LXXXIX.—*The Combustion of Carbon.*

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THE question as to what is the first reaction that takes place when carbon burns in oxygen has long been a subject of controversy.

The commonly accepted view is that the first product is carbon dioxide, which, in contact with an excess of incandescent carbon, is immediately reduced to carbon monoxide, thus *:

On the other hand, the classical investigations of Dixon on the rates of explosion of mixtures of gaseous carbon compounds with oxygen, and of H. B. Baker on combustion in dried oxygen, support the belief that carbon burns directly to carbon monoxide:

and that any carbon dioxide found in the products is only formed by the secondary combustion of the monoxide:

Dixon's work leaves no room for doubt but that in the burning of *gaseous* carbon, carbon monoxide is produced before carbon dioxide; for example, in the explosion of cyanogen (Dixon, Strange, and Graham, Trans., 1896, 59, 759) it is shown that the velocity of the explosion-wave is higher when the gas is half-burnt to carbon monoxide than when there is enough oxygen present to burn it completely. Moreover, the substitution of inert nitrogen for the additional molecular volume of oxygen required for complete combustion produces less retardation. So far as the propagation of the explosion-wave is concerned, therefore, the second molecule of oxygen is inert. This is well shown by the following rates of explosion:

Mixture of gases	$\text{C}_2\text{N}_2 + \text{O}_2$.	$\text{C}_2\text{N}_2 + 2\text{O}_2$.	$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$.
Rate of explosion (metres per second) ...	2728	2321	2398

Further, the flame is not only propagated more quickly, but the pressure is higher and the reaction sooner completed in the first than in the second case. The only conclusion to be drawn from these results is that the formation of carbon monoxide precedes that of carbon dioxide.

* This view seems to have been controverted by Tunner so long ago as 1861, and in 1872, Sir Lowthian Bell, in his "Chemical Phenomena of Iron Smelting" (Section II, pp. 4—9), argued strongly in favour of the view that carbon monoxide and not carbon dioxide is the initial product of the combustion of carbon.

H. B. Baker's experiments (*Phil. Trans.*, 1888, **179**, A, 571) certainly point to the conclusion that when solid carbon burns in oxygen its combustion is effected in two stages; that it forms first carbon monoxide, which, if circumstances are favourable, undergoes further oxidation to carbon dioxide.

C. J. Baker (*Trans.*, 1887, **51**, 249) undertook experiments with the object of ascertaining the nature of the gases produced on heating carbon that had absorbed oxygen at low temperatures. He found, as had been stated by Angus Smith (*Proc. Roy. Soc.*, 1863, **12**, 424), that moist oxygen which had been absorbed by carbon at -12° was given up as carbon dioxide when the carbon was heated to 100° . On the other hand, C. J. Baker found that dried carbon which had absorbed dried oxygen (dried by phosphoric oxide) at $+12^{\circ}$ yielded only traces of gas on heating until a temperature of 450° was reached. The gases then obtained consisted mainly of carbon monoxide. He drew the conclusion that carbon is burned directly to carbon monoxide by the absorbed oxygen.

The experimental evidence in support of the view that carbon dioxide is the first product of the burning of solid carbon is derived chiefly from some work by J. Lang (*Zeitsch. physikal. Chem.*, 1888, **2**, 168), which can be summarised as follows:

(1) Oxygen was passed over gas-carbon contained in a glass tube heated to 500° , at which temperature it was found that the gas-carbon could not reduce carbon dioxide. The products of combustion varied with the speed of passage of the oxygen, the carbon monoxide formed being less the slower the gas-stream, and disappearing altogether with very slow streams.

The conclusion drawn by Lang from these experiments was that the carbon monoxide found with quick streams was produced by the reduction of the carbon dioxide first formed, owing to local heating of the carbon. With very slow streams no local heating would occur, and therefore there was no reduction of carbon dioxide.

(2) A mixture of oxygen and carbon monoxide was passed at different speeds over carbon heated at 500° . With slow gas streams the whole of the oxygen was converted into carbon dioxide, and the carbon monoxide passed through the tube unchanged. With rapid streams more carbon monoxide was found in the products than was present in the original mixture, some of the carbon dioxide first formed being reduced by the carbon.

Lang therefore concluded that, since the oxygen was converted into carbon dioxide under such conditions that the carbon monoxide present was not acted on, the carbon dioxide must have been formed without the intermediate formation of carbon monoxide.

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Dixon, in a paper entitled "The mode of burning of carbon" (Trans., 1899, 75, 630), criticised Lang's conclusions. He pointed out that the first series of experiments merely showed that carbon dioxide was the *final* product when oxygen was passed slowly over coke heated at 500°, and that there was no direct contradiction of the supposition that carbon monoxide was the first product of oxidation of the coke, the carbon monoxide molecules thus formed being further oxidised to carbon dioxide. Lang's second series of experiments, which appeared to dispose of this possibility, Dixon was unable to confirm; and he gave results of experiments which were at variance with those of Lang.

Since this paper of Dixon's, there does not appear to have been any further attempt to produce experimental evidence in favour of the view that carbon burns first to form carbon dioxide; but it cannot be said that the alternative, which the work of Dixon and Baker supports, has received universal acceptance. Haber, for example ("Thermodynamics of Technical Gas Reactions," Eng. Ed., p. 255), considers the primary reaction to be:

the adjustment of the equilibrium being brought about by the secondary reaction:

This adjustment would or would not take place according as the carbon dioxide had time to react or not.

Whilst it appeared to be impossible to obtain *direct* evidence as to the first product of oxidation of solid carbon, we hoped that, indirectly, a study of the relative rates at which the various reactions between oxygen, carbon, carbon monoxide, and carbon dioxide proceeded under the same experimental conditions, might enable us to form some opinion as to which were the more likely to take precedence at different temperatures.

If it could be shown that either reaction (a) or reaction (c) (p. 846) proceeded at a temperature at which, under the same experimental conditions, the rates of reactions (b) and (d) were inappreciable, the problem would be solved.

It may be said at once that we have been unable to arrive at a complete solution of the problem in such a simple manner; for at no temperature at which the rate of oxidation of carbon is appreciable could we obtain conclusive evidence of the primary formation, *to the exclusion of the other*, of either carbon monoxide or carbon dioxide.

Our experiments show (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures, under conditions which do not admit of the reduction of carbon dioxide by

carbon. On the other hand, (2), carbon dioxide is undoubtedly produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that carbon monoxide is first formed and then oxidised to carbon dioxide.

When carbon is burned at low temperatures, therefore, carbon dioxide and carbon monoxide are produced *simultaneously*.

The question naturally arises as to what reaction between oxygen and carbon can account for this simultaneous production of the two oxides. The conclusions to which we have come regarding this problem, together with a description of the experiments on which these conclusions are founded, form the subject of a separate paper.

EXPERIMENTAL.

P. Farup (*Zeitsch. anorg. Chem.*, 1906, **50**, 276) has determined the rate of reaction between oxygen and graphite (arc-lamp carbon) at temperatures of 455°, 485°, and 515°; and between air and graphite at 485° and 515°. The air or oxygen was passed in a continuous stream through a heated bulb-tube of porcelain containing the graphite in the form of a rod. Experiments, in the same apparatus, were also made by Farup on the rate of reduction of carbon dioxide by graphite. He found that the rate of reduction of carbon dioxide at 850° was about the same as the rate of oxidation of graphite at 450°; and that the temperature-coefficient k_{t+10}/k_t of the latter reaction over the range 450—500° was about 1.50.

Our determinations were made with highly purified wood charcoal under the same experimental conditions, and in the same apparatus as those of the rate of reduction of carbon dioxide already described (this vol., p. 835).

A given volume of air or oxygen was circulated continuously through the carbon contained in a porcelain tube, and heated in an electric resistance furnace. The weight of carbon used in each experiment was about 2.5 grams, and it was sieved through a 10- and on a 30 mesh sieve so as to be of uniform size. It occupied the middle 9 cm. of the length of the porcelain tube, which was of 1.2 cm. bore.

A series of three by-passed sampling-tubes, and a by-passed absorption-tube, were included in the circuit of the gases (see diagram on p. 844), and could be used or omitted as required for different experiments. The absorption-tube, *R*, for the removal of carbon dioxide as soon as formed, was placed between the reaction tube and a calcium chloride drying-tube. It consisted of a cylindrical vessel, 27 cm. long and 4 cm. in diameter. Soda-lime mixed

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with small pieces of potassium hydroxide filled this vessel to within 5 or 6 cm. from each of the ends, which contained pure stick potassium hydroxide broken into pieces about 4 mm. cube. This admixture of potassium hydroxide with the soda-lime prevented moisture, given off from the latter when carbon dioxide is absorbed, from being carried away by the gases, which were further dried by the calcium chloride.

We will first give the details of a series of three determinations of the rate of oxidation of carbon by air at 350°, 400°, and 500° respectively. In the experiments at 350° and 400° the sampling-tubes were shut off from, and the absorption-tube turned on to, the circuit, and the rate of oxidation determined from readings of the pressure inside the apparatus at given intervals of time. In the experiment at 500°, in which there was a considerable formation of carbon monoxide, both sampling-tubes and absorption-tube were employed, and the rate of disappearance of oxygen determined from the partial pressures at given intervals of time. These partial pressures were calculated from the total pressures in the apparatus, and the analyses of the samples of gases shut off periodically during the course of the experiment.

We have already commented on the fact that, in determining the relative rates of gaseous reactions taking place on or with a surface, it is essential that the surface should be in the same condition before each experiment is begun. In our experiments on the rate of reduction of carbon dioxide by carbon, this was effected by heating the carbon (in the reaction-tube) to 1100°, and exhausting at that temperature. In the present experiments on the oxidation of carbon, treatment of the carbon in this manner destroyed their relative value, for a reason that will appear later.

Starting with a carbon surface that had been exhausted at 1100°, it was found necessary, in order to obtain comparable values for the rate of reaction at different temperatures, to make a series of consecutive determinations at the experimental temperature, keeping that temperature rigidly constant between each determination. The first three or four determinations showed a rapidly decreasing rate of reaction, but after a time a value was obtained which did not vary from one experiment to another.

This constant rate was regarded as the "normal" rate of reaction at the particular temperature employed; thus, the experiments detailed below are the final ones of series made at each temperature with successive charges of air until a constant rate of reaction was obtained.

In the tables that follow:

t = the time in minutes from the beginning of each experiment.

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P = the total pressure in the apparatus, determined from manometer readings, and corrected for a temperature of 0° .

P_{O_2}, P_{CO} = the partial pressures of oxygen and carbon monoxide.

k_{O_2} = the rate of disappearance of oxygen, calculated from the partial pressures (concentrations) by means of the expression $1/t \log C_o/C_i$ ($t=1$ minute).

Experiments with Air.

$T = 350^\circ$.

t .	P (mm.).	P_{O_2} (mm.).	k_{O_2} .
0	406.4	78.4	—
360	402.7	74.7	0.0000583
720	399.7	71.7	0.0000583
1440	394.0	66.0	0.0000517
2880	383.1	55.1	0.0000517
3240	378.7	50.7	0.0000583

The final gas contained 0.20 per cent. of carbon monoxide, corresponding with a partial pressure of 0.75 mm.

$T = 400^\circ$.

t .	P (mm.).	P_{O_2} (mm.).	k_{O_2} .
0	417.8	87.7	—
120	405.2	75.1	0.000562
240	395.0	64.9	0.000545
360	385.6	65.5	0.000550
480	376.0	46.5	0.000574
600	370.0	39.9	0.000570
720	364.0	33.9	0.000573

The final gas contained 0.60 per cent. of carbon monoxide, equivalent to a partial pressure of 2.2 mm.

$T = 500^\circ$.

t .	P (mm.).	Gas analysis, per cent.		P_{CO} (mm.).	P_{O_2} (mm.).	k_{O_2} .
		CO.	O ₂ .			
0	465.2	nil	20.7	—	96.4	—
30	435.0	8.6	4.3	37.4	18.7	0.0237
45	424.3	9.1	2.1	38.6	8.9	0.0230
60	418.3	9.8	0.8	41.0	3.3	0.0244
120	408.4	9.0	nil	36.7	—	—

It is to be noted, in the first place, that the temperature-coefficient k_{t+10}/k_t , calculated from the mean values of k at the three temperatures recorded, is 1.52; that is to say, practically identical with that found by Farup for the oxidation of graphite over about the same range of temperature.

Comparison with the relative rates of reduction of carbon dioxide at different temperatures, shows that under the same conditions of

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experiment the rate of oxidation of carbon at 500° is about equal to the rate of reduction of carbon dioxide at 1130° .

The most important result is, however, the formation of so much carbon monoxide during the oxidation of carbon at 500° . Whilst at 350° and 400° traces of carbon monoxide were found in the gases at the end of fifty-four and twelve hours' circulation respectively, at 500° the gases at the end of thirty minutes contained as much as 8.6 per cent.

Supposing that the first reaction between oxygen and carbon produces carbon dioxide, and that any carbon monoxide found in the final products arises from the reduction of some of this carbon dioxide by excess of carbon, two assumptions can be made as to the means by which the reduction is effected.

It can be assumed that the air in the experiment at 500° was transformed, after it had passed through the first few centimetres of the column of carbon, into a mixture containing about 20 per cent. of carbon dioxide and 80 per cent. of nitrogen, no carbon monoxide having yet been formed. Partial reduction of the carbon dioxide then took place during the passage of this mixture through the remainder of the carbon heated at 500° .

This cannot be the case, however, for we have shown that the rate of reduction of carbon dioxide under like experimental conditions is hardly appreciable even at 850° .

The second assumption, that used by Lang (*supra cit.*) of local heating up of the carbon due to its rapid oxidation, is more difficult to dispose of.

Calculation from the partial pressures in the experiment at 500° shows that at the end of thirty minutes an amount of carbon monoxide equivalent to 37.4 mm. had been produced, and that at the same time carbon dioxide equivalent to 48.9 mm. had been formed and absorbed by the soda-lime and potassium hydroxide. That is to say, if it is assumed that carbon dioxide was the sole first product of oxidation of the carbon, about 28 per cent. of it had been reduced.

For this amount of reduction to take place in thirty minutes, we calculate (from the ascertained rates of reduction of carbon dioxide under the same conditions of experiment) that the carbon would have to be raised locally to a temperature of over 1175° .

Before discussing the matter further, we will give one of the results of a series of experiments made with pure oxygen. The experiment chosen is one of several made at a temperature of 500° , at which temperature a considerable quantity of carbon monoxide is formed. The time of circulation of the gases was the same as

in the experiments with air, and the carbon dioxide formed was removed in the same manner. The result was as follows: *

Experiment with Oxygen.

$$T = 500^{\circ}.$$

<i>t.</i>	<i>P</i> (mm.).	<i>PO</i> ₂ (mm.).	<i>PCO</i> (mm.).	<i>kO</i> ₂ .
0	372.8	372.8	—	—
30	160.4	73.0	87.4	0.0236

The gases at the end of the experiment contained 54.5 per cent. of carbon monoxide.

The rate of disappearance of oxygen is no greater in this experiment with pure oxygen than in the comparative experiment with air at 500°. This result agrees with numerous other comparative experiments that we have made with oxygen and with air at temperatures below 500°.

If at these comparatively low temperatures there were any pronounced local heating, one would expect to find that the mixture of an inert gas with the oxygen would, by minimising the amount of local heating, decrease the rate of oxidation. Any decrease in the rate, due to such cause, should, moreover, be very marked; for we have shown that an increase in the temperature of the carbon of 50° between 350° and 500° increases the rate of reaction five- or six-fold.

The fact that the rate of oxidation when either air or pure oxygen is used is the same, the rate of disappearance of oxygen being directly proportional to its partial pressure (concentration) in both cases, brings us to the conclusion that no local heating of the carbon can account for the formation, by reduction of carbon dioxide, of so much carbon monoxide as is shown in these experiments at 500°. That when the oxygen first enters the column of carbon some rise in temperature must take place owing to the heat of the reaction, is incontrovertible; but it would appear that a rapid dissipation of this heat takes place throughout the mass of the carbon, and through the walls of the containing vessel, and that such carbon molecules as may be raised to a temperature sufficiently high to reduce carbon dioxide are few in number.

The question now arises whether, if oxidation of the carbon monoxide could be prevented, any carbon dioxide would be found

* No samples were taken during the course of this experiment, for the rapid rate of disappearance of oxygen prevented such samples from being in any way representative of the total contents of the apparatus, and therefore rendered them useless for the purpose of calculating the partial pressures of oxygen and carbon monoxide at different intervals of time.

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in the products of combustion of carbon. That is to say, granted that the carbon monoxide found in the products of combustion does not arise from the reduction of carbon dioxide, does the carbon dioxide found arise solely from the oxidation of carbon monoxide?

We have attempted to answer this question by experimenting with mixtures of carbon monoxide and oxygen, and determining their rates of combination when circulated over carbon heated at different temperatures. The experiments were made in the same apparatus and under the same conditions as those already described.

In the three experiments described below a mixture of carbon monoxide and oxygen in combining proportions ($2\text{CO} + \text{O}_2$) was circulated through carbon heated at 250° , 300° , and 400° respectively. The time of circulation of the gases was, as before, thirty-five minutes. The carbon dioxide formed was removed by the absorption tube.

Experiments with Carbon Monoxide and Oxygen.

$$T = 250^\circ.$$

	P_{CO} (mm.).	P_{O_2} (mm.).
Original	265.5	125.4
Final, after 288 hours	251.6	105.2
Difference.....	13.9	20.2

The 13.9 mm. of carbon monoxide that have disappeared required 6.9 mm. of oxygen to form carbon dioxide. This leaves 13.3 mm. of oxygen that have combined with the carbon forming, ultimately, carbon dioxide. The ratio between these two quantities is 1.93.

Similarly, for the experiments at 300° and 400° the ratios were:

$$T = 300^\circ.$$

$$\text{Ratio: } \frac{\text{Oxygen combined with carbon}}{\text{Oxygen combined with carbon monoxide}} = 1.55.$$

$$T = 350^\circ.$$

$$\text{Ratio: } \frac{\text{Oxygen combined with carbon}}{\text{Oxygen combined with carbon monoxide}} = 0.84.$$

Let us consider first the experiment at 250° . Pure oxygen circulated through carbon heated at 250° produces mainly carbon dioxide, as the following experiment (made under the same conditions as all the others) shows:

Experiment with Oxygen.

$$T = 250^{\circ}.$$

<i>t.</i>	<i>P</i> (mm.).	<i>P</i> _{CO} (mm.).	<i>k</i> O ₂
0	390.5	—	—
1440	386.8	—	0.0000028
2880	383.9	—	0.0000025
4320	381.0	—	0.0000025
5760	375.6	—	0.0000030
8700	366.6	2.0	0.0000029

The gases at the end of this experiment were found to contain 0.60 per cent. of carbon monoxide, equivalent to a partial pressure of 2.0 mm. This was formed whilst 23.9 mm. of oxygen were burnt. That is to say, about 4 per cent. only of the oxygen burnt appeared in the products of combustion as carbon monoxide.

If it is assumed that the first reaction between carbon and oxygen produces carbon monoxide, and that any carbon dioxide found is due to the subsequent oxidation of this carbon monoxide by excess of oxygen, it would appear that the rate at which carbon monoxide combines with oxygen over the carbon surface at 250° must be much faster than its rate of formation from carbon.

To return to the experiment with carbon monoxide and oxygen over carbon at 250°. The result shows that the rate of combination of the oxygen with the carbon was 0.00000281.* This is about the same rate as was found when pure oxygen was used.

On the other hand, the rate of disappearance of oxygen in combination with carbon monoxide was 0.00000142; that is to say, about *half as fast* as the rate of combination of oxygen with carbon.

This fact would appear at once to discount the hypothesis that carbon monoxide is formed first when oxygen combines with carbon; but, as Dixon in his criticism of Lang's work points out, the *nascent* carbon monoxide molecules may combine with oxygen rapidly on or near the surface of the carbon, whilst the carbon monoxide originally present is comparatively inert.

Let us now compare the results of the three experiments with a mixture of carbon monoxide and oxygen. The ratio between the rate of combination of oxygen with carbon and the rate of combination of oxygen with carbon monoxide is 1.9 at 250°. At 300° it is 1.5, and at 400° it is 0.8. Now if carbon monoxide is the sole first product of combustion of carbon, this decrease in the ratio with increasing temperature must mean either (1) that the rate of combustion of carbon monoxide increases more rapidly between

* Calculated from the expression $1/t \log C_0/C_t$, the fall in concentration of the oxygen due to combination with carbon being 13.3 mm. at the end of 288 hours.

250° and 400° than does the rate of combustion of carbon; or (2) that the higher the temperature (within the limits 250° to 400°) the greater is the number of nascent carbon monoxide molecules that escape oxidation at the surface.

Neither of these explanations is satisfactory. The first demands that the lower the temperature of oxidation of carbon the greater the quantity of carbon monoxide in the products, whereas the reverse is the case. The second implies that the more rapidly the nascent carbon monoxide molecules are carried away from the surface the greater is the number that remain unoxidised. If this were so, a rapid stream of air or oxygen passed through carbon heated at, say, 400°, should yield more carbon monoxide in proportion to carbon dioxide than a slow stream. We have found the reverse to be the case.

We arrive, therefore, at the conclusion given in the theoretical portion of this paper, that when carbon burns at low temperatures there is a simultaneous production of the two oxides.

ALTOFTS.