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Fluorochlorobromides of Silicon

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By the use of methods previously employed successfully in the preparation of mixed halides of silicon, such as the fluorochlorides, fluorobromides, and chlorobromides, we have prepared for the first time halides of silicon containing three different halogens, namely, $SiFClBr_2$ and $SiFCl_2Br$.[1] In the course of this work new methods of preparation of the silicon chlorobromides also have been developed.

In a previous paper[2] we have described the reaction of silicon tetrabromide with antimony trifluoride, in the absence of any catalyst, by which a mixture of fluorobromides of silicon was obtained. It seemed wholly reasonable, therefore, to expect that the partial fluorination of a chlorobromide, such as $SiClBr_3$ or $SiCl_2Br_2$, should yield products containing three different halogens. The following experimental work bears out the correctness of this assumption.

A. Reactions of Antimony Trifluoride with Silicon Chlorobromides

The silicon chlorobromides needed for these experiments were prepared by the following methods, of which all but the first have not been described previously.

1. A mixture of chlorine and bromine was passed over metallic silicon at 700°, and the products were subjected to repeated distillation. In this way silicon chlorotribromide (b. p. 126–130°) and silicon dichlorodibromide (b. p. 102–106°) were obtained, together with some trichlorobromide and tetrabromide.

2. A mixture of the three chlorobromides of silicon was also prepared by refluxing silicon tetrabromide for forty-eight hours in an atmosphere of chlorine, contained in a sealed liter bulb, a microburner supplying the heat and the upper portion of the flask serving as a condensing surface. The mixture was separated by fractional distillation.

3. It was found that the reaction of antimony trichloride, mixed in the proper proportions with silicon tetrabromide, and subjected to the proper mode of distillation, may also serve as a convenient method for preparing any one of the three chlorobromides, $SiCl_3Br$, $SiCl_2Br_2$ or $SiClBr_3$, in yields of approximately 80%.[3]

4. A liquid mixture of bromine and hexachlorodisilane, Si_2Cl_6, was dropped from a separatory funnel into a horizontal Pyrex tube maintained at 500° in a gas furnace. A slow stream of pure carbon dioxide passing through the tube carried the products of the reaction to condensers, cooled by ice, and thence to a drying tube. As the mixture of liquids entered the heated tube vaporization occurred, followed immediately by reaction accompanied by flame. The free bromine left in the reaction products was removed quantitatively by shaking with mercury. From an original 100 g. of Si_2Cl_6 and 65 g. of bromine which was actually used in the reaction, about 40 g. was obtained of each of the three substances, silicon tetrachloride, trichlorobromide and dichlorodibromide.

In a similar manner, 90 g. of octachlorotrisilane, Si_3Cl_8, with 44 g. of bromine (1:1.1 mol.) gave as final, colorless products:

	B. p., °C.	Grams
$SiCl_4$	57	20
$SiCl_3Br$	80	30
$SiCl_2Br_2$	105	18
$SiClBr_3$	128	8
Si_2Cl_6	147	6

A small, higher boiling residue was also obtained

During a period of one hour 230 g. of sublimed antimony trifluoride was added gradually with rapid stirring to 900 g. of silicon chlorotribromide, $SiClBr_3$, contained in a three-necked flask, which was provided with a mercury-sealed stirrer and connected to a series of condensing traps provided with circular coils. Distillation of the product formed in the first condenser, maintained at 0°, yielded about 75 g. of silicon fluorochlorodibromide, $SiFClBr_2$, b. p. 59.5°; and from the second condenser, maintained at −65°, about 20 cc. of a liquid was obtained which contained no bromine and proved to be a mixture of the fluorochlorides, SiF_2Cl_2 and SiF_3Cl, in molar proportions approximately 2:1.

The fact that a dichloro compound is formed from a monochloro compound in this process may be explained when it is realized that antimony trichloride, formed in the interaction of SbF_3 and $SiClBr_3$, is capable of bringing about replacement of bromine atoms by chlorine in such compounds as silicon tetrabromide, as stated above. Consequently, in the reaction of antimony trifluoride with silicon chlorotribromide the formation of a dichloro compound is to be interpreted as due to side reactions in which both antimony trifluoride and antimony trichloride are involved in interaction with $SiClBr_3$.

In a similar manner, 130 g. of antimony trifluoride was added to 400 g. of silicon dichlorodibromide, $SiCl_2Br_2$, over a period of eighty minutes, the condensers being cooled with ice and with a mixture of carbon dioxide and alcohol, respectively. The contents of the first receiver

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[1] The third possible compound containing the same elements, SiF_2ClBr, has not as yet been isolated, although several methods for its preparation have been tried.

[2] Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

[3] From a mixture of equal weights of $SiBr_4$ and PCl_5 heated for one hour, a mixture of $SiClBr_3$ and $SiCl_2Br_2$ was also obtained.

consisted of 40 g. of a liquid boiling at about 39°. Repeated distillation of this mixture finally yielded 10 g. of pure $SiFCl_2Br$, b. p. 35.1 ± 0.2° at 752 mm. (corr.). The analyses of the new compounds, as well as determinations of their molecular weights and vapor pressures, are given below (section D).

B. Chlorination of Silicon Fluorobromides

Silicon fluorotribromide and chlorine were mixed in a liter globe in the molar ratio $4SiFBr_3:3Cl_2$, the initial pressure of chlorine being two atmospheres. Although reaction began upon standing at room temperature, the globe was gently heated at the bottom with a very small flame for two hours; at the end of this period the reaction was complete. Mercury was then introduced into the cooled globe and the free bromine quantitatively removed thereby. Distillation of the product yielded a mixture of nearly equal weights of $SiFClBr_2$ and $SiFCl_2Br$, together with some $SiFCl_3$, and a residue containing a small quantity of unchanged $SiFBr_3$. The chief reaction may be represented as

$$4SiFBr_3 + 3Cl_2 \longrightarrow 2SiFClBr_2 + 2SiFCl_2Br + 3Br_2$$

The reaction between gaseous silicon difluorodibromide and chlorine proceeded very slowly at temperatures below 400°. Radiation with a 500-watt lamp for several hours did not noticeably increase the rate of reaction. When a mixture of SiF_2Br_2 and chlorine in the molar ratio of 3:2 was passed repeatedly through a 20-mm. Pyrex tube, 80 cm. long, placed in a furnace at 500°, the reaction was sufficiently rapid for study. Bromine was liberated copiously, and its removal from the products was effected by shaking with an excess of mercury. The resulting gas mixture, after being transferred to the usual fractionating system, gave a fraction which proved to be substantially pure silicon difluorodichloride (v. p. 59 mm. at −78°) and a small residue consisting mainly of silicon difluorodibromide. Hence the original reaction taking place proceeded essentially as follows

$$SiF_2Br_2 + Cl_2 = SiF_2Cl_2 + Br_2$$

and no fluorochlorobromides were formed in this case.

C. Reaction of Antimony Trichloride with $SiFBr_3$

In view of the fact, referred to in section A, that antimony trichloride brings about the replacement of bromine by chlorine in silicon tetrabromide, it was felt that interaction of antimony trichloride and $SiFBr_3$ might yield fluorochlorobromides. In one experiment 50 g. of the fluorotribromide was added to 30 g. of anhydrous antimony trichloride in a 50-cc. flask, provided with a 15-cm. fractionating column (8 mm. o. d.) containing within it a glass rod and aluminum spiral. The mixture was heated cautiously with a microburner and a distillate passed over at 58–64°, the products consisting of $SiFCl_2Br$, $SiFClBr_2$ and unchanged $SiFBr_3$, in the approximate ratio of 2:1:1. The fluorochlorodibromide was purified by distillation, and its boiling point was determined as 59.5 ± 0.2° at 760 mm. It was quite free from silicon tetrachloride (b. p. 56.8°).

In another experiment a water-jacketed fractionating column (45 cm. long and 6 mm. o. d., without spiral) was used, the temperature of the jacket being kept at 35°. In this experiment a mixture of 50 g. of $SiFBr_3$ and 43 g. of $SbCl_3$ was warmed very cautiously in the 50-cc. flask for one hour, the antimony trichloride remaining solid. The original distillate, weighing 32 g., in this case passed over between 34–38°, and consisted of $SiFCl_2Br$, $SiFCl_3$ and $SiFClBr_2$ in the approximate ratio 8:3:1.

D. Analysis and Properties of Silicon Fluorochlorobromides

In the analysis of the two fluorochlorobromides the sample, contained in a small weighed bulb, supplied with a cap consisting of a 20 mm. ground joint and stopcock, was hydrolyzed by ice-cold water, which was caused to enter the bulb by opening the stopcock under the water, the bulb being cooled. The products of hydrolysis are silicic, hydrochloric, hydrobromic and hydrofluoric acids. If the temperature is low and the concentration of hydrofluoric acid is small, very little fluosilicic acid is formed.

The analysis itself consisted of weighing the silica; of liberating bromine by means of cold 10% potassium permanganate solution and nitric acid, and after extraction of the bromine with carbon tetrachloride, determining it iodimetrically; and of determining the chlorine in solution as silver chloride after treatment with nitrous acid. Direct determination of fluorine was made in the case of $SiFClBr_2$, by hydrolyzing the sample, and after the filtration of the silica, which was washed with hot water, the filtrate was made alkaline and heated to 90° to convert any fluosilicate into fluoride. The filtered solution was acidified with acetic acid in the correct excess, and an excess of a solution of calcium chloride was added. After standing for two weeks, the precipitated calcium fluoride was filtered, washed, ignited and weighed. A summary of the analytical results is given in Table I.

The molecular weights, determined by the gas density method, as described in our previous paper (1), are also shown in the table.

TABLE I

ANALYTICAL RESULTS AND MOLECULAR WEIGHTS

Substance	Si, %	F, %	Cl, %	Br, %	Mol. wt.
$SiFClBr_2$	11.87	..	14.78	66.13	246.8
	10.97	7.78	14.57	65.81	245.8
Calcd.	11.58	7.84	14.63	65.94	242.3
$SiFCl_2Br$	13.64	..	...	...	...
	14.11	..	35.41	40.02	202.8
	...	..	36.02	40.15	202.0
Calcd.	14.18	9.60	35.84	40.38	197.9

The fluorochlorobromides of silicon are colorless, mobile liquids, which hydrolyze instantly when their vapors are allowed to come into contact with moist air, resembling the other known fluorohalides of this element in this and other respects. They do not attack pure mercury at room temperature.[4]

The vapor pressure of silicon fluorodichlorobromide was measured by the static method, that of the fluorochlorodibromide was measured both by the static and by a dynamic method, previously described.[1] The plotting of log P against $1/T$ gave very satisfactory straight lines, and the pressure data are summarized in the following table.

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(4) A stopcock lubricant consisting of 95% white vaseline and 5% paraffin was found to be very satisfactory in resisting attack by these substances.

TABLE II

VAPOR PRESSURE DATA

Substance	B. p., °C.	Log P	ΔH, cal.	Trouton's constant
$SiFClBr_2$	59.5	$7.5669 - (1558/T)$	7,095	21.38
$SiFCl_2Br$	35.4	$7.0982 - (1301/T)$	5,954	19.30

The melting points were determined by the method described by Skau,[5] the specimens being sealed in wafer-thin ampoules provided with thermocouple wells in which a copper-constantan thermocouple was inserted. Heating and cooling curves were then taken potentiometrically in the Skau apparatus. The melting points so determined are −112.3 ± 0.2° and −99.3 ± 0.2° for $SiFCl_2Br$ and $SiFClBr_2$, respectively.

Summary

1. Two fluorochlorobromides of silicon have been prepared for the first time, silicon fluorochlorodibromide, $SiFClBr_2$, and silicon fluorodichlorobromide, $SiFCl_2Br$. These substances are the first halides of silicon to be reported in which silicon is linked to three different halogen atoms.

2. The new compounds were prepared by three methods: the fluorination of silicon chlorobromides, the chlorination of silicon fluorotribromide, and the reaction of antimony trichloride with silicon fluorotribromide. The formulas of the compounds were established by analysis and molecular weight determinations.

3. $SiFClBr_2$ is a colorless, mobile liquid of b. p. 59.5°, m. p. −99.3°. Its vapor pressure is represented by the equation, $\log P = 7.5669 - (1558/T)$. $SiFCl_2Br$, also a colorless, mobile liquid, boils at 35.4°, and melts at −112.3°. Its vapor pressure is given by the equation, $\log P = 7.0982 - (1301/T)$.

4. Both liquids hydrolyze completely in moist air. In ice-cold water the hydrolysis products are silicic, hydrochloric, hydrobromic and hydrofluoric acids, with practically no fluosilicic acid.

5. Incidental to the main objective of the work, several new methods of preparing the three chlorobromides of silicon were developed, including the reaction of antimony trichloride or phosphorus trichloride with silicon tetrabromide; the refluxing of silicon tetrabromide for forty-eight hours in a sealed container in an atmosphere of chlorine; and the reaction of hexachlorodisilane with bromine.

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(5) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

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Atomic Weight of Lead from Galena, Great Bear Lake, N. W. T., Canada

BY JOHN PUTNAM MARBLE[1]

The fundamental assumption on which we base the "lead-ratio" method for measuring geologic time is that a given mineral has neither lost nor gained lead, uranium, or thorium since its first crystallization. As the writer recently pointed out,[2] further evidence on this point, either general or specific, is greatly desired in determining the age of the pitchblende at Great Bear Lake, Canada.

One of the mineral systems at this locality is a replacement band of sulfides in the country rock, which is cut by the pitchblende veins. Mr. Hugh S. Spence of the Mines Branch, Canada Department of Mines kindly furnished a generous sample of this material, with the following description:[3]

"Fine-grained galena from chalcopyrite-galena band in the country rock, cut by the No. 2 Vein at LaBine Point, Great Bear Lake, N. W. T., in the No. 2 pit on the easterly (siliceous) portion of the vein. The pieces were taken from the band approximately at the contact with the vein, and the galena carries some fine native silver, presumably introduced from the vein."

The question at once arises: "Is the lead in this ore 'common' lead, 'uranium' lead, or a mixture of the two?" If the first, it offers a source for the "common" lead found in the pitchblende;[4] if the second or third, it indicates that more or less lead may have been leached from the pitchblende, which would make it valueless as an "age-index" mineral.

Preliminary work showed that if the sample contained uranium or thorium, the amounts were too

(1) Research Associate, Committee on Determination of Geologic Time.

(2) J. P. Marble, THIS JOURNAL, **58**, 434 (1936).

(3) Personal communication; *see also* H. S. Spence, Sec. III, Investigations in Min. Res. and Mining Indus., Ottawa, 1931, p. 61.

(4) (a) J. P. Marble, THIS JOURNAL, **56**, 854 (1934); (b) F. W. Aston, *Proc. Roy. Soc.* (London), **A140**, 535 (1933); (c) F. Hecht and E. Kroupa, *Z. anorg. allgem. Chem.*, **226**, 248 (1936).