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The Dehydrofluorination of Complexes of Silicon Tetrafluoride with Nitrogen- and Oxygen-containing Donor Ligands

A.A.Ennan, L.A.Gavrilova, and V.O.Gel'mbol'dt

Data on the dehydrofluorination of complexes of silicon tetrafluoride with N- and O-donor ligands in the absence of a solvent and in benzene, and on the alcoholysis and hydrolysis of silicon tetrafluoride, have been reviewed. The probable mechanism of dehydrofluorination has been discussed.
The bibliography contains 88 references.

CONTENTS

I. Introduction 843
II. The dehydrofluorination of amine complexes of silicon tetrafluoride in the absence of a solvent and in benzene 843
III. The dehydrofluorination of alcohol complexes of silicon tetrafluoride. The hydrolysis of silicon tetrafluoride 847
IV. The mechanism of the dehydrofluorination of complexes of silicon tetrafluoride 848

I. INTRODUCTION

Earlier reviews[1-5] and a monograph[6] summarised data on the properties and structures of the complexes of silicon tetrafluoride with organic bases, but do not give sufficient information on the dehydrofluorination of these complexes. These processes, however, form the basis for the preparation of various fluoro-organosilicon compounds with covalent Si–N and Si–O bonds, of practical interest (fluorosilylamines, hexafluorodisilazanes, oligomeric and polymeric cyclic and linear fluorosilazanes, and alkoxysilanes). Dehydrofluorination reactions are also of undoubted theoretical interest in the study of the relationship between the type of coordination polyhedron of the mixed-ligand fluorocomplex of silicon and the nature of the ligands present. The pioneers in the study of the dehydrofluorination of complexes of silicon tetrafluoride with alkylamines were the group of English workers in London University headed by Aylett, who published their first papers in the mid-sixties. Their success was largely due to their experience with related silicon–nitrogen monomers and polymers.[7,8]

The present review systematises and summarises the results of studies of the dehydrofluorination of complexes of silicon tetrafluoride with nitrogen- and oxygen-containing donor ligands, published up to and including 1984.

II. THE DEHYDROFLUORINATION OF AMINE COMPLEXES OF SILICON TETRAFLUORIDE IN THE ABSENCE OF A SOLVENT AND IN BENZENE

The high strength of Si–F bonds and the stability of the complexes of silicon tetrafluoride with alkylamines[9] made it necessary to use fairly severe conditions to achieve dehydrofluorination: the complexes, or stoichiometric SiF_4–amine mixtures, were heated for a long time at a comparatively high temperature in the presence of special dehydrofluorinating agents, such as $LiAlH_4$, $NaBH_4$, $NaNH_2$, B_2H_6, LiH, Na, Al, and Mg.[10-13]

Heating the complexes of SiF_4 with secondary or primary amines in the presence of hydrogen fluoride acceptors to 180–220° leads to the removal of one or two molecules of hydrogen fluoride to give tri- and difluorosilylamines or hexafluorodisilazanes:[10,11]

$$SiF_4(R_2NH)_2 \rightarrow R_2NSiF_3 + HF + R_2NH$$
$$SiF_4(R_2NH)_2 \rightarrow (R_2N)_2SiF_2 + 2HF$$
$$2SiF_4(RNH_2)_2 \rightarrow RH(SiF_3)_2 + 2HF + 3RNH_2 \ .$$

The composition of the dehydrofluorination products is determined not only by the number of hydrocarbon groups in the molecules of the amine ligands but also by the characteristics of the dehydrofluorinating agent used. Thus the reaction of silicon tetrafluoride with dimethylamine in the presence of $LiAlH_4$ or B_2H_6 (190–200°) gives dimethylaminotrifluorosilane and bis(dimethylamino)difluorosilane; with Na (25°) or Al (350°), bis(dimethylamino)difluorosilane is obtained; and traces of tris(dimethylamino)fluorosilane $(Me_2N)_3SiF$ are obtained only on prolonged heating (340 h) in the presence of Na (25°). The complexes with ammonia or with primary amines give substituted hexafluorodisilazanes $RN(SiF_3)_2$ (R = H, Me, Et, Ph), unstable aminotrifluorosilanes ($EtNHSiF_3$,[12] $PhNHSiF_3$,[11] or condensed products of the disproportionation of the hexafluorodisilazanes. An increased tendency to form the last compounds was observed for the derivatives $RN(SiF_3)_2$ with R = H, Ph:

$$n\,RN(SiF_3)_2 \begin{cases} \longrightarrow SiF_3NR(SiF_2NR)_{n-1}SiF_3 + (n-1)SiF_4 \\ \longrightarrow (RNSiF_2)_n + n\,SiF_4 \end{cases},$$

The disproportionation of N-alkylhexafluorodisilazanes $RN(SiF_3)_2$ (R = Me, Et) has also been described;[13] the intermediate products $SiF_3NRSiF_2NRSiF_3$ were isolated.

A number of suggestions have been made[11] about the role of different acceptors in the binding of hydrogen fluoride by the dehydrofluorinating agents. Thus $LiAlH_4$ reacts with silicon tetrafluoride and methylamine according to the scheme:

$$4SiF_4 + 2MeNH_2 + LiAlH_4 \rightarrow 2MeN(SiF_3)_2 + LiF + AlF_3 + 4H_2$$

and with secondary amines (R = Me, Et) according to the scheme:

$$(6-2n)SiF_4 + 4R_2NH + LiAlH_4 \rightarrow (6-2n)(R_2N)_nSiF_{4-n} + LiF + AlF_3 + 4H_2 .$$

The thermal decomposition of lithium aluminium hydride in turn is accompanied by the transformations:[14]

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 3H_2 + 2Al$$
$$Li_3AlH_6 \rightarrow 3LiH + {}^3/_2H_2 + Al \ .$$

The LiH and Al formed have an increased reactivity, and can react with amines and SiF_4. The possible reaction of $LiAlH_4$ with amines to give $LiAlH_{4-n}(NR_2)_n$ at increased temperatures is not excluded; under these conditions, the complexes $SiF_4(R_2NH)_2$ can dissociate, and the partial pressure of the amine becomes considerable, and $LiAlH_4$ does not decompose. Dehydrofluorination can evidently take place with the participation of both $LiAlH_4$ and the products of its thermochemical transformations (including organometallic compounds with Li–N[15] and Al–N[11] bonds); however, the contribution of these reactions is not known.

In dehydrofluorination, sodium hydroborate behaves like $LiAlH_4$, but the yield of dehydrofluorination products is slightly lower. The main reaction is complicated by the decomposition of $NaBH_4$ to give borazoles or aminoboranes. When diborane is used as dehydrofluorinating agent, boron trifluoride complexes which are much more stable than the corresponding silicon tetrafluoride derivatives are formed, and the boron trifluoride complexes, for the same reason, are present in the reaction products even in an appreciable excess of SiF_4:

$$6SiF_4 + B_2H_6 + (3n + 2)\,R_nNH_{3-n} \rightarrow 3n\,R_nN(SiF_3)_{3-n} + 6H_2 + 2BF_3 \cdot R_nNH_{3-n}.$$

The complexes of primary amines, depending on the type of hydrocarbon group, either give low yields of silazanes (R = Me) or do not form silicon–nitrogen compounds at all (R = H, Pr, Ph). In the latter case, borazoles are formed.

Aluminium, magnesium, and zinc powders, in contact with gaseous mixtures of SiF_4 and $MeNH_2$ at increased temperatures, can bind HF:

$$M + nHF + MF_n + n/2\,H_2.$$

The intensification of dehydrofluorination using metals at comparatively high temperatures (>300°) is evidently due to the breakdown of the oxide film on the metal surface.

As already noted, sodium under mild conditions reacts extremely slowly according to the scheme:

$$SiF_4 + n\,Me_2NH + n\,Na \rightarrow (Me_2N)_n SiF_{4-n} + n\,NaF + \frac{n}{2}H_2$$

An excess of dimethylamine brings about the disproportionation of the initially formed Me_2NSiF_3 (base catalysis), so that $(Me_2N)_2SiF_2$ predominates in the dehydrofluorination products:

$$2Me_2NSiF_3 \rightarrow (Me_2N)_2SiF_2 + SiF_4$$

The addition of an excess of methylamine to the reaction gives volatile oligomeric silazanes, which tend to lose silicon tetrafluoride to give cyclosilazanes $(MeNSiF_2)_n$.[11]

With increase in temperature (300–400 °C), more extensive thermochemical transformations of the complexes take place to give polymers containing the $-RNSiF_2-$ fragment. A method for synthesising polymeric silicon–nitrogen compounds by the thermal decomposition of adducts or stoichiometric mixtures of SiF_4 with primary or secondary amines in sealed ampoules in the presence of bases such as $NaNH_2$ or $LiAlH_4$ has been patented.[16,17] In a typical example, the thermal decomposition of the complex $SiF_4(MeNH_2)_2$ in the presence of sodamide (350°, 10 h) gives a brown polymer powder:

$$SiF_4(MeNH_2)_2 + 2NaNH_2 \rightarrow 1/n\,(MeNSiF_2)_n + 2NaF + 2NH_3 + MeNH_2.$$

The process can be carried out in two stages: the first stage gives N-methylhexafluorodisilazane (250°, 2 h), which is purified by fractional vacuum distillation and which undergoes further thermal decomposition (100°, 6 h):

$$4SiF_4 + 2MeNH_2 + LiAlH_4 \rightarrow 2MeN(SiF_3)_2 + LiF + AlF_3 + 4H_2$$
$$MeN(SiF_3)_2 \rightarrow SiF_4 + 1/n\,(MeNSiF_2)_n.$$

Selection of the thermal decomposition conditions and the dehydrofluorinating agents makes it possible to vary the mechanical characteristics of the polymeric products from soft to elastic and hard. The polymers with a high molecular mass have a high thermal stability (they do not melt or decompose when heated to 500°), are insoluble in most organic solvents, and are stable to hydrolysis (including the action of aqueous alkali solutions), but decompose in contact with solid alkali.

Published data[10,11,16,17] strengthened the view that in dehydrofluorination it is necessary to use hydrogen fluoride acceptors of basic character. In 1970,[18] however, the ability of silicon tetrafluoride complexes (by themselves or in an excess of SiF_4) to undergo "spontaneous dehydrofluorination" was observed. Similar results were obtained in Ref. 19; heating silicon tetrafluoride with trimethylhydrazine or unsymmetrical dimethylhydrazine gave $Me_2NN(Me)SiF_3$ and $Me_2NNHSiF_3$ respectively. The term "spontaneous dehydrofluorination"[18] (that is dehydrofluorination in the absence of special dehydrofluorinating agents) apparently does not fully reflect the essential features of the processes taking place, since no account is taken of the ability of the complexes to act as HF acceptors:

$$SiF_4(R_nNH_{3-n})_2 + 2HF \rightarrow (R_nNH_{4-n})_2SiF_6.$$

Trifluorosilylamines and hexafluorodisilazanes can be obtained by the thermal decomposition of complexes of silicon tetrafluoride with primary and secondary amines in sealed ampoules;[18,20] the presence of an excess of silicon tetrafluoride leads to an increase in the yield of the desired products. The complexes of secondary amines are converted fairly rapidly (1.5–8 h) into the corresponding trifluorosilylamines, and silicon tetrafluoride in turn combines with the dialkylammonium fluoride formed:

$$SiF_4(R_2NH)_2 \rightleftarrows R_2NSiF_3 + R_2NH_2F$$
$$SiF_4 + 2R_2NH_2F \rightleftarrows (R_2NH_2)_2SiF_6.$$

Experiments with the complexes of diethylamine and pyridine proved that the first reaction is reversible.[20] The thermal decomposition of these compounds in a melt gave the corresponding trifluorosilylamines; the original complexes were formed when the products of each reaction were kept at room temperature for several days.

Table 1. Reaction conditions and yields of products in the thermal decomposition of the complexes of silicon tetrafluoride with secondary amines.[20]

Complex	t, °C	τ*, h	Product	Yield, %
$SiF_4(Me_2NH)_2$ (liquid)	175	1.5	Me_2NSiF_3	52
$SiF_4(Et_2NH)_2$ (solid)	40	21.5	Et_2NSiF_3	10
$SiF_4(Et_2NH)_2$ (liquid)	110–120	4.5	Et_2NSiF_3	100
$SiF_4(Et_2NH)_2$ (gas)	175–190	7.5	—	0
$SiF_4(Pr_2NH)_2$ (solid)	100	3	Pr_2NSiF_3	100
$SiF_4(Bu_2NH)_2$ (solid)	120	3.5	Bu_2NSiF_3	100
$SiF_4(C_4H_8NH)_2$ (liquid)	145	6	$C_4H_8NSiF_3$	1
$SiF_4(C_5H_{10}NH)_2$ (solid)	120	8	$C_5H_{10}NSiF_3$	traces
$SiF_4(C_5H_{10}NH)_2$ (liquid)	175–185	3.8	$C_5H_{10}NSiF_3$	16

*τ is the reaction time.

The data in Table 1 show that the yields of trifluorosilylamines increase with increase in the length of the hydrocarbon groups in the amine molecule, and are very low for derivatives of cyclic amines $(CH_2)_nNSiF_3$ (n = 4, 5).

Unfortunately, an objective estimation of the yield of the dehydrofluorination products is difficult, since the time and temperature conditions for different syntheses vary over wide ranges. No justification has been given for the selection of the conditions for carrying out a given reaction.

A combination of differential thermal analysis, differential thermogravimetric analysis, infrared spectroscopy, and elemental analysis made it possible to refine the dehydrofluorination scheme[21–23] and to establish the temperature ranges for achieving it (Table 2) in the thermal decomposition of the complexes of secondary amines:

$$SiF_4(R_2NH)_2(\text{solid}) \rightarrow SiF_4(R_2NH)_2(\text{liquid}) \rightarrow R_2NSiF_3(\text{gas}) + HF(\text{gas}) + R_2NH(\text{gas, liquid})$$

$$\frac{SiF_4(R_2NH)_2(\text{liquid}) + 2HF(\text{gas}) \rightarrow (R_2NH_2)_2SiF_6(\text{liquid})}{3SiF_4(R_2NH)_2(\text{liquid}) \rightarrow 2R_2NSiF_3(\text{gas}) + (R_2NH_2)_2SiF_6(\text{liquid}) + 2R_2NH(\text{gas})}$$

Table 2. Thermal analysis of the complexes of silicon tetrafluoride with secondary alkylamines.[22,23]

Complex	Endothermic effects		Mass loss, %		Assignment*
	t_0, °C	t_{max}, °C	found	calculated	
$SiF_4(Et_2NH)_2$	200	220	15	0	*a*
	—	255	65	61	*b*
	—	275	100	100	*c*
$SiF_4(Bu_2NH)_2$	165	180	7	0	*a*
	220	250	68	63	*b*
	—	270	98	100	*c*
$SiF_42(C_{10}H_{21})_2NH$	160	180	3	0	*a*
	220	235	28	36	*b*
	—	275	95	100	*c*
$SiF_4(C_5H_{10}NH)_2$	175	210	5	0	*a*
	—	265	56	62	*b*
	—	280	100	100	*c*
$SiF_42(PhCH_3)_2NH$	200	215	3	0	*a*
	235	260	52	40	*b*
	—	285	—	—	*c*
	—	305	100	100	*d*

*a = fusion, b = dehydrofluorination, c = dissociation, d = boiling of the amine.

Thus the silicon tetrafluoride complex itself acts as a dehydrofluorinating agent. The possible use of a silicon tetrafluoride complex as dehydrofluorinating agent was reported earlier.[24]

Table 3. Reaction conditions and yields of products in the thermal decomposition of complexes of silicon tetrafluoride with primary amines.[20]

Complex	t, °C	τ, h	Product	Yield, %
$SiF_4(MeNH_2)_2$(gas)	220	2.5	—	0
$SiF_4(EtNH_2)_2$(gas)	190—200	10	—	0
$SiF_4(PrNH_2)_2$(solid)	200	8.2	$PrN(SiF_3)_2$	3
$SiF_4(PrNH_2)_2$(gas)	190—200	10	—	0
$SiF_4(BuNH_2)_2$(solid)	190—200	8.2	$BuN(SiF_3)_2$	6
SiF_4(i-$BuNH_2)_2$(solid)	190—200	8	i-$BuN(SiF_3)_2$	30
SiF_4(i-$BuNH_2)_2$(liquid)	220—240	24	i-$BuN(SiF_3)_2$	75
SiF_4(t-$BuNH_2)_2$(solid)	190—200	8	t-$BuNHSiF_3$	60
SiF_4(t-$BuNH_2)_2$(liquid)	220—240	24	t-$BuNHSiF_3$	86
SiF_4(t-$BuNH_2)_2$(solid)	180—200	12	—	0

Complexes of primary amines undergo dehydrofluorination in sealed ampoules over a longer period (8–24 h) (Table 3). The process is complicated by the ability of the trifluorosilylamines formed in the first stage to be transformed into the more stable hexafluorodisilazanes:

$$SiF_4(RNH_2)_2 \rightarrow RNHSiF_3 + RNH_3F$$

$$SiF_4 + 2RNHSiF_3 + SiF_4(RNH_2)_2 \rightarrow 2RN(SiF_3)_2 + 2RNH_3F \ .$$

Thermogravimetric data[22,23] (Table 4) give grounds for modifying the scheme for the thermal decomposition of the complexes of primary amines as follows:

$$2SiF_4(RNH_2)_2(\text{solid}) \rightarrow RN(SiF_3)_2(\text{gas}) + 2HF(\text{gas}) + 3RNH_2(\text{gas})$$

$$\frac{SiF_4(RNH_2)_2(\text{solid}) + 2HF(\text{gas}) \rightarrow (RNH_3)_2SiF_6(\text{solid})}{3SiF_4(RNH_2)_2(\text{solid}) \rightarrow RN(SiF_3)_2(\text{gas}) + 3RNH_2(\text{gas}) + (RNH_3)_2SiF_6(\text{solid})} \ .$$

Table 4. Thermal analysis of complexes of silicon tetrafluoride with primary alkylamines.[22,23]

Complex	Endothermic effects		Mass loss, %		Assignment
	t_0, °C	t_{max}, °C	found	calculated	
$SiF_4(EtNH_2)_2$	140	170	53	59	*b*
	250	280	100	100	*c*
$SiF_4(PrNH_2)_2$	150	178	57	61	*b*
	245	280	100	100	*c*
SiF_4(i-$PrNH_2)_2$	120	165	55	61	*b*
	250	270	100	100	*c*
$SiF_4(BuNH_2)_2$	175	195	58	61	*b*
	250	278	100	100	*c*
SiF_4(i-$BuNH_2)_2$	110	145	57	61	*b*
	230	275	100	100	*c*
$SiF_4(C_7H_{15}NH_2)_2$	135	165	59	62	*b*
	245	280	100	100	*c*
$SiF_4(C_8H_{17}NH_2)_2$	140	175	57	62	*b*
	235	280	100	100	*c*
$SiF_4(PhCH_2NH_2)_2$	205	230	56	62	*b*
	260	285	100	100	*c*

The structure of the amine determines not only the yield but also the composition of the dehydrofluorination products.[20] Thus for the complex SiF_4(t-$BuNH_2)_2$ containing the bulky t-butyl group, the reaction is complete with the formation of t-$BuNHSiF_4$, whereas the dehydrofluorination of the complexes $SiF_4(BuNH_2)_2$ and SiF_4(i-$BuNH_2)_2$ gives N-butylhexafluorodisilazanes. The formation of N-alkylhexafluorodisilazanes is represented as the stepwise replacement of the hydrogen atoms on the nitrogen by trifluorosilyl groups. In the thermal decomposition of the complex SiF_4(i-$BuNH_2)_2$ with an excess of SiF_4, the products included, in addition to hexafluorodisilazane, an oligomeric oil formed by the disproportionation of the primary product:

$$\text{i-}BuN(SiF_3)_2 \rightarrow SiF_4 + 1/n\,(\text{i-}BuNSiF_2)_n \ .$$

The prolonged thermal decomposition of the complexes $SiF_4(RNH_2)_2$ (R = H, Me, Bu, Ph) at comparatively high temperatures in a nitrogen atmosphere (Table 5)[25] is accompanied by more extensive dehydrofluorination to give stable solid polymeric products: white $(NSiF)_n$, yellow-brown $(MeNSiF_2)_n$, and dark violet $(PhNSiF_2)_n$. Poly-(n-butyldifluorosilazane) was isolated as a high-boiling (350–400°) oligomeric oil and a white waxy non-volatile powder:

$$2SiF_4(NH_3)_2 \rightarrow NH_4F + (NH_4)_2SiF_6 + 1/n\,(NSiF)_n$$

$$2SiF_4(RNH_2)_2 \rightarrow 2RNH_3F + (RNH_3)_2SiF_6 + 1/n\,(RNSiF_2)_n \ .$$

Polymeric fluorosilazanes remain unchanged when heated in a stream of dry nitrogen to 500°, but they can be hydrolysed by strong alkalis. The reaction of dry oxygen with $(NSiF)_n$ at 500° gives silicon dioxide and an unidentified compound containing nitrogen, oxygen, and fluorine.

Table 5. Reaction conditions and the yield of polymeric products in the thermal decomposition of complexes of silicon tetrafluoride with ammonia and primary amines.[25]

Complex	t, °C	τ, h	Product	Yield, %
$SiF_4(NH_3)_2$	160--170	162	$(NSiF)_n$	21
$SiF_4(NH_3)_2$	290—310	21	$(NSiF)_n$	20
$SiF_4(NH_3)_2$	290—310	44	$(NSiF)_n$	14
$SiF_4(NH_3)_2$	250—280	66	$(NSiF)_n$	18
$SiF_4(MeNH_2)_2$	250—280	84	$(MeNSiF_2)_n$	38
$SiF_4(BuNH_2)_2$	250—280	72	$(BuNSiF_2)_n$	37
$SiF_4(PhNH_2)_2$	250—280	72	$(PhNSiF_2)_n$	37

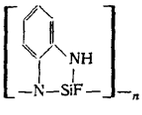
Thermogravimetric, infrared spectroscopic, chemical analysis, and X-ray diffraction data have been used to propose a scheme for the thermal decomposition of the complex $SiF_4(NH_3)_2$ [26] differing from that in Ref. 25. It was shown that the thermal decomposition takes place in stages to give ammonium hexafluorosilicate and a polymer with the composition $(NHSiF_2)_n$ (identified from the similarity of its infrared spectrum to the published spectrum[27]); $HN(SiF_3)_2$ was detected as an intermediate product. Ammonium fluoride was not detected among the thermal decomposition products, as confirmed indirectly in Ref. 28. Thermodynamic calculations for the thermal decomposition of the complex $SiF_4(NH_3)_2$ ($\Delta H^\circ_{decomp} = 2.5$ kJ mole^{-1}, $\Delta S_{decomp} =$ 12 kJ mole^{-1} K^{-1}) show that the extremely high thermal stability of the complexes is due mainly to kinetic factors.[25]

Harris and Rudner[29,30] were the first to show that the complexes of SiF_4 with primary amines can be dehydrofluorinated in the presence of tertiary amines: trimethylamine, triethylamine, or di-isopropylethylamine; trimethylphosphine can also be used.[29] The syntheses were carried out in benzene at room temperature, that is under much milder conditions than dehydrofluorination by thermal decomposition:

$$3SiF_4 + RNH_2 + 2R_3N \rightleftarrows 1/n\,(RNSiF_2)_n + 2\,(R_3NH)\,SiF_5$$

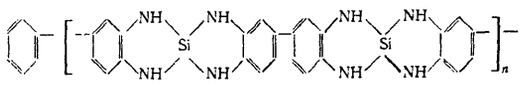
$$(m+1)\,SiF_4 + RNH_2 + 2R_3N \rightleftarrows 1/n\,(RNSiF_2)_n + \frac{2}{m-1}\,(R_3NH)_{m+1}\,Si_nF_{5m+1}^{-m+1)} .$$

The possibility of the process taking place according to one of the above schemes is determined by the nature of the tertiary amine. The dehydrofluorination of the complexes of methylamine, aniline, and 2-amino-4-chlorotoluene gave mixtures of cyclofluorosilazanes ($n = 3$–5). The oligomer $(MeNSiF_2)_n$ could not be converted[30] into a heat- and water-resistant polymeric product of the type described by Aylett and co-workers.[16,17] The dehydrofluorination of complexes of silicon tetrafluoride with multidentate amines (*o*-phenylenediamine, 3,3',4,4'-tetra-aminobiphenyl) in the presence of triethylamine fairly easily yields the silazane polymers



$n = 10$—5000

and



$n = 2$—1000

which react with a side product of the reaction, trimethylammonium fluorosilicate, to give an oil insoluble in benzene.

Somewhat later, the "spontaneous dehydrofluorination" of complexes of SiF_4 with primary and secondary alkylamines under mild conditions was described.[21,23,31,32] Complex formation by silicon tetrafluoride with ethylamine is accompanied by dehydrofluorination even at 25°;[21] in an excess of SiF_4, the dehydrofluorination of $SiF_4(EtNH_2)_2$ is complete:

$$SiF_4 + 2EtNH_2 \rightarrow SiF_4(EtNH_2)_2$$

$$2SiF_4(EtNH_2)_2 + SiF_4 \rightarrow EtN(SiF_3)_2 + (EtNH_3)_2SiF_6 .$$

Similarly, in boiling benzene (80°) in the presence of silicon tetrafluoride, the complex $SiF_4(Et_2NH)_2$ undergoes dehydrofluorination according to the scheme:

$$2SiF_4(Et_2NH)_2 + SiF_4 \rightarrow 2Et_2NSiF_3 + (Et_2NH_2)_2SiF_6 .$$

In general, the dehydrofluorination of complexes $SiF_4(RNH_2)_2$ (R represents a group with the normal structure C_nH_{2n+1}, $n = 2$–4) is favoured by heating the reaction mixture and an excess of silicon tetrafluoride; with increase in the length of the hydrocarbon group in the amine ligands ($n > 4$), the dehydrofluorination takes place at room temperature and at all SiF_4 : amine ratios. Increase in the degree of branching (and hence in the steric effect) of the hydrocarbon group gives the same effect. Thus the dehydrofluorination of the complex $SiF_4(i\text{-}BuNH_2)_2$ takes place at 25° in an excess of the amine. The dehydrofluorination of t-$BuNH_2$ is so vigorous that it is practically impossible to isolate the complex $SiF_4(t\text{-}BuNH_2)_2$ in pure form even with cooling of the reaction medium. Under these conditions, t-butylammonium hexafluorosilicate is precipitated, and t-$BuNHSiF_3$ was identified in the solution by infrared spectroscopy. In boiling benzene, hexafluorodisilazane accumulates in the liquid phase, and is probably produced by the disproportionation of the initially formed t-butyltrifluorosilylamine:

$$2t\text{-}BuNHSiF_3 \rightarrow t\text{-}BuN(SiF_3)_2 + t\text{-}BuNH_2 .$$

As in the thermal decomposition of the complexes of silicon tetrafluoride with the isomeric butylamines,[18,20] the structure of the amine (the steric effect of the substituents on the nitrogen atom, E_N [33]) influences the dehydrofluorination rate and the composition of the reaction products. In particular, the complexes of primary amines with groups having a normal structure, and also isopropylamine and isobutylamine ($E_N = -0.93$ and -1.10 respectively) form hexafluorodisilazanes; with t-butylamine, where the substituent has a greater steric effect ($E_N = -1.54$), trifluorosilylamine is formed. It is reasonable to assume that the complexes $SiF_4(RNH_2)_2$ with ligands having a normal structure, in the first stage of the dehydrofluorination, also give unstable $RNHSiF_3$, which rapidly disproportionate to give more stable hexafluorodisilazanes. The stabilisation of products of t-$BuNHSiF_3$ type is most probably due to the sharp increase in interligand interactions in the fragment  [34] on going from t-$RNHSiF_3$ to t-R_2NSiF_3.

The dehydrofluorination of the complexes $SiF_4(R_2NH)_2$ (R represents a group with a normal structure C_nH_{2n+1}, $n = 2$, 4, 10, 18; R = CH_2Ph; $R_2NH = C_5H_{10}NH$) in benzene solution generally takes place under milder conditions than the corresponding transformations of the complexes of primary amines: at room temperature and in an excess of

SiF_4, or even at molar ratios SiF_4 : amine < 2.[23] As with the complexes of primary amines, increase in the length of the hydrocarbon group R in the ligand molecules intensifies the dehydrofluorination of the complexes $SiF_4(R_2NH)_2$. Thus elemental analysis and infrared spectroscopy show that the reaction of silicon tetrafluoride with dibutylamine in benzene gives a precipitate containing not only $SiF_4(Bu_2NH)$ but also the hexafluorosilicate $(Bu_2NH_2)_2SiF_6$, and in the products of the reaction of SiF_4 with $(C_{10}H_{21})_2NH$ and $(C_{18}H_{37})_2NH$, the corresponding dialkylammonium hexafluorosilicates predominate.

The possibility of carrying out the above reactions of "mild" dehydrofluorination (in contrast to the "severe" thermal decomposition processes) is most likely due to the specific properties of benzene as reaction medium.[35] The energy capacity of the benzene molecules[35] gives their large number the function of a buffer; by absorbing the excess energy, liquid benzene prevents elastic collisions of the reagent molecules and increases the probability of reactive collisions, that is it facilitates the formation of activated complexes.

Finally, mention may be made of the problems of identifying dehydrofluorination products; the novel character of the experimental material and the difficulty of isolating the individual compounds, which tend to undergo hydrolysis and disproportionation, complicate their analysis. Nevertheless, spectroscopic methods have been used successfully to identify monomeric, oligomeric, and polymeric fluorosilyl and fluorosilazane derivatives. The strong bands in the infrared spectra of trifluorosilylamines at about 850 cm^{-1} and 960 cm^{-1} are assigned[20] to the symmetric and antisymmetric $\nu(SiF)$ vibrations, and the splitting of the ν_{as} band into two components (958 cm^{-1} and 980 cm^{-1} for Me_2NSiF_3) is attributed to a decrease in the symmetry of the R_2NSiF_3 molecule as a result of restricted rotation about the Si–N bond. For trifluorosilylamines, the series of fairly strong bands in the range 1000–1300 cm^{-1} (1051, 1172, and 1221 cm^{-1} for Et_2NSiF_3) has been assigned to the CNC fragment stretches.[20,23]

The hexafluorodisilazanes $RN(SiF_3)_2$ give $\nu_{as}(SiF)$ and $\nu_{as}(Si_2N)$ bands in the range 910–1030 cm^{-1}, and $\nu_s(SiF)$ bands in the range 790–845 cm^{-1}.[11,20,23,36]

For linear and cyclic fluorosilazanes $(RNSiF_2)_n$ and related compounds, the most informative range is 800–1060 cm^{-1}, in which the Si–F and Si–N bond vibrations appear. As with the compounds of the previous class, the interpretation of the spectra is complicated by the similarity in the Si–F and Si–N bond stretching frequencies and by overlapping and splitting of the bands. In the spectra of linear fluorosilazanes, the bands have been tentatively assigned as follows: $\nu_{as}(Si_2N)$ 930–980, $\nu_s(Si_2N)$ 600–620 cm^{-1}, $\nu_{as}(SiF)$ and $\nu_s(SiF)$ 800–900 cm^{-1}.[15,17]

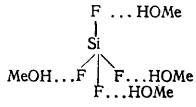
The parameters of the ^1H and ^{19}F NMR spectra of various trifluorosilylamines, and also $MeN(SiF_3)_2$, $(Me_2N)_2SiF_2$, and $(MeNSiF_2)_3$, have been published.[38,39] The values of the constants $J(^{29}Si–^{19}F)$ are highly characteristic for each type of compound containing the groups SiF_3 and $-SiF_2-$ (202–206 Hz and 218–219 Hz respectively).[39]

The parameters of the infrared and ^{19}F NMR spectra of "complex" trialkylammonium fluorosilicates with the stoichiometric composition $(R_3NH)_3Si_2F_{11}$ and $(R_3NH)_4Si_3F_{16}$, which are side products of the dehydrofluorination, have been discussed.[30,40–43] In the absence of structural data, these compounds with anions having the empirical formula $Si_nF_{5n+1}^{-(n+1)}$ (n = 2 or 3) can be regarded as double salts $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$ or as salts of polymeric octahedral ions with bridging fluorine atoms. The spectral parameters of the "complex" fluorosilicates (infrared: bands at 720, 790, and 880 cm^{-1} $\nu(SiF)$ and 450 and 480 cm^{-1} $\delta(SiF)$; ^{19}F NMR: two singlet signals with chemical shifts of 126–128 p.p.m. and 135–136 p.p.m. relative to $CFCl_3$) do not provide any evidence for a polymeric anion structure with Si–F–Si fragments, and are consistent with the alternative structures $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$. The data in Refs. 38–43 illustrate clearly the value of spectroscopic methods in the identification of dehydrofluorination products. The ^{19}F NMR spectra may be particularly useful in the study of the structure and the quantitative estimation of the yields of fluorine-containing products when mixtures of substances difficult to separate are formed.

III. THE DEHYDROFLUORINATION OF ALCOHOL COMPLEXES OF SILICON TETRAFLUORIDE. THE HYDROLYSIS OF SILICON TETRAFLUORIDE

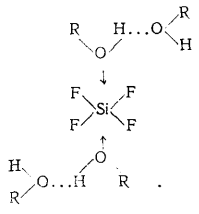
The state of silicon tetrafluoride in solution in aliphatic alcohols, and the question of the possible alcoholysis of SiF_4 in these systems, have been the subject of prolonged discussion.[4] Alcohols, which are bases of medium strength, absorb silicon tetrafluoride to give unstable complexes with the composition $SiF_4.4ROH$.[44,45] This stoichiometry of the complexes was confirmed[46] in detailed experiments on the tensimetric titration of silicon tetrafluoride with methanol and of methanol with silicon tetrafluoride. The reported preparation of complexes with the compositions $SiF_4.6MeOH$ and $SiF_4.8MeOH$[47] is apparently erroneous.

A tetrahedral structure has been proposed[46] for the complex $SiF_4.4MeOH$ with four strong hydrogen bonds between fluorine atoms and methanol molecules:



The spectral characteristics (infrared, ^1H NMR) of the complex given in Ref. 46, however, can be interpreted as providing evidence for alternative structures. Since silicon tetrafluoride shows appreciable Lewis acidity,[3] its reaction with alcohols only by hydrogen bond formation is unlikely. In fact, analysis of the low-temperature ^{19}F NMR spectra of solutions of SiF_4 in alcohols ROH (R = Me, Et, Pr, Bu, i-Bu) showed the presence of the complexes *trans*-$SiF_4.(ROH)_2$, *trans*-$SiF_4(ROH)(H_2O)$, and *trans*-$SiF_4(H_2O)_2$.[48,49] The concentrations of the complexes of the last two types were much lower than that of the purely alcohol complexes; the appearance of hydrated forms in the solutions is attributed to dehydration of the alcohols, catalysed by silicon tetrafluoride.[45,46]

^{19}F NMR established the nature of the coordination of only the inner-sphere alcohol ligands forming the SiF_4O_2 coordination sphere. Later, however, infrared spectroscopic data for saturated solutions of SiF_4 in methanol, ethanol, and isopropyl alcohol[50] confirmed the proposed[48,49] *trans*-octahedral structure of the alcohol complexes. The splitting of the $\nu(CO)$ band into two components in the infrared spectra of alcoholic solutions of silicon tetrafluoride is due to the structural non-equivalence of the alcohol molecules in the complex: two molecules form Si ← O coordinate bonds, and the other two are in the outer sphere. The bonding between the outer-sphere alcohol molecules and the first coordination sphere involves intermolecular hydrogen bonds, where the proton donors are the coordinated alcohol molecules:



It has been claimed[51] that, unlike other silicon tetrahalides, SiF_4 in alcoholic solutions does not undergo alcoholysis. Later measurements[46] of the electrical conductivity of methanol solutions of SiF_4.MeOH showed that the complex is a very weak electrolyte, that is the inner-sphere alcohol molecules show little tendency to lose protons. The reported[52] rapid dehydrofluorination in the SiF_4–MeOH system to give $MeOSiF_3$ and small quantities of $(MeO)_2SiF_2$

$$MeOH+SiF_4\rightarrow MeOSiF_3+HF$$

$$MeOSiF_3+MeOH\rightarrow (MeO)_2SiF_2+HF$$

is somewhat surprising. The reaction conditions were not given,[52] however. Other data[46,48–51] indicate that under ordinary conditions the solvolysis of silicon tetrafluoride in alcohols is not accompanied by appreciable dehydrofluorination, that is the equilibrium

$$SiF_4+n\mathrm{ROH}\rightleftarrows SiF_{4-n}(OR)_n+n\mathrm{HF}$$

is displaced to the left. This is evidently due both to the high strength of the Si–F bond (539–564 kJ mole^{-1}) compared with, for example, the Si–Cl (359–380 kJ mole^{-1})[53] and to the inability of alcohols to form stable oxonium complexes with HF. As already noted, the last factor (that is the presence of a hydrogen fluoride acceptor) has a decisive influence on the course of the dehydrofluorination.

The dehydrofluorination of alcohol complexes of silicon tetrafluoride is readily carried out in the presence of strong bases—ammonia or aliphatic amines. Alcohol complexes of SiF_4 undergo dehydrofluorination under the influence of trialkylamines to give alkoxysilanes and trialkylammonium fluorosilicates:[30]

$$5SiF_4+4\mathrm{ROH}+4R_3N\rightarrow Si(OR)_4+4(R_3NH)SiF_5 .$$

The bulky di-isopropylethylamine forms a stable pentafluorosilicate, and triethylammonium pentafluorosilicate is stable in benzene and acetonitrile solutions, but when the solvent is removed it loses SiF_4 to give the doube salt $(Et_3NH)_2SiF_6.2(Et_3NH)SiF_5$.[43] Similarly, all attempts to isolate trimethylammonium pentafluorosilicate gave a product with the composition $(Me_3NH)_3Si_2F_{11}$, probably the double salt $(Me_3NH)_2SiF_6.(Me_3NH)SiF_5$. To investigate the influence of the nature of the amine on the composition of the dehydrofluorination products, SiF_4–EtOH–(primary, secondary, or tertiary amine) systems were studied.[54] The dehydrofluorination in these systems can be described by the equations:

$$3SiF_4+4R_{3-n}NH_n+4\mathrm{EtOH}\rightarrow Si(OEt)_4+2(R_{3-n}NH_{n+1})_2SiF_6$$

$$11SiF_4+12R_3N+12\mathrm{EtOH}\rightarrow 3Si(OEt)_4+4(R_3NH_3)_3Si_2F_{11} .$$

The reaction takes place according to the first scheme when primary and secondary amines are used ($n = 1, 2$); with tertiary amines ($n = 0$), the reaction takes place according to both schemes.

The behaviour of aliphatic diamines,[55,56] 2,2′-iminodi(ethanol), 2,2′,2″-nitrilotri(ethanol),[57] and highly basic N-containing heterocyclic compounds (imidazole, benzimidazole, and its derivatives)[58] in the dehydrofluorination of alcohol complexes of SiF_4 is analogous to that of aliphatic monoamines.

A reaction related to the dehydrofluorination of alcohol complexes of silicon tetrafluoride is the hydrolysis of SiF_4, usually described[59] by the scheme:

$$2SiF_4+2H_2O\rightarrow SiO_2+SiF_6^{2-}+2H^++2\mathrm{HF} .$$

This is an overall equation, and does not reflect the complex set of equilibria in the SiF_4–H_2O system.[4] In acidic silicon–fluoride solutions, various methods have established the existence of the complex $SiF_4(H_2O)_2$,[60–62] whose formation can be regarded as the primary stage of the dehydrofluorination in the reaction of silicon tetrafluoride with water.

Dehydrofluorination in the SiF_4–ROH–amine and SiF_4–H_2O systems is of interest for the utilisation of silicon tetrafluoride, of which a large tonnage is produced as a waste product in the manufacture of phosphorus fertilisers.[6] According to patents,[63–65] the dehydrofluorination of alcohol complexes takes place according to the scheme:

$$3SiF_4+4\mathrm{ROH}+4NH_3\rightarrow Si(OR)_4+2(NH_4)_2SiF_6 .$$

The yields of tetra-alkoxysilanes are 70–95%. Tetra-alkoxysilanes are used in the synthesis of organosiloxane oligomers and polymers. Silicon tetrafluoride reacts with alcohols in the presence of Zn or Fe;[66] the zinc and iron hexafluorosilicates formed in addition to $Si(OR)_4$ have been proposed for the protection of constructional materials. A method for preparing tetra-alkoxysilanes by the reaction of alcoholic solutions of SiF_4 with alkali and alkaline earth metal sulphides, oxides, carbides, chlorides, carbonates, and cyanides has been patented.[67,68] The reaction is described by the scheme:

$$SiF_4+4\mathrm{ROH}+4MA\rightarrow Si(OR)_4+4MF+4HA ,$$

and is accompanied by the formation of the metal fluoride or hexafluorosilicate and the volatile compound HA, for example H_2S, C_2H_2, etc.

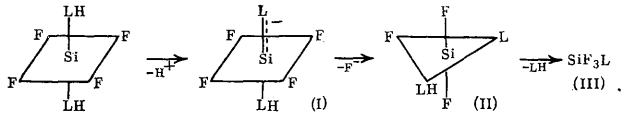
Schemes have now been developed on the industrial scale for utilising silicon tetrafluoride, based on its hydrolysis[69] to give finely dispersed silicon dioxide, H_2SiF_6, and Na_2SiF_6. The last of these is used on an increasing scale to obtain synthetic cryolite and aluminium fluoride. SiF_4 is hydrolysed by water vapour or in the flame obtained by burning hydrogen or a hydrocarbon mixture.[70] Silicon dioxide is separated from the gas mixture on ceramic filters, and the HF is adsorbed on solid sodium fluoride, followed by its thermal regeneration. A patent[71] has proposed a rapid flow method for depositing a film of silicon dioxide on silicon semiconducting devices; a mixture of SiF_4, water vapour, and a carrier gas at temperatures of 700–1000 °C is passed over the semiconducting wafer.

IV. THE MECHANISM OF THE DEHYDROFLUORINATION OF COMPLEXES OF SILICON TETRAFLUORIDE

It has been suggested that the dehydrofluorination of amine and alcohol complexes of silicon tetrafluoride and the hydrolysis of SiF_4 should be regarded from the viewpoint of a single mechanism[4,46,49,72] taking account of the specific nature of the bonds in the fluoro-complexes of non-transition elements. Traditional views of the nature of the bonds in compounds of the type SiF_4X_2 and SiF_4X[1–3] assume that the 3*d* AO of silicon take part in the bonding and have integral populations. As noted in Ref. 73, however, for five-coordinate fluoro-complexes of silicon it is possible to put forward a counter-argument to practically all the evidence for the participation of the 3*d* AO of silicon in bond formation. According to Williams,[74] the exaggeration of the role

of the outer *nd* AO in the chemistry of non-transition elements results from a historically determined tendency to interpret the octahedral structure of complexes taking account of only two-centre two-electron bonds (sp^3d^2 hybridisation of the AO of the central atom), and not delocalised multi-centre bonds. Recently, Musher's alternative hypervalent bond model has been used increasingly to describe the electronic and geometric structure of fluoro-complexes of *p* elements.[75] This model is based on Rundle's postulate[76] that the complex-forming element A with a restricted *ns*, *np* valence basis set, in addition to ordinary two-electron two-centre bonds A–F, also forms three-centre four-electron bonds F–A–F. This model has been used successfully[77–79] to analyse the characteristic features of the structure of silatranes, (aroyloxymethyl)trifluorosilanes with a five-coordinate silicon(IV) atom, and pseudo-octahedral complexes of tin(IV).

By analogy with published data,[79] the structure of the original complexes $SiF_4(LH)_2$ (L = RNH, R_2N, RO, HO) with *trans*-orientation of the ligands can be regarded as based on two three-centre hypervalent fragments F–Si–F with almost pure *p* character in the equatorial plane; the axial fragment LH–Si–LH is formed by two ordinary bonds with the participation of sp_z-hybrid orbitals of the silicon atom. Dehydrofluorination takes place as a result of the protonic dissociation of one inner-sphere ligand, brought about by the base:



The appearance in the coordination polyhedron of silicon of the π-donor acido-ligand L, which requires the participation of the corresponding equatorial p orbital of silicon for the formation of the π-component of the Si–L bond, leads to a decrease in the strength of the Si–F σ-bonds (*cis*-weakening[80,81]). This favours the removal of one fluoride ion from the coordination sphere of the intermediate (I). The five-coordinate intermediate (II) in turn loses the weakly bonded molecular ligand LH and is transformed into the four-coordinate reaction product (III).

The dehydrofluorination reactions examined in the present review illustrate the configurational lability of fluoro-complexes of silicon(IV), that is the ability of the silicon atom to adopt different coordination numbers (CN) from 4 to 6, depending on the nature of the ligands co-existing in the complex. The phenomenon of configurational lability is due to the orbital-deficient nature of the silicon atom as a non-transition element, and is revealed by the ready decrease in the CN of silicon and increase in the multiplicity of the bond with the ligand as a result of its deprotonation. Dehydrofluorination reactions with a decrease in the CN of the central atom are also extremely typical of the analogous fluoro-complexes of phosphorus(V).[82–86] On the other hand, dehydrofluorination reactions are less characteristic of the fluoro-complexes of the heavier analogues of silicon and phosphorus, that is germanium(IV) and antimony(V).[30,87] The relative stabilisation of the six-coordinate fluoro-complexes of these elements is evidently due to the increase in the valence basis set of the central atoms.[49,88]

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Mechnikov Odessa State
University