# CCCLVII.—*The Combustion of Charcoal in Oxygen, Nitric Oxide, and Nitrous Oxide. Part II. The Effect of Temperature.*

By MADHAVLAL SUKHLAL SHAH.

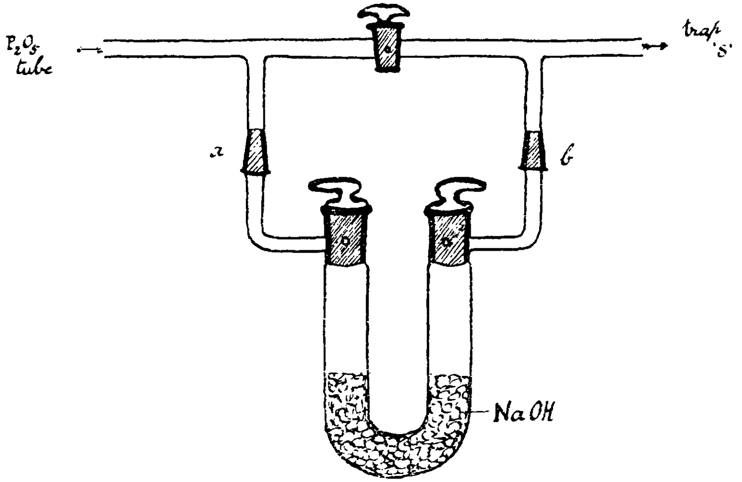
IN the preceding paper the author has shown that the combustion of charcoal in oxygen, nitric oxide, and nitrous oxide depends upon the fixation of oxygen in charcoal. Attempts are now described (*a*) to obtain further information about the flame combustion of charcoal in oxygen and nitrous oxide, and (*b*) to find an explanation for its flameless combustion in nitric oxide. As in the previous investigation, pure sugar charcoal and purified gases were used. The recorded volumes of gases are reduced to 0° and atmospheric pressure.

## *Section A. The Decomposition of Nitrous Oxide.*

The thermal decomposition of nitrous oxide has been found to be bimolecular by Hunter (*Z. physikal. Chem.*, 1905, **53**, 441), Hinshelwood and Burk (*Proc. Roy. Soc.*, 1924, **106**, 284), and by Briner, Meiner and Rothen (*Helv. Chim. Acta*, 1926, **9**, 409); the reaction is $2N_2O \longrightarrow 2N_2 + O_2$ (I). Moreover, the last-named workers found that nitrous oxide in a rapid stream and above 700° gives nitric oxide: $2N_2O \longrightarrow N_2 + 2NO \longrightarrow 2N_2 + O_2$ (II); in presence of quartz or platinum the amount of nitric oxide was greatly reduced. Richardson and Woodhouse (*J. Amer. Chem. Soc.*, 1923, **45**, 2638) showed that charcoal was not oxidised in a mixture of carbon dioxide and nitrous oxide at 425°, and the author, having found (preceding paper, p. 2667) by using the streaming method that the evolution of nitrogen and carbon monoxide and dioxide from charcoal and nitrous oxide commences at about 460—470°, thought that the decomposition of nitrous oxide was a thermal effect and that surface action had little or no influence on it. He now finds, however, from experiments on the decomposition of nitrous oxide in a silica vessel either in absence or in presence of charcoal, that the decomposition is a surface effect, that the oxidation of charcoal is perceptible even at 300—350°, and that various other substances promote the decomposition, thoria being more active than charcoal.

*Procedure.*—In the initial experiments the reaction was studied in a closed system partly by a manometric method. The change in pressure was found to correspond with a bimolecular change only when the charcoal had been previously digested with nitrous oxide at the temperature of the experiment. The manometric method, however, is inadequate, for the change in pressure is the effect of several simultaneous reactions, including fixation of gas in charcoal; hence the gases produced were analysed and the charcoal was carefully examined.

FIG. 1.



The apparatus and experimental method were the same as described in the preceding paper (Fig. 7), the manometric connexion *M* being included : change in pressure (cm. of mercury) was noted at intervals of 5 minutes. Two series of experiments were conducted. Charcoal, previously exhausted at 1100°, was allowed to react with nitrous oxide which was admitted always at atmospheric pressure, and the reaction was arrested at the end of one hour by using liquid air to solidify carbon dioxide and unchanged nitrous oxide in the trap, *S*; the pressure of the uncondensed gases, nitrogen and carbon monoxide, gave an indication of the extent to which the reaction had occurred.

Blank experiments were made to test the effect of the silica vessel on the thermal decomposition of nitrous oxide. According to Briner, Meiner, and Rothen (*loc. cit.*) there was a risk of formation of nitric oxide which might lead to nitrogen peroxide. This was tested for as follows. The arrangement shown in Fig. 1 was inserted between the phosphoric oxide tube and the trap *S* of the apparatus. The U-tube, which was detachable at the ground joints *a* and *b*, contained coarsely powdered, moist sodium hydroxide for absorbing nitrogen peroxide (Barnes, *J. Soc. Chem. Ind.*, 1926, **45**, 259T). The tube was evacuated and weighed before and after the experiment, but no increase in weight was found and no nitrite could be detected, hence no peroxide was formed.

TABLE I.

*The decomposition of nitrous oxide in a silica vessel.*

| Temp. of expt. | $N_2O$ admitted, c.c. | Increase in press., after 1 hour. | Gas removed, c.c. | Composition of gas. | | | % $N_2O$ decomp. |
|---|---|---|---|---|---|---|---|
| | | | | $N_2O$. | $N_2$. | $O_2$. | |
| 500° | 28·4 | 0·2 | 28·6 | 28·2 | 0·2 | 0·2 | 0·70 |
| 550 | 26·4 | 2·1 | 26·9 | 25·7 | 0·9 | 0·3 | 3·38 |
| 600 | 25·4 | 7·0 | 27·2 | 22·4 | 3·2 | 1·6 | 12·10 |
| 625 | 24·0 | 7·0 | 27·1 | 19·3 | 5·0 | 2·2 | 20·58 |
| 650 | 24·6 | 19·0 | 31·0 | 12·0 | 13·0 | 5·0 | 52·00 |
| 675 | 23·8 | 24·0 | 30·9 | 7·9 | 15·6 | 7·4 | 66·38 |
| 700 | 22·8 | 33·0 | 31·9 | 3·4 | 19·6 | 8·9 | 85·21 |
| 750 | 20·9 | 32·0 | 30·0 | 0·8 | 20·0 | 9·5 | 96·15 |

The data given in Table I show that in absence of charcoal the decomposition of nitrous oxide in a silica vessel is slow at 500° but rapid at 700°. The results of similar experiments in the presence of charcoal are given in Table II and, together with those of Table I,

TABLE II.

*The decomposition of nitrous oxide in a silica vessel, charcoal* (5 g.) *being present.*

(i) Products removed at temperature of decomposition, *t*°.

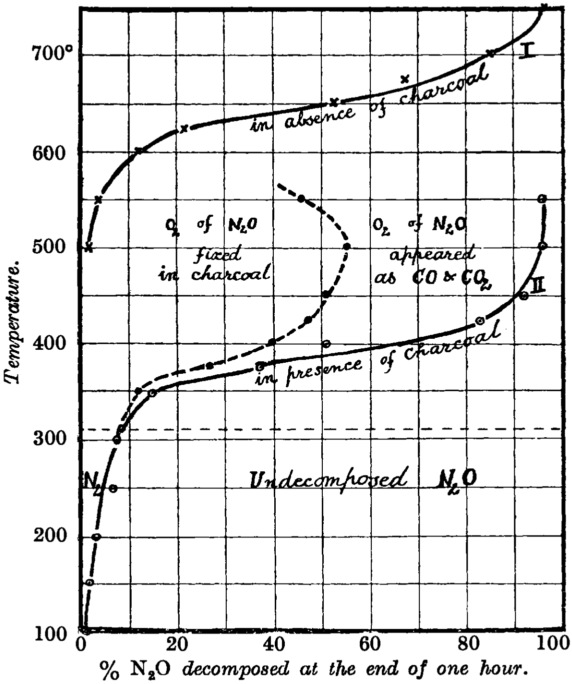
| Temp., *t*°. | $N_2O$ admitted, c.c. | Press. increase in 1 hr., cm. | Composition of gas removed at *t*°, c.c. | | | | | % $N_2O$ decomp.* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $CO_2$ | CO. | $N_2O$. | $N_2$. | Total. | To CO, $CO_2$, & $N_2$. | To $N_2$ & $O_2$. | Total. |
| 100° | 150·0 | — | — | — | 150·2 | 0·3 | 150·5 | — | 0·2 | 0·2 |
| 150 | 95·0 | — | — | — | 94·6 | 0·6 | 95·2 | — | 0·6 | 0·6 |
| 200 | 61·0 | — | — | — | 59·4 | 1·8 | 61·2 | — | 2·9 | 2·9 |
| 250 | 53·0 | — | — | — | 49·2 | 3·4 | 52·6 | — | 6·5 | 6·5 |
| 300 | 44·2 | — | — | — | 41·0 | 3·3 | 44·3 | — | 7·5 | 7·5 |
| 350 | 41·5 | — | 0·7 | — | 35·4 | 6·0 | 42·1 | 3·4 | 11·1 | 14·5 |
| 375 | 35·0 | 0·6 | 1·9 | — | 21·6 | 13·0 | 36·5 | 11·0 | 26·6 | 37·6 |
| 400 | 33·0 | 5·5 | 3·5 | — | 13·2 | 19·9 | 36·6 | 21·4 | 39·2 | 60·6 |
| 425 | 31·0 | 12·0 | 5·1 | 1·0 | 5·3 | 26·0 | 37·3 | 35·9 | 47·5 | 83·4 |
| 450 | 30·0 | 13·0 | 5·6 | 1·1 | 2·4 | 27·7 | 36·8 | 40·8 | 51·2 | 92·0 |
| 500 | 28·6 | 18·0 | 5·7 | 1·1 | 1·3 | 26·9 | 34·9 | 44·3 | 50·8 | 95·1 |
| 550 | 26·0 | 15·0 | 6·3 | 0·8 | 1·3 | 24·8 | 33·2 | 51·3 | 43·7 | 95·0 |

* The oxygen produced in the second method of decomposition remains fixed in the charcoal.

(ii) Products removed between $t°$ and 900°.

| Temp. of expt., $t°$. | Comp. of gas removed between $t°$ and 900°, c.c. | | | | % of original $N_2O$ of which oxygen appears as CO + $CO_2$ at 900°. |
|---|---|---|---|---|---|
| | $CO_2$. | CO. | $N_2$. | Total. | |
| 100° | — | 0·4 | 0·4 | 0·8 | 0·2 |
| 150 | — | 0·6 | 0·4 | 1·0 | 0·6 |
| 200 | 0·3 | 0·9 | — | 1·2 | 2·5 |
| 250 | 0·2 | 2·1 | 0·1 | 2·4 | 4·8 |
| 300 | 0·2 | 2·1 | 0·1 | 2·4 | 5·7 |
| 350 | 0·2 | 3·3 | 0·1 | 3·6 | 8·9 |
| 375 | 0·2 | 9·4 | 0·4 | 10·0 | 25·4 |
| 400 | 0·1 | 11·3 | 0·4 | 11·8 | 34·8 |
| 425 | 0·1 | 13·7 | 0·4 | 14·4 | 44·6 |
| 450 | 0·15 | 13·0 | 0·3 | 13·4 | 43·6 |
| 500 | 0·1 | 10·6 | 0·2 | 10·9 | 41·6 |
| 550 | 0·1 | 7·1 | 0·3 | 7·5 | 28·5 |

FIG. 2.



are plotted in Fig. 2. The two series of experiments lead to the following conclusions.

(1) The reaction between charcoal and nitrous oxide begins with the fixation of oxygen, which is small at low temperatures and increases rapidly as the temperature is raised.

(2) The quantity of nitrogen produced at each temperature is a

measure of the nitrous oxide decomposed. Up to 300°, the corresponding amount of oxygen is fixed in charcoal and the evolution of oxides of carbon is not observed. Richardson and Woodhouse (*loc. cit.*) failed to detect the primary stage of this reaction below 425° because (*a*) their charcoal had been exhausted at 450°; (*b*) the nitrous oxide was taken from a cylinder without further purification; (*c*) the production of carbon dioxide was used as the test for the oxidation of charcoal.

(3) Above 300°, oxygen begins to appear as oxides of carbon, the velocity of the reaction increasing rapidly with rise of temperature.

(4) The amount of carbon monoxide produced is small and fairly constant, but that of dioxide steadily increases, thus indicating that the monoxide first formed is subsequently oxidised.

(5) In Fig. 2 the broken-line curve shows that the amount of oxygen fixed in charcoal gradually increases with rise in temperature, reaches a maximum at 500°, and then diminishes; thus a distinct change occurs in the surface of the charcoal above 500°.

(6) The portion lying between this curve and the decomposition curve shows the quantity of oxygen which appears as oxides of carbon; if the dotted curve is prolonged it is found to meet the temperature axis at about 700°, whereas flame is first observed at 710°.

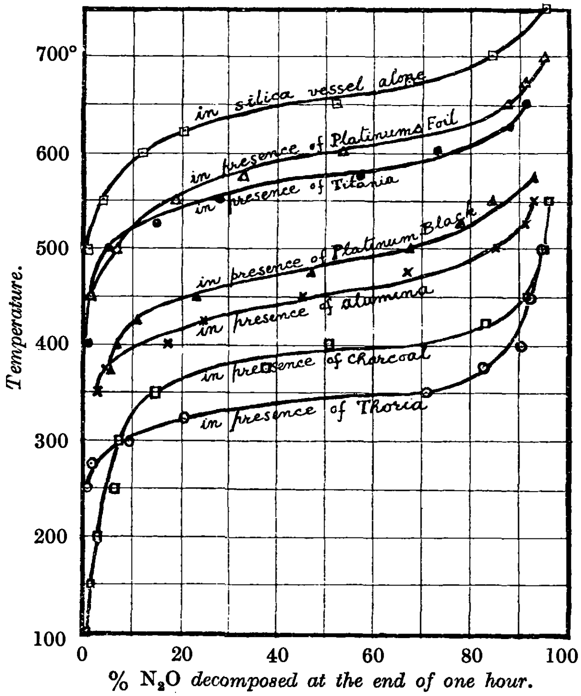
(7) Curves I and II are similar: the presence of charcoal lowers the temperature of decomposition of nitrous oxide in a silica vessel by about 250°.

*The Decomposition of Nitrous Oxide in Presence of Various Catalysts.*—On the suggestion of Professor H. B. Baker, F.R.S., a study was made of the effect of various catalysts, *viz.*, thoria, alumina, titania, platinum foil, and platinum-black. The alumina and titania were obtained from Messrs. Hopkin and Williams, and the thoria from Kahlbaum. Platinum-black was prepared according to Loew's method (*Ber.*, 1890, **23**, 289). 5 G. of the catalyst were used in each case excepting that of platinum-black, of which only 2 g. were used. Before each experiment the catalyst was heated to 1000° in the silica tube and exhausted completely by means of the Sprengel pump.

In experiments on the combustion of a mixture of hydrogen and nitrous oxide (*Chem. News*, 1909, **99**, 125), Baker had found that the mixture did not react ordinarily at 530° in a Jena-glass tube, and that a similar gas mixture reacted without explosion in presence of thoria and with explosion in presence of radium bromide. It is now found that thoria decomposes nitrous oxide, the mechanism being a surface effect.

The apparatus and procedure were as described above, unchanged nitrous oxide being removed after 1 hour by means of liquid air, and other gases analysed. The catalyst was finally heated to 1000° and in no case was any gas evolved. The percentage of nitrous oxide decomposed in each case, including that of charcoal, is represented in Fig. 3; the curves bear a general resemblance to one another, and thoria is seen to be the most effective catalyst and silica the least. The inference can be drawn that thoria promotes the reaction between hydrogen and nitrous oxide in Baker's experiments (*loc. cit.*), for it brings about the decomposition of the latter gas at a low temperature.

FIG. 3.



### *Section B. The Reaction between Charcoal and Nitrous Oxide.*

With a view to confirm the rôle played by fixed oxygen in the reaction, and in order to obtain further information as to the products of the reaction, experiments were conducted with a larger volume of nitrous oxide than had been possible in one operation in the small silica tube. Charcoal and nitrous oxide were allowed to react at

470° as before, and after complete evacuation, the treatment with nitrous oxide was repeated. Three series of experiments were performed: in series I the treatment was carried out 5 times, and in II and III, 10 and 15 times, respectively. Then, after evacuation at 470°, the temperature of the furnace was raised to 600°, 750°, and 900—950°, the gas being removed at each stage by the Sprengel pump and analysed.

Similar experiments were performed with charcoal and (*a*) carbon monoxide and (*b*) carbon dioxide, but no gas was evolved when the temperature was raised. The charcoal that had been treated at 470° with nitrous oxide, but not those treated with carbon monoxide and dioxide, yielded gases at higher temperatures.

The results are exemplified by the longest series (III), shown in Table III. For instance, in Expt. 10, charcoal, which had been treated with nitrous oxide and exhausted at 470° in nine successive experiments, was allowed to react with nitrous oxide (32·8 c.c.) in the silica bulb. During 1 hour, the oxygen of 44·1% of this nitrous

### TABLE III.

*The repeated treatment of charcoal with nitrous oxide.*

*Series III.*

A. The reaction at 470°.

| Expt. No. | $N_2O$ admitted, c.c. | Composition of gas evolved at 470°, c.c. | | | | | % $N_2O$ decomposed.* | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $CO_2$. | CO. | $N_2O$. | $N_2$. | Total. | To $N_2$ & $O_2$. | To $N_2$, CO, & $CO_2$. | Total. |
| 1 | 31·6 | 6·4 | 1·4 | 2·6 | 29·3 | 39·7 | 47·4 | 44·5 | 91·9 |
| 2 | 31·8 | 7·7 | 1·6 | 3·7 | 28·2 | 41·2 | 35·2 | 53·2 | 88·4 |
| 3 | 31·6 | 7·7 | 1·9 | 6·1 | 25·4 | 41·1 | 24·7 | 55·9 | 80·6 |
| 4 | 31·7 | 6·9 | 1·6 | 7·0 | 24·8 | 40·3 | 29·6 | 48·4 | 78·0 |
| 5 | 32·9 | 6·4 | 1·5 | 9·0 | 24·2 | 41·1 | 29·6 | 43·0 | 72·9 |
| 6 | 32·8 | 6·5 | 2·0 | 10·1 | 23·6 | 42·2 | 25·3 | 44·7 | 70·0 |
| 7 | 32·8 | 6·5 | 1·5 | 10·3 | 22·2 | 40·5 | 24·1 | 45·2 | 69·3 |
| 8 | 32·5 | 6·4 | 1·4 | 10·2 | 22·4 | 40·4 | 25·5 | 44·2 | 69·7 |
| 9 | 32·9 | 6·6 | 1·4 | 10·8 | 22·3 | 41·1 | 23·3 | 44·1 | 67·4 |
| 10 | 32·8 | 6·4 | 1·7 | 10·8 | 22·3 | 41·2 | 23·3 | 44·1 | 67·4 |
| 11 | 33·0 | 7·1 | 1·6 | 10·9 | 22·4 | 42·0 | 19·8 | 47·5 | 67·3 |
| 12 | 32·7 | 7·0 | 1·7 | 11·0 | 22·2 | 41·9 | 19·6 | 47·2 | 66·8 |
| 13 | 33·3 | 6·8 | 1·9 | 11·0 | 22·7 | 42·4 | 21·1 | 46·2 | 67·4 |
| 14 | 33·5 | 7·0 | 1·6 | 11·8 | 22·3 | 42·7 | 19·7 | 47·7 | 65·4 |
| 15 | 33·6 | 7·3 | 1·6 | 10·8 | 22·8 | 42·5 | 19·6 | 48·2 | 67·8 |

* The oxygen produced in the first method of decomposition is retained by the charcoal.

B. The gas collected at 600°, 750°, and 900—950°.

| Temp. | Composition of gas evolved, c.c. | | | | |
|---|---|---|---|---|---|
| | $CO_2$. | CO. | $N_2O$. | $N_2$. | Total. |
| 600° | 13·2 | 12·0 | — | 0·2 | 25·4 |
| 750 | 2·9 | 27·7 | — | 0·4 | 31·0 |
| 900—950 | 0·0 | 11·6 | — | 2·0 | 13·6 |

oxide appeared as carbon monoxide and dioxide, and that of 23·3% remained fixed in charcoal and was only partially liberated as carbon monoxide and dioxide when the charcoal was heated to higher temperatures.

Thus, the results of the repeated treatment of charcoal with nitrous oxide may be summarised as follows. (i) The fraction of nitrous oxide decomposed diminishes progressively at first and approaches constancy after about five treatments. (ii) The *fraction* of oxygen fixed in charcoal in each successive experiment also diminishes steadily until it attains a constant value (about 20%); the *total* amount of oxygen thus fixed, however, increases with successive treatments. (iii) The capacity of charcoal for fixing oxygen increases continuously, for it is still pronounced in the fifteenth experiment, although carbon dioxide and monoxide had been evolved in quantity and the charcoal had already fixed a large amount of oxygen in earlier experiments. This shows, incidentally, that carbon dioxide and monoxide are actually evolved before the saturation capacity of charcoal is reached. (iv) The amount of carbon monoxide produced in these experiments at 470° is constant and small, whereas that of the dioxide is constant and large. Moreover, the composition of the gas evolved when the charcoal is heated in a vacuum confirms the previous conclusion that the reaction proceeds with the evolution of nitrogen and the fixation of oxygen, just as in the reaction between charcoal and oxygen or nitric oxide. A similar retention of gas is not observed in the repeated treatment of charcoal with carbon monoxide and dioxide.

### *Section C. The Spectroscopic Examination of* (a) *Charcoal and* (b) *Carbon Monoxide burning in Nitrous Oxide*

(with R. H. PURCELL).

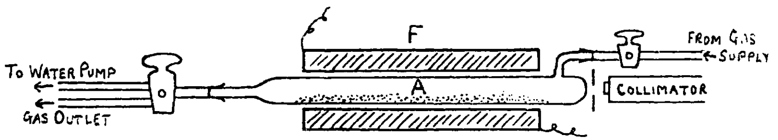
The flame spectra of carbon monoxide when burning in air, in oxygen, and in nitrous oxide were examined by Smithells (*Phil. Mag.*, 1901, vi, **1**, 476), who recorded a continuous spectrum, and by Weston (*Proc. Roy. Soc.*, 1925, **109**, 176), who showed that in the flame of undried carbon monoxide, two sets of independent reactions occur simultaneously, *viz.*, (i) direct interactions between carbon monoxide and oxygen, which give rise to continuous and banded parts of the spectrum; and (ii) interactions between carbon monoxide and water which produce the steam lines in the spectrum.

The present work was carried out mainly to ascertain if the flame combustion of charcoal in oxygen and nitrous oxide consists in the oxidation of carbon monoxide. The flashes obtained in the combustion of (*a*) charcoal and (*b*) carbon monoxide in nitrous oxide have been photographed on a small Hilger quartz spectrograph. The apparatus is shown in Fig. 4. A diaphragm was used in front of the slit to enable comparison spectra to be taken and a copper arc was used for reference purposes.

(a) *Charcoal in Nitrous Oxide.*—Charcoal, obtained from recrystallised sucrose, was strongly ignited in a silica dish. The silica tube was heated electrically and maintained at 700—750°. Nitrous oxide was then admitted from the gas cylinder through a water bubbler and its flow regulated under reduced pressure by means of the water pump until the flashes occurred intermittently. Plate I shows an enlargement obtained from a 6-hours' exposure.

(b) *Carbon Monoxide in Nitrous Oxide.*—Nitrous oxide and carbon monoxide were collected over water in separate reservoirs and mixed before admission to the silica tube maintained at 750°. The proportion of each gas in the mixture was carefully adjusted and the pressure regulated by means of the water pump so that intermittent flashes were steadily produced. Plate II corresponds to an exposure of 4 hours.

FIG. 4.



These photographs show that the spectra of charcoal and of carbon monoxide burning in nitrous oxide are similar, and since they resemble those obtained from the carbon monoxide flame in oxygen, air, and nitrous oxide, it is highly probable that the flame combustion of charcoal consists in the oxidation of carbon monoxide.

The observations recorded in this and in the previous paper taken together lead to the following explanation of the mechanism of reaction between charcoal and nitrous oxide.

The first stage is the evolution of nitrogen and the fixation of oxygen in charcoal. This fixation may be assumed to be due to the formation of the complex $C_xO_y$, suggested by Rhead and Wheeler (J., 1913, **103**, 461) :

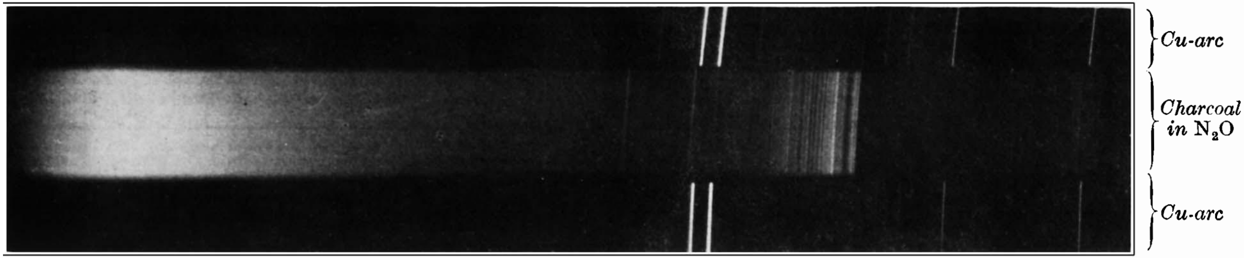
$$xC + yN_2O \longrightarrow C_xO_y + yN_2 \quad . \quad . \quad . \quad . \quad \text{(i)}$$

The complex then decomposes with the production of carbon monoxide and dioxide :

$$C_xO_y \longrightarrow uCO + vCO_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

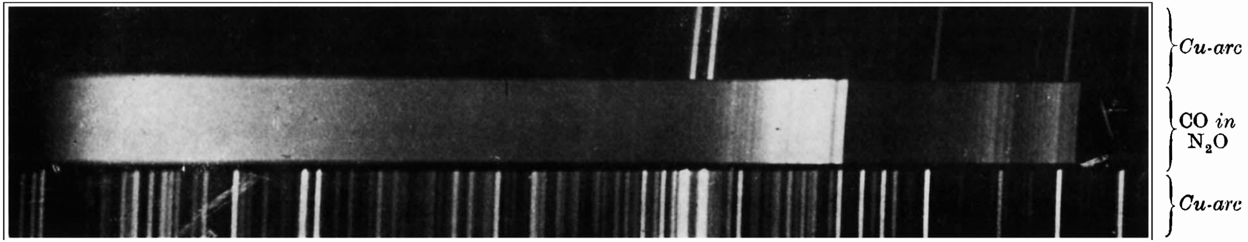
A fresh surface is thus exposed so that more nitrous oxide can be continuously decomposed. Reaction (ii) is accompanied by the subsequent oxidation of carbon monoxide in the gaseous phase.

PLATE I.



(A) *Charcoal in nitrous oxide.*

PLATE II.



(B) *Carbon monoxide in nitrous oxide.*

[*To face p.* 2684.]

When the temperature of reaction has greatly increased, more nitrous oxide is decomposed: the resulting oxygen forms the complex and oxidises carbon monoxide. At 710°, when these reactions proceed rapidly, charcoal burns with the production of a flame owing to the rapid escape of carbon monoxide from the surface of charcoal and its subsequent oxidation in the gaseous state. It is suggested that the blue phosphorescence observed in a slow stream of nitrous oxide above 540° (see preceding paper, p. 2667) is due to the slow oxidation of carbon monoxide.

### *Section D. The Reaction between Charcoal and* (a) *Oxygen at* −190° *and* −78°, *and* (b) *Nitric Oxide at Various Temperatures.*

(a) *The Reaction between Charcoal and Oxygen.*—Two series of experiments were conducted at −190° and −78° mainly to find whether oxygen is fixed by charcoal at low temperatures or not. The reaction was allowed to proceed for 1 hour with a limited amount of oxygen, but as this gas could not be pumped off at −190°, the temperature was raised to − 78° or to 0° whilst the 'Hyvac' pump was in operation. Evolution of oxygen from the charcoal was slow at −78°, but almost the whole of it was evolved within 2 hours at 0°. The connexion with this pump was then closed, the Sprengel pump was applied, and the temperature of the reaction vessel was gradually raised; no gas was evolved up to 500°, but between this and 600° a slight increase in pressure occurred. The temperature was therefore raised to 900° and the evolved gas collected and analysed:

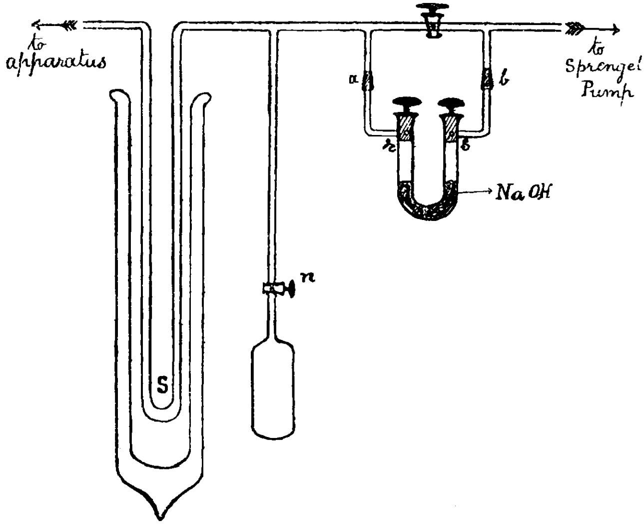
| | | | | |
|---|---|---|---|---|
| Oxygen admitted .................. | 535 c.c. at −190°. | | 522 c.c. at −78°. | |
| Gas evolved at 900° (c.c.) ...... | $CO_2$. | CO. | $CO_2$. | CO. |
| | 0·4 | 4·9 | 0·6 | 5·6 |

The tendency of charcoal to fix oxygen becomes very weak at these low temperatures, and it is highly probable that even these small amounts are fixed during the rise of temperature to 0°. Thus oxygen is not appreciably sorbed by charcoal below 0°.

(b) *The Reaction between Charcoal and Nitric Oxide.*—The present experiments, in continuation of those described in the preceding paper, were carried out with a view to study the retention of nitric oxide by charcoal and also the flameless combustion of charcoal in this gas. In general there are two ways in which nitric oxide can be retained by charcoal: the charcoal may fix nitric oxide molecules upon its surface by means of chemical forces of attraction just as oxygen is retained, or the oxygen fixed in charcoal, as a result of chemical reaction between charcoal and nitric oxide, may still possess properties whereby it retains nitric oxide.

If the process depends upon the direct influence of charcoal, it may be expected that (i) the nitric oxide will be retained by charcoal at a temperature such that it is not reduced, and (ii) the quantity of nitric oxide fixed will not vary much below 125°, owing to the absence of such reactions as $2NO + O_2 = 2NO_2$, $NO + NO_2 = N_2O_3$, or $NO_2 + NO_2 = N_2O_4$. If, on the contrary, an intermediate layer of oxygen produced by reduction of nitric oxide is responsible for its retention, the results will be that (i) the nitric oxide will not be fixed at a temperature where it is not reduced by charcoal; (ii) the amount of nitric oxide fixed will differ enormously at various temperatures because the above-mentioned concurrent reactions would proceed in the pores of charcoal; and (iii) the chemical forces of attraction between charcoal and oxygen might either grow weaker than those between oxygen and nitric oxide, with the result that nitrogen peroxide would be produced, or might grow stronger and result in the production of carbon dioxide.

FIG. 5.



In order to test which of the two explanations is in better agreement with the experimental facts, the reaction between charcoal and nitric oxide has been examined at various temperatures from −190° to 600°, and it was first proved that the surface of the silica vessel did not cause appreciable decomposition of the gas below 900°.

*Procedure.* The apparatus used was that described in Fig. 7 of the preceding paper. An alteration, to facilitate the estimation of nitrogen peroxide in the presence of carbon dioxide and nitric oxide, consisted of the insertion (see Fig. 5) on the pump side of the apparatus of a bulb with a tap *n* and of a U-tube containing sodium hydroxide.

Purified nitric oxide was admitted at barometric pressure, and the reaction with charcoal (5 g.), previously exhausted at 1100°, was allowed to proceed. At the end of 1 hour, the reaction was stopped by opening the tap *m* (Fig. 7, *loc. cit.*) and immersing the trap *S* in liquid air, which removed carbon dioxide and a considerable amount of nitric oxide. The charcoal was then evacuated for 2 hours, whereby nitrogen and such nitric oxide as remained in the gaseous state were collected. The temperature of the furnace was then raised and the gas that was fixed in charcoal was estimated from the analysis of the gas obtained on subsequent evacuation at 900°.

The presence of blue nitrogen trioxide in the liquid-air trap showed that nitrogen peroxide had been formed, but this was observed only in experiments where the temperature had been raised suddenly from −190° or −78° to 0° or 150°.

Two methods were tried for determining nitrogen trioxide: (1) The connexion with the bulb (Fig. 5) was opened and the condensed gas in *S* (*i.e.*, $N_2O_3$,$CO_2$, and NO) was transferred to the bulb by immersing it in liquid air; this was then replaced by a carbon dioxide–ether mixture, and carbon dioxide and nitric oxide were removed by pumping. At the end of the experiment, the bulb which contained the trioxide was disconnected, weighed, evacuated, and re-weighed, the difference giving the amount of nitrogen trioxide. (2) After the complete removal of nitrogen and nitric oxide, the U-tube containing coarsely powdered sodium hydroxide (Fig. 5) was left open for absorbing carbon dioxide and nitrogen trioxide. The taps *r* and *s* were closed and the increase in weight of the tube was noted. The carbonate and nitrite now contained in the alkali were estimated in the usual way by means of standard acid and permanganate.

Carbon dioxide in admixture with nitric oxide was estimated by absorption with potassium hydroxide, and nitric oxide in admixture with nitrogen by means of an alkaline solution of sodium sulphite, followed by ferrous sulphate treatment.

The results of one set of experiments are given in Table IV.

*Formation of Nitrogen Peroxide.*—The formation of nitrogen peroxide throws considerable light on the mechanism of adsorption and chemical reaction with nitric oxide, and the conditions determining it were therefore investigated. The reservoir *C* (Fig. 6) containing pure nitric oxide was connected through a sodium hydroxide tube to the apparatus at *k*. The apparatus was first of all evacuated, and the sugar charcoal (5 g.) contained in the silica tube was exhausted at 1100° for 4 hours by means of the Hyvac

## TABLE IV.

(i) *Experiments at* −190°, −78°, *and* 0°.

| Temp. of expt. ............... | −190°. | | | | | −78°. | | | | | 0°. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NO admitted ................. | 565 c.c. | | | | | 541 c.c. | | | | | 260 c.c. | | | | |
| | Composition of gas evolved, c.c. | | | | | Composition of gas evolved, c.c. | | | | | Composition of gas evolved, c.c. | | | | |
| Temp. of evacuation. | $CO_2$. | CO. | NO. | $N_2$. | Total. | $CO_2$. | CO. | NO. | $N_2$. | Total. | $CO_2$. | CO. | NO. | $N_2$. | Total. |
| −190° | — | — | — | — | Nil | — | — | — | — | — | — | — | — | — | — |
| − 78 | — | — | — | — | — | 2·7 | — | 8·2 | 103·8 | 114·7 | — | — | — | — | — |
| 0 | 4·1 | — | 328·3 | 80·3 | 412·7 | 4·1 | — | 125·3 | 7·2 | 136·6 | 2·4 | — | 23·0 | 63·0 | 88·4 |
| 150 | 19·8 | — | 49·8 | 7·2 | 86·8 | 52·1 | — | 108·6 | 14·2 | 174·9 | 20·7 | — | 85·3 | 6·5 | 112·5 |
| 450 | 17·9 | 8·4 | — | 3·0 | 29·3 | 24·5 | 8·6 | — | 4·0 | 37·1 | 21·3 | 6·7 | — | 3·0 | 31·0 |
| 900 | 12·0 | 67·6 | — | 0·6 | 80·2 | 14·6 | 61·8 | — | 6·8 | 83·2 | 9·2 | 47·7 | — | 13·3 | 70·2 |
| Total vol. of $NO_2$ as calc. from $N_2O_3 \longrightarrow NO_2+NO$ | 3·8 c.c. | | | | | 2·0 c.c. | | | | | Negligible. | | | | |

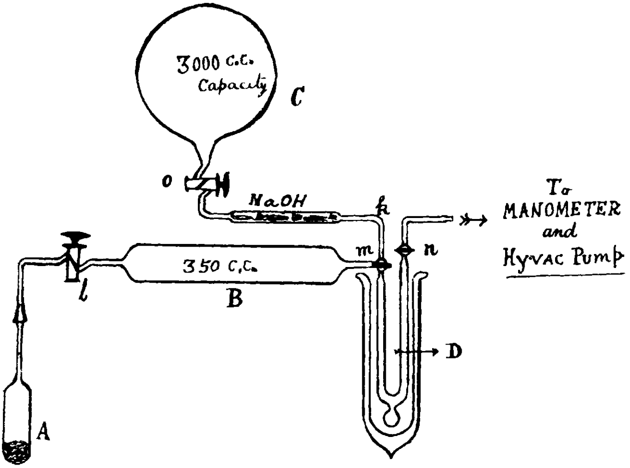
(ii) *Experiments at other temperatures.*

| Temp. of evacuation, $t$°. | NO admitted, c.c. | Composition of gas removed, c.c. | | | | | Composition of gas evolved between $t$° and 900°, c.c. | | | | | % NO decomp. | % NO retained at $t$° and evolved as NO, $CO_2$, CO, and $N_2$ at 900°. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CO_2$. | CO. | NO. | $N_2$. | Total. | $CO_2$. | CO. | NO. | $N_2$. | Total. | | |
| 50° | 116·0 | 1·8 | — | 15·1 | 37·7 | 54·6 | 27·3 | 27·3 | 12·0 | 7·3 | 73·9 | 65·0 | 23·7 |
| 100 | 82·6 | 10·4 | — | 9·5 | 28·6 | 52·5 | 14·2 | 21·3 | 2·4 | 6·4 | 48·3 | 69·8 | 18·5 |
| 150 | 68·0 | 8·7 | — | 4·0 | 26·7 | 44·4 | 12·3 | 21·5 | 0·9 | 5·0 | 39·7 | 78·5 | 16·3 |
| 200 | 58·4 | 5·3 | — | 2·4 | 23·9 | 34·1 | 9·0 | 23·1 | 1·1 | 3·0 | 41·2 | 81·8 | 12·2 |
| 300 | 47·8 | 6·1 | — | 3·1 | 20·0 | 30·2 | 5·2 | 22·0 | 0·4 | 2·0 | 33·4 | 83·7 | 9·2 |
| 400 | 37·8 | 8·9 | — | 1·6 | 16·3 | 26·8 | 3·0 | 11·5 | 0·0 | 2·7 | 17·4 | 86·2 | 14·3 |
| 500 | 34·4 | 6·5 | 0·2 | 0·3 | 15·0 | 22·0 | 2·5 | 12·6 | 0·3 | 2·6 | 17·4 | 87·7 | 12·5 |
| 600 | 26·0 | 9·0 | 1·2 | 0·0 | 11·4 | 20·6 | 0·6 | 6·6 | 0·0 | 1·6 | 8·8 | 87·2 | 12·3 |

pump. The taps *l*, *m*, and *n* were then closed and the tube *A* was allowed to cool. Nitric oxide was now admitted from the reservoir, *C*, to the bulb, *B*. Sodium hydroxide absorbed any traces of nitrogen peroxide. The taps, *m* and *o*, were closed, and the purity of the nitric oxide was tested by immersing the U-tube, *D*, in liquid air: if nitrogen tetroxide was present, it imparted a colour to the liquid owing to formation of trioxide.

The silica tube, *A*, was now immersed in a carbon dioxide–ether mixture, and after ½ hour the absorption of nitric oxide was allowed to proceed by opening the tap *l*. After 3 hours the silica tube, *A*, was removed from the freezing mixture, and the U-tube immersed in it and kept over-night, during which time some nitrogen trioxide condensed.

FIG. 6.



The special features of these experiments taken together are as follows.

(1) Nitric oxide is reduced by charcoal at all temperatures from —78° upwards; the nitrogen produced is a measure of the extent of decomposition, most of the corresponding oxygen remaining fixed in charcoal.

(2) Some nitric oxide is retained by charcoal along with this oxygen even after 2 hours' evacuation; the amount so retained diminishes progressively as the temperature is raised.

(3) The nitric oxide so fixed is liberated (i) as such, (ii) as peroxide, or (iii) as carbon dioxide and nitrogen according to the conditions of the experiment: the second alternative occurs in low-temperature experiments when the temperature is suddenly raised from —190°

or −78° to 0° or 150°, and the peroxide then combines with nitric oxide, giving trioxide; the other two alternatives obtain at high temperatures.

(4) No carbon monoxide is produced below 500°. The retention of nitric oxide on the surface of charcoal and the formation of carbon dioxide at low temperatures show that carbon monoxide is oxidised by nitric oxide at the time of its formation in the pores of the charcoal. Some carbon monoxide is evolved in the experiments at 600°, probably because the amount of nitric oxide held on the surface is insufficient for its complete oxidation.

(5) At the temperature of liquid air, no nitric oxide could be removed on pumping: it remains condensed in the pores of charcoal (its b. p. is −150°). The reaction occurs at and above −78°, however.

These observations, along with those recorded in the preceding paper on the reaction between charcoal and nitric oxide, indicate that these two substances react with evolution of nitrogen: $x\mathrm{C} + y\mathrm{NO} \longrightarrow \mathrm{C}_x\mathrm{O}_y + \frac{1}{2}y\mathrm{N}_2$; the oxygen and some of the nitric oxide are retained by the charcoal; even at −78° the fixation of these two gases occurs simultaneously. This, taken in conjunction with other facts, *viz.*, (*a*) that nitric oxide is continuously absorbed by charcoal at 0° (see Table II, Part I); (*b*) that it is partially removed on evacuation at various temperatures; and (*c*) that it gives rise to nitrogen peroxide under one set of conditions and to carbon dioxide and nitrogen under another, suggests that nitric oxide is retained on the surface of charcoal through the intermediate layer of oxygen.

It therefore appears that the mechanism of adsorption is substantially as suggested in deduction (iii) (p. 2686), oxygen atoms produced by reduction of part of the nitric oxide forming a layer which retains a further molecular layer of nitric oxide, thus: $\cdot\cdot\cdot\underset{:}{\overset{:}{\mathrm{C}}}\cdot\cdot\cdot\underset{:}{\overset{:}{\mathrm{C}}}\cdot\cdot\mathrm{O}\cdot\cdot\mathrm{NO}$. At low temperatures there is a tendency to the formation of nitrogen peroxide (accompanied by secondary reactions such as the production of trioxide), which leaves the charcoal surface free to absorb nitric oxide again, and the continuance of this process accounts for the extensive absorption of nitric oxide observed at 0°. Above 50°, however, carbon dioxide and nitrogen are produced owing to a different scission of the surface complex, and a fresh surface is exposed.

Experiments with charcoal and (*a*) oxygen and (*b*) nitric oxide show that (i) the union between carbon and oxygen is stronger at high temperatures than at low, and (ii) charcoal retains oxygen *per se* much less readily than that formed from nitric oxide. Moreover, the facts that the fixation of oxygen is extensive in experiments with oxygen or nitric oxide at 0° and with nitrous oxide at 470°, and that nitric oxide molecules are always retained along with the fixed oxygen on the surface of charcoal, suggest that the fixed oxygen is more likely to exist, not in the form of a compound, $C_xO_y$, such as is assumed by Rhead and Wheeler (*loc. cit.*), but in a " special state," under the influence of the surface atoms of charcoal, as suggested by Keyes and Marshall (*J. Amer. Chem. Soc.*, 1927, **49**, 158).

## *Summary and Conclusions.*

The conclusion to be drawn from the present work is that the initial stage in the combustion of charcoal in oxygen, nitrous oxide, or nitric oxide is the same, *i.e.*, the fixation of oxygen. The combustion in nitrous oxide depends mainly on the decomposition of the gas accompanied by fixation of oxygen, and is therefore similar to that in oxygen. This is followed by the formation of carbon monoxide and dioxide, which takes place at 280° in oxygen and at 460° in a stream of nitrous oxide. The vigour of combustion is dependent on the rate of formation of carbon monoxide, and the subsequent oxidation of this gas is the cause of the flame observed in oxygen or nitrous oxide.

The mechanism of reaction with nitric oxide is slightly different, for charcoal retains this gas as well as oxygen. The reaction then proceeds between charcoal and these fixed gases, and the ultimate products, except at low temperatures, are carbon dioxide and nitrogen. So strong is the retention of nitric oxide that even in a rapid stream of the gas carbon monoxide is not detected, and the combustion proceeds without phosphorescence or the production of a flame.

These observations help to check previous hypotheses as to the mode of burning of charcoal in oxygen.

The first explanation, that carbon dioxide is the primary product and the monoxide results from its reduction, is untenable in the light of the experiments with carbon dioxide at 0° and at 470° as compared with those with oxygen : carbon dioxide is not retained by charcoal, and the amount of monoxide produced by its reaction with charcoal at 470° is much less than is evolved from fixed oxygen (see Tables III, IV, and VII, Part I). Moreover, if the explanation were true, the combustion of charcoal in oxygen or nitrous oxide would be similar to that in nitric oxide, which is not the case.

The second explanation, that carbon monoxide is first formed and the dioxide results from secondary oxidation through the agency of water molecules, is more tenable but cannot be examined without further knowledge of the function of water vapour. It is suggested that carbon monoxide may be oxidised at the time of its formation by oxygen held in a superincumbent layer on the surface of charcoal, just as it is oxidised by nitric oxide in the surface reaction of that gas with charcoal.

The author does not agree with Rhead and Wheeler's suggestion (*loc. cit.*) that in the complex, on which the oxidation of charcoal depends, " several carbon molecules hold one oxygen molecule " ; he prefers Langmuir's suggestion that " on the surface of charcoal one adsorbable atom or molecule of the gas would be bound for each carbon atom," and concurs with the further suggestion of Keyes and Marshall that the oxygen fixed by charcoal exists in a special state so that the first layer can adsorb other molecules (or atoms). From the author's experiments, it appears that the oxygen derived from nitric oxide and fixed in charcoal is able to attach nitric oxide to itself. Moreover, because of the possibility of obtaining nitrogen trioxide from charcoal and nitric oxide, it appears that at least one layer of nitric oxide is attached to the innermost layer of the surface.

There are grounds for believing that the oxygen fixed in any one layer from the pure gas is much less in quantity than oxygen and nitric oxide fixed in a similar layer from nitric oxide; also, owing to the greater chemical activity of nitric oxide, the number of superincumbent layers of this gas is much greater than that of oxygen. Further, at low temperatures the amount of oxygen held in the first layer is less than in the second and succeeding layers, with the result that much of it is recovered as such on pumping. With increasing temperature, increasing quantities of oxygen are held in the first layer and decreasing quantities in the others, until finally at high temperatures only one layer is formed; consequently at first the gases evolved on heating contain increasing proportions of monoxide and dioxide, but later the dioxide decreases and ultimately the monoxide is the sole product.

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