

markedly different from that of the light lanthanides. The results obtained for the intermediate carbide phases should facilitate interpretation of analogous data collected for other heavy lanthanides.

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Silicon-Fluorine Chemistry. IX. The Reactions of Silicon Difluoride and Silicon Tetrafluoride with Water and Some Reactions of Tetrafluorodisiloxane

J. L. Margrave, K. G. Sharp, and P. W. Wilson

Contribution from the Chemistry Department, Rice University, Houston, Texas 77001. Received September 9, 1969

Abstract: The reactions of silicon difluoride and silicon tetrafluoride with water have been investigated. The compound 1,1,1',1'-tetrafluorodisiloxane has been isolated from the reaction of silicon difluoride with water. The mass spectrum, infrared spectrum, nmr spectrum, and some of the chemical properties of this compound are reported.

Although a large number of the reactions of silicon difluoride has been investigated,¹ the reaction of silicon difluoride with water has not been previously described. When most silicon halides are hydrolyzed polymeric oxides are formed. It is possible that silicon difluoride also would react in this manner to give Si-O-F polymers. Such polymers were produced in the reaction of silicon difluoride with oxygen.² The methanolysis reaction of silicon difluoride was reported recently and two new compounds were isolated from the reaction products.³ It thus seemed possible that the controlled hydrolysis of silicon difluoride would also produce nonpolymeric products.

Since a considerable quantity of silicon tetrafluoride is always present in silicon difluoride reactions, there will necessarily be a simultaneous reaction between the silicon tetrafluoride and water when the hydrolysis of silicon difluoride is carried out. When silicon tetrafluoride reacts with an excess of water, silicon dioxide and fluorosilicic acid are produced.⁴ However, Chaigneau has reported that silicon tetrafluoride reacts with wet magnesium sulfate to give fluorosiloxanes.⁵ It therefore seemed advisable to study the reaction of silicon tetrafluoride with water to determine what products would be formed under the conditions used in this investigation.

Experimental Section

The silicon difluoride was produced as described previously by passing silicon tetrafluoride over a column of silicon heated to 1250°. Water vapor was introduced into the stream of silicon difluoride and silicon tetrafluoride leaving the furnace and the resultant mixture was condensed. The apparatus was designed to

minimize the time between mixing and condensation. By means of ballast bulbs fitted with needle valves the ratio of silicon difluoride to water could be adjusted to any selected value. In any particular experimental run the value of this ratio was held constant, but it was varied over a number of runs from 1:1 to 7:1.

After the reaction was completed the resultant condensate was warmed to room temperature and any volatile products were collected. The products were purified by either trap-to-trap distillation or by the Cady codistillation method.⁷ The Cady method was particularly valuable in these experiments since the various reaction products were eluted as well-separated peaks.

A reaction between water and silicon tetrafluoride was, as expected, observed in the experiments described above. This reaction was further investigated by mixing silicon tetrafluoride and water in the gas phase, condensing and reevaporizing the mixture several times, and examining the products. Silicon tetrafluoride was always present in excess as this limited the amount of polymer formed.

The reactions of tetrafluorodisiloxane reported were studied by condensing the tetrafluorodisiloxane and the second reagent into a 20-cc glass ampoule and allowing the mixture to stand at room temperature until products were formed.

The infrared spectra were obtained using the Beckman spectrophotometers IR-8 and IR-11. The mass spectra were obtained on a Bendix Time-of-Flight Model 14-107 mass spectrometer, and the nmr spectra were taken on a Varian Model A-56/60A nmr spectrometer.

Results and Discussion

A. Reaction of Silicon Fluorides with Water. A multicolored polymer was produced by cocondensing water and silicon difluoride at -196°; when the water and silicon difluoride were present in approximately equimolar amounts the condensate was white, when silicon difluoride was in slight excess the condensate was green, and when silicon difluoride was in large excess the condensate was yellow. In most experiments bands of all three colors were seen.

When the condensate was warmed to room temperature, it gradually turned white and evolved volatile compounds. A considerable quantity of white polymer always remained after removal of volatile products. This polymer differed from those obtained in other reactions of silicon difluoride studied in that it was not

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pyrophoric.⁶ The infrared spectrum of this residual polymer showed absorptions in the regions of Si-F and Si-O stretching vibrations but none in the region of Si-H stretches.

In all the reactions of silicon difluoride with water studied, regardless of the ratio of silicon difluoride with water used, the major product was 1,1,1',1'-tetrafluorodisiloxane. This was apparently the only volatile product formed by the reaction of silicon difluoride with water and a mechanism whereby it might have been formed will be discussed later. Other products obtained were trifluorosilane, hexafluorodisiloxane, and perfluorotrisiloxane. The latter two compounds were probably formed by the reaction of silicon tetrafluoride with water.

The mass spectrum of the tetrafluorodisiloxane is listed in Table I. Mass spectra taken at lower electron

Table I. Mass Spectrometric Ion Abundances for (HF₂Si)₂O^a

<i>m/e</i>	Assignment	Intensity
47	SiF ⁺	100
48	SiFH ⁺	15
66	SiF ₂ ⁺	27
67	SiF ₂ H ⁺	95
82	OSiF ₂ ⁺	4
83	OSiF ₂ H ⁺	58
111	OSi ₂ F ₂ H ⁺	24
129	OSi ₂ F ₃ ⁺	92
130	OSi ₂ F ₃ H ⁺	69
131	OSi ₂ F ₃ H ₂ ⁺	74
148	OSi ₂ F ₄ ⁺	97
149	OSi ₂ F ₄ H ⁺	69
150	OSi ₂ F ₄ H ₂ ⁺	36

^a Measured at 50 eV.

voltages showed that the peak at *m/e* 150 is due to the molecular ion. The large peak at *m/e* 83 (SiF₂HO⁺) indicates that the compound is symmetrical.

The identity of the main product as 1,1,1',1'-tetrafluorodisiloxane is confirmed by its nmr spectrum. The ¹⁹F spectrum is a doublet centered at 134 ppm (upfield from CCl₃F) and the ¹H spectrum is a triplet at 4.0 ppm (downfield from (CH₃)₄Si). The splitting in both multiplets was 97 ± 1 cps. These spectra are expected for an AX₂ system. In both spectra satellites due to *J*_{F-²⁹Si} were observed, the coupling constants being 370 cps in the ¹H spectrum and 270 cps in the ¹⁹F spectrum.

The infrared spectrum of the tetrafluorodisiloxane was determined and is tabulated in Table II. The strong absorption at 2307 cm⁻¹ is due to Si-H stretching vibrations, that at 1166 cm⁻¹ is due to Si-O stretching vibrations, and those in the region 1050-850 cm⁻¹ are due to Si-F stretches.

When silicon tetrafluoride was treated with water the major product was hexafluorodisiloxane. This was conclusively demonstrated by the mass spectrum of the reaction products. Although hexafluorodisiloxane appeared to be quite stable in the gas phase, when condensed and revaporized it decomposed into silicon tetrafluoride and a white polymer. This behavior made it almost impossible to obtain hexafluorodisiloxane uncontaminated by silicon tetrafluoride. The mass spectrum and nmr spectrum of hexafluorodisiloxane have been reported.^{5,8} The infrared spec-

Table II. Infrared Spectrum of Some Halodisiloxanes^{a,b}

(HF ₂ Si) ₂ O	(F ₈ Si) ₂ O	(ClF ₂ Si) ₂ O
636 w	672 w	595 s
848 s	839 s	600 s
887 s	913 w	605 s
987 s	984 m	700 w
1029 w	1032 ^c m	758 m
1166 s	1040 w	853 w
1400 w	1205 s	867 w
1800 w	1242 m	888 w
2307 m	1268 m	915 m
		957 m
		1010 s
		1187 s
		1140 w

^a Gas cell, 10 cm, 1-cm pressure, KBr windows; spectra in cm⁻¹.
^b Strong, s; medium, m; weak, w. ^c Probably due to SiF₄ impurity.

trum of Si₂O₂F₆ has not been previously reported; the principal bands of the spectrum are given in Table II. The spectrum showed absorptions between 839 and 1032 cm⁻¹ due to Si-F stretching vibrations⁶ and at 1200-1270 cm⁻¹ due to Si-O stretches.

In addition to hexafluorodisiloxane, a second product was formed in the reaction of silicon tetrafluoride with water, although its yield was very low. Mass spectrometry showed the compound to be SiF₃OSiF₂OSiF₃. This compound was quite unstable and could not be purified. Samples were always contaminated by large amounts of silicon tetrafluoride and hexafluorodisiloxane. The infrared spectrum of the mixture showed absorptions, in addition to those of silicon tetrafluoride and hexafluorodisiloxane, at 782 (m), 1192 (s), 1290 (m), and 1309 (m) cm⁻¹.

The products formed when silicon tetrafluoride is hydrolyzed are similar to those obtained from hydrolysis of silicon tetrachloride; Goubeau and Warncke⁹ have shown that careful hydrolysis of silicon tetrachloride produces hexachlorodisiloxane and SiCl₃-OSiCl₂OSiCl₃.

In many of the reactions of silicon difluoride described to date, the products obtained have conformed to the general formula A(SiF₂)_nB where *n* ≥ 2. It has been suggested that these products are formed in the following manner.^{10,11} When the mixture of silicon difluoride and the second reagent are cooled to -196° two silicon difluoride molecules dimerize to form diradicals ·SiF₂SiF₂·. These diradicals then react with the other reagent to give products containing at least two silicon atoms. Solan and Timms,¹² however, have found that the reaction of silicon difluoride with germane does not fit this pattern. Similarly, the reaction of silicon difluoride with water seems not to proceed *via* a diradical mechanism.

Since the major product obtained from the reaction of silicon difluoride with water is 1,1,1',1'-tetrafluorodisiloxane, it is most likely formed by the following reaction route

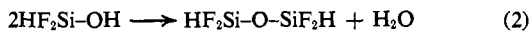
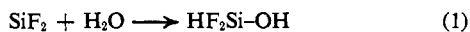
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The condensation of silanols is known to be rapid unless special circumstances such as steric hindrance slow the reaction.¹³ If diradicals were the reacting species, the product formed would have been $\text{HF}_2\text{-SiSiF}_2\text{-O-SiF}_2\text{SiF}_2\text{H}$. There was no evidence that this compound or any closely related compound had been formed. This is a strong argument that diradicals do not figure significantly in this reaction.

It is also possible that a silicon difluoride monomer reacts with water to form a silanol (as in reaction 1), and a second monomer then reacts with the silanol to form the disiloxane. However, as above, diradicals



are not involved in this mechanism.

B. Some Reactions of 1,1,1',1'-Tetrafluorodisiloxane.

One of the aims of this project was to study the chemical properties of the products obtained. Consequently the reactions of tetrafluorodisiloxane were investigated with the purpose of determining whether the presence of fluorine in the molecule had a significant effect on the lability of the hydrogen atom or the reactivity of the Si-O bonds.

1. Reaction with Chlorine. Reaction was rapid, leading to hydrogen chloride and 1,1'-dichloro-1,1,1',1'-tetrafluorodisiloxane. The latter compound has only been prepared previously by the partial fluorination of hexachlorodisiloxane.¹⁴ The infrared spectrum of the compound is listed in Table II. In comparison with the infrared spectrum of tetrafluorodisiloxane, the spectrum of $\text{SiF}_2\text{ClOSiF}_2\text{Cl}$ showed no absorption at 2300 cm^{-1} but included a new absorption at 600 cm^{-1} , indicating that the Si-H bond had been replaced by an Si-Cl bond.

The most important features of the mass spectrum of dichlorotetrafluorodisiloxane were a low intensity parent ion at m/e 218, a low intensity ion at m/e 199 corresponding to the loss of a fluorine atom, and a high intensity ion at m/e 183 corresponding to the loss of a chlorine atom. At lower m/e ratios the spectrum was very similar to that of tetrafluorodisiloxane.

$\text{SiF}_2\text{Cl-O-SiF}_2\text{Cl}$ may well be a useful reagent for the preparation of other fluorodisiloxanes as the chlorine can easily be exchanged for other groups by passing the compound over solid silver, mercury, and lead salts.¹⁵

2. Reaction with Methanol. Reaction was rapid; the products were hydrogen and a compound that was shown by its mass spectrum to have the structure $\text{CH}_3\text{O-SiF}_2\text{-O-SiF}_2\text{-OCH}_3$. This compound was very unstable, and rapidly decomposed to give white poly-

mers, methoxytrifluorosilane, and dimethoxydifluorosilane. The properties of the latter two compounds have been described elsewhere.³

Since both $\text{CH}_3\text{OSiF}_2\text{OSiF}_2\text{OCH}_3$ and $\text{SiF}_3\text{OSiF}_2\text{-OSiF}_3$ decompose readily, it appears that chains consisting of alternating oxygen and silicon difluoride units are unstable. A similar instability has been noted for the chlorosiloxanes, although these appear to be more stable than the fluorosiloxanes.⁹

3. Reaction with Boron Trifluoride. Disiloxanes generally react with boron trifluoride to give fluorosilanes and siloxyboron fluorides.¹⁶ However, after 24 hr boron trifluoride had not reacted with tetrafluorodisiloxane.

4. Reaction with Lithium Aluminum Hydride. LiAlH_4 reacted quickly with the tetrafluorodisiloxane to give a mixture of fluorosilanes. No reduced disiloxanes were produced.

5. Reaction with Calcium Hydride. Since lithium aluminum hydride reacted rapidly with tetrafluorodisiloxane to cleave the Si-O bond, a reaction with the milder reducing agent calcium hydride was investigated. After 24 hr no reaction had occurred. Hagenmuller and dePape have reported that silicon tetrafluoride is only slowly reduced by calcium hydride but they did obtain a 12% yield of silane in a 24-hr reaction.¹⁷

6. Reaction with Hydrogen Chloride. Most siloxanes react with hydrogen halides to give halosilanes; fluorosiloxanes are generally especially reactive.¹⁶ However, no reaction was observed between tetrafluorodisiloxane and hydrogen chloride after 24 hr.

7. Reaction with Phenylboronic Acid. In reaction 2 above, tetrafluorodisiloxane was shown to react with -OH groups to eliminate hydrogen. It was of interest to see if tetrafluorodisiloxane would react with -OH groups other than those of alcohols. The dibasic acid, phenylboronic acid, was chosen since reaction might lead to a six-membered ring. However, no reaction was observed between tetrafluorodisiloxane and phenylboronic acid after 24 hr.

The overall picture drawn from the reactions of 1,1,1',1'-tetrafluorodisiloxane studied is that the reactivities of the Si-H and disiloxane groups are not greatly affected by the substituent fluorine atoms. The large difference in electronegativity between silicon and fluorine should give the Si-F bond a highly ionic character and consequently affect the other substituents on the silicon through inductive effects.¹⁸ However, the polarity of the Si-F bond can be significantly lowered by $p \rightarrow d\pi$ bonding from the halogen to the silicon; this effect is larger for fluorine atoms than for other halogen atoms. The overall effect of fluorine substitution may thus be rather small.

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