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The Structure and Mechanism of Formation of Pyrolytic Carbon from Cyanogen

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The structures of carbon deposits formed by pyrolysis of cyanogen on a carbon filament have been investigated by electron diffraction and the influence of cyanogen pressure and filament temperature has been determined. All the deposits show the existence of graphite layer planes and both the crystal size and the degree of preferred orientation parallel to the axis of the substrate increase with temperature of deposition. Possible mechanisms are discussed for the formation of carbon from cyanogen, methods of growth of deposits both along and normal to the graphite *c* axis being proposed.

Carbons produced by the decomposition of organic vapours on heated substrates, particularly carbon filaments, have been extensively studied (Grisdale, Pfister & van Roosbroeck, 1951; Tesner & Echeistova, 1952; Brown, Hall & Watt, 1953; Brown & Watt, 1958; Cullis, Manton, Thomas & Wilman, 1959; Blackman, Saunders & Ubbelohde, 1961). One factor which is of primary importance in determining the structure of the deposited carbon is the physical condition obtaining at the point of deposition, the carbons produced on a solid surface differing fundamentally from those formed in the gas phase. In the first case, the carbon is laid down in small crystallites which have a high degree of orientation and is easily graphitized at 2500 °C or above. Gas phase carbon is, however, a carbon black in which the individual particles are spherical, and does not graphitize well even at 3000 °C.

The physical properties of pyrolytic carbons depend too to a considerable extent on the temperature of deposition. A striking change has been found to occur as this temperature passes through a critical region around 1900 °C (Blackman, Saunders & Ubbelohde, 1961). Carbons prepared from methane below this temperature have low bulk densities, show only a comparatively small degree of preferred orientation and contain appreciable amounts of residual hydrogen. Deposition at higher temperatures results in carbons with bulk densities and other properties which tend towards those of perfect graphite. It seems probable that, at about 1900 °C, the rates of thermal annealing processes become of the same order as the rates of deposition of carbon, thus causing defect structures to be removed as rapidly as fresh deposits are laid down.

The influence of the starting material from which carbons are formed is, however, much less clear. Comparison of the carbonaceous deposits produced by pyrolysis of some hydrocarbons and chlorohydrocarbons shows that the more highly chlorinated compounds give rise to carbons in which the crystallites are smaller and the preferred orientation is less marked than in those derived from compounds containing little or no chlorine (Cullis, Manton, Thomas

& Wilman, 1959). In contrast, other work on the pyrolysis of a wide variety of hydrocarbons suggests that at temperatures above 900 °C the nature of the gaseous compounds from which carbons are formed has little effect on the resulting deposits (Conroy, Slysh, Murphy & Kinney, 1959).

In the majority of studies of the formation of pyrolytic carbon, hydrocarbons or their simple derivatives have been used as starting materials. It was considered of interest therefore to investigate the production of carbon from a compound containing no hydrogen. The thermal decomposition of cyanogen is reported in the older literature (*e.g.* Meyer & Goldschmidt, 1882; Berthelot, 1905) but there appears to be little previous work on the breakdown of this compound on a heated substrate. It was thus decided to study its pyrolysis on a carbon filament heated to temperatures in the range 1500 to 2100 °C and to compare the structure of the deposits obtained with those derived from more conventional starting materials.

Experimental

Apparatus

Since no appreciable pyrolysis of cyanogen was found to occur on vitreous surfaces up to the limiting temperatures at which these could be used, the compound was decomposed on a heated carbon filament. The reaction vessel used (Fig. 1) was a 1-litre pyrex glass globe containing an extruded cellulose carbon filament, 5·6 cm in length and 0·025 cm in diameter. The filament was connected *via* carbon blocks and tungsten leads to the 240-V A.C. mains. The pressure of cyanogen introduced was measured on a mercury manometer and the temperature of the filament was determined by means of an optical pyrometer.

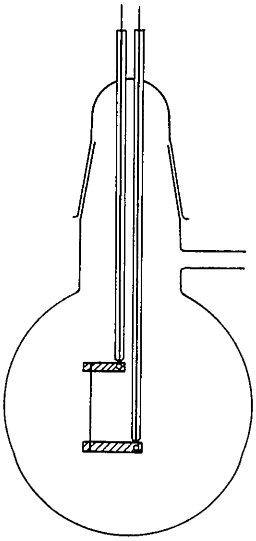

Fig. 1. The reaction vessel.

Materials

The most satisfactory method for the preparation of cyanogen gas was found to be the controlled thermal decomposition of silver cyanide. This compound was first heated to 200 °C *in vacuo* for one hour to remove moisture. A bath of molten potassium nitrate at 350 °C was then placed around the tube containing the silver cyanide and its temperature was gradually raised. Cyanogen began to be evolved at *ca.* 380 °C and was condensed in a second tube immersed in liquid oxygen. The product, which at −186 °C was a white solid, was carefully distilled, large head and tail portions being rejected, and was then transferred to a storage globe. The cyanogen thus obtained was analysed by gas-liquid chromatography (on a column containing MS 550 silicone oil as the stationary phase) and was found to be extremely pure.

Procedure

Cyanogen was admitted to the reaction vessel at different initial pressures (100–600 mmHg) and with different filament temperatures (1500–2120 °C). During the course of a run, the deposited carbon caused the voltage across the filament to decrease and thus resulted in a gradual drop in the filament temperature; the voltage was therefore continuously adjusted in order to keep the filament temperature constant. At the end of a run, when the filament had cooled down, the residual cyanogen was pumped off, the filament was removed and the resulting carbon deposits were examined in a Siemens Elmiskop Ia electron microscope. Electron diffraction patterns at grazing incidence were thus obtained, an electron accelerating voltage of 100 kV being employed. The instrument constant, λL, where λ is the wavelength of the electrons and L is the camera length, was 2·5 Å.cm.

Results and discussion

Fig. 2 shows a typical carbon deposit obtained at a filament temperature of 1900 °C; the graphite 'whiskers' (*cf.* Meyer, 1957, 1958) which were frequently formed on the surface are clearly visible. Electron diffraction patterns for the deposits obtained at temperatures ranging from 1500 to 2120 °C all show diffractions due to the even orders of the reflexion from the (001) planes. The order of size of the crystallites may be estimated from the half-breadth of these reflexions, although the degree of accuracy obtainable is not high. The existence of preferred orientation can be deduced from the variation of the intensity around the ring; no such preferred orientation exists in the substrate.

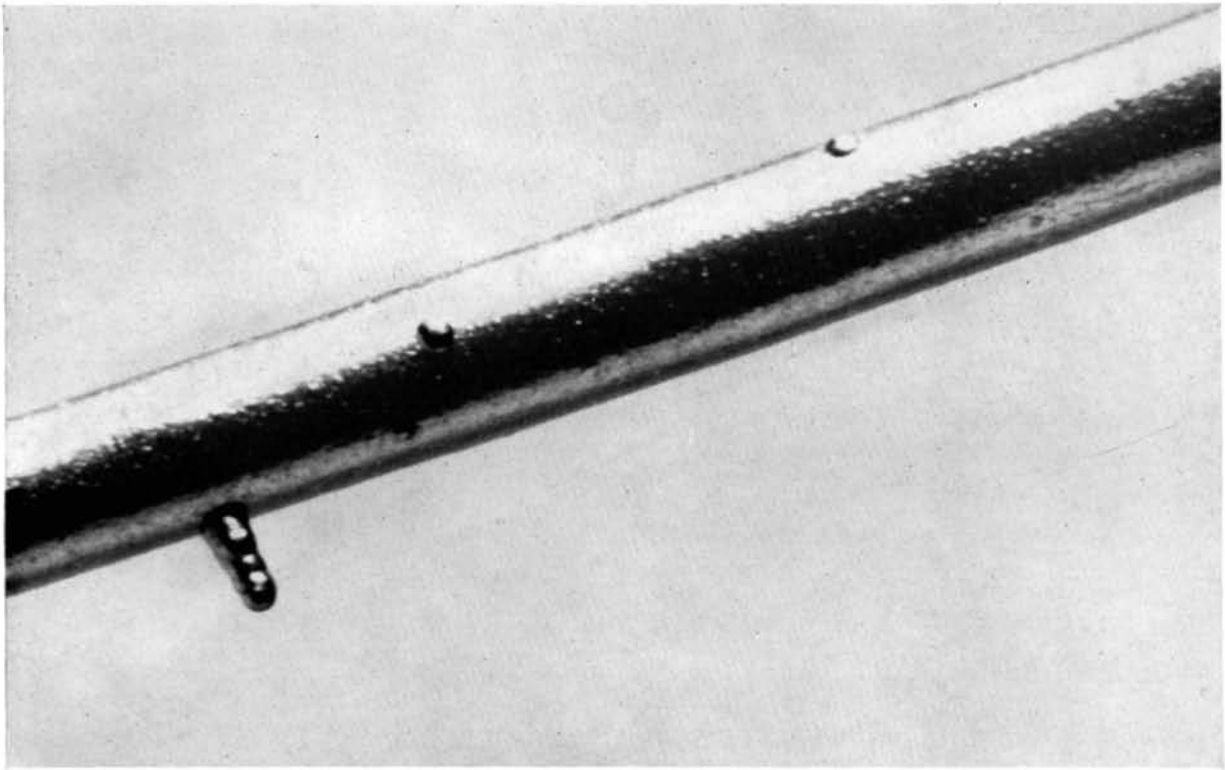

Fig. 2. Carbon deposit from cyanogen on to carbon filament at 1920 °C. Magnification: × 50.

In all the deposits, the (001) planes in the crystallites tend to be parallel to the substrate.

Table 1 summarizes some information regarding the structure of the carbon deposits formed at different temperatures. The electron-diffraction patterns show the existence of graphite layer planes in all cases. Both the size of the crystallites and the degree of preferred orientation parallel to the axis of the substrate increase with the temperature of deposition. On the other hand, the initial pressure of cyanogen has over the range investigated little or no influence on the structure of the resulting deposits.

Table 1. *Order of crystal size and degree of orientation in the carbon deposits*

Temperture of decomposition	Order of crystal size normal to (001) plane	Order of crystal size normal to (100) plane	Degree of (001) orientation	*hkl* reflexions
1500 °C	100 Å	50 Å	Slight	Absent
1620	200	100	Slight	Absent
1730	300	100	Slight	Absent
1855	300	150	Fairly strong	Absent
1990	400	200	Fairly strong	Absent
2120	500	200	Fairly strong	Absent

The observed influence of temperature clearly reflects the mobility of the carbon atoms or other fragments on the surface of the substrate and the growing crystals at the time of deposition. The higher the mobility, the more perfectly crystalline will the crystallites be, owing to the greater ability of the atoms to move to preferred positions of low potential energy in the crystallites rather than to remain at the sites at which they are deposited.

The deposits obtained from cyanogen do not, however, show the presence of the three-dimensional order which is characteristic of the ideal graphite structure. This is inferred from the absence of *hkl* reflexions in all the diffraction patterns, including those for carbon deposits obtained at temperatures above 1900 °C. It appears therefore that the deposits are turbostratic (Warren, 1934; Biscoe & Warren, 1942) and non-graphitizable (Franklin, 1951*a*, *b*).

Carbons formed by pyrolysis of the vapour of chlorinated hydrocarbons (Cullis, Manton, Thomas & Wilman, 1959) have been shown to consist of randomly oriented crystallites and it has been suggested that the relatively large chlorine atom restricts the movement of carbon fragments at the time of deposition, resulting in the formation of a disordered deposit. In the same way, it would be expected that the presence of nitrogen on or near the surface would tend to limit the mobility of the deposit-forming groups. Three-dimensional order is thus absent in the deposits obtained from cyanogen even at temperatures where carbon deposits formed from hydrocarbons begin to show evidence of the ideal graphite structure. Although the best compound to compare with cyanogen would be acetylene, there does not appear to be any information regarding the structure of pyrolytic carbons produced from this hydrocarbon at temperatures comparable to those used in the present work. Several X-ray studies of the carbons formed by pyrolysis of methane at high temperatures show clearly however the existence of some *hkl* reflexions above 1900 °C (*e.g.* Brown & Watt, 1958; Guentert & Cvikevich, 1960; Blackman, Saunders & Ubbelohde, 1961; Guentert, 1962).

There are of course various possible mechanisms for the formation of solid carbon from the present starting material but the two most likely are as follows:

(1) A cyanogen molecule may become chemisorbed on two adjacent surface carbon atoms, the original C–C bond being broken and two adsorbed CN groups being formed (Fig. 3). (Alternatively of course CN radicals, formed by prior thermal dissociation of cyanogen in the gas phase (White, 1940), may be the species which undergo adsorption). The sites at which

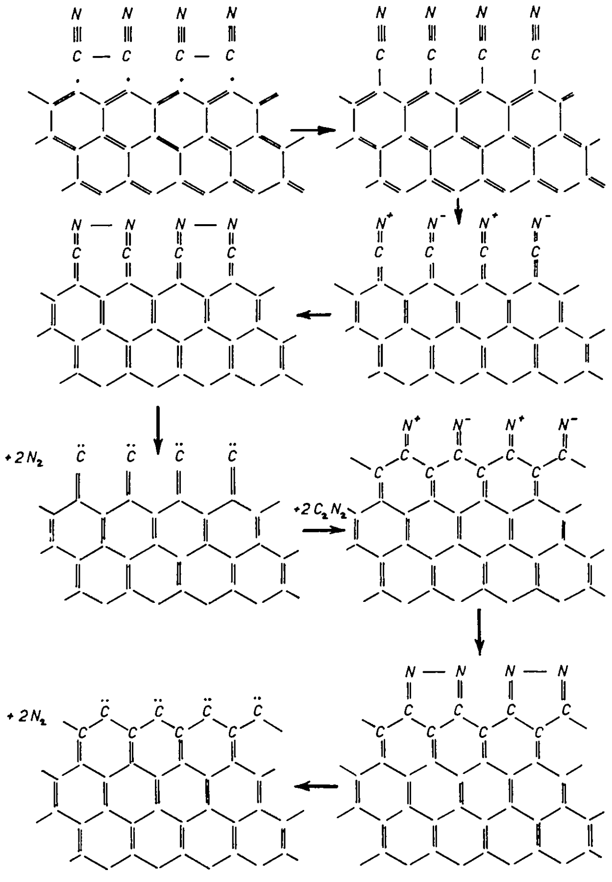

Fig. 3. Suggested mechanism for the growth of graphite hexagon planes during the pyrolysis of cyanogen.

this occurs must possess free unpaired electrons and will probably be the edges of graphite crystallites. Interaction between the nitrogen atoms of adjacent adsorbed groups may result in the formation of a N–N bond, and molecular nitrogen may then be desorbed, leaving free electrons on each of the two carbon atoms present originally in the cyanogen molecule. Further adsorption of cyanogen can then take place on these carbon atoms causing the progressive building up of the carbon hexagon network.

Cyanogen could also be adsorbed at lattice imperfections, two CN groups being formed as before. Steric factors will, however, probably prohibit the rapid desorption of nitrogen in this configuration. It is therefore probable that the CN groups will migrate to positions of lower potential energy at which desorption of nitrogen is facilitated. Favourable positions are again likely to be the edges of complete hexagon planes. The mechanism of desorption will then be the same as before, and the graphite hexagons will increase in size as the reaction proceeds.

(2) The initial growth of the carbon deposits in a direction perpendicular to the axis of the substrate will probably occur by a different mechanism. In this case it is necessary for an unsaturated nucleus to be formed on the surface of the filament before the hexagon plane can begin to build up as in (1). A six-membered ring of carbon atoms could be formed by the condensation on the surface of three molecules of cyanogen. Nitrogen could then be desorbed, the ring becoming weakly bonded to the hexagon plane of the substrate by interaction between one or more of the free valencies formed in the desorption process and the free valencies associated with the plane. Several such ring structures could condense together as a result of movement over the surface, the new layer plane being built up, as before, from cyanogen molecules adsorbed from the gas phase. This process will occur to a greater extent on crystallites which are originally parallel to the surface of the substrate, deposition on those situated at an angle to the surface being rapidly terminated by the growth of neighbouring crystallites. This would account for the preferred orientation of the deposited carbon parallel to the axis of the substrate.

Thus the simultaneous occurrence of (1) and (2) would lead to the growth of a carbon deposit both along and perpendicular to the graphite *c* axis, with the layer planes parallel to the surface on which the deposit is formed but not arranged in any crystallographic order with respect to each other.

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