CCXXVI.—*The Decomposition of Carbon Monoxide in the Silent Electric Discharge. Part III.*

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THE continuation of the experiments described in Parts I and II of this series (J., 1925, **127**, 2052; 1927, 857) has led to an accumulation of information relating both to the unresolved controversy between Berthelot (*Compt. rend.*, 1890, **110**, 609, 684) and Schutzenberger (*ibid.*, pp. 560, 681; **111**, 14) on the formation of the brown solid known as Brodie's suboxide by ozoniser discharges in carbon monoxide, and to the recent contention of Ott (*Ber.*, 1925, **58**, 772; J., 1928, 1378) that this brown substance is identical with polymerised malonic anhydride (carbon suboxide, C_3O_2).

The first analyses of the brown solid were made by Schutzenberger, who found that at least 1·5% of hydrogen was always present despite elaborate precautions to dry the monoxide from which the solid had been produced. He also observed that the velocity of decomposition became exceedingly slow when dry mercury was used instead of aqueous electrolyte for the electrodes, and that the decomposition could barely be effected with electrodes of metal foil. He concluded that the presence of water was essential to the decomposition, and that, under the influence of the electric field, either hydrogen or water was transported through the glass containing walls to the reaction space. The slight decomposition observed in experiments with metallic electrodes was consequently attributed to traces of water initially in the apparatus.

Schutzenberger's analyses also indicated an excess of oxygen, much greater than the equivalent of the amount of hydrogen found, and a deficit in the amount of carbon. When the monoxide was replaced by nitrogen no water was found after six hours' discharge. These results were thought to establish that oxygen and hydrogen only were transported into the reaction space, where the hydrogen combined with the monoxide, and that carbon was transported outwards. In the experiments with nitrogen, however, no attempts were made to prove the entry of oxygen and hydrogen into the reaction space.

It is interesting to note that Schutzenberger's hypothesis may have been suggested by Warburg's discovery some years previously of the electrolytic transport of sodium through the walls of a highly evacuated glass bulb (*Wied. Ann.*, 1884, **21**, 622; 1890, **40**, 1). It will be shown that the production of malonic anhydride (carbon suboxide) during the decomposition of carbon monoxide in the discharge affords a satisfactory explanation of Schutzenberger's results.

Berthelot criticised the work of Schutzenberger on the ground that the presence of water was due to the insufficient drying of the initial reactant and of glass and mercury surfaces; he held that the extremely hygroscopic nature of the solid product accounted for its water content, and discountenanced Schutzenberger's hypothesis, but he omitted to discuss the results which were thought to establish the " electrolytic transport " of oxygen and of carbon through the ozoniser walls.

Meyer reinvestigated Schutzenberger's claim in 1913 (*Ber.*, **46**, 1110), using water electrodes, and hydrogen in place of carbon monoxide. He found that the amount of water which was transferred through the walls of the ozoniser, if any, did not exceed 0·0001 g. in 5 hours; this is approximately 1/100 of the amount reported by Schutzenberger.

Experiments have, therefore, been carried out to determine the influence of the nature of the electrodes on the velocity of decomposition, in which both mercury and electrolyte electrodes were employed with the same ozoniser, care being taken to ensure that the condensation in each case took place under identical electrical conditions. Analyses of the products of decomposition were made in order to establish that this process can occur in the absence of water. In order to obtain a true estimation of the water actually present in the solid and not that absorbed during its manipulation, it is essential that the combustion of the solid must be effected without removing it from the ozoniser; for this purpose a new type of ozoniser has been devised.

EXPERIMENTAL.

The general disposition of the apparatus was identical with that described in Part II of this series, with the addition of phosphoric oxide tubes in the outlet tube of the circulator in order to ensure the dryness of the gas returning to the main system: the reaction vessel and the apparatus immediately adjoining it were, however, of a different type and are shown in Fig. 1.

The vessel *B*, which contained the gas while it was subjected to the discharge, was a Siemens type of ozoniser, constructed of soft glass, in which it was possible to effect the combustion of the brown solid produced therein. In all experiments the inner electrode served as the high-tension electrode, the outer electrode being earthed and also water-cooled. The dimensions of the ozoniser were: length, 45·7 cm.; external diameter of outer and inner tubes, 2·54 and 1·7 cm., respectively. Heating of the ozoniser during baking-out processes and combustions was effected by a cylindrical furnace which could be slipped over it from beneath. The furnace consisted of a tube of fire-clay, wound on the outside with nichrome wire and placed in a tin case packed with asbestos; its temperature was measured by means of a platinum–platinum-rhodium thermocouple.

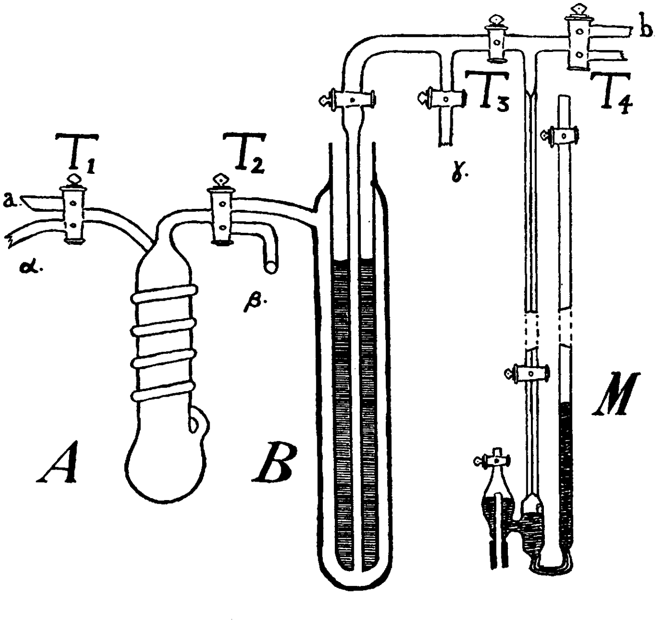
As in the former experiments, an automatic Sprengel pump circulated the gas continuously through the discharge, the gas on leaving the reaction vessel being led through the trap *A* which could be immersed in liquid air, and then to the circulator. A mercury manometer, *M*, was attached to the system as before.

Oxygen-free carbon monoxide was produced by the method described previously, in which recrystallised formic acid was allowed to drop into an evacuated flask containing warm concentrated sulphuric acid. The gas was passed over solid caustic potash and phosphoric oxide and was finally stored under pressure over dry mercury.

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

FIG. 1.

Circulating gases enter this apparatus at b *and leave at* a.



Reaction-velocity Experiments.—The whole of the apparatus from the manometer to the gas container was continuously evacuated for several hours by means of an oil pump connected through several phosphoric oxide tubes to the tube γ, the ozoniser being heated to 400° : the vacuum was then tested over 24 hours. In order to ensure the dryness of all the gas admitted to the apparatus, the following procedure was adopted. The trap *A* was immersed in liquid air and tap T_2 closed ; a small amount of carbon monoxide was then allowed to enter *via* tap T_1 from the gas holder. This gas had been in contact with phosphoric oxide for some time and was allowed to remain in *A* for some minutes before being admitted (*via* T_2) to the ozoniser and manometer section. When pressure equilibrium had been attained, tap T_2 was closed and the process repeated until the apparatus was filled with monoxide at a pressure approximating to 500 mm. at room temperature. The electrolyte levels, which unavoidably altered slightly during an experiment, were adjusted as carefully as possible in order to obtain constant initial electrode dimensions. The voltage was maintained constant by frequent adjustment of the governing resistances, but fluctuations of the order of $2\frac{1}{2}\%$ in the main supply were unavoidable.

The pressure was recorded at one-minute intervals for the first 15 minutes, and thereafter at longer intervals. The results are shown in Table I, the electrode material for Expts. I, II, and III being dilute sulphuric acid, and for Expt. IV dry mercury: the experiments were carried out successively without removing the solid produced.

TABLE I.

Potential applied to reaction vessel, 8·0 kilovolts, r.m.s.

Time (mins.).	I.	II.	III.	IV.
	Pressure (mm.).			
0	504·5	502·5	505·0	505·9
5	500·0	497·5	500·0	501·0
10	490·5	489·0	490·5	495·0
15	483·0	481·5	482·3	488·0
20	476·0	473·5	473·5	481·3
25	469·0	466·1	466·2	475·0
30	462·0	460·0	459·1	469·0
45	446·0	444·0	443·0	451·0
60	(435·5)	432·0	430·1	435·0
75	422·5	423·9	421·0	423·0

It will be seen that, despite the difficulty of obtaining identical conditions for these experiments, the results indicate that the velocity is independent of the nature of the electrode. This is in agreement with the results of Berthelot, and the contention of Schutzenberger that the velocity is specific to the electrode material must therefore be attributed to variations in the potential applied to the electrodes, a quantity which neither author attempted to measure.

These experiments also show that with mercury or with electrolyte electrodes, carbon monoxide, dried finally by slow passage through a spiral immersed in liquid air, decomposes readily in the ozoniser. Since the ozoniser had been evacuated at 400° previous to Expt. I, the only water present is that combined in the glass of the ozoniser and that carried over from the liquid-air trap. Unless it be assumed that the discharge liberates water from the glass, it is clear that decomposition takes place in the presence of an amount of water exceedingly small compared with that cited by Schutzenberger as essential to the decomposition.

Prolongation of the discharge revealed points of some interest: after the first 90 minutes, the pressure–time curves begin to diverge slightly, the condensation velocity in each successive experiment being slightly greater than in the previous one. This phenomenon may be connected with the observation that in these experiments the brown solid was not deposited on the walls of the ozoniser as a film, as was the case when the streaming method was employed, but formed " centres," and in the succeeding experiments the fresh solid was deposited on these nuclei, leaving the clear portions of the walls comparatively free from the condensed solid.

Further, no evidence was obtained for the existence of an equilibrium indicated by a cessation of pressure change which has been reported by most previous workers : in Expt. IV, after 18 hours' discharge, the pressure was still falling at a steady, albeit small, rate.

It is interesting to note that a difference in location of the external " corona " or purple glow which occurred on the outermost ozoniser surface was attendant upon the change in electrode material. In Expts. I—III (acid electrodes) the glow occurred at the level of the upper surface of the inner electrode, and in Expt. IV (mercury electrodes) at the surface of the outer electrode, although the inner electrode was, in all cases, of identical length, its upper surface being several cm. above that of the outer electrode.

Water Content of the Solid Phase.—In these experiments, which were performed in order to determine the atomic ratio H : C in the brown solid resulting from the decomposition of carefully dried carbon monoxide, the procedure was as follows. The decomposition was carried out at approximately 500 mm. pressure, the gas being circulated at about $2\frac{1}{2}$ litres per hour. The potash tubes were cut out, all condensable gaseous products being collected in the liquid-air trap. As the pressure fell, amounts of monoxide were added from the calibrated gas holder until a measured volume had been used. The final addition was made so that the total pressure was about 5% higher than the required final pressure.

In order to determine the time at which the discharge was to be discontinued, *i.e.*, when the measured volume of monoxide had been condensed, corrections were necessary for the actual liquid-air level, and for loss of monoxide during circulation. The discharge was switched off just before the completion of a run, to allow the ozoniser to attain room temperature, and then resumed until the pressure had fallen to the calculated value.

The liquid-air level correction was determined by plotting the pressure of a given volume of gas, which read 500 mm. at a given level, as a function of the liquid-air level. The correction for the loss of carbon monoxide was necessitated by the fact that, if the monoxide alone was circulated in the system, a small but constant decrease in pressure occurred amounting to 25 mm. in 20 hours.

The cause of this disappearance is as yet unknown: no dioxide is produced in the process, but it was noticed that the walls of the outlet tube of the circulator became coated in places by a white film.

At the finish of a run, the white solid mass in the liquid-air trap was allowed to evaporate (*via* tube β) successively through a bubbler containing about 25 c.c. of a solution of dry aniline (1 vol.) in dry xylene (2 vols.), a weighed potash bubbler as used in combustions, and lastly, a tube containing soda–lime. The gases were finally swept out of the tubes by means of a dry nitrogen stream: a preliminary test showed that no increase in weight of the potash bubbler occurred when a carbon dioxide-free gas was passed through the system; hence an estimation of the carbon dioxide produced in the reaction could be effected.

Combustion. The carbon monoxide remaining in the apparatus from tap T_2 to tap T_3, together with the nitrogen in the trap, was removed by passing through the apparatus a slow stream of oxygen. This oxygen, prior to its entry *via* tube α, was led through strong potash solution, concentrated sulphuric acid, a tube containing copper oxide heated to dull redness, several tubes packed with phosphoric oxide, and finally a weighed pentoxide tube. A blank showed that this last tube suffered no increase in weight after an hour's passage of oxygen. To tube γ were attached by means of pressure tubing two weighed pentoxide tubes, a combustion tube containing 8″ of heated copper oxide, a potash bubbler, and a soda–lime tube.

The most difficult procedure was the complete removal of the acid constituting the inner electrode: neglect to do this effectively in the preliminary experiments caused breakage of the ozoniser. The difficulties were overcome in the following manner. A length of very fine quill tubing was inserted in the inner compartment and connected by supported pressure tubing to the water pump; in this way the bulk of the acid was removed, the remainder being removed by washing out successively with water, alcohol, and ether. Finally the tube was completely dried by being maintained at 100° in the earlier parts of the combustion, while a gentle stream of dry nitrogen was passed through the quill tubing.

The temperature, as indicated by the thermocouple, was then allowed to rise slowly until it reached 400°, at which it was maintained for about an hour. At the end of that time the combustion was complete; the current controlling the heating was switched off, and the oxygen stream allowed to continue until the ozoniser had attained room temperature.

The desired atomic ratio of the solid could then be calculated from the increments in weight of the pentoxide tubes and the potash bubbler. The results of certain experiments are contained in Table II.

TABLE II.

Expt.	CO decomposed (c.c. at N.T.P.).	CO_2 produced (g.).	CO_2 resulting from combustion (g.).	H_2O resulting from combustion (g.).	Ratio, H : C.
S	233·0	0·1030	0·3480	0·0114	0·1631
I	284·7	0·1305	0·3456	0·0079	0·1116
II	283·1	0·0757(?)	0·3812	0·0005	0·0064
III	288·6	0·1052	0·3935	0·0048	0·0596
IV	288·0	0·1102	0·3880	0·0005	0·0063

S = Schutzenberger's data.

An interesting phenomenon occurred during the combustion in Expt. I, but was not noticed in succeeding experiments. At 200°, a purple-red substance appeared to be condensing in the form of liquid drops into the upper part of the ozoniser, *i.e.*, that above the furnace; its colour gradually became black, and then it apparently solidified; finally it was oxidised with the residue inside the furnace as the temperature rose.

Discussion.

The water content of the brown solid obtained in Expts. II and IV has thus been shown to be of the order of 5×10^{-4} g., the corresponding atomic ratio H : C being $6{\cdot}3 \times 10^{-3}$. These values are extremely small compared with those obtained by previous workers. Lunt and Venkateswaran (Part II, *loc. cit.*), who carried out combustions of the solid in the usual manner, obtained values of H : C varying from 0·67 to 0·78, whereas those obtained by Schutzenberger were of the order of 0·1; the last author effected estimations by disconnecting the reaction vessel at the end of a run, weighing, and wrapping the whole in platinum foil before inserting it in a large tube in which the combustion was done in the ordinary way. The high values obtained by previous workers must therefore be attributed mainly to the absorption of water vapour from the atmosphere during manipulation of the solid. In view of the intensely hygroscopic nature of the solid, it is surprising that Schutzenberger should obtain a value as low as that quoted.

The water contents shown in Table II correspond to the decomposition of about 300 c.c. of monoxide in a total volume of approximately 25 litres of gas which had passed through the discharge. If comparison be made with Schutzenberger's results, it will be seen that the amount of water associated with the decomposition is 1/100 of that which that author thought to be essential, or 1/30 if the comparison be made with reference to the total volume of gas decomposed in the two cases. Direct evidence thus shows that decomposition takes place in the presence of an amount of water exceedingly small in comparison with that held by Schutzenberger to be essential.

It is interesting to consider what amounts of water could have been conveyed by the circulating gases to the ozoniser during the discharge and in the subsequent manipulation prior to and during the combustion. Although the gas initially in the circulating system had been previously dried by passage over phosphoric oxide, and allowed to enter the ozoniser only after passage through a spiral immersed in liquid air, the direction of circulation (see Fig. 1) was such that the gas flowed over 1 metre of phosphoric oxide before again being fed into the ozoniser: the maximum partial pressure of water is therefore that due to the oxide. This has been shown by Morley (*J. Amer. Chem. Soc.*, 1904, **26**, 1173) to correspond with a content of less than 1 mg. of water vapour in 40,000 litres. The velocity of circulation was approximately $2\frac{1}{2}$ litres per hour and the duration of experiment 10 hours: it is thus clear that no appreciable amount of water could have been conveyed to the ozoniser in this way. Since the carbon monoxide added to the circulating stream, *viz.*, 288 c.c., and the oxygen used during combustion, *viz.*, 2 litres per hour for 6 hours, were also dried by slow passage over a long column of phosphoric oxide before being admitted to the ozoniser, it is impossible to ascribe the water content of 5×10^{-4} g. to the residual moisture in these gases.

Since the ozoniser had been previously evacuated at 400°, it is extremely improbable that a further evolution of water is produced by the thermal effects of the discharge, but the possibility must not be overlooked that the electrical discharge itself may effect a further release of the water combined in the glass. The fact that Meyer (*loc. cit.*) showed that no such phenomenon occurred in the case of his experiments on hydrogen may be due to his use of a relatively weak induction-coil discharge. The action of the more intense discharge employed in these experiments is being further investigated, for the data now available indicate that this type of discharge is capable of releasing appreciable amounts of water from the glass walls of the ozoniser, since the only remaining source of water is that combined in the glass.

Examination of the Solid Phase.—It was decided to carry out certain preliminary experiments in order to confirm the properties of the brown solid as described by previous workers. Some of the solid, prepared and collected as in Part II of this series, was therefore shaken with water and warmed; carbon dioxide was evolved and a deep brown, acid solution smelling of caramel was obtained, together with a dark brown, insoluble residue which could not be filtered off. After boiling, therefore, the fine insoluble particles were allowed to settle and the brown solution was decanted off. The residue was periodically boiled and agitated with water during 19 days, at the end of which period the water had assumed a pale yellow tinge but the residue had become black. The brown solution was also boiled periodically, and it is important to note that during each ebullition fine black particles closely resembling carbon separated out; after these had settled the solution was decanted off and the process repeated; after this treatment had been continued for some time the solution gradually attained an eosin-red colour by transmitted light. It had also clarified and when diluted was of an orange colour. With a series of electrolytes this diluted solution formed brown amorphous precipitates, but these redissolved completely to give a brown solution, when treated with dilute sulphuric acid.

Experiments were then performed to confirm the identity of the acid obtained in the aqueous solution of the solid : after decolorisation, as described by Lunt and Venkateswaran, the solution gave the reactions of oxalic acid. By extraction with dry ether in a Soxhlet apparatus, the solid resulting from the evaporation to dryness of an aqueous solution of 1 g. of the brown solid yielded a small quantity of colourless crystals, m. p. 98—99°. In view of the similarity of these results to those obtained by previous workers, no further evidence seems to be necessary to establish that the acid discovered by Brodie is oxalic acid.

The Production of Malonic Anhydride.—Ott (*loc. cit.*) described the production of unimolecular malonic anhydride, C_3O_2, by the action of the silent electric discharge upon carbon monoxide. He did not state the electrical conditions employed, but experiment shows that C_3O_2 is produced under the same conditions as those obtaining for the experiments of Table II.

The condensable gases from the discharge were collected in the vessel *A*, cooled in liquid air, and allowed to evaporate, and the gases were then driven by a nitrogen stream through a bubbler containing a solution of dry aniline in dry xylene; the white flakes obtained, when washed with ether and dried, had m. p. 224°, mixed m. p. with malonanilide (m. p. 223°), 224—225°. The formation of C_3O_2 in the gaseous phase is thus definitely confirmed.

This discovery sheds interesting light upon the Schutzenberger-Berthelot controversy. Schutzenberger found that nearly half of the oxygen which was necessary to convert the monoxide into the dioxide was not accounted for at the expense of the monoxide condensed; as the remaining gas was pure monoxide, he concluded that this excess oxygen had been conveyed through the glass from the exterior under the action of the discharge : but this conception had also to explain the simultaneous disappearance of 8—10 mg. of carbon. If it be assumed that unimolecular C_3O_2 was obtained in Schutzenberger's experiments, it may readily be seen that the estimation of this substance as carbon dioxide explains the anomalous results obtained. For, let the mass of C_3O_2 produced be x g., and the total mass of gas estimated as CO_2 be m g., then the apparent loss of carbon will be given by the expression :

$$12(m - x)/44 + 36x/68 - 12m/44.$$

Schutzenberger found this to amount to 8 to 10 mg. Solution of the equation gives $x = 0{\cdot}039$ g. Hence, the apparent introduction of oxygen will amount to $0{\cdot}039(32/44 - 32/68) = 0{\cdot}0103$ g.—a value in good agreement with those obtained by Schutzenberger, *viz.*, 0·015—0·016 g.

It would appear, therefore, that the discovery that malonic anhydride is produced when carbon monoxide is subjected to the action of the silent electric discharge offers a satisfactory explanation of the results which gave rise to the protracted controversy between Berthelot and Schutzenberger.

Polymerised Malonic Anhydride.—Diels and Wolff (*Ber.*, 1906, **39**, 689), in announcing their discovery of malonic anhydride, pointed out that this substance, whether in the liquid or gaseous state, polymerised to form a dark red amorphous substance of the approximate formula $(C_3O_2)_x$, although it also contained some hydrogen. Subsequently, Diels and Meyerheim (*Ber.*, 1907, **40**, 355) showed that the polymeride was very hygroscopic and that in dissolving in cold water it liberated carbon dioxide. This observation seems to have received no confirmation from subsequent workers. Diels was struck by the similarity of the polymeride to the brown solid obtained by Brodie, but as little was known regarding either substance, speculation was useless ("Die Kohlensuboxyde," Donath and Burian, Stuttgart, 1924). Experiments have been made by the present authors to ascertain how far the similarity holds.

A quantity of malonic anhydride was prepared by the method of Diels and Meyerheim (*loc. cit.*) as modified by Edwards and Williams (J., 1927, 855); the gas was liquefied by means of an alcohol–solid carbon dioxide bath in a tube which was subsequently sealed off and placed in the ice chest for a day. At the end of that time the bulk of the malonic anhydride had polymerised; a brownish-black solid having a somewhat crystalline appearance had taken the place of the liquid, while from the gaseous phase the polymeride had separated in brown centres together with a light brown film which extended over the surface of the glass. On admitting air to the tube this film immediately became coloured a fine red.

With cold water, the freshly prepared polymeride partly dissolved forming a rich carmine-red liquid which was slightly acid; carbon dioxide was evolved and the solid dissolved completely on warming. The caramel-like smell characteristic of the aqueous solution of the brown solid was not observed. Experiment showed that carbon dioxide was the only gas evolved and that approximately 1 mol. was evolved when 3 mols. of the polymeride (calculated as C_3O_2) were treated with water. On treating the solution with electrolytes, *e.g.*, solutions of sodium chloride, silver nitrate, etc., and boiling, coagulation occurred with the deposition of red-brown flocks, the solution being completely decolorised. Further, by dialysis through a collodion membrane complete coagulation occurred. The polymeride on standing became less soluble in cold water, but on boiling complete solution always took place. It may be presumed that the eosin-red colour of the solution is due to the presence of colloidal carbon. It has been mentioned that the aqueous solution of the polymeride was faintly but distinctly acid. Williams and Edwards, who took great care to obtain pure malonic anhydride, also state this to be the case (private communication). It was therefore important to discover if oxalic acid had been produced as in the case of the solid obtained from carbon monoxide.

On evaporation of the solution to dryness on the water-bath, a brownish-black residue was obtained which on treatment with water gave a slightly acid solution which decolorised acid permanganate, but when neutralised gave no precipitate with calcium chloride. Dialysis experiments gave no further evidence. As a final experiment, the solid remaining after evaporation to dryness of a solution of about 2 g. of the polymeride was extracted with dry ether in a Soxhlet apparatus. On evaporation of the ether, no oxalic acid crystals were obtained, as was the case with the solid obtained by means of the discharge, but only a yellow resinous material.

Polymerised malonic anhydride, therefore, on treatment with water yields carbon dioxide, an eosin-red solution which contains colloidal particles, and traces of an acid which is not oxalic acid.

Nature of the Solid Phase.—Since the discovery of malonic anhydride, many workers have called attention to the similarity between its polymeride and the brown solid obtained by the decomposition of carbon monoxide by the silent electric discharge. Ott (*loc. cit.*) suggests that the brown solid is polymerised malonic anhydride since the weight of this substance which would be formed according to the equation $4CO = C_3O_2 + CO_2$, calculated from the observed amount of carbon dioxide produced, is found to be approximately equal to the sum of the weights of the gaseous malonic anhydride produced and of the brown solid deposited.

The malonic anhydride which is produced in the discharge may obviously suffer polymerisation and partial decomposition, since at 37° the thermal decomposition is rapid; and it may be anticipated that the action of the discharge would be to accelerate both these processes. The brown solid is therefore probably a mixture which contains some polymerised malonic anhydride. Decomposition of the anhydride itself would result in the formation of carbon: a mechanism is thus provided which would account for the origin of the small black particles which constitute the insoluble residue of the brown solid, and of those which separate from the brown solution on boiling. It remains to account for the extremely hygroscopic nature of the brown solid, and for its reaction with water giving oxalic acid. In two experiments a ring of white solid was observed at the bottom of the ozoniser; this is in agreement with the observation of Schutzenberger (*Compt. rend.*, 1890, **110**, 560). It is conceivable that this white substance will account for those properties of the brown solid just mentioned. It has not yet been possible to determine the conditions under which the phenomenon is reproducible.

Summary.

Experiments with reference to the Schutzenberger–Berthelot controversy concerning the decomposition of carbon monoxide in the silent electric discharge have shown that the velocity does not depend on the nature of the electrodes, that decomposition takes place readily even when elaborate precautions are taken to exclude moisture, and that the presence of malonic anhydride in the decomposition products offers a simple explanation of the analytical results of Schutzenberger. It has also been shown that the brown solid produced from carbon monoxide in the discharge is not identical with polymerised malonic anhydride.

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