## LVII.—*Some Reactions of the Halogen Acids.*

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It had been noticed by one of us that when phosphorus pentoxide was used for drying gases, there was in certain cases an indication that a considerable amount of gas was taken up. It was found, for instance, on passing a stream of air through phosphorus pentoxide tubes, which had been used for drying chlorine, sulphur dioxide, and hydrogen chloride respectively, that these gases continued to be carried over by the air for several hours. This was thought to arise from a mere mechanical retention of the gases, but as the quantities expelled were large, it was desirable to determine the character and

extent of the absorption. This seemed especially necessary, seeing that the problem of the reaction of dry gases on one another is one of great importance, and phosphorus pentoxide has been relied upon in experiments of a delicate nature where perfect desiccation was required.

For the purpose of determining the extent to which this retention of the gas took place, dry chlorine, hydrogen chloride, and sulphur dioxide respectively, were passed over a long layer of phosphorus pentoxide in a drying tube, which was weighed from time to time. It was found that, although the experiment was continued several hours, no marked increase of weight occurred. These observations appeared therefore to be in contradiction to those previously made.

Recently, however, we have been engaged in studying the relative values of desiccating agents, and the results which were obtained, when working with phosphorus pentoxide in particular, led us to reopen the question as to the action of this substance on gases.

*Action of Hydrogen Chloride on Phosphorus Pentoxide.*

Our method of experiment was to introduce into the gas over mercury a quantity of phosphorus pentoxide in a glass tube, open at both ends so as to give free access to the gas. With oxygen, hydrogen, sulphur dioxide, carbon dioxide, chlorine, and sulphuretted hydrogen, no absorption was observed, although the gases were left in contact with phosphorus pentoxide for several weeks.

With hydrogen chloride, however, a considerable absorption was noticed, and this went on from day to day, commencing very slowly, rising to a maximum, diminishing again, and finally ceasing.

Observations of the amount of absorption were made at convenient intervals, and the results are embodied in the following table, the volumes being in all cases reduced to normal temperature and pressure.

| I. | | | II.* | | |
|---|---|---|---|---|---|
| Time elapsed. | Absorption. | Rate in c.c. per hour. | Time elapsed. | Absorption. | Rate in c.c. per hour. |
| 27 hours ... | 6·8 c.c. | 0·36 | 143 hours .. | 112·6 | 0·72 |
| 48 „ ... | 18·3 „ | 0·55 | 167 „ .. | 124·4 | 0·57 |
| 70 „ ... | 35·0 „ | 0·76 | 239 „ .. | 138·6 | 0·19 |
| 77 „ ... | 44·5 „ | 1·35 | 309 „ .. | 148·5 | 0·14 |
| 103 „ ... | 74·3 „ | 1·16 | 452 „ .. | 158·5 | 0·07 |
| 119 „ ... | 95·3 „ | 1·28 | 572 „ .. | 163·7 | 0·04 |

* Readings in the second series of observations after the $P_2O_5$ tube had been in a vacuum (see p. 757).

The slow rate of absorption during the time of the first few observations is worthy of remark; though it may merely indicate that it was necessary for the hydrogen chloride to expel the air mechanically retained by the phosphorus pentoxide, before it could come into intimate contact with the latter. This would also explain why no marked increase in weight was observed when the gases were simply passed over a layer of phosphorus pentoxide.

The next question was, to determine what was the nature of the action which took place between the hydrogen chloride and the phosphorus pentoxide. That this was something more than a mere mechanical retention of the gas was indicated by the fact, that when the phosphorus pentoxide was taken out of the hydrogen chloride absorption tube and left in a Torricellian vacuum for some days, no gas was given off. The phosphorus pentoxide was therefore again placed in an atmosphere of hydrogen chloride, and, as seen from Table II, continued to take up more of the gas.

The only similar case of reaction with phosphorus pentoxide is, as far as we are aware, that noticed by Gladstone (*J. Chem. Soc.*, 1866, **19**, 290, and 1868, **21**, 64),* in which dry ammonia is taken up with formation of diamidopyrophosphoric acid.

To determine quantitatively the amounts of phosphorus pentoxide and hydrogen chloride which enter into the reaction, well-stoppered bottles were filled by displacement with hydrogen chloride, and a quantity of phosphorus pentoxide quickly inserted from a weighed tube. The amount of pentoxide added was thus known. The bottles were opened from time to time under mercury until there was no further absorption; at this stage, all the phosphorus pentoxide had become liquid. The amount of the absorption was thus measured.

As an instance of the results obtained by this method, the following numbers may be given :—Phosphorus pentoxide taken = 0·1255 gram, hydrogen chloride absorbed = 28·5 c.c., that is, 1 gram of phosphorus pentoxide takes up 227 c.c. of hydrogen chloride.

These numbers agree very nearly with the equation—

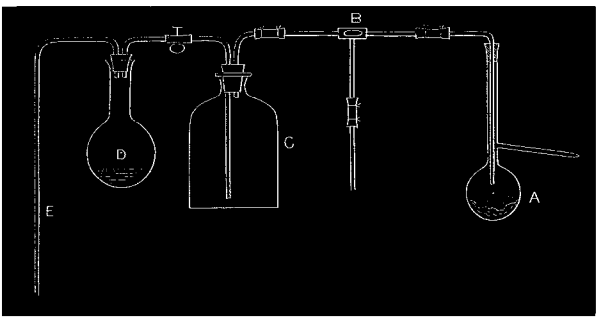
$$2P_2O_5 + 3HCl = POCl_3 + 3HPO_3.$$

Calculating from this equation, 0·1255 gram phosphorus pentoxide should take up 29·7 c.c. of hydrogen chloride; a result which agrees

* Professor Thorpe has called our attention to the fact that Mallet (*Chem. News*, **44**, 164) had observed that hydrogen fluoride was taken up by phosphorus pentoxide, from which he concluded that the pentafluoride of phosphorus was formed. Moissan has however shown (*Ann. Chim. Phys.* [6], **12**, 486) that phosphorus trifluoride combines readily with oxygen, forming a stable oxyfluoride, $POF_3$, analogous to the oxychloride, and it would thus seem very probable that the retention of hydrogen fluoride observed by Mallet was due to the formation of this oxyfluoride.

very nearly with that found, especially when we take account of the small errors inherent in the method of experiment.

It was difficult in this way to obtain a sufficient quantity of the compound to determine its nature. An apparatus such as is shown in the figure was therefore constructed, and as this form, which our experiments showed to be most convenient, may be found useful in cases where a regulated supply of gas free from air is required, we describe it.




A is a fractionating bulb, into which a quantity of phosphorus pentoxide was introduced, B is a three-way tap, C a large bottle serving as a reservoir for the hydrogen chloride, and D a flask containing sulphuric acid and common salt. After attaching the bulb A, containing the pentoxide, the whole apparatus was filled by displacement with hydrogen chloride, and the side tube of A sealed up. Any excess of hydrogen chloride may escape by the tube E dipping under mercury. The whole apparatus is thus sealed off from the air. The course of the reaction may be examined by allowing the vertical limb of the three-way cock B to dip under mercury, which thus showed how the absorption was proceeding. By means of the three-way tap, supplies could be drawn periodically from the reservoir to replace the gas taken up by the phosphorus pentoxide, and the reservoir could be replenished by warming the flask D.

When the reaction appeared complete, the bulb A was detached, a thermometer introduced, and the liquid distilled off, precautions being taken to prevent ingress of moisture. The liquid boiled at 108°, and showed all the properties of phosphorus oxychloride. A residue of metaphosphoric acid was left in the bulb.

From these experiments it appears that a reaction, analogous to that of Kolbe and Lautemann (*Annalen*, **113**, 240) for obtaining phosphorus oxychloride, occurs spontaneously when hydrogen chloride is left in contact with phosphorus pentoxide, and is complete if sufficient time be allowed.

Having established, therefore, the reaction in the case of hydrogen chloride, it was interesting to observe what took place in the case of the other halogen acids. These were experimented on in the same way. In the case of hydrogen bromide, absorption took place and the phosphorus pentoxide became liquid, the reaction beginning slowly and increasing to a maximum, as in the case of hydrogen chloride. Complete absorption, however, is effected much more slowly in the case of hydrogen bromide.

With hydrogen iodide, no absorption could be observed, so that although the circumstances seem especially favourable for the production of an oxy-compound, no such body is formed.

*Action of Hydrogen Chloride on Mercury in presence of Oxygen.*

Although it is known that hydrogen chloride has no action on mercury, it had been noticed that in some of the experiments with this gas, the mercury had been attacked, and this occurred only where oxygen was present.

Richardson has recently shown (Trans., 1887, 801), that hydrochloric acid, when mixed with excess of oxygen and exposed to light, yields chlorine; but we found that, even with small quantities of oxygen, the mercury was attacked, and became coated with a white salt.

48 c.c. hydrogen chloride and 30 c.c. oxygen, dried over calcium chloride, were introduced along with a small quantity of mercury into a stoppered vessel and exposed to diffused daylight for three weeks to allow of the reaction reaching its limit.

The vessel was then opened under mercury. Only 5 c.c. of gas remained, and the whole of the hydrogen chloride had disappeared, as there was no further absorption on the introduction of water. The chlorine had manifestly been taken up by the mercury, and oxygen equal to half the volume of the hydrogen chloride had disappeared, part of which only could have combined with the hydrogen.

In order to obtain a quantity of the mercury compound, a large cylinder was filled with a mixture of hydrogen chloride and oxygen, and a few globules of mercury introduced. The mercury was frequently shaken to renew the surface, the charge of hydrogen chloride being renewed from time to time. When sufficient of the compound appeared to be formed, it was collected, and any globules of mercury adhering to it were removed as completely as possible by amalgamation with silver. Analysis, however, showed that the compound still contained free mercury.

The analysis was performed by heating the substance (previously

dried over phosphorus pentoxide) with quicklime, collecting and weighing the mercury, and estimating the chlorine in the residue.

0·2890 gram substance yielded 0·2347 mercury.
0·0359 chlorine.

The difference, 0·0184, could consist only of oxygen or water. This evidence, taken in conjunction with that derived from the volumes of the gases concerned in the reaction, lead to the equation—

$$2Hg + 2HCl + O_2 = Hg_2OCl_2,H_2O.$$

It seems, therefore, that in such an experiment there is formed an oxychloride resembling the oxycyanide, $Hg_2O(CN)_2$.

Berthelot, we found (*Ann. Chim. Phys.* [5], **23**, 100), had already noticed that mercury was attacked in some cases by hydrogen chloride, and set down the compound formed as calomel, but gives little experimental evidence in support of this.

The reaction proceeds in the dark as well as when exposed to light, and indeed powerful sunlight seems, if anything, unfavourable to it.

It was found by these experiments that if excess of oxygen is present, all the hydrogen chloride is used up, and *vice versâ*. If, however, a considerable amount of nitrogen is present as when air is mixed with the hydrogen chloride, the reaction proceeds much more slowly, and all the oxygen is not taken up even in presence of considerable excess of hydrogen chloride.

The reaction of course goes on much more slowly if excess of hydrogen chloride is present. In one case, a mixture containing only 9 per cent. of oxygen was left in contact with mercury; at the end of three weeks, nearly half the oxygen remained, the total amount of gas entering into combination being only 20 c.c. out of the 150 c.c. used.

*Action of Hydrogen Bromide and Hydrogen Iodide on Mercury.*

A mixture containing 33 vols. of oxygen to 45 of hydrogen bromide was taken and kept in contact with mercury in the dark. The whole of the hydrogen bromide was found to have disappeared, 37 c.c. of gas remaining. On testing this gas for oxygen with a glowing splinter, a powerful detonation occurred, showing the presence of a considerable quantity of free hydrogen; it appeared, in fact, that whereas in the case of hydrogen chloride the whole of the hydrogen combined with the oxygen, with hydrogen bromide only part of it was thus transformed.

Hydrogen iodide, as is well known, acts directly on mercury; the green mercurous iodide is first formed very rapidly, and this is converted by excess of hydrogen iodide into the red iodide. This

takes place even if the mercurous compound has been dried at 100°. The mercuric iodide is reconverted into the mercurous compound on adding excess of mercury.

Chlorine, if allowed to act on mercury in the cold, forms mercuric chloride, even in presence of a considerable excess of mercury.

Whilst the work was proceeding, we communicated with Dr. Richardson, thinking that he might have made some observations in the same direction, and we have to acknowledge the great courtesy with which he placed such facts as he had noticed at our disposal, desiring that they should appear in conjunction with ours. We cannot do better than quote his words: "Mercury in contact with hydrobromic acid and hydriodic acid (in presence of oxygen) readily decompose in the light, also, however, in the dark." "Hydrobromic and hydriodic acids, dry and free from oxygen, were almost completely decomposed in the dark; copper completely decomposes hydriodic acid."

The reactions observed open out an interesting field for studying the course of chemical reaction, and one in which we look forward with interest for the results of Dr. Richardson's investigations of the part played by light in these phenomena.