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TETRASULFUR TETRANITRIDE (S_4N_4) AND HEPTASULFUR IMIDE (S_7NH)

Berkeley, California

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UCRL-11294

Chapter in book - Inorganic Synthesis

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Milagros Villena-Blanco and William L. Jolly

January 1964

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Submitted by Milagros Villena-Blanco* and William L. Jolly*

Checked

Tetrasulfur tetranitride can be prepared in good yield by the method described by Becke-Goehring.[1] However, because of certain ambiguities and omissions in the method, chemists unfamiliar with the synthesis usually obtain very poor yields of the product. In this revision of the method, we emphasize the points which, if neglected, can cause difficulty.[2] Because S_4N_4 is explosive, and because the large amounts of material involved in the earlier method are unwieldy, we have scaled down the synthesis.

If high yields of S_4N_4 are desired, the reaction mixture should not be cooled below 20°.† The only purpose served by placing the reaction flask in a cold-bath is to prevent the temperature from rising so high that appreciable amounts of solvent vaporize; however, excessive solvent

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* Department of Chemistry, and Inorganic Materials Research Division of the Lawrence Radiation Laboratory, University of California, Berkeley, California.

† Arnold[3] suggests operating in the temperature range 20-50°.

vaporization can be prevented by reducing the flowrate of the ammonia or by using an ambient-temperature water bath. When S_7NH is the only product desired, then it is advantageous to cool the reaction mixture in an ice bath. The total yield of S_7NH increases by 40% and the total yield of S_4N_4 decreases by 65% on changing from no cooling to ice-bath cooling.

As long as the reaction mixture is at ambient temperatures or higher, there is no harm in passing an excess of ammonia gas through the mixture. The yields of S_4N_4 and S_7NH are unaffected by the passage of excess ammonia.

It has been pointed out that the passage of ammonia should be continued until the reaction mixture is colored "salmon red".[1,3] This color may be better described as "golden poppy" (color plate 9L12 in the "Dictionary of Color"[4]), or, very roughly, as "Kodak yellow". The sequence of colors through which the reaction mixture passes preliminary to turning golden poppy varies with the temperature, the ammonia flowrate, and whether or not the sulfur chloride has been chlorinated. Inasmuch as yellow colors which might be mistaken for the final "golden poppy" color

often appear before the completion of the reaction, it is recommended that the completion of the reaction be confirmed by testing the reaction mixture for the presence of excess ammonia. A test for this purpose is described in the Procedure.

The preliminary chlorination of the S_2Cl_2 to SCl_2 may be omitted, if desired, but the total yield of S_4N_4 is thereby reduced by a factor of two. If S_7NH is sought, the chlorination must be omitted, because only trace amounts of S_7NH form in the reaction between SCl_2 and ammonia.

The reaction mixture becomes very thick and difficult to stir. If, in order to facilitate stirring, the reaction mixture is diluted with carbon tetrachloride, an appreciable fraction of the S_4N_4 and practically all of the S_7NH end up in the carbon tetrachloride phase. It is then necessary to work up this carbon tetrachloride solution as well as the precipitate.

A. Tetrasulfur Tetranitride, S_4N_4

Procedure

Fifty ml. (84 g., 0.62 mole) of disulfur dichloride and 1400 ml. of dry carbon tetrachloride* are added to a 2-l. three-necked flask. A paddle stirrer is inserted through the main neck, and a gas inlet tube is inserted through one of the side necks. While stirring the mixture briskly, a stream of chlorine is passed into the solution until a distinctly green layer of chlorine gas is observed over the solution. (The color of the solution changes from yellow to orange-red). The flow of chlorine is stopped, and the gas delivery tube is connected to a cylinder of ammonia. The flask is immersed to the level of the carbon tetrachloride solution in a water-bath of running tap water, and ammonia is passed through the stirred solution.** The ammonia is passed as rapidly as possible without causing material to splash from the flask or allowing the temperature of the reaction mixture to rise above 50°.

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* Carbon tetrachloride may be dried by allowing it to stand over anhydrous calcium sulfate (Drierite) for several days.

** The heat of reaction will prevent the temperature of the reaction mixture from falling below 20° even though the water-bath temperature is less than 20°. The water bath may be omitted, but then the flow of ammonia gas must be reduced in order to maintain the temperature below 50°.

After approximately two hours, when the entire reaction mixture has turned a "golden poppy" color, about 2 ml. of the reaction mixture is withdrawn into an inverted pipet and then shaken with 10 ml. of water. If the pH of the aqueous extract, as measured with pH-paper or a pH-meter, is greater than 8, the flow of ammonia is stopped. Otherwise the flow is continued until the pH of an aqueous extract is greater than 8.

The reaction mixture is filtered on a large sintered-glass or Büchner funnel, and the damp solid material is vigorously slurried with 1 l. of water for 5-10 minutes. The remaining solid is filtered off and allowed to air-dry thoroughly for a day or two. The dry material is placed in an extraction thimble and extracted with 400 ml. of dry dioxane* in a Soxhlet extractor until the eluate is only weakly colored orange-yellow.† Upon cooling the eluate to room temperature, some of the S_4N_4 will crystallize out. This material is filtered off and air-dried, and the

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* Dioxane may be dried by refluxing over sodium-lead alloy, followed by distillation.

† If the extraction is stopped too soon, S_4N_4 will be left in the thimble, if the extraction is prolonged, the product will be contaminated with sulfur.

filtrate is evaporated to dryness at a temperature lower than 60°. (Evaporation at room temperature at atmospheric pressure is slow, but satisfactory.) The residue from the evaporation is recrystallized from hot benzene to remove sulfur. A combined yield of 16 g. of S_4N_4 is generally obtained.*

Properties

Tetrasulfur tetranitride, as prepared by the above procedures, usually has a melting point of 178-179°. However, by repeated recrystallization from benzene, or by purification on an alumina chromatographic column, S_4N_4 with a melting point as high as 187-187.5° has been obtained.[2] It has been observed that the sensitivity of S_4N_4 toward both shock and temperature increases with its purity. Even the small amount of material contained in a melting point capillary can explode violently.

The infrared spectrum of S_4N_4 is given by Lippincott and Tobin[5]; prominent absorption bands occur at 347, 552, 557, 696, 719, and 925 cm^{-1}.

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* About 4 g. of product is lost in the CCl_4 filtrate and in the process of recrystallization.

B. Heptasulfur Imide, S_7NH

Procedure

Fifty ml. (84 g., 0.62 mole) of disulfur dichloride and 1400 ml. of dry carbon tetrachloride are added to a 2-l. three-necked flask. A paddle stirrer is inserted through the main neck, and a gas inlet tube connected to an ammonia cylinder is inserted through one of the side necks. The flask is immersed to the level of the carbon tetrachloride solution in an ice bath, and, when the solution has reached a temperature of 5° or lower, ammonia is passed as rapidly as necessary in order to maintain the temperature of the reaction mixture at approximately 10°. The ice bath is removed after about 30 minutes, when the reaction mixture has a dark chocolate color,* and the ammonia flow rate is then regulated so as to maintain the temperature between 20° and 30°.

The flow of ammonia is continued until a "golden poppy" color is reached. About 1½ hr. are required for the reaction.

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* The sequence of colors is brown, khaki, chocolate, olive drab, tan, and golden poppy.

The reaction mixture is filtered on a large sintered-glass or Büchner funnel, and the solid material is washed with about 100 ml. of carbon tetrachloride. The solid material on the funnel may be worked up by a procedure similar to that described in the previous section if it is desired to recover the S_4N_4.* Otherwise it is discarded. The combined filtrate and wash is evaporated to dryness at a temperature lower than 60°. The residue from the evaporation is shaken or vigorously stirred for an hour with 250 ml. of peroxide-free ether in a stoppered flask. After filtering the ether solution, it is evaporated to dryness. The residue from the ether evaporation contains about seven grams of S_7NH mixed with smaller amounts of sulfur and S_4N_4. By recrystallizing the material from hot acetone three or four times, approximately one gram of pure S_7NH (with a melting point above 110°) may be recovered. If quantitative recovery of a pure product is desired, the residue from the ether evaporation may be dissolved in a minimum volume of carbon tetrachloride (about 500 ml.)

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* A yield of approximately 5 g. may be expected. This yield may be increased to 8 g. if the solid is combined with the residue from the ether extraction.

and separated in several batches by elution chromatography on a silica gel column. About 150 ml. of the saturated carbon tetrachloride solution may be passed through a column 24 cm. long and 75 mm. wide in each batch separation. Elution with carbon tetrachloride yields a band of sulfur followed closely by a band of S_7NH. S_7NH in the eluate may be detected by mixing a small volume of the eluate with an equal volume of methanolic KOH. A red-violet color forms in the presence of S_7NH. When heated, the mixture turns yellow, as it also does in the presence of sulfur alone.

Properties

S_7NH is a pale yellow, almost colorless solid of melting point 113.5°. The compound may be distinguished from sulfur by its infrared spectrum.[6] Absorption bands occur at 805, 1290, and 3300 cm^{-1}.

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

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