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CONVENIENT METHODS FOR PREPARING $S_3N_2Cl_2$ AND S_4N_3Cl

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Contribution from the Department of Chemistry and
Inorganic Materials Research Division of the Lawrence Radiation
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When a suspension of ammonium chloride in S_2Cl_2 is refluxed, the principal reaction products are NSCl and HCl[1]:

$$NH_4Cl + 2\,S_2Cl_2 \longrightarrow 3\,S + NSCl + 4\,HCl\,.$$

If a sufficiently large amount of ammonium chloride is used, transparent orange crystals of $S_3N_2Cl_2$ form in the condenser above the level of the refluxing liquid soon after the beginning of the reflux. When practically all the S_2Cl_2 has been consumed, the $S_3N_2Cl_2$ which has formed in the condenser may be removed. However, if S_4N_3Cl is the desired product, the reaction flask is replaced by a flask containing carbon tetrachloride, and the carbon tetrachloride is boiled so that the refluxing liquid washes the crystals into the flask. During this process the crystals first turn green (S_3N_2Cl) and finally yellow (S_4N_3Cl).

It is believed that the vapors of S_2Cl_2 and NSCl react to form the $S_3N_2Cl_2$:

$$2\,NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2\,.$$

This reaction does not begin immediately upon refluxing the mixture of ammonium chloride and S_2Cl_2 because of the presence of chlorine[2] in the effluent gases. Chlorine is known[1] to react with $S_3N_2Cl_2$ according to the equation,

$$Cl_2 + S_3N_2Cl_2 \longrightarrow 2\ NSCl + SCl_2 .$$

However, when the concentration of sulfur in the S_2Cl_2 increases sufficiently to prevent, or almost prevent, the evolution of chlorine, the $S_3N_2Cl_2$ deposition begins. Two types of experiments attest to this interpretation of the delayed deposition of $S_3N_2Cl_2$. First, when relatively small amounts of ammonium chloride are used, no $S_3N_2Cl_2$ is deposited even when the refluxing is continued until the ammonium chloride is completely consumed. (In such cases, the concentration of sulfur never becomes high enough to prevent effectively the evolution of chlorine.) Second, when sulfur is added to the reaction mixture, the time to the first appearance of $S_3N_2Cl_2$ is greatly reduced.[3] Indeed $S_3N_2Cl_2$ is produced when sulfur is added to a reaction mixture that ordinarily does not produce $S_3N_2Cl_2$.

When $S_3N_2Cl_2$ is heated to 80-95° <u>in vacuo</u>, greenish-black S_3N_2Cl is formed:[1]

$$3\ S_3N_2Cl_2 \longrightarrow 2\ S_3N_2Cl + 2\ NSCl + SCl_2 .$$

We believe that this pyrolysis is the best method for preparing S_3N_2Cl. When S_3N_2Cl is heated to 130-150° *in vacuo*, a variety of products, including NSCl and SCl_2, are evolved, and a residue of pure S_4N_3Cl is formed. In view of these facts and the fact that a dark green intermediate is observed during the refluxing of carbon tetrachloride with $S_3N_2Cl_2$, we believe that the over-all conversion of $S_3N_2Cl_2$ to S_4N_3Cl by boiling carbon tetrachloride proceeds *via* S_3N_2Cl. Meuwsen[5] carried out this same conversion, but he stated that the reaction proceeds smoothly only in the presence of S_2Cl_2, and he did not report the intermediate formation of S_3N_2Cl.

Experimental

Preparation of S_4N_3Cl. — Fifty grams of NH_4Cl and 25 ml. of S_2Cl_2 were placed in a 500 ml. round bottomed flask fitted with an air condenser (75 cm. long and 22 mm. in diameter) to the top of which a calcium sulfate drying tube was attached. The mixture was refluxed gently using a heating mantle. The heating was adjusted so that the level of the refluxing S_2Cl_2 was just above the neck of the flask. During approximately 16 hours of refluxing, orange crystals of S_3N_2Cl collected in the air condenser. At the end of this time the heating was stopped and the apparatus was allowed

to stand overnight so that most of the liquid adhering to the crystals could drain away. (This liquid contained appreciable amounts of dissolved hydrogen chloride which, if not removed, resulted in a product contaminated with ammonium chloride.) The reaction flask was removed and immediately replaced with a similar flask containing 100 ml. of dry carbon tetrachloride (freshly distilled from $CaSO_4$). The carbon tetrachloride was then refluxed up into the air condenser over the crystalline deposit. The material first turned dark green and partly bright yellow and fell into the flask. Shaking the assembly or even inserting a long glass rod down the air condenser was sometimes necessary in order to assist the sublimate down into the reflux flask. The carbon tetrachloride was boiled until all the dark material was converted into a bright yellow solid (approx. 4 hrs.). The solid S_4N_3Cl was filtered from the carbon tetrachloride while it was still warm; it was washed with dry carbon tetrachloride, and finally dried in a vacuum desiccator. Yield: 4.5 g.

Anal.— Calculated for S_4N_3Cl: N, 20.38; S, 62.34; Cl, 17.24. Found: N, 21.02; S, 62.09; Cl, 17.58. The infrared spectrum (KBr disc) showed peaks at 8.55, 10.0, and 14.75 μ, and was identical with the infrared spectrum of a sample of S_4N_3Cl prepared in the usual way.[6]

When 5.35 g. of ammonium chloride was refluxed wtih 35 ml. of S_2Cl_2 for 36 hrs. in the manner described above, all the ammonium chloride was consumed and a solution of sulfur in S_2Cl_2 remained. No $S_3N_2Cl_2$ was formed in the air condenser. In a reaction similar to the above, but in which 6.4 g. of elementary sulfur was added to the reactants, crystals of $S_3N_2Cl_2$ began to form after 1.5 hrs. refluxing.

Preparation of $S_3N_2Cl_2$.— The orange $S_3N_2Cl_2$ which formed in the reaction between S_2Cl_2 and NH_4Cl (described above) could be isolated in a pure state by rapidly removing the reaction flask, closing the open end of the air condenser and then quickly replacing the drying tube with a connection to the vacuum line. By evacuating the tube and pumping for approximately 30 minutes, the volatile impurities were removed. The $S_3N_2Cl_2$ was scraped from the inside of the air condenser in a "dry bag" flushed with dry nitrogen. All operations involving $S_3N_2Cl_2$ should be made in a dry atmosphere, since the compound is very sensitive to atmospheric moisture. Yield: approximately 14 g.

Anal.— Calculated for $S_3N_2Cl_2$: S, 49.29; N, 14.36; Cl, 36.34. Found: S, 49.0; N, 14.27; Cl, 36.64. m.p. (sealed tube) 90-92°. The compound is not stable for prolonged periods even in a dry atmosphere, but

may be kept for about 10 days without serious decomposition.

Thermal decomposition of S_3N_2Cl.— Dark green S_3S_2Cl (1.95 g.) (prepared by thermal decomposition of $S_3N_2Cl_2$. Anal.— Calcd. for S_3N_2Cl: N, 17.54; Cl, 22.24. Found: N, 17.95; Cl, 21.80) was thermally decomposed *in vacuo* at 130-150°. The volatile products (0.65 g.) were collected in a -78° trap and were identified by their infrared spectrum as NSCl,[7] and SCl_2.[8] By allowing the trap to stand at room temperature overnight the NSCl formed the non-volatile trimer $(NSCl)_3$ from which 0.145 g. of SCl_2 was readily separated. The solid non-volatile residue from the pyrolysis was bright yellow S_4N_3Cl (1.03 g.).

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References

(1) K. D. Maguire, J. J. Smith, and W. L. Jolly, to be published.

(2) Most of the chlorine probably arises from the decomposition of The S_2Cl_2. When S_2Cl_2 is fractionally distilled at atmospheric pressure, SCl_2 comprises the first fraction. Because SCl_2 is known to decompose appreciably to chlorine[3], and because in these syntheses the more volatile vapors are being carried away by a stream of hydrogen chloride, it is reasonable to expect chlorine in the initial off-gases.

(3) J. W. George, Progress in Inorganic Chemistry, 2, 33 (1960).

(4) Presumably sulfur reduces the concentrations of SCl_2 and Cl_2 in the liquid S_2Cl_2 by shifting the equilibria $S_2Cl_2 = S + SCl_2$ and $S_2Cl_2 = 2\,S + Cl_2$.

(5) A. Meuwsen, Ber., 65, 1724 (1932).

(6) M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen", Akademie-Verlag, Berlin, 1957, p. 155.

(7) O. Glemser and H. Richert, Z. anorg. allgem. Chem., 307, 313 (1961).

(8) G. M. Barrow, J. Phys. Chem., 59, 987 (1955).

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