

CXXVI.—*The Decomposition of Carbon Monoxide
in the Corona due to Alternating Electric Fields.
Part II.*

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IN the first communication of this series (J., 1925, 127, 2052) an account was given of the decomposition of a fixed amount of carbon monoxide, enclosed in the annular space of a Siemens ozoniser,

when subjected to ionisation by collision produced by alternating electric fields of frequency 250 cycles per sec. The decomposition was accompanied by the formation of a brown solid on the walls of the ozoniser, and equilibrium was attained when the residual gas contained 1 part of carbon dioxide to approximately 12 parts of the monoxide. Those experiments showed also that the composition of the brown solid, which was calculated from the results of analysis of the residual gases at equilibrium, varied with the initial pressure of the carbon monoxide, the ratio of carbon to oxygen increasing as the initial pressure of the monoxide diminished. In addition, it was found that the composition of the solid was independent of the potential applied to the ozoniser electrodes in the range examined, *viz.*, 4000—9000 volts.

Further experiments at the same frequency have now been carried out with the aim of more completely elucidating the nature of this substance. The apparatus has been modified in order to produce relatively large amounts, of the order of several grams, and to ensure that the "suboxide" should be formed at a constant partial pressure of the monoxide and in the absence of appreciable quantities of the dioxide. The conditions of formation are therefore more exactly defined than in the earlier experiments in which the carbon dioxide produced was not removed. Despite the improved technique, the preparation of the suboxide in quantity is a slow process, and is rendered difficult by a tendency to decompose spontaneously in air.

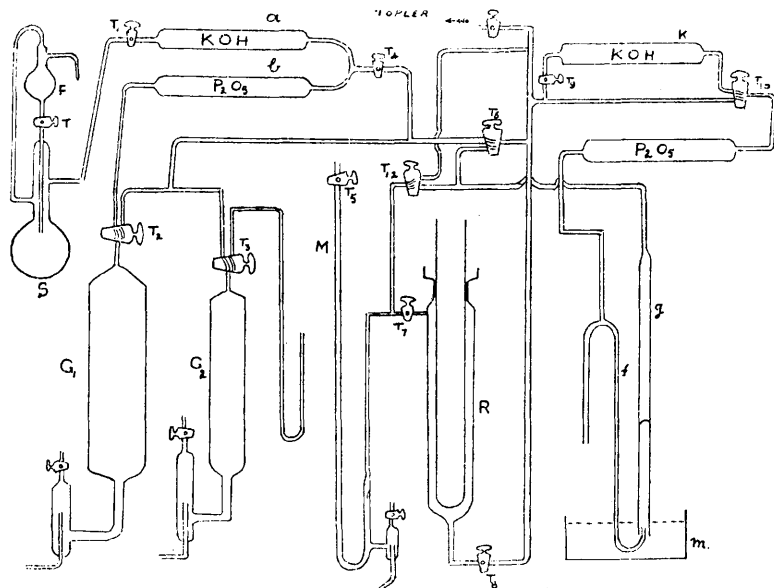
EXPERIMENTAL.

The electrical technique employed was identical with that described in Part I of this series.

Reaction Vessel.—The vessel which contained the gas while it was subjected to the discharge (Fig. 2) was that employed previously, *viz.*, a Siemens ozoniser constructed of glass, and connected to the auxiliary apparatus as represented in Fig. 1. The inner tube, t_1 , was ground to fit the outer tube, t_2 , at one end, thus facilitating the removal of any substance formed in the annular space between the tubes. It was filled with mercury, which served as the high-tension electrode, E_1 . A glass tube containing mercury surrounded the outer tube and formed the low-tension electrode, E_2 , which was earthed. The electrodes were water-cooled and their temperatures were recorded by alcohol thermometers. The external diameters of the two tubes of the reaction vessel were 25.5 and 15.2 mm., respectively, and the internal diameters were 23.3 and 12.7 mm., the thicknesses being thus 1.1 and 1.25 mm., respectively. The total volume included between the stopcocks was 81 c.c., and the effective length of the electrode was 33 cm.

An automatic Sprengel pump, *fg*, circulated the gas continuously through the discharge. The gas was led from the reaction vessel by the tap, *T*₈, through some 6 feet of tubing containing caustic potash, *K*, and then over phosphorus pentoxide to the fall tube, *g*, of the Sprengel pump. From the pump the gas flowed to the reaction vessel *via* the taps *T*₁₂ and *T*₇. The circulating system was connected by the taps *T*₁₂ and *T*₆ to gas holders containing the monoxide, *G*_{1*G*₂, in such a manner that this could be fed in as rapidly as the dioxide was removed by the potash. In this way an approximately constant pressure was maintained in the gas sub-}

FIG. 1.



General diagram showing connexions of different parts of the apparatus.

jected to the discharge. A mercury manometer, *M*, was attached to the system as before.

Preparation of Carbon Monoxide.—The gas was produced free from oxygen by the method described previously, in which recrystallised formic acid contained in the bulb, *F*, was allowed to drop into an evacuated flask, *S*, containing warm concentrated sulphuric acid.

Procedure.—In order to facilitate the rapid formation of the suboxide, the highest available potential was employed in all experiments, *viz.*, 10,000 volts r.m.s.; the corresponding current varied slightly with the pressure from 9—10 milliamps.

The method adopted for preparing quantities of about 2 g. of the suboxide consisted in circulating carbon monoxide continuously through the reaction vessel until about 5 litres had been consumed, the potash tube for absorbing carbon dioxide being connected in the circulating system. The supply of monoxide was adjusted to

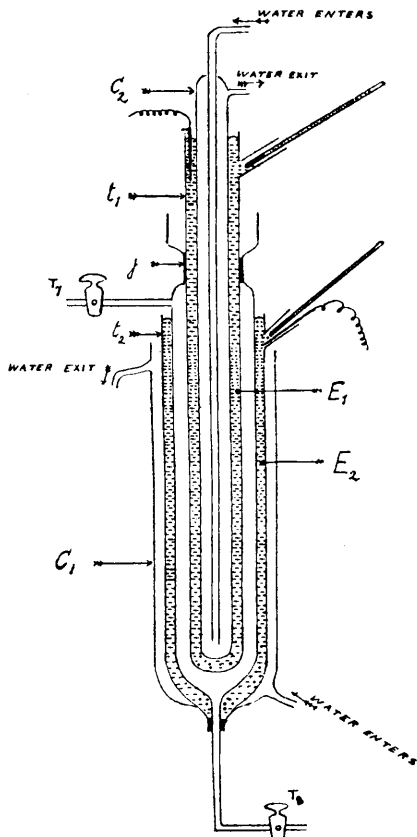


FIG. 2.

Reaction vessel.

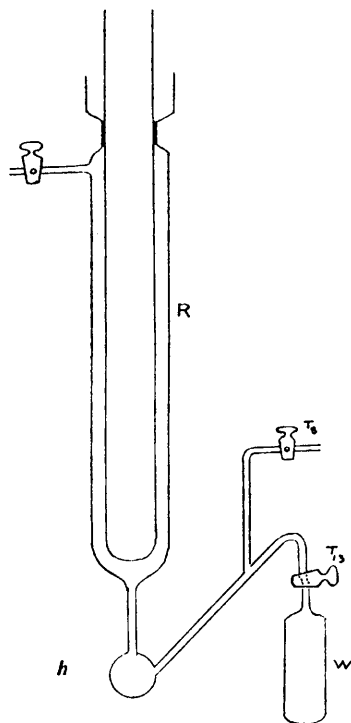


FIG. 2A.

maintain the pressure constant within ± 5 mm. Hg. After the discharge was stopped, the reaction vessel was disconnected from the circulating system and filled with dry air. The inner tube was then removed from the outer tube, and the suboxide scraped off as rapidly as possible on account of its very hygroscopic nature and transferred to a vacuum desiccator containing phosphorus pentoxide. As soon as the inner tube had been withdrawn, the grease was

removed from the ground joint of the outer tube, which was then filled with pure dry ether, and the solid adhering to the walls was loosened by rubbing with a clean dry copper rod. The ether and the solid were transferred to a flask and the former was removed by distillation, the residue being placed in a vacuum desiccator to remove the last traces of ether. The ether which had been in contact with the solid was not coloured, and on evaporation to dryness left no residue. The brown solid is therefore insoluble in ether, the use of which, to protect the solid from atmospheric contamination, would appear to be permissible.

In order to ascertain whether the conditions of experiment were substantially identical with those described in Part I, a fixed amount of carbon monoxide, at an initial pressure of 528.4 mm. Hg, was exposed to the discharge until equilibrium was reached, as indicated by the cessation of pressure change. The ratio of monoxide to dioxide in the residual gas was 11.4, which is in satisfactory agreement with the mean value, 11.58, previously obtained at an initial pressure of 501 mm. Hg.

Preliminary Examination of the Solid.—The experiments described in this section were carried out on the solid prepared by circulating carbon monoxide through the discharge at a constant pressure of 500 mm., the dioxide formed being removed continuously by potash. On treatment with water, the solid gave a brown, acidic solution having the smell of caramel, and a dark brown residue which was insoluble even in boiling water. Titration of this solution by standard alkali indicated that its acidity did not change with time. An examination of the solution under the ultramicroscope revealed the presence of colloidal particles. Prolonged boiling of the brown aqueous solution with purified animal charcoal did not decolorise it. The treatment of the solution with purified norit, freed from lime and silica, was more successful. Some five or six treatments with fresh norit were necessary, however, to give a nearly colourless solution. It was extremely tedious to prepare a colourless solution. The nitrates of aluminium, sodium, and thorium were also effective in partly decolorising the solution. Dialysis through a collodion membrane, although satisfactory in other ways, was too slow to be serviceable. The nearly colourless solution of the suboxide obtained by any of these methods was acid to litmus and reduced acidified potassium permanganate solution. When neutralised with ammonia the solution gave with calcium chloride a white, crystalline precipitate insoluble in acetic acid, and a white precipitate with silver nitrate, indicating that the original solution contained oxalic acid.

On concentrating the nearly decolorised solution of the brown solid obtained by treatment with norit, colourless crystals were

obtained, m. p. 96—100° (m. p. of hydrated oxalic acid, 100°). Similar crystals were obtained by extracting with dry ether, in a Soxhlet apparatus, the solid remaining when the brown aqueous solution of the suboxide was evaporated to dryness. After recrystallisation from dry ether, colourless crystals were obtained which, alone or when mixed with pure hydrated oxalic acid, melted at 98—99°. The crystals were compared microscopically with those of oxalic, malonic, and succinic acids, and found to be very similar to the first. The *p*-toluidine derivative, after recrystallisation from absolute alcohol, had m. p. 265—266° (oxalo-*p*-toluidide melts at 266—267°).

The silver or calcium salt precipitated from the neutralised, nearly colourless solution of the brown solid carried with it the residual colouring matter in the solution. The silver salt thus obtained could not therefore be used to determine accurately the equivalent of the acid. It would appear, however, that ignition of the calcium salt leads to values for the oxalic acid content of the solution, but such data are reserved for a later communication. The equivalent of the acid has, however, been determined by igniting the silver salt, dried at 100°, obtained from two different dialyses of a solution of the brown solid through a collodion membrane [Found : equiv., (a) 45.8, (b) 46.9. $(\text{CO}_2\text{H})_2$ requires 45.0].

When the nearly colourless solution of the brown solid, obtained by treatment with norit, was titrated with permanganate, the end-points were indefinite, but this could not be traced to the effect of the norit. Since the brown, aqueous solution of the suboxide and the insoluble residue could be slowly and completely decolorised by acidified permanganate even in the cold, it would appear that the indefinite end-points might be due to the imperfect decoloration of the solution before titration. In view of the difficulty of obtaining a perfectly colourless solution and of the probable loss by adsorption on the norit, this method of decoloration was abandoned as unsuitable for further quantitative investigations. Nevertheless, a rough estimation was carried out and the results, although only approximate, are considered in the next section.

During attempts to scrape off the brown solid from the walls of the ozoniser, a curious phenomenon was observed on two occasions. The solid adhering to the outside of the inner tube was scraped with a nickel spatula into a glass basin. Almost immediately the solid in the basin glowed and gave off a white cloud with evolution of heat, and a dark, spongy mass resembling charcoal remained. When the contents of the basin were treated with water, the spongy mass floated and the water was not coloured, but was found to contain oxalic acid. It was thought that this curious phenomenon

might have been due to the accidental presence of moisture on the spatula or in the glass basin. When the brown solid was treated with water or methyl alcohol, a gas containing carbon dioxide was evolved, accompanied by a hissing noise which was more pronounced in the case of methyl alcohol. In order to ascertain if the gas was entirely carbon dioxide, a small glass bulb, *h* (Fig. 2A), was inserted between the reaction vessel, *R*, and the tap, *T*₈. Through a side tube of the bulb, water could be distilled into it from the vessel *W*, containing air-free water, and by placing a beaker of hot water underneath the bulb the water from the bulb could be distilled into the ozoniser. After some brown solid had been formed in the ozoniser and the latter evacuated, water was distilled into it as described. The gas evolved was carbon dioxide with a trace of carbon monoxide.

It follows from these preliminary experiments that the brown solid on treatment with water produces carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and an insoluble, brown residue.

Quantitative Examination of the Brown Solid.—In order to determine whether the composition of the solid, produced under the conditions already described, varied with the pressure of the monoxide, as indicated by the earlier experiments (Part I), four samples prepared at 200, 350, 500, and 690 mm. were analysed by combustion in a stream of dry oxygen. The results showed that the substance contained carbon, hydrogen, and oxygen. Assuming that all the hydrogen in the material before combustion is present as water (possibly due to the absorption of atmospheric moisture during the transference from the reaction vessel and subsequent weighing), the atomic ratios of oxygen to carbon in the four samples of the brown solid were calculated to be, respectively, 0.58, 0.60, 0.60, and 0.59, each value being a mean of two determinations. There is thus a remarkable constancy in the ratio, corresponding to an empirical formula C_5O_3 , throughout the range of pressure investigated; and it would appear that the compositions of the substances produced might be represented by the empirical formula $C_5O_{3,x}H_2O$. These conclusions suggest also that the product formed by streaming the gas through the discharge is not identical with that obtained from an enclosed mass of gas exposed to the discharge (compare Part I).

It has been mentioned that, under certain conditions, the brown solid reacts with water, evolving carbon dioxide. It was therefore necessary to determine whether any carbon dioxide was similarly evolved in the formation of the substance, $C_5O_{3,x}H_2O$, during the unavoidable hydration of the brown solid in manipulation. Analysis

of samples of the solid, prepared at 500 mm., collected from the inner tube of the reaction vessel in the presence of moist air, and from the outer tube under dry ether, showed that the latter contained the smaller amount of water, as calculated from the hydrogen content; the results corresponded with the empirical formulæ $C_5O_3, 1.95H_2O$ and $C_5O_3, 1.65H_2O$, respectively. They show that the ratio of carbon to oxygen is constant and independent of the water content of the substance, and they therefore afford evidence that carbon dioxide had not been liberated during the hydration of the brown solid. Experiments are in progress to determine whether the hydrogen content of the solid can be traced solely to the absorption of atmospheric moisture, or if it is due, in part, to the liberation of water from the walls of the reaction vessel during the discharge.

The increase in weight which took place when a known amount of the solid was exposed to moist air at atmospheric pressure is given in Table I.

TABLE I.

(Initial weight of solid = 0.02848 g.)

Time of exposure (hrs.)	0.5	1.75	2.5	3.5	27	70
Total increase in weight (mg.)	5.4	8.8	12.6	15.4	15.4	15.2

The substance was treated subsequently with excess of water, and the solution evaporated to dryness in a steam-oven; it had then suffered a total loss in weight of 0.00922 g., or 32.38%; 0.2427 g. of the same sample of brown solid, on direct treatment with water and subsequent evaporation to dryness, lost 0.0788 g., or 32.47% in weight. If it be assumed, in accordance with the experiments just described, that the increase in weight in moist air is due to the absorption of water only, then the observed increase corresponds to a change in composition from $C_5O_3, 1.70H_2O$ to $C_5O_3, 4.21H_2O$.

A further series of combustions was then carried out on samples obtained by treatment of the brown solid with water and subsequent evaporation to dryness in a steam-oven. The ratios of oxygen to carbon, computed as before, varied in an apparently chaotic manner with the pressure at which the brown solid had been formed. It would appear, however, that this erratic variation may be attributed to slow atmospheric oxidation of the suboxide residue after treatment with water and subsequent evaporation to dryness. Three successive combustions were carried out on the suboxide residue (original solid prepared at 200 mm.) so obtained, one in the forenoon, one in the afternoon, and the third on the next day. During this period the bulk of the substance, from which samples were taken for combustion, was exposed to the

atmosphere in a steam-oven (100°). The results (Table II) show that whilst the proportion of hydrogen is fairly constant, that of oxygen progressively increases, indicating that the brown solid after treatment with water absorbs oxygen while in contact with the atmosphere at 100° . No precautions were taken, in the experiments in which chaotic results were obtained, to insure that such atmospheric oxidation was avoided, or that the time of drying in the steam-oven was constant.

TABLE II.

Sequence of experiments.	I.	II.	III.
Carbon	1.00	1.00	1.00
Hydrogen	0.77	0.78	0.78
Oxygen	0.66	0.69	0.71

The results of these combustion experiments may now be summarised. In the pressure range investigated, the brown solid, after treatment with water and subsequent evaporation to dryness in a steam-oven, yields a substance which contains carbon, hydrogen, and oxygen, and slowly absorbs oxygen in air at 100° , but no definite composition can be assigned to it until samples have been prepared under conditions such that the possibility of oxidation is excluded during the treatment with water and subsequent drying.

Some further experiments, in which the volume of the monoxide consumed in the discharge was measured, were carried out on the evolution of gas which takes place when the brown solid is treated with water. After the discharge had been discontinued, the reaction vessel was evacuated; air-free water was then distilled into the vessel in the manner already described. After $\frac{1}{2}$ hour had elapsed, the gases formed were pumped out and analysed, the results obtained being given in Table III. In the experiment (see below) in which 16.05 c.c. of gas were thus obtained, a further quantity of water was distilled into the reaction vessel, and the gases were pumped out after $\frac{1}{2}$ hour. Less than 0.1 c.c. of gas, which proved to be carbon dioxide, was obtained. Repetitions of this procedure over a period of 5 days resulted in the formation of 3.0 c.c. of carbon dioxide.

TABLE III.

Pressure of CO (mm.).	200.	350.	500.
Volume of CO consumed (c.c. at <i>N.T.P.</i>) ...	74.0	130.0	111.3
Volume of CO ₂ formed (c.c. at <i>N.T.P.</i>).....	10.55	19.05	16.05
Volume of CO formed (c.c. at <i>N.T.P.</i>)	0.30	0.25	0.60

These results suggest that there is a rapid reaction associated with the formation of carbon dioxide together with small amounts of the monoxide, and a slow reaction also producing carbon dioxide.

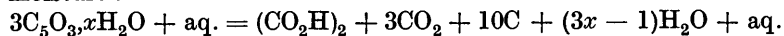
It is important to note that the volume of dioxide produced by the rapid reaction is very nearly 1/7th of the volume of the monoxide used in the formation of the brown solid.

The behaviour of the nearly colourless aqueous solution of the brown solid towards permanganate solution has already been described. By rapid titration with standard permanganate solution, two approximate determinations have been carried out on the amount of oxalic acid formed when the solid is dissolved in water. Two samples of the solid, prepared at 500 mm., were found by combustion to have the empirical compositions (a) $C_5O_3 \cdot 1.70H_2O$, (b) $C_5O_3 \cdot 1.69H_2O$. About 0.5 g. of the solid was dissolved in water, and the solution diluted to 100 c.c.; 20 c.c. of this solution were decolorised by 0.25 g. of norit, a little dilute sulphuric acid was added, and the solution was heated to boiling and titrated rapidly. The results showed that 0.6490 g. of (a) and 0.5178 g. of (b) yielded 0.1180 and 0.0933 g., respectively, of oxalic acid calculated as anhydride, C_2O_3 . Titration of a solution containing a similar amount of pure oxalic acid, which had been treated in the above manner with norit, showed that 1% of the oxalic acid had been adsorbed by the norit. The values obtained above for the equivalent weight of oxalic anhydride in the solution are therefore probably low by this amount.

On the basis of the provisional hypothesis that the empirical formula $C_5O_3 \cdot xH_2O$ can be assigned to the brown solid, the amounts of oxalic anhydride ($M = 72$) which are equivalent to 1 g.-mol. of " C_5O_3 " contained in the brown solid used in the above experiments are calculated to be (a) 25.22 g., and (b) 24.93 g., *i.e.*, approximately 3 mols. of empirical composition $C_5O_3 \cdot xH_2O$ react with water to give 1 mol. of oxalic acid. Since the empirical composition of the solid is represented by $C_5O_3 \cdot xH_2O$, and since the hydrogen content must arise from the absorption of water by one or both of the processes already mentioned, it would appear that the formation of the brown solid may be represented by the equation $7CO = C_5O_3 + 2CO_2$. It will be recalled that in the reaction between water and the brown solid in the reaction vessel approximately 1 vol. of carbon dioxide was liberated for every 7 vols. of monoxide consumed in producing the solid. This observation suggests (the small amount of monoxide formed at the same time being neglected) that in the reaction with water each mol. of " C_5O_3 " reacts forming 1 mol. of carbon dioxide.

By combining the results obtained from combustion, from titration of the nearly decolorised aqueous solution, and from the reaction with water, the following equation is advanced tentatively to represent the action of water on the brown solid after it has been removed

from the reaction vessel and exposed for a short time to atmospheric moisture :



The production of free carbon, according to this equation, would account for the readiness with which the substance absorbs oxygen after treatment with water. Experiments are now in progress to determine the nature of the insoluble material formed when the brown solid is treated with water, and will form the subject of a future contribution.

Summary.

(1) A preliminary quantitative investigation has been carried out on the properties of the substance formed when carbon monoxide, at pressures from 200 to 690 mm. Hg, is subjected to ionisation by collision when streamed through an alternating electric field of the order of 20,000 volts per cm., and of frequency 250 cycles per sec.

(2) After removal from the reaction vessel, the substance has the empirical composition $C_5O_3 \cdot xH_2O$.

(3) The substance reacts with water, forming carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and a dark, insoluble residue.

The authors wish to express their indebtedness to the Royal Commissioners of 1851 for a Senior Studentship which has enabled one of them (R. W. L.) to continue this research, and particularly to Professor F. G. Donnan, F.R.S., for his deep interest and advice during the development of this work.

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