ART. XLVI.—*Communications from the Laboratory of Williams College.* No. VI.—*Concerning Phosphorus Oxychloride;* by IRA REMSEN.

THE fact was recently established* that carbon monoxide, though it must be considered as an unsaturated compound, does not readily combine with the oxygen from ozone to form the saturated dioxide. Indeed it was impossible to discover any conditions under which such a combination takes place.

Although it is known that ozone does readily oxydize many substances, it seemed to me desirable to further test its action upon bodies which are generally recognized as unsaturated. For this purpose I have first employed phosphorus trichloride in the hope of obtaining the oxychloride, $POCl_3$. The method of formation of the oxychloride thus indicated would be interesting from more than one stand-point, as will be pointed out below.

It has already been shown by Brodie† that, when oxygen is passed into phosphorus trichloride at the boiling temperature of the latter, a partial transformation into the oxychloride takes place; and Michaelis‡ subsequently showed that this transformation or oxydation is exceedingly incomplete, even though the process be continued for two or three days. An analogous experiment has also been performed by Henry,§ who proved that, when sulphur and phosphorus trichloride are heated together in a sealed tube at 130°, the sulphochloride $PSCl_3$ is formed. It is plain that, in both of these experiments, one of the forces which opposes the combination is that which binds together the atoms of oxygen in the molecule of oxygen, and the atoms of sulphur in the molecule of sulphur; and hence, if we could employ free atoms of oxygen or sulphur instead of their molecules, we would expect the action to take place much more readily. In the case of sulphur, it is not possible, as far as we know at present, to obtain free atoms or unstable molecules which by their breaking up yield free atoms. In ozone, however, we have such an unstable molecule of oxygen. As we have seen in the experiment with carbon monoxide, above referred to, ozone does not always appear to furnish free atoms of oxygen when we might expect it to, and hence the formation of phosphorus oxychloride by the action of ozone could not be predicted with any certainty. Experiment proved, however, that the formation actually does take place with

* This Journal, vol. xi, p. 136.
† Odling's Handbook, i, 297.
‡ Gmelin-Kraut's Handbuch der Chemie, I, i, 391.
§ Berliner Berichte, ii, 638.

great ease, and that phosphorus oxychloride may be obtained in this way in any quantity.

Pure phosphorus terchloride boiling at 77° was placed in a flask. In the cork of the flask were three openings. In one of these was inserted a thermometer which dipped into the liquid; in another was a tube, leading from the ozone-generator, which served to conduct the ozone into the liquid; in the third was placed a tube which in turn was connected with an inverted Liebig's condenser, the latter serving to condense and return to the flask any vapors that might be formed. Oxygen, thoroughly dried by sulphuric acid and calcium chloride, was now passed through the tube which served as ozone-generator. At first I employed a Siemen's ozone-tube which was connected with an induction-coil. The action in this case was not marked, although I soon observed that the thermometer indicated a rise in the temperature of the trichloride. At the beginning of the operation the temperature of the liquid in the flask was the same as that of the air in the room, viz: 15°. In a short time it rose to 36° where it remained stationary, as long as ozone was conducted into the liquid. As soon as the current was stopped, the temperature began to fall and continued to fall gradually until the ordinary temperature was reached.

In about an hour the process was interrupted, and the liquid subjected to distillation. Its boiling point was markedly changed. Only a drop or two passed over before the thermometer indicated 80° and then the mercury rose gradually to 110° when all had passed over. About half the liquid boiled below 90°. This was again subjected to the action of ozone, but now instead of using Siemen's tube, as at first, Wright's tube connected with the Holtz electrical machine was used, and with much better results. The arrangement of the apparatus in this second experiment was the same as in the first. The temperature of the liquid in this case also began to rise as soon as the ozone was passed into it. In a few minutes the thermometer, which at the beginning of the operation indicated 15·5° stood at 44°, where it continued to stand with slight fluctuations during the entire process. At the surface of the liquid the increase in the temperature was so marked, that a portion was converted into vapor, which was returned to the flask by means of the condenser. In the flask, a few drops of a yellowish, resinous material made their appearance, principally at the end of the ozone delivery-tube. The quantity of this substance formed was so small, as to preclude the possibility of an investigation. On repeating the experiment subsequently, this substance always appeared as a product. Whatever it is, it seems to be somewhat volatile with the vapor of the oxychloride of phosphorus.

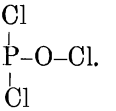
The passage of ozone into the flask was continued for about half an hour in the second experiment, and the product was then examined. About three quarters of the liquid now boiled above 100°, and it did not commence to boil below 85°. By the first distillation it was thus separated into two parts, one boiling below 100°, and the other boiling above 100°. The latter, without further treatment, was at once analyzed. A small quantity was weighed in a sealed bulb, and the bulb then broken under water. After decomposition, pure nitric acid was added and the solution then precipitated with silver nitrate.

0·251 grams of the substance gave 0·6842 grams AgCl = 0·1692 grams Cl.

This corresponds to 67·41 per cent of chlorine, while phosphorus oxychloride contains 69·37 per cent of chlorine and the trichloride 77·4 per cent chlorine. This analysis could hardly be expected to give more satisfactory numbers, as very little precaution was taken to separate the pure oxychloride from the mixture. It proves, however, that the liquid under examination contains markedly less chlorine than the trichloride with which we started, and nearly the same amount as the oxychloride which we would expect to be formed under the circumstances described. The deficit in chlorine may be accounted for by considering the yellow resinous material, above referred to, as being free from chlorine and being also somewhat volatile with the vapors of phosphorus oxychloride.

In addition to the above facts, it was found that the liquid was decomposed slowly by cold water—much less readily than the trichloride—and as a product of the decomposition with water, a large amount of phosphoric acid was formed. Taking then everything into consideration, there cannot be much doubt that, when ozone acts upon phosphorus trichloride, the latter is readily converted into the oxychloride.

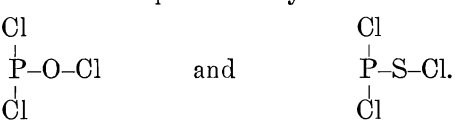
The reaction is analogous to those referred to above, viz: the production of the oxychloride by the action of oxygen upon boiling trichloride, and that of the sulphochloride by the action of sulphur on the trichloride at 130°. Further, it is analogous to the reaction which gives rise to the formation of phosphorus perchloride by the action of chlorine upon the trichloride. The most natural thought that suggests itself is that all these bodies have a constitution similar to that of phosphorus perchloride, and that, in the above reactions, phosphorus passes from the triad to the pentad condition. Those who hold the view that the valence of an element is invariable are inclined to consider phosphorus oxychloride as having a structure essentially different from that of the perchloride, and they write its formula thus:



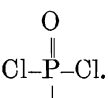
According to this, phosphorus is trivalent in the oxychloride, the same as in the trichloride. The grounds for this assumption are as follows:

1. The oxychloride can be converted into the form of vapor without undergoing decomposition, which shows that it cannot belong to the class of compounds known as molecular compounds, inasmuch as these latter are decomposed into simpler molecules by the action of heat. But, if it is not a molecular compound its structure must be similar to that of phosphorus trichloride, which is the type of the atomic compounds of phosphorus.

2. Thorpe* has recently shown that the specific volume of oxygen in phosphorus oxychloride is 7·89 and that of sulphur in the thiochloride 22·66. These values agree closely with those formerly found by Kopp for oxygen and sulphur which are united with another element with only one affinity each. From this the conclusion is drawn that in phosphorus oxychloride and thiosulphide, the oxygen and sulphur are united to phosphorus by only one affinity each, and hence that the structures of these bodies are represented by the formulas:

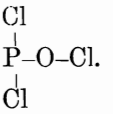


It may be remarked in regard to the former of these grounds that Würtz† has shown that phosphorus perchloride itself, the most decided representative of molecular compounds, may, under proper conditions, be converted into the form of vapor without undergoing decomposition, and hence there is no good reason for assuming that the perchloride differs from ordinary chemical compounds in any essential particular. If, however, the perchloride is a true chemical compound, an atomic in contradistinction from a molecular compound, then phosphorus is in it quinquivalent, while it is certainly trivalent in the trichloride. If, further, we once grant that phosphorus can and does act as a quinquivalent element, we would naturally suppose it to act so in the oxychloride, and hence to the latter would be given the formula,

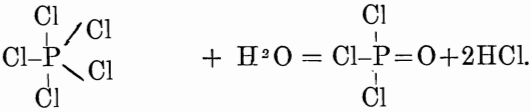


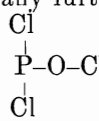
* Berliner Berichte, viii, 326. † Comptes Rendus, lxxvi, 601.

This formula is more in accordance with known facts than the former one. We can much more readily understand how a compound of this formula may be produced by the action of water on phosphorus perchloride, than we could understand its formation if its formula were



Thus we have:



Here the oxygen atom from the water simply takes the place of two chlorine atoms without any further disturbance of the molecule. But, if the formula  is correct, then it is plain that the reaction with water is much more complicated.

So too the formation of the oxychloride from the trichloride by the action of ozone is much more comprehensible, on the assumption that the reaction consists simply in the taking up of an atom of oxygen, without any accompanying displacement and subsequent binding of chlorine.

In regard to the experiments of Thorpe, it may be said that, if Kopp's principle is correct, i. e., if the specific volume of an atom is determined by the manner in which it is held in combination, and, if Thorpe's numbers are correct, then there can be no doubt that the conclusion drawn by him is also correct. While there is no reason for doubting the correctness of the numbers obtained by Thorpe, we may perhaps be justified in not accepting Kopp's principle as so firmly established, that we can employ it as a means of proving the correctness or incorrectness of formulas which seem to be well established by other means.

March, 1876.