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The Structure and Crystal Growth of Carbon Deposits Formed by Pyrolysis of some Hydrocarbons and Chlorohydrocarbons

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Studies have been carried out, of the influence of the chlorine content of both aliphatic and aromatic compounds on the structure of the carbon deposits formed on a silica surface by pyrolysis at 850–950 °C. The results show that the more highly chlorinated compounds give rise to carbons in which the crystals are smaller and the preferred orientation and (001) habit of the crystallites are less marked than in those derived from organic compounds containing little or no chlorine. The differences in carbon structure are ascribed to the decreased mobility of the carbon atoms in presence of hydrogen chloride or chlorine.

Introduction

The structure of carbonaceous deposits formed during pyrolytic processes depends not only on the temperature of formation but also, frequently, on the nature of the material undergoing decomposition. In general, carbons formed by thermal decomposition of inorganic compounds usually possess a high degree of atomic arrangement into crystalline aggregates. For example, the carbon formed at 500 °C. on a catalyst (Hofmann & Wilm, 1936) by the reaction:

$$2\,CO = C+CO_2$$

has layer-plane spacings of the same value (3·4 Å) as for carbons prepared by breakdown of organic compounds at 1700 °C. Similarly, highly crystalline carbons are obtained at a relatively low temperature from austenite (Northcott, 1923) and metallic carbides (Westbecker, 1904; Hahn & Strutz, 1907).

In general, however, carbon formed by pyrolysis of hydrocarbons (e.g. White & Germer, 1941; Iley & Riley, 1948) is not markedly different from that formed from carbon monoxide under comparable conditions of temperature and pressure. By comparison, carbons prepared by pyrolysis of polyvinylidene chloride at 1000 °C. contain groups of from two to four parallel graphite-like layers in a carbon matrix which gives only a gas-like contribution to the total X-ray scattering; on further heating at the same temperature the main structural change is the growth of the small graphite-like layers at the expense of the non-organized carbon (Franklin, 1950(*a*), (*b*)).

Presumably, in the decomposition of hydrocarbons, any gases present—the amounts of which left in the solid may be quite large (Riley, 1938)—tend to inhibit the ordering process by saturation of the valencies of the carbon atoms on the surface of the growing crystallites. The carbonaceous deposits prepared from other organic compounds generally contain substantial amounts of other elements besides hydrogen which are present in the original material. In studies of the thermal decomposition of certain chlorohydrocarbons, for example, it is found that appreciable quantities of chlorine remain in the solid (Cullis & Priday, 1954), the presence of which clearly tends to affect the structure of the deposited carbon. This paper describes the first attempt to study systematically the effect of the chlorine content of organic compounds on the structure of the carbon formed by their pyrolysis. The results obtained in this work show clearly the considerable extent to which the presence of this element in the starting material influences the resulting carbon structure.

Experimental

Apparatus

Gases and vapours were admitted to a heated silica reaction vessel (volume, ca. 300 ml.) suspended in an electric furnace the temperature of which was automatically controlled. Into the reaction vessel was inserted a translucent silica rod to the end of which was sealed a piece of smooth transparent silica (1 mm. wide × 2·5 cm. long). All organic compounds were introduced into the reaction vessel at a pressure of 50 mm. Hg (at the reaction temperature) and decomposition was assumed to be complete when no further pressure change occurred (generally 6–24 hr.). At the end of reaction, the reaction vessel was evacuated and a further quantity of organic vapour was admitted. This procedure was repeated three times and the reaction vessel, while still evacuated, was allowed to cool to room temperature. The silica rod was then carefully withdrawn and the carbon deposited on its end was examined by the 'reflection' electron-diffraction technique. An accelerating potential of 60–70 kV. and a camera length of 47 cm. were used.

Materials

(*a*) *Methane*. The gas was obtained directly from a cylinder, the specification being >98·5% methane. Mass-spectrometric analysis showed that effectively the only impurity was ethane, and no attempt was made to remove the higher homologue. The gas was

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

	Temperature of decomposition	Order of crystal size normal to		Degree of (001)	Figure
Compound	(°C.)	(001) plane (Å)	(100) plane (Å)	orientation	No.
CH_4	875	50	100	Fairly strong	1(*a*)
CH_3Cl	842	30	70	Slight	1(*b*)
CH_2Cl_2	842	30	70	Nil	1(*c*)
$CHCl_3$	875	(30)	(50)	Nil	1(*d*)
CCl_4	875	Not determined		Nil	1(*e*)
CH_4	932	>100	200	Strong	2(*a*)
CH_3Cl	932	100	150	Slight	2(*b*)
CH_2Cl_2	932	30	100	Nil	2(*c*)
$CHCl_3$	932	20	100	Nil	2(*d*)
CCl_4	932	Silica pattern only shown			
C_6H_6	932	150	200	Strong	3(*a*)
C_6H_5Cl	932	150	200	Fairly strong	3(*b*)
o-$C_6H_4Cl_2$	932	150	150	Slight	3(*c*)

passed through a column of magnesium perchlorate followed by a trap cooled in liquid nitrogen.

(*b*) *Methyl chloride.* This compound was prepared by the action of dimethyl sulphate on anhydrous aluminium chloride at room temperature (Shamshurin, 1939). The gas was passed first through magnesium perchlorate and then through soda lime which removed any hydrogen chloride formed in the reaction; it was finally fractionally distilled into a storage globe.

(*c*) *Methylene chloride, chloroform and carbon tetrachloride.* The purest available commercial samples were carefully fractionated. Middle fractions were re-distilled in vacuo into a storage bulb where they were freed from dissolved air by repeated freezing and melting under vacuum. The 'outgassing' procedure was carried out before each run.

(*d*) *Benzene, chlorobenzene and o-dichlorobenzene.* Commercial samples were first purified by washing with concentrated sulphuric acid, 5 % aqueous sodium bicarbonate solution and finally water. After they had been dried (Na_2SO_4), the liquids were distilled and a constant-boiling fraction was collected. This fraction was then re-distilled into a storage bulb and the liquid was 'outgassed' as previously described.

Results and discussion

Typical electron-diffraction photographs obtained from the deposits studied are shown in Figs. 1, 2 and 3. All the carbons obtained show diffractions due to the even orders of the reflection from the (001) planes. The order of size of the crystallites may be estimated from the half-breadth of these and other diffractions, although the degree of accuracy obtainable from such reflection photographs is not high. The existence of preferred orientation can be deduced from the presence of 'arcing' or, in other words, variation of the intensity round the ring. In all the deposits which showed such preferred crystal orientation, the (001) planes in the crystallites tended to be parallel to the substrate. Generally the spread of orientation in the specimens was found to be up to ±30° from the mean. In all cases where strong (001) orientation was observed, the diffraction arcs (especially the 00*l*) showed a strong broadening and displacement towards the shadow edge of the pattern, due to refraction by (001) boundary faces of the crystals. Patterns from unoriented deposits showed no indication of such pronounced (001) crystal habit.

Table 2. *Indices of main diffractions observed in the carbon deposits*

Compound	Temperature of decomposition (°C.)	Indices *hkl* of diffraction rings present*	Figure No.
CH_4	875	002, 004, 100, 110	1(*a*)
CH_3Cl	842	002, 004(*w*), 100, 110	1(*b*)
CH_2Cl_2	842	002, 100, 110	1(*c*)
$CHCl_3$	875	002, 100(*w*), 110(*w*)	1(*d*)
CCl_4	875	004(*vw*)	1(*e*)
CH_4	932	002, 004(*w*), 100, 110, *hkl*(*w*)	2(*a*)
CH_3Cl	932	002, 100(*w*), 110(*w*)	2(*b*)
CH_2Cl_2	932	002, 100, 110	2(*c*)
$CHCl_3$	932	002, 100, 110	2(*d*)
CCl_4	932	Silica pattern only shown	
C_6H_6	932	002, 004, 006, 100(*w*), *hkl*(*w*)	3(*a*)
C_6H_5Cl	932	002, 004, 006(*w*), 100(*w*), *hkl*(*w*)	3(*b*)
o-$C_6H_4Cl_2$	932	002, 004(*w*), 100(*w*)	3(*c*)

* (*w*) = weak; (*vw*) = very weak.

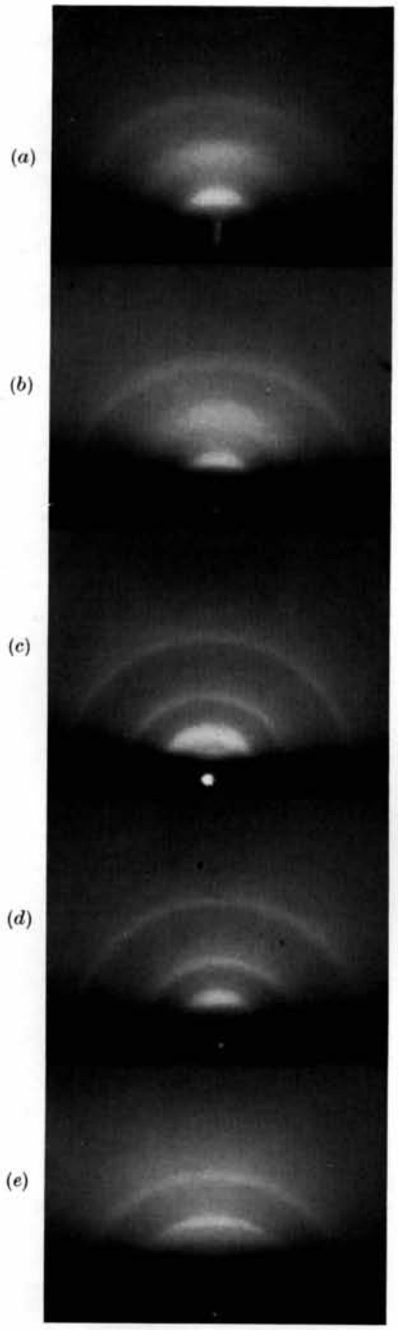

Fig. 1. Carbon deposits from pyrolysis of (*a*) CH_4, (*b*) CH_3Cl, (*c*) CH_2Cl_2, (*d*) $CHCl_3$, (*e*) CCl_4, at about 850 °C. (Table 1). $L \simeq 50$ cm.; ~ 55 kV.

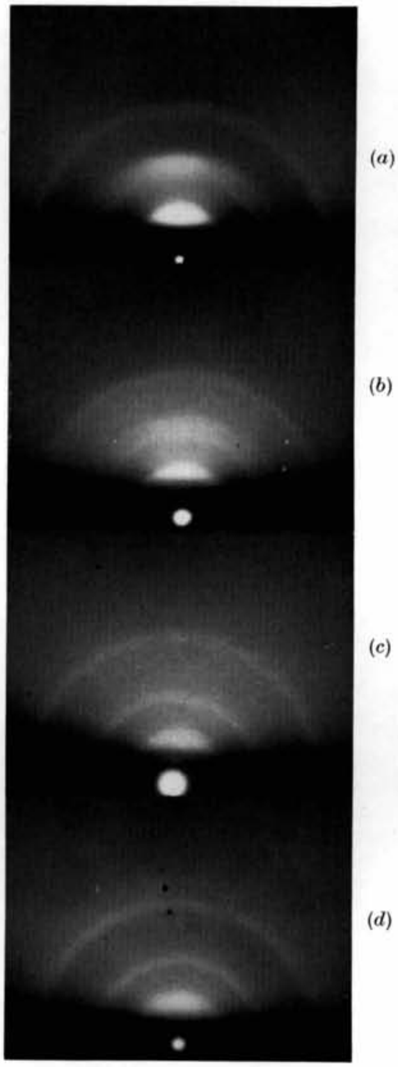

Fig. 2. Carbon deposits from pyrolysis of (*a*) CH_4, (*b*) CH_3Cl, (*c*) CH_2Cl_2, (*d*) $CHCl_3$, at 932 °C. $L \simeq 50$ cm.; ~ 55 kV.

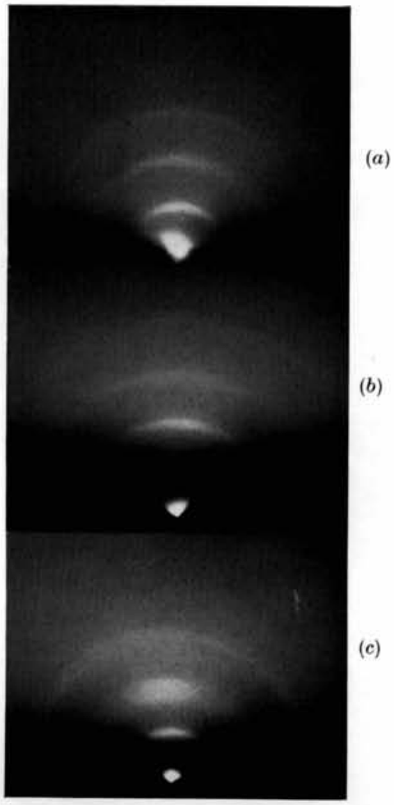

Fig. 3. Carbon deposits from pyrolysis of (*a*) C_6H_6, (*b*) C_6H_5Cl, (*c*) *o*-$C_6H_4Cl_2$, at 932 °C. $L \simeq 50$ cm.; ~ 55 kV.

Table 1 gives details of the crystal size wherever it can be estimated, and of the presence or absence of orientation in the various carbon deposits studied. Table 2 shows the main diffraction rings present for each carbon examined; it was not found possible to obtain a satisfactory deposit from carbon tetrachloride at 932 °C. Where the diffractions obtained are weak (Table 2) values of the crystal size are only rough (Table 1). There is a definite trend in the variation of crystal size with the carbon source at 932 °C., the crystallites being smaller the higher the chlorine content of the organic compound.

All the carbon deposits obtained possessed a graphite-like layer lattice in which successive layers are stacked parallel to each other in the individual crystallites with a spacing equal to, or possibly slightly greater than, the corresponding spacing in the graphite crystal (Warren, 1941; Biscoe & Warren, 1942). There is no marked indication of rotational shift of successive layer-planes; in other words, the intensity contour across the $hk0$ rings appears to be as symmetrical as that of the $00l$ rings.

The carbons formed from methane, benzene and chlorobenzene possess a more normal graphite structure than those obtained from the other organic compounds studied. This is indicated by the presence of diffractions of the hkl type in addition to those of the $hk0$ and $00l$ types; thus successive layers of (001) carbon sheets are stacked parallel to one another without rotation to form relatively perfect graphite crystals with the layer planes tending to be parallel to the substrate surface. For the carbons formed from methylene chloride, chloroform and carbon tetrachloride, the electron-diffraction patterns obtained give no indication of any preferred orientation. The deposits from methyl chloride and *o*-dichlorobenzene show a small amount of preferred orientation and hence belong to a class intermediate between the two extremes. The indications are that only a trace of preferred orientation of the crystallites is present; in other words, the deposits are nearly randomly oriented.

These results reflect the mobility of the carbon atoms (or other fragments of the carbon skeleton of the molecules) on the surface of the substrate and the growing crystals at the time of deposition or formation. The higher this degree of mobility, the more perfect crystalline form will the crystallites possess, due to the ability of the atoms to move to preferred positions of low potential energy in the crystallites rather than to remain at the site at which they are deposited. Consequently, a high degree of mobility of the deposit-forming atoms is associated with (i) the formation of a small number of large crystallites rather than with a larger number of smaller crystallites, (ii) the presence of a preferred orientation of the crystallites and (iii) the development of smooth faces of the (001) type.

During the building-up of a crystal, the unsatisfied valencies at the surface may be satisfied either by further atoms of the same type or by other atoms or molecules which may be present. From the results given in Table 1, it appears that the presence of an excess of hydrogen in the gaseous reaction products does not reduce appreciably the perfection of the crystallites formed. Thus the carbon deposits from methane, benzene and chlorobenzene possess a more extensive graphite crystal development and habit than those obtained from the other sources. Hydrogen atoms will of course tend to satisfy some of the crystallite surface valencies, but due to their small volume, will allow carbon atoms still to maintain sufficient mobility on the surface to take up a preferred structural position. The presence of hydrogen chloride or chlorine adsorbed on the growing crystals, due to their larger molecular volumes, reduces the mobility of the carbon atoms causing them to take up less preferred positions. This results in the absence of any preferred orientation, the formation of crystallites of smaller size and the absence of well-defined smooth (001) faces.

Thin deposits formed more slowly than usual did not develop appreciably larger crystal size. This finding appears to indicate that the effect of the other gases present was not merely to slow down the crystallization but to limit it by a more or less static form of adsorption. This might be expected to lead to the observed considerable gas content of the deposits.

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References

Biscoe, J. & Warren, B. E. (1942). *J. Appl. Phys.* **13**, 364.

Cullis, C. F. & Priday, K. (1954). *Proc. Roy. Soc.* A, **224**, 308, 544.

Franklin, R. E. (1951*a*). *Acta Cryst.* **4**, 253.

Franklin, R. E. (1951*b*). *Proc. Roy. Soc.* A, **209**, 196.

Hahn, C. & Strutz, C. (1907). *Chem. Ztg.* **31**, Rep. 33.

Hofmann, U. & Wilm, D. (1936). *Z. Elektrochem.* **42**, 504.

Iley, R. & Riley, H. L. (1948). *J. Chem. Soc.* p. 1362.

Northcott, L. (1923). *J. Iron Steel Inst.* **108**, 491.

Riley, H. L. (1938). *Trans. Faraday Soc.* **34**, 1011.

Shamshurin, A. A. (1939). *J. Gen. Chem. U.S.S.R.* **9**, 2207.

Warren, B. E. (1941). *Phys. Rev.* **9**, 693.

Westbecker, J. (1904). *Z. Elektrochem.* **10**, 837.

White, A. H. & Germer, L. H. (1941). *J. Chem. Phys.* **9**, 492.