CCXXXIII.—*The Interaction of Carbon Tetrabromide with Sulphur and Selenium.*

By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and JOHN RICHARD ROWLANDS.

BARTAL has studied the action of carbon tetrabromide on sulphur (*Ber.*, 1905, **38**, 3067) and selenium (*Chem.-Ztg.*, 1906, 810). In the former experiment an intimate mixture of carbon tetrabromide (1 mol.) and sulphur (2 atoms) reacted at 160°, and liquid products were collected up to 195°, leaving a dark blue solid, consisting of free carbon, and a blue compound, $C_9Br_4S_4$, soluble only in molten phenol. The liquid product on distillation yielded (1) a red liquid (b. p. 47—64°) consisting of carbon disulphide, free bromine, and a trace of substance supposed to be sulphur monobromide, and (2) a fraction (b. p. 165—185°) which, when freed from bromine, appeared as a red oily liquid that on solution in ether and addition of alcohol yielded a compound $C_2S_3Br_6$, m. p. 123°.

A mixture of carbon tetrabromide (1 mol.) and selenium (2 atoms), treated in a similar manner, yielded only a small quantity of liquid product at 190°, and the black solid residue, after extraction with carbon disulphide to remove traces of selenium mono- and tetra-bromides and carbon tetrabromide, appeared as a dark grey solid consisting essentially of two compounds: one, extracted with molten phenol, had the composition $C_{10}Se_5Br$; and the other, $C_9Se_4Br_2$, was a dark grey insoluble powder which on heating with very concentrated caustic soda solution yielded the compound C_4Se.

The reinvestigation here reported of the products formed under various conditions by the reaction of carbon tetrabromide with sulphur and with selenium has shown that in the former reaction the products are always sulphur monobromide, carbon disulphide, bromine, and free carbon; whilst selenium yielded its mono- and tetra-bromides, together with quantities of non-volatile residue insoluble in all solvents and apparently mainly a mixture of carbon and selenium. No indication has been observed of the more complex compounds reported by Bartal.

EXPERIMENTAL.

Preparation of Carbon Tetrabromide.—Carbon tetrabromide was prepared by a modification of the method of Habermann (*Ber.*, 1874, **6**, 549) as fine white crystals, m. p. 91° (yield 90%), by thoroughly agitating bromoform (2·5 c.c.) for several hours with bromine (5 c.c.) dissolved in *N*-sodium hydroxide (300 c.c.). It

was washed well with water and dried over phosphoric oxide before use.

The Reaction of Carbon Tetrabromide with Sulphur.—Carbon tetrabromide (332 g.; 1 mol.) and flowers of sulphur (128 g.; 4 atoms) heated in a distillation flask with a free flame yielded liquid products containing much free bromine up to 120°, and left a small residue consisting of sulphur (m. p. 119°, recrystallised from light petroleum) and a little black solid (4 g.) which, after refluxing with carbon disulphide and alcohol, contained a trace of sulphur but no bromine. The liquid product on fractionation through an 18-in. glass-bead column yielded a large bulk (120 c.c.) of red liquid, b. p. 46—56°, containing much free bromine, from which, after repeated washing with dilute caustic soda, carbon disulphide (20 c.c.; b. p. 46·5—47·0°) was obtained. A dark red liquid tail-fraction (5 c.c.; b. p. 140—190°) contained much free bromine and was attacked, slowly by water and immediately by caustic soda, with deposition of sulphur.

Repetition of this experiment with 1 mol. (332 g.) of carbon tetrabromide and 2 atoms of sulphur (64 g.) gave similar products, but the tail-fraction (b. p. 90—170°), unlike the corresponding distillate obtained in the previous experiment, contained dissolved carbon tetrabromide.

The proportion of high-boiling liquid in the product was increased by refluxing carbon tetrabromide (110 g.; 1 mol.) with excess of sulphur (42 g.; 4 atoms) at 160° for several hours: the product on cooling was a brown-red liquid apparently containing no free bromine. On distillation, the fraction of b. p. 45—70° (15 c.c.), although containing some free bromine, consisted largely of carbon disulphide, but the main fraction (b. p. 130—180°; 30 c.c.) appeared partly to decompose with liberation of bromine. Aqueous caustic soda decomposed it immediately, depositing a plastic insoluble variety of sulphur, but it was only slowly attacked by water. After repeated washing with water to remove free bromine, it was dried over calcium chloride and appeared as a ruby-red oily liquid (*d* 2·6, the same as that given for S_2Br_2), with a smell suggestive of sulphur monochloride, and contained no carbon: it was slowly attacked by alcohol with deposition of sulphur (Found, in two separate preparations: Br, 72·1, 72·5; S, 26·1, 27·7. Calc. for S_2Br_2: Br, 71·5; S, 28·5%).

The Reaction of Carbon Tetrabromide with Selenium.—A mixture of carbon tetrabromide (1 mol.) and grey selenium (3 atoms) heated in sealed tubes at 250° for 20 hrs. yielded a black solid mass from which drained a small quantity of a dark red oil (*d* 3·6, the same as that given for Se_2Br_2), which was decomposed slowly by water and

caustic soda, and immediately by alcohol : it contained no carbon (Found : Br, 55·2; Se, 45·0. Calc. for Se_2Br_2 : Br, 50·3; Se, 49·7%). The black solid, after extraction with carbon disulphide to remove the last traces of selenium monobromide, was insoluble in all known solvents, and contained free selenium which could readily be extracted with concentrated nitric acid. The same experiment, repeated at 180°, gave selenium monobromide in a larger yield but containing dissolved carbon tetrabromide.

A mixture of carbon tetrabromide (111 g.; 1 mol.) and excess of selenium (107 g.; 4 atoms), when heated until it gave no further distillate, yielded selenium monobromide (20 c.c.) containing a little dissolved carbon tetrabromide, and an orange-yellow hygroscopic solid (20 g.) very soluble in water and organic solvents, which was well washed with carbon tetrachloride and dried over calcium chloride (Found : Br, 80·8; Se, 19·8. Calc. for $SeBr_4$: Br, 80·0; Se, 20·0%). The solid residue in the flask, after extraction with carbon disulphide, was apparently mainly grey selenium.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling one of us (J. B. P.) to take part in the work.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, May 24th,* 1929.]