

with vigorous to violent boiling. The flask must sometimes be somewhat cooled. Toward the end of the reaction, which occurs within 5 to 10 minutes, the liquid becomes orange-yellow. At that point the boiling ceases, indicating that all of the PCl_3 is transformed into PSCl_3 .

The cooled liquid is now poured into a large separatory funnel, a large amount of water is added, and the funnel is carefully shaken to avoid too heavy an emulsion. This dissolves the AlCl_3 , PCl_3 , H_3PO_3 and HCl , producing an immediate decolorization of the product. The PSCl_3 settles out as the bottom. It is separated, dried with CaCl_2 and distilled.

The yield is as high as 120 g. (97%).

SYNONYM:

Phosphorus sulfochloride.

PROPERTIES:

Colorless, mobile liquid; fumes in air; sharp odor, not disagreeable when diluted; lachrymator. With water, decomposes slowly in the cold, quickly when heated, to give HCl , H_2S and H_3PO_4 . On heating with sodium hydroxide, $\text{Na}_3\text{PO}_3\text{S}$ is formed (see p. 569). Miscible with CS_2 .

M.p. -35°C , b.p. 125°C (corr.); d 1.668.

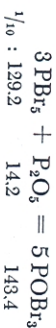
REFERENCES:

- I. German Patent 675,303, Class 12 i, Group 31, May 5, 1929 (Inventor: G. Schrader).
- II. F. Knotz. Österr. Chemiker-Z. 50, 128 (1949).

Phosphoryl (V) Bromide

POBr_3

According to Hönigschmid and Hirschbold-Witner, the reaction of PBr_5 with P_2O_5 , proposed by Berger, is the best procedure for the preparation of POBr_3 :



A round-bottom flask, joined to a reflux condenser with a ground joint, is the reactor. A mixture of PBr_5 and P_2O_5 (mole ratio 5 : 1), with a small excess of the latter [$e.g.$, 250 g. of PBr_5 and

20 g. of P_2O_5 —preferably from a new package] is heated in an oil bath, with the temperature gradually increased to 150°C . Care must be taken to prevent escape of the bromine. The reaction is complete after five hours. Then 10 g. of Br_2 and a corresponding quantity of P_2O_5 are added to the molten product. The mixture is refluxed for seven hours at 150°C . This oxidizes the intermediate PBr_3 to PBr_5 and transforms the latter into POBr_3 . The final product is distilled at 12 mm. A tube containing NaOH must be inserted between the aspirator and the distillation apparatus. The first cut contains Br_2 and some PBr_3 . The completely colorless POBr_3 is obtained almost quantitatively. It is best to cool the receiver with an ice-salt mixture. The yield is 200 g. (73%, based on the PBr_5 used).

The traces of PBr_3 can only be removed by fractionating the POBr_3 six times in high vacuum.

PROPERTIES:

Very sensitive to elevated temperature, at which it decomposes with yellowing. For this reason it should never be melted with a flame, but only with hot water.

Large, flaky crystals, M.p. 55°C , b.p. 193°C ; d 2.82.

Decomposes slowly in water, forming H_3PO_4 and HBr . Soluble in ether.

REFERENCES:

- O. Hönigschmid and F. Hirschbold-Witner. Z. anorg. allg. Chem. 243, 355 (1940).
- F. Berger. Compt. Rend. Hebd. Séances Acad. Sci. 146, 400 (1908).

Thiophosphoryl (V) Bromide

PSBr_3

Thiophosphoryl bromide can be obtained by the reaction of phosphorus pentasulfide with phosphorus pentabromide:



The reaction vessel is a distillation flask provided with a P_2O_5 drying tube. The flask is charged with 31 g. of dry, red P and cooled in a bath. Then 400 g. of Br is added, followed by 100 g. of P_2S_5 . The mixture is then heated for two hours on a water bath and finally with an open flame, until completely