613. *Sulphur Chloride Pentafluoride: New Preparative Methods.*

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The preparation of sulphur chloride pentafluoride by the reaction of chlorine trifluoride with sulphur or sulphur tetrafluoride, and of chlorine monofluoride with sulphur tetrafluoride is described. These routes give the compound in considerably greater yields than those hitherto described and are more convenient.

Sulphur chloride pentafluoride has been prepared in poor yield by the reaction of fluorine with sulphur dichloride at $-10°$,[1] and has also been obtained as a product of the reaction of chlorine with disulphur decafluoride.[2] The former preparation is tedious and inefficient while the latter depends on the poorly available disulphur decafluoride, a by-product from the preparation of sulphur hexafluoride from fluorine and sulphur.[3] The present paper describes three new methods by which sulphur chloride pentafluoride can be prepared conveniently and in good yield.

Fluorination of sulphur dichloride with chlorine trifluoride was first tried since this reaction would be less exothermic than that with fluorine and might thus have given better yields. However, when chlorine trifluoride (diluted with nitrogen) was passed over the surface of liquid sulphur dichloride at various temperatures, only sulphur tetrafluoride was produced at temperatures below 20° while at higher temperatures increasing amounts of sulphur hexafluoride were obtained; no sulphur chloride pentafluoride was formed in these experiments.

Since chlorine trifluoride could act simultaneously both as a chlorinating and fluorinating agent its reaction with elemental sulphur was examined. Chlorine trifluoride diluted 1 : 4 by volume with nitrogen was passed over sulphur in a copper tube. At low flow rates of chlorine trifluoride, *i.e.*, <2·7 l./hr., the only products were sulphur tetrafluoride and the sulphur chlorides:

$$4ClF_3 + 5S \longrightarrow 3SF_4 + 2SCl_2$$

$$SCl_2 + S \longrightarrow S_2Cl_2$$

At higher flow rates (2·7—17·5 l./hr.) increasing quantities of sulphur chloride pentafluoride were produced, reaching a maximum yield of 30%, and then sulphur hexafluoride was produced at the expense of both sulphur chloride pentafluoride and sulphur tetrafluoride.

The sulphur chloride pentafluoride produced by this method always contains sulphur tetrafluoride and usually significant amounts of sulphur hexafluoride. Attempts to isolate sulphur chloride pentafluoride directly from this mixture by fractional distillation under pressure were unsuccessful owing to the formation of azeotropes which were not investigated in detail. Pure sulphur chloride pentafluoride was, however, obtained by chemical removal of the sulphur tetrafluoride[1] followed by the fractional distillation under pressure of the resulting binary mixture. It is noteworthy that with chlorine trifluoride flow rates of <2·5 l./hr., removal of the sulphur chlorides from the products by fractional condensation left sulphur tetrafluoride of >99% purity. Thus under these conditions the reaction provides a convenient preparation of pure sulphur tetrafluoride.

Since sulphur tetrafluoride is readily available by the above reaction or that of sulphur dichloride with sodium fluoride,[4] it would be a convenient starting material for the preparation of sulphur chloride pentafluoride. When mixed with gaseous chlorine trifluoride in a copper vessel no reaction occurred at room temperature, but at 180° the two compounds

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[1] Roberts and Ray, *J.*, 1960, 665.
[2] George and Cotton, *Proc. Chem. Soc.*, 1959, 317.
[3] Denbigh and Whytlaw-Gray, *J.*, 1934, 1346.
[4] Tullock, Fawcett, Smith, and Coffman, *J. Amer. Chem. Soc.*, 1960, **82**, 539.

reacted smoothly, to give an equimolar mixture of sulphur chloride pentafluoride and sulphur hexafluoride:

$$2SF_4 + ClF_3 \longrightarrow SF_5Cl + SF_6$$

Although sulphur chloride pentafluoride and sulphur hexafluoride are readily separated by fractional distillation under pressure this route is relatively inefficient since half the sulphur tetrafluoride is converted into an unwanted by-product. However, reaction of sulphur tetrafluoride with chlorine monofluoride gives sulphur chloride pentafluoride almost exclusively. Thus, when a equimolar mixture of sulphur tetrafluoride and chlorine monofluoride (prepared *in situ* from chlorine and chlorine trifluoride at 350°) sealed in a nickel tube was heated, reaction took place rapidly on reaching 350° and gave a *ca.* 95% yield of sulphur chloride pentafluoride. Sulphur hexafluoride, chlorine, and unchanged sulphur tetrafluoride and chlorine monofluoride were the only other products:

$$ClF_3 + Cl_2 \longrightarrow 3ClF$$
$$ClF + SF_4 \longrightarrow SF_5Cl$$

This reaction was made the basis of a continuous process which produced sulphur chloride pentafluoride in 85% overall yield from chlorine trifluoride.

The larger quantities of sulphur chloride pentafluoride made available by the above routes have enabled more accurate determinations of some physical properties to be made; values for the melting point, density, and critical temperature are given here for the first time. M. p. —64°; b. p. —19·1°; v. p. over the range —60° to —20° is given by $\log p_{\text{mm.}} = 7{\cdot}145 - 1083/T$ (°K); Trouton constant 19·5; density over the range —60° to —20° is given by $1{\cdot}861 - 0{\cdot}0015T$ (°C); critical temperature 117·7° ± 0·2°.

EXPERIMENTAL

Chlorine trifluoride supplied by General Chemicals Division, Imperial Chemical Industries Limited, was used without further purification. Pure sulphur tetrafluoride was prepared from sulphur and chlorine trifluoride as described below.

Gas-chromatographic analyses were carried out with a column (12′ long by ¼″ in diameter) of " Chromosorb " (Johns Manville Co. Ltd.) on to which 30% w/w of " Florube A " grease (Imperial Chemical Industries Limited) had been adsorbed. This column resolved sulphur hexafluoride, sulphur tetrafluoride, and sulphur chloride pentafluoride, but chlorine, chlorine monofluoride, and chlorine trifluoride had similar retention times and could only be resolved collectively from the other compounds.

Reaction of Chlorine Trifluoride with Sulphur Dichloride.—The experimental technique used was identical with that used by Roberts and Ray for the reaction of fluorine with sulphur dichloride.[1] At temperatures below 20° only sulphur tetrafluoride was produced. At higher temperatures increasing amounts of sulphur hexafluoride were formed but no sulphur chloride pentafluoride was detected.

Reaction of Chlorine Trifluoride with Sulphur.—A copper tube *ca.* 3′ long by 1½″ in internal diameter was charged with *ca.* 1 kg. of sulphur in lumps of ⅓″ diameter, spread evenly along its length. A 4″ long copper coil, connected to a cold-water supply, was wound on so that it was possible to slide it along the tube and keep it at the point where the reactant gases first met the sulphur bed. One end of the tube was connected by copper tubing (¼″ bore) *via* separate flow-meters to cylinders of chlorine trifluoride and nitrogen. The other end was similarly connected to two glass traps cooled severally to −80° and −183° by solid carbon dioxide and liquid air. A sampling point for the removal of the products for gas-chromatographic analysis was placed between the two product traps. A $ClF_3 : N_2$ ratio of 1 : 4 by volume was used in all experiments.

In an experiment, the apparatus was swept out with nitrogen, the chlorine trifluoride flow set at a given rate, and after one hour had been allowed for steady conditions to be attained samples of the products were taken for gas-chromatography. The products collected at −183° were also directly analysed in some experiments; the sulphur chlorides produced were retained quantitatively at −80°, while the fluorinated products were swept through to the −183° trap by the nitrogen stream. At chlorine trifluoride flow-rates of up to 2·7 l./hr. sulphur tetrafluoride was the only fluorine-containing product detected. At higher flow rates first sulphur chloride pentafluoride up to a maximum yield of 30%, and then sulphur hexafluoride were obtained. Thus an experiment in which a flow rate of 16·25 l./hr. of chlorine trifluoride was maintained for 4 hr. (268 g., 2·90 moles) gave 176 g. of sulphur chlorides (mainly sulphur monochloride) and 248 g. of fluorine-containing products. The latter were distilled on to an excess of trifluoride to remove sulphur tetrafluoride (160 g., 1·48 moles, 68%) as the solid complex BF_3,SF_4.[5] The residue, after removal of the excess of boron trifluoride by scrubbing with water, gave on trap-to-trap distillation sulphur hexafluoride (4 g., 0·03 mole, 2%) and sulphur chloride pentafluoride (80 g., 049 mole, 28%). Yields are based on chlorine trifluoride taken.

Attempts to separate the mixture of sulphur tetrafluoride, sulphur chloride pentafluoride, and sulphur hexafluoride by fractional distillation under pressure through a 3′ × 1″ column packed with $\frac{1}{8}$″ mild steel rings were unsuccessful. Evidence was obtained for the formation of a ternary azeotrope and a binary azeotrope of sulphur tetrafluoride and sulphur hexafluoride.

Reaction of Chlorine Trifluoride and Sulphur Tetrafluoride.—The reaction vessel was a copper tube 3′ long and 4·5″ in diameter, blanked off at one end, sealed at the other with a "Fluon"-packed needle-valve, and fitted with a "Budenberg" chlorine-pressure gauge. The tube was evacuated and chlorine trifluoride admitted directly from a cylinder to give one atm. pressure. Sulphur tetrafluoride was then added to two atm. gauge-pressure, giving a $SF_4 : ClF_3$ molar ratio of 2 : 1. The tube was heated in an electric furnace to 180° and kept at this temperature until no further change in pressure occurred (*ca.* 1 hr.). After cooling to room temperature gas-chromatography of the products showed that almost complete reaction to give equimolar quantities of sulphur hexafluoride and sulphur chloride pentafluoride had occurred; unchanged sulphur tetrafluoride (1%) and a trace of chlorine or chlorine fluorides were the only other products detected.

Reaction of Chlorine Monofluoride with Sulphur Tetrafluoride.—The experimental method used for the static reaction was similar to that given above except that a 300-ml. nickel reaction vessel was used. Chlorine trifluoride was admitted to the evacuated tube to one atm. pressure and chlorine then added to one atm. gauge pressure, giving an equimolar mixture. The temperature of the reactor was raised to 350° and then lowered to room temperature, the pressure inside being 2 atm. (gauge) owing to the formation of chlorine monofluoride. Sulphur tetrafluoride was then added to give a total pressure of 5 atm. (gauge) and the reaction vessel was heated once more to 350°. On cooling to room temperature, the pressure fell to 2 atm. (gauge). Gas-chromatography showed the products to contain sulphur chloride pentafluoride (90%), unchanged sulphur tetrafluoride (5%), sulphur hexafluoride (2%), and either chlorine or chlorine monofluoride.

For the continuous reaction two connected nickel tubes, 4′ long × $2\frac{1}{2}$″, were used, heated by separate electric furnaces. The reactants were metered from storage cylinders by means of capillary flow-meters whose construction was such that neither chlorine trifluoride nor sulphur tetrafluoride came into contact with their glass parts.[6] Chlorine trifluoride (0·18 l./min.) and chlorine (0·22 l./min.) were mixed and passed into the first reactor kept at 350° to produce chlorine monofluoride. An excess of chlorine was used in order to ensure that no unchanged chlorine trifluoride reacted at the next stage. The gases from the first reactor were mixed with sulphur tetrafluoride (0·54 l./min.) and passed into the second reactor, the optimum temperature for which was found to be 375°. The effluent gases were washed counter-currently with water in a tower 4′ long and 4″ in diameter packed with porcelain rings, dried by passage through a bed of calcium sulphate and condensed in traps cooled in liquid air. The material thus produced contained up to 5% of sulphur hexafluoride but no other impurity. Distillation under pressure through the column described above gave pure sulphur chloride pentafluoride in 85% overall yield based on sulphur tetrafluoride. Gas-chromatography of the products before washing showed that >95% conversion into sulphur chloride pentafluoride took place in the reaction vessel. Control experiments established that a *ca.* 10% loss of sulphur chloride pentafluoride occurred in the wash-tower owing to solubility in water. In a typical experiment

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[5] Bartlett and Robinson, *Proc. Chem. Soc.*, 1957, 230.

[6] Imperial Chemical Industries Limited, Data Sheet for Chlorine Trifluoride.

520 g. of sulphur tetrafluoride fed into the reaction vessel during 4 hr. gave 660 g. of pure sulphur chloride pentafluoride, an overall yield of 84·5%.

Measurement of Physical Properties.—The vapour-pressure of sulphur chloride pentafluoride was determined (±0·1 mm.) by means of an isoteniscope immersed in a bath whose temperature could be held constant to ±0·1° over the range used.

Density was measured by observing the length of known weight of liquid in a calibrated capillary tube.

The critical temperature was measured by observing the temperature at which the meniscus of a sample sealed in a glass capillary tube disappeared.

The authors thank Messrs. H. F. Leach and S. J. Webster for the physical data quoted.

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[*Received, March* 15*th*, 1962.]