Reaction of Carbon with Nitrogen

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Studies of the reaction of carbon with nitrogen from 1000 to 2200°C show that appreciable interaction takes place at temperatures as low as 1400°C. With one of the two types of graphite investigated, the rate of formation of cyanogen passes through a well-defined maximum at *ca.* 1600°C. The reaction is retarded by trace quantities of oxygen and accelerated by relatively large amounts of water vapour, and the rate is proportional to the nitrogen pressure over the range 0-35 mm. The results are discussed in relation to those for other carbon-gas reactions and a mechanism is proposed which is consistent with the experimental findings.

In recent years results obtained on the interaction of gases with solid carbon have helped to elucidate the microcrystalline structure of carbon and the mechanism of gas-solid reactions in general.[1] The reactions of carbon with oxygen, carbon dioxide, steam, hydrogen and nitrous oxide all take place rapidly at temperatures below 1000°C, but the reaction with nitrogen does not occur appreciably under comparable conditions. Earlier workers could find no chemical evidence for the formation of cyanogen even at much higher temperatures,[2] although an intense cyanogen spectrum was observed when dry nitrogen was passed through a carbon arc.[3] More recently Fink and Wroughton [4] have detected cyanogen in the products formed in the carbon + nitrogen reaction above 2200°C. Berkowitz [5] has investigated the reaction mass-spectrometrically at temperatures from 1900 to 2200°C and has detected a variety of intermediate species.

The present work was designed to obtain reliable values for the rates of formation of cyanogen over a wide range of temperatures and under both equilibrium and non-equilibrium conditions. The behaviour of two different graphites (EY 9A and pile grade A) has been investigated and the effects of trace amounts of oxygen and water vapour on the reaction have been determined.

EXPERIMENTAL

FLOW SYSTEM

GENERAL DESIGN OF APPARATUS

A flow system was used to study the reaction between carbon and nitrogen at atmospheric pressure. Nitrogen from a cylinder entered the system via reducing and needle valves. It passed first through 2-ft long columns of sofnolite and magnesium perchlorate, which remove carbon dioxide and water respectively, then through a similar column of freshly prepared manganous oxide,[6] which reduces the concentration of oxygen to less than 1 p.p.m., and finally through a second column of magnesium perchlorate.

Known small amounts of oxygen could be re-introduced by passage of the purified gas over the surface of the electrolyte (0·158 % aq. soln. of $Ba(OH)_2$) in the anode compartment of an electrolytic cell. The cell was placed immediately before the second column of magnesium perchlorate. In order to re-introduce known small amounts of water vapour, the pure dry nitrogen, after leaving the second column of magnesium perchlorate was passed through a bed of either zinc sulphate heptahydrate or sodium hydroxide maintained at a constant temperature; both compounds were found to provide a steady rate of release of water vapour over reasonably long periods of time. The nitrogen (with or without added oxygen or water vapour) then entered the reaction vessel via a capillary flowmeter and the effluent gases were finally passed through three glass wash-bottles, one of which was connected in parallel with the other two in series. These were each of *ca.* 500 ml capacity with a sintered-glass disc (average pore size: 100-120 microns) fitted just above the base. Each of the wash-bottles normally contained 100-200 ml of appropriate solutions for the absorption of the reaction products.

REACTION VESSEL AND FILAMENT ASSEMBLY

The reaction vessel (fig. 1) consisted essentially of a 2-l. Pyrex globe through which nitrogen could be passed continuously and containing a carbon filament which could be heated electrically. The flask was fitted at opposite ends with large ground-glass cones through which the filament assembly could be inserted. Once the filament was in position, each end could be closed and the vessel made gas-tight by attachment of corresponding ground-glass sockets which were provided with water jackets to prevent the lubricant becoming too mobile during heating of the filament.

Since it was often necessary to maintain the carbon filament at high temperatures for considerable periods, the filament supports also tended to become very hot. In order to exclude all foreign substances which might cause side-reactions, carbon was used as the constructional material for the major part of the filament assembly. The graphite filaments A were in the form of helices with square cross-sections and of the dimensions given in table 1. Each end was fitted into a groove machined into a rectangular carbon block B and the filament was then secured by four thin carbon plates which fitted over the ends of the helix and were screwed into the blocks by graphite screws. Into threaded holes in the centre of each block were then screwed two carbon rods C, which in turn were fixed to tungsten rods. The filament assembly was set up independently before it was inserted into the outer Pyrex vessel.

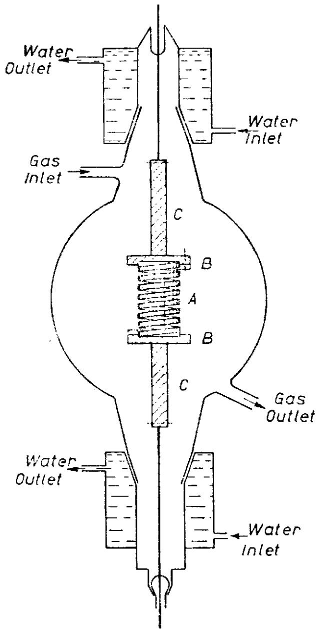

FIG. 1.—The flow system reaction vessel.

TABLE 1.—DIMENSIONS OF THE GRAPHITE FILAMENTS

	EY 9A	pile-grade A
external diam., mm	32	25
cross-section of helix, mm^2	2	3
distance between turns, mm	2	2·5
no. of turns heated	5	11

The filaments were heated by the output from a 5 kVA stepdown transformer connected to the 250-V a.c. mains. Current control was provided by a heavy duty rheostat placed in series with the transformer and filament and capable of carrying a current somewhat in excess of 50 A. The temperature of the filament was measured with an optical pyrometer which was accurate to ±10° at 1500°C and to ±20° at 2000°C. The temperature distribution down the filament was fairly uniform and in no case exceeded 20° between the central and the end turns. No correction was applied for the non-perfect " black body " radiation of the filament.

PROCEDURE

The filament was outgassed for about 10 h at 2000°C in nitrogen before runs were started. At the beginning of a run the nitrogen flow rate was adjusted to the required value, the systems for the introduction of oxygen and water-vapour being included or by-passed as appropriate. Suitable absorbent solutions were placed in the wash-bottles and the filament current was switched on and adjusted until the filament was at the desired temperature. After *ca.* 15 min, when steady flow conditions had been obtained, the effluent gases were passed through the appropriate absorbent solutions, aliquots of which were periodically extracted and analyzed. The following analytical procedures were used.

(i) CYANOGEN AND HYDROGEN CYANIDE.—Cyanogen is the principal product of the reaction between carbon and nitrogen, although previously,[4] appreciable amounts of hydrogen cyanide were also detected. To separate the two possible products, use was made of the fact that hydrogen cyanide, but not cyanogen, reacts with silver nitrate to form silver cyanide,[7] whereas both compounds are converted to cyanide ion on reaction with dilute alkali. Thus, if the effluent gas stream is allowed to flow for a given time through two wash-bottles in series containing in turn acidified 0·1 N $AgNO_3$ and 0·1 N NaOH solutions and then for a further given time through a single wash-bottle containing 0·1 N NaOH solution, the hydrogen cyanide and cyanogen can be separately determined.

The concentration of cyanide ion in the absorbent alkali solution was determined by conversion to cyanogen chloride with chloramine-T and subsequent reaction with a mixture of mono- and bis-pyrazolones.[8, 9] The extinction coefficient of the resulting blue dye was measured at a wavelength of 6320 Å in a Unicam SP 500 spectrophotometer, and as little as 0·1 μg of cyanide per ml of solution could be determined.

OXYGEN.—The concentration of oxygen introduced into the nitrogen stream was determined by means of a Hersch cell.[10] In order to carry out a determination, the cell was flushed with the gas to be analyzed by several evacuation-admission cycles and the cathode and anode were then connected across a 100-ohm resistance, the potential across which was measured at intervals by means of a thermocouple potentiometer. The amount of oxygen present was calculated from the area under the resulting discharge current-time curves.

WATER VAPOUR.—Water vapour was condensed out of the nitrogen stream by passage through a trap immersed in liquid nitrogen. The contents of the trap were dissolved in a known amount of anhydrous acetone and the water content of the resulting solution was determined by allowing a measured volume to react with acetyl chloride and pyridine and back-titrating the acetic acid formed with standard alkali.[11]

STATIC SYSTEM

A static system was used to study the reaction at low pressures. Purified nitrogen was admitted to a reaction vessel containing a carbon filament which could be heated electrically. The reaction products formed were condensed out and their pressure was subsequently measured.

The reaction vessel (fig. 2) consisted essentially of a 1-l. Pyrex flask with a narrow appendix extending from the base and a wide ground-glass cone sealed to the top. The vessel was made vacuum-tight by attachment of a ground-glass socket, through the closed end of which were sealed two tungsten electrodes. The ends of the electrodes were attached to carbon blocks. A carbon filament, made of non-graphitic extruded cellulose and 56 mm long and 0·25 mm diam. was clamped at each of its ends between the main carbon blocks and two smaller carbon blocks. In order to avoid the production of glow discharge at the relatively low gas pressures employed, the filament was heated by direct current from the 230-V d.c. mains.

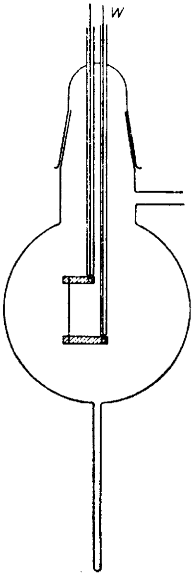

FIG. 2.—The static system reaction vessel.

Before a series of runs was started, the carbon filament was outgassed for 2 h at 2000°C under vacuum. Then before any given run, the system was evacuated and the reaction vessel appendix was immersed in liquid oxygen. Nitrogen was admitted to the reaction vessel to the desired pressure and the filament current was switched on for a given length of time. After the reaction vessel had cooled to room temperature and all the products had diffused into the appendix, the residual nitrogen was pumped off and the condensed products were allowed to warm up to room temperature, the pressure developed being measured by means of a McLeod gauge. Blank runs were carried out to ensure that there was no condensable material either present initially in the nitrogen or evolved from the filament and supports when they were heated under vacuum. All experiments in the static system were carried out at a single temperature, viz., 2000°C.

RESULTS

FLOW SYSTEM

NATURE OF THE PRODUCTS.—Since most carbons contain small amounts of hydrogen, two possible products, cyanogen and hydrogen cyanide, may be formed in the carbon-nitrogen reaction. The analytical procedures employed show, however, that, with both the graphites used, cyanogen is the sole product over the whole range of experimental conditions investigated.

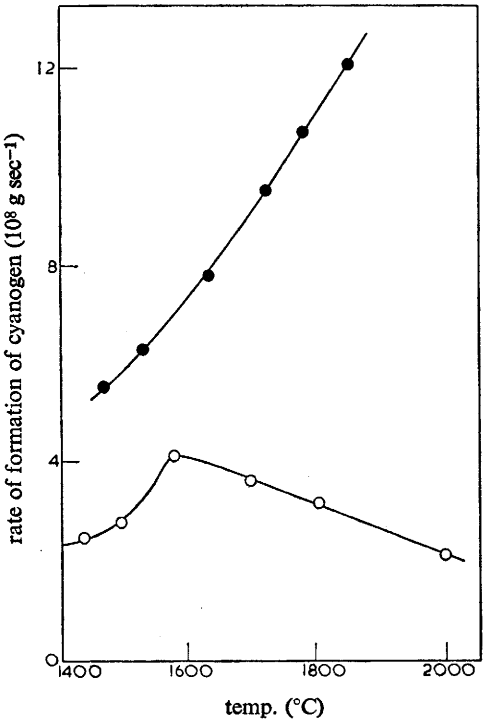

FIG. 3.—The influence of temperature on the rate of formation of cyanogen.
○, EY 9A graphite filament; ●, pile-grade A graphite filament.

INFLUENCE OF GAS FLOW RATE.—The rate of formation of cyanogen at a given filament temperature (deduced from the slopes of plots of cyanogen formed against time) increases with nitrogen flow rate from 3 to 6 ml sec^{-1} but at higher values (6-10 ml sec^{-1}) becomes independent of the gas flow. Presumably at the lower flow rates equilibrium tends to be set up and some of the cyanogen formed decomposes again into its elements, whereas at the higher flow rates, such decomposition is prevented by the rapid removal of the products from the reaction zone. In all subsequent experiments, therefore, the gas flow was kept constant at 7 ml sec^{-1}.

INFLUENCE OF TEMPERATURE.—Rates of formation of cyanogen were measured at filament temperatures from 1400 to 2000°C. The earliest runs with a given filament gave abnormally high and generally rather random rates of reaction but subsequent runs (after *ca.* 50 h of heating of the filament) gave more reproducible results. The observed variation of rate with temperature for fully acclimatized filaments is shown in fig. 3. With EY 9A graphite the rate increases with temperature up to 1600°C but thereafter decreases rapidly. The rate of reaction of pile grade A graphite increases continuously between 1500 and 1800°C; it was not practicable to study the reaction of this graphite at higher temperatures owing to the low electrical resistance of the only available filament of this material. According to the results shown in fig. 3, pile-grade A graphite is apparently more re-reactive than EY 9A graphite in the temperature range investigated and only with the latter does the rate pass through a maximum with increasing temperature. No hysteresis effect was observed with either graphite.

INFLUENCE OF OXYGEN.—The effects were determined of small amounts of oxygen on the rate of formation of cyanogen. In all cases investigated, oxygen exerts a marked retarding effect on the carbon-nitrogen reaction. Some typical results are shown in fig. 4.

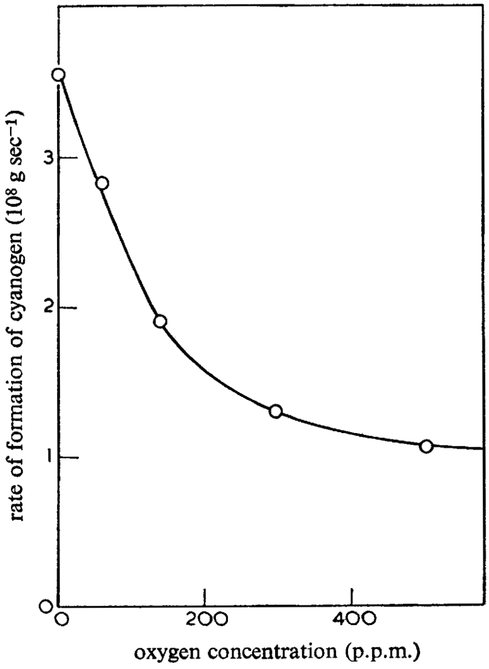

FIG. 4.—The influence of oxygen concentration on the rate of formation of cyanogen. EY 9A graphite filament; temp. 1700°C.

INFLUENCE OF WATER VAPOUR.—Although it was only possible to determine quantitatively the total CN-containing products formed in the presence of added water vapour, qualitative analysis indicates that some hydrogen cyanide is formed as well as cyanogen. The typical results in table 2 show that small additions of water vapour increase the total rate of formation of species containing the CN grouping.

TABLE 2.—THE INFLUENCE OF ADDED WATER VAPOUR ON THE RATE OF REACTION OF PILE-GRADE A GRAPHITE AT 1630°C

% volume of water vapour	rate of reaction (10^8 g CN^- sec^{-1})
0	15·6
0·32	21·2
0·70	33·2

STATIC SYSTEM

INFLUENCE OF NITROGEN PRESSURE.—The rate of formation of cyanogen (the sole product detected) was measured as a function of the nitrogen pressure. The results in fig. 5 show that the rate increases linearly with the pressure of the reacting gas. Such behaviour is characteristic of heterogeneous reactions in which a single gas is weakly absorbed on the surface of a solid. From the data in fig. 5 the first-order velocity constant under the conditions used is $1{\cdot}11 \times 10^{-7}$ sec^{-1} at 2000°C.

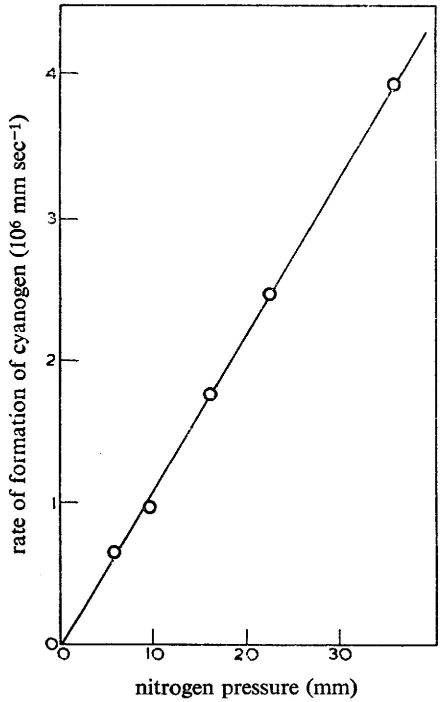

FIG. 5.—The influence of nitrogen pressure on the rate of formation of cyanogen. Extruded cellulose filament; temp. 2000°C.

DISCUSSION

The results obtained show that carbon reacts with nitrogen at an appreciable rate at temperatures considerably lower than the minimum reaction temperatures found by previous workers.[4] One striking similarity of the carbon-nitrogen reaction to other carbon gas reactions [12-15] is the maximum in the rate-temperature curve for EY 9A graphite (fig. 3). Previously, this maximum has been attributed to deactivation of the surface at high temperatures [16-18] and this factor probably also plays some part in the carbon-nitrogen reaction. Thus, above 1600°C the rate of healing of the active centres becomes greater than the rate of the gasification process so that the rate of reaction decreases. The very high rates observed with new filaments is no doubt due to the preferential attack by nitrogen at non-graphitic centres. These centres will be more reactive than less defective areas but will eventually be removed, as cyanogen, leaving a more perfectly crystalline surface of diminished reactivity.

The apparently higher rates of reaction with pile-grade A graphite (fig. 3) are probably due to its greater surface area. Thus the measured heated geometric areas of the pile-grade A and EY 9A graphite filaments used are 91·0 and 34·5 cm² respectively. The true surface areas are very much greater than this. Surface area measurements by the B.E.T. method can be carried out at low temperatures but the results are of doubtful significance when applied to solids undergoing gasification at high temperatures. The geometric surface areas are probably in these circumstances just as reliable, and if account is taken of the different values for the two filaments used, there does not appear to be much difference between the reactivities towards nitrogen of pile grade A and EY 9A graphites.

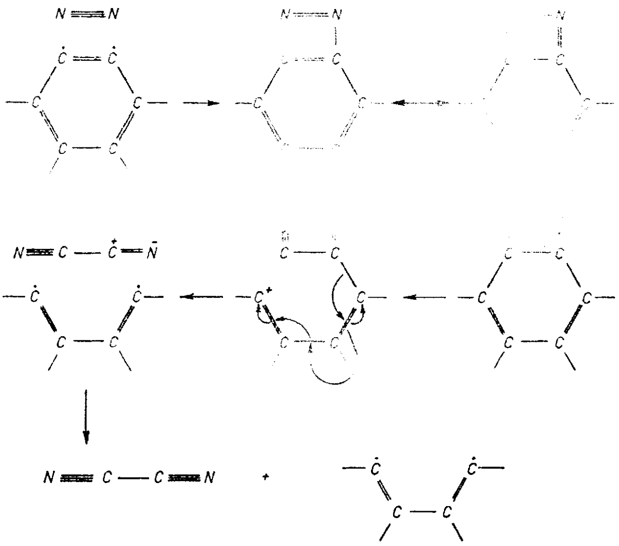

FIG. 6.—A suggested mechanism for the reaction of carbon with nitrogen.

The first-order kinetic behaviour observed at low gas pressures (fig. 5) suggests that nitrogen is only weakly adsorbed by carbon at high temperatures and that the rate of reaction is controlled either by the rate of adsorption of gas molecules or by the rate of interaction in the adsorbed layer. The precise nature of the active centres at which adsorption occurs is not known but most of the results can be accounted for if it is assumed that these centres possess a free-radical structure and that their concentration on the surface is relatively low. Such structures are likely to be situated at the edges of crystallites, having been formed as a result of the removal of foreign atoms from the surface during the initial degassing process and would be expected to constitute highly active centres for a gasification reaction.

The presence of a species, such as oxygen, would tend to retard the reaction with nitrogen, since oxygen, in view of its electronic structure, would be preferentially adsorbed at such free radical centres. This would account for the observed marked decrease in rate in the presence of small amounts of oxygen (fig. 4). On the other hand, addition of water vapour would accelerate the reaction due to the creation, as a result of the carbon-water vapour reaction, of an increased number of centres at which adsorption of nitrogen can take place. Such a suggestion is consistent with the large-scale disintegration of the graphite structure which takes place after a run with water vapour present and which leads to the surface of the graphite filament, which is normally a lustrou grey colour, appearing black and " sooty ".

Thus the carbon-nitrogen may perhaps be envisaged as occurring via the stages shown in fig. 6. The rate-determining step is the adsorption of nitrogen on two adjacent carbon atoms each having a free electron. The resulting adsorption complex can have a number of resonance structures and the fission of the bond between the two nitrogen atoms will be brought about by the transfer of electrons to the adsorbate from the graphite layer plane. The latter possesses a benzenoid structure which facilitates such transfer processes. Thus, once the nitrogen has been adsorbed, cyanogen is rapidly formed and volatilizes leaving the carbon surface with two free electrons and a structure essentially similar to that which it possessed before reaction.

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