[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS COLLEGE.]

THE ACTION OF THIONYL AND SULFURYL CHLORIDES ON SULFUR AND PHOSPHORUS.

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In 1882 Köchlin and Heumann[1] described an investigation of the action of sulfuryl chloride on several substances, among which were sulfur and phosphorus. Inasmuch as the experiments described were carried on under ordinary atmospheric pressure, the temperature could not have been higher than 69°, the boiling point of the reagent. According to Köchlin and Heumann, sulfuryl chloride reacts only slowly with yellow phosphorus, but with well-dried red phosphorus the reaction proceeds readily even at the ordinary temperature, with the formation of phosphorus trichloride. This compound was separated from the excess of sulfuryl chloride by fractional distillation. Reaction proceeds according to the equation

$$2P + 3SO_2Cl_2 = 2PCl_3 + 3SO_2.$$

The failure of yellow phosphorus to react was considered to be due to the limited surface of contact. Sulfuryl chloride was found by Köchlin and Heumann to be without action on sulfur at the boiling point of the former.

The action of thionyl chloride on sulfur was described by Prinz[2] in 1884. The experiments were carried out in sealed glass tubes. At 100° the sulfur was found to dissolve to form a clear solution but upon cooling it separated in the form of crystals. After heating the tubes for a time at 180°, the sulfur was found to have reacted according to the equation

$$2SOCl_2 + 3S = 2S_2Cl_2 + SO_2.$$

So far as the authors of this article are able to find, no attempts have been made to bring about reaction between thionyl chloride and phosphorus either red or yellow.

The experiments described in this paper were carried out in sealed glass tubes at temperatures varying from 70° to 180°. The sulfur flowers and red phosphorus were carefully dried over sulfuric acid; the yellow phosphorus was dried on filter paper. Except where otherwise stated, an excess of the reagent was employed.

Sulfuryl Chloride and Sulfur.—Tubes containing sulfuryl chloride and sulfur were heated at temperatures varying between 75° and 150°. At temperatures from 75° to 85°, the sulfur was found to dissolve in the liquid and to crystallize out upon cooling. Upon opening the tubes no indication of chemical reaction was noted. At 95° to 98° reaction was found to take place slowly for upon cooling tubes which had been heated at these temperatures for several hours, only about one-fifth of the sulfur separated out.

[1] *Ber.*, **15**, 1736 (1882).
[2] *Ann.*, **223**, 355 (1884).

At temperatures of 125° and above, all the sulfur went into solution within 2 hours but did not crystallize out when the tubes were cooled. Reaction apparently was complete. The color of the solution in these tubes varied from light yellow to dark amber, depending upon the relative amounts of sulfur and sulfuryl chloride employed. A rough fractional distillation of the solution led to the identification of sulfur monochloride and the excess of sulfuryl chloride. Sulfur dioxide was likewise present to considerable extent. Reaction evidently proceeds according to the equation

$$SO_2Cl_2 + 2S = S_2Cl_2 + SO_2.$$

Sulfuryl Chloride and Phosphorus.—As previously mentioned this reaction was investigated by Köchlin and Heumann who found the product of the reaction to be phosphorus trichloride. Inasmuch as sulfuryl chloride is a good oxidizing agent, the authors of this paper considered that the reaction with excess of sulfuryl chloride should proceed further and that the ultimate product formed should be phosphorus pentachloride. Accordingly a number of tubes were prepared with red phosphorus and an excess of the reagent. After the tubes were heated for a time at 120°, the phosphorus was found to have gone entirely into solution with the formation of phosphorus trichloride, as described by Köchlin and Heumann. Higher temperatures were then tried. At 180° reaction proceeds further, for after heating for a time at this temperature the tubes were found to contain a small amount of a light yellow crystalline deposit which proved to be phosphorus pentachloride. The supernatant liquid contained the greater part of the phosphorus in the form of trichloride. From this it is seen that phosphorus trichloride is oxidized to phosphorus pentachloride by excess of sulfuryl chloride, but that reaction is far from complete at 180°. Equations for the action of sulfuryl chloride on phosphorus are as follows:

$$3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$$

$$PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$$

The complete reaction of an excess of sulfuryl chloride on phosphorus may be expressed in a single equation as follows:

$$2P + 5SO_2Cl_2 = 2PCl_5 + 5SO_2$$

After completing the above experiments with red phosphorus, other tubes were prepared using yellow phosphorus. Reaction was found to take place readily at a temperature of 125° with formation of phosphorus trichloride according to the equation given above for red phosphorus. As stated heretofore, Köchlin and Heumann found that sulfuryl chloride and yellow phosphorus react very slowly. This difference in results is undoubtedly due to the fact that Köchlin and Heumann carried on their experiments under ordinary pressure, hence at a temperature not exceeding 69°, whereas the authors of the present paper employed a temperature of 125°.

Thionyl Chloride and Sulfur.—The reaction of thionyl chloride on sulfur was described by Prinz as previously mentioned. This work has been repeated by the authors with precisely the same results as those described by Prinz. At temperatures from 150° to 180°, reaction takes place giving sulfur dioxide and sulfur monochloride.

Thionyl Chloride and Phosphorus.—Although this reaction has never been investigated, the action of thionyl chloride on phosphorus trichloride was described by Michaelis[1] in 1871. According to Michaelis, when phosphorus trichloride and thionyl chloride are heated together in the proportion of 3 molecules of the former to one of the latter, reaction takes place with the formation of phosphorus pentachloride, phosphorus oxychloride and phosphorus sulfochloride, as shown by the equation

$$3PCl_3 + SOCl_2 = PCl_5 + POCl_3 + PSCl_3.$$

Reaction however, is not complete even after heating for 15 or 20 hours.

This reaction differs greatly from the thionyl chloride reactions heretofore studied by the authors, hence the work has been repeated, tubes being prepared with phosphorus trichloride and thionyl chloride in the proportions employed by Michaelis. These tubes were heated for 16 hours at temperatures from 80° to 160°, after which they were found to contain a yellowish crystalline substance together with the supernatant liquid. The solid proved to be phosphorus pentachloride. On account of the small amount, it was impossible to fractionate the supernatant liquid with any degree of completeness. Nevertheless a rough fractionation yielded a small quantity having a boiling point above 110°. When this was decomposed in water, considerable hydrogen sulfide was liberated, undoubtedly due to phosphorus sulfochloride which is decomposed by water according to the equation

$$PSCl_3 + 4H_2O = H_3PO_4 + 3HCl + H_2S.$$

It has been impossible to identify positively the phosphorus oxychloride but the lower boiling portion of the liquid was found to contain both thionyl chloride and phosphorus trichloride. From this it appears that the reaction as described by Michaelis is correct but incomplete at the temperature employed.

Several tubes were prepared with the element phosphorus and a considerable excess of thionyl chloride. After heating for 2 hours at 125°, the phosphorus was found to have gone completely into solution. This was true with both the yellow and red varieties of the element. Reaction proceeds according to the equation

$$2P + 4SOCl_2 = 2PCl_3 + 2SO_2 + S_2Cl_2.$$

Other tubes were heated for several hours at a temperature close to 180°. These were found upon cooling to contain small amounts of phosphorus

[1] *Z. Chem. Ph. Math.*, **7**, 151 (1871); abstract, *Bull. soc. chim.*, [2] **15**, 185 (1871).

pentachloride. Sulfur dioxide was evolved to a slight extent when the tubes were opened. The supernatant liquid consisted chiefly of the excess of thionyl chloride and phosphorus trichloride, but in addition sulfur monochloride also was detected. It was thought that the oxidizing action of the excess of thionyl chloride on the phosphorus trichloride had proceeded according to the equation

$$3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2,$$

which is quite different from that given by Michaelis. However, it is certain that reaction does not follow the above equation quantitatively, inasmuch as in every case decomposition of the liquid contents of the tubes by means of water gave appreciable quantities of hydrogen sulfide, indicating that to some extent at least, reaction follows the equation given by Michaelis.

Summary.

Thionyl and sulfuryl chlorides react with sulfur at temperatures from 150° to 180° with formation of sulfur dioxide and sulfur monochloride. Under similar conditions both reagents react with phosphorus, either red or yellow, with the formation of phosphorus trichloride. Prolonged heating tends to cause the trichloride to become pentachloride, but the reaction is far from complete even after heating for several hours at 160° to 180°.

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THE USE OF METALLIC SILVER AS A REDUCING AGENT IN THE VOLUMETRIC ESTIMATION OF IRON.

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I. Purpose of the Investigation.

Several investigators have studied the reaction between metallic silver and solutions of ferric salts, and have shown that it proceeds to an equilibrium, in which at room temperature a considerable concentration of ferric salt is usually present. This fact apparently renders silver unsuitable as a reducing agent for the quantitative estimation of iron. However, if the silver-ion concentration in the solution is reduced (*e. g.*, by precipitation) the equilibrium may be shifted until only inappreciable quantities of ferric iron remain in the solution. Thus Hoenig[1] has shown that in the presence of a sufficient concentration of hydrochloric acid, ferric chloride may be reduced to the ferrous state by metallic silver with sufficient completeness to permit the quantitative estimation of the iron by titration with potassium permanganate after filtering off the silver chloride and the excess of silver.

[1] *Z. anal. Chem.*, **54**, 441 (1915).