274. *The Deposition of Carbon on Vitreous Silica.*

By R. Iley and H. L. Riley.

Three types of carbon deposited from methane, propane, butane, and ethylene and from benzene vapour in the temperature range 800—1300° on a fused-silica surface have been examined by *X*-ray diffraction. These carbons, vitreous and columnar, soft black pulverulent, and filamentous, are all microcrystalline, similar in crystallite size to carbons made by carbonisation. The crystallites present in the vitreous and filamentous varieties have dimensions which increase with the temperature of deposition and which are larger than those present in the soft black variety. The carbons resemble macrocrystalline graphite in their reactivity to gaseous oxygen. The formation of a new white form of carborundum by the interaction of ethylene and silica at 1200—1300° is also reported.

Most of the methods available for the preparation of the so-called " amorphous " carbons can be classified under two headings, *viz.*, (1) *carbonisation* (*i.e.*, the pyrolytic decomposition of carbonaceous matter, exclusively in the condensed phase) and (2) *carbon deposition* (*i.e.*, the homogeneous or heterogeneous decomposition of carbonaceous gases and vapours). The *X*-ray crystal chemistry of carbonisation has been studied in the Northern Coke Research Laboratory (Blayden, Gibson, and Riley, " The Ultra-Fine Structure of Coal and Cokes ", B.C.U.R.A., London, 1944, 176—231; *J. Inst. Fuel*, 1945, War Time Bulletin; Gibson, Holohan, and Riley, *J.*, 1946, 456) and by U. Hofmann and Sinkel (*Z. anorg. Chem.*, 1940, **245**, 85). Hofmann and his co-workers have also studied the *X*-ray crystallography of carbon deposition. Following K. A. Hofmann and Rochling (*Ber.*, 1923, **56**, 2071), K. A. Hofmann and U. Hofmann (*ibid.*, 1926, **59**, 2433) investigated the deposition on inert surfaces of a black highly lustrous form of carbon from hydrocarbon gases at temperatures from 650° upwards. In order to avoid soot formation, the gas or vapour was led into a heated crucible at a slow uniform velocity : aliphatic hydrocarbons were preferred to aromatic. Nitrogen was used as a carrier gas, and it was claimed that small proportions of oxygen, carbon dioxide, and water vapour promoted the formation of the black lustrous variety by reacting with any soot which was formed. Surfaces of porcelain, quartz, fluorspar, carborundum, diamond, zinc blende, and gold (also silver, but this was not so effective) all became coated with a lustrous black layer, which appeared smooth and polished under the microscope and was about 3 μ thick. On rough surfaces, such as unglazed procelain, calcined magnesia, asbestos, retort carbon, or Acheson graphite, a metallic grey layer was formed, sometimes similar in appearance to platinum. This grey variety was also formed on smooth surfaces at higher temperatures or when high concentrations of organic vapours were used. The carbon content of the black lustrous modification was 98·8—99%;

the deficit was considered to be largely moisture and perhaps a trace of hydrogen : its reactivity to oxidising agents was similar to that of retort carbon. *X*-Ray examination indicated an average crystallite dimension of the order of 38 A. Hofmann (*Ber.*, 1928, **61**, 1180, 2183) and Hofmann and Wilm (*Z. physikal. Chem.*, 1932, *B*, **18**, 401; *Z. Elektrochem.*, 1936, **42**, 504) have examined carbons deposited on iron from carbon monoxide and report the following variations of crystallite dimensions ($L_a \times L_c$ in A.) with temperature of formation : 400°, 40 × 35; 420°, 60 × 70; 550°, 150 × 160; 700°, 120 × 180. They found that the dimensions of the carbon crystallites deposited from light petroleum (b. p. 60—70°) on a porcelain surface were much smaller than those deposited on an iron surface : the voluminous soots deposited at 900° from light petroleum containing a trace of iron pentacarbonyl and entrained in nitrogen, like those deposited on iron powder, gave relatively sharp *X*-ray diffractions. Hofmann, Ragoss, and Sinkel (*Kolloid-Z.*, 1941, **96**, 231) have shown that commercial carbon blacks undergo little crystallite growth on being heated to 1300° for 10 hours : 24 hours at 3000° brings about thermal recrystallisation to an extent limited by the size of the discrete poly-crystalline particles present in the original soot. Koch-Holm (*Mitt. Siemens-Konz.*, 1927, **6**, 188) prepared carbons by the thermal decomposition of hydrocarbons without a catalyst at temperatures from 1200° to 2700° and found that crystallite dimensions increased with increasing temperature of formation. Biscoe and Warren (*J. Appl. Physics*, 1942, **13**, 364) studied the crystallite dimensions of various carbon blacks and the changes which occurred on heating a reinforcing channel black to various temperatures between 760° and 2800° : the average crystallite dimensions ($L_a \times L_c$) of the original sample were 20·0 × 12·7 which increased to 65·2 × 40 A. after 2 hours' heating at 2800°. Ruess (*Monatsh.*, 1946, **76**, 253) has recently reported the results of further *X*-ray investigations on lustre carbons prepared by depositing carbon from propane on fused silica at 850° ($L_a \times L_c$, 21·5 × 31 A.) and 930° (31·0 × 18 A.) : the latter results are in good agreement with those described below. Ruess reports an additional broad diffraction, indexed as ($00\frac{1}{2}$), in the powder photographs of his carbons : his specimens were, however, contained in glass capillary tubes. No such additional band has been observed in our investigations.

The present investigations were carried out in order to ascertain to what extent the crystallographic properties of the deposited carbon are determined by the nature of the parent carbonaceous gas or vapour, and to learn something of the part played by a refractory surface in the mechanism of the reaction. It is well known that during the deposition of carbon from carbon monoxide on an iron surface, the iron plays a definite part in the reaction, probably involving the formation and decomposition of cementite, and that the iron is intimately dispersed in the deposited carbon : fused silica is known to suffer deterioration in carbonaceous gases at high temperatures and it appeared possible that this might be due to some kind of interaction.

EXPERIMENTAL.

The carbon deposition was carried out in a long electrically heated vitreosil tube of 0·8″ internal diameter. Inside this tube was another of the same material, 6″ long, and of 0·4″ internal and 0·6″ external diameter, provided with lugs so that an annulus was left between the two tubes. Much of the carbon was deposited on this inner tube which could be removed easily from the up-stream end of the larger tube with little disturbance of the deposited carbon. The temperature was measured by means of a platinum–platinum-rhodium thermocouple surrounded by a vitreosil sheath situated axially in the tube. The following gases were used : methane (from a cylinder of the compressed gas and more than 98% pure), pyrogas (largely propane), calor gas (largely butane), ethylene (from a cylinder of the compressed gas), and benzene vapour entrained in nitrogen. In some experiments the gases were dried by passage through a tower of calcium chloride, in others they were saturated with water vapour at room temperature, and in others 10% by volume of ammonia was added. The gases were passed through the cracking tube at a constant rate of 25 l. (measured at room temperature) per hour.

The character of the carbon deposited varied with its position in the tube. Three types of carbon were formed : (1) a shiny, vitreous variety (probably similar in nature to Hofmann's " Glanzkohlenstoff "), which when formed in thick layers developed a columnar structure, (2) a soft, velvet-black, pulverulent variety, and (3) a filamentous variety. The vitreous and columnar forms tended to be deposited in the hotter zone, and the filamentous variety to grow from the down-stream end of the hot zone in the direction of the current. All three forms of carbon, deposited on the thermocouple sheath, are shown in Plate I : this deposit was formed at 1200° from ethylene saturated with water vapour at room temperature. Plate II shows a fern-like growth (about twice actual size) which was formed inside the inner vitreosil tube when dry propane was passed through the apparatus at a temperature of 1200°. Plate III shows much finer fibres deposited from methane at 1000° on the down-stream end of the inner silica tube. A compact bundle of these fibres was collected and formed into a rod by means of a little gum arabic. Plate IV shows the fibre photograph obtained from this specimen : it was made using unfiltered cobalt-*K* radiation and a film-to-specimen distance of 48 mm., and indicates that the carbon present is the ordinary " amorphous " variety with the *c* axes of the crystallites tending to be perpendicular to the fibre axis, *i.e.*, the hexagon layer planes more or less parallel to the fibre axis, and that the maximum deviation is about 20°. A fibre photograph of the columnar variety of carbon showed much less pronounced but quite definite indications of a similar preferred orientation.

The extent of the contamination of the deposited carbon with silica was influenced by the previous history of the vitreosil tube : that deposited on a new tube contained about 0·4—0·5% of SiO_2, whereas with a vitreosil tube which had been used several times the contamination was more than 10%. The vitreosil surfaces, on continued use, gradually became pitted. In one experiment at 1200°, in which ethylene saturated with water vapour was passed through the tube, in addition to the carbon deposit, there was a white, fluffy, mould-like growth on the central outer surface of the inner vitreosil tube. An *X*-ray powder photograph proved this to be cubic carborundum : although the substance was micro-crystalline, the back reflexions in the powder photograph were sharp. The growth was quite unlike the greenish-yellow carborundum formed when carbon reacts with silica at somewhat higher temperatures : it was quite soft to the touch and readily gave an extruded rod for *X*-ray examination when mixed with a little dilute gum arabic. It was not found possible to repeat this experiment, possibly because the silica tube surface must be in a specially active condition to permit the formation of silicon carbide at 1200° ; by increasing the temperature to 1300°, however, the same phenomenon was observed when a seasoned vitreosil tube was used.

Table I gives typical analyses of a number of carbons all prepared in the same silica tube. They are

TABLE I.

Sequence of Expt.	Gas.	Condition.	Temp.	Type of carbon.*	Ash, % (SiO_2).	C, %. (Ash-free, dry.)	H, %. (Ash-free, dry.)
1	Propane	Moist	1000°	L.	0·98	99·4	0·47
1	,,	,,	1000	B.p.	3·1	98·4	0·91
2	Ethylene	Dry	1200	F.	0·51	99·2	0·46
2	,,	,,	1200	B.p.	0·44	99·1	0·80
3	Ethylene	Moist	1200	L.	1·03	99·4	0·56
4	Propane	Moist	1200	L.	3·3	99·0	0·86
5	,,	Dry	1200	F.	5·5	99·1	0·49
5	,,	,,	1200	B.p.	10·6	99·4	0·47

* L. = lustrous; B.p. = black pulverulent; F. = filamentous.

low in oxygen, and the silica content increases with the repeated use of the fused silica tube, probably because of some opening up of the surface by chemical interaction.

The crystallite dimensions were determined as previously described (Blayden, Gibson, and Riley, *loc. cit.*), using a cylindrical camera (radius 45·43 mm. and cobalt-K_α radiation), from the corrected half-peak widths, β, of the diffractions; the Jones formula $\beta = 1{\cdot}0\lambda/L \cos \theta$ was used for the 002 diffraction, and the Warren formula $\beta = 1{\cdot}84\lambda/L \cos \theta$, for the 10 diffractions; θ is the *X*-ray wavelength, λ the Bragg angle, and L the crystallite dimension in the direction concerned. The results obtained are given in Table II.

DISCUSSION.

An examination of the crystallite dimensions recorded in Table II leads to the following conclusions. The parent organic gas or vapour and the added ammonia and water vapour show no systematic effect upon the crystallographic character of the deposited carbons. The *c* dimensions of both the vitreous and the soft black varieties prepared at temperatures of 1000—1300° show a spread of about 6 A., and the *a* dimensions a smaller spread of about 4 A. The *a* and the *c* dimensions of the vitreous variety of deposited carbon have a distinct tendency to increase as the temperature of formation increases from 800° to 1300°. The *a* and the *c* dimensions of the soft black variety of deposited carbon, on the other hand, display no such clear tendency. The *c* dimensions of the vitreous carbons are, on the average, systematically greater than those of the soft black variety, by some 4 A. at 1000° increasing to about 6 A. at 1300°. The *a* dimensions of these two varieties of carbon show a similar difference but of a somewhat smaller magnitude. The crystallite dimensions of the filamentous carbons are similar to those of the vitreous and columnar varieties. This indicates that the difference in the crystallographic properties of the vitreous and soft black varieties cannot be explained by any gross difference in the experimental conditions of deposition : Plate I shows that the deposition of the three varieties has occurred in the order : vitreous, soft black, filamentous. The less compact and sooty character of the soft black carbon is consistent with its lower crystallinity.

Another interesting feature of the above results is that the *a* dimensions are of the same magnitude, to within a few A., as those obtaining in carbons prepared by carbonising cellulose, lignin, coal, etc., up to corresponding temperatures of 1000—1300°, whereas carbons deposited on iron from carbon monoxide at much lower temperatures contain crystallites possessing very much larger *a* dimensions. A probable explanation of this difference is that carbon atoms adsorbed on or in an iron surface are more mobile than those on a silica surface and so permit greater crystal growth : it is also likely that hydrogen atoms can inhibit crystal growth by combining with the peripheral carbon atoms of the crystallites. The above results indicate that

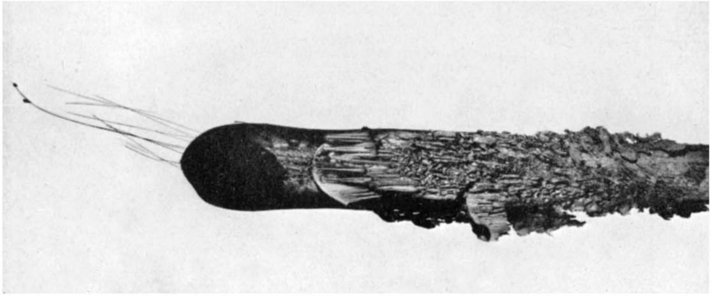

Plate I.

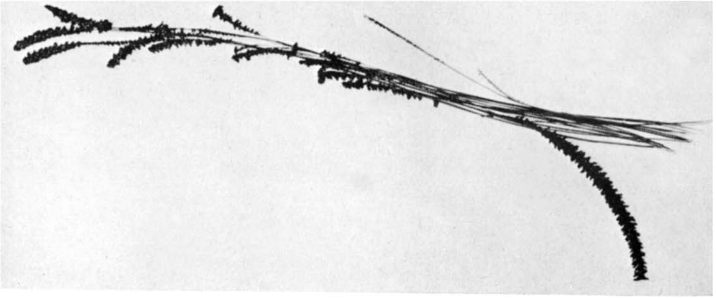

Plate II.

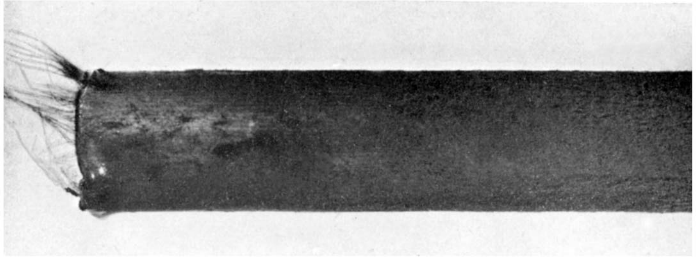

Plate III.

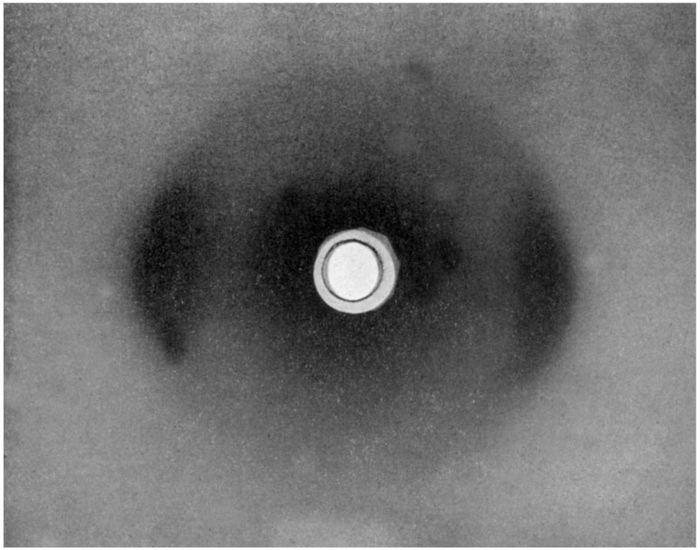

Plate IV.

[*To face p.* 1364.

TABLE II.

			Vitreous carbons.							Soft black carbons.						
			Half-peak width, mm.		Lattice parameter, A.		Crystallite size, A.			Half-peak width, mm.		Lattice parameter, A.		Crystallite size, A.		
Gas.	Addition.	Temp.	10.	002.	*a*.	*c*/2.	*a*.	*c*.	Ignition temp.	10.	002.	*a*.	*c*/2.	*a*.	*c*.	Ignition temp.
Methane	Dry	1000°	5·03	4·84	2·43	3·43	33·5	17·7	572°	5·07	5·28	2·44	3·47	33·3	16·2	500°
	Dry	1000	5·05	4·89	2·44	3·47	33·4	16·6	—	—	—	—	—	—	—	—
	NH_3	1000	5·11	5·17	2·44	3·44	33·0	16·6	565	—	—	—	—	—	—	—
	H_2O	1000	4·75	5·24	2·41	3·65	35·5	16·3	—	—	—	—	—	—	—	—
	Dry	1100	4·6	3·85	2·43	3·47	36·8	22·6	551	5·22	5·74	2·47	3·58	32·4	14·8	520
	Dry	1200	4·72	3·98	2·46	3·50	35·8	21·8	—	5·33	5·55	2·40	3·44	31·7	15·3	—
	Dry	1300	4·78	3·89	2·43	3·43	35·4	22·4	648	4·67	5·43	2·45	3·46	36·2	15·7	—
Ethylene	Dry	1000	5·36	4·62	2·43	3·44	31·5	18·6	—	5·05	6·91	2·45	3·56	33·4	12·3	525
	NH_3	1000	4·86	4·16	2·43	3·45	34·8	20·8	540	5·13	6·57	2·43	3·56	32·9	12·9	535
	H_2O	1000	4·98	4·30	2·44	3·55	33·9	20·1	630	—	—	—	—	—	—	—
	Dry	1100	4·89	4·17	2·46	3·46	34·6	20·8	617	5·41	6·44	2·42	3·51	31·2	13·2	529
	Dry	1200	4·63	4·25	2·45	3·47	36·6	20·3	586	5·56	6·35	2·42	3·47	30·3	13·4	512
	NH_3	1200	4·89	4·04	2·44	3·47	34·6	21·5	546	5·36	6·31	2·42	3·43	31·5	13·5	474
	H_2O	1200	5·06	4·00	2·43	3·43	33·4	21·7	605	—	—	—	—	—	—	—
	Dry	1300	4·06	4·06	2·43	3·45	41·9	21·4	630	—	—	—	—	—	—	—
Benzene	Dry	1000	5·37	4·79	2·45	3·44	31·4	18·0	—	5·58	5·50	2·45	3·44	30·2	15·5	—
	Dry	1100	—	4·44	2·44	3·46	—	19·4	—	5·48	6·00	2·43	3·47	30·8	14·2	514
	Dry	1200	4·91	3·71	2·40	3·38	34·4	23·6	582	5·27	5·42	2·40	3·50	32·0	15·7	501
	Dry	1300	4·67	3·07	2·41	3·40	36·2	29·0	614	—	—	—	—	—	—	—
Propane	Dry	800	5·26	5·20	2·41	3·45	32·9	16·5	561	—	—	—	—	—	—	—
	Dry	1000	5·16	5·28	2·44	3·45	32·7	16·2	—	—	—	—	—	—	—	—
	NH_3	1000	4·71	4·63	2·44	3·45	35·9	18·6	582	—	—	—	—	—	—	—
	H_2O	1000	4·70	5·77	2·43	3·46	36·0	23·2	610	—	—	—	—	—	—	—
	Dry	1200	4·66	4·40	2·43	3·45	36·3	19·6	—	—	—	—	—	—	—	—
	NH_3	1200	4·82	4·24	2·44	3·46	35·2	20·4	545	5·78	5·97	2·42	3·44	29·1	14·3	524
	H_2O	1200	4·55	4·34	2·43	3·49	37·2	19·9	532	5·17	6·46	2·42	3·52	32·7	13·1	530
Butane	Dry	1000	5·00	5·46	2·43	3·43	33·7	15·6	576	—	—	—	—	—	—	—
	Dry	1100	5·07	4·07	2·45	3·50	33·3	21·2	620	4·89	5·78	2·42	3·50	32·6	14·7	520
	Dry	1200	4·66	4·14	2·45	3·45	36·7	20·9	610	5·13	6·14	2·44	3·58	32·9	13·9	522
	Dry	1300	4·75	3·08	2·46	3·40	35·7	28·9	612	5·18	5·03	2·44	3·44	32·6	17·0	—
Filamentous carbon.																
Methane	Dry	1000	5·58	4·46	2·42	3·33	30·2	19·3	—							
Methane	Dry	1000	5·03	4·34	2·43	3·43	33·5	19·9	—							
Propane	Dry	1200	4·56	4·40	2·43	3·45	37·2	19·6	560							
Ethylene	Dry	1200	4·62	4·25	2·45	3·45	36·7	20·4	—							

the mechanism of crystal growth obtaining in these deposition reactions is probably similar in some respects to that obtaining in carbonisation.

The ignition temperatures of some of the deposited carbons were determined by the semimicro-method described by Blayden, Riley, and Shaw (*Fuel*, 1943, **22**, 32, 64), and the results are recorded in Table II. The soft black carbons have lower ignition temperatures than the vitreous carbons prepared at corresponding temperatures : on ignition they also tended to burn more rapidly than the vitreous carbons. These results indicate that the deposited carbons, particularly the vitreous variety prepared at 1300°, are closely akin to natural graphite in reactivity with oxygen (cf. Riley, *Quart. Reviews*, 1947, **1**, 59).

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KING'S COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE-UPON-TYNE, 1.

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