CLXXXVII.—The Influence of Gaseous Oxides of Nitrogen on the Rate of Interaction of Chlorine and Hydrogen.

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HITHERTO it has been shown that both oxygen (Bunsen and Roscoe, Phil. Trans., 1857, 147, 390) and nitrogen chloride (Burgess and Chapman, Trans., 1906, 89, 1399) retard the union of hydrogen and chlorine in light, and that, although the inhibitive influence of the former is considerable, that of the latter is incomparably greater. On the other hand, the observed retardation of the same reaction by nitrogen and carbon dioxide was so small that we have been forced to conclude that these gases function as diluents only. The fact that the property of inhibiting the union of hydrogen and chlorine is strictly limited to a few substances, and is not possessed in varying degrees by gases in common, suggests that it is the result of some chemical relation, definable in general terms, between the gas exhibiting the property and one of more of the constituents of the interacting system. It is possible that the inhibitor must be capable of reacting with one or more of the other gases present. Such a condition is obviously satisfied by oxygen and nitrogen chloride.

As this conjecture is supported by facts recently disclosed in the study of the effect of the gaseous oxides of nitrogen on the rate of union of chlorine and hydrogen, it is advanced tentatively as a hypothesis which will at least serve to indicate the line of investigation that we intend to pursue.

In the presence of water, nitric oxide and chlorine interact, and a brown gas, probably nitrogen peroxide, results. A considerable period of time elapses before the last trace of this gas is absorbed by the chlorine water in the vessel containing it. If a comparatively small volume of nitric oxide is introduced into a mixture of chlorine and hydrogen, the resulting brown gas inhibits the interaction of the chlorine and hydrogen in the light. When, on standing for several hours, the nitrogen peroxide has dissolved, the electrolytic gas almost recovers its former sensitiveness. In its power to retard the interaction of chlorine and hydrogen, nitrogen peroxide appears to lie between nitrogen chloride and oxygen. Like oxygen, nitrogen peroxide will, under the conditions necessary for the interaction of chlorine and hydrogen, act on hydrogen chloride, so that it belongs to that class of substances to which the property of inhibition is supposed to be limited.

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Nitrogen monoxide, although an oxidising agent, acts merely as a diluent. Nitrous oxide is, however, an extremely stable and inert substance at the ordinary temperature. It is probable that it will only part with its oxygen at elevated temperatures.

The three known inhibitors, therefore, contain either loosely combined atoms of oxygen or loosely combined atoms of chlorine. They are all three capable of oxidising hydrogen chloride, and if it is assumed that a comparatively large amount of energy is dissipated in the process of oxidation, an intelligible explanation is afforded of the means by which the inhibitor is enabled to discharge the efficient energy of the chlorine.

The facts published in our last paper on the retarding effect of oxygen (this vol., 959) are in complete harmony with the theory. The communication in question contained experimental evidence which pointed to the conclusion that a very small (perhaps an infinitely small) amount of light energy was sufficient to cause the union of considerable amounts of chlorine and hydrogen in a mixture of the gases containing no oxygen or other inhibitor. On the other hand, to oxidise with gaseous oxygen an equivalent quantity of hydrogen chloride in the presence of chlorine, must necessitate the expenditure of a considerable amount of efficient energy. It is, therefore, not surprising that oxygen, although an inhibitor, is not removed from a mixture of hydrogen and chlorine at a measurable rate in the presence of light.

EXPERIMENTAL.

The apparatus was the same as that employed to measure the retarding effect of oxygen. The electrolytic gas was so free from inhibitive impurities removable by the action of light that no induction period could be observed when the actinometer filled with the mixture was exposed to light. The nitric oxide was prepared by the action of dilute nitric acid on a saturated solution of ferrous sulphate, and was collected in a large gasholder filled with water. After standing in the presence of the water for several hours, some of the gas was allowed to pass into a smaller gasholder filled with a boiled solution of sodium arsenite, in the presence of which reagent it was allowed to remain for several days in order to remove any nitrogen chloride which might be present. As the light emitted from the standard Hefner lamp was inconveniently feeble for these experiments, an electric glow-lamp of 25 c.p., placed at a distance of 2 metres from the insolation vessel, was substituted for it. Under the influence of the light from this lamp, the index of the actinometer moved at the rate of 40 cm. in one minute. A measure

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of nitric oxide, equal to 1/300th of the total volume, was admitted. The mixture was then exposed to the light of the glow-lamp for half an hour, during which period there was no detectable movement of the index. If the original mixture had been exposed to the light for the same length of time, about one-third of the electrolytic gas would have been converted into hydrogen chloride. After the illumination of half an hour, the mixture was allowed to stand in the dark for two and a-half hours, and then re-exposed to light; during twenty-five minutes there was no combination. The actinometer was then left for thirteen hours in the dark. On exposure to light there was instantaneous formation of hydrogen The movement of the index was at first slow, but it chloride. gradually increased until the sensitiveness of the mixture was almost as great as that observed before the nitric oxide had been added.

In a second experiment the procedure was slightly varied. Fresh water was introduced into the actinometer, which was subsequently filled with sensitive electrolytic gas. The index liquid moved 34 cm. in one minute when the insolation vessel was exposed to the light of the glow-lamp; but after the mixture had been left for almost twelve hours in darkness, the nitrogen peroxide had almost completely disappeared from the gas. The sensitiveness, which was at first only 3 cm. per minute, increased gradually and rather irregularly to its original value.

In a third experiment it was found that a mixture of the same composition began to combine after five hours' continuous exposure to light. A soluble product of the interaction of moist nitric oxide and chlorine, presumably nitrogen peroxide, is therefore capable of inhibiting the combination of chlorine and hydrogen.

In the experiments with nitrous oxide, some difficulty was presented in the preparation of the gas sufficiently pure for our purpose. Very small quantities of foreign substances in the ammonium nitrate, from which the nitrous oxide is prepared, tend to facilitate side reactions when the salt is decomposed by heating. The ammonium nitrate was therefore crystallised four times from pure water. In the preparation of the nitrous oxide, great care should be taken to prevent rapid decomposition of the salt. In spite of the precautions taken to ensure purity, we have not succeeded in preparing a sample of the gas quite free from nitric oxide.

In the experiments performed to test the influence of the nitrous oxide on the rate of interaction of chlorine and hydrogen, the source of light was a Hefner lamp, placed at a distance of 60 cm. from the insolation vessel of the actinometer. The details of an experiment are recorded below.

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The sensitiveness of the electrolytic gas was 4.40 cm. per minute. After adding to the electrolytic gas 1/300th of its volume of nitrous oxide, it was found that hydrogen chloride was still formed in the light, the rate of its formation corresponding to a movement of the index of 0.36 cm. per minute. On standing for 12.5 hours in darkness, the sensitiveness was 2.30 cm. per minute, but it rose gradually to 4.00 cm. per minute. That the observed retardation immediately after the addition of the nitrous oxide was not caused by the nitrous oxide itself, but by a small amount of nitric oxide, is evident from the circumstance that the effect almost entirely disappeared after the insolation vessel had been allowed to remain in darkness for half a day. Another experiment, in which a volume of nitrous oxide equal to as much as 1/20th of the internal capacity of the insolation vessel was added, furnished similar results.

Conclusions.

1. A gaseous product of the interaction of moist chlorine and nitric oxide (presumably nitrogen peroxide) inhibits the interaction of chlorine and hydrogen.

2. The inhibitive gas is after several hours almost completely absorbed by the chlorine water.

3. Nitrous oxide is a mere diluent. The rate of interaction of chlorine and hydrogen is not appreciably affected by the presence of a comparatively large volume of the gas.

4. It is considered as probable that the action of the inhibitor is such that the efficient energy of the chlorine derived directly from the light is dissipated by its bringing about a chemical change in which the inhibitor takes part.

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