

110. *Studies in Graphite Formation. Part II. The Chemical Nature of Graphite and Amorphous Carbon.*

By A. E. BALFOUR, H. L. RILEY, and R. MORRIS ROBINSON.

CARBON with an electrical conductivity almost equal to that of Ceylon graphite is obtained when hexaiodobenzene is decomposed at 770° (Ciusa, *Gazzetta*, 1928, **58**, 222), a temperature at which carbonaceous substances containing hydrogen yield carbon of relatively high specific resistance. Hofmann and Frenzel (*Ber.*, 1930, **63**, 1248) have shown that carbon deposited on iron from carbon monoxide gives an 83·3% yield of graphitic oxide when subjected to Brodie's reaction, whereas carbon from petroleum soot gives only a 20·2% yield. It is well known (cf., *inter alia*, Burgess and Wheeler, *J.*, 1910, **97**, 1917; Stock, Lux, and Rayner, *Z. anorg. Chem.*, 1931, **195**, 158) that the volatile matter evolved in the carbonisation of substances such as coal, at temperatures above 700°, is principally hydrogen. These facts, and others given below, indicate that in the formation of carbon, by the pyrolysis of carbonaceous material, the presence of hydrogen plays a very important part.

It has been assumed by many workers that amorphous carbon consists of very small crystals of graphite more or less contaminated with complex hydrocarbons. This assumption is only partly true, for it is shown here, on both theoretical and experimental grounds, that small quantities of hydrogen play a fundamental part in modifying the properties of the graphite crystal lattice.

Adam (*Trans. Faraday Soc.*, 1934, **30**, 57) pointed out that if we fix our attention on one of the carbon atoms in a hexagon plane of the graphite lattice, it becomes apparent that its three valency bonds lead to three aromatic hexagons, suggesting a similarity, "though this may be only superficial," between the structure of graphite and of triphenylmethyl. A comparison of the properties of graphite with those of the triarylmethyls leaves little doubt that this formal similarity is reflected in a very fundamental way in the chemical properties of these substances.

The presence of three aromatic radicals attached to the same carbon atom brings about a pronounced modification in the properties of the fourth valency (cf. *inter alia*, Ingold, *Ann. Reports*, 1928, **25**, 150); for instance, (a) hexaphenylethane dissociates into free radicals in non-ionising solvents and into both positive and negative triphenylmethyl ions in ionising solvents; (b) triphenylmethyl chloride gives, in liquid sulphur dioxide, a conducting solution which contains the ions Ph_3C^+ and Cl^- ; (c) triphenylmethyl forms compounds with the alkali metals which dissociate in liquid ammonia forming positive alkali-metal ions and negative triphenylmethyl ions; (d) triphenylmethane acts as a weak acid; (e) hexaphenylethane takes up oxygen from the atmosphere spontaneously to form a peroxide. Each of these fundamental properties can be paralleled closely from the chemistry of graphite. (a) The crystal structure and chemical properties of graphite

(*vide infra*) indicate that each hexagon plane can act as a macro-free radical. It is of interest that polynuclear aromatic systems act more powerfully than phenyl in promoting the dissociation of hexa-arylethanes (cf., *inter alia*, Ingold, *loc. cit.*). (b) Frenzel and Hofmann (*Z. Elektrochem.*, 1934, **40**, 511) prepared graphite bisulphate in which the carbon hexagon planes remained intact, the hydrogen sulphate ions having penetrated between them, increasing their distance apart. Ruff and Bretschneider's graphite monofluoride (*Z. anorg. Chem.*, 1934, **217**, 1) is a similar type of compound, though much more stable. In these compounds, the hexagon planes are playing the part of macro-positive radicals. (c) Fredenhagen and Cadenbach (*Z. anorg. Chem.*, 1927, **158**, 249) and Fredenhagen and Suck (*ibid.*, 1929, **178**, 353) have prepared the compounds C_8K and $C_{16}K$, and Schleede and Wellmann (*Z. physikal. Chem.*, 1932, *B*, **18**, 1) have shown that in these compounds the alkali-metal atoms had penetrated and formed layers between the hexagon carbon planes. These compounds are obviously analogous to the alkali-metal triphenylmethides, and the hexagon planes are acting as macro-negative radicals. (d) Lengyel (*ibid.*, 1931, **154**, 371) has shown that the potential of a graphite electrode is determined by the p_H of the solution and is not influenced by the pressure of gaseous hydrogen surrounding the electrode. Bangham and Stafford (*J.*, 1925, **127**, 1085) found that graphite will adsorb hydrogen ions, but not molecular hydrogen, from the gas phase. These phenomena indicate that graphite possesses a definite affinity for hydrogen ions. (e) The nature of graphitic oxide has recently been studied in detail by Hofmann and Frenzel and their collaborators (*Ber.*, 1930, **63**, 1248; *Z. Elektrochem.*, 1931, **37**, 613; *Kolloid Z.*, 1932, **58**, 7; *Annalen*, 1934, **510**, 1) and by Thiele (*Z. Elektrochem.*, 1934, **40**, 26). Hofmann and his co-workers deduce from their X-ray studies that the oxygen atoms in graphitic oxide, of empirical formula C_3O , are attached to the carbon atoms in the planes by an ethylene-oxide type of linkage. In view of the aromatic character of the hexagon planes, it is more probable that the oxygen is peroxidic in character. Such a view is not contrary to the experimental results of the above workers and is in accord with the explosive property of graphitic oxide and with the fact that, when shaken with water (or certain organic liquids), it is completely dispersed into micelles possessing only single hexagon layers (Kohlschütter and Haenni, *Z. anorg. Chem.*, 1919, **105**, 121). The swelling of graphitic oxide in water and its final dispersion is, on the above view, a dissociation of the graphitic peroxide into macro-free radicals or ions brought about by the fission of the weakened $-O-O-$ bond. The 8% of water remaining in the oxide even after prolonged drying, which has been shown by Hofmann and his co-workers to be present as H_2O molecules, is probably there as solvated water. This view of the peroxidic character of graphitic oxide brings its properties into line with the general properties of aromatic peroxides (Goldschmidt and Steigerwald, *Annalen*, 1924, **438**, 202) and of the ketyls, and it also indicates that graphitic oxide is the analogue of Gomberg's hexaphenylethane peroxide. That graphite does not take up oxygen in a manner similar to hexaphenylethane is possibly connected with the size of the graphite crystallites, which probably determines the magnitude of the energy barrier to the penetration of oxygen molecules between the hexagon planes. Acheson graphite does not sorb molecular oxygen, but active carbons have been prepared which, after sorbing oxygen, exploded on heating (Ruff and Bretschneider, *loc. cit.*), a behaviour reminiscent of graphitic oxide (see also Meyer, *Z. physikal. Chem.*, 1932, *B*, **17**, 385; Berl, Andress, Rheinhardt, and Herbert, *ibid.*, 1932, *A*, **158**, 273).

The above considerations leave no doubt as to the pronounced aromatic character of the carbon hexagon planes in pure graphite. Their striking stability is a consequence of the large number of resonance forms in which the planes can exist. The amphoteric character of the planes suggests the possibility of the existence of inter-planar resonance forms. At the inter-planar distance of 3.4 Å., ordinary valency forces would be very weak. The general stability of graphite crystals [cf. coronene (hexabenzobenzene, Scholl and Meyer, *Ber.*, 1932, **65**, 902), which sublimes in vacuum at 500°] suggests that more than van der Waals forces are involved in the bonding of the planes together (cf. Lennard-Jones, *Trans. Faraday Soc.*, 1934, **30**, 58; Hückel, *ibid.*). There can, however, be little doubt that inter-planar resonance is concerned in the bonding of foreign atoms and radicals between the planes, because of the curious, step-wise manner in which the potassium

graphite compound, C_8K , and graphite bisulphate decompose. Schleede and Wellmann (*loc. cit.*) showed that when C_8K was decomposed by heating, alternate layers of potassium atoms were expelled to form $C_{16}K$. Graphite bisulphate decomposes on hydrolysis in a somewhat similar step-wise manner (Frenzel and Hofmann, *Z. Elektrochem.*, 1934, 40, 511).

The relatively high stability of graphite monofluoride and the great tautomeric activity of hydrogen suggest that the graphite crystal lattice will be capable of bonding atoms of hydrogen between the hexagon planes in a very stable manner, and, further, that the presence of relatively small amounts of hydrogen ($< 1\%$, cf. the compounds C_8K and $C_{16}K$) will have a very pronounced effect upon the properties of the carbon.

Those types of carbon usually referred to as "amorphous" all contain appreciable quantities of hydrogen. The above theory of the inter-planar bonding of this hydrogen offers a simple explanation as to why these carbons differ so pronouncedly in chemical and physical properties from pure graphitic carbon. The high stability of the hexagon planes in pure graphite is due to their aromatic character. The inter-planar bonding of hydrogen must reduce the stability of the hexagon planes, because the fourth valencies of some of the carbon atoms are brought into play, and this will reduce the number of resonance forms in which the planes can exist. There will, of course, be a corresponding increase in the number of inter-planar resonance forms; *i.e.*, the presence of tautomeric hydrogen between the planes reduces their aromatic character, with consequences illustrated by the following examples.

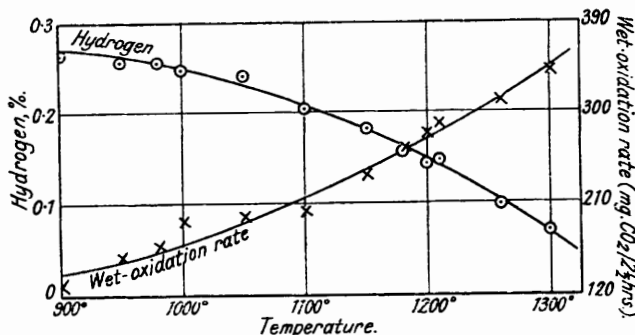
Pure graphite gives excellent yields of graphitic oxide when subjected to Brodie's reaction, whereas most of the so-called amorphous carbons give very poor yields or none at all. This difference in behaviour is no doubt due to the more stable aromatic hexagon planes in graphite withstanding the action of the oxidising solution more successfully than the less stable, more aliphatic planes in "amorphous" carbon. The latter is much more reactive to gaseous oxygen below 1000° than is graphite; there is considerable evidence to indicate that the reverse state of affairs exists at higher temperatures. The above theory readily accounts for this: the less stable nature of the hexagon planes in "amorphous" carbon permits of their edge-wise combustion, whereas with graphite rapid combustion will only occur when the oxygen can penetrate freely between the planes, *i.e.*, at high temperatures (cf. Meyer, *loc. cit.*). Ruff and Bretschneider (*loc. cit.*) have shown that carbon burns in fluorine in two ways, *viz.*, (a) by a smooth reaction yielding volatile carbon fluorides, and (b) explosively, through the intermediate formation of the solid compound, graphite monofluoride, in which the fluorine atoms are bonded between the hexagon planes.

The above considerations indicate that the hexagon planes of graphite can act as macro-free radicals, and it is therefore probable that the paramagnetic nature of oxygen is an important factor in the combustion of graphite. It is significant, in this connexion, that chlorine dioxide, which contains an odd number of electrons, is the reagent most generally employed in the preparation of graphitic oxide.

In order to obtain still further confirmation of the above views as to the importance of small amounts of hydrogen in determining the properties of carbon, a large bulk sample of sugar charcoal was prepared at approximately 900° , and small samples of this were heated in vacuum for 3 hours at a series of temperatures above 900° . The hydrogen content, the susceptibility to oxidation by the chromic-phosphoric solution (Blayden and Riley, *J. Soc. Chem. Ind.*, 1935, 54, 159T; Balfour and Riley, *J.*, 1935, 1723), and the specific resistance of the resulting carbons were determined. Hydrogen content and wet-oxidation rate are plotted against temperature in Fig. 1. The complementary nature of these two curves is obvious. The slope of the wet-oxidation curve indicated that a specimen of carbon, free from hydrogen, would react very rapidly, possibly explosively, with the solution of chromic acid in phosphoric acid. This proved to be the case when a sample of kish (carbon which had crystallised from molten pig iron) was subjected to this test. During the first 20 minutes of the test, carbon dioxide was evolved from a graded 1-g. sample at the rate of 3,000 mg. per $2\frac{1}{2}$ hrs., then the remaining carbon suddenly swelled up rapidly, completely filling the reaction vessel (approximately 150 c.c.), probably owing to the formation of graphitic oxide or some similar compound. This result is interesting in view of Thiele's

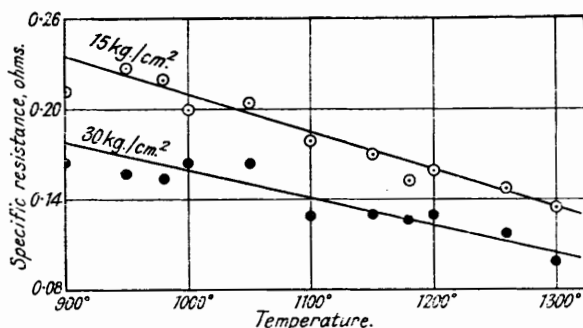
statement (*loc. cit.*) that graphite does not swell when anodically polarised in syrupy phosphoric acid, whereas swelling occurs in concentrated sulphuric and nitric acids.

FIG. 1.



These curves, and those of the specific electrical resistance of the samples of carbon under two external pressures (Fig. 2), show that decrease in hydrogen content is accompanied by an increase in the wet-oxidation rate and the electrical conductivity, *i.e.*, an increase in the graphite content of the samples.

FIG. 2.



Experiments in which the carbon samples were heated in a vacuum for different periods indicated that after 3 hours either the hydrogen content had reached an equilibrium value or only a very slow elimination of hydrogen occurred after this period. The following results were obtained.

Temp.	Time of heating, hrs.	H, %.	Wet-oxidation rate (mg. CO ₂ /2½ hrs.).	Temp.	Time of heating, hrs.	H, %.	Wet-oxidation rate (mg. CO ₂ /2½ hrs.).
1000°	3	0.249	194	1200°	1.5	0.163	242
	6	0.232	198		3	0.133	279
			6		0.142	274	

A factor involved in determining the extent of graphitisation and the size of the graphite crystallites produced when an organic compound is carbonised, is the chemical nature of the compound employed. Another factor is obviously the speed of carbonisation. Before hydrogen can be stably bonded in the carbon lattice, the establishment of some arrangement approximating to the hexagon planes of graphite is necessary. This will occupy an appreciable time, for it involves the interaction of a large number of carbon atoms. The escape of hydrogen from the solid phase probably depends upon the formation of molecular hydrogen or simple hydrocarbons, involving the interaction of only a small number of atoms. Rapid carbonisation, therefore, will increase the probability of the escape of hydrogen, as less time will be available for the formation of the hexagon layer structure. Consequently, rapid carbonisation should yield a more highly graphitised

carbon. To test this view, two cokes A and B were prepared by carbonising two samples of the same coal in a nitrogen-filled electric furnace, A being placed in a furnace already at 900° and kept there for an hour; and B being put into a cold furnace, heated at the rate of 3° a minute to 900°, and kept at this temperature for one hour. Examination of the resulting cokes gave the following results.

	H, %.	Wet-oxidation rate (mg. CO ₂ /2½ hrs.).
Coke A (rapid carbonisation)	0.58	180
Coke B (slow carbonisation)	0.89	106

The effect of rate of carbonisation upon the graphite content of the resulting cokes is further illustrated by Fig. 3, in which maximum carbonising temperature is plotted against wet-oxidation rate. The continuous curve shows the results obtained on rapidly coking a Northumberland coal at different temperatures, and the broken line those when the same

FIG. 3.

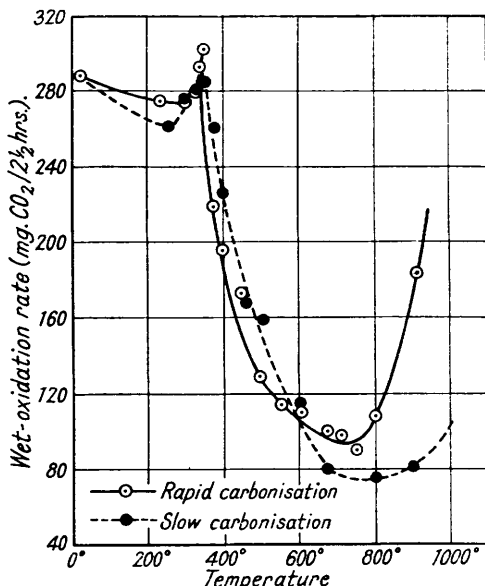
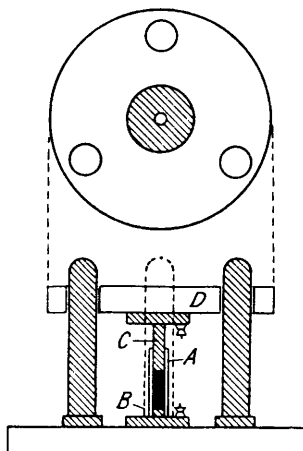


FIG. 4.



coal was carbonised slowly, *i.e.*, being heated at the rate of 5° a minute up to the various temperatures shown. The relative position of the two curves at temperatures above 650° indicates that rapid carbonisation produced the more highly graphitised coke. The curves in Fig. 3 are typical of a large number which have been obtained from the study of various coals. The form of these curves has been discussed in Part I (*loc. cit.*).

The above theoretical considerations and experimental results leave little doubt as to the fundamentally important part which hydrogen plays in the transformation of an organic compound into elementary carbon. Many of the substances usually termed "amorphous carbon" are compounds possessing a crystal lattice similar to that of graphite, with hydrogen firmly bonded between the hexagon planes. The curves shown in Fig. 3 and in Fig. 4 of Part I (*loc. cit.*) indicate that this carbon-hydrogen compound possesses considerable stability and commences to decompose only between 600° and 700°. The actual temperature is probably determined to some extent by the size of the crystallites present in the sample. The work of Berl, Address, Rheinhardt, and Herbert (*loc. cit.*), Hofmann and Wilm (*ibid.*, 1932, 18, 401), and Arndt and Pollack (*Z. anorg. Chem.*, 1931, 201, 81) appears to indicate that the presence of hydrogen has only a small effect upon the distance apart of the hexagon planes of the graphite lattice, for many of the samples of carbon examined by those workers undoubtedly contained appreciable quantities of hydrogen (cf. Hofmann and Groll, *Ber.*, 1932, B, 65, 1257). It is possible that the inter-

planar bonding of hydrogen gives rise to the "mesomorphic state" suggested by Berl and co-workers (*loc. cit.*). Crystallite growth and the presence of hydrogen are probably intimately connected at temperatures below 1300° (see Wesselowski and Pertzow, *Z. anorg. Chem.*, 1934, 216, 228, and Arndt and Pollack, *loc. cit.*, for studies of graphitisation at higher temperatures), and the disregard of the fundamental importance of the presence of small traces of hydrogen renders the interpretation of X-ray data, with reference to the size of the crystallites, uncertain.

Further evidence in support of the existence of a stable carbon-hydrogen compound is provided by the fact that anthracite and not graphite is apparently the end point in the process of coal formation. Apart from the relatively rare occurrence of igneous intrusions, it is generally agreed that coal deposits have not been subjected to temperatures much above the normal, *i.e.*, in the course of geological time the coal has not been subjected to a temperature sufficiently high to bring about the decomposition of the stable carbon-hydrogen compound (cf. Weinschenk, *Abh. Bayr. Akad.*, 1900, 21, 233, quoted by Kohlschütter, *Z. anorg. Chem.*, 1919, 105, 35).

EXPERIMENTAL.

A large stock sample of sugar charcoal was prepared by carbonising successive quantities of sucrose in an electrically heated muffle furnace for about 6 hours at approximately 900°. The product was crushed and sieved on a 20 I.M.M. sieve, the more finely divided product being returned to the muffle with the next charge. The whole sample was thoroughly mixed. About 10 g. of this stock sample were placed in a silica test-tube and heated for 3 hours in vacuum (0.01 mm.) in an electrically heated tube furnace. The carbon was allowed to cool in a dry atmosphere, and its hydrogen content determined by the combustion of a 2-g. sample, blank combustions being performed at frequent intervals in order that the results could be corrected accurately. The percentages of hydrogen were calculated on an ash-free basis, the sugar charcoal containing approximately 4% of ash. All the experiments were carried out in duplicate, and results were obtained over the range 900—1300°. The wet-oxidation rate of each sample was determined as described by Blayden and Riley (*loc. cit.*).

The specific resistances of the various specimens of carbon were determined by means of the apparatus shown in Fig. 4. A few grams of the sample, graded between 60 and 100 I.M.M. sieves, were dried in vacuum at 300° immediately before the determination. A thin layer of the carbon was placed in the thick-walled glass tube, *A*, resting on the cylindrical brass electrode, *B*, which fitted closely inside the glass tube. Another cylindrical brass electrode, *C*, of the same diameter, was placed in position, and a suitable weight placed on the platform *D*. The latter was tapped gently until the resistance of the column of carbon, as measured by a Wheatstone's bridge, became constant. The distance between the contact ends of the two electrodes was measured by means of a cathetometer. The height of the column of sugar charcoal was increased by the addition of a further quantity of the sample, and the resistance was measured in a similar manner. This procedure was repeated until the length of the column was approximately 2 cm. The length and the resistance of the first column of sugar charcoal were subtracted from subsequent readings, to eliminate end effects, and the mean specific resistance was calculated. Further measurements were made with a higher pressure. The original bulk sample of sugar charcoal had a hydrogen content of 0.273%, a wet-oxidation rate of 146 mg. CO₂/2½ hrs., and a specific resistance of 0.24 ohm at 15 kg./cm.² and 0.20 ohm at 30 kg./cm.².

The rapid and slow carbonisations were carried out in the electrical furnace described in Part I (Balfour and Riley, *loc. cit.*). The Northumberland coal employed in these experiments had the following composition: ash, 3.9; moisture, 5.4; volatile matter (less moisture), 36.0; C, 82.9; H, 5.4; N, 1.7; S, 2.1; O, 7.9%.

One of us (R. M. R.) is indebted to the Research Council of the British Iron and Steel Federation for a maintenance grant. Our thanks are also due to the Research Committee of Armstrong College for a grant, and to the Northern Coke Research Committee, in whose laboratory this work was carried out, for permission to publish it.