solution. The filtrate is allowed to stand in a tightly sealed flask at room temperature or on ice until crystallization occurs. After several hours, yellow needles of $(NH_4)_2S_5$ are formed. These are stable for a fairly long time if submerged in the mother liquor in the absence of air, but they decompose very rapidly when dry to form NH_3, H_2S and S. The product is isolated by rapid suction-filtration through filter paper, removal of adhering mother liquor by pressing between filter papers, and consecutive washing with ether-methanol (5 : 1), absolute ether and anhydrous chloroform. The still moist product is allowed to stand in a vacuum desiccator over CaO which has been wetted with some concentrated ammonium hydroxide. However, because of decomposition, it contains about 10% of elemental sulfur after five hours. Freshly prepared $(NH_4)_2S_5$ should give a clear solution in 5% ammonium hydroxide.

SYNONYM:

Diammonium pentasulfane.

PROPERTIES:

Yellow to orange-yellow crystals; very easily decomposed to NH_3, H_2S and S. Melts in a sealed tube at 95°C to form a red liquid; decomposes on heating in an open tube. Rapidly precipitates S with water; soluble in ammonium hydroxide (see above).

REFERENCE:

H. Mills and P. L. Robinson, J. Chem. Soc. (London) 1928, 2326.

Dichloromonosulfane

SCl_2

I.
$$\underset{32.07}{S} + \underset{70.91}{Cl_2} = \underset{102.98}{SCl_2}$$

Coarsely ground roll sulfur (200 g.) is placed in a one-liter, round-bottom, ground glass flask equipped with a side arm serving as gas inlet. A reflux condenser is set in the ground joint and a thermometer is fastened in such a way that it protrudes from the flask into the lower part of the condenser. From the upper end of the condenser an outlet tube leads to the hood through a wash bottle containing H_2SO_4. A fast stream of carefully dried Cl_2 gas is passed through the S until the contents of the flask have completely liquefied, forming crude S_2Cl_2 (heat is evolved). Then a

spatula tip (about 0.1 g.) of Fe powder or anhydrous $FeCl_2$ or $FeCl_3$ is added and the gas flow is continued for another 0.5 hour; during this time the reaction mixture is gradually cooled to 20°C by immersing the flask in water. The dark red liquid which forms, and which contains S_2Cl_2 and Cl_2 in addition to the SCl_2, is left to stand for about one hour. Then 2 ml. of PCl_3 is added and the solution is distilled through a small fractionating column. The middle fraction boiling between 55 and 62°C is collected in a receiver containing a few drops of PCl_3 and is again fractionated. A very pure product with a constant boiling point of 60°C is obtained. The yield is about 70%.

The substance is stable for a few days when stored in glass vessels in the presence of a few drops of PCl_3. Pure SCl_2 can always be recovered from the mixtures with S_2Cl_2 and Cl_2 that form on prolonged standing by distillation with PCl_3.

II. $$\underset{135.04}{S_2Cl_2} + \underset{70.91}{Cl_2} = \underset{205.95}{2\,SCl_2}$$

The substance can also be prepared starting directly with S_2Cl_2. Otherwise, the procedure is the same as in method I.

SYNONYM:

Sulfur dichloride.

PROPERTIES:

Dark-red liquid with a pungent, chlorinelike odor; it decomposes readily, reversing reaction II, to form S_2Cl_2 and Cl_2; sensitive to atmospheric moisture. M.p. −121°C, b.p. +59.6°C; d (20°C) 1.621.

Reacts with water with precipitation of sulfur and formation of $H_2S_2O_3$, $H_2S_nO_6$ and H_2SO_4; soluble in n-hexane without decomposition.

REFERENCES:

H. Jonas and H. Stöhr, unpublished, private communication.
See also Naturforschung und Medizin in Deutschland 1939-1946 (FIAT-Review), 23, 191.

Dichlorodisulfane

S_2Cl_2

$$\underset{64.13}{2\,S} + \underset{70.91}{Cl_2} = \underset{135.04}{S_2Cl_2}$$

Sulfur is melted in a flask equipped with a side arm and a neck elongated into a gradually narrowing tube. By tilting the flask, the

walls are coated with a uniform layer of sulfur melt. After cooling, the flask is mounted vertically in such a way that the tube end passes through a rubber stopper into another flask below. From the latter, a gas outlet tube passes through a drying tube directly to the hood. A moderately rapid stream of carefully dried Cl_2 is introduced through the side arm of the top flask and the walls of that flask are simultaneously heated to 50-80°C by fanning with a flame. Once the reaction is in progress, the S_2Cl_2 product flows into the lower flask in a rapid succession of drops. The orange-red substance is still contaminated by dissolved starting materials. Some sulfur is added and it is distilled at atmospheric pressure. The portion which distills above 137°C is refractionated over sulfur at about 12 mm. in an apparatus with ground glass joints; b.p. of the pure product is 29-30°C at this pressure.

This material is used on a large scale in industry as a solvent for sulfur in the vulcanization of rubber.

SYNONYMS:

Disulfur dichloride; older designations "sulfurous chloride" and "sulfur monochloride."

PROPERTIES:

Golden yellow, oily liquid; when less pure, orange to reddish because of SCl_2 impurities; fumes in moist air, unpleasant pungent odor. M.p. −77°C, b.p. (760 mm.) +138°C; d (20°C) 1.6773.

Hydrolyzes with water to form HCl, SO_2 and H_2S; these then convert to S, $H_2S_2O_3$ and $H_2S_nO_6$. Readily soluble in CS_2.

REFERENCE:

Abegg, Handbuch der anorganischen Chemie, Vol. IV, 1, p. 287.

Dichlorotri-, -tetra-, -tenta-, -hexa-, -hepta- and -octasulfane

S_3Cl_2, S_4Cl_2, S_5Cl_2, S_6Cl_2, S_7Cl_2, S_8Cl_2

If the ratios of the reactants are reversed, then the general synthetic method used in the preparation of the sulfanes (p. 353) can also be used for the preparation of the chlorosulfanes. The sulfane component is added to an excess of chlorosulfane at low temperature and after the reaction

$$(a-2)\,Cl_2S_n + Cl{-}S_n{-}\boxed{Cl + H}{-}S_m{-}\boxed{H + Cl}{-}S_n{-}Cl = Cl_2S_{2n+m} + 2\,HCl + (a{-}2)\,Cl_2S_n$$

(n = 1, 2; m = 1, 2, 3, 4, 5, 6).

is complete, excess chlorosulfane $(a - 2)Cl_2S_n$ is distilled off.

With suitable choice of reactants and careful following of