136. *Sulphur Chloride Pentafluoride: Preparation and Some Properties.*

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A new compound, sulphur chloride pentafluoride, has been obtained by fluorination of sulphur dichloride. It is a colourless gas, b. p. −21°, which is stable to acids but rapidly hydrolysed by alkalis.

Sulphur readily forms a hexafluoride, but with chlorine its valency never exceeds two. Sharpe [1] has suggested that this may be due to the greater energy of S–F bonds and the lower dissociation energy of the fluorine molecule which more than compensate for the additional energy required to raise a sulphur atom from the ground state to a $3s^1 3p^3 3d^2$ valency state required by sulphur hexafluoride. Craig and Magnusson [2] considered the same problem in terms of the influence of chlorine and fluorine atoms on the 3*d*-orbitals of sulphur and concluded that for effective use of these orbitals in bond formation the atoms attached to sulphur should be small and strongly electronegative. They also suggested that the presence of four or five fluorine atoms might give sufficient stabilisation to enable compounds such as SF_4Cl_2 and SF_5Cl to exist.

A possible experimental approach is to study the reaction of sulphur dichloride with

[1] Sharpe, *Quart. Rev.*, 1957, **11**, 49.
[2] Craig and Magnusson, *J.*, 1956, 4895.

fluorine; this has been done, and the compound sulphur chloride pentafluoride has been isolated from the products of this reaction.[3]

At room temperature sulphur chloride pentafluoride is a colourless gas with a characteristic and unpleasant odour; it condenses to a liquid of b. p. −21° which solidifies at −64°. It is stable up to 250° in a glass or nickel vessel, but decomposes at 200° in the presence of metals such as copper and mercury which react with chlorine:

$$2SF_5Cl \longrightarrow SF_4 + SF_6 + Cl_2$$

It is stable to acids, but it is slowly hydrolysed by water and rapidly by alkalies:

$$8OH^- + SF_5Cl \longrightarrow SO_4^{2-} + Cl^- + 5F^- + 4H_2O$$

It is thus more reactive than either sulphur hexafluoride or disulphur decafluoride.

The infrared absorption spectrum of sulphur chloride pentafluoride shows three main bands, at 905, 854, and 706 cm.$^{-1}$; as would be expected these are similar to the S–F stretching modes of disulphur decafluoride [4] which occur at 940, 827, and 682 cm.$^{-1}$.

Experimental

Microanalyses are by Dr. A. F. Colson and the infrared absorption spectroscopy by Mr. L. H. Cross.

Preparation of Sulphur Chloride Pentafluoride.—The reaction vessel was a 2-ft. length of copper tube of ¼ in. bore, formed into a loose helix and immersed in a cooling-bath. About 6 in. from one end a branch of similar tubing was welded in, the junction being below the surface of the cooling-bath; a thermocouple was also fastened to the tube at this point. Fluorine from an electrolytic cell was passed over sodium fluoride to remove hydrogen fluoride, diluted with an equal volume of nitrogen, and passed into the reaction tube at the end nearer the branch. A second stream of nitrogen was saturated with sulphur dichloride vapour at 30° and passed into the reaction tube through the side-branch. The products were condensed in a series of liquid-air traps connected to the other end of the reaction tube.

Experiments were carried out over a range of temperature from −30° to +40° with different ratios of fluorine to sulphur dichloride; the best yield of sulphur chloride pentafluoride was obtained with the reaction tube at −10° and a molar ratio $F_2 : SCl_2$ between 3 and 4. In a typical run under these conditions fluorine (31·5 g., 0·83 mole) and sulphur dichloride (21·8 g., 0·21 mole) were passed into the reaction tube during 6 hr. Nitrogen was then swept through the apparatus and the traps until the excess of fluorine was removed, and the contents of the traps were allowed to volatilise into a gas-holder, leaving a small residue of sulphur monochloride and sulphur dichloride. The gaseous products were washed first with a saturated solution of ferrous sulphate in 2N-sulphuric acid to remove chlorine and to hydrolyse sulphur tetrafluoride, and then with a saturated solution of sodium dichromate in 6N-sulphuric acid to remove sulphur dioxide resulting from the hydrolysis of sulphur tetrafluoride. The residual gas was dried with anhydrous magnesium perchlorate and separated by gas chromatography at room temperature on a 1 in. diameter column packed with " Chromosorb " (Johns Manville Co., Ltd.) containing 40% w/w " Florube " grease type A (Imperial Chemical Industries Limited). The first fraction eluted from the column was sulphur hexafluoride; the second fraction (1·7 g.), with a retention time 3·0 times that of the first, was *sulphur chloride pentafluoride* (Found: S, 20·3; Cl, 22·2; F, 57·7%; *M*, 163. SF_5Cl requires S, 19·7; Cl, 21·9; F, 58·4%; *M*, 162·5).

The vapour pressure was measured with a mercury manometer connected to a bulb immersed in a cooling-bath, the temperature of which was measured with a previously calibrated alcohol thermometer. The results can be summarised in the form [vapour pressure (mm.) at $T°$ K]: $\log_{10} p = -1005/T + 6{\cdot}87$. The b. p. was found by extrapolation to be −21°; the latent heat of vaporisation, calculated from the slope, is 4560 cal. per mole, and the Trouton constant is 18·2.

The m. p. of a number of different samples of the compound was measured with a calibrated alcohol thermometer and found to be −64° ± 1°.

The infrared absorption spectrum was observed in a 10-cm. cell with rock-salt windows and a Grubb–Parsons double-beam infrared spectrometer. The spectrum showed bands at 1754vw,

[3] B.P. Appln. 31,320/1958.

[4] Dodd, Woodward, and Roberts, *Trans. Faraday Soc.*, 1957, **53**, 1545.

1698w, 1656vw, 1610w, 1531w, 1513w, 1455vw, 1305vw, 1282vw, 1253w, 1212vw, 1204vw, 1168vw, 1157vw, 1138vw, 1103vw, 1045vw, 990vw, 975vw, 960vw, 905vs, 860, 854, 849vs, 807, 801, 795m, 712, 706, 696s cm.$^{-1}$.

Chemical properties. A bulb containing liquid sulphur chloride pentafluoride was broken under an excess of aqueous sodium hydroxide. The resulting solution was found to contain sulphate, chloride, and fluoride in the ratio 1 : 0·95 : 5·1.

A sample of sulphur chloride pentafluoride was heated to 250° in a stainless-steel pressure vessel for 24 hr. On cooling, the sample was recovered. A second sample was heated to 200° in a copper vessel for 1 hr.; on cooling the residual gas was analysed by gas chromatography and infrared spectroscopy and found to be a mixture of sulphur hexafluoride, sulphur tetrafluoride, and chlorine.

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