Richards and Thompson in the spectra of organochlorosilanes should be assigned to the Si–H bending vibration rather than, as suggested by them, to a vibration of the Si–Cl bond.

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Improved Procedure for Synthesis of P-32 Phosphorus Oxytrichloride[1]

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The research and development program at this Laboratory on phosphate-type plasticizers and turbine-oil rust inhibitors has made mandatory the obtaining of P-32 labeled phosphorus oxytrichloride of high specific activity and chemical purity. Published methods[2-4] for the synthesis of this intermediate compound suffer from a number of disadvantages, the most important being the need for cumbersome and elaborate equipment, and the loss of from one- to two-thirds of the radioactivity during the synthesis, due considerably to the prolonged contact of $H_3P^{32}O_4$ or metal phosphates with glass at elevated reaction temperatures.

After preliminary unsuccessful attempts to increase the radioactive yield of available procedures by treating PCl_5 with H_3PO_4, HPO_3 and P_2O_5 carrier,[5] respectively, an improved method has been evolved to overcome the above-mentioned difficulties. Use of this procedure has resulted in the synthesis of P-32 phosphorus oxytrichloride with a specific activity of 25 mc./mmole. The material is obtained in 95–99% yield and retains 95–97% of the initial radioactivity. Inactive $POCl_3$ produced by this method was assayed at 97 ± 1% purity, by determination of chloride and phosphate.

Quantities as small as 0.40 g. (0.27 ml.) of the compound have been successfully prepared. The total time required for all operations is from 4 to 8 hours, depending upon the specific activity level desired.

Experimental

A typical run is described below.

Dehydration of Aqueous P-32 Phosphoric Acid.—Ten millicuries of an aqueous solution of P-32 phosphoric acid[6] with a specific activity of 0.025 mg. P/mc. (5.8 mc./ml. of solution), O.R.N.L. Cat. No. P-32 P-1, was transferred to a tared 25-ml. two-necked flask possessing ₸ 19/22 joints. One neck was stoppered, and the other fitted with a still head, a 105° angle vacuum adapter and an appropriate receiver, and lyophilization of the solution to a residue of 0.224 g. (12.4 mmoles) was accomplished by application of a vacuum and suitable freezing baths. Lyophilization of the solution beyond about 0.05 g. is possible, but impractical; for samples of this size, calculation of the millimoles of reactants would include millimoles of $H_3P^{32}O_4$, neglected above.

Synthesis of P-32 Phosphorus Oxytrichloride.—The stopper and adapter were replaced by a double-surface condenser with attached drying tube and a hopper, which was constructed from a ₸ 19/22, double jointed drying tube by grinding a slightly oversized glass rod into the barrel with emery and alundum. The rod was held firmly in place by use of a sleeve adapter on the top joint and a short length of rubber tubing.

The hopper was charged with 2.70 g. (13.0 mmoles) of reagent grade PCl_5, and the P-32 $H_3P^{32}O_4$ was frozen by immersion of the flask in a Dry Ice–acetone-bath. The reaction was initiated by adding a small quantity (*ca.* 0.1 g.) of PCl_5, removing the freezing bath, and allowing the mass to thaw slightly. The cycle of alternate freezing and addition of PCl_5 was continued until the reaction was controllable without freezing; the remainder of the PCl_5 was then added as rapidly as possible.

The flask was then allowed to warm to room temperature and cautiously brought to reflux for a period of 15 minutes. The flask was then cooled, and immersed in the Dry Ice–acetone-bath; warm water was circulated through the condenser, to distil any adhering P-32 $POCl_3$ into the flask. The flask was then fitted for lyophilization, run at 1 mm. pressure, maintaining the temperature of the still flask at −5°; yield 1.89 g. (99% of theoretical) of P-32 $POCl_3$ of specific activity 0.78 mc./mmole (96% activity retained) with a chemical purity of 97 ± 1%. The specific activity of the compound was determined by conversion into P-32 tricresyl phosphate and an assay thereof.

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[1] The opinions or assertions herein are those of the authors, and are not to be construed as reflecting those of the Navy Department or the Naval Service at large.

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[6] Obtained from the Carbide and Carbon Chemical Co., Oak Ridge, Tennessee.

The Ammonolysis of Hexachlorodisiloxane

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A study of the ammonolysis of Si_2OCl_6 and of the pyrolysis of the product was undertaken, following similar studies which have been reported with $SiCl_4$,[1-3] with Si_2Cl_6,[4] and with $SiHCl_3$.[5] It was expected in view of the earlier work that ammonolysis of hexachlorodisiloxane, Si_2OCl_6, should lead to $(Si_2ON_3H_3)_x$ at room temperature, and that this product on heating should form an oxynitride, $(Si_2ON_2)_x$. Compounds of silicon containing oxygen and nitrogen have been reported,[6] but oxygen in these cases was believed to be present as silica contamination.

Experimental

All reactions were carried out in carefully dried apparatus with a minimum of atmospheric exposure. Several samples of hexachlorodisiloxane were obtained, some from commercial sources, another from Dr. Herbert H. Anderson, and some by preparation as required. They were purified by fractional distillation (b.p. 134° at 760 mm.) and kept in sealed glass tubes. When needed, these tubes were cooled in liquid nitrogen, opened and sealed to the apparatus with Cenco Plicene. The apparatus was evacuated and the sample distilled into the reaction vessel under reduced pressure.

Commercial ammonia was distilled into a storage tube, in which it was dried over sodium; before use of the ammonia, non-condensable gases were pumped off.

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