CCCXLIV.—*The Action of Sulphur Monochloride on Antimony Pentachloride.*

By JAMES RIDDICK PARTINGTON.

A COMPOUND of sulphur tetrachloride and antimony pentachloride was first described by Rose (*Pogg. Ann.*, 1837, **42**, 517). He stated that chlorine had no appreciable action on antimony trisulphide in the cold, but on heating in one place reaction began and finally a nearly white amorphous powder remained. This was dissolved in dilute nitric acid, oxides of nitrogen being evolved, and antimony was precipitated as sulphide, which was reduced to metal in hydrogen and weighed. Hydrogen sulphide was removed from the filtrate by copper nitrate, and chlorine precipitated with silver nitrate. In the filtrate from the silver chloride, sulphate was precipitated as the barium salt. From this complete analysis of the substance, Rose found Sb, 25·67; S, 7·63; Cl, 66·70%. Apparently Rose assumed the substance to be formed according to the equation $Sb_2S_3 + 11Cl_2 = 2SbCl_5,3SCl_4$, and as this formula would require Sb, 21·75; S, 8·59; Cl, 69·66%, he assumed that his material contained some antimony trichloride.

Ruff and Fischer (*Ber.*, 1904, **37**, 4513) obtained a compound of antimony pentachloride and sulphur tetrachloride by adding chlorinated sulphur monochloride, containing 68·9% of chlorine, to a solution of antimony pentachloride in sulphuryl chloride. The substance separated in "fine needles." It was decomposed in a current of moist air, sulphur separating. The apparatus was then washed out with fuming nitric acid, and the liquid warmed. From one specimen the chlorine was precipitated as silver chloride, and from another, the antimony as sulphide: the sulphur was not estimated. Their results (corrected for the new atomic weight of antimony) were: Cl, 67·76; Sb, 26·96; S (by diff.), 5·28%. $SbCl_5,SCl_4$ requires Sb, 25·74; S, 6·78; Cl, 67·48%, and they adopt this formula, stating it to be "also derselben die schon Rose gefunden hat," whereas Rose's formula was $2SbCl_5,3SCl_4$.

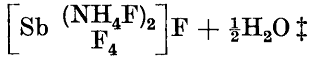
Ruff and Fischer state that the substance melts at 125—126° in a sealed tube in an atmosphere of chlorine to a yellow liquid, but their statement is confused, since they proceed to explain that the solid begins to sublime at 150°, and "der Schmelzpunkt bezieht sich auf die sublimierte Substanz." It is shown in the present communication that the substance actually is $SbCl_5,SCl_4$, and that it melts at about 157° and does not sublime unchanged.

Since the existence of the compound $SbCl_5,SCl_4$ has sometimes been regarded as evidence of the existence of SCl_4 in the separate state, it seemed desirable to examine the action of antimony pentachloride on sulphur monochloride. The confirmation of the existence of such a compound as $SbCl_5,SCl_4$ was also of some importance, since it seems difficult to represent the structure of such a molecule on any formulation not involving links of *single* electrons. Such anomalies and apparent exceptions to the theory that co-ordination is due to the donation of a pair of electrons by one atom to form a covalent bond, are, however, by no means uncommon, as the following examples show :

(I.) $SbCl_5,6NH_3$*

$$\left[\mathrm{Sb}\ \begin{matrix}(\mathrm{ClH,Quinoline})_2\\ \mathrm{Cl}_4\end{matrix}\right]\mathrm{Cl} + H_2O$$ † (II.)

(III.)



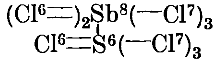
$$\left[\mathrm{Sb}\ \begin{matrix}(\mathrm{NH_4F})_2\\ \mathrm{F}_4\end{matrix}\right]\mathrm{F} + \tfrac{1}{2}H_2O$$ ‡

That it is the antimony which is functioning as the centre of co-ordination in these compounds seems probable, and if further evidence is required it might be supplied by the existence of such compounds as the following, some of which are very stable: $SbCl_5,HCN$; $SbCl_5,PCl_5$; $SbCl_5,POCl_3$; $SbCl_5,NO$; $SbCl_5,2ICl$; $SbCl_5,3ICl$; $HSbCl_6$ and its salts; $SbCl_5,(C_2H_5)_2O$.

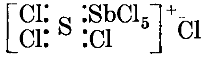
If we leave out of account the two compounds containing iodine chloride and the compound $SbCl_5,6NH_3$ (which, it is just possible, may be $SbCl_3,4NH_3 + 2NH_4Cl$), it is seen that, in all the substances quoted in which quinquevalent antimony functions as a centre of co-ordination, it does so with a co-ordination number of 6, and also that it does not seem easy to represent these compounds as formed by the donation of pairs of electrons to complete the external electronic structure of antimony to the xenon formation unless it is assumed that some chlorine atoms are held by single-electron linkages.

The compound $SbCl_5,SCl_4$ may, for example, be represented by the formula (IV) with the notation used by Sugden (J., 1927, 1173), but this formula seems very artificial. A more satisfactory formula might, no doubt, be devised. If the compound is assumed to be a salt, which is just possible from the conductivity measurements, we might represent it as (V), in which sulphur is the centre

(IV.)



$$\begin{array}{c}(\mathrm{Cl}^6{=})_2\mathrm{Sb}^8(-\mathrm{Cl}^7)_3\\ \mathrm{Cl}^6{=}\mathrm{S}^6(-\mathrm{Cl}^7)_3\end{array}$$



$$\left[\begin{matrix}\mathrm{Cl}\!:\\ \mathrm{Cl}\!:\end{matrix}\ \mathrm{S}\ \begin{matrix}:\!\mathrm{SbCl}_5\\ :\!\mathrm{Cl}\end{matrix}\right]^+\mathrm{Cl}^-$$

(V.)

of co-ordination with a co-ordination number of 4. In this case the antimony is surrounded by twelve electrons. The cubic form

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* Ephraim, "Inorganic Chemistry," English edtn., p. 650.

† Weinland and Schmidt, *Z. anorg. Chem.*, 1905, **44**, 37.

‡ Marignac, *Annalen*, 1868, **145**, 237.

of the crystals would then lead us to suspect, from the Buys-Ballot law, that the ion in square brackets packs, as a tetrahedral unit, into a cubic lattice (compare Pauling, *J. Amer. Chem. Soc.*, 1929, **51**, 1010, 2868).

It is suggested that the compound $\mathrm{SbCl_5,SCl_4}$ should be represented (without regard to possible electron arrangements) as a saturated co-ordination nucleus, $\left[\mathrm{Sb}\,\begin{smallmatrix}\mathrm{Cl_5}\\ \mathrm{SCl_4}\end{smallmatrix}\right]$, in which $\mathrm{SCl_4}$ occupies one co-ordination position. Werner ("Neuere Anschauungen," 1909, p. 77) explains its structure differently, representing it as $\mathrm{Cl_3}\overset{+}{\mathrm{S}}\overset{-}{[\mathrm{SbCl_6}]}$. It is assumed that in compounds such as $\mathrm{SCl_4}$ the halogen atoms are held by progressively weakening affinities, so that "in the limiting compounds one atom of halogen has the capacity of exercising a supplementary valency." He refers to the compound as "salt-like" and compares it with the compound of triphenylmethyl chloride, $\mathrm{(C_6H_5)_3CCl,SnCl_4}$. "The affinity of the carbinol carbon is so strongly taken up by the three phenyl groups that only a smaller share of affinity is at the disposal of the fourth valency. In consequence, the atoms linked to this valency remain unsaturated and are capable of forming addition compounds . . . the atomic compounds expressed by simple valency bonds can have different affinity values according to the particular compounds." The results of the experiments now communicated suggest, however, that $\mathrm{SbCl_5,SCl_4}$ has no salt-like properties and is probably a typical non-polar compound with an uncharged nucleus.

EXPERIMENTAL.

When antimony pentachloride is mixed with sulphur monochloride, there is a considerable evolution of heat and the mixture forms a pale yellow paste: 5 c.c. of each liquid were taken and the pasty product was dissolved in 40 c.c. of sulphuryl chloride in a stoppered bottle. The bottle containing the dark yellowish-brown liquid was kept in a desiccator containing phosphoric oxide for a week. Crystals separated on the side of the bottle in considerable amount. They were clear amber-yellow cubes or cubes with octahedral facets, 2—3 mm. long, and exhibiting a play of colours in light. The strongly fuming liquid was rapidly poured off, and the crystals were washed with a little sulphuryl chloride. The bottle was then fitted with a cork carrying two tubes, through one of which a slow current of air (dried by passing over phosphoric oxide) was passed, the bottle at the same time being placed in water at 50°. The crystals fell quite dry to the bottom of the bottle, the sides of which remained perfectly clear. The stopper was then inserted and the substance could be kept indefinitely. On exposure to air it fumed strongly and rapidly liquefied, sulphur separating.

A small quantity of the substance was quickly transferred to a previously weighed, stoppered weighing bottle, which was again weighed. The whole of the substance in this bottle was quickly dissolved in dilute nitric acid, nitrous fumes being evolved, and a clear solution was obtained, as Rose states. This solution, however, rapidly deposited a white powder, which could be dissolved by warming with a little tartaric acid. The clear solution was made up to a known volume and aliquot portions were taken for analysis. Chlorine was weighed as silver chloride, sulphur as barium sulphate, and antimony as trisulphide (Clowes and Coleman, "Quantitative Analysis," 12th edit., 1924, p. 116). The results [Found: Sb, (*a*) 24·81, (*b*) 26·23; Cl, (*a*) 66·32, (*b*) 66·25; S, (*a*) 6·98, (*b*) 6·94%] lead to the formula $SbCl_5,SCl_4$, and the substance is no doubt formed by the reaction $5SbCl_5 + S_2Cl_2 = 2(SbCl_5,SCl_4) + 3SbCl_3$. No conclusion as to the possible existence of SCl_4 may therefore be drawn from the existence of this compound, since it is readily formed from S_2Cl_2.

The physical properties of the substance differed considerably from those described by Ruff and Fischer. The "white needles" they mention are probably the white powder which first separates. The melting point also differed: at 125° the crystals, in a loosely corked tube, were quite unchanged in appearance and did not alter until the temperature reached 157°, whereat they softened with decomposition, fusion being complete at 163° with considerable decomposition.

The crystals were insoluble in carbon disulphide, and were scarcely attacked by concentrated sulphuric acid, in which they remained with a very slight evolution of gas, until the temperature reached 110°, whereupon they disappeared, fumes of hydrogen chloride being evolved. In dry benzene the crystals at once liquefied, hydrogen chloride being evolved, and the dark greenish-black liquid first formed slowly became clear yellow when the action ceased. The lower yellow layer when separated from the benzene slowly turned very viscous. It contained carbon, chlorine, and sulphur, but was not further investigated. The only solvent found for the compound $SbCl_5,SCl_4$ was sulphuryl chloride, which dissolved it sparingly to form a pale yellow liquid. The specific conductivity of the specimen of sulphuryl chloride used was $3·02 \times 10^{-6}$ ohm^{-1} at 25°, and that of the saturated solution at the same temperature $7·05 \times 10^{-6}$ ohm^{-1}: Walden (Abegg's "Handbuch," IV, i, 1, p. 313) gives $0·3 \times 10^{-7}$ ohm^{-1} for very pure sulphuryl chloride. Although sulphuryl chloride is a weak ionising solvent, the figures just given seem to show that the compound $SbCl_5,SCl_4$ has no salt-like properties and is non-polar.

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