Both types of electrodes give the same electromotive force within narrow limits.

3. Densities of aqueous solutions of hydrobromic acid over the above temperature and concentration ranges were determined.

4. The standard potential of the cell was evaluated from 0 to 60° at 5° intervals. Its value at any temperature within the above limit is given by equation (6).

5. The activity coefficient was computed by the extended Debye and Hückel theory (Eqs. (8) and (9)). As in the case of hydrochloric acid, the mean distance of approach of the ions was found to be constant from 0 to 60°.

6. The relative partial molar heat content and specific heat of hydrobromic acid was computed from these data. Comparison was made with like quantities for hydrochloric acid solutions, also computed from electromotive force measurements.

NEW HAVEN, CONN. RECEIVED MARCH 24, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 53]

Fluorobromides of Silicon

BY WALTER C. SCHUMB AND HERBERT H. ANDERSON

By the application of two methods previously used successfully in the preparation of the fluorochlorides of silicon[1] we have prepared the three analogous fluorobromides, $SiFBr_3$, SiF_2Br_2 and SiF_3Br. The first method consisted of the cleavage of hexafluorodisilane, Si_2F_6, by an excess of bromine. The two substances were allowed to mix in the gaseous condition in a cylindrical glass bulb and by heating at one point combustion occurred, the flame passing quietly through the whole bulb and the red color of the gaseous mixture becoming very much lighter. The excess of bromine was removed quantitatively by prolonged shaking with mercury in a flask. When the product was subjected to fractionation, in addition to the inevitable silicon tetrafluoride, a mixture in approximately equal amounts of difluoro- and trifluorobromide was obtained.

The second method consisted of the action of metal fluorides upon silicon tetrabromide, including the fluorides of zinc, titanium, silver and antimony. Of these, silver fluoride reacts too violently and titanic fluoride too slowly for satisfactory results. Because of the recent extension of the Swarts reaction[2] by Booth[1b] and co-workers to a variety of inorganic halides, resublimed antimony trifluoride was employed in most of the subsequent experiments. The usual catalyst, antimony pentachloride, could not be employed in this reaction, as at 100° interaction with silicon tetrabromide destroys the pentachloride with copious liberation of bromine. For a similar reason, antimony pentafluoride was not tried. Antimony pentabromide has not been isolated and free bromine itself does not noticeably aid the reaction.

After testing the effect upon the yields of mixed halides of variation in experimental conditions, the best results were obtained as follows. The antimony fluoride was added in 0.5 to 1.0-g. portions, at a rate of about 100 g. per hour, to 1000 g. (an excess) of bromine-free silicon tetrabromide maintained at the boiling point of the solution, which was contained in a three-necked flask, provided with a mercury-sealed stirrer and connected with three condensing traps provided with circular coils. The first trap, held at 20°, retained nearly all the $SiBr_4$ and $SiFBr_3$, with some dissolved material, chiefly SiF_2Br_2. The second and third traps were at -60 and $-65°$ (lower temperatures would cause solidification of the condensate). Uncondensed silicon tetrafluoride passed on through drying tubes and on escaping from the apparatus through an inverted funnel was hydrolyzed by a dilute solution of ammonia.

In each run a total of 300 g. of antimony fluoride was used; more silicon tetrabromide was added at intervals as needed, since some silicon tetrabromide was continuously distilled into the first trap. The yields obtained per 100 g. of antimony fluoride were the following: 30–40 g. of $SiFBr_3$, 8–18 g. of SiF_2Br_2 and 5–12 g. of SiF_3Br. The rate of addition of antimony trifluoride, the temperature, and the effectiveness of stirring, all

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[1] (a) Schumb and Gamble, THIS JOURNAL, **54**, 3943 (1932); (b) Booth and Swinehart, *ibid.*, **57**, 1333 (1935).

[2] Swarts, *Bull. Acad. Roy. Belg.*, **24**, 309, 474 (1892).

appear to be important in obtaining satisfactory results.

The fractionation of the mixture of products was carried out at constant temperature (−78.5 and 0°), the constancy of vapor pressure with continuous withdrawal of material being the criterion of purity. The apparatus used for this purpose was the same in principle as that described by Schumb and Gamble.[1] It was possible to purify the $SiFBr_3$ fraction by distillation at atmospheric pressure, using an air-cooled fractionating column.

The analysis of these three substances was carried out by a modification of that employed with the fluorochlorides.[1a] Samples of $SiFBr_3$ condensed in small weighed tubes were cooled by solid carbon dioxide and the tubes opened under ice-cold distilled water. From the weights of silica and of silver bromide and the total acidity the percentages of the constituent elements were calculated. Titration with silver nitrate in the presence of potassium chromate was used as an alternative method for the determination of bromine. For the other two fluorobromides the hydrolysis was carried out in a bulb provided with ground joint and stopcock, which was weighed against a similar counterpoise before and after admission of the gaseous sample. The gas was then condensed with liquid air and water admitted into the bulb. The results are in sufficiently close agreement with the theoretical values to establish definitely the composition of the compounds.

All three of the fluorobromides are colorless substances, which in the gaseous condition are hydrolyzed immediately by moist air. In the pure condition they do not attack mercury appreciably at ordinary temperatures over a period of several days.

ANALYTICAL DATA

		% Si	% Br	% F
$SiFBr_3$	I	10.18	83.04	6.73
	II	9.52	82.94	6.81
	Calcd.	9.78	83.60	6.62
SiF_2Br_2	I	12.13	70.42	16.67
	II	12.70	71.30	16.58
	Calcd.	12.42	70.76	16.82
SiF_3Br	I	16.65	48.81	34.94
	II	16.92	47.61	34.96
	Calcd.	17.01	48.44	34.55

The molecular weights of the substances were determined by the gas density method.

MOLECULAR WEIGHT DATA

	Volume, cc.	Temp., °C.	Pressure, mm.	Weight of gas, g.	Mol. wt., calcd.	Calcd.
$SiFBr_3$	208.10	90.2	772.7	2.0030	282.0	286.8
	208.10	91.2	772.7	2.0663	291.1	
SiF_2Br_2	208.10	22.7	722.9	1.8986	232.8	225.9
	208.10	22.0	726.7	1.9135	232.9	
SiF_3Br	208.10	23.9	756.1	1.3906	163.7	165.0
	75.00	25.0	310.2	0.2082	166.3	

The vapor pressures of SiF_3Br and SiF_2Br_2 were measured by the static method, with constant volume manometer and the usual accessories. The vapor pressure of $SiFBr_3$ was measured by a dynamic method determining the boiling point at a fixed pressure of inert gas (carbon dioxide).[3] To maintain constant pressure a 3-liter bulb was used and a condenser filled with an alcohol–carbon dioxide mixture was interposed between the boiling liquid and the manometer. Sufficient time was permitted for equilibrium to be reached and standardized thermometers were used in all cases. The effectiveness of the apparatus was checked by independent runs with distilled water.

VAPOR PRESSURE DATA

$SiFBr_3$		SiF_2Br_2		SiF_3Br	
Temp., °C.	Press., mm.	Temp., °C.	Press., mm.	Temp., °C.	Press., mm.
84.0	765.7	21.4	984.0	−39.9	810.8
76.1	586.0	13.2	750.7	−43.9	692.7
65.5	420.8	0.0	449.2	−45.6	648.8
47.2	213.5	−18.7	197.1	−49.9	539.2
32.3	118.5	(+13.7)	(760.0)	−54.6	426.2
(83.8)	(760.0)			−62.2	298.8
				−68.6	215.4
				(−41.7)	(760.0)

The following equations represent the above data.

$$\log p = 7.6721 - (1710/T) \text{ for } SiFBr_3$$
$$\log p = 7.4080 - (1298.3/T) \text{ for } SiF_2Br_2$$
$$\log p = 7.0415 - (962.7/T) \text{ for } SiF_3Br$$

The *melting points* were determined with a precision of 0.5° in the case of SiF_3Br and $SiFBr_3$, and of but 1° in the case of SiF_2Br_2, this substance

SUMMARY OF PHYSICAL DATA

	$SiFBr_3$	SiF_2Br_2	SiF_3Br
M. p., °C.	−82.5 ± 0.5	−66.9 ± 1	−70.5 ± 0.5
B. p., °C.	+83.8 ± 0.2	+13.7 ± 0.2	−41.7 ± 0.2
λ, cal.	7,833	5,929	4,405
Trouton's const.	21.94	20.67	19.04
$\log p$	$7.6721 - \frac{1710}{T}$	$7.4080 - \frac{1298.3}{T}$	$7.0415 - \frac{962.7}{T}$
B. p.–m. p., °C.	166.3	80.6	28.8

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(3) See, for example, Mack and France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1930, p. 47.

showing a tendency to decompose on standing. The samples, sealed in thin-walled tubes, were allowed to warm up very gradually in an alcohol bath contained in a large transparent Dewar tube; a calibrated toluene thermometer was used to read the temperature.

Summary

Three new fluorobromides of silicon, $SiFBr_3$, SiF_2Br_2 and SiF_3Br, have been prepared, analogous to the previously known fluorochlorides, and their chief physical properties have been determined.

The cleavage of Si_2F_6 with bromine yields SiF_3Br and SiF_2Br_2, together with SiF_4. The fluorination of silicon tetrabromide with antimony trifluoride (without a catalyst) yields all three mixed halides. Suitable experimental conditions for the preparation of these compounds are given.

CAMBRIDGE, MASS. RECEIVED APRIL 6, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF BRITISH COLUMBIA]

Systems of Sulfur Dioxide and Monolefins. I. Caprylene and Sulfur Dioxide

BY W. F. SEYER AND LISLE HODNETT

A series of investigations has been carried out on the relationships existing between sulfur dioxide and normal paraffin hydrocarbons. It was found that the critical solution temperature was a function of molecular weight.[1] It then became desirable to know whether similar conditions were true for the unsaturated derivatives of the normal paraffins having one double bond, *i. e.*, monolefins. In the case of cetene ($C_{16}H_{32}$) and sulfur dioxide, the curve defining the limits of the coexistence of the two liquid phases has the same general shape as that of any two partially miscible liquids.[2] Freezing point measurements carried out on mixtures of sulfur dioxide and amylenes in this Laboratory indicated that these substances were miscible in all proportions, hence it was estimated that partial miscibility ought to begin at about a chain length of eight carbon atoms. F. de Carli has stated that caprylene was only slightly soluble in liquid sulfur dioxide and formed a yellow solution, which he regarded as a sign of compound formation.[3]

Experimental

The general procedure in determining the freezing and miscibility points was the same as that already described when dealing with the normal hydrocarbons. A difficulty, however, was encountered in the purification of the olefin that was not met with in the case of $C_{16}H_{32}$, nor in the case of the normal hydrocarbons, but was similar to that which was experienced when dealing with cyclohexene. When ordinary caprylene is mixed with sulfur dioxide it takes on a deep red color. A small amount of this red compound dissolves in the sulfur dioxide layer giving it a yellow tinge. In a previous experiment[4] it was found that the presence of minute quantities of air in cyclohexene–sulfur dioxide mixtures, caused immediate condensation of the cyclohexene and sulfur dioxide[4] producing a reddish colored compound, whose composition has been established by Marvel and coworkers.[5]

In this particular case oxygen was found to be the catalyst that induced reaction which was absent when all work was done in an inert atmosphere of nitrogen. From the work of I. L. Ryden and C. S. Marvel it would appear that the coloration of the caprylene–sulfur dioxide mixtures is due to the formation of polysulfones.[6]

The course of the reaction was undoubtedly due to the presence of peroxides in the caprylene because much coloration took place upon refluxing it over metallic sodium and formation of a red amorphous compound continued as long as a positive test for peroxides was obtained. The test employed was that recommended by Conant and Peterson[7] in which a solution of ferrous ammonium sulfate and ammonium thiocyanate is used. The original material gave a deep red color with this reagent even after it had been distilled, but after it had been refluxed over sodium in an inert atmosphere for six or seven hours no color developed.

Materials

The caprylene used was obtained from the Eastman Kodak Co. It had a boiling point lying between 124–126° which could not be changed materially by the ordinary laboratory rectification methods. The material was very similar to that used by Brühl,[8] who claimed that caprylene was a mixture of the two isomeric compounds of 1- and 2-octene and reported the refractive index as $n^{20}\text{D}$ 1.4132. Our own had slightly higher value, $n^{20}\text{D}$ 1.4137, after purification.

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[1] Seyer and Todd, *Ind. Eng. Chem.*, **23**, 325–327 (1931).

[2] Seyer and Hugget, *Trans. Roy. Soc. Canada*, **18**, Sec. III, 209 (1924).

[3] F. de Carli, *Gazz. chim. ital.*, **57**, 347–355 (1926).

[4] Seyer and King, THIS JOURNAL, **55**, 3140 (1933).

[5] D. S. Frederick, H. D. Cogan and C. S. Marvel, *ibid.*, **56**, 1815 (1934).

[6] L. L. Ryden and C. S. Marvel, *ibid.*, **57**, 2311 (1935).

[7] J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932).

[8] J. W. Brühl, *Ann.*, **235**, 11 (1886).