II. PREPARATION WITH WHITE PHOSPHORUS

Two solutions in CS_2 are prepared. One contains 1 g. of white P and the other 12.27 g. of I_2. The solutions are mixed without loss, and the mixture is processed further as under I.

PROPERTIES:

Dark red, columnar crystals. M.p. 61°C. Quick decomposition in moist air and must therefore be stored over $CaCl_2$.

REFERENCE:

F. E. E. Germann and R. N. Traxler. J. Amer. Chem. Soc. 49, 307 (1927).

Phosphorus (V) Oxide

P_2O_5 (P_4O_{10})

Purification of the commercial product. Ordinary commercial P_2O_5 usually contains lower oxides of P, especially P_2O_3, and sometimes also white P. When P_2O_5 is used as a drying agent, these impurities sometimes exert a harmful influence because of their reducing action. To test for the lower oxides, P_2O_5 is dissolved in water, forming a solution which easily reduces a 10% $AgNO_3$ solution, and a Hg(II) salt solution on boiling. If lower P oxides are present a distinct odor of PH_3 is given off when the aqueous solution is evaporated and then moderately warmed. To prepare pure P_2O_5, the commercial product is sublimed in a stream of well-dried oxygen at bright red heat, according to Finch and Peto, and also Whitaker. A T-shaped iron tube is used for this purpose (see Fig. 194); it is connected to a glass tube. The apparatus, particularly the iron tube, must be thoroughly cleaned and dried. The commercial product to be sublimed is gradually added from *a* and trapped in collecting bulb *b*. From 200 g. of impure P_2O_5, about 70 g. of pure P_2O_5 can be obtained in two hours (cf. also Part I, p. 81).

Modifications of phosphorous pentoxide. Phosphorus pentoxide forms three solid modifications, of which the metastable M form is the ordinary commercial P_2O_5. This modification crystallizes as rhombohedra with a molecular lattice (P_4O_{10}) and sublimes readily at 250°C and 10 mm. (Glixelli and Boratynski). Above 260°C and even more quickly above 500°C, form M changes into form R. The latter crystallizes in a three-dimensional atomic lattice of PO_4 tetrahedra and is less volatile. A form S, which

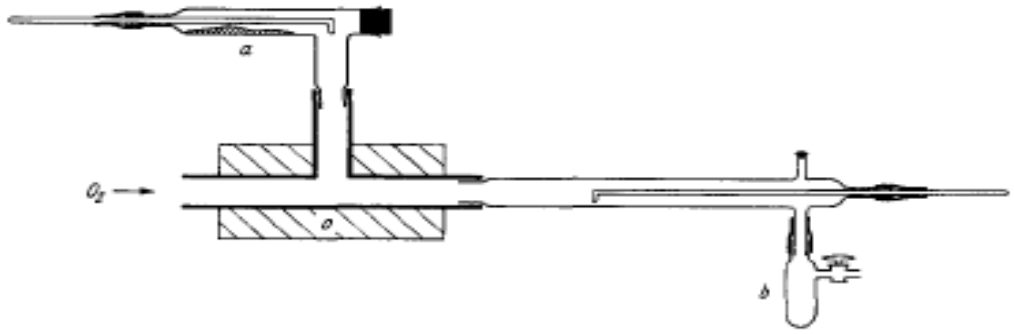

Fig. 194. Purification of P_2O_5 by sublimation. *a*) Starting material; *b*) collecting bulb for purified material; *c*) electric furnace.

crystallizes in a layer lattice, and a few vitreous forms are also known (De Decker and McGillavry; Hill, Faust and Hendricks).

To prepare the stable modification, crystals of the M modification, obtained by sublimation in a stream of dry O_2 at about 320°C, are placed under a stream of dry O_2 in a Vycor tube 2 × 23 cm. The latter is fused shut after evacuation. After heating for five days at 500–530°C in a horizontal position, the section of the tube containing the best crystals is heated for 2.5 hours at 350–400°C, while the other end remains at room temperature.

SYNONYM:

Tetraphosphorus decaoxide.

PROPERTIES:

Modification M is brittle; R and S form hard crystals, which deliquesce after a few hours in the air and undergo considerable swelling in water. The density of R is 2.72, that of M 2.30 (calculated from x-ray data).

REFERENCES:

G. I. Finch and R. H. K. Peto. J. Chem. Soc. (London) 121, 692 (1922).
H. Whitaker. J. Chem. Soc. (London) 127, 2219 (1925).
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H. C. J. de Decker and C. H. McGillavry. Rec. Trav. Chim. Pays-Bas 60, 153 and 413 (1941); Nature 164, 448 (1949).
W. L. Hill, G. T. Faust and S. B. Hendricks. J. Amer. Chem. Soc. 65, 794 (1943).