CXXXVII.—*The Reactions of the Halogens with Carbon Sulphidoselenide.*

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IN continuation of previous work (this vol., p. 56) carbon sulphidoselenide has been found to react readily and exothermally with chlorine and bromine. It does not react with iodine, even at 120° in sealed tubes, and although iodine dissolves in the liquid, it may be completely removed by extraction with aqueous caustic soda.

As was anticipated, the reactions with chlorine and bromine show some resemblance to the corresponding reactions of carbon disulphide. Whereas carbon disulphide yields with chlorine thiocarbonyl tetrachloride, $CSCl_4$ (Klason, *Ber.*, 1887, **20**, 2377), and with bromine carbon disulphotetrabromide, CS_2Br_4 (Hell and Ureck, *Ber.*, 1876, **9**, 788), carbon sulphidoselenide on chlorination at the ordinary temperature gives thiocarbonyl tetrachloride and selenium tetrachloride, and with bromine it yields *thiocarbonyl tetrabromide* (apparently hitherto unknown) and selenium tetrabromide, or, under certain conditions, a solid intermediate *compound*, $C_2S_2SeBr_6$.

Aqueous solutions of the halogen acids do not react with carbon sulphidoselenide even after several hours' heating at 120°.

EXPERIMENTAL.

Reactions with Chlorine.—A solution of carbon sulphidoselenide in carbon tetrachloride, when saturated with chlorine, deposited a fine white solid which, when filtered, washed with carbon tetrachloride, and dried on a porous plate in a desiccator, was very hygroscopic and fumed continuously on exposure to the air (Found : Se, 34·9; Cl, 65·0. Calc. for $SeCl_4$: Se, 35·8; Cl, 64·2%).

Carbon sulphidoselenide (20 c.c.) suspended in water was treated with a slow current of chlorine. After some time a white precipitate was formed which slowly dissolved to give a clear supernatant solution. When the solution had been kept saturated with chlorine for 48 hours, the residual liquid (20 c.c.) was separated, washed with aqueous caustic soda, dried with calcium chloride, and distilled. It yielded a bright yellow, oily liquid, b. p. 147—149°, having a penetrating and disagreeable smell (Found : C, 6·5; S, 16·8; Cl, 75·8. Calc. for $CSCl_4$: C, 6·5; S, 17·2; Cl, 76·3%). Vapour-density measurements by Dumas's method gave values for the molecular weight of 210 at 170° and 198 at 200° (Calc. for $CSCl_4$, 186·0).

The density of the liquid, determined in a 10 c.c. glass pyknometer, was $d_{4^\circ}^{20^\circ}$ 1·6996; $d_{4^\circ}^{25^\circ}$ 1·6923. By using the method of capillary rise in three tubes, the mean value of the surface tension at 20° was found to be $\gamma = 35{\cdot}02$ dynes/cm., whence the molecular parachor, $M\gamma^{\frac{1}{4}}/D$, is 266·1. The value calculated for thiocarbonyl tetrachloride, assuming the mercaptan structure, is 4·8 (C) + 46·5 (S) + 217·2 (4 × Cl) = 268·5; and the agreement of this figure with the value found clearly confirms the formula $CCl_3{\cdot}S{\cdot}Cl$.

Reactions with Bromine.—Addition of excess of bromine to carbon sulphidoselenide dissolved in carbon tetrachloride yielded an orange-yellow precipitate which was filtered off, washed with carbon tetrachloride, and dried in a desiccator (Found : Se, 19·1; Br, 81·0. Calc. for $SeBr_4$: Se, 19·8; Br, 80·2%); it fumed continuously in air and was extremely hygroscopic, forming, when exposed to moist air for a few minutes, a yellow oil.

Carbon sulphidoselenide (20 c.c.) was suspended in water, and bromine (70 c.c.) was added, as required for the reaction $CSSe + 4Br_2 \longrightarrow CSBr_4 + SeBr_4$. The viscous oil formed (35 c.c.), after being kept under water for 2 days, washed with aqueous caustic soda, and dried over calcium chloride, yielded a clear, red liquid with a strong smell resembling that of yellow phosphorus. The liquid distilled mainly between 155° and 165°, but distillation, even under reduced pressure, caused progressive decomposition, so that free bromine was found in the head fraction and a white solid separated in the residue. This solid, recrystallised from aqueous alcohol, had m. p. 90·0° (Found: C, 3·5; Br, 96·2. Calc. for CBr_4 : C, 3·6; Br, 96·4%).

A quantity of the red oil, which had not been distilled, when washed thoroughly with aqueous caustic soda and dried was considered to be reasonably pure (Found: C, 3·5; S, 9·4; Br, 87·4. $CSBr_4$ requires C, 3·3; S, 8·8; Br, 87·9%). The density determined in pyknometers was $d_{4^\circ}^{20^\circ}$ 3·0240, and the surface tension determined by the method of capillary rise was $\gamma_{20^\circ} = 47{\cdot}74$ dynes/cm. From these data the molecular parachor $M\gamma^{\frac{1}{4}}/D = 316{\cdot}4$, in reasonable agreement with the value 323·3 calculated for the formula $CBr_3{\cdot}S{\cdot}Br$.

Carbon sulphidoselenide (10 c.c.), suspended in water, was treated with bromine (20 c.c.), and the thick oil was kept for several hours. It then set to a solid which crystallised from benzene as a fine white substance (54 g.) having a strong phosphorus-like smell (Found: C, 3·7; S, 10·0; Se, 12·2; Br, 74·9. $C_2Br_6S_2Se$ requires C, 3·7; S, 9·9; Se, 12·2; Br, 74·2%). It would appear that this *substance* is formed according to the reaction $2CSSe + 5Br_2 \longrightarrow C_2S_2SeBr_6 + SeBr_4$. Cryoscopic measurements of the molecular weight in benzene gave low results, suggesting that dissociation occurs in solution. The solid distils under reduced pressure to form a dark red oil which has the same composition as the original solid but does not crystallise unless kept under water. It seems likely that this substance exists in two forms, one of which is liquid; and this view is supported by its behaviour on melting. If the solid is slowly and steadily heated, it melts sharply at 90·0°, but if it is maintained at a lower temperature for some minutes it will liquefy slowly even at 78°.

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