Trifluoroiodosilane and Difluorodi-iodosilane: Their Properties and Use in Preparing Fluorosilicon Derivatives with Si–N, Si–O, and Si–S Bonds

By **Bernard J. Aylett,* Ian A. Ellis,** and **John R. Richmond,** Chemistry Department, Westfield College, London NW3 7ST

Fluoroiodosilanes $SiF_{4-x}I_x$ (x = 1 or 2) have been prepared by cleavage of the corresponding dimethylaminofluorosilanes with HI; their physical properties are reported. They react respectively with HgO to give $(SiF_3)_2O$ and oligomeric fluorosiloxanes, and with water to give $(SiF_3)_2O$ (initially) and fluorosiloxane polymers. The nature of volatile oligomers formed in these and other reactions is discussed. Trifluorosilyl pseudohalides SiF_3CN and SiF_3NCS are prepared from SiF_3I and corresponding Hg^{II} or Ag^{I} compounds. With HgS, SiF_3I, and SiF_2I_2 form silathianes, believed to be $(SiF_3)_2S$ and $(SiF_2S)_2$. Trifluoroiodosilane reacts with NMe_3 to give a 1:2 adduct, probably $(SiF_3,2NMe_3)^+I^-$, with $NHMe_2$ to give SiF_3NMe_2, and with ammonia to give polymeric fluorosilazanes.

WHILE iodosilanes have proved valuable in the preparation of many SiH_3– and SiH_2= derivatives,[1] little corresponding use has been made of fluoroiodosilanes.[2] This is probably because of their reputation of being difficult to prepare and of readily disproportionating. It will be shown that this is largely unmerited.

Fluoroiodosilanes were first made [3] by redistribution between SiF_4 and SiI_4 at 700 °C; they also resulted [4] when aluminium(III) iodide reacted with SiF_4 or Na_2SiF_6 at 300°. More recently the reactive species SiF_2 has been found [5] to combine with iodine yielding SiF_3I and SiF_2I_2.

Since the Si–N bond is readily cleaved by hydrogen halides,[6] dialkylaminofluorosilanes are possible starting

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[1] (*a*) A. G. MacDiarmid, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 207; (*b*) B. J. Aylett, *ibid.*, 1968, **11**, 249.

[2] For a recent isolated example, see: R. R. Schrieke and B. O. West, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 141.

[3] H. H. Anderson, *J. Amer. Chem. Soc.*, 1950, **72**, 2091.

[4] M. Schmeisser and H. Jenkner, *Z. Naturforsch.*, 1952, **7B**, 191.

[5] J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1813.

[6] V. Bažant, V. Chvalovský, and J. Rathouský, ' Organosilicon Compounds,' Czechoslovak Academy of Sciences, Prague, 1965.

materials for fluoroiodosilanes.[7] We report the use of this method to prepare SiF_3I and SiF_2I_2, and a number of their reactions.

EXPERIMENTAL

General.—Normal high-vacuum and dry-box techniques were used, together with a 5-ft low-temperature column for difficult separations.[8] Halocarbon grease (Kel-F) was essential for taps, *etc.*, when handling fluorosilicon-sulphur and -pseudohalide compounds. I.r. spectra were obtained with Perkin-Elmer 337 or 521 instruments.

N-Dimethylaminotrifluorosilane and bis(dimethylamino)-difluorosilane were prepared [9] by heating dimethylamine, an excess of tetrafluorosilane, and lithium tetrahydroaluminate in a sealed tube at 475 K for 10 h. Amines were dried (CaH_2) and repeatedly fractionated *in vacuo*. Mercury(II) and silver(I) salts were dried by long pumping (and heating if necessary), then by treatment with a little SiF_3I; silver compounds were protected from light.

Preparation of SiF_3I.—(*a*) Dimethylaminotrifluorosilane (4·46 mmol) and HI (10·50 mmol) were sealed together and allowed to warm from 77 K to room temperature (10 min). The products were: excess of HI, trifluoroiodosilane [3·70 mmol, 71%, held at 133 K, passes through 153 K baths (Found: *M*, 207. SiF_3I requires *M*, 212)], small amounts of SiF_4, SiF_2I_2, and $SiFI_3$, also dimethylammonium iodide (i.r.).

TABLE 1

Gas-phase i.r. spectra (cm^{-1}) of fluorosiloxanes (4000—400 cm^{-1})

$(SiF_3)_2O$		$(SiF_3O)_2SiF_2$ [a]	$SiF_3OSiF_2SiF_3$ [b]	A [c]	B [c]	C [c]	D [c]	E [c]
This work	Ref. 16							
1268w	1268m	1309m						
1242w	1242m	1290m				1235w	1232w	
1205s,br	1205s	(1205)		1202s	1200s,br	1182s,br	1180s,br	1170s,br
	1040w	1192s	1172s	1162s,br	1160sh,br	1015vs	1013vs	1020sh
1020vs	1032m	(1032)		1125m		986w	985m	990vs,br
982w	984m	(984)	983s	1020vs	1020vs	936m	935m	881 }
	913w		884m	945m	945m	870m	870m	875 } m
837ms	839s	(839)	842m	865m	865m	654w	652w	870 }
	672w	782m	663w	665w	665w	470m,br	470w,br	
428m,br				430s,br	430s,br	400m,br	400m,br	425w

[a] Ref. 16. [b] Ref. 20. [c] KEY. A *ex* $SiF_2I_2 + HgO$, more volatile fraction, decomposed to solid + SiF_4. B *ex* $SiF_2I_2 + HgO$, less volatile fraction, decomposed to solid + SiF_4. C *ex* $SiF_2(NMe_2)_2 + H_2O$, held at 135 K, passed 177 K, decomposed to solid but essentially no SiF_4. D *ex* $(SiF_3)_2O + SiF_3I$ on storage, held at 153 K, passed 177 K, decomposed to solid but essentially no SiF_4. E *ex* SiF_3I + NO (*hν*), pumped from column at 145 K, decomposed to solid but essentially no SiF_4.

(*b*) Aluminium powder (3 mmol), iodine (2 mmol), and SiF_4 (50 mmol) were heated together in a thick-walled tube for 65 h at 620 K. The tube was then allowed to cool slowly to room temperature (2 h) and the contents were fractionated to yield excess of SiF_4, $(SiF_3)_2O$, SiF_3I (*ca.* 0·1 mmol), and SiF_2I_2 (*ca.* 0·1 mmol). The major silicon-containing product was SiI_4.

Physical Properties of SiF_3I.—Values of the saturated v.p. in the range T = 139—227 K determined the equation: $\log_{10} p(\text{mm}) = 7{\cdot}593 - 1110/T$. Only a trace of SiF_4 was detected at the end of the experiment. Thus the b.p. (extrap.) = 236 K (lit.,[3] 245—253 K), ΔH_{vap} = 21·2 kJ mol^{-1}, and ΔS_{vap} = 89·7 J K^{-1} mol^{-1}. The m.p. (Stock method) was 199·5 ± 0·5 K (lit.,[3] *ca.* 181 K). Band positions in the i.r. spectrum (1000sh, 996vs, 862vs, 857vs, 852vs, 492sh, 481s, 477s, and 472s cm^{-1}) agreed closely with those recently reported,[5] although the intensities appeared different.

Preparation of SiF_2I_2.—Bisdimethylaminodifluorosilane (4·0 mmol) and HI (17·4 mmol) were allowed to warm from 77 K to room temperature and then remain together for 10 min. Fractionation yielded an excess of HI, a trace of SiF_4, SiF_3I (0·4 mmol), SiF_2I_2 [3·2 mmol, 80%, passes 227 K, held at 177 K (Found: *M*, 317. SiF_2I_2 requires *M*, 320)], and $SiFI_3$ (0·4 mmol).

Physical properties of SiF_2I_2. V.p. data in the range 250—296 K (limited by decomposition) suggested an extrapolated b.p. of *ca.* 360 K. The m.p. was 191·0 ± 0·5 K (lit.,[3] 190 K); the i.r. absorptions (971sh, 967s, 961sh, 886s, 881s, 877sh, 597w, 492vs, 485vs, and 443m cm^{-1}) agreed reasonably well with published values [5] apart from relative intensities and the very strong doublet reported here at 485 cm^{-1}. All the bands appeared markedly asymmetric.

Reactions with Water.—SiF_3I (0·02 mmol) and water (0·01 mmol), both in the vapour phase, were mixed in a 10-cm i.r. gas cell; the course of the reaction was monitored by rapid scanning of the range 1600—800 cm^{-1}. Immediate formation of $(SiF_3)_2O$ was observed, a little white solid began to deposit after 2 min, and all the water was consumed after 4 min.

In a similar reaction, vapour of SiF_2I_2 and of water produced an immediate deposit of white solid; SiF_4 was formed and SiF_2I_2 disappeared during 5 min. No $(SiF_3)_2O$ or appreciably volatile fluorosiloxane oligomers were found, but a product that at first could just be transferred *in vacuo* later lost SiF_4 and became involatile. Heating of the solid residues to *ca.* 475 K yielded a little SiF_4 as the only volatile product.

Reactions with Mercury(II) *Oxide.*—(*a*) A mixture of SiF_3I vapour (0·09 mmol) and nitrogen was twice passed over mercury(II) oxide (80 mmol) supported on glass wool. The sole volatile product was $(SiF_3)_2O$ (0·04 mmol, >80%), while the mercury compound's colour changed from orange to deep red.

(*b*) SiF_2I_2 vapour (0·22 mmol) was passed several times over HgO (75 mmol). The volatile products comprised $(SiF_3)_2O$, SiF_xI_{4-x} (x = 2—4), and also two fluorosiloxane fractions A (passed 209 K, held at 177 K) and B (held at 209 K). Their i.r. spectra are given in Table 1.

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[7] J. J. Moscony and A. G. MacDiarmid, *Chem. Comm.*, 1965, 307.

[8] D. F. Shriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969.

[9] M. Allan, B. J. Aylett, and I. A. Ellis, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 261.

Photolysis of SiF_3I *and* NO.—SiF_3I (2·2 mmol) and NO (2·2 mmol) were irradiated in the gas phase (quartz tube, Hg-sensitized, 1 atm) for 15 min with a 1 kW source. The products were fractionated to yield: N_2 (0·4 mmol), N_2O, NO, SiF_4, SiF_3I, SiF_2I_2 (trace), $(SiF_3)_2O$, HgI_2, and a volatile fluorosiloxane E (see Table 1; *M*, 170 ± 20), slightly less volatile than $(SiF_3)_2O$.

Reactions with Mercury(II) *Sulphide*.—(*a*) SiF_3I vapour (4 mmol) was passed several times at *ca.* 5-cm pressure over mercury(II) sulphide (100 mmol). The mercury compound developed dark red and greenish yellow regions, and the volatile products were excess of SiF_3I, SiF_4, $(SiF_3)_2O$ (trace), and presumed hexafluorodisilathiane $F_3Si{\cdot}S{\cdot}SiF_3$(I) [mainly held at 153 K (Found: *M*, 200. Si_2F_6S requires *M*, 202)].

(*b*) SiF_3I (6 mmol) and HgS (40 mmol) were sealed together and allowed to react for 18 h at 278 K; a liquid phase was always present. The products were SiF_4, $(SiF_3)_2O$ (trace), and presumed tetrafluorocyclodisilathiane $F_2Si{\cdot}S{\cdot}SiF_2{\cdot}S$ (II) [held at 153 K (Found: *M*, 198. $Si_2F_4S_2$ requires *M*, 196)].

(*c*) When SiF_2I_2 (1·2 mmol) vapour was passed over HgS (80 mmol), there was negligible reaction. The two compounds were then sealed together for 18 h at 298 K: the major volatile product was compound (II), although some SiF_4, $(SiF_3)_2O$, and compound (I) were also present. When the solid residue was warmed and pumped, further amounts of (I) and (II) were produced.

I.r. spectra of compounds (I) and (II) are given in Table 2.

TABLE 2

Gas-phase i.r. spectra of fluorosilathianes (4000—400 cm^{-1})

$(SiF_3)_2S$	$(SiF_2S)_2$	
	1108vw	2 × 554?
995sh 990vs	1008vs	ν_{as}(SiF)
	888m	
881 873 vs 866	850 846 s 842	ν_s(SiF)
568sh 561s 554sh	554s	ν_{as}(SiSSi)

These samples had been purified by distillation by fractionation on the low-temperature column; attempts at purification by g.l.c. (silicone oil) at 298 K led to decomposition.

Into gaseous (presumed) $(SiF_3)_2S$ (I, 0·09 mmol) in a 10-cm i.r. cell were injected successive aliquots (*ca.* 0·03 mmol) of pyridine vapour carried in nitrogen. After the first and second, white solid was formed, and i.r. bands due to (I) diminished in intensity, while a band at 1032 cm^{-1} (SiF_4) increased. After the third, no bands due to (I) were visible, and that due to SiF_4 had weakened.

Reaction of SiF_3I *and Mercury*(II) *Cyanide*.—Vapour of SiF_3I (1·2 mmol) was passed over $Hg(CN)_2$ (100 mmol); red HgI_2 was immediately formed. The volatile products were SiF_4, $(SiF_3)_2O$ (trace), unused SiF_3I, and presumed trifluorosilyl cyanide (III) [mainly held at 139 K (Found: *M*, 108. $CNSiF_3$ requires *M*, 111), i.r. (gas phase, cm^{-1}): 1010vs (ν_{as}SiF); 890ms, 881s, 875ms (RQP, ν_sSiF); 602sh, 597m, 588sh (RQP, νSiC)]. Compound (III) rapidly reacted with Apiezon grease to give HCN; alone, it decomposed to form a yellow involatile solid and traces of SiF_4 when condensed at 77 K or when stored in the gas phase at more than *ca.* 5 cmHg. The solid absorbed (i.r., mull) at 3325m, 3110s, 3070s, 1680s, 1585m, 1510m, 1300w, 1274m, 1260sh, 1092m, 1064m, 1008m, 951m, 664sh, 649s cm^{-1}, with an additional band (KBr disc) at 1405 cm^{-1}. It slowly turned brown *in vacuo*, and its alkaline hydrolysate gave a positive test for CN$^-$.

A similar reaction between SiF_3I vapour and AgCN also yielded compound (III), while treatment of either $Hg(CN)_2$ or AgCN with liquid SiF_3I produced only the yellow solid referred to above. Gaseous HCl slowly reacted with the yellow solid; after 20 h, some HCN and fluorochlorosilanes were present (i.r.).

Reaction of SiF_3I *and* HCN.—Equimolar amounts of SiF_3I and HCN reacted in a 10-cm gas cell (total pressure, *ca.* 5 cm). After 15 h at room temperature, a yellow solid (i.r.: 3030sh, 2980sh, 2910vs, 2840sh, 2760m, 2660mw, 2590m, 2525m, 1900w, 1550m, 1530w, 1475m, 1287m, 1133s, 1050w,br, 948m cm^{-1}) had formed, although most (>75%) of the reactants were intact; no volatile Si–CN product was detected. When treated with water vapour, the solid evolved a little HCN.

Reaction of SiF_3I *and Mercury*(II) *Thiocyanate*.—SiF_3I (0·9 mmol) was condensed on to $Hg(NCS)_2$ (30 mmol) and the mixture allowed to warm slowly to room temperature. The volatile products were: SiF_4, $(SiF_3)_2O$ (trace), and trifluorosilyl thiocyanate (0·2 mmol, 20%; Found: *M*, 142; calc. for SiF_3NCS, 143); its i.r. absorptions were generally as in ref. 10, except that the bands there reported near 3540 cm^{-1} are probably due to HNCS. With Apiezon grease, SiF_3NCS yielded HNCS, while as a liquid or a gas at high pressures, it changed into a yellow-brown solid without simultaneous formation of volatile products. The solid evolved HNCS on treatment with water vapour, and the residue contained fluorosiloxanes and SiF_6^{2-} (i.r.).

Reaction of SiF_3I *and Trimethylamine*.—Gaseous SiF_3I (3·04 mmol) was injected into NMe_3 (6·21 mmol) contained in a 2 l flask attached to an i.r. cell. A pale yellow solid formed in the vessel, while the only volatile product was NMe_3 (0·13 mmol; combining ratio, 1 : 2·00). The solid's i.r. spectrum (3000m, 2950s, 2735s, 1470vs, 1405m, 1388w, 1252w, 1239m, 1120w, 1028w, 972vs, 964s, 951vs, 940vs, 925sh, 819s, 761m, 585s,br, 463vs,br cm^{-1}) remained unchanged after pumping for 1 h; after 30 min without pumping a trace of SiF_4 was apparent. There was no indication that the adduct dissolved in NMe_3, even with the latter in large excess.

When exposed to water vapour, the adduct immediately became white, and the i.r. spectrum showed bands assigned to $NHMe_3^+$, SiF_6^{2-}, and fluorosiloxane polymers.

Another sample of adduct (2·20 mmol) reacted with chlorine (3·06 mmol) at room temperature. Iodine was immediately formed, and the more volatile products comprised SiF_4 (trace) and excess of chlorine (2·03 mmol). The combining mole ratio of adduct to Cl_2 is thus 1 : 0·47.

Reaction of SiF_3I *and Dimethylamine*.—(*a*) Gaseous SiF_3I (0·1 mmol) and $NHMe_2$ (0·8 mmol) were mixed in an i.r. cell. White solid immediately formed, some being on the windows. An i.r. spectrum run at once showed a complex mixture of products including $SiF_2(NMe_2)_2$ (diagnostic bands at 1315, 915, and 880 cm^{-1}, but no SiF_3NMe_2 (diagnostic bands at 980, 958, and 879 cm^{-1}). Volatile products were then removed by pumping for 10 min; during their fractionation, solids were deposited and the only final volatile product was $NHMe_2$. The solid left in the cell at this stage showed bands attributable to Me_2NH_2I, together with others at 3260s, 1325m, 1108m, 1028s,

[10] W. Airey and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 2865.

912m, 798vs, 775vs, and 560s cm^{-1}. On further pumping, these additional bands disappeared.

(*b*) Gaseous SiF_3I (1·8 mmol) and $NHMe_2$ (0·9 mmol) were similarly mixed. Volatile products were removed and shown to include SiF_3NMe_2 and a little $SiF_2(NMe_2)_2$, while the solid residue was solely Me_2NH_2I.

Reaction of SiF_3I *with Ammonia.*—(*a*) SiF_3I vapour (2·26 mmol) was led into a 2 l flask containing ammonia (3·41 mmol). White solid was deposited, leaving unchanged SiF_3I (0·25 mmol), SiF_4, and a small amount of a substance held at 153 K [i.r. (cm^{-1}): 3400w, 1380w, 1232m, 1138s, 1008vs, 975m, 885w, 822m, 749w] which could not be completely separated from SiF_3I and rapidly decomposed during attempted fractionation. The white solid showed i.r. bands attributed to NH_4^+ and a little SiF_6^{2-}; it smelt slightly of ammonia, and dissolved in water to give initially a clear solution, which later became turbid. When treated with conc. H_2SO_4, the solid frothed and yielded iodine.

(*b*) Ammonia (3·64 mmol) entered an i.r. cell containing SiF_3I vapour (0·22 mmol). A white solid formed over the walls and windows of the cell, and the sole volatile product was ammonia (3·21 mmol). The solid gave i.r. bands attributed to NH_4I, with additional broad bands at 1600m, 930s, 890s, 730s, and 610m cm^{-1}. When the solid was exposed to water vapour, ammonia was evolved, and broad bands at 690s and 480s appeared, while that at 730 cm^{-1} (SiF_6^{2-}) intensified.

The combining ratios of SiF_3I to NH_3 in (*a*) and (*b*) were 1 : 1·70 and 1 : 1·95 respectively.

RESULTS AND DISCUSSION

Dimethylaminotrifluoro- and bisdimethylaminodifluoro-silane reacted readily with a slight excess of hydrogen iodide below room temperature to give the corresponding fluoroiodosilanes in good yield [equation (1)]; the case where $x = 1$ has been briefly mentioned

$$SiF_{4-x}(NMe_2)_x + 2xHI \longrightarrow SiF_{4-x}I_x + xNH_2Me_2I \quad (1)$$
$$(x = 1, 71\%;\ x = 2, 80\%)$$

by Moscony and MacDiarmid.[7] This reaction, formally the reverse of that often used to make Si–N bonds,[11] now appears to offer the best route to pure fluoroiodosilanes.

Experiments using a larger excess of HI led to more highly iodinated products. Thus SiF_3NMe_2 and a two-fold excess of HI over that demanded by equation (1) gave only a 25% yield of SiF_3I but a mol ratio (SiF_4 : $SiFI_3$) of *ca.* 1 : 5. This shows that simple disproportionation of SiF_3I (which would produce more SiF_4 than $SiFI_3$) cannot be the only way in which $SiFI_3$ is formed; possibly species such as $NH_2Me_2^+HI_2^-$ can act as iodinating agents.* Similar effects were shown by $SiF_2(NMe_2)_2$ and HI in excess; with this system, deficit of HI was also undesirable, since it led to the formation of a poorly volatile liquid, believed to be $SiF_2(NMe_2)I$, that caused rapid disproportionation of SiF_2I_2 during fractionation.†

Attempts to prepare fluoroiodosilanes from aluminium, iodine, and SiF_4 by a modification of Schmeisser's method [4] met with only limited success. Slow reaction did occur above 200°, but the chief iodinated product was always SiI_4, even with a large excess of SiF_4. Also $(SiF_3)_2O$, always formed when SiF_3I (or SiF_4) is heated in glass, was difficult to separate completely from SiF_3I. This criticism must apply to any high-temperature route to fluoroiodosilanes.

Both SiF_3I and SiF_2I_2 appear to be normal unassociated liquids. While SiF_3I is thermally stable up to its b.p. (236 K), SiF_2I_2 begins to disproportionate in the liquid phase above *ca.* 270 K. Liquid samples of SiF_3I at 298 K in small sealed tubes suffered less than 10% decomposition after 2 weeks, no doubt because of the high pressure of SiF_4 in the tube.

With water, in the vapour phase, SiF_3I is converted completely and within a few minutes into hexafluorodisiloxane, which itself slowly undergoes base-catalysed disproportionation [12-14] to give solid fluorosiloxanes [equation (2)]. Analogously, SiF_2I_2 is hydrolysed

$$2SiF_3I + H_2O \longrightarrow (SiF_3)_2O + 2HI \xrightarrow{[H_2O]} \frac{1}{x}(SiF_2O)_x + SiF_4 \quad (2)$$

directly to oligomeric and polymeric fluorosiloxanes; the SiF_4 also produced may arise from water-promoted disproportionation of either SiF_2I_2 directly or intermediates such as $SiF_3O(SiF_2O)_nSiF_3$ (derived from SiF_2I_2 and some SiF_3I). These reactions parallel those long known for mono- and di-halogenosilanes.[15]

Reactions of Fluoroiodosilanes with Heavy-metal Compounds.—Reaction (3), with X = H, has proved a valuable route to new silyl derivatives.[1] Generally the reaction proceeds if Y is more electronegative than I; Ag^I behaves similarly to Hg^{II}. In the present study, reaction (3) with X = F has been investigated; some

$$2SiX_3I + HgY_2 \longrightarrow 2SiX_3Y + HgI_2 \quad (3)$$

parallel studies have recently been reported.[10] We find that SiF_3I and SiF_2I_2 react readily with mercury (and in some cases silver) compounds to yield SiF_3– or SiF_2= derivatives, but that these are often of limited thermal stability.

Fluorosilicon-oxygen Compounds.—Mercury(II) oxide reacted vigorously with SiF_3I alone to give SiF_4 and white solids. However, when SiF_3I vapour was diluted with nitrogen, reaction (3) (X = F, Y = O/2) gave

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* SiF_3I and HI alone do not react.

† No doubt because Si–NMe_2 derivatives can act as Lewis bases, albeit feebly.[15]

[11] B. J. Aylett, in 'Preparative Inorganic Reactions,' ed. W. L. Jolly, Interscience, New York, 1965, vol. II.

[12] M. Allan, B. J. Aylett, and I. A. Ellis, *Chem. and Ind.*, 1966, 1417.

[13] J. Goubeau and H. Grosse-Ruyken, *Z. anorg. Chem.*, 1951, **264**, 230.

[14] H. S. Booth and R. S. Osten, *J. Amer. Chem. Soc.*, 1945, **67**, 1092.

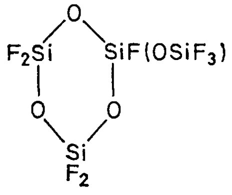
[15] A. Stock, 'Hydrides of Boron and Silicon,' Cornell University Press, Ithaca, N.Y., 1933; H. J. Campbell-Ferguson, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2121.

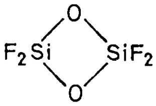
$(SiF_3)_2O$ as the sole volatile product. A similar reaction with SiF_2I_2 was more complex. Disproportionation evidently occurred, since $(SiF_3)_2O$ and a mixture of fluoroiodosilanes were detected. Two presumed fluorosiloxane fractions A (more volatile) and B (less volatile) could be isolated: it is possible these were mixtures, although their i.r. spectra were reproducibly and distinctly different (Table 1).

Although $(SiF_3)_2O$ is reasonably well documented, much less is known of other fluorosiloxanes. Margrave *et al.*[16] have isolated impure $(SiF_3O)_2SiF_2$ as well as $(SiF_3)_2O$ from the hydrolysis of SiF_4, thus confirming and amplifying earlier reports.[13,14,17] Oxidation of SiF_4 in a glow discharge [18] yields $(SiFO_{3/2})_x$, while a microwave discharge acting on SiF_4 in a silica tube leads to linear and cyclic fluorosiloxanes.[19] Recent studies [20] on the reactive species SiF_2 have show that, with SOF_2, it forms $(SiF_3)_2O$, $(SiF_3O)_2SiF_2$, and $Si_2F_5OSiF_3$, while the presence of $SiF_3SiF_2SiF_2OSiF_3$ and cyclic $(SiF_2O)_n$ ($n = 2$ or 3) was inferred from mass spectra.* Oxygen and SiF_2 gave similar products,[20] also polymeric $(SiF_2O)_x$; the polymer gave oligomers $(SiF_2O)_n$ ($n = 2$—5) on heating. It was suggested that cyclic fluorosiloxanes are more stable thermally than the linear species. In all these studies, however, only $(SiF_3)_2O$ could be isolated in a pure state, underlining the practical difficulties involved.

Table 1 lists available i.r. data for $(SiF_3)_2O$ and the fluorosiloxanes reported in refs. 16 and 20, this work, and some related studies. The strong band for $(SiF_3)_2O$ found in this study at 1020 cm^{-1} is considered to be genuine, whereas ref. 16 lists only a moderate band at 1032 cm^{-1}, attributed 'probably to SiF_4'. We assign the bands at 1020 and 837 cm^{-1} to asymmetric and symmetric Si–F stretching modes respectively, noting the resemblance to $(SiF_3)_2NH$ (1005 and 825 cm^{-1}) [21] and $(SiF_3)_2NMe$ (1016 and 822 cm^{-1}).[21]

It appears that while fluorosiloxanes C and D are identical, there are four volatile species distinct from $(SiF_3)_2O$, $(SiF_3O)_2SiF_2$, and $Si_2F_5OSiF_3$, *viz.* A, B, (C + D), and E. We propose that those species giving SiF_4 on decomposition have SiF_3O- groups, while the others do not; either class may also possess $-SiF_2O-$ and $-\overset{|}{Si}FO-$ groups.† Taking also the volatilities and methods of preparation of fractions A—E into account, it seems likely that A and B are predominantly cyclic compounds with some pendant SiF_3O- groups, and have the general formula $[SiF_x(OSiF_3)_{2-x}O]_n$ [*e.g.* (i)], while (C + D) and E are cyclic $(SiF_2O)_n$ species. The molecular weight of E [which is of similar volatility to $(SiF_3)_2O$] corresponds to $n = 2$ (ii), hence for (C + D) probably $n = 3$. The fall in $\nu_{as}(SiOSi)$ observed in passing from $(SiF_3)_2O$ to (C + D) to E is then reasonably interpreted in terms of increasing ring strain as the $\widehat{SiOSi}$ angle decreases from its 'free' value [23] of at least 155° in $(SiF_3)_2O$. Moreover both A and B show two bands in this region, at about 1200 and 1160 cm^{-1}, which may be assigned to SiF_3-O-Si_{ring} and $Si_{ring}-O-Si_{ring}$ stretching vibrations respectively.


(i)


(ii)

Fluorosilicon–Sulphur Species.—In a gas–solid reaction, SiF_3I reacted rapidly with mercury(II) sulphide to give a volatile product (I) presumed to be hexafluorodisilathiane, $(SiF_3)_3S$ [equation (3), X = F, Y = S/2].‡ In contrast, liquid–solid reactions between SiF_3I or SiF_2I_2 and HgS gave a product (II) of similar volatility and molecular weight,§ but with a distinctly different i.r. spectrum, believed to be tetrafluorocyclodisilathiane, $(SiF_2S)_2$. This compound has already been reported [25] from the reaction of SiF_4 and SiS_2 at 1000°; it was said to decompose slowly (14% in 14 days at room temperature), but no i.r. spectrum or chemical properties were given.¶

Both (I) and (II) were unchanged after 20 h in the gas phase at 25°, in glass vessels at *ca.* 5 cm Hg. When (I) was heated at 150° or kept in the liquid phase at room temperature, it gave SiF_4, (II), and a white solid. Under the same conditions, (II) gave a little SiF_4 and white solid only. When (I) was stored in the gas phase in contact with Apiezon grease, about 25% decomposed after 17 h at 25°, yielding H_2S; (II) behaved similarly. These facts are consistent with the earlier conclusions as

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* It seems possible, however, that ions of cyclic species may arise thus: $SiF_3OSiF_2OSiF_3 + e^- \longrightarrow SiF_4 + (SiF_2O)_2^+ + 2e^-$.

† Fluorosilazanes are known to behave similarly: $(SiF_3)_2NMe$ and SiF_3NMe_2 readily lose SiF_4,[12] but cyclic $(SiF_2NMe)_n$ does not.[21,22]

‡ Much more vigorous conditions were needed for the corresponding reaction [24] between $SiCl_3I$ and Ag_2S.

§ Calculated mol. wts. for $(SiF_3)_2S$ and $(SiF_2S)_2$ are very similar to each other and to the experimental values.

¶ The only other previously-reported fluorosilicon–sulphur compounds are $SiHF_3SH$ and SiF_2HSiF_2SH, made from SiF_2 and H_2S; n.m.r. but not i.r. spectra were recorded: K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, 1969, **8**, 2655.

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to the nature of (I) and (II). We may therefore write provisional equations (4) and (5).

$$2\text{HgS} + 2\text{SiF}_2\text{I}_2 \longrightarrow 2\text{HgI} + (\text{SiF}_2\text{S})_2 \qquad (4)$$

$$\begin{array}{ccll} (\text{SiF}_3)_2\text{S} & \longrightarrow & (\text{SiF}_2\text{S})_2 + \text{SiF}_4 & \quad (5\text{a}) \\ (\text{I}) & & \downarrow \ (\text{II}) & \\ & & (\text{SiF}_2\text{S})_x & \quad (5\text{b}) \end{array}$$

Reaction (5), which also evidently occurred during the liquid–solid reaction of SiF_3I and HgS, is analogous to the disproportionation of $(\text{SiH}_3)_2\text{S}$,[26] $(\text{SiF}_3)_2\text{O}$,[12-14] and $(\text{SiF}_3)_2\text{NMe}$.[12] There is some evidence that reaction (5b) is reversible on heating, reminiscent of the ring-chain equilibria of organosiloxanes and organosilathianes;[27] $(\text{SiF}_2\text{O})_x$ (ref. 20 and this work) and $(\text{SiCl}_2\text{S})_x$ (ref. 28) appeared to behave similarly. Both presumed $(\text{SiF}_3)_2\text{S}$ and $(\text{SiF}_2\text{S})_2$ were strongly held by mercury(II) residues from their preparation, in keeping with the well-known Lewis-base behaviour of sulphur(II) compounds towards Hg^{II}.

The Lewis-acid nature of presumed $(\text{SiF}_3)_2\text{S}$ was shown by adding to its vapour in an i.r. gas-cell successive amounts of pyridine vapour. White solid formed immediately; SiF_4 appeared in the gas phase, and increased in concentration while the amount of $(\text{SiF}_3)_2\text{S}$ diminished. Only when all $(\text{SiF}_3)_2\text{S}$ had disappeared was SiF_4 removed (as $\text{SiF}_4,2\text{NC}_5\text{H}_5$). A parallel exists in the reaction of $(\text{SiH}_3)_2\text{S}$ with trimethylamine [approximate equation (6)],[26] but it seems surprising in the present

$$(\text{SiH}_3)_2\text{S} + 0{\cdot}75\ \text{NMe}_3 \longrightarrow \text{SiH}_4 + \frac{1}{n}(\text{SiH}_2\text{S},0{\cdot}75\text{NMe}_3)_n \qquad (6)$$

case that $(\text{SiF}_2\text{S})_x$ is apparently a stronger acid than SiF_4 towards pyridine.

Other, unsuccessful, routes to $(\text{SiF}_3)_2\text{S}$ were explored. SiF_3I and H_2S in the gas phase did not react, while SiF_3NR_2 (R = Me or Et) or $\text{SiF}_4,2\text{NC}_5\text{H}_5$ when heated with H_2S yielded only polymeric Si–S compounds.

Apart from bands in the expected positions for ν_{as} and ν_{s}(SiF) (Table 2), the main feature of the i.r. spectra of $(\text{SiF}_3)_2\text{S}$ and $(\text{SiF}_3\text{S})_2$ was a strong band at 561 and 554 cm^{-1} respectively [*cf.* $(\text{SiH}_3)_2\text{S}$, 515 (ref. 29), 517 (ref. 30); $(\text{SiMe}_3)_2\text{S}$, 488 (ref. 31); $(\text{SiMe}_2\text{S})_2$, 528 cm^{-1} (ref. 32)] assigned in each case to ν_{as}(SiSSi).* The symmetrical mode is expected to be weak, and has not been observed. For $(\text{SiH}_3)_2\text{S}$, the *P–R* branch separation for ν_{as}(SiSSi) is 14·5 cm^{-1}, and hence the bond angle $\text{Si}\hat{\text{S}}\text{Si}$ was inferred[29] to be about 100° (subsequently confirmed[33] by electron diffraction). The corresponding separation in $(\text{SiF}_3)_2\text{S}$ is also 14 cm^{-1}, but it seems unlikely that the pseudo-triatomic approximation used in ref. 29 will be applicable here.

Fluorosilicon Pseudohalides.—SiF_3I readily reacted with mercury(II) cyanide and thiocyanate according to equation (3) (X = F; Y = CN or NCS); the silver(I) salts were also effective, and SiF_3NCS has been independently prepared[10] from AgNCS and SiF_3Br. I.r. absorptions and molecular weights of the products were consistent with those expected for trifluorosilyl cyanide and isothiocyanate. Both compounds appeared to polymerize in the liquid phase or in the gas phase at all but low pressures; † the former compound also lost some SiF_4. It has been reported[35] that SiH_3CN also forms a brown solid on storage, with some loss of SiH_4, while SiH_3NCS shows evidence of association[35] in the liquid phase but does not seem to form a solid polymer (although HNCS does).

The solid derived from SiF_3CN showed i.r. absorptions at 1680 and 1405 cm^{-1} similar to those reported[36] for triazine in-plane ring vibrations, suggesting that tris-(trifluorosilyl)triazine had been formed. Reaction with HCl gave the products expected for SiF_3-ring cleavage, accompanied by some depolymerization. In the case of the solid from SiF_3NCS, it seems likely that self-insertion involving Si–N and N=C bonds (similar to the well-known reaction of PhNCS with Si–N compounds[37]) has led to linear or cyclic $-\text{N}(\text{SiF}_3)\text{C}(\text{S})-$ derivatives. Hydrolysis of both solids $(\text{SiF}_3\text{Y})_x$ gave HY and the expected mixture of fluorosiloxanes and SiF_6^{2-}. A different solid, identified as polymeric $(\text{HCN})_x$, resulted from the reaction of SiF_3I and HCN in the gas phase.

Reaction of SiF_3I *with Nitrogen Bases.*—A slight excess of trimethylamine reacted rapidly with SiF_3I in the gas phase to give the adduct $\text{SiF}_3\text{I},2\text{NMe}_3$. This was almost involatile at room temperature, but very slowly lost SiF_4. As usual, the adduct was more readily hydrolysed than the parent compound. With an excess of chlorine, the adduct underwent rapid displacement of iodine (but not NMe_3) with presumed formation of the corresponding adduct of SiF_3Cl [equation (7)]. Fergus-

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* The authors of ref. 32 assigned the spectrum of $(\text{SiMe}_2\text{S})_2$ on the basis of D_{2h} symmetry (*i.e.* with a planar ring) and hence labelled the band at 528 cm^{-1} as B_{3u}. Additional bands in this region would be expected if the ring were non-planar; in their absence, we tentatively assign $(\text{SiF}_2\text{S})_2$ in a similar way.

† This probably explains why no ν(C≡N) band was observed at the low pressures necessarily used with SiF_3CN; the band is weak in gas-phase spectra of HCN and SiH_3CN.[34]

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son *et al.*[38] have shown that SiF_3Cl can form both 1 : 1 and 1 : 2 adducts with trimethylamine; another report[39]

$$2SiF_3I,2NMe_3 + Cl_2 \longrightarrow 2SiF_3Cl,2NMe_3 + I_2 \quad (7)$$

suggests that SiF_3Br and NMe_3 initially form a 1 : 1 adduct, but it seems likely in this case that disproportionation was complete before an excess of amine had been added.

The i.r. spectrum of $SiF_3I,2NMe_3$ is complex and not readily correlated with that[40] of $SiH_3I,2NMe_3$ (no doubt because of mixing);[41] the only clear feature is that bands in the Si–F stretching region are generally lowered in frequency compared with SiF_3I itself. However, it seems very likely by analogy with the SiH_3I adduct [formulated[42] as $(SiH_3,2NMe_3)^+I^-$] and with $(SiCl_3,2NMe_3)^+ClO_4^-$[43] that $SiF_3I,2NMe_3$ is also ionic, with five-co-ordinate silicon.

A deficit of dimethylamine reacted with SiF_3I in the same way as that reported[39] for SiF_3Br [equation (8)]. With an excess of dimethylamine, the reaction proceeded

$$SiF_3I + 2NHMe_2 \longrightarrow SiF_3NMe_2 + NH_2Me_2I \quad (8)$$

differently: base-catalysed disproportionation removed any free SiF_3NMe_2, and only a little $SiF_2(NMe_2)_2$ was initially detected [$SiF_2(NMe_2)_2$ is a weaker Lewis acid, and less susceptible to disproportionation,[12,39] than SiF_3NMe_2]. The solid product, besides NH_2Me_2I, contained a compound identified by its i.r. spectrum and volatility as $SiF_4,2NHMe_2$.[44] Thus reaction (9) is indicated, followed by further disproportionation of $SiF_2(NMe_2)_2$ during fractionation. Grosse–Ruyken and

$$2SiF_3NMe_2 + 2NHMe_2 \longrightarrow SiF_4,2NHMe_2 + SiF_2(NMe_2)_2 \quad (9)$$

Kleesaat[39] interpreted results of gas titrations in terms of a rather weak 1 : 1 adduct between SiF_3NMe_2 and $NHMe_2$; this is not necessarily inconsistent with the present work, since such an adduct would have been removed by pumping before the i.r. spectrum of the solid was recorded. However, we obtained no evidence for such an adduct (or for any solid adduct from SiF_3NMe_2 and trimethylamine).

Reaction of SiF_3I with ammonia was harder to elucidate, since the chief products were ammonium salts and polymers containing Si, N, F, and H. Only with an excess of SiF_3I was there evidence for a volatile product, with an i.r. spectrum consistent with that expected for SiF_3NH_2. This compound always decomposed during attempted separation and it seems clear that SiF_3-analogues of di- and tri-silylamine, if they exist, will be extremely labile.*

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