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.

Acknowledgment.—The authors wish to acknowledge with great appreciation the efforts of Mr. A. R. Allison of this Laboratory and Mr. V. Saitta of the Bureau of Ships, Washington, D. C., in fostering the application of radioisotopes to naval material development.

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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.

[2] B. Axelrod, *J. Biol. Chem.*, **176**, 295 (1948).

[3] J. E. Gardiner and B. A. Kilby, *Research*, **2**, 590 (1949).

[4] J. E. Gardiner and B. A. Kilby, *J. Chem. Soc.*, 1769 (1950).

[5] J. L. Kalinsky and B. Gilbert, unpublished work, showed that one-third of the radioactivity was retained by the reaction flask.

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

The Ammonolysis of Hexachlorodisiloxane

BY WALTER C. SCHUMB AND ROBERT A. LEFEVER

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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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[1] F. Lengfeld, *Am. Chem. J.*, **21**, 531 (1899).

[2] E. Vigouroux and Hugot, *Compt. rend.*, **136**, 1670 (1903).

[3] M. Blix and W. Wirbelauer, *Ber.*, **36**, 4220 (1903).

[4] R. Schwarz and W. Sexauer, *ibid.*, **59B**, 333 (1926).

[5] O. Ruff and E. Geisel, *ibid.*, **38**, 2235 (1905).

[6] L. Weiss and T. Engelhardt, *Z. anorg. allgem. Chem.*, **65**, 38 (1909).

Silicon analyses were made in several different ways in the course of the work, and the results obtained thereby were found to be in satisfactory agreement. For example, in one method fusion of a sample with sodium hydroxide or carbonate, solution of the melt, acidification with nitric acid and removal of chloride as silver chloride in the conventional manner, were followed by addition of perchloric acid to the filtrate, evaporation, and dehydration of the silica. The determination of chlorine and silicon on the same sample, in this way, was found to be satisfactory.

In the determination of nitrogen, the ammonolysis products and intermediate compounds were weighed in small glass containers and added directly to 20% sodium hydroxide solution in a Kjeldahl flask, from which the evolved ammonia was distilled into standard acid. Ammonium chloride nitrogen could be distinguished from nitrogen present as a constituent of the silicon compound by titrating the latter with standard acid after hydrolysis of the sample with water. Fusion of the sample with sodium hydroxide was found to cause quantitative evolution of ammonia from the nitride and the oxynitrides. Fusions were carried out in a nickel tube and the evolved ammonia was carried into standard acid with dry nitrogen.

Ammonolysis.—A 25-ml. sample of Si_2OCl_6 was distilled into a 250-ml. round-bottom flask and cooled to 0°. Ammonia at one atmosphere pressure was gradually admitted until the initial, vigorous reaction appeared to cease. The flask was allowed to warm and remain at room temperature overnight under an atmosphere of ammonia. After 24 hours, excess ammonia was removed by alternately evacuating and flushing the apparatus with dry nitrogen. Samples were removed for analysis in a dry-box. *Anal.* Calcd. for $1/x(Si_2ON_3H_3)_x + 6NH_4Cl$: Si, 12.8; total N, 28.8; "basic" N, 9.6; Cl, 48.5. Found: Si, 12.8; total N, 28.6; "basic" N, 8.9; Cl, 48.8. A second, 20-ml. sample was ammonolyzed in the same manner and gave the following results: Si, 12.4; total N, 28.4; "basic" N, 9.6; Cl, 48.4.

In a calibrated system, a measured amount of ammonia was added to a 1.98-g. sample of Si_2OCl_6 at −60°. A total of 2.8 moles of ammonia per mole of oxychloride was absorbed as rapidly as added. An additional 0.1 mole reacted as the temperature was gradually increased to about −30°, at which point an additional 1.7 moles reacted (Si_2OCl_6 melts at −33°). As the temperature was allowed to increase to room temperature, further ammonia was absorbed until, after 7 hours, a total of 9.0 moles of ammonia per mole of oxychloride had reacted. Further ammonia could not be caused to react. Analysis of the product gave: Si, 13.0; total N, 28.7; "basic" N, 9.5; Cl, 48.5, in good agreement with the calculated values indicated above.

The ammonolysis products were white solids composed of various sized particles ranging from coarse lumps to finely divided material. They were hydrolyzed readily when treated with water and evolved ammonia when dissolved in aqueous sodium hydroxide. Although excess ammonia had been removed, a strong odor of ammonia could be detected on exposure to the air, indicating hydrolysis from moisture. Attempts to remove ammonium chloride by prolonged leaching with liquid ammonia at about −40° resulted in a reduction of chlorine percentages of only about 50%. Such a result might be expected in view of the polymeric nature of the product. X-Ray powder patterns on the ammonia-washed material gave strong diffraction lines for ammonium chloride.

Intermediate Products.—In addition to polymerized triimidodisiloxane, $(Si_2ON_3H_3)_x$, several intermediate products were obtained by deammonation of the initial ammonolysis product of hexachlorodisiloxane, by heating the product to fixed, elevated temperatures (from 550–700°) under vacuum or in a current of nitrogen until the sublimation of ammonium chloride appeared to cease. In some cases, this was followed by treatment with ammonia, also at elevated temperatures. The fluffy, white powders that resulted from this procedure were essentially free from ammonium chloride, as shown by the absence of the appropriate X-ray diffraction pattern. Hydrolysis by contact with water was now only gradual; that from moisture of the air was negligible. However, decomposition with acids and bases was rapid and complete. A typical analysis gave data corresponding to an empirical formula $(Si_2O_{1.19}N_{2.60}H_{2.60}Cl_{0.41})_x$. This product resulted from the ammonolysis of Si_2OCl_6, starting at −22°, where 7 moles of ammonia was required per mole of Si_2OCl_6. At room temperature a total of 9 moles of ammonia was found to have reacted, and although the temperature was then increased to 60° and held for 0.5 hr., further ammonia could not be caused to react. At 250° and about 1 mm. pressure, ammonium chloride sublimed and 1.5 moles of ammonia was evolved per mole of oxychloride. After sublimation of ammonium chloride appeared to have ceased, the temperature was raised to 550° and held for two hours. A measured amount of ammonia (0.71 mole per mole of Si_2OCl_6) was then introduced, and an immediate further sublimation of ammonium chloride occurred. Analysis of the resulting product gave the empirical formula recorded above.

Silicon Oxynitride.—When a sample of the intermediate product with a composition corresponding to the empirical formula $(Si_2O_{1.19}N_{2.60}H_{2.60}Cl_{0.41})_x$, was heated in a continuous flow of nitrogen to 1300–1350° for 3 hours, the product was found on analysis to contain 54.2% Si, 25.1% N and 2.2% Cl, corresponding to an empirical formula $(Si_2O_{1.20}N_{1.85}Cl_{0.06})_x$, which approaches the requirements of an oxynitride, Si_2ON_2, somewhat contaminated with silica and chloride.

A sample of Si_2OCl_6 was ammonolyzed at room temperature in a fused silica tube and then directly heated to 1250° under an atmosphere of ammonia. After 8 hours at this temperature, the tube was cooled and the product reheated at 1350° in a second tube for 6 hours in a current of nitrogen. Analysis of the product gave: Si, 55.6; N, 26.1; $Cl < 0.1\%$. These data correspond to an empirical formula $(Si_2O_{1.15}N_{1.88})_x$, or a product composed of 93% oxynitride, Si_2ON_2 and 7% SiO_2. The silica, however, is not necessarily to be considered present as such in the product.

These high-temperature products were identical in appearance with the intermediate materials and similar to them in behavior toward water, acids and alkali. Hot concentrated sulfuric acid caused gradual decomposition with the formation of silica and ammonium sulfate; concentrated sodium hydroxide solution caused evolution of ammonia; and 48% hydrofluoric acid rapidly and completely decomposed them.

X-Ray powder patterns indicated that these products were amorphous, and attempts to produce crystallinity by heating at 1350° (maximum time 60 hours) in a nitrogen atmosphere failed. However, when a sample of this material was heated in an induction furnace for one hour at 1500° under a nitrogen pressure of 170 mm., the product gave weak X-ray diffraction lines identifiable as due to the nitride, Si_3N_4. A second sample, similarly heated at 1600° for one hour under 230 mm. nitrogen pressure, was sealed in a thin-walled Pyrex capillary and exposed in a Debye–Scherrer X-ray camera to Cu K_α radiation (Ni filter) for 10 hours (39 peak k.v., 19 ma.). The resulting interplanar spacings compared closely with the corresponding values for Si_3N_4, determined in the same manner.[7]

Discussion

From the observed quantity of ammonia reacting with weighed samples of hexachlorodisiloxane and from analytical data obtained from the products, it is concluded that at room temperature nine moles of ammonia react with each mole of Si_2OCl_6, according to the equation

$$Si_2OCl_6 + 9NH_3 \longrightarrow \frac{1}{x}(Si_2ON_3H_3)_x + 6NH_4Cl$$

During the sublimation of ammonium chloride from the ammonolysis products of silicon tetrachloride, it was reported[8] early that chlorine-containing silicon compounds were formed, but halide retention has since been generally attributed to the presence of ammonium chloride. However, it has been confirmed in the present work that halide removal by sublimation as the ammonium salt in the presence of nitrogen, or of hydrogen, or under vacuum

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(7) We are indebted to the Carborundum Company, Niagara Falls, N. Y., for a sample of the nitride, analysis of which indicated about 93% purity. The complete Si_3N_4 diffraction pattern is relatively complex, consisting of over 100 diffraction lines.

(8) P. Schützenberger, *Compt. rend.*, **89**, 644 (1879); P. Schützenberger and A. Colson, *ibid.*, **92**, 1508 (1881).

proved difficult, whereas complete sublimation under an atmosphere of ammonia may be realized more rapidly and at lower temperatures.[9] This suggests that the halogen was not present as the ammonium salt but rather as a constituent of the silicon compound. The absence of X-ray diffraction lines in the intermediate products referred to above indicates that ammonium chloride was not present in concentrations sufficient to account for the observed chloride contents (11–15%). Furthermore, the sudden evolution of ammonium chloride when intermediate products were treated with ammonia suggests the occurrence of a reaction.

The amorphous nature of the compounds when heated to 1300–1350° indicates that they are essentially oxynitrides of silicon. The absence of X-ray diffraction lines for any crystallographic modifications of SiO_2 even in compounds heated to higher temperatures indicates that silica is not present as such. Decomposition of these compounds with the formation of Si_3N_4 in the temperature range of 1500–1600° is to be expected in view of the fact that the decomposition pressure of Si_3N_4 becomes appreciable, approaching 15 mm. at the latter temperature.[10]

Acknowledgments.—Financial assistance in this investigation was received in the form of a grant from the Owens-Illinois Glass Company, Toledo, Ohio. The authors wish to thank Professor David P. Shoemaker of this Department for assistance with crystallographic aspects of the work.

[9] E. Lay, "Über Silicium-Stickstoff-Wasserstoff Verbindungen," Leopold-Buchdruckerei, München, 1910.

[10] W. Hincke and L. Brantley, THIS JOURNAL, **52**, 48 (1930).

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The Refractive Indices of Aqueous Solutions of H_2O^{18} and CO_2

BY H. E. WATSON

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As the generally accepted value for the refractive index of H_2O^{18} could not be reconciled with the results obtained when examining light water, a redetermination of this quantity has been undertaken. About 80 deuterium-free samples from 200 p.p.m. light to 800 p.p.m. heavy and of varying degrees of purity have been examined in a Rayleigh interferometer, the purity being checked by conductivity measurements. The change in refractive index at 18°, with white light, for a molecular proportion y of H_2O^{18}, was found to be $0.00008y$, the factor being only one-tenth of the accepted value.

Measurements were greatly facilitated by the use of an interferometer cell machined from solid copper and silver-plated, temperature equilibrium being reached in about three minutes.

Observations on water containing CO_2 kept in contact with silica and metals have been made in order to determine the effect of possible impurities. For dilute CO_2 solutions, the relation $\kappa^2 = -4.6\ \delta n$ held good with an error of about 10%, κ being the conductivity in reciprocal megohms at 18° and δn the difference between the refractive index of the solution and that of pure water, multiplied by 10^7.

Introduction

Lewis and Luten[1] measured the effect of H_2O^{18} on the refractive index of water, using a Rayleigh-Zeiss interferometer and a sample said to contain 0.5% of H_2O^{18}. No details of the preparation or purification of this sample were given. It was deduced that if y was the molecular proportion of H_2O^{18} in a sample of water, the difference in the refractive indices of this sample and water containing the same amount of D_2O but no H_2O^{18}, was $0.0008y$. A formula was given for determining the amounts of H_2O^{18} and D_2O in water from measurements of the density and refractive index. On attempting, a few years later, to use this formula for estimating the H_2O^{18} content of deuterium-free water, the author could find no change in the refractive index with density and it appeared that refractive index measurements were useless for analytical purposes. In 1939, Brodsky and Scarre[2] made further interferometer measurements with 3 samples heavier than water by 200 p.p.m. or less, which gave discordant results. They deduced that Lewis and Luten's factor should be 0.00069 ± 0.0001, but do not appear to have tested the purity of their samples or to have taken adequate steps to ensure the normality of the D_2O in them.

As measurement of the refractive index is a convenient method of estimating the concentration of D_2O in water if the correction for H_2O^{18} is known, it was decided to make further determinations of the latter quantity. As expected, these proved to be by no means easy, since the effect of traces of impurity in the solutions was much greater than that of the H_2O^{18}. The nature of the impurities was not obvious, but as CO_2 was always present and no data could be found for the refractive index of its solutions, a number of these were examined. The results indicated that in some cases the containing vessel was attacked, and further measurements were made to estimate the magnitude of this effect.

Experimental

All refractive index differences δn are for white light and are expressed in units of 1×10^{-7}. All conductivities κ are in reciprocal megohms at 18°.

A Rayleigh interferometer was used for the refractive index measurements, a consistency of 1 scale division or $^1/_{58}$ of a band, being obtained. With a 10-cm. cell, this corresponded with a change of 1.0×10^{-7} in refractive index. It was consequently necessary that the temperature of the two solutions should be the same within 0.001°. This was achieved by using as the interferometer cell a solid bar of copper 1.5″ square. A length of 10 cm. was cut off and two parallel holes $^5/_{16}$″ in diameter drilled through it, the centers being 0.5″ apart to correspond with the separation of the two light beams. A slot was milled out underneath the holes for the lower beams. The ends were ground parallel, polished, and closed with two optically flat glass plates. The joints were watertight, but to avoid possible displacement they were cemented with a trace of cellulose varnish. The effective length was 100.00 ± 0.01 mm., and the difference between the lengths of the cells less than one wave length. The capacity was 5 cc. and filling was effected through 0.25″ holes drilled through the top of the block near one end. These were closed with loosely fitting flanged plugs of polythene. The internal tubes were at first silver plated and later gilt. The whole block was cased in insulating material and equilibrium was reached in about three minutes. For some of the experiments with CO_2, a con-

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[2] A. E. Brodsky and O. S. Scarre, *Acta Phys. Chim. URSS*, **10**, 729 (1939).