## 590 REYNOLDS: SILICON COMPOUNDS

## LV.—Researches on Silicon Compounds and their Derivatives. II. A New Chlorobromide of Silicon.

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I HAVE already pointed out that silicon tetrabromide is a more manageable reagent than the chloride for use with organic substances (Trans., 1887, 202). But the bromide does not appear to have been produced in quantity from the date of its discovery by Serullas in 1831 (Ann. Chim. Phys., 47, 87), until I obtained more than a kilogram of it by a slight modification of Serullas' process. In the course of the purification of this large quantity five years ago, I separated a liquid from which I have lately obtained the new chlorobromide of silicon described in this paper.

The crude tetrabromide was prepared by the action of the vapour derived from commercial bromine on a mixture of silica with carbon, heated in a good wind furnace. The best results were obtained when the mixture was most intimate, and this was secured by making a paste of gelatinous silica, the purest form of lampblack, and syrup of cane-sugar; this mass was formed into pellets, then dried and ignited.

The purification of the silicon bromide was carried out in the following way:—A current of dry hydrogen was led through the warmed liquid, in order to remove most of the free bromine; the residue was then shaken up with metallic mercury which completely decolorised the liquid, and the latter was then subjected to fractional distillation in a dry atmosphere. Out of 1.2 kilos. of liquid only a few drops passed over below 140°, but a considerable fraction was obtained between 140° and 144°, and another between 145° and 148°, after which the temperature rose rapidly to 153°. The last distillate consisted of nearly pure tetrabromide, which completely solidified to a

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beautiful crystalline mass at  $-12^{\circ}$ . The fraction between  $140^{\circ}$  and  $144^{\circ}$  did not afford any crystals when kept for several hours below  $-14^{\circ}$ ; nor did the higher fraction either.

The liquid of lower boiling point\* was then separated by repeated fractionation into a small quantity of a substance which boiled below 140°, a relatively large amount boiling between 140—141°, and some more tetrabromide.

The liquid boiling at  $140-141^{\circ}$  is colourless and fumes in the air like the tetrabromide. Its sp. gr. is  $2\cdot432$ ; that of the tetrabromide being  $2\cdot82$ . When added to water, it is quickly decomposed, and affords a mixture of silicic, hydrobromic, and hydrochloric acids.

The following determinations were made with this compound :--

- I. 4.5259 grams were added to water in a platinum dish; when decomposition was complete, the liquid was evaporated to dryness and the residue ignited; it was then moistened with ammonium hydrate and ignited again for half an hour. SiO<sub>2</sub> weighed 0.9211 gram = 9.57 per cent. of Si.
- II. 3.4225 grams similarly treated gave 0.698 of  $SiO_2 = 9.59$  of Si. Mean of the two experiments 9.58 of Si. The formula SiClBr<sub>3</sub> requires 9.35 per cent. of Si.
- III. 2.8325 grams were added to water, and the liquid, when cold, was diluted to 500 c.c.
- a. The weights of silver required to precipitate the chlorine and bromine in two separate quantities of 100 c.c. each were determined. The mean value found was 4.09146 grams of silver for the above weight of chlorobromide; consequently 100 parts = 144.4 of silver. The formula SiClBr<sub>3</sub> requires 142.13 of silver.
- b. 200 c.c. were just neutralised by ammonium hydrate, the solution boiled for some time, then filtered to remove silica, and the filtrate precipitated by excess of silver nitrate. The mixed precipitate of AgBr and AgCl weighed 2.6746 grams, or 6.6865 for the total weight of chlorobromide taken; this corresponds to 235.1 for 100.

The percentage composition of the substance is :---

	$SiClBr_3$	
	requires.	Found.
Si	9.35	9.57
C1	11.67	12.12
Br	78.98	<b>78</b> ·53

\* A similar fraction was separated from a quantity of crude tetrabromide made for me by Dr. Schuchardt.

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The vapour-density of the compound by Meyer's method, and in aniline vapour, proved to be 10.43. Theory requires 10.47.

The liquid analysed is therefore *silicon chlorotribromide* containing traces of a body richer still in silicon and chlorine. Its chlorine has obviously been derived from the crude bromine used in the preparation of the tetrabromide. The chlorotribromide is, then, the chief product of the action of chlorine on the silica and carbon mixture in presence of a large excess of bromine.

By the isolation of the chlorotribromide we are now acquainted with a complete series of the compounds possible between silicon tetrachloride on the one hand and tetrabromide on the other. The chlorobromide SiCl<sub>3</sub>Br was obtained by Friedel and Ladenburg (Ann. Chim. Phys. [4], 27, 416) as the chief product of the action of bromine on silicon trichlorosulphydrate and on silicon chloroform; in the latter case, they also obtained the chlorobromide SiCl<sub>2</sub>Br<sub>2</sub>. The boiling points of the series of compounds are given in the following table:—

В. р.
59°
80
100
141
153

It would be of interest to compare the boiling points of the silicon haloïds with those of the corresponding carbon compounds; but the data for the latter are not all obtainable.

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