds				
Pitch from low temperature tar[e]	83.52	84.5	22.0	4.1	9.7
Pitch from high temperature tar[f]	91.52	135.5	23.0	7.9	13.0
Triphenylene	94.70	169.6	77.8	67.2	75.2
Hexaethylbenzene	87.72	11.0	2.9	0.0	0.0

[a] 100 g. used in each case. [b] Corrected for the solubility of the ammonium mellitate. [c] 7.6 g. of unoxidized graphite remained. [d] Prepared by carbonizing the pitch from the low temperature tar at 700°. [e] The residue remaining at 400° from the distillation of tar from a low temperature carbonization process. [f] The residue remaining at 400° from the distillation of tar from a high temperature carbonization process.

tially graphitic character of all carbonaceous materials which have been heated to elevated temperatures.

In the oxidation of a molecule built up of condensed C_6-rings the yield of mellitic acid, if exclusively peripheral oxidation is assumed, will be a function of the molecular weight. The type of condensed ring structure which should furnish the maximum yield of mellitic acid is triphenylene (9,10-benzophenanthrene) in which 12 out of 18 carbon atoms should be recovered as mellitic acid. The addition of more rings can result only in a structure in which a smaller fraction of the carbon will be recovered as mellitic acid and a larger fraction as carbon dioxide. It is, of course, not certain that oxidation of large condensed structures would be exclusively peripheral, but such appears probable. This point of view is borne out by the relatively high yields of mellitic acid obtained from the carbon black and from the 700° coke, both of which, because of their mode of formation, probably consist of condensed units of relatively low molecular weight.

Active carbons have been reported to give high yields of mellitic acid on oxidation. The sample studied gave much lower yields than either the carbon black or the 700° coke from the Pittsburgh coal.

Cokes prepared at 700 to 1000° give relatively good yields and are cheap and convenient raw materials for the preparation of mellitic acid by this procedure.

The pitch from the low temperature carbonization process gives poor yields, probably because of the absence of purely aromatic structures of the proper size. Oxidation of the product obtained by carbonization of this pitch at 700° results in a three-fold increase in the yield of mellitic acid, due to conversion of hydroaromatic to aromatic structures as well as to further condensation. A significantly greater yield of mellitic acid was obtained by oxidation of the high temperature pitch. Both ultimate composition and mode of formation of this pitch indicate a condensed aromatic structure.

The actual recovery of mellitic acid from the triphenylene is 44.8% of theory, which becomes 47.5% if corrected for the solubility of ammonium mellitate. In the oxidation of hexaethylbenzene carbon dioxide was formed almost exclusively and no mellitic acid was recovered.[8]

In addition to mellitic acid, in many cases significant amounts of other acids were formed. The amounts can be found in each case by adding 4 g. to the mellitic acid recovered and subtracting the sum from the total acids in the third column of the table. These acids have not yet been characterized completely, but aliphatic acids such as oxalic are absent and it appears probable that they contain significant amounts of the simpler benzene carboxylic acids. It will be observed that relatively large amounts of these acids are formed in the oxidation of the coals, the low temperature pitch and the petroleum coke, and almost none from the natural graphite or any coke which has been formed at 1000°. An interesting difference between anthracite and graphite lies in the formation of significant amounts of acids other than mellitic by oxidation of the former.

Large variations are found in the weight of the residue remaining after the nitric acid oxidation. Triphenylene, the high temperature pitch and the petroleum coke yielded large residues following the nitric acid stage, indicating a similarity of structure.

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Summary

The yield of mellitic acid from coals increases with increasing rank. The yields of mellitic acid obtained from all carbonaceous materials which have been heated to 1000° are of the same order as from the graphite. A carbon black from natural gas gave the highest yield of any carbonaceous material. Triphenylene was oxidized to mellitic acid with a yield of 44.8%. Hexaethylbenzene yielded chiefly carbon dioxide and no mellitic acid was recovered. Commercial high temperature coke is a convenient starting material since it reacts at a controllable rate with fuming nitric acid and requires relatively small amounts of permanganate to complete the oxidation.

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(8) No perceptible oxidation took place when alkaline permanganate alone was employed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FISK UNIVERSITY]

Reactions in the Presence of Metallic Halides. II. The Behavior of Fluorides and the Reactivity of the Halogens[1]

BY N. O. CALLOWAY

Introduction

Many papers have appeared dealing with the various types[2] of organic reactions which occur in the presence of metallic halides. Yet, little attention has been paid to the fluorides with exception of the use of boron fluoride in alkylations.[3] As a part of a general study on the Friedel–Crafts and related syntheses a report is made here on the fluorides as compared with the other halides.

We have found that the organic fluorides behave normally, acyl and alkyl halides yielding with benzene and aluminum chloride the typical ketone and hydrocarbon, respectively, in accordance with the following general schemes.

$$C_6H_6 \xrightarrow[AlCl_3]{CH_3COF} C_6H_5COCH_3$$

$$C_6H_6 \xrightleftharpoons[AlCl_3]{n\text{-}C_4H_9F} C_6H_5C_4H_9$$

It was found that aluminum fluoride would not catalyze the reaction in either acylation or alkylation using either organic fluorides or chlorides.

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(1) For the first paper see Calloway and Green, THIS JOURNAL, 59, 809 (1937).

(2) Calloway, *Chem. Rev.*, 17, 327 (1935).

(3) McKenna and Sowa, THIS JOURNAL, 59, 470 (1937). See preceding papers also.