LX.—*The Interaction of Hydrogen and Chlorine. The Nature of Photochemical Inhibition.*

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It has been already remarked (Trans., 1909, **95**, 1717) that the gases which are known to retard or prevent the photochemical interaction of hydrogen and chlorine are, without exception, easily reducible substances, and it has been inferred that probably the retarding effect is indirectly due to the reduction of the inhibitor by hydrogen or hydrogen chloride.

The ground for the above conclusion concerning inhibitors was the following ascertained facts. Oxygen, nitrogen chloride, and the gas formed by the action of moist chlorine or nitric oxide (nitrogen peroxide or nitrosyl chloride) acted as inhibitors, whilst carbon dioxide, nitrogen, and nitrous oxide were mere diluents. That nitrous oxide should appear amongst the list of diluents is not contrary to expectation, since this gas is, in most circumstances, chemically inert. Oxygen is by far the most feeble inhibitor, and it is also the least chemically active.* Nitrogen chloride and

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* As yet, no disappearance of oxygen from an illuminated mixture of hydrogen and chlorine containing it has been detected; but sufficiently forcible a priori considerations can be adduced in support of the assumption that oxygen will slowly react with hydrogen chloride in the presence of chlorine under the influence of light.

nitrogen peroxide or nitrosyl chloride are reduced with comparative ease, and they are also powerful inhibitors.

In order further to test the truth of the statement that easily reducible gases are in general inhibitors, we have examined the influence of small quantities of the three gases, ozone, chlorine peroxide, and chlorine monoxide, on the rate of interaction of chlorine and hydrogen. Ozone and chlorine peroxide prevent almost entirely the formation of hydrogen chloride, whilst chlorine monoxide has no effect. In order to observe the effect of ozone, the mixture must be exposed to light shortly after the ozone has been added; for, if the mixture is kept in the dark for a few hours, the ozone contained in it is completely destroyed. On the other hand, chlorine peroxide is perfectly stable in the presence of the moist electrolytic gas, provided that the mixture is protected from the influence of light. That the addition of chlorine monoxide to a mixture of chlorine and hydrogen would not appreciably affect the rate of formation of hydrogen chloride under the influence of light might have been predicted, since it is almost certain that moist chlorine itself is really an equilibrium mixture of chlorine, water vapour, the vapour of hypochlorous acid, chlorine monoxide, and hydrogen chloride.

An hypothesis capable of explaining the fact that easily reducible gases are, in general, inhibitors is needed. At first sight it might seem possible that the inhibitor simply destroys the hydrogen chloride produced by the photochemical interaction of the chlorine and hydrogen in such a manner as to leave the total volume of gas unchanged. For example, with ozone as an inhibitor, the reactions expressed by the following equations might be conceived to take place:

$$H_2 + Cl_2 = 2HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$3O_3 + 2HCl = 4O_2 + H_2O + Cl_2 \quad . \quad . \quad . \quad (ii)$$

The two foregoing equations are equivalent to the single equation:

$$\underbrace{H_2 + 3O_3}_{4 \text{ vols.}} = \underbrace{4O_2 + H_2O}_{4 \text{ vols.}}.$$

Such a simple hypothesis, however, is not by itself sufficient to account for the facts. For, to explain the extremely long "induction periods" observed, it must also be postulated that the change expressed by equation (i) proceeds at a slower rate than the same reaction under like condition in a mixture of chlorine and hydrogen containing no ozone. A satisfactory theory must involve other considerations not expressible by chemical equations: the energetics of the phenomenon cannot be ignored.

It is possible that a complete theory must include electrical conceptions; but so far our attempts to formulate an electrochemical hypothesis have only involved us in a maze of assumptions and speculations apparently incapable of experimental verification. We have therefore adopted, for the present, a working hypothesis, in which the photochemical character of the phenomenon is emphasised. According to this hypothesis the energy which enters the system through the chlorine molecules is distributed between the various constituents of the system. If no inhibitor is present an extremely small amount of the transformed energy is sufficient to bring about the union of finite quantities of hydrogen and chlorine. But if an inhibitor is present, the efficient energy is partly (in most cases almost entirely) employed in promoting its reduction, and a considerable amount of energy is degraded in bringing about the reduction of small quantities of the inhibitor.* The assumption that a comparatively large amount of energy is required to reduce a small quantity of inhibitor is in some cases capable of experimental verification. The experiments undertaken with this object in view do not naturally fall within the scope of this paper, and they therefore will be reserved for a future communication.

EXPERIMENTAL.

The Inhibitory Effect of Ozone.

In the following experiments we have measured the effect of ozone on the rate of combination of the electrolytic gases under similar experimental conditions to those which obtained in our work on the retarding influence of nitric oxide on the velocity of formation of hydrogen chloride.

Ozone has entirely fulfilled our expectations in acting similarly to nitric oxide, and its behaviour taken with that of oxygen has afforded an interesting comparison. The measure of its inhibitory power differs very little from that of nitric oxide. In so far as there is a difference, ozone is the more powerful inhibitor.

The apparatus was the same as that employed in the previous investigation on nitric oxide. As ozonised oxygen frequently contains minute quantities of the oxides of nitrogen derived from a trace of nitrogen contained in the oxygen from which it is prepared, the gas from the ozoniser was passed through a wash-bottle containing concentrated sulphuric acid, which is a very effective absorbent of nitrogen peroxide, and was then allowed to

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* It will be observed that the hypothesis does not preclude the possibility of an oxidisable gas acting as an inhibitor provided that it satisfies the necessary conditions.

bubble slowly through water, acidified with sulphuric acid, into a small gas-holder. When the water was saturated with ozone, the supply of gas was shut off, and the ozone kept in the gas-holder for periods varying from two to ten days. By observing these precautions it was hoped that nitrogen peroxide would be completely removed. It may here be observed that potassium hydroxide solution cannot be employed to absorb the oxides of nitrogen, since ozone is extremely unstable in the presence of alkalis.

The measure of ozonised oxygen added amounted to about 1/300th of the total volume of gas in the insolation vessel. In all the experiments the source of light was a 25 c.p. electric lamp, as the more constant Hefner lamp was found to be too feeble for the investigation of the inhibitory effects.

In the preliminary experiment one measure of ozonised oxygen was added to the sensitive mixture in the actinometer in each case. Experiments were performed in which the original sensitiveness of the electrolytic gas varied from 6 to 21 cm. per minute with the lamp placed at a distance of one metre from the insolation vessel. The exposure was half an hour commencing immediately after the addition of the ozone, and in no case could any movement of the index be detected during that period.

In a second series of experiments concentrated sulphuric acid was substituted for the acidified water in the gas-holder. The ozonised oxygen was retained in the gas-holder for ten days before use. Some of the experiments are recorded in detail below:

(*a*) The sensitiveness of the gas was 2·1 cm. per minute with the lamp at a distance of one metre. After the addition of a measure of ozone the insolation vessel was exposed for one hour to the light of the lamp placed at a distance of 30 cm. No movement of the index could be detected. The mixture was then left in the dark for ten hours. On re-exposure to light, combination started immediately, the maximum rate of union of 1 cm. of the index per minute being rapidly attained. Ozone therefore disappears from the gaseous mixture in the dark.

(*b*) The sensitiveness of the gas was 5 cm. of the index per minute, the lamp being at a distance of one metre from the insolation vessel. The distance of the lamp from the insolation vessel was then reduced to 20 cm. A measure of ozone was added to the electrolytic gas in the dark, and the mixture exposed to the rays of the lamp. At the end of one hour and twenty minutes the index liquid began to move very slowly, and at the end of one hour and thirty minutes was moving at the rate of 3 mm. per minute.

(*c*) A measure of ozone was added to the insolation vessel, which was then allowed to remain in the dark for eighteen hours. Subsequent exposure to light proved that the ozone had completely disappeared; there was no "induction period."

(*d*) After the addition of a measure of ozone the mixture was allowed to remain in the dark for an hour and forty-five minutes only, before being exposed to the light of the lamp at a distance of 20 cm. The length of the "induction period" was between twenty and thirty minutes.

Acidified water was again substituted for concentrated sulphuric acid in the small gas-holder, and the experiments were repeated. The readings obtained in one experiment are recorded *in extenso*.

The original rate of combination of the chlorine and hydrogen was 4·5 cm. of the index per minute, with the lamp at a distance of 100 cm. from the insolation vessel. This distance was now decreased to 20 cm., and ozone added:

Time of exposure in minutes.	Scale reading, in cm.	Rate of combination, in cm.
51	1·50	0·00
54	1·70	0·20
57	2·00	0·30
60	2·35	0·35
63	2·60	0·25
66	2·90	0·30
69	3·30	0·40
72	3·70	0·40
75	4·15	0·45
99	14·15	1·25

The rate of combination then increased rapidly to 5 cm. per minute. With the lamp at the original distance of 100 cm. from the insolation vessel, the maximum rate of combination was 9 mm. per minute.

It was finally necessary to show that the means adopted to remove traces of the oxides of nitrogen from the ozonised oxygen were sufficiently effective. To do this oxygen previously mixed with 5 per cent. of nitric oxide was bubbled through water into the small gas-holder, and allowed to remain in the presence of water for one day. Sensitive electrolytic gas in the insolation vessel, mixed with two measures of this oxygen, failed to exhibit any sign of an "induction period." The inhibitory agent in the above experiments was therefore ozone.

The Inhibitory Effect of Chlorine Dioxide.—The chlorine dioxide was prepared from potassium chlorate and concentrated sulphuric acid. The potassium chlorate was recrystallised from boiling water. In the later experiments potassium chlorate, crystallised from an aqueous solution which had been saturated with chlorine and boiled for many hours in a flask provided with a ground-in reflux condenser, was used. In the same experiments the sulphuric acid was several times saturated with chlorine and heated before being used. The chlorine dioxide was prepared by adding in small quantities well dried and finely powdered potassium chlorate to concentrated sulphuric acid contained in a small bulb surrounded by a freezing mixture. The bulb, while still surrounded by the freezing mixture, was connected by means of a ground glass joint with that part of the apparatus designed for adding a measured quantity of gas to the actinometer. The temperature of the bulb was then raised to about 30°, and chlorine dioxide was evolved. The results of a few experiments are recorded below.

A sufficient volume of chlorine dioxide was mixed with the electrolytic gas in the insolation vessel to give a mixture containing one volume of chlorine dioxide to fifty volumes of electrolytic gas. For intervals amounting in all to over seventy hours and extending over five days, the mixture was exposed to the rays of a 25 c.p. tantalum glow lamp placed as near as possible to the glass window of the tank in which the insolation vessel was immersed. At the end of the seventy hours' exposure to light, the gas began to combine slowly under the influence of the rays from the glow lamp. The activity of the mixture gradually increased, and ultimately attained a maximum value equal to about 1/40th of the original sensitiveness of electrolytic gas.

In another experiment one measure of chlorine dioxide only was added to the electrolytic gas in the insolation vessel. The original sensitiveness of the electrolytic gas corresponded with a movement of 36 cm. of the index per minute with the 25 c.p. carbon filament lamp at a mean distance of 20 cm. from the insolation vessel. For four days there was no sign of combination, the total exposure to light during this period amounting to about fifty hours. The tantalum lamp was then placed as near to the insolation vessel as the tank permitted, and under these conditions slow combination was noted. The rate of interaction of the chlorine and hydrogen increased at first very slowly, and then more rapidly up to a maximum of about 3 cm. per minute.

An interesting result, which we are unable at present to explain, is obtained when very small quantities of chlorine dioxide are mixed with the electrolytic gas. With such a mixture interaction of the chlorine and hydrogen proceeds at a slow and uniform rate for an hour or more, and then there is a sudden increase in the velocity of combination.

The Influence of Chlorine Monoxide.—Chlorine monoxide was found to have no inhibiting effect on the union of chlorine and hydrogen. In several preliminary experiments chlorine was passed through a glass tube packed with mercuric oxide, and about 2 c.c.

of the resulting gas were passed into the insolation vessel. The mixture thus obtained did not exhibit the phenomenon of induction, but it was found to be four times less sensitive than the original gas. The fall in sensitiveness was almost certainly due to some oxygen derived from the partial decomposition of the chlorine monoxide.

In the next experiment the chlorine monoxide was liquefied in order to free it from oxygen, and 2 c.c. of the vapour were driven into the insolation vessel. On exposure of the resulting mixture to light, there was no induction period, and in this case only a slight retardation. After the liquid chlorine monoxide had been evaporating some time and all the oxygen had been driven out of the bulb which contained the chlorine monoxide, a further amount of vapour was added; there was no induction period, and no further retardation. Finally, a large volume of chlorine monoxide (about 25 per cent. of the volume of the insolation vessel) was added. There was neither an "induction period" nor a measurable decrease in sensitiveness. Chlorine monoxide has therefore no effect on the rate of combination of hydrogen and chlorine in light.

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