Reaction of Silicon Difluoride with Halogens: a Reinvestigation‡

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Reactions of SiF_2 with halogens have been reinvestigated by both co-condensation and gas-phase methods. The co-condensation method yields a number of fluorohalogenosilanes including mono-, di-, and higher silane derivatives. These compounds contain SiF, SiF_2, and SiF_3 units. The reactivity towards SiF_2 decreases from chlorine through bromine to iodine. While chlorine and bromine give rise to a number of fluorohalogenosilanes, iodine yields only the monosilane derivatives. In contrast, the gas-phase reactions do not progress to any appreciable extent. The products have been characterized by mass spectrometry and ^{19}F and ^{29}Si n.m.r. spectroscopy. Many have been identified for the first time.

Except towards oxygen, silicon difluoride exhibits very low reactivity in the gas phase towards many reagents. However, when co-condensed, it reacts readily with a large variety of inorganic and organic compounds to yield novel compounds containing $(SiF_2)_n$ units.[1] Some of these compounds cannot at present be prepared by any other synthetic route. This difference in reactivity may be attributed to either concentration effects and/or to the presence of triplet species of the type $F_2\dot{S}i(SiF_2)_n\dot{S}iF_2$ in the condensate as compared to the singlet species $:SiF_2$ present in the gas phase.

There are very few reports concerning the reaction of SiF_2 with halogens. Pease[2] mentioned these reactions with an emphasis on the preparation of difluorodihalogenosilanes. Later Margrave *et al.*[3] studied the reaction of SiF_2 with iodine in detail and were able to identify only SiF_2I_2 and SiF_3I among the reaction products. This led these authors to conclude that diradicals of the type $\dot{S}iF_2\dot{S}iF_2$ do not play a significant role in this reaction.

In view of the known reactivities of both SiF_2 and the halogens, we might expect the formation of a wide variety of fluorohalogenosilanes containing Si–Si units in these reactions. Moreover, all the halogen reactions reported so far were studied by the method of co-condensation. There is no information about the reactivity of SiF_2 with halogens in the gas phase. This lack of information prompted us to reinvestigate these reactions and characterize them in more detail.

Experimental

Apparatus and Measurements.—All the volatile products were handled in a conventional greaseless vacuum line. Silicon difluoride was prepared by the standard method[4] of reduction of SiF_4 with elemental silicon at 1 150 °C. Mass spectra were recorded on a DuPont 21-490 mass spectrometer with samples introduced by evaporation at room temperature. The n.m.r. samples were prepared by evaporating and condensing the sample, solvent ($CDCl_3$), and the respective internal standard into n.m.r. tubes and sealing the tubes under nitrogen at slightly below room temperature. All the samples were kept at −196 °C prior to analysis. Fluorine-19 n.m.r. spectra were recorded on a Varian XL-200 instrument (188.2 MHz) with CCl_3F as the internal standard, ^{29}Si spectra on both Varian XL-200 (39.74 MHz) and Bruker WP-80 (15.9 MHz with $SiMe_4$ as the internal standard) instruments. High-field shifts are taken as negative.

Reagents.—Silicon tetrafluoride was obtained from Matheson and purified by low-temperature fractionation before use. Chlorine, bromine, and iodine (Reagent Grade) were obtained from commercial sources and used as such. Dibromodifluorosilane was prepared by the reaction of SiF_2 with Br_2 and purified by repeated fractional distillation at low temperature.

General Procedure for the Reaction of SiF_2 *with Halogens and* SiF_2Br_2*: Co-condensation Method.*—The appropriate halogen was co-condensed in a flask at −196 °C with the mixture of SiF_4 and SiF_2[4] emerging out of the reactor tube. Chlorine and bromine were evaporated at room temperature, while iodine was vapourized from a heated bulb. Coloured deposits were obtained, which varied from greenish yellow to reddish white and dark purple in the cases of chlorine, bromine, and iodine respectively. In a typical run, SiF_4 (0.178 mol) was passed through a furnace and co-condensed with the halogen (0.16 mol) over a period of 2 h. In the case of the reaction of SiF_2 with SiF_2Br_2, the latter (0.07 mol) was evaporated from a trap maintained at −20 °C and then co-condensed with the mixture of SiF_4 and SiF_2 (0.09 mol SiF_4) to yield a reddish white deposit (1 h). The pressure in the reaction zone was kept below 0.2 Torr throughout the experiment. The coloured deposits turned white when warmed to room temperature, accompanied by the liberation of volatile compounds. The volatile products were partially separated by low-temperature fractionation by passage through a series of U-tubes maintained at different temperatures. Because of the complexity of the mixture of products obtained in each reaction and the similarities in the vapour pressures of the different compounds, complete separation of individual compounds was not possible. In addition, some unreacted halogen usually remained dissolved in the mixture of products and could not be separated by simple fractionation. The excess of halogen was removed by shaking the mixture with mercury for a brief period and immediately transferring the products to another trap. There was no evidence that mercury reacted with the products.

The reactions were done with various amounts of reactants, but SiF_4 was always kept in excess. Because of the complexities mentioned earlier, we could not make any quantitative measurement of the yield of the products.

Gas-phase Reactions.—These reactions were done with chlorine and bromine, in the same ratios as used for co-condensation. The appropriate halogen was allowed to mix with the mixture of SiF_4 and SiF_2 in a 2-l globe. The mixture was allowed to stand overnight at a pressure of 2 Torr at room temperature. It was then fractionated and subjected to mass spectral analysis.

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‡ *Non-S.I. unit employed:* Torr ≈ 133 Pa.

Table 1. N.m.r. data for (SiF_2 + X_2) reaction products: monosilane derivatives

	^{19}F				^{29}Si			
	δ/p.p.m.		$^1J(SiF)$/Hz		δ/p.p.m.		$^1J(SiF)$/Hz	
Compound	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
SiF_4		−163.30[c]		175.03[d]		−113.70		169.70
SiF_3Cl		−134.63		228.00		−86.10		228.00
SiF_2Cl_2	−111.04	110.64	274.70	273.60	−59.47	−59.40	275.75	273.60
$SiFCl_3$	−93.23	−92.25	315.0	311.50	−36.58	−36.50	314.30	311.50
$SiCl_4$					−18.56	−19.99		
SiF_3Br	−126.71	−123.91	258.40	252.70		−86.80		252.70
SiF_2Br_2	−95.11	−94.58	320.10	318.80	−72.01	−71.80	320.0	318.80
$SiFBr_3$	−76.24	−76.62	368.10	368.70		−71.40		368.70
$SiBr_4$						−93.60		
SiF_3I	−109.90	−106.90[e]	292.70	296.00[e]	−101.61		293.90	
SiF_2I_2	−75.20	−73.50[e]	372.70	375.00[e]	−135.93		372.46	
$SiFI_3$	−66.00		421.10		−213.85		424.29	
SiI_4						−351.71		

[a] Present work. [b] Refs. 5 and 6. Reported values are with reference to SiF_4; ^{19}F values have been converted into the CCl_3F scale here by taking δ(SiF_4) as −163.3 p.p.m. [c] C. H. Dungan and J. R. Van Wazer, 'Compilation of Reported ^{19}F NMR Chemical Shifts,' Wiley-Interscience, New York, 1969. [d] J. W. Emsley, L. Philips, and V. Wray, 'Fluorine Coupling Constants,' Pergamon, London, 1977, pp. 712, 713. [e] Ref. 3.

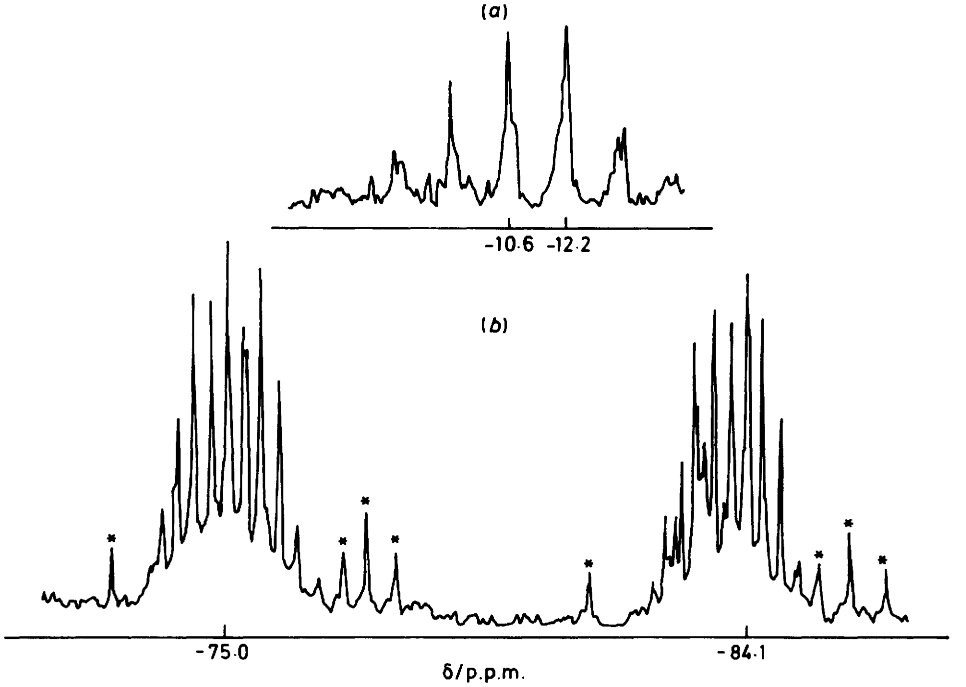

Figure. Silicon-29 n.m.r. spectrum of $(SiF_3)_3SiCl$: (*a*) $(SiF_3)_3$*Si*Cl; (*b*) central part of the multiplet of quartets assigned to the SiF_3 group. Asterisks indicate peaks probably due to other compounds

Results

All the three halogens reacted with SiF_2 giving rise to a large number of products. The nature of the products formed did not vary with the relative proportions of the reactants, but the overall yield increased with increasing halogen:SiF_4 ratio and also from iodine to chlorine. Also it was observed that the amount of non-volatile white solid, presumably polymeric $(SiF_2)_n$, increased from chlorine to iodine and in the co-condensation of SiF_2 and SiF_2Br_2.

The products formed can be classified as mono-, di-, and higher silane derivatives. Mass spectral (m.s.) studies were helpful to some extent in characterizing the compounds, though not conclusive. Many of the chloro compounds, including higher silane derivatives, gave a characteristic molecular ion peak. However, in the cases of bromo- and iodo-silanes, only the monosilanes gave parent-ion peaks. The higher silanes underwent extensive fragmentation giving rise to complex spectra, which provided only a general indication of the compounds present. More conclusive evidence came from n.m.r. data. On the basis of all the available data, some reasonable conclusions can be drawn about the nature of the products formed.

Reaction of SiF_2 *with Chlorine.*—All three chlorofluoromonosilanes were formed, SiF_2Cl_2 being the major product (Table 1). Chlorotrifluorosilane was identified only by m.s. (m/z = 120) since it was formed in small amounts. Another

Table 2. Silicon-29 n.m.r. data for ($SiF_2 + X_2$) reaction products higher silane derivatives[a]

	δ/p.p.m.			J/Hz	
Assignment	SiF_3	SiF_2	SiX_n	^1J(SiF)	^2J(SiF)
$\mathrm{F_3Si{-}SiF_3}$[b]	−77.90			321.80	
$\mathrm{ClF_2\mathit{Si}{-}SiF_2Cl}$		−47.35 (tt)		356.40	78.20
$\mathrm{ClF_2Si{-}\mathit{Si}F_2Cl}$		−47.56 (t)		361.0	
$\mathrm{F_3\mathit{Si}{-}SiCl_3}$	−78.73 (q)			357.5	
$\mathrm{F_3Si{-}\mathit{Si}Cl_3}$			−6.33 (q)		55.6
$\mathrm{Cl_2F\mathit{Si}{-}SiCl_3}$[c]				374.9	
$\mathrm{Cl_2FSi{-}\mathit{Si}Cl_3}$			−1.98 (d)		53.6
$\mathrm{Cl_3Si{-}SiCl_3}$[b]			−8.00		
$\mathrm{Br_3\mathit{Si}{-}SiBr_3}$			−36.50 (s)		
$\mathrm{F_3\mathit{Si}{-}SiF_2{-}SiF_3}$[b]	−79.70			344.40	
$\mathrm{F_3Si{-}\mathit{Si}F_2{-}SiF_3}$[b]		−17.7		356.60	
$\mathrm{F_3\mathit{Si}{-}SiBr_2{-}SiBr_3}$	−83.9 (q)			352.0	
$\mathrm{F_3Si{-}\mathit{Si}Br_2{-}SiBr_3}$			−30.27 (q)		50.80
$\mathrm{F_3Si{-}SiBr_2{-}\mathit{Si}Br_3}$[d]			−28.28 (q)		
$\mathrm{(\mathit{Si}F_3)_3SiCl}$	−79.53 (mq)				
$\mathrm{(SiF_3)_3\mathit{Si}Cl}$			−11.39 (dct)		62.77

[a] q = Quartet, t = triplet, tt = triplet of triplets, mq = multiplet of quartets, dct = decet, d = doublet, and s = singlet. [b] Ref. 6. [c] δ(SiF) −22.36 (d) p.p.m. [d] ^3J(SiF) 6.5 Hz.

Table 3. Fluorine-19 n.m.r. data for ($SiF_2 + X_2$) reaction products: higher silane derivatives[a]

	δ/p.p.m.		J/Hz		
Compound	SiF_3	SiF_2	^1J(SiF)	^2J(SiF)	^3J(FF)
$\mathrm{F_3Si{-}SiF_3}$[b]	−121.05 (s)		321.80		
$\mathrm{ClF_2Si{-}SiF_2Cl}$		−113.90 (s)	358.00	76.60	19.2
$\mathrm{F_3Si{-}SiCl_3}$	−125.79 (s)		350.60	61.40	
$\mathrm{Cl_2FSi{-}SiCl_3}$[c]					
$\mathrm{F_3Si{-}SiF_2Br}$	−121.99 (t)	−118.51 (q)			20.43
$\mathrm{F_3Si{-}SiF_2{-}SiF_3}$	−123.36 (t)	−136.90 (spt)			10.40
$\mathrm{ClF_2Si{-}SiF_2{-}SiCl_3}$		−111.84 (t) −123.64 (t)			18.30
$\mathrm{F_3Si{-}SiBr_2{-}SiBr_3}$	−124.43 (s)		352.00	50.60	
$\mathrm{F_3Si{-}SiF_2{-}SiBr_3}$	−120.27 (t)	−133.30 (q)			10.07
$\mathrm{F_3Si{-}SiBr_2{-}SiF_3}$	−120.99 (s)		362.50		
$\mathrm{(SiF_3)_3SiCl}$	−125.6 (s)				

[a] s = Singlet, t = triplet, q = quartet, and spt = septet. [b] Ref. 5. [c] δ(SiF) −102.79 (s) p.p.m.

monosilane derivative detected among the reaction products was $SiCl_4$ (m/z = 168).

Among disilane derivatives, $\mathrm{ClF_2Si{-}SiF_2Cl}$ (**1**), $\mathrm{Cl_2FSi{-}SiCl_3}$ (**2**), and $\mathrm{F_3Si{-}SiCl_3}$ (**3**) were characterized, showing molecular ion peaks at m/z = 202, 250, and 218 respectively. Compound (**1**) showed the expected triplet of triplets in its ^{29}Si n.m.r. spectrum (Table 2). The n.m.r. parameters of compound (**2**) were in good agreement with those reported.[5,6] The ^{29}Si n.m.r. spectrum of the sample containing (**3**) was very complex because of the presence of many other products, however we were able to pick out a pair of quartets with δ and J values attributable to (**3**). Other disilanes such as Si_2F_5Cl and Si_2F_6 were detected by m.s. (m/z = 186 and 170 respectively).

The only trisilane derivative which could be characterized was $\mathrm{ClF_2Si{-}SiF_2{-}SiCl_3}$. No molecular ion peak for this compound was detected. A tetrasilane derivative was tentatively identified as $\mathrm{(SiF_3)_3SiCl}$. The ^{29}Si n.m.r. spectrum of this compound (Figure) is quite complex and needs elaborate analysis involving computer-simulation studies. One part of the spectrum consists of a quartet of multiplets attributable to the SiF_3 group. Each multiplet seems to be comprised of septets. The other part of the spectrum appears to be a decet and may be attributed to the $\geqslant$SiCl group.

The mass spectra of less volatile fractions showed very weak peaks at m/z = 334, 382, and 400. These might be attributed to the molecular ion peaks for compounds such as $Si_4F_8Cl_2$, $Si_4F_5Cl_5$, and $Si_5F_{10}Cl_2$ respectively. The ^{19}F n.m.r. spectra also showed many other peaks, particularly singlets, which we were unable to assign to any particular compound.

Reaction of SiF_2 *with Bromine.*—Here also SiF_2Br_2 was the major product among the monosilane derivatives. Among disilane derivatives Si_2F_5Br and Si_2Br_6 were characterized. The δ value of Si_2Br_6 agrees well with the reported[6] value of −35.56 p.p.m. The existence of Si_2F_6 and $Si_2F_3Br_3$ was detected by m.s. (m/z = 170 and 350 respectively).

The completely fluorinated Si_3F_8 was one of the trisilane derivatives. Its ^{19}F n.m.r. δ values (Table 3) are somewhat lower than those reported[4] [−126.0 (t) and −139.0 p.p.m. (spt)]. This might be due to the presence of other compounds. The other compounds characterized were $\mathrm{Br_3Si{-}SiBr_2{-}SiF_3}$, $\mathrm{F_3Si{-}SiBr_2{-}SiF_3}$, and $\mathrm{F_3Si{-}SiF_2{-}SiBr_3}$.

Reaction of SiF_2 *with Iodine.*—Only monosilane derivatives, SiF_3I, SiF_2I_2, and $SiFI_3$, were characterized among the reaction products. The ^{19}F n.m.r. spectrum of the less volatile fraction containing $SiFI_3$ also showed weak singlets at higher fields. These are probably due to some higher fluoroiodosilanes.

Reaction of SiF_2 *with* SiF_2Br_2.—The condensate was reddish white but became white when warmed to room temperature. No bromine was evolved during the reaction. A large amount of a white solid $(SiF_2)_n$ was left behind after the removal of volatile products. Most of the SiF_2Br_2 was recovered unchanged. These observations indicate that there was no appreciable reaction. The ^{19}F n.m.r. spectra showed SiF_2Br_2 as the major component.

Gas-phase Reactions.—During the experiment a thin layer of solid was observed on the inside walls of the vacuum line. The bromine reaction did not yield any bromofluorosilanes, while the chlorine reaction gave only traces of SiF_3Cl and SiF_2Cl_2.

Discussion

From our results it is evident that the reactivity towards SiF_2 decreases from chlorine through bromine to iodine, as indicated by the overall yield, the number of products formed, and the amount of unchanged polymeric $(SiF_2)_n$ remaining. The halogens behave similarly as far as the formation of monosilane derivatives is concerned, each yielding all three possible fluorohalogenosilanes.

When the formation of higher silanes is considered the halogens are found to behave differently. Chlorine and bromine give rise to more of these products than does iodine. This is understandable considering the relative Si–X bond energies, which decrease from chlorine to iodine. The thermal stabilities of higher silane derivatives are likely to follow a similar trend. Even if such compounds were formed initially, there is the possibility of their decomposition or rearrangement in the complex reaction mixture and consequently they could have escaped detection. We were able to observe some weak singlets in the ^{19}F n.m.r. spectrum of the products of the iodine reaction. These might be due to some higher fluoroiodosilanes. However, the lack of fine structure and satellites for these singlets prevented their assignment to any particular compound.

It is interesting that the products formed in these reactions contain SiF, SiF_2, and SiF_3 units, in contrast to the behaviour of SiF_2 in many of its reactions [1] where the products contain only $(SiF_2)_n$ units. An unexpected aspect of the halogen reactions is the formation of non-fluorinated silicon halides such as $SiCl_4$ and Si_2Br_6. It is quite possible that other halides like Si_2Cl_6 and $SiBr_4$ might have been formed in small amounts and escaped observation. Another noteworthy observation is the formation of perfluorosilanes such as Si_2F_6 and Si_3F_8, the latter was formed in substantial amounts in the bromine reaction and could be detected by n.m.r. spectroscopy. According to a previous report,[1] these perfluorosilanes are formed only in traces in the warming-up of the condensate of SiF_2 and SiF_4 but in substantial amounts upon heating $(SiF_2)_n$ polymer at 250—350 °C *in vacuo*. In the present case, they are formed even before the condensate reaches room temperature.

The gas-phase reactions indicate that chlorine and bromine do not react with SiF_2 to any appreciable extent. Chlorine seems to be somewhat more reactive, in the sense that we were able to detect small quantities of chlorofluorosilanes. The bromine reaction did not yield any bromofluorosilanes. This lack of reactivity is surprising considering the affinity of halogens towards silicon. One possible reason may be the low concentration of the reactants in the gas phase.

We have observed that SiF_2X_2 is the major product in all the halogen reactions. There is a possibility that SiF_2X_2 is formed first by the reaction of SiF_2 and X_2, and the other silane derivatives are formed by reactions between SiF_2X_2 and SiF_2. To test this we attempted the reaction of SiF_2Br_2 and SiF_2, but there was no appreciable reaction. It is quite likely that the reaction occurs just before condensation when the concentration of the reactants is high enough, or during the warming-up of the condensate. It may involve complete redistribution of Si–X bonds (X = F, Cl, Br, or I) giving rise to various types of silicon halides. The fact that compounds containing Si–Si units were formed indicates that species such as $\dot{S}iF_2$–$\dot{S}iF_2$ are involved in these reactions. There is no reason to believe that only monomeric SiF_2 is involved.

Other important features of the present work are that many of the compounds have been characterized and n.m.r. parameters determined for the first time. Although all the three fluoroiodosilanes have been known for quite some time, their ^{29}Si n.m.r. parameters had not been determined and also the ^{19}F n.m.r. parameters for $SiFI_3$. We were able to isolate these compounds and determine all these values. Many of the higher fluorosilanes have been identified and characterized for the first time. As far as we know there are no previous reports for compounds such as ClF_2Si–SiF_2Cl, F_3Si–$SiCl_3$, ClF_2Si–SiF_2–$SiCl_3$, F_3Si–SiF_2Br, Br_3Si–$SiBr_2$–SiF_3, F_3Si–$SiBr_2$–SiF_3, and F_3Si–SiF_2–$SiBr_3$. The compound $(SiF_3)_3SiCl$ has been tentatively characterized from its n.m.r. data. Chlorofluorosilanes containing more than three silicon atoms have been detected by m.s.

Acknowledgements

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