[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF BLACKBURN COLLEGE]

The Redistribution Reaction in Substituted Fluorosilanes. Iodofluorosilanes

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Calingaert and co-workers have studied the redistribution reaction in mixed alkyl derivatives of mercury, lead and silicon.[1] We demonstrated the redistribution reaction—which involves no net heat of reaction, and involves entropy only—among inorganic compounds containing halides or pseudo halides and showed that equilibrium required random distribution of mixed halides in various series of compounds of silicon and of carbon[2,3,4] (which did not at the time include fluorides). This paper in turn explores the redistribution reaction in substituted fluorosilanes, and thereby presents a previously unproven—and occasionally the best—method of preparation for substituted fluorosilanes; all three iodofluorosilanes are isolated for the first time.

Preparation of Pure Compounds Needed for Redistribution Studies

Bromofluorosilanes from $SiBr_4$ and SiF_4.—As a substitute for the stoichiometrically less efficient reaction between $SiBr_4$ and SbF_3,[5] the reaction between tetrabromosilane and tetrafluorosilane was studied. A steel tube 70 cm. long and 3 cm. in i. d., with one end closed, contained barium fluosilicate, which at a red heat slowly yielded gaseous tetrafluorosilane, which, regulated by a safety tube, passed through a bubbler containing concentrated sulfuric acid and then entered a Pyrex glass tube 70 cm. long and 2.3 cm. in i. d., the central 50 cm. of which were inside an electric sleeve heated to 700°. Liquid tetrabromosilane, regulated in flow by a stopcock, dripped into the cold zone of the tube and with the assistance of the heat from a microburner vaporized at the outer edge of the hot zone maintained by the electric sleeve; thus a mixed vapor incipiently containing only the two tetrahalides flowed slowly through a zone at 700°. Without any attempt to maintain a constant ratio of the two tetrahalides, in a two-hour period 200 g. of $SiBr_4$ and approximately 40 g. of SiF_4 started through the hot zone. In the hot zone redistribution took place, and thereby all three bromofluorosilanes were formed. Upon flowing through the last quarter of the Pyrex tube—*i. e.*, the side remote from the tube containing the barium fluosilicate—the gaseous mixture containing three bromofluorosilanes as well as both tetrahalides cooled down; all the $SiBr_4$ and most of the $SiFBr_3$ condensed in an air-cooled receiver, and thereafter nearly all the SiF_2Br_2 and most of the SiF_3Br condensed in a receiver immersed in solid carbon dioxide and alcohol, while the SiF_4 escaped, uncondensed, from the end of the flow system. This process yielded 40 g. of $SiFBr_3$, 30 g. of SiF_2Br_2 and 30 g. of SiF_3Br, which upon distillation at 76 cm. boiled at 83.8–84.4°, 12–15°, and −43 to −41°, respectively; these samples served in the studies of the redistribution reaction.

Fluoroisocyanatosilanes.—Although all three fluoroisocyanatosilanes were obtained through the redistribution of $Si(NCO)_4$ and SiF_4 in a small-scale experiment, the main investigation employed the reaction of $Si(NCO)_4$ with SbF_3, during the course of which rather pure $SiF(NCO)_3$ and $SiF_2(NCO)_2$[6] were prepared; these samples served in the studies, in 1947, of the redistribution reaction among fluoroisocyanatosilanes.

Fluoroiodosilanes.—These new compounds will be described fully in a later portion of this publication; all three compounds were prepared simultaneously from SiF_4 and SiI_4 at 700°, in a process which was comparable to that used with the bromofluorosilanes above, and which therefore will not be described in detail.

Redistribution Studies (see Table I)

Because of the vast differences in boiling points, and because SiF_4 sublimes at 760 mm. pressure, an altered method of analytical procedure was used: 15–20 g. of the pure compound was slowly and regularly admitted to the hot tube at 700° by the use of a stopcock and gravity feed if a liquid—or, if a gas at room temperature, by controlled distillation of the sample from a small bulb partially filled with liquid, at a temperature corresponding to the boiling point.

TABLE I

REDISTRIBUTIONS AT 700° WITHOUT A CATALYST AT ONE ATMOSPHERE

Compound	Mole %	$SiBr_4$	$SiFBr_3$	SiF_2Br_2	SiF_3Br	SiF_4
			Bromofluorosilanes			
$SiFBr_3$	Obs.	32	43	20	5	(0)
	Calcd.	31.6	42.2	21.1	4.7	0.4 (For F = 0.25)
SiF_2Br_2	Obs.	4	25	40	23	8
	Calcd.	6.3	25.0	37.5	25.0	6.3 (For F = 0.50)
SiF_3Br	Obs.	0.3	6	17	45	31
	Calcd.	0.4	4.7	21.1	42.2	31.6 (For F = 0.75)
			Isocyanatofluorosilanes			
Compound	Mole %	$Si(NCO)_4$	$SiF(NCO)_3$	$SiF_2(NCO_2)$	$SiF_3(NCO)$	SiF_4
$SiF(NCO)_3$	Obs.	26	45	22	7	(0)
	Calcd.	31.6	42.2	21.1	4.7	0.4 (For F = 0.25)
$SiF_2(NCO)_2$	Obs.	7	28	35	23	7
	Calcd.	6.3	25.0	37.5	25.0	6.3 (For F = 0.50)

During a period of sixty minutes the incipiently pure compound, representing a definite mole fraction of fluorine, entered a zone at 700° and then flowed slowly through the tube; during the slow passage through this zone at 700° redistribution occurred. Thereupon, the flowing mixture of compounds which resulted from redistribution cooled

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[1] Calingaert, *et al.*, THIS JOURNAL, **61**, 2748, 2755, 2758, 3300 (1939).

[2] Anderson, *ibid.*, **66**, 934 (1944).

[3] Forbes and Anderson, *ibid.*, **66**, 931 (1944).

[4] Forbes and Anderson, *ibid.*, **67**, 1911 (1945).

[5] Schumb and Anderson, *ibid.*, **68**, 994 (1936).

[6] Forbes and Anderson, *ibid.*, **69**, 1241 (1947).

down, and some liquid condensed along the Pyrex tubing which led to a trap (the trap had two ${}^{10}/_{30}$ standard taper ground joints, one for the insertion of a male through joint of the same size, and the other for a means of escape of uncondensed SiF_4). This trap, held at −75°, condensed everything except SiF_4 which was absorbed in a weighed tube containing soda lime and estimated from the gain in weight.

After completion of the redistribution, the trap was disconnected from the high temperature system, weighed to 0.01 g. and then connected to a 40-cm.-long column of 4-mm. i. d.; the temperature within the column could be controlled by the temperature of a reservoir of alcohol in a jacket of 20 cm. height, which was above the column. In the typical run the lowest boiling mixed halide was distilled—such as SiF_3Br at −45 to −39°—and then the column allowed to reach a temperature midway between the boiling points of the two lowest-boiling mixed halides (during which very little material distilled); thereupon, the trap unit was cooled and weighed to the nearest 0.01 g., and the consequent loss in weight ascribed to the compound which had just been distilled. Next, the difluoro compound was distilled at the appropriate temperature, and then the trap unit again cooled and weighed; this represented the weight of the difluoro derivative. At this stage it was advantageous in some instances to, if the mole fraction of the monofluoro derivative and that of the tetrabromide (or tetraisocyanate) were high, transfer to a smaller one-piece microdistillation unit and visually estimate the volumetric ratio of the two components after distillation, from which the mole ratio could be computed.

Tetrafluorosilane and Tetrachlorosilane.—These two compounds underwent the redistribution reaction, but at easily attainable temperatures the rate was quite slow. Because of experimental obstacles, no runs were made at temperatures above 740°; it is estimated that a flow rate comparable to that mentioned above would be consistent with random distribution of fluorochlorosilanes *only* if the reaction temperature were in the range 900–1000°. At 740° and a very slow passage through the tube approximately 12–15% of the tetrachlorosilane was converted into trichlorofluorosilane, $SiFCl_3$, of boiling point range 11–14°; moreover, some SiF_2Cl_2 was evident in each of two runs. Previously[7] we concluded "The readiness of rearrangement increases from carbon to tin and from chlorine to iodine, and is in general favored by increasing atomic volume. . . ." Thus the slower rate of redistribution of SiF_4 and $SiCl_4$ as compared with that of systems involving bromide, isocyanate or iodide is in keeping with trends already observed.

When coupled with our previous results the present redistributions, both qualitatively and quantitatively studied, are ample to allow the conclusion that beyond much doubt random distribution represents the condition of equilibrium in any system of mixed silicon halides not containing alkyl groups or isothiocyanate.

Therefore it appeared unnecessary to demonstrate random distribution either in the slowly rearranging chlorofluorosilanes or in the iodofluorosilanes which were quite sensitive either to oxygen or to traces of moisture.

Iodofluorosilanes

Preparation.—Tetraiodosilane, a pale yellow solid, was prepared from silicon tetrachloride: first, through reaction of the tetrachloride with a slight excess of aniline, then with treatment of the resultant tetraanilide with an excess of dry hydrogen iodide; after filtration of anilinium iodide, the solution and numerous washings with carbon disulfide were evaporated; finally, the tetraiodosilane was distilled in an all-glass apparatus at low pressure, in the presence of copper turnings. Because of difficulties mechanically and because of the adsorption of tetraiodosilane on the anilinium iodide, the over-all yield was only approximately 35%.

In much the same method as that employed in the bromofluorosilanes, except that the main part of the apparatus consisted of a continuous piece of Pyrex glass which included the bulb containing the tetraiodosilane, the tube heated to 700° and the air-cooled first receiver (which held the liquid products), the iodofluorosilanes were prepared; in the first run 80 g. of SiI_4 and a stream of SiF_4 yielded 3.4 ml. of $SiFI_3$, b. p. 185°, 2.4 ml. of SiF_2I_2, b. p. 85°, and approximately 3 ml. (at −78°) of SiF_3I, of b. p. less than −10°; in the second run, with new equipment and a higher mole fraction of fluorine, the products were 1.4, 1.8 and 10 ml., respectively. Tetrafluorosilane was allowed to escape uncondensed at the end of the apparatus. Brown silicon powder was present in the part of the tube which had been at 700°, despite careful sweeping out of the SiF_4 generator and also sweeping out of the rest of the equipment with carbon dioxide; free iodine, present in the products, may indicate a dissociation of tetraiodosilane into silicon and iodine at 700°.

The two liquid products were distilled in special all-glass stills under the conditions specified in Table II. There was no sign of any instability under these conditions; the low pressure of distillation of $SiFI_3$ was useful in reducing the distillation temperature and therefore reducing the redistribution which takes place at the temperature of distillation. Strangely, SiF_2I_2 did not wet glass easily. However, the gas SiF_3I did not appear to be very stable under distillation at 760 mm.; in contrast to the behavior of the other two iodofluorosilanes, iodotrifluorosilane did not appear to have a sharp boiling point. After a preliminary distillation through a plain column 40 cm. long of 4 mm. i. d. at a temperature range of −30 to −20°, the compound was redistilled at a somewhat faster rate with a thermometer bulb immersed in the liquid; nearly all the material distilled in the range −20 to −28°, but there was no constancy of boiling point which is typical of stable compounds. Such a behavior is comparable to that of $SiF_3(NCO)$,[8] that of $PF_2(NCO)$,[9] and that of PF_2Br.[10] All the iodofluorosilanes are colorless and hydrolyze quite rapidly. Both liquids were easily miscible with carbon disulfide, but SiF_3I was completely miscible with carbon disulfide only at approximately −40° or above; below this, as judged from approximately equal volumes, the two formed a partially miscible system and either an opalescence or two layers resulted.

Analysis.—Tetraiodosilane and ethanol furnish some ethyl iodide, and therefore such a system was unsuited for analysis. It was necessary to hydrolyze the individual iodofluorosilane in ice-cold water, and then titrate both the hydriodic and the hydrofluoric acids, together with a small amount of fluorosilicic acid, with phenolphthalein as indicator. An excellent modification consisted of crushing a bulblet of wafer (soft) glass under an ice-cold sodium hydroxide solution of 80% of the expected equivalence; such a process, with phenolphthalein present, served both to catch the acids and to indicate the progress of the hydrolysis and the desorption of acid from the silica gel. The end-point consisted of a faint pink which was stable for five minutes at 60°. Thereupon, the best way to determine the iodine appeared to be to liberate the iodine with ferric nitrate—perhaps ferric sulfate would have been better—and extract very carefully with carbon tetrachloride; after repeated extraction the iodine was titrated rather rapidly with sodium thiosulfate, using starch as an indicator. Other methods did not work, and even this method suffered from the disadvantage that traces of nitric acid apparently extracted in the carbon tetrachloride, and in a slow reaction this shifted the true end-point with the thiosulfate, although the error was not large. Calcd. for $SiFI_3$: neut. equiv., 106.9; I, 89.0; mol. wt., 427.8. Found: neut. equiv., 106.4, 107.0; I, 88.5, 89.2; mol. wt., 412. Calcd. for SiF_2I_2: neut. equiv., 80.0; I, 79.4; mol. wt., 319.9. Found: neut. equiv., 79.7, 80.5; I, 79.2, 79.4; mol. wt., 332. Calcd. for SiF_3I; neut. equiv., 53.0; I, 59.8; mol. wt., 212.0. Found: neut. equiv., 51.6; I, 59.5; mol. wt., 208. These analyses show that

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[7] Forbes and Anderson, THIS JOURNAL, **67**, 1914 (1945).

[8] Forbes and Anderson, *ibid.*, **69**, 1241 (1947).

[9] Anderson, *ibid.*, **69**, 2495 (1947).

[10] Booth and Frary, *ibid.*, **61**, 2934 (1939).

the three formulas are correct, and that the gas was essentially-pure SiF_3I, despite instability. Because of the ease of liberation of iodine and because of the limited stability of the monoiodo compound, the melting points are only approximate: −41° for $SiFI_3$; −83° for SiF_2I_2; roughly −92° for SiF_3I.

Table II lists boiling points and densities for the series.

TABLE II

IODOFLUOROSILANES

Compound	B. p., °C.	Density	Distillation range, °C./mm.
SiI_4	290	....	....
$SiFI_3$	188 ± 1	3.164 (30°)	84.0–85.0/24
SiF_2I_2	84.5 ± 0.5	2.41 (25°)	84.5–84.8/756
SiF_3I	−24 ± 4	....	−28 to −20/756
SiF_4	−95[a]	....	....

[a] Extrapolated.

Discussion

1. Fluorine, chlorine, bromine, iodine and isocyanate are all similar in the redistribution reaction, which occurs with fluorochlorosilanes, bromofluorosilanes, iodofluorosilanes and isocyanatofluorosilanes at 700° without a catalyst.

2. It is obvious that the redistribution reaction is advantageous in preparing all of the ternary fluorides except the chlorofluorosilanes.

3. When coupled with our previous results and those, although qualitative only, of Besson,[11] a more complete understanding of mixed halides of silicon is reached—in (probably) all cases of silicon compounds containing halogens or isocyanate (this excludes isothiocyanate, alkyl or aryl groups) random distribution represents the condition of equilibrium.

4. In the previous reactions such as $Si_2F_6 + Br_2 \rightarrow SiF_4 + SiF_3Br + SiF_2Br_2$[12] or the analogous reaction with chlorine,[13] two conclusions are indicated as valid: first, theoretically, if equilibrium had been reached, then $SiFX_3$ and SiX_4 derivatives would have to be present in accordance with random distribution, which, however, *could not be attained* because the temperature was not high enough for equilibrium; second, the existence of three products is best explained in terms of free radicals as shown

$$Si_2F_6 \longrightarrow 2SiF_3$$
$$2SiF_3 + Cl_2 \longrightarrow 2SiF_3Cl$$

and

$$Si_2F_6 \longrightarrow SiF_4 + SiF_2$$
$$SiF_2 + Cl_2 \longrightarrow SiF_2Cl_2$$

5. In contrast to the results reported in our redistribution studies and those reported by Calingaert and co-workers, the study of Sauer and Hadsell[14] indicates a non-random redistribution of methylchlorosilanes. There is no irrefutable explanation of their findings, which may reflect the high pressure used—50 to 100 atmospheres—or possibly some selection related to the non-linear progression in boiling points of methylchlorosilanes. Further study along related lines is planned here.

Summary

1. At 700° or above certain substituted fluorosilanes, including bromofluorosilanes, isocyanatofluorosilanes, chlorofluorosilanes and (new) iodofluorosilanes undergo the redistribution reaction.

2. It is evident that the redistribution reaction is highly advantageous and efficient in the preparation of bromofluorosilanes, isocyanatofluorosilanes and especially iodofluorosilanes.

3. Random distribution—such as found previously by Calingaert and co-workers, and also by us—governs the redistribution of any pure compound or any mixture in the series of bromofluorosilanes or isocyanatofluorosilanes. Random distribution probably applies to all mixed halides of silicon which do not contain isothiocyanate, alkyl or aryl groups.

4. Three new iodofluorosilanes—the last ternary silicon halides to be isolated—were the products of the redistribution of SiF_4 and SiI_4, and are as follows: stable triiodofluorosilane, $SiFI_3$, b. p. 84–85° at 24 mm., or 188° at 752 mm.; stable diiododifluorosilane, SiF_2I_2, b. p. 84.5° at 756 mm.; not-very-stable iodotrifluorosilane, SiF_3I, b. p. approximately −24°. All the iodofluorosilanes are colorless and hydrolyze readily.

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(11) Besson, *Compt. rend.*, **112**, 611, 788, 1314, 1447 (1891).

(12) Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

(13) Schumb and Gamble, *ibid.*, **54**, 3943 (1932).

(14) Sauer and Hadsell, *ibid.*, **70**, 3590 (1948).