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Silicon Tetrafluoride Adducts

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The review deals with the compositions, properties, structures, and thermodynamics of silicon tetrafluoride adducts with organic molecules containing electron-donating nitrogen, oxygen, phosphorus, or sulphur atoms. Particular attention has been paid to reactions involving the conversion of the adducts of nitrogen-containing bases into fluorine-containing compounds with a covalent silicon-nitrogen bond. The comparative estimates of the electron-accepting properties of silicon tetrafluoride and other silicon tetrahalides obtained by different workers are discussed.
The bibliography includes 126 references.

CONTENTS

I. Introduction 539
II. Stoichiometry 539
III. Properties 542
IV. Stereochemistry 544
V. Thermodynamics 546

I. INTRODUCTION

In the manufacture of simple superphosphate a considerable amount of fluorine-containing compounds, mainly silicon tetrafluoride, which is the principal potential source of industrial fluorine[1], are released into the gas phase. Evidently this is why there has been no weakening of interest in various aspects of the chemistry of silicon tetrafluoride, which was discovered almost 200 years ago.

Among the numerous aspects of silicon tetrafluoride chemistry, particular attention has been devoted to the study of its complex-forming capacity: silicon tetrafluoride, which is very inert with respect to exchange reactions, enters readily into addition reactions with organic electron-donating molecules (R), forming adducts with the composition $SiF_4 nR$ (n = 1 or 2). Very many original studies have been made on silicon tetrafluoride adducts but in monographs on the chemistry of silicon and fluorine these compounds are either not considered at all or ar discussed very briefly. Even in reviews[2,3] on the chemistry of silicon complexes the problem is given very scanty attention.

This review constitutes a first attempt at a systematic and general account of the available literature data on the composition, properties, and structures of silicon tetrafluoride adducts. Account is taken of almost all the original studies on the chemistry of silicon tetrafluoride adducts published up to 1st June, 1973. In accordance with the definition of an adduct proposed by Cotton and Wilkinson[4], we shall consider solid compounds of definite composition formed by silicon tetrafluoride with organic molecules containing an electron-donating nitrogen, oxygen, phosphorus, or sulphur atom, which have been isolated in a pure state.

II. STOICHIOMETRY

Under normal conditions, silicon tetrafluoride is a colourless gas; its melting point is −90°C.[5] It has been established by electron diffraction[6] that gaseous silicon tetrafluoride has the symmetry of a regular tetrahedron with an Si–F distance of 1.54 ± 0.2 Å. In the ground state tetrahedral silicon tetrafluoride has the electronic configuration $(1a)^2(1t_2)^6(2a)^2(2t_2)^6(1e)^4(3t_2)^6(t_1)^6$.

Calculations have shown[7] that the 3*d* atomic orbitals of the central silicon atom in the silicon tetrafluoride molecule are populated to a large extent, which is evidence for a significant involvement of the orbitals in the formation of chemical bonds. Despite the presence of an electron octet, the silicon atom in the molecule is capable of increasing its coordination number from four to six by utilising two of the five vacant 3*d* orbitals and it has been noted[8] that σ-bonding with participation of the silicon 3*d* orbitals is due mainly to the presence of highly electronegative groups located at this atom. From this standpoint, silicon tetrafluoride should behave as an "ideal" silicon halide for the formation of complexes with electron-donating molecules via σ-bonding with expansion of the silicon octet.

The simplest compound of this type is the adduct $SiF_4.2NH_3$, which is a white powder; it was synthesised at the beginning of the past century[9]. It was established later[10] that, on mixing dry SiF_4 with an excess of dry NH_3, only one compound with the composition $SiF_4.2NH_3$ is formed in the solid phase; it sublimes *in vacuo* at 60–65°C and does not undergo ammonolysis even on heating in an excess of ammonia up to 300°C. In contrast to the tetrafluoride, the remaining silicon tetrahalides form with ammonia compounds having the composition $SiX_4.6NH_3$ (X = Cl, Br, or I).[11]

Aliphatic amines react with silicon tetrafluoride like ammonia. Adducts of silicon tetrafluoride with trimethylamine (Me_3N) have been investigated in greatest detail. It has been reported[12] that silicon tetrafluoride reacts with trimethylamine to form a white solid compound $SiF_4.Me_3N$, whose vapour pressure is 45 mmHg at room temperature and 0.1 mmHg at 78°C. The existence of this compound was subsequently confirmed by Berg[5]. However, Wilkins and Grant[13] discovered two compounds in the SiF_4–Me_3N system: $SiF_4.Me_3N$ and $SiF_4.2Me_3N$†, whose existence has been confirmed from the vapour pressure–composition isotherm and by cryoscopic measurements. Both adducts are white crystalline substances, which sublime congruently at atmospheric pressure and melt congruently at higher pressures. Subsequently Schnell[14] reported that the adduct

†Henceforth we shall refer to these adducts as a 1 : 1 and 1 : 2 type respectively.

$SiF_4.2Me_3N$ is deposited as a dense white precipitate when silicon tetrafluoride is passed into a solution of trimethylamine in petroleum ether. When a benzene solution of trimethylamine is used, the product is the compound $SiF_4.Me_3N$, which is readily soluble in benzene, carbon tetrachloride, petroleum ether, and carbon disulphide, while the 1 : 2 adduct is much less soluble in these solvents.

Subsequent investigations[15] confirmed Schnell's conclusions, but the SiF_4–Me_3N system proved to be the only one so far for which the existence of adducts of two types may be regarded as finally proved. Information has also been published on the synthesis of dimethylamine adducts of the 1 : 2 and 2 : 3 types[16], but subsequently these results were not confirmed. Hagen and Callaway[11] showed that dimethylamine forms with silicon tetrafluoride only an adduct of the 1 : 2 type. Methylamine, whose adduct $SiF_4.2MeNH_2$ has been investigated in fair detail, reacts with silicon tetrafluoride similarly[11,17,18]. The synthesis of the compounds $SiF_4.Am$ and $SiF_4.2Am$ (Am = mono-, di-, and triethylamines and mono-, di-, and tri-ethanolamines) has been reported[19].

Alicyclic amines (piperidine, pyrrolidine[20], and aziridine[21]) also form 1 : 2 adducts with silicon tetrafluoride. The earlier data concerning the synthesis of 1 : 2 adducts with ammonia, methylamine, dimethylamine, trimethylamine, pyrrolidine, and piperidine were confirmed recently[22] and the hitherto unknown compounds $SiF_4.2NH_xR_{3-x}$ ($x = 1$, R = Et, n-Pr, or n-Bu; $x = 2$, R = Et, n-Pr, n-Bu, i-Bu, or t-Bu) and $SiF_4.2NMe_xEt_{3-x}$ (x = 0–2), obtained by the direct interaction of the reactants in the gas or liquid phase, were described. On the basis of these data, the authors[22] concluded that the formation of 1 : 2 adducts is characteristic of the silicon tetrafluoride–aliphatic monoamine systems and data[2] concerning the formation of a 2 : 3 methylamine adduct are explained by the hydrolysis of the 1 : 2 adduct by atmospheric moisture. One must agree with this conclusion, since the range of amines employed by Aylett et al.[22] and other investigators[11,17–21] was sufficiently large to extend the observed behaviour to the entire series of aliphatic amines.

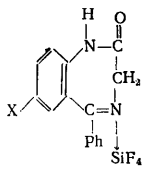
Aliphatic diamines react with silicon tetrafluoride as bidentate ligands, forming 1 : 1 adducts. Ethylenediamine reacts with silicon tetrafluoride in this way, forming a solid white adduct, which sublimes at 225°C and 0.2 mmHg[24]. Adducts of the 1 : 1 type have also been described for piperazine[21] and a number of tetramethylalkylenediamines of the type $Me_2N(CH_2)nNMe_2$, where n = 1, 2, 3, 4, or 6.[25] It is striking that hydrazine reacts with silicon tetrafluoride like the monoamines, forming a white non-hygroscopic compound $SiF_4.2N_2H_4$, which sublimes congruently at 100°C and decomposes on heating above 200°C.[23] Owing to its low molecular dimensions, hydrazine is probably unable to occupy two coordination sites at once about the silicon atom and for this reason behaves as a monodentate ligand. The behaviour of phenylhydrazine, which behaves as a bidentate ligand forming a 1 : 1 adduct with silicon tetrafluoride[21], is therefore incomprehensible. Since there are reliable data concerning the composition of the $SiF_4.2N_2H_4$ adduct[23], which were confirmed by other results[17], we believe that the observed[21] composition of the phenylhydrazine adduct requires an additional test.

Proceeding now to the consideration of the stoichiometry of the adducts of nitrogen-containing heterocycles, we may note that this problem has given rise to the greatest degree of disagreement. An example is provided by the controversy concerning the composition of the silicon tetrafluoride adduct with pyridine (Py). As early as 1888, Comey and Smith[26] described a white compound $SiF_2.2Py$ in powder form, obtained by passing silicon tetrafluoride through a benzene solution of pyridine and noted that it decomposes rapidly. Pyridine is evolved at the same time and a compound close in composition to $2SiF_4.3Py$ is produced. These observations were subsequently confirmed by Wannagat and Schwarz[27], but a final conclusion about the individuality of the compound $2SiF_4.3Py$ was not reached. Thus, taking into account the data[28,29] concerning the existence of the compound $SiF_4.Py$ in the silicon tetrafluoride–pyridine system, three types of adducts have been described altogether. On the other hand, the majority of investigators have reported the existence of only one adduct of the 1 : 2 type[30–33]. In order to resolve the above contradictions, Guertin and Onyszchuk[20] investigated the direct interaction of the two reactants in the gas phase, used for the synthesis a solution of pyridine and ether, and also applied the tensimetric titration method. In all of the above instances they obtained a solid white product of composition $SiF_4.2PY$, which sublimes congruently *in vacuo* at 60–80°C. They emphasised[20] that the method of synthesis of the 2 : 3 [26] and 1 : 1 [28,29] adducts was most carefully repeated, but in all cases only one compound $SiF_4.2Py$ was obtained. On the basis of their results, Guertin and Onyszchuk concluded that other workers who reported the formation of the 1 : 1 and 2 : 3 adducts failed to take into account the loss of pyridine as a result of the hydrolysis of $SiF_4.2Py$. Aylett et al.[22] subsequently agteed with this conclusion. They studied the silicon tetrafluoride–pyridine system in the range of temperatures from 196°C to room temperature and in all cases obtained the compound $SiF_4.2Py$, which melts at 189°C (170–180°C according to Guertin and Onyszchuk[20]) in a sealed capillary. However, Aylett et al.[22] also succeeded in obtaining compounds of other compositions by means of special procedures, but all these proved to be unstable and slowly lost silicon tetrafluoride, forming the adduct $SiF_4.2Py$. Thus we believe that the problem of the stoichiometry of the adducts in the silicon tetrafluoride–pyridine system may be regarded as finally solved in favour of the formation of only one stable compound of the 1 : 2 type.

There was a similar controversy in yet another instance. Thus Comey and Jackson[16] drew attention to the fact that, although pure quinoline does not react with silicon tetrafluoride, when the latter is passed through a benzene solution of quinoline the product is an acicular deposit of $2SiF_4.3C_9H_7N$, which sublimes without decomposition. These results were disproved by Wannagat and Schwarz[27], who pointed out that quinoline does not react with silicon tetrafluoride and the adduct described by Comey and Jackson[16] is quinolinium hydrofluoride formed as a result of the hydrolysis of silicon tetrafluoride when moist quinoline is employed. However, this report was also rejected by Gutmann et al.[21] who reported that, when a benzene solution of quinoline is employed, a 1 : 2 adduct is formed. Subsequently Wannagat et al.[34] reinvestigated the silicon tetrafluoride–quinoline system and confirmed the conclusions of Gutmann et al.[21], stating that their earlier results were erroneous. It is appropriate to mention here also the extremely interesting study by Schnell[35], according to whose results the interaction of isoquinoline with silicon tetrafluoride yields a 1 : 2 adduct. The same investigator reported[14] the existence of the adduct $SiF_4.2\beta\text{-}MeC_9H_4N$, but he presented no data concerning the conditions of the synthesis and properties of this compound.

In general one may assume that the formation of 1 : 2 adducts is characteristic of nitrogen-containing hetero-

cycles as well as of aliphatic and alicyclic amines. Only 2,4-dimethylpyridine and 8-hydroxyquinoline, for which Muetterties[29] described 1 : 1 adducts, constitute an exception to this general rule. The addition of a second amine molecule probably does not occur in this case owing to steric hindrance. The finding that complex polyatomic species, such as 1,4-benzo-2-diazepinium ions, also form 1 : 1 adducts with silicon tetrafluoride[36] supports this hypothesis:



(X = Me, Cl, NO_2) .

Judging from infrared spectroscopic data[36], the tertiary nitrogen atom and not the amide group is responsible for a coordination in these compounds.

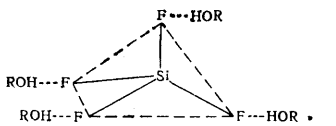
As expected, all the heterocyclic diamines investigated hitherto (2,2′-bipyridyl[21,37,38], 4,4′-bipyridyl[39], and 1,10-phenanthroline[30]) form 1 : 1 adducts with silicon tetrafluoride. Aromatic diamines behave similarly. Among these, the adduct of *o*-phenylenediamine has been most completely investigated. The compound SiF_4.*o*-PDA‡ was obtained for the first time by Gutmann et al.[21], whose finding was subsequently confirmed by Harris and Rudner[40] and also by the authors of the present review[41]. The latter showed that 1 : 1 adducts are also formed by *m*- and *p*-phenylenediamines. All the compounds were obtained by passing gaseous silicon tetrafluoride through benzene solutions of the corresponding diamines. It is therefore surprising that a precipitate is not formed on treating a benzene solution of 3,3′, 4,4′-tetra-aminobiphenyl with silicon tetrafluoride[40], although under the same conditions benzidine, which has a similar structure, gives rise readily to a 1 : 1 adduct[42].

In general the problem of the stoichiometry of the adducts of silicon tetrafluoride with aromatic diamines involves no disagreements, which cannot be said of the adducts of aromatic monoamines, although historically these adducts were in fact the first to attract attention. As early as 1888, Comey and Jackson[16] obtained white or slightly coloured compounds of composition $2SiF_4.3Am$ (Am = aniline, *p*-bromoaniline, *p*-chloroaniline, *p*-toluidine, *o*-toluidine, diphenylamine, and *NN*-dimethylaniline) and described in detail their properties. Later Gutmann et al.[21] showed that, on passing gaseous silicon tetrafluoride through benzene solutions of *p*-chloroaniline, *p*-aminophenol, β-naphthylamine, and *p*-aminobenzoic acid at room temperature, cryptocrystalline 1 : 2 adducts are formed in all cases, but *o*-nitroaniline gives rise to the compound $SiF_4.H_2NC_6H_4NO_2$.

It has also been reported that 1 : 2 adducts are formed by *NN*-dimethylaniline[29], *o*-aminophenol, and 2-amino-4-chlorotoluene[40]. On the other hand, when silicon tetrafluoride was passed through boiling benzene solutions of the initial amines, 1 : 1 adducts of *p*-anisidine[43] and α-naphthylamine[44] were obtained and at room temperature products of the 2 : 3 type were synthesised.

Unfortunately, information about the influence of the conditions of synthesis and of the structure of the initial amine on the composition of the adduct formed in silicon tetrafluoride–aromatic amine systems is extremely limited, so that the general conclusions of Aylett et al.[22] appear to be insufficiently well-founded.

It is noteworthy that the investigations[16,21,29,40,43,44] have been carried out using solutions of the amines in aprotic solvents, mainly benzene, in which silicon tetrafluoride is almost insoluble[45]. The situation is different when aliphatic alcohols, in which silicon tetrafluoride dissolves readily, are employed. Under these conditions, the products[46,47] are the complexes $SiF_4.4ROH$ formed as a result of strong hydrogen bonding[49]§:



We established that in alcoholic solutions aromatic amines (Am) react with silicon tetrafluoride as follows[50-52]:

$$SiF_4 \cdot 4ROH \rightleftarrows SiF_4 + 4ROH , \quad (1)$$

$$SiF_4 + 2Am \rightleftarrows SiF_4 \cdot 2Am , \quad (2)$$

$$SiF_4 \cdot 4ROH + 2Am \rightleftarrows SiF_4 \cdot 2Am + 4ROH , \quad (3)$$

with formation of a precipitate consisting of the adduct $SiF_4.2Am$ (Am = aniline, *p*-aminophenyl difluoromethyl sulphone, *m*- and *p*-nitroanilines, *o*- and *p*-aminobenzoic acids, *m*-trifluoromethylaniline, *p*-aminoazobenzene, *o*-, *m*-, and *p*-anisidines, *o*-, *m*-, and *p*-aminophenols, *p*-bromoaniline, *p*-chloroaniline, *o*-, *m*-, and *p*-toluidines, *p*-phenetidine, diphenylamine, and *N*-ethylaniline). In this case the proportions of the initial reactants influence appreciably the rate of complex formation, which makes it possible to employ the proposed technique in the investigation of the kinetic parameters of the reaction.

As a result of higher steric hindrance in the case of the tertiary amines *NN*-dimethyl-, *NN*-dipropyl-, and *NN*-dibutyl-anilines and *NN*-dimethyl-*p*-toluidine, these amines do not form solid products with silicon tetrafluoride either in alcoholic or benzene solutions[52]. *o*-Aminobenzenethiol behaves analogously, although, as mentioned above, under analogous conditions *o*-aminophenol forms a compound with the composition $SiF_4.2H_2NH_6H_4OH$.[40]

Apparently the only known adduct of silicon tetrafluoride with amides is the compound $SiF_4.2Me_2NCHO$, obtained by passing silicon tetrafluoride through a benzene solution of *NN*-dimethylformamide[53,54]. It has also been reported that acetamide absorbs about one quarter of a mole of silicon tetrafluoride with formation of a white solid product[55], while formamide[54] and urea[16] decompose under the influence of silicon tetrafluoride even at room temperature. In contrast to aliphatic amides, aromatic amides, for example chloroacetamidobenzophenones in which the nitrogen atom is conjugated with the π-electron system of the benzene ring, do not form any solid product with silicon tetrafluoride[36]. In this case steric hindrance cannot be of decisive importance, because chloroacetamidobenzophenones are models of 1,4-benzodiazepin-2-ones, which, as mentioned above, form 1 : 1 adducts with silicon tetrafluoride.

On the basis of the results of early studies[45,55], it was believed for a long time that silicon tetrafluoride is incapable of coordination with molecules containing an electron-donating oxygen atom. Muetterties[29] described

‡PDA = phenylenediamine.

§Borodin et al.[48] investigated the silicon tetrafluoride–ethanol system by ^{19}F NMR, but were unable to reach definite conclusions concerning the structure of the alcohol complex of silicon tetrafluoride.

"weak complexes" of silicon tetrafluoride with acetylacetone and tropolone and noted that these complexes are unstable even at room temperature. It has also been reported that under certain conditions silicon tetrafluoride promotes the dissociation of the C–O bond in epoxide molecules [56], but in this case adducts were not isolated. It has been established only in recent years that silicon tetrafluoride reacts with certain oxygen-containing donors (methylene and trimethylene oxides, tetrahydrofuran, tetrahydropyran, and methyl ether), forming white solid 1 : 2 adducts [57,58], which are stable only at room temperature.

According to Guertin and Onyszchuk [58], the adducts of pyridine, dimethylamine, triphenylphosphine, and tricyclohexylphosphine oxides [59] and dimethyl sulphoxide [60] as well as the dimethylformamide adduct described above should also be classified as compounds in which the oxygen atom is responsible for the formation of the coordinate bond. All these compounds react vigorously with silicon tetrafluoride, forming 1 : 2 adducts, which, like the dimethylformamide adduct, are white cryptocrystalline substances insoluble in ether, toluene, benzene, etc. The compounds are much more stable than the adducts of alicyclic ethers. Thus the adduct of dimethyl sulphoxide sublimes congruently at 107–111 °C, while $SiF_4.2Ph_3PO$ and $SiF_4.2(C_6H_{11})_3PO$ decompose with liberation of the initial reactants at 158–161° and 167 °C respectively. The above differences between the stabilities can probably be explained by the increase of the electron-donating capacity of the oxygen atom as a result of the shift of the electron density of the phosphorus, sulphur, or nitrogen atom linked to oxygen. This explanation is supported by the finding that solid products are not formed in the case of diphenyl sulphoxide [61], in which such conjugation should be much weaker than in dimethyl sulphoxide.

The first attempt to synthesise an adduct with an Si ← P coordinate bond was unsuccessful: trimethylphosphine (Me_3P) does not react with silicon tetrafluoride at 25 °C. [62] Subsequently Beattie and Ozin [15,63] obtained at low temperatures the compounds $SiF_4.Me_3P$ and $SiF_4.2Me_3P$. However, the attempt to obtain triphenylphosphine adducts were unsuccessful even on cooling the reaction mixture to −96 °C. [64]

Together with the adducts of "simple" molecular donors, compounds of silicon tetrafluoride with complex ligands—dicyanobis-(1,10-phenanthroline)iron(II) (A) and dicyanobis-(4,7-diphenyl-1,10-phenanthroline)iron(II) (B)—of compositions $SiF_4.A$, $2SiF_4.A$, and $SiF_4.B$ have been described; they are cryptocrystalline powders, very sensitive to atmospheric moisture [65]. Another example of an adduct of silicon tetrafluoride with a complex ligand is the compound $SiF_4.Pt(PPh_3)_2$, colourless crystals of which have been obtained by treating a benzene solution of tris-(triphenylphosphine)platinum(0) with silicon tetrafluoride at room temperature [64]:

$$(Ph_3P)_3Pt + SiF_4 \rightarrow (Ph_3P)_2Pt \cdot SiF_4 + Ph_3P \ . \qquad (4)$$

III. PROPERTIES

Like the initial silicon tetrafluoride, its adducts are readily hydrolysed by water with the formation of the hexafluorosilicate ion, which is characteristic of silicon tetrafluoride [10,23,34,35]:

$$3(SiF_4 \cdot 2Am) + 2H_2O \rightarrow 2(AmH)_2SiF_6 + SiO_2 + 2Am \ . \qquad (5)$$

The quantitative experiments of Aylett et al. [22] showed that the hydrolysis of $SiF_4.2NH_3$ and $SiF_4.2MeNH_2$ is described by the equation for first-order kinetics and that the rate constants at 25 °C are 1.0×10^{-3} and 1.9×10^{-3} s^{-1} respectively. For other adducts, there are only qualitative data, on the basis of which Aylett et al. [22] arranged the 1 : 2 adducts in the following sequence in terms of their resistance to hydrolysis¶: $NH_3 > MeNH_2 \sim EtNH_2 > > i\text{-}BuNH_2 > Me_2NH \sim Et_2NH > Me_3N \sim EtMe_2N \sim Et_2MeN \sim \sim Et_3N$ and $Me_3N > C_5H_5N$. When the adduct reacts with hydrofluoric acid, only the fluorosilicates of the corresponding base cations are formed, for example those of hydrazinium [23] or pyridinium [20]:

$$SiF_4 \cdot 2Am + 2H_3O^+ + 2F^- \rightarrow \underset{\downarrow -2H_2O}{2AmH^+ + SiF_6^{2-}} + 2H_2O \rightarrow (AmH^+)_2SiF_6^{2-} \ . \qquad (6)$$

More powerful electron pair acceptors (anhydrous hydrogen chloride and boron trifluoride) are probably capable of displacing silicon tetrafluoride quantitatively from its adducts, but such reactions have been described only for $SiF_4.2C_5H_5N$ (Wannagat et al. [66]) and $SiF_4.2M_2H_4$ (Aggarwal and Onyszchuk [23]). At room temperature gaseous boron trichloride displaces silicon tetrafluoride from its adducts with bis(triphenylphosphine)platinum [67]:

$$(Ph_3P)_2Pt \cdot SiF_4 + BCl_3 \rightarrow (Ph_3P)_2Pt \cdot BCl_3 + SiF_4 \ . \qquad (7)$$

The reactions involving the substitution of one amine by another in the adducts have been studied in much greater detail. The first such reaction was reported by Gutmann et al. [21], who found that, on treatment with dry ammonia, the adduct $SiF_4.2(CH_2)_2NH$ decomposes with liberation of free aziridine:

$$SiF_4 \cdot 2(CH_2)_2NH + 2NH_3 \rightarrow 2(CH_2)_2NH + SiF_4 \cdot 2NH_3 \ . \qquad (8)$$

A similar reaction takes place when the hydrazine and pyridine adducts are treated with free ethylenediamine [20]:

$$SiF_4 \cdot 2C_5H_5N + H_2N(CH_2)_2NH_2 \rightarrow SiF_4 \cdot H_2N(CH_2)_2NH_2 + 2C_5H_5N \ . \qquad (9)$$

Aylett et al. [22] found that for the adducts of aliphatic amines the initial bases can be arranged in the following sequence in terms of their relative strengths in the substitution reaction: $NH_3 \gg MeNH_2 > PhNH_2 > Me_2NH > > Me_3N$; $MeNH_2 > Et_3N$. A similar sequence had been established also for aromatic amine adducts. The substitution of one amine by another takes place almost quantitatively via the mechanism

$$SiF_4 \cdot 2Am + 2Am' \rightarrow SiF_4 \cdot 2Am' + 2Am \ , \qquad (10)$$

in the following sequence on treatment of the adduct of a weaker base by a stronger base: benzylamine > *p*-anisidine, *p*-toluidine > aniline > *p*-chloroaniline, *p*-bromoaniline > *p*-aminoazobenzene > *p*-aminobenzoic acid > > *p*-nitroaniline, i.e. the possibility of the substitution reaction is determined in this case by the basicity of the initial amine [68].

Among other known reactions of silicon tetrafluoride adducts, dehydrofluorination is of particular interest as a method of converting the adducts into simple fluorine-containing compounds with a covalent silicon–nitrogen bond: F_3SiNR_2 (fluorosilylamines) and $(F_3Si)_2NR$ (fluorosilazones). Compounds of this kind are formed as a result of the loss of one or two molecules of hydrogen fluoride on heating the adducts of primary or secondary amines to 200 °C in the presence of powerful reducing agents, for

¶Only the base is indicated.

example $LiAlH_4$, B_2H_6, $NaBH_4$, LiH, $NaNH_2$, Al, or Mg [69-71]:

$$SiF_4 \cdot 2HNR_2 \xrightarrow{-HF} F_3SiNR_2 + HNR_2 , \quad (11)$$

$$SiF_4 \cdot 2HNR_2 \xrightarrow{-2HF} F_2Si(NR_2)_2 , \quad (12)$$

$$2(SiF_4 \cdot 2H_2NR) \xrightarrow{-2HF} (F_3Si)_2NR + 3H_2NR . \quad (13)$$

On further heating of the adducts of primary amines to 300–400°C in the presence of the above reducing agents, more far-reaching reactions take place and polymeric compounds of the type $(-F_2SiNR-)_n$ are formed. Their chains are made up of alternating difluorosilyl and substituted imino-groups [70,71]:

$$SiF_4 \cdot 2MeNH_2 + 2NaNH_2 \rightarrow (-F_2SiNMe-) + 2NaF + 2NH_3 + MeNH_2 . \quad (14)$$

Harris and Rudner [40,72,73] found that the adducts of primary amines readily split off hydrogen fluoride on treatment with tertiary amines, for example trimethylamine, triethylamine, or ethyldi-isopropylamine, with formation of cyclosilazanes and the corresponding pentafluorosilicates:

$$RNH_2 + 2R_3N + 3SiF_4 \rightleftarrows \frac{1}{n}(RNSiF_2)_n + 2R_3NH^+SiF_5^- \quad (15)$$

or of the ammonium salts of other fluorosilicic acids, for example with the anion $Si_2F_{11}^-$:

$$RNH_2 + 2R_3N + (m+1)SiF_4 \rightleftarrows \frac{1}{n}(RNSiF_2)_n + \frac{2}{m+1}(R_3NH^+)_{m+1}Si_mF_{(5m+1)}^{-(m+1)} \quad (16)$$

depending on the structure and properties of the tertiary amine used in the reaction. The reaction proceeds in benzene solution in an atmosphere of silicon tetrafluoride at room temperature, under milder conditions than the analogous reactions of the adducts of phosphorus pentafluoride [74] or boron trifluoride [75].

The above equations (15) and (16) provide a fairly general scheme for the reactions occurring in the dehydrofluorination process, whose mechanism has been hardly investigated. One can only presume that in these processes the dehydrofluorinating agent is not the tertiary amine itself but its adduct, since in all the published instances [40,72,73] the fluorosilicates of the corresponding bases and not the hydrofluorides are formed together with cyclosilazanes. This hypothesis is also supported by the employment of the adduct $SiF_4.Me_3N$ as a dehydrofluorinating agent in the synthesis of polyfluoroalkylketens and polyfluoroalkylsulphenes [76]. It has been noted that the fluoride ion liberated as a result of dehydrofluorination is bound firmly to the adduct, as a result of which the process becomes irreversible.

Fluorine-containing silicon–nitrogen compounds can also be obtained by the direct interaction of silicon tetrafluoride with alkali metal amides, for example with sodium bis(trimethylsilyl)amide [78] or lithium alkylamides [79]. It has been believed for a long time that the aminolysis of an Si–F bond in silicon tetrafluoride proceeds only in the presence of dehydrofluorinating agents. At the same time, the aminolysis of an Si–F bond occurs when primary amines act on alkylfluorosilanes [80] and phenylfluorosilanes [81-83], so that a similar reaction is presumably feasible also for silicon tetrafluoride. In this connection particular interest attaches to the report by Aylett et al. [84]†, who found that fluorosilylamines can be obtained by heating the adducts of certain alkylamines without using any dehydrofluorinating agents. It is recommended that the adducts be heated in a sealed tube in the presence of an excess of silicon tetrafluoride at 100–200°C. Trifluorosilylamines are formed from the adducts of secondary amines:

$$SiF_4 \cdot 2R_2NH \rightarrow F_3SiNR_2 + R_2NH_2F \quad (17)$$

and the excess SiF_4 is combined with formation of the corresponding hexafluorosilicate:

$$2R_2NH_2F + SiF_4 \rightarrow (R_2NH_2)_2SiF_6 . \quad (18)$$

Pentafluorosilicates are hardly formed in this reaction. When primary amine adducts are heated, the situation is complicated because of the formation of products with a tendency towards further dehydrofluorination and disproportionation. It has been noted [84] that the yield of the corresponding hexafluorodisilazane $(SiF_3)_2NR$ depends mainly on the structure of the initial amine. Indeed the yields of the hexafluorodisilazanes obtained from the adducts of n-alkylamines (Table 1, Nos. 9–12) are much lower than for the adduct of a secondary amine—isobutylamine (Table 1, Nos. 13 and 14). In conformity with the above finding, when the adduct of t-butylamine is heated, a fairly high yield of trifluorosilylamine is produced via the reaction

$$SiF_4.2t\text{-}BuNH_2 \rightarrow t\text{-}BuNHSiF_3 + t\text{-}BuNH_3F, \quad (19)$$

since the increase of the steric effect of the substituent on passing to the t-butyl group not only increases the yield of the final product but also alters the reaction mechanism.

Table 1. Conditions governing the synthesis and yields of trifluorosilylamines and hexafluorodisilazanes [84].

No.	Adduct pyrolysed	Temp., °C	Time, h	Product	Yield, %
1	$SiF_4.2Et_2NH$(solid)	40	21.5	Et_2NSiF_3	10*
2	$SiF_4.2Et_2NH$(liq.)	110-120	4.5	Et_2NSiF_3	100*
3	$SiF_4.2Et_2NH$(gas)	175-190	7.5	...	0
4	$SiF_4.2n\text{-}Pr_2NH$(solid)	100	3	$n\text{-}Pr_2NSiF_3$	100*
5	$SiF_4.2n\text{-}Bu_2NH$(solid)	120	3.5	$n\text{-}Bu_2NSiF_3$	100*
6	$SiF_4.2C_4H_8NH$(liq.)	145	6	$C_4H_8NSiF_3$	~1*
7	$SiF_4.2C_5H_{10}NH$(solid)	120	8	$C_5H_{10}NSiF_3$	traces
8	$SiF_4.2C_5H_{10}NH$(liq.)	175-185	3.8	$C_5H_{10}NSiF_3$	16*
9	$SiF_4.2EtNH_2$(solid)	190-200	8	...	0
10	$SiF_4.2n\text{-}PrNH_2$(solid)	200	8.2	$n\text{-}PrN(SiF_3)_2$	1**
11	$SiF_4.2n\text{-}PrNH_2$(gas)	190-290	10	...	0
12	$SiF_4.2n\text{-}BuNH_2$(solid)	190-200	8.2	$n\text{-}BuN(SiF_3)_2$	2**
13	$SiF_4.2iso\text{-}BuNH_2$(solid)	190-200	8	$iso\text{-}BuN(SiF_3)_2$	10**
14	$SiF_4.2iso\text{-}BuNH_2$(liq.)	220-240	24	$iso\text{-}BuN(SiF_3)_2$	25**
15	$SiF_4.2t\text{-}BuNH_2$(solid)	190-200	8	$t\text{-}BuNHSiF_3$	60***
16	$SiF_4.2t\text{-}BuNH_2$(liq.)	220-240	24	$t\text{-}BuNHSiF_3$	86***

*Yield calculated by Eqn. (17);
**yield obtained from the conversion of the amine;
***yield calculated by Eqn. (19).

According to a patent [85], the thermal transformations of the adduct $SiF_4.2NH_3$ are particularly far-reaching, so that silicon–nitrogen films are deposited as a result of the pyrolytic decomposition of this compound. On the other hand, tensimetric measurements have shown [22] that the

†These results have been described in detail in a paper [126] published after the present review had been prepared for the press.

adducts of ammonia, methylamine, dimethylamine, trimethylamine, and pyridine dissociate almost completely into the initial reactants on heating:

$$SiF_4.2Am(solid) \rightleftharpoons SiF_4(gas) + 2Am(gas). \quad (20)$$

The diethylamine adduct melts initially and then decomposes via the mechanism

$$SiF_4.2Et_2NH(liq.) \rightleftharpoons SiF_4(gas) + 2Et_2NH(gas). \quad (21)$$

The adducts of high-boiling amines, for example of triethylamine and diethylmethylamine, decompose on heating via a somewhat different mechanism:

$$SiF_4.2Am(solid) \rightleftharpoons SiF_4(gas) + 2Am(liq.), \quad (22)$$

The last mechanism was proposed previously by the present author to describe the thermal reactions of the isomeric phenylenediamine complexes of silicon tetrafluoride [41] and was subsequently proved [68] for a number of adducts of aromatic amines with the composition $SiF_4.2Am$ (Am = *p*-nitroaniline, diphenylamine, *p*-aminobenzoic acid, *m*-aminophenol, and *N*-ethylaniline). It was reported in the same communication that the adducts of aniline, *p*-phenetidine, *p*-toluidine, *p*-chloroaniline, and *p*-anisidine dissociate on heating in accordance with reaction (20). When the adduct is heated, the amine passes to the gas phase together with silicon tetrafluoride and then interacts with the latter, reforming the adduct at lower temperatures; the adduct is deposited on the less heated components of the sublimation tube, so that the overall process resembles sublimation. In general, although the thermal reactions of silicon tetrafluoride adducts have been clearly inadequately investigated, the sum total of the results quoted permits the conclusion that the pathways and extent of these reactions are determined primarily by the structure of the initial amine.

The basicity and the structure of the initial amine are the controlling factors also in the reactions of silicon tetrafluoride adducts with alcohols and phenols. According to patent data [86], when the ammonia adduct is heated in alcohols, complete alcoholysis of silicon tetrafluoride takes place with formation of a fully substituted orthosilicic acid ester and ammonium hexafluorosilicate:

$$3SiF_4 + 4NH_3 + 4ROH \rightarrow Si(OR)_4 + 2(NH_4)_2SiF_6. \quad (23)$$

The esters of n-propyl, isopropyl, n-butyl, isobutyl, and pentyl alcohols were later obtained in the same way [87], but the possibility of employing aniline and pyridine in reaction (23) suggested in the patent quoted above was not subsequently confirmed. As mentioned previously, aniline and its substituted derivatives form 1 : 2 adducts in alcoholic solutions [52]. Silicon tetrafluoride does not undergo alcoholysis in the presence of pyridine either, although the adducts of tertiary aliphatic amines do react with alcohols and phenols in accordance with Eqns. (24) and (25):[40]

$$5SiF_4 + 4R_3N + 4ROH \rightleftarrows Si(OR)_4 + 4R_3NH^+SiF_5^-, \quad (24)$$

$$\frac{5m+1}{m+1}SiF_4 + 4R_3N + 4ROH \rightleftarrows Si(OR)_4 + \frac{4}{m+1}(R_3NH^+)_{m+1}Si_mF_{5m+1}^{-(m+1)}. \quad (25)$$

When triethylamine and ethyldi-isopropylamine are employed, the reaction proceeds with formation of pentafluorosilicic acid salts [Eqn. (24)] and in the case of triethylamine the products are salts containing the anion $Si_2F_{11}^{3-}$ [Eqn. (25)], which had not been described previously.

Dehydrofluorination is not the only method for the conversion of silicon tetrafluoride adducts into fluorine-containing compounds with a covalent silicon–nitrogen bond.

In contrast to silicon tetrafluoride, its adducts react with disilazanes and cyclosilazanes, forming the corresponding fluorosilazanes. This property of the silicon tetrafluoride adduct was established for the first time by Wannagat and Bürger [88], who obtained difluorobis(trimethylsilylamino)silazane on heating to 100°C a suspension of the adduct $SiF_4.2NH_3$ in hexamethyldisilazane:

$$SiF_4 \cdot 2NH_3 + 2(Me_3Si)_2NH \rightarrow (Me_3SiNH)_2SiF_2 + 2Me_3SiF + 2NH_3. \quad (26)$$

The adducts $SiF_4.2MeNH_2$, $SiF_4.2N_2H_4$, and $SiF_4.2C_5H_5N$ react similarly with hexamethyldisilazane, forming a mixture of fluorosilylamines of the type $(Me_3SiNH)_nSiF_{4-n}$, where $n = 1-3$. [18] Special mention should be made of the fact that, although pyridine does not in fact contain reactive hydrogen atoms, its adduct reacts with hexamethyldisilazane via the mechanism

$$SiF_4 \cdot 2C_5H_5N + n(Me_3Si)_2NH \rightarrow (Me_3SiNH)_nSiF_{4-n} + n\,Me_3SiF + 2C_5H_5N. \quad (27)$$

In this case the main product is difluorobis(trimethylsilylamino)silane ($n = 2$) and also small amounts of trifluorotrimethylsilylaminosilane and fluorotris(trimethylsilylamino)silane ($n = 3$). On heating to 120°C, the ammonia adduct reacts also with cyclosilazanes to form fluorosilazanes of the type $FMeSi(NHSiMe_2)_nF$ ($n = 1$, 2, or 3) among which an *SiSi*-difluoropolysilazane $(-F_2SiNH-)_x$ was isolated.

IV. STEREOCHEMISTRY

It has been noted above that monodentate ligands usually form 1 : 2 adducts with silicon tetrafluoride. Presumably the silicon atom passes to the sp^3d^2 hybridised state as a result of the acceptance of two electrons from the electron-donating atoms (for 1 : 1 adducts, the corresponding transition to the sp^3d hybridised state is postulated), i.e. silicon behaves similarly to transition elements. This explanation was put forward for the first time by Piper and Rochow [54], who found that the infrared spectra of the adducts $SiF_4.2NH_3$ and $SiF_4.2Me_2NCHO$ show very intense broad absorption bands with a maximum in the region of 750 cm^{-1}, which were identified as the ν(Si–F) bands of the hexacoordinate silicon atom. The authors [54] reached this conclusion on the basis of the comparison of the absorption bands corresponding to the stretching vibrations of the Si–F bonds in the ifrared spectra of gaseous SiF_4 and the octahedral SiF_6^{2-} anion. In the first case [89] these bands are observed at 1031 and 800 cm^{-1} whereas ν(Si–F) for the hexafluorosilicate ion is usually [90] in the region of 740 cm^{-1}. Subsequent studies showed that the intense absorption in the region of 740 cm^{-1} is characteristic also of other silicon tetrafluoride adducts. On this basis, it has been concluded [2,14,17,21,23,35,60,91] that the compounds investigated have an octahedral structure.

The octahedral structure has now been adopted for hexacoordinate silicon tetrafluoride compounds, but the problem of the relative positions of the ligands in the adduct molecules still remain controversial. From the examination of the octahedral model alone, different stereoisomeric distributions of the ligands are clearly possible (Fig. 1).

Beattie et al. [92] employed the infrared spectroscopic method to solve the problem of the ligand positions. They found by a [normal] coordinate analysis of the vibrations of the *cis*- and *trans*-models of the molecules of adducts of the type $SiF_4.2R$ that the infrared spectrum of the *cis*-form must be more complex: neglecting the possible band splittings, one may expect the presence in the infrared spectrum of three active high-frequency vibrations, while

only one vibration should be active in this region for the highly symmetrical *trans*-form.

Continuing these investigations, Beattie and Webster[30] identified by comparative analysis the absorption bands in the infrared spectra of the adducts $SiF_4.2Py$ and $SiF_4.2Ph_3PO$ and, on the basis of the number of these bands, concluded that both compounds obtained have the *trans*-octahedral structure. Subsequently the configurations of a number of other adducts, which are listed in Table 2, were determined similarly.

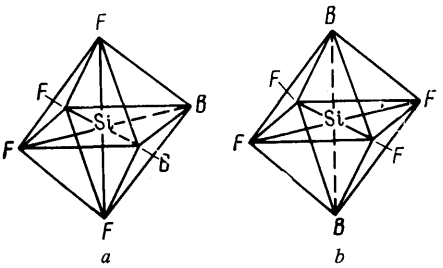


Figure 1. Configuration of hexacoordinate silicon tetrafluoride compounds: *a*) *cis*-octahedron (C_S); *b*) *trans*-octahedron (C_{2v}).

Comparative analysis of the data in Table 2 shows that the probabilities of the formation of the *cis*- and *trans*-configurations of the hexacoordinate silicon tetrafluoride compounds are almost the same. However, one must stipulate that these stereochemical differences have not so far been explained and given a theoretical interpretation.

Table 2. The results of infrared spectroscopic studies of the configurations of octahedral adducts of the type $SiF_4.2R$.

Compound	Configuration	References	Compound	Configuration	References
$SiF_4.2NH_3$	*cis*	17*, 23	$SiF_4.N_2H_4$	*cis*	17, 23
$SiF_4.2ND_3$	*cis*	17	$SiF_4.2C_5H_5N$	*trans*	30, 93
$SiF_4.2MeNH_2$	*cis*	11, 17	$SiF_4.2Me_2NCHO$	*cis*	53
$SiF_4.2Me_2NH$	*cis*	11	$SiF_4.2Ph_3PO$	*trans*	30
$SiF_4.2Me_3N$	*trans*	15	$SiF_4.2Me_2SO$	*trans*	94
$SiF_4.2Me_3P$	*trans*	15			

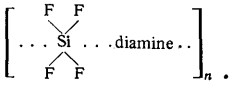
*The authors[17] also investigated the wide-band ^{19}F NMR spectrum of this adduct.

The attempt to estimate theoretically the relative stabilities of the *cis*- and *trans*-isomers of the adducts $SiF_4.2Py$ and $SiCl_4.2Py$ by an approximate parametric calculation of the energies of the $p\pi$–$d\pi$ bonds with additional ligands was understandably greeted with much interest. Rami and Hensen[95] examined two models in which the pyridine ligand is involved via two or one atomic p orbitals of the π type (apart from the atomic σ orbitals forming σ-bonds with the silicon atom), but they were nevertheless unable to predict the stereochemistry of the adducts investigated and noted that the choice of configuration may be determined by other causes. Moreover, as has been pointed out correctly[20,23,93], one cannot solve unambiguously the problem of the configuration of the adduct on the basis of infrared spectroscopic data alone. Even the identification of the absorption bands corresponding to ν(Si–F) is usually difficult owing to the strong absorption by the ligands and the frequency shift due to the degeneracy of the vibrations[20,30]. Moreover, gaseous silicon tetrafluoride reacts with NaCl glasses, as a result of which the intensity of the band in the region of the ν(Si–F) absorption is appreciably enhanced[96]. Analogous difficulties arise also in the analysis of the infrared spectra of other coordination compounds of this type[97].

An X-ray diffraction study has been made so far only of one adduct ($SiF_4.2Py$), the structure of which was determined with the aid of the refined three-dimensional Patterson method and three-dimensional Fourier syntheses[98]. It was shown that the configuration of this adduct is centrosymmetric and *trans*-octahedral, of the type proposed previously[30,93] on the basis of infrared spectroscopic data. Analogous *trans*-octahedral configurations have also been demonstrated for the adducts $SiCl_4.2Py$,[99] $GeCl_4.2Py$,[100] $SnCl_4.2Py$, $SnBr_4.2Py$, $SeCl_4.2Py$, and $TeCl_4.2Py$.[101]

In the case of the diamine adducts reliable data are available only for the silicon tetrafluoride compound with 2,2′-bipyridyl. The ^{19}F NMR spectrum of the adduct $SiF_4.C_{10}H_8N_2$ dissolved in chloroacetonitrile shows at room temperature two equal-intensity triplets, which enabled the authors[37] to conclude that the compound has the *cis*-configuration. A little later the validity of this conclusion was confirmed by X-ray diffraction analysis, which showed that the molecules of the $SiF_4.C_{10}H_8N_2$ adduct are monomeric with a *cis*-disposition of the bipyridyl nitrogen atoms. The Si–N distances are 1.982 and 1.972 Å and the Si–F distances are longer by 0.025 Å for the axial fluorine atoms than for the equatorial atoms. The adducts of 2,2′-bipyridyl with germanium and tin tetrafluorides have an analogous structure[38].

Judging from the infrared spectroscopic data, the adducts of silicon tetrafluoride with 1,10-phenanthroline[30] and ethylenediamine[23] also have the *cis*-configuration. Aggarwal and Onyszchuk[23] noted that additional evidence in support of the *cis*-configuration is provided by the fact that the ethylenediamine molecule is too small to span two coordination sites in the *trans*-configuration. Earlier Gutmann et al.[21] attributed a "polymeric" structure of the following type to the 1 : 1 adducts of diamines:



These workers also assumed the octahedral configuration of the silicon atom but they quote no additional considerations in its support. This structure was later proposed for the isomeric silicon tetrafluoride adducts with phenylenediamine on the basis of a comparison of their thermal stabilities[41]. Evidently the problem of the type of coordination of the primary diamine adducts could be solved successfully with the aid of infrared spectroscopy, but unfortunately such studies have not yet been made.

There is much less information in the literature about the structures of the 1 : 1 adducts formed by silicon tetrafluoride with monodentate ligands. As mentioned above, sp^2d hybridisation has been attributed to the silicon atom in such compounds as a result of the involvement of one of its vacant $3d$ orbitals. Linnett and Mellish[102] showed that

the most probable locations of electrons with identical spins in the $sp^3d_{Z^2}$ configuration are the corners of a trigonal bipyramid. The most probable locations for the $sp^3d_{X^2-Y^2}$ configuration are provided by a tetragonal bipyramid in which the four electrons located in the base are not coplanar with the central nucleus, forming an angle of approximately 105° with the nucleus and with the electron located at the vertex. The trigonal bipyramidal (D_{3h}) and tetragonal pyramidal (C_{4v}) models for a molecule of the type SiX_5 are presented in Fig. 2.

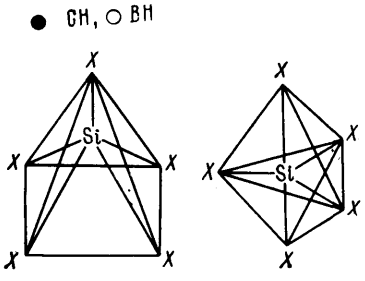


Figure 2. Tetragonal pyramidal and trigonal bipyramidal models for the pentacovalent silicon atom.

Thus, in agreement with theoretical predictions, the pentacoordinate silicon tetrafluoride compounds of the type $SiF_4.R$ can exist in the form of four geometrical isomers which correspond to the symmetry point groups C_{2v}, C_{3v}, C_{4v}, and C_s. According to Nakamoto[103], the numbers of the normal vibrations active in the infrared and Raman spectra of the above configurations are different, so that the configurations can be distinguished on the basis of Raman and infrared spectra (Table 3).

Table 3. The Si–F stretching vibrations in pentacoordinate silicon tetrafluoride compounds.

Bond	Symmetry			
	C_{2v}	C_{3v}	C_{4v}	C_s
$Si-F_{ax}$	A_1+B_{1s}	A_1	. . .	A′
$Si-F_{eq}$	A_1+B_2	A_1+E	$A_1+B_1^*+E$	$2A'+A''$

*The vibration is active only in the Raman spectrum, the remaining vibrations are active in both infrared and Raman spectra.

It has been suggested that the data in Table 4 be used for the identification of the ν(Si–F) absorption bands in the infrared spectra of compounds in which the coordination numbers of the silicon atom are different[64].

On the basis of these concepts, Beattie and Ozin[15] investigated the infrared spectra of the adducts $SiF_4.Me_3N$ and $SiF_4.Me_3P$ in the region of the Si–F stretching vibrations. They found that, judging from the number of absorption bands corresponding to ν(Si–F), the structure of a trigonal bipyramid (C_{3v}) can be attributed to the adducts, but the authors themselves noted that the evidence for this conclusion is inadequate. It is noteworthy that the trigonal bipyramidal structure has been demonstrated for the pentacoordinate compounds $GeCl_4.NMe_3$ (Bilton and Webster[106]) and $CHF_2CF_2SiH_3.NMe_3$ (Cook et al.[107]). This structure has also been proposed for $SiF_4.Pt(PPh_3)_2$.[64]

Table 4. The dependence of the ν(Si–F) frequency on the coordination number of the silicon atom.

Compound	Coord. No.	ν(Si-F), cm^{-1}		References
		antisym.	sym.	
SiF_4	4	1030	...	89
$PhSiF_3$	4	862	970	104
SiF_5^-	5	785	874	105
$SiF_4.Pt(PPh_3)_2$	5	780	875	64
SiF_6^{2-}	6	740	...	90
$SiF_4.2NH_3$	6	725	...	23

V. THERMODYNAMICS

The fundamental thermodynamic parameters for the dissociation of the adducts in accordance with Eqn. (20) have been determined by a number of workers from the results of tensimetric[10,13,22,25,108] and calorimetric[32,109–111] measurements (Table 5).

Table 5. The principal thermodynamic parameters of the dissociation reaction $SiF_4.2Am(solid) \rightleftharpoons SiF_4(gas) + 2Am(gas)$.

Adduct	$\Delta H°$, kcal $mole^{-1}$	$\Delta G°_{298}$, kcal $mole^{-1}$	$\Delta S°_{298}$, kcal $mole^{-1}$ deg^{-1}	References
$SiF_4.2NH_3$ (solid)	52.7±1.9 54.6	19.7±2.3 20.2	111±13 —	22 10, 112
$SiF_4.2MeNH_2$ (solid)	58.1±1.9	20.5±2.5	126±13	22
$SiF_4.2Me_2NH$ (solid)	55.2±0.7 54.8±1.0	15.8±0.9 —	132±5 —	22 25
$SiF_4.2Et_2NH$ (solid) $SiF_4.2Et_2NH$ (liq.)	53.2±1.7 10.7±0.9*	10.3±2.2 5.3±1.3	144±11 18±6	22 22
$SiF_4.2C_5H_5N$ (solid)	51.1±0.7 53.1±0.3 37.1±0.3	16.1±0.9 — —	117±5 — —	22 110 111
$SiF_4.2Me_3N$ (solid)	40.5±0.4 41.5	6.1±0.6 —	116±3 —	22 13
$SiF_4.2Et_2NMe$ (solid)	8.6±0.3** 23.0±0.5	0.3±0.5 −2.0±1.0	28±2 84±5	22 22
$SiF_4.2Et_3N$ (solid)	12.5±0.5** 27.5±0.5	−2.0±0.4 1.6±1.0	49±2 105±5	22 22

*By Eqn. (21).
**By Eqn. (22).

Vandrish and Onyszchuk[110] noted that the following thermodynamic cycle must be considered:

$$SiF_4(gas) + 2Am(soln.) \xrightarrow{\Delta H_1} SiF_4.2Am(solid),$$
$$\downarrow \Delta H_2 \qquad\qquad \uparrow \Delta H_4$$
$$SiF_4(gas) + 2Am(gas) \xrightarrow{\Delta H_3} SiF_4.2Am(gas).$$

Hence

$$\Delta H_3 = \Delta H_1 - 2\Delta H_2 - \Delta H_4 , \qquad (28)$$

where ΔH_1 is the enthalpy of formation of the solid adduct, ΔH_2 the enthalpy of desolvation of the ligand, ΔH_4 the crystal lattice energy determined by the dipole–dipole interaction and intramolecular hydrogen bonds, and ΔH_3 the enthalpy of formation of the adduct in the gaseous phase determined by the energy of the Si ← N donor–acceptor bond and intermolecular hydrogen bonds, if the latter exist.

Bearing in mind that the adducts investigated dissociate fully in the gas phase, Aylett et al.[22] concluded that $\Delta H_3 \ll \Delta H_4$ and that ΔH_4 is determined by the energy of the hydrogen bonds, the existence of which in the adducts of ammonia, hydrazine[17], methylamine[22], and primary aromatic amines[91] has been established by infrared spectroscopy. This conclusion agrees well with the finding that the values of ΔH^0 for the solid adducts of ammonia and primary and secondary amines differ little from one another but are appreciably higher than for tertiary amines (Table 5), although the electron-donating properties of pyridine resemble those of primary amines. The anomalous behaviour of pyridine can be readily explained on Mulliken's hypothesis[114] that the pyridine molecule can function not only as an n-donor but also as a π-donor, although the donor–acceptor bond in the adduct is formed via the nitrogen atom.

Unfortunately there are no methods so far for a direct measurement of ΔH_4. Therefore it is usually assumed that it varies little in a series of adducts with the same structures and similar molecular weights[115]. On the basis of these postulates and taking into account the results of earlier studies[32,109,111], Vandrish and Onyszchuk[110] estimated the relative electron-accepting capacities in the series of silicon and germanium tetrahalides investigated, with respect to pyridine and isoquinoline. They found that, as in the reaction with trimethylamine[108], $GeF_4 > SiF_4$, but were unable to reach any conclusions about the variation of the electron-accepting capacity in the series of silicon tetrahalides.

In view of the fundamental importance of this problem, the question of the reliability of the data merits consideration. Gur'yanov et al.[116] recently made a critical assessment of the methods described in the literature for the determination of the enthalpies of formation ΔH^0_{gas} of donor–acceptor compounds in the gas phase from the experimental heat change with the aid of a thermodynamic cycle. They noted that the hypothesis of the similarity of the crystal lattice energies is not always valid, because of difference between the enthalpies of sublimation in a series of similar compounds may be significant and comparable to ΔH^0_{gas} for these compounds[117]. Therefore, in using the heats of formation of the solid adducts as a measure of their relative stabilities, which has been done in a number of studies[109-111,113,118], very great caution must be exercised.

We believe that the attempt by Hensen and Sarholz[119] to estimate the relative electron-accepting capacities of silicon tetrahalides with respect to pyridine on the basis of the shift of the π–π^* transition band in the ultraviolet spectra of free and coordinated pyridine is even more controversial. These workers measured the ultraviolet absorption spectra of suspensions of many adducts in Nujol and found the halides can be arranged in the following sequence in terms of their electron-accepting capacity: $SiF_4 \simeq BF_3 < SiHCl_3 < GeCl_4 < SiCl_4 < SiBr_4$. On the basis of analogous measurements, the authors[39] later reported that the electron-accepting capacity with respect to 4,4′-bipyridyl decreases in the sequence $BF_3 < SiF_4 < SiBr_4$. It is noteworthy that Hensen and Sarholz's data[119] agree well with the conclusions of Wannagat et al.[111], but are in conflict with the results of later thermochemical measurements by Vandrish and Onyszchuk[110]. The latter workers also noted that a relation between the shifts in the ultraviolet spectra, the π-bonding effect, and the enthalpies of dissociation of adducts of the type $SiX_4.2Py$, formed mainly via σ bonds, has not so far been established, so that the earlier conclusions[39,119] require additional confirmation.

As mentioned above, the silicon tetrafluoride adducts with nitrogen-containing donors are much more stable than those with oxygen-containing donors (cf. Tables 5 and 6).

Table 6. Heats of dissociation of the adducts via the reaction $SiF_4.2ether(solid) \rightleftharpoons SiF_4(gas) + 2ether(gas)$ [58].

Adduct	$\Delta H°$, kcal mole^{-1}	Adduct	$\Delta H°$, kcal mole^{-1}
$SiF_4 \cdot 2(CH_2)_2O$	10.7±0.2	$SiF_4 \cdot 2(CH_2)_5O$	10.9±0.3
$SiF_4 \cdot 2(CH_2)_3O$	13.6±0.1	$SiF_4 \cdot 2Me_2O$	9.0±0.1
$SiF_4 \cdot 2(CH_2)_4O$	11.7±0.1		

Unfortunately in this case too the crystal lattice energies are unknown and the differences between the enthalpies of dissociation are too small to reach final conclusions about the relative electron-donating capacities of the ethers investigated. The most stable of the compounds listed, $SiF_4.2(CH_2)_3O$, does not decompose up to 13.6°C, while the remaining adducts exist only below 0°C.

It is noteworthy that BF_3 and GeF_4 form more stable adducts with ethers than does silicon tetrafluoride. Thus the compounds $GeF_4.2R$ (R = methyl ether, tetrahydropyran, or tetrahydrofuran) remain solid at 25°C, although in the case of epoxy-ethane the adduct decomposes at temperatures above −78°C.[57] The boron trifluoride compounds with Me_2O, $(CH_2)_4O$, and $(CH_2)_5O$ are stable liquids at 25°C, the first two distilling without decomposition[120]. The differences between the electron-accepting capacities of the above fluorides are shown particularly clearly with respect to 1,4-dioxane. Although silicon tetrafluoride does not react with the latter even at −94°C, GeF_4 forms with it a 1 : 1 adduct, which sublimes at 125°C and BF_3 forms 1 : 1 and 1 : 2 adducts, the first of which is a white powder at 25°C and the second a colourless liquid[58]. On the basis of a comparison of the behaviour of SiF_4 and GeF_4 with respect to oxygen-containing donors, Aggarwal and Onyszchuk[121] concluded that germanium tetrafluoride is a more powerful electron acceptor than silicon tetrafluoride. This can be explained by the decrease of $p\pi$–$d\pi$ binding on passing from silicon tetrafluoride to germanium tetrafluoride.

Interesting conclusions concerning the variation of electron accepting capacity in the series of silicon tetrahalides were arrived at on the basis of measurements of the vapour pressures of the adducts of SiF_4, $SiCl_4$, and $SiBr_4$ with trimethylamine and trimethylphosphine. Assuming that of two adducts which have similar structures and molecular weights, the thermodynamically more stable adduct has a lower vapour pressure, Beattie and Ozin[63] obtained the following sequences: $SiF_4 \ll SiCl_4$, $SiBr_4$ with respect to trimethylphosphine, $SiF_4 > SiCl_4 > SiBr_4$ with respect to trimethylamine, and $Me_3P \gg Me_3N$ with respect to $SiCl_4$ and $SiBr_4$. Beattie and Ozin[63]

examined the influence of steric factors, the possibility of the formation of bonds not involving the *d* orbitals, and the differences between the rearrangement energies of silicon tetrafluoride and other silicon tetrahalides, but they were still unable to show which of these factors determined the relative electron-accepting capacities with respect to each of the ligands indicated.

Silicon is a typical element of the class of "hard" acids, for which N ≫ P > As > Sb. At the same time the "hardness" of an acid is a function of the oxidation state of the central atom and depends to an equal extent on the nature of the groups linked to this atom [122]. Evidently the anomalous sequence of changes in the stability of the silicon tetrahalide adducts described above is determined by the differences between the electron-accepting capacities of the silicon atom in silicon tetrafluoride and other silicon tetrahalides ($SiCl_4$ and $SiBr_4$), which makes the study of the electron-accepting capacity of silicon tetrafluoride particularly interesting.

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The review has shown that the individual aspects of the chemistry of silicon tetrafluori have now been investigated in fair detail. This applies primarily to problems of the stoichiometry and thermal transformations of adducts with nitrogen-containing donors. The interaction of silicon tetrafluoride with oxygen-containing donors has been less thoroughly studied, although there are literature data concerning the high catalytic activity of silicon tetrafluoride in the esterification of carboxylic acids [55,123,124] and in the polymerisation of epoxides [56,125]. There are few data on the reactions of silicon tetrafluoride with other donors, for example phosphorus- and sulphur-containing donors, and also with complex ligands, which hinders a comparative assessment of the electron-accepting capacities of silicon tetrafluoride and other silicon tetrahalides. The lack of thermodynamic quantities characterising directly the strength of the Si ← N, Si ← P, etc. coordinate bonds is particularly serious, which precludes any quantitative assessment of the electron-accepting capacity of silicon tetrafluoride. On the whole, we believe that, together with thermodynamic studies, the investigation of the structures of the 1 : 1 adducts of monoamines and diamines and also fo the reactions of the adducts with formation of fluorine-containing silicon–nitrogen compounds, which frequently exhibit enhanced thermal and hydrolytic stabilities [72,88], is especially interesting at the present stage.

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