

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

## Fluoroisocyanates of Silicon

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During the past seven years, a number of new volatile mixed compounds of silicon, germanium and phosphorus, containing halogen atoms together with cyanate or thiocyanate groups, have been prepared in these Laboratories. Their relative stabilities could not always be predicted in advance, even after making allowance for differing distillation temperatures. As expected, similar compounds of quadrivalent elements become less stable as the radius of the central atom is increased, also, in general, as the average electronegativity of the substituents decreases. Thus phosphoryl chlorodibromide is less stable than phosphoryl dichlorobromide, but on the other hand phosphorus difluorobromide is less stable than phosphorus fluorodibromide.<sup>1</sup> A marked difference in the volumes of attached groups seems to be inimical to stability, as is evident in the series SiHX<sub>3</sub>. The preparation and study of volatile fluoroisocyanates and fluoroisothiocyanates of various elements have been undertaken, for one reason, to clarify further the problems suggested above.

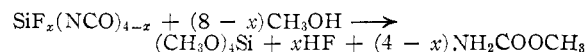
## Experimental

**Preparation of the Silicon Fluoroisocyanates.**—Adapting a method previously developed for preparation of silicon fluorobromides,<sup>2</sup> 100 g. of sublimed antimony trifluoride was gradually added to 185 ml. (265 g.) of silicon isocyanate steadily boiling in a three-necked flask. The isocyanate was itself a middle fraction, essentially free from benzene, chloroisocyanates and the higher-boiling normal cyanate. A mercury-sealed stirrer provided relief for pressures temporarily greater than atmospheric. About 90 g. of volatile reaction products were bled off between 110 and 165°. The solid antimony triisocyanate<sup>3</sup> which separated out was often converted, with swelling, into non-volatile orthocyanate (or a polymer). These solids retarded the mixing of the reactants and probably reduced the yields. Silicon tetrafluoride was allowed to escape without condensation. Three well-defined fractions were obtained, and formulated as follows: SiF<sub>3</sub>NCO, 12 g. condensed with Dry Ice; SiF<sub>2</sub>(NCO)<sub>2</sub>, 18 g.; SiF(NCO)<sub>3</sub>, 40 g. In a second experiment, similar except for an hour of refluxing at 110–130° during distillation, the corresponding yields were lower—12, 10 and 21 g., respectively. An experiment at diminished pressure and temperature, as in a typical analogous fluorination by Booth and co-workers,<sup>1</sup> was carried out next. To favor isolation of the monofluoro derivative, 100 g. of antimony trifluoride was added in one lot to 300 ml. of silicon isocyanate, and the mixture refluxed under 40 mm. pressure. With distillation-head temperatures between 85 and 97°, condensation with Dry Ice isolated 70 g. of crude mono- and 10 g. of crude difluorodisocyanate. All the tri- and doubtless a part of the difluoro compound were lost through failure to condense.

After repeated distillation, a final fraction of the fluoro-triisocyanate was collected between 134.0 and 134.4°; also one of the difluorodisocyanate between 68.5 and 68.7°, both at 757 mm. The purification of these two

stable compounds utilized equipment comparable with that described by Rose.<sup>4</sup> Silicon trifluoroisocyanate, thanks to its low boiling point (about -6°), was redistilled without substantial decomposition, and stored as a gas in large bulbs. During several weeks at room temperature, a liquid, presumably a mixture of less highly fluorinated compounds, separated out in the bulbs originally containing the trifluoroisocyanate, and the total pressure decreased progressively. The residual gas was found to be mainly silicon tetrafluoride. A freshly prepared 15-g. sample of crude silicon trifluoroisocyanate, refluxed for three hours with a column packed in Dry Ice to allow escape of tetrafluoride, yielded 0.8 g. of difluorodisocyanate, 3.0 g. of fluorotriisocyanate and 2.3 g. of tetraisocyanate, indicating that about 9.0 g. of tetrafluoride had formed and escaped. Indeed, a sample of gas collected late in the distillation had a molecular weight of 108 as against 104 for tetrafluoride. A new sample (about 30 g.) was therefore subjected to a straight distillation, and the liquid collected between -8 and 10° was at once redistilled limiting the b. p. range to -7.5 to -4.5° for fifteen minutes. The value -6.0 ± 1.0° was taken as the normal boiling point. The product was collected and preserved in Dry Ice. Analyses for fluorine and for nitrogen, in addition to a molecular weight determination, were undertaken at once. Decomposition of another portion at 0° was followed manometrically; at zero time, in Dry Ice pressure was negligible; after three minutes at 0°, 1012 mm.; after thirty minutes 1217 mm., after sixty minutes 1306 mm. A stable liquid boiling at -6° should have a vapor pressure of about 980 mm. at 0.0°.

**Analytical Methods.**—The hydrolysis of a silicon fluoroisocyanate according to the equation SiF(NCO)<sub>3</sub> + 4H<sub>2</sub>O → H<sub>4</sub>SiO<sub>4</sub> + HF + 3HNCO is vigorous but some fluosilicic acid is formed by a secondary reaction, and the isocyanic acid is subject to further hydrolysis. A sample of silicon isocyanate was dissolved in absolute methanol, and successive portions were tested with silver nitrate until—after three hours—only an opalescence was produced. The alcoholysis of fluoroisocyanates proceeds as follows



To determine hydrofluoric acid, weighed portions treated as above, and added to water, were titrated with sodium hydroxide to a phenolphthalein end-point. Methyl carbamate is reasonably stable in water, and its hydrolysis products would introduce no error. Nitrogen, and also molecular weights, were determined according to Dumas. *Anal.* Calcd. for SiF(NCO)<sub>3</sub>: F, 11.0; N, 24.3; mol. wt., 173.1. Found: F, 10.9; N, 24.1; mol. wt., 179. Calcd. for SiF<sub>2</sub>(NCO)<sub>2</sub>: F, 25.3; N, 18.7; mol. wt., 150.1. Found: F, 24.9; N, 18.7; mol. wt., 156. Calcd. for SiF<sub>3</sub>(NCO): F, 44.8; N, 11.0; mol. wt., 127.1. Found: F, 44.2; N, 10.6, 10.8; mol. wt., 129. These values justify the formulas assigned.

**Physical properties** were measured on the day of the final distillation so as to avoid disproportionation. All the compounds are colorless liquids, having the peculiar "isocyanic acid" odor. Calibrated thermometers were used in all measurements; densities were obtained using a 2-ml. special micropycnometer, subject to a volume error not greater than one part in 5000. The scale of the Abbe refractometer was checked with water. The data in Table I show the gradations in properties from silicon tetrafluoride to silicon tetraisocyanate.

Boiling points of the mixed compounds calculated by linear interpolation between the sublimation point of silicon tetrafluoride and the boiling point of silicon isocyanate are

(1) Booth and Frary, *THIS JOURNAL*, **61**, 2934 (1939); see also Booth and Morris, *ibid.*, **58**, 90 (1936).

(2) Schunib and Anderson, *THIS JOURNAL*, **58**, 994 (1936).

(3) Anderson, *THIS JOURNAL*, **64**, 1757 (1942).

(4) Rose, *Ind. Eng. Chem.*, **28**, 1210 (1936).

TABLE I

Compound	B. p., °C.	M. p., °C.	Density, 20°	$n$	Molar refraction, ml.
SiF <sub>4</sub>	-95 <sup>a</sup>	-90	...	....	8.40 <sup>a</sup>
SiF <sub>3</sub> (NCO)	-6.0 ± 2	.....	...	....	.....
SiF <sub>2</sub> (NCO) <sub>2</sub>	68.6	-75 ± 1.5	1.437	1.3536	22.69
SiF(NCO) <sub>3</sub>	134.3	-29.2 ± 1	1.456	1.4161	29.99
Si(NCO) <sub>4</sub>	185.6	26.0	1.442 <sup>a</sup>	1.4610	37.29

<sup>a</sup> Extrapolated.

-25, 45 and 115°, respectively—about 20° below the observed values. The variations in liquid densities are unusually small. The maximum at the monofluoro compound is justified by the even progression of the molar refractions ( $n^2$  formula), which also are close to the calculated values 22.85 and 30.07 ml. The vapor pressure equation for silicon difluorodisocyanate is  $\log p = 8.33860 - 1864.9/T$ , whence  $\Delta H$ , the heat of vaporization, is 8,550 cal. and the Trouton constant 25.0. For silicon fluorotriisocyanate,  $\log p = 8.65169 - 2351.1/T$ ,  $\Delta H = 10,760$  cal. and  $\Delta H/T = 26.4$ .

**Chemical Properties.**—The trifluoro compound, only, is unstable at room temperatures. All three mixed compounds are vigorously hydrolyzed by water, and rapidly decomposed by absolute methanol. They do not react at room temperature with hydrocarbon solvents or with mercury. The mono and difluoro compounds are, like silicon isocyanate, miscible in all proportions with benzene, carbon tetrachloride, bromobenzene, ethylene dibromide and 1,4-dioxane at 20°. These two fluoro compounds, unlike silicon isocyanate, exhibit partial miscibility, only, with carbon disulfide. By titration of hydrofluoric acid after alcoholysis, it was found that the carbon disulfide layer saturated at 24° contains 13 volume per cent. of the monofluoro compound and that the corresponding layer saturated at 24° contains 8 volume per cent. of the difluoro compound. At 45° this had increased to about 20 volume per cent. (one rough observation) indicating that the temperature coefficient of miscibility is large. A single experiment confirmed the prediction that the solubility of the trifluoro compound in carbon disulfide would be very limited.

### Discussion

The ease of fluorination of silicon isocyanate

(5) Sublimation point, Patnode and Papish, *J. Phys. Chem.*, **34**, 1494 (1920).

(6) Gaseous state, Klemm and Henkel, *Z. anorg. Chem.*, **213**, 115 (1933).

without a catalyst suggests that the strength of the bonds in that compound may correspond more nearly to silicon bromide than to silicon chloride. According to Kopp's law,  $V_F = 8.7$  ml.,  $V_{Cl} = 22.2$  ml.,  $V_{Br} = 27$  ml. and  $V_{NCO} = 37.2$  ml. In these binary silicon compounds, boiling points follow the volumes, not the masses of the attached units. The unexpectedly high boiling points of the mixed compounds may be due, in part, to the difference in size of the groups. Further possibilities are being tested by work on other mixed compounds containing fluorine. Also, we expect to follow the stabilities of the mono- and difluoro compounds over a long period of time. Additional study of solubilities and solubility trends of mixed silicon compounds in carbon disulfide might be profitable.

### Summary

Silicon isocyanate reacts with antimony trifluoride in the absence of a catalyst to produce all the three fluoroisocyanates. The yield of silicon fluorotriisocyanate was improved by fluorination under diminished pressure.

The normal boiling point of silicon fluorotriisocyanate, SiF(NCO)<sub>3</sub>, is 134.3°, that of silicon difluorodisocyanate, SiF<sub>2</sub>(NCO)<sub>2</sub>, is 68.6°, and that of silicon trifluoroisocyanate, SiF<sub>3</sub>NCO, is -6°. All these boiling points are some twenty degrees above predicted values. Several physical properties were measured.

No rearrangement of the mono- or difluoroisocyanate was noted, but the rate of disproportionation of the trifluoro compound at its boiling point set a limit to the purity attainable. Similarly, phosphorus fluorodibromide is known to be more stable than phosphorus difluorobromide.

All three mixed compounds are completely miscible with a number of organic solvents, but solubility in carbon disulfide decreases as the number of fluorine atoms increases.

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