

167. Amorphous Carbon.

By THOMAS D. SMITH.

Carbons, prepared by carbonisation of organic compounds, have been examined by X-ray diffraction and gas adsorption. The presence of oxygen in the organic molecule profoundly affects the crystallographic character of the resultant chars. Surface areas of these chars vary appreciably: very large areas may be due to the presence of a highly porous three-dimensional cross-linked structure; small areas occur when the material decomposes in the fused state.

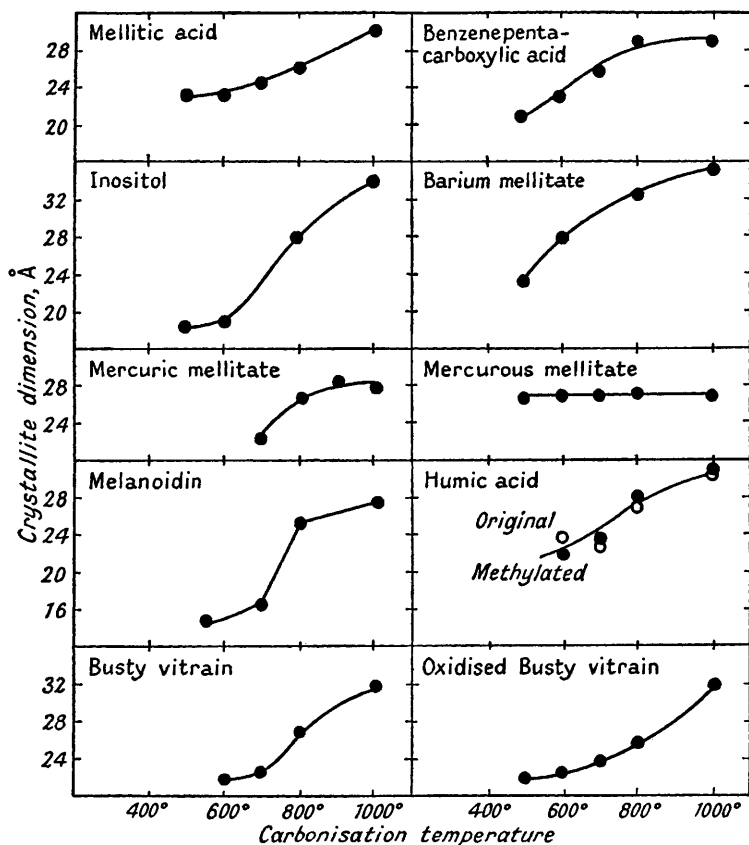
It has been suggested (Riley, *Quart. Reviews*, 1947, I, 59) that amorphous carbons are built up of two types of structure, *viz.*, (1) a turbostratic, lamellar, graphite-like structure, and (2) a disordered, three-dimensional cross-linked structure. The latter has been described as a three-dimensional repetition of *o*-tetraphenylene residues. The evidence for this view has been assembled from detailed X-ray examination of a large number of amorphous carbons prepared from a variety of organic substances (Blayden, Gibson, and Riley, "Ultra-Fine Structure of Coals and Cokes," B.C.U.R.A., London, 1947, 178; *J. Inst. Fuel*, 1945, War Time Bulletin, 117; Gibson, Holohan, and Riley, *J.*, 1946, 456). The method of examination consists in measuring the half-peak widths of the diffraction bands and calculating from these the dimensions of the average, hypothetical, cylindrical crystallites. It is thus possible to follow the growth of the crystallites with increasing temperature of carbonisation. The average height (*c* dimension) of the crystallites is calculated from the corrected half-peak width of the 002 diffraction halo by means of Jones's formula $\beta = 1.0\lambda/L_c \cos \theta$; the average diameter (*a* dimension) is calculated from the half-peak width of the 10 cross-lattice diffraction halo by Warren's formula $\beta = 1.84\lambda/L_a \cos \theta$.

These studies have been extended to a series of amorphous carbons prepared by carbonisation of organic compounds of high oxygen content. The surface areas have been determined by adsorption of nitrogen. The following materials were carbonised at 5° per minute in an atmosphere of nitrogen, up to various temperatures: mellitic acid,

barium mellitate, mercuric and mercurous mellitate, inositol, benzenepentacarboxylic acid, quinol humic acid, methylated humic acid, melanoidin, and oxidised Busty vitrain. Figs. 1 and 2 summarise the results of the crystallite-growth studies.

Although the individual characteristics, molecular sizes, and shapes of the original materials differed considerably, all the chars exhibited almost constant c dimensions; the a dimensions in general showed a growth from about 20 Å at 400° to about 32 Å at 1000°. The behaviour of the c dimensions is in striking contrast to that exhibited by chars obtained by carbonising materials of low oxygen content (*e.g.*, dibenzanthrone, pitch extract, bituminous coal), but is similar to the behaviour of the cellulose chars previously studied. It is significant that none of the chars contained less than 4% of oxygen (by difference).

FIG. 1. "a" Dimensions.



The pitches, peat, dibenzanthrone etc., yield chars having a turbostratic structure which is mobile in that growth can take place along the c axis. On the other hand, cellulose and the materials listed in Figs. 1 and 2 yield chars having, even at low temperatures, a rigid structure. The presence of oxygen apparently inhibits growth along the c axis. Constant c dimensions were obtained whether the oxygen-containing compounds decomposed in the solid state (as in the case of humic acid, mellitic acid, and mellitates), or in the fused state (inositol and benzenepentacarboxylic acid).

The mechanism by which oxygen causes rigidity in carbon crystallites is obscure but is possibly due to some form of cross-linking between the lamellar planes. Oxidation of a Busty vitrain for 100 days at 150° appeared to convert a turbostratic lattice into a system of rigid carbon crystallites (Fig. 2). The c dimensions of the chars from methylated

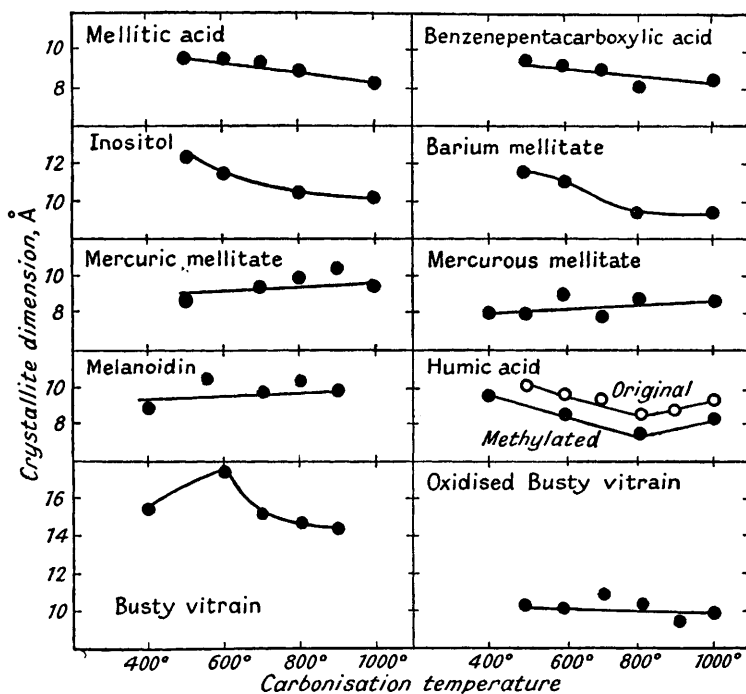
humic acid were consistently about 1 Å less than those from the original material. This difference, although small, may indicate that introduction of the methoxyl groups caused an increase in the disordering of the crystallites.

The surface structure of the carbons was examined by adsorption of nitrogen at the temperature of liquid nitrogen. Sigmoidal (type 2) isotherms were obtained in every case. The total surface areas of the carbons were calculated by the Brunauer-Emmett-Teller equation:

$$V = \frac{V_m C X [1 - (n + 1)X^n + nX^{n+1}]}{(1 - X)[1 + (C - 1)X - CX^{n+1}]}$$

where V_m is the volume of gas adsorbed at N.T.P. when the surface is covered by a monolayer, V the volume adsorbed at pressure p , X the relative pressure, n the number of

FIG. 2. "c" Dimensions.



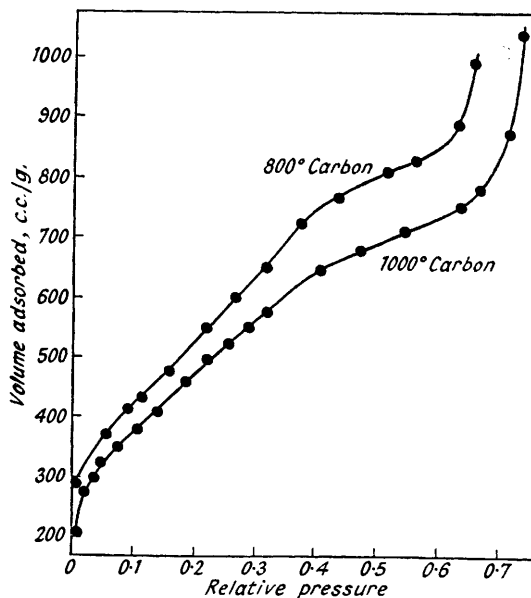
layers to which the gas is limited, and C is a constant dependent on the heat of adsorption.

The simple limiting form of the B.-E.-T. equation did not give linear graphs owing to the small value of n . Similarly, the Harkins-Jura equation did not apply (Smith and Bell, *Nature*, 1948, **162**, 109). Joyner, Weinberger, and Montgomery's method (*J. Amer. Chem. Soc.*, 1945, **67**, 2182) was used to derive the value of V_m ; 16.2 sq. Å was taken as the area of surface covered by one molecule of adsorbate.

The values of V_m , n , and specific surface area are given in the Table. The high surface area of the barium mellitate chars might have been expected, as it is well known that when carbonaceous materials are carbonised with inorganic salts an increase in the surface area is obtained. However, surfaces of this magnitude, particularly those occurring in hexachlorobenzene carbons, can hardly be accounted for by the prismatic and basal surfaces of minute graphite crystallites; they indicate intracrystalline penetration of the adsorbate. This lends additional weight to the cross-linked aromatic structure suggested by Gibson, Holohan, and Riley, which possesses a highly developed pore structure. The isotherms of the hexachlorobenzene carbons show a slight but distinct tendency to flatten out at about

0.5 relative pressure (Fig. 3). More definite plateaux, but of the same nature, were obtained by Zettlemoyer and Walker (*Ind. Eng. Chem.*, 1947, **39**, 69) in a study of active magnesia. Such isotherms probably indicate that two types of adsorbing surface are present, one existing as pores of fairly uniform diameter, the other as pores having a random size distribution.

FIG. 3. Adsorption isotherms on carbons from hexachlorobenzene.



Surface areas from the B.-E.-T. equation.

Sample	Carbonisation temp.	V_m , c.c./g.	n	Specific surface area, sq. m./g.
Mellitic acid	500°	153	1.4	670
	1000	147	1.3	640
Inositol	500	50	4.0	218
	600	86	3.6	375
	1000	15	9.0	65
Barium mellitate	600	153	2.7	665
	800	379	3.0	1650
	1000	312	2.7	1355
Mercuric mellitate	800	110	1.8	480
Mercurous mellitate	800	179	1.9	780
Benzenepentacarboxylic acid	1000	3.7	3.2	16
Hexachlorobenzene	800	488	5.5	2125
	1000	425	4.0	1850
Cellulose	1000	1.5	3.0	66.5
Melanoidin	800	1.9	2.3	8

The very low surface area of the benzenepentacarboxylic acid chars was probably due to the charring's having occurred in a fused state. A shiny, highly swollen coke was produced. The formation of a carbon under these conditions must tend to inhibit the production of an inner surface.

EXPERIMENTAL

Mellitic acid was prepared by Juettner's method (*J. Amer. Chem. Soc.*, 1937, **59**, 208). 200 G. of high-temperature coke, on oxidation with fuming nitric acid (3 l.) containing ammonium vanadate (0.5 g.), followed by alkaline permanganate, gave after electro dialysis (2—3 amp.; 66 hours) a white, crystalline ammonium salt, which did not contain any oxalic

acid. The free acid was obtained by electro dialysis (Found : C, 42.1; H, 1.8. Calc. for $C_{12}H_6O_{12}$: C, 42.1; H, 1.75%).

The acid (m. p. 283—286°, decomp.) was identified by esterifying it with diazomethane and recrystallising of the hexamethyl ester from methyl alcohol; m. p. 87.

Benzenepentacarboxylic acid (B.D.H.) was purified by recrystallisation from absolute ethyl alcohol.

Barium mellitate was prepared by addition of an aqueous solution of "AnalaR" barium chloride in slight excess to an aqueous solution of ammonium mellitate. The dense, white, flocculent precipitate was thoroughly washed with hot water and dried at 105°. Under the microscope it was seen to consist of minute, acicular crystals (Found : C, 17.6; Ba, 51.2; H_2O , 6.8. Calc. for $C_{12}O_{12}Ba_3 \cdot 3H_2O$: C, 18.0; Ba, 51.4; H_2O , 6.7%). This salt was carbonised in the standard way, and the chars were thoroughly extracted with boiling hydrochloric acid.

Mercurous mellitate was prepared by adding an excess of mercurous nitrate, dissolved in very dilute nitric acid, to a hot solution of mellitic acid. The white precipitate, which coagulated on stirring, was filtered off, washed thoroughly, and dried at 110° (Found : Hg, 73.1. Calc. for $C_{12}O_{12}Hg_6 \cdot 6H_2O$: Hg, 73.1%). On carbonisation it yielded a carbon in which mercury could not be detected; a considerable amount of mercury condensed on the cooler parts of the furnace tube, doubtless owing to decomposition of the oxides.

Mercuric mellitate was prepared by adding hot mercuric chloride solution to a hot solution of ammonium mellitate. A heavy white precipitate was produced which was filtered off, thoroughly washed, and dried at 140° (Found : Hg, 57.3. Calc. for $C_{12}O_{12}Hg_3 \cdot 6H_2O$: Hg, 57.5%). On carbonisation in nitrogen, as with the mercurous salt, it afforded globules of mercury in the cool regions of the furnace tube leaving chars containing no detectable quantity of mercury.

Quinol humic acid was prepared by alkaline persulphate by Eller and Koch's method (*Ber.*, 1920, **53**, 1469) (Found : C, 57.55; H, 3.1. Calc. for $C_6H_4O_3$: C, 58.05; H, 3.25%). It was methylated five times by suspending it in dioxan and treating it with an ethereal solution of diazomethane, the methoxyl content rising to 7.1%.

Melanoidin complex was prepared by heating an aqueous solution of dextrose (6 g.) with glycine (15 g.) for 2 hours. The solution became dark brown. On evaporation, a brittle, brown solid remained (4.6 g.).

Hexachlorobenzene carbon was produced by the method of Gibson, Holohan, and Riley (*J.*, 1946, 461), and heated in nitrogen to various temperatures in the usual way.

The isotherms were determined by adsorption of nitrogen at liquid-nitrogen temperature in an apparatus of similar design to that of Brunauer and Emmett (*J. Amer. Chem. Soc.*, 1934, **56**, 35; 1937, **59**, 1553) as modified by Harkins and Jura (*ibid.*, 1944, **66**, 1366). All samples of carbon were degassed at 200° for 4 hours under a very high vacuum.

The foregoing investigation was part of the fundamental research programme of the British Coke Research Association, and the author thanks Mr. H. E. Blayden, Dr. J. Gibson, and Dr. H. L. Riley for advice and encouragement.

NORTHERN COKE RESEARCH LABORATORIES,
KING'S COLLEGE, NEWCASTLE-ON-TYNE.

[PRESENT ADDRESS: PHOTO PRODUCTS DIVISION,
E. I. DU PONT DE NEMOURS & Co.,
PARLIN, NEW JERSEY, U.S.A.]

[Received, August 13th, 1951.]