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SHORT COMMUNICATION

Reaction of Thiophosphoryl Fluoride with Metals and Metal Oxides

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While investigating the chemistry[1,2] of thiophosphoryl fluoride, it is observed that it would react slowly (48 hours) with metals like copper and silver at ordinary temperature(25°C) producing metal sulphide and phosphorus trifluoride. The reaction becomes fast at 100° C. Similar results are obtained with iron and nickel at this elevated temperature. The sulphur is exchanged for oxygen, when thiophosphoryl fluoride reacts with silver oxide forming phosphoryl fluoride and silver sulphide. Such exchange is sluggish in the case of other metal oxides. The results of these investigations are reported in this paper.

EXPERIMENTAL

A. Reaction of thiophosphoryl fluoride with metals:

Thiophosphoryl fluoride is prepared and stored in glass globes as described in an earlier communication [1]. A known amount of the gas (≈100 mg.) is taken in an evacuated pyrex reaction tube fitted with appropriate ground joints and stop cocks. About a gramme of the metal powder is taken in the reaction tube before introducing the gas. The tube is introduced into a suitable furnace maintained at 110°C.

Trial runs indicated that the reaction will be complete only after 4 hours in the case of silver and copper. Five hours are required for the completion of the reaction in the case of iron and nickel. At the end of this period, the products are isolated, identified and estimated in the following way.

The volatile gaseous product is frozen in a separate trap cooled in liquid nitrogen. The ir spectrum of the sublimed gaseous product is recorded on a Carl Zeiss spectrophotometer. The ir spectrum indicates the absence of thiophosphoryl fluoride for which the reported[3] peaks are: 989(vs), 981(vs), 973(vs), 952(vs), 945(vs), 703(m), 695(m), 686(m), 448(s), 431(s), 402(w), and corresponds to phosphorus trifluoride. Peaks observed are: 486(s), 692(w), 860(vs), 890(vs), 1198(w), 1228(w), 1710(w). Reported [4] peaks are: 486(s), 693(w), 860(vs), 891(vs), 1196(w), 1238(w), 1713(w).

The phosphorus and fluorine content of these gaseous products are estimated after absorbing the gas in sodium hydroxide solution(2N). Fluoride content is estimated spectrophotometrically [5] and phosphorus as ammonium phosphomolybdate [6]. The analytical results confirm that the gaseous product is phosphorus trifluoride. The solid residue left in the reaction tube is treated with hydriodic acid(40%) and the hydrogen sulphide evolved is estimated iodometrically. The sulphide content corresponds to the sulphur content of the thiophosphoryl fluoride taken for the experiment.

The results of the experiments carried out with metal powders, copper, silver, iron and nickel show that the reduction of thiophosphoryl fluoride is quantitative in each

case. The amount of metal sulphide formed corresponds to the stoichiometric expectations in the form of equation,

$$PSF_3 + M \longrightarrow MS + PF_3$$

(M = Cu, Ag, Ni, Fe)

The phosphorus trifluoride formed during this reaction does not seem to react with any of the metals. However, it is known that phosphorus trifluoride would react with metals under drastic experimental conditions, such as higher temperatures and pressures [7,8].

Thiophosphoryl fluoride itself is found to react with the silica of the pyrex tube at about 200°C and therefore the present series of experiments are not conducted above 100°C. The decomposition of thiophosphoryl fluoride on the surface of glass resulted in the formation of variety of products such as sulphur dioxide, phosphorus pentafluoride, phosphoryl fluoride, silicon tetrafluoride, elemental sulphur and phosphorus as identified by their characteristic ir spectra and qualitative analysis.

B. Reaction of thiophosphoryl fluoride with silver oxide.

When the experiment is carried out with silver oxide silver sulphide and phosphoryl fluoride are produced under similar experimental conditions according to the equation,

$$PSF_3 + Ag_2O \longrightarrow POF_3 + Ag_2S$$

Phosphoryl fluoride is identified by its ir spectrum. Peaks observed are: 475(s), 483(m), 692(w), 831(s), 878(s), 930(w) 990(vs), 1275(w), 1335(m), 1417(s), 1460(w), 1742(w), 1858(m). Peaks reported [9] are: 473(s), 485(m), 690(w), 830(s),

875(s), 946(w), 990(vs), 1275(w), 1330(m), 1415(s), 1462(w), 1740(w), 1855(m).

It is reasonable to infer that exchange between oxygen and sulphur takes place instead of reduction. The reaction is found to be quantitative. The reaction of thiophosphoryl fluoride with other metal oxides is found to be very slow even at 100°C and is not quantitative.

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