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Chapter in book "Inorganic Synthesis"

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PHOSPHINE

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January 1964

PHOSPHINE

$$4\ H_3PO_3 \longrightarrow 3\ H_3PO_4 + PH_3$$

SUBMITTED BY SUDARSHAN D. GOKHALE*† AND WILLIAM L. JOLLY*

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Phosphine can be prepared by various methods,[1,2] e.g. by the action of water on calcium phosphide, by the action of hot alkaline solutions on elemental phosphorus, by the reaction of phosphorus trichloride with lithium hydroaluminate, and by the pyrolysis of hypophosphorous acid, phosphorous acid, or one of their salts. We have found the pyrolysis of phosphorous acid to be most convenient for the laboratory preparation of phosphine.

Procedure

About 34 g. (0.41 mole) of dry crystalline phosphorous acid is placed in a long-necked 500-ml. round bottomed flask which is connected

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to a vacuum line by a tube about 60 cm. long and 2 cm. in diameter. A 0° - 360° thermometer is placed with its bulb resting on the inner wall of the flask and with its upper end extending into the connecting tube. Some glass-wool is placed in the upper part of the connecting tube to prevent any acid spray from passing into the vacuum line. The flask is evacuated through a series of three traps. It is advisable that the first trap have a large diameter (at least 25 mm.) to avoid choking due to the condensation of water. The first trap is cooled with a dry-ice-acetone mixture (-78°) and the next two traps are cooled with liquid nitrogen (-196°). Pumping is maintained throughout the preparation. The small amount of hydrogen which forms during the synthesis passes through the traps and is pumped out of the system; the other volatile products collect in the cold traps. The flask is slowly heated by a heating mantle controlled with an autotransformer. The phosphorous acid crystals melt completely near 74°, and the liquid starts boiling near 180°. Evolution of phosphine begins at about 200°. The temperature rise between 175° -200° should be very gradual, otherwise the acid starts

boiling and frothing very suddenly - resulting in incomplete condensation of the products in the traps, contamination of the vacuum line, and lower yields. The temperature of the flask should be maintained at 205° -210° for about 30 minutes, at which time most of the PH_3 will have been given off. The acid becomes very frothy and slowly turns to a red viscous mass. Finally the temperature is raised to about 350° to obtain the maximum yield of phosphine, and the heating is then stopped. The water and traces of P_2H_4 which collect in the first trap are discarded. The phosphine which collect in the last two traps, is purified by distilling *in vacuo* through a -126° trap (methyl cyclohexane slush). The reaction flask is filled with nitrogen gas after it has cooled to room temperature; it is then removed from the vacuum line.

Properties

The vapor pressure of phosphine prepared in this way was found to be 170 ±1 mm. at -111.6° (CS_2 slush). The literature value is 171 mm.[3] The infrared spectrum shows absorption at the following frequencies (in cm^{-1}): 2327 (m), 1121 (m), 900 (m).[4] An actual spectrum is given in the paper by P. A. Tierney et al.[5]

This work was performed under the auspices of the United States Atomic Energy Commission.

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