Tetrafluorosilane–Amine Adducts: Stoicheiometry, Thermodynamics of Dissociation, Stability, and Hydrolysis

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Tetrafluorosilane combines with the following amines under varying conditions to give 1 : 2 adducts: NH_xMe_{3-x} (x = 0—3), NH_xEt_{3-x} (x = 0—2), NH_2R (R = Pr^n, Bu^n, Bu^s, Bu^t, or Ph), NHR_2 (R = Pr^n or Bu^n; R_2 = C_4H_8 or C_5H_{10}), NC_5H_5, NMe_xEt_{3-x} (x = 1 or 2), and with $NHR{\cdot}[CH_2]_n{\cdot}NHR$ (n = 2, R = Me or Et; n = 3, R = Me) to give 1 : 1 adducts. Solid tetrafluorosilane also reacts with a deficit of liquid pyridine to yield an approximately 1 : 1 adduct. Solid–vapour or liquid–vapour equilibria are reported for adducts of NH_xMe_{3-x} (x = 0—3), NH_xEt_{3-x} (x = 0 or 1), $NMeEt_2$, and NC_5H_5; the extent of dissociation in the vapour phase is estimated, and values of ΔH, ΔG, and ΔS for dissociation from the condensed phase are calculated. Competition experiments indicate the order of adduct stability: $NH_3 \geqslant NH_2Me > NH_2Ph > NHMe_2 > NMe_3$. First-order rate constants for hydrolysis of $SiF_4,2NH_3$ and $SiF_4,2NH_2Me$ are $1{\cdot}0 \times 10^{-3}$ and $1{\cdot}9 \times 10^{-3}$ s^{-1} at 25 °C; qualitatively hydrolysis becomes more rapid in the order ammonia < primary amines < secondary amines < tertiary amines. Ease of dissociation and hydrolysis are related to hydrogen-bonding and steric factors.

ALTHOUGH adducts of tetrafluorosilane and ammonia or amines have been known for many years[1] and usually are formed readily at room temperature, surprisingly little is known of their chemistry. In particular, quantitative information about their dissociation, order of stability, and ease of hydrolysis has been sparse and sometimes contradictory.

In the course of our studies of these adducts we have already briefly described some aspects of their behaviour, particularly their dehydro-fluorination.[2] Others, especially Onyszchuk and Wannagat and their co-workers, have published closely related studies:[3-12]

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[1] (*a*) J. Davy, *Phil. Trans.*, 1812, **1**, 352; (*b*) J. L. Gay-Lussac and L. J. Thenard, *Mém. Phys. Chem. Soc., Arcueil*, 1809, **2**, 317; (*c*) A. M. Comey and C. L. Jackson, *Amer. Chem. J.*, 1888, **10**, 165; (*d*) A. M. Comey and F. W. Smith, *ibid.*, p. 294.

[2] (*a*) M. Allan, B. J. Aylett, and I. A. Ellis, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 261; (*b*) U.S.P. 3,234,148/1966; B.P. 1,041,791/1966; (*c*) B. J. Aylett, I. A. Ellis, and C. J. Porritt, *Chem. and Ind.*, 1970, 499.

[3] J. M. Miller and M. Onyszchuk, *J. Chem. Soc.* (*A*), 1967, 1132.

[4] J. P. Guertin and M. Onyszchuk, *Canad. J. Chem.*, 1969, **47**, 1275.

[5] G. Vandrish and M. Onyszchuk, *J. Chem. Soc.* (*A*), 1970, 3327.

[6] G. G. Strathdee, Ph.D. Thesis, McGill University, 1967.

[7] U. Wannagat, H. Bürger, and F. Höfler, *Monatsh.*, 1968, **99**, 1186, 1198.

[8] U. Wannagat, F. Vielberg, H. Voss, K. Hensen, and W. Sarholz, *Monatsh.*, 1969, **100**, 1127.

[9] H. Bürger, W. Sawodny, and F. Höfler, *Monatsh.*, 1965, **96**, 1437.

[10] H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1966, 1508; 1967, 705.

[11] J. J. Harris and B. Rudner, *J. Amer. Chem. Soc.*, 1968, **90**, 515; *J. Inorg. Nuclear Chem.*, 1972, **34**, 75.

[12] (*a*) A. A. Ennan and B. M. Kats, *Zhur. neorg. Khim.*, 1971, **16**, 1462; (*b*) A. P. Hagen and B. W. Callaway, *J. Inorg. Nuclear Chem.*, 1972, **34**, 487.

these will be discussed later. We now report in detail some thermodynamic and other properties.

EXPERIMENTAL

General Techniques.—All volatile reagents were manipulated in a high-vacuum system; solids were handled in a dry-box. Vapour pressures of adducts that were appreciably volatile only above room temperature were measured in Pyrex tensimeters. A bulb of known capacity (0·5—1·0 l) was connected to a spoon-gauge and jacket; the reactants were measured, distilled into the bulb, and there formed the adduct. It was found helpful to interpose a magnetic break-seal between the bulb and spoon-gauge to protect the latter from rapid pressure changes occurring during reaction. The seal was then opened, and the tensimeter heated in an air oven. A high-speed fan ensured that variation of air temperature in the oven was less than ±0·5 °C at 200 °C. At temperatures above *ca.* 110 °C, it was essential to heat the spoon-gauge jacket additionally with a heating tape to *ca.* 30 °C above the oven temperature (see Results section). Temperatures were determined by a thermometer and thermocouples to 0·5 °C. Vapour pressures of adducts below room temperature were measured with a wide-bore mercury manometer and calibrated alcohol thermometers. Measurements of both saturated and unsaturated vapour pressures at various temperatures were thus obtained: from the latter, apparent degrees of dissociation in the gas phase were estimated.

I.r. spectra were obtained on Perkin-Elmer 137, 337, and 521 instruments. Samples were prepared in a dry-box, which in the case of adducts of dimethylamine and trimethylamine contained the amine vapour.

Analysis.—Adducts yielded either tetrafluorosilane when treated with concentrated sulphuric acid or amine when heated with sodium fluoride at 200 °C. Alternatively, volatile amines resulting from alkaline hydrolysis were estimated by acid titration; fluoride in the hydrolysate was titrated against thorium nitrate solution, buffered at pH 4 with alizarin sulphonate as indicator.

Materials.—Tetrafluorosilane was prepared by the pyrolysis of dry barium hexafluorosilicate at 400 °C; the gas was then dried (P_4O_{10}) and fractionated repeatedly through −134 °C. Amines were pure commercial samples, which were fractionated *in vacuo*, dried (CaH_2), then treated with a small amount of tetrafluorosilane and re-fractionated.

System SiF_4–NH_3.—Gas-phase titrations with varying ratios of reactants confirmed a combining ratio (SiF_4 : base) of 1 : 2·0, as did a liquid-phase reaction between SiF_4 (15 mmol) and ammonia (2·8 mmol) in a sealed tube (150 ml) at 100 °C for 1 h. The solid (Found: SiF_4, 75·0; F, 55·2; NH_3, 24·1. Calc. for $SiF_4,2NH_3$: SiF_4, 75·4; F, 55·0; NH_3, 24·4%) gave i.r. spectra (Nujol, KBr disc) in agreement with ref. 9 rather than refs. 13 and 14, although the strong peak at 619 cm^{-1} reported in the first was not observed.

Values of the saturated vapour pressure in the range 313—425 K determined the equation: $\log p/\text{mmHg} = 11{\cdot}23 + 3836/T$ [lit.,[15] $\ln p = 25{\cdot}06 - 8050/(T - 21{\cdot}9)$]. Unsaturated vapour of concentration $3{\cdot}19 \times 10^{-3}$ mol l^{-1} had the following apparent molecular weights at the temperatures shown: 46·6, 213 °C; 46·4, 231 °C, 46·1, 254 °C; 46·1, 283 °C; 46·1, 303 °C; 46·1, 325 °C; and 46·0, 333 °C (Calc. for fully dissociated $SiF_4,2NH_3$: *M*, 46·0).

System SiF_4–NH_2Me.—Both gas-phase titrations and liquid-phase reactions in sealed tubes, with reacting ratios between 1 : 3 and 2 : 1 gave exclusively the 1 : 2·0 adduct (Found: SiF_4, 62·3; NH_2Me, 37·3; F, 45·5. Calc. for $SiF_4,2NH_2Me$: SiF_4, 62·6; NH_2Me, 37·4; F, 45·8%). I.r. absorptions (cm^{-1}) were at: (mull) 3315s, 3270s, 3190m, 3048m, 3024m, 2680vw, 2425vw, 1606s, 1478s, 1339s, 1310s, 1280sh, 1102s, 1068s, 1017s, 970w, 816s, br, 771vs, 703s, 602vs, 474s, 414s; (KBr disc) 3280s, br, 3205s, br, 3155s, 3008s, 2961s, 2912w, 2655w, 2405w, 1604vs, 1468s, 1406w, 1332vs, 1105s, 1068m, 1019s, 921m, 815vs, br, 760vs, 702vs, 608vs, 479s, and 410s. The adduct sublimed almost quantitatively at 80 °C *in vacuo* to give a product with an identical i.r. spectrum. It was essentially insoluble in chloroform, carbon tetrachloride, benzene, carbon disulphide, hexane, acetonitrile, and ether, but reacted with ethanol.

Values of the saturated vapour pressure defined the equation $\log p/\text{mmHg} = 12{\cdot}35 - 4230/T$ in the range 333—395 K. Unsaturated vapour of concentration $1{\cdot}08 \times 10^{-3}$ mol l^{-1} had the following apparent molecular weights: 57·6, 177 °C; 56·3, 198 °C; 56·2, 211 °C; 55·9, 227 °C; 56·3, 249 °C; 56·2, 268 °C; 56·1, 277 °C; and 55·5, 297 °C (Calc for fully dissociated $SiF_4,2NH_2Me$: *M*, 55·3).

System SiF_4–$NHMe_2$.—Both gas- and liquid-phase reactions, with either reagent in excess, gave exclusively the 1 : 2·0 adduct (Found: F, 39·6%. Calc. for $SiF_4,2NHMe_2$: F, 39·0%). I.r. absorptions (mull, cm^{-1}) were at: 3290s, 3000m, 2675w, 2440w, 1480s, 1330s, 1240w, 1140w, 1120m, 1030s, 920s, 805vs, 775vs, and 725w. The adduct sublimed unchanged and quantitatively at 60 °C. It was slightly soluble in an excess of dimethylamine.

Values of the saturated vapour pressure in the range 321—365 K defined the equation: $\log p/\text{mmHg} = 12{\cdot}79 - 4023/T$. Unsaturated vapour of concentration $1{\cdot}39 \times 10^{-3}$ mol l^{-1} had the following apparent molecular weights: 66·5, 162 °C; 66·1, 165 °C; 65·5, 191 °C; 65·6, 209 °C; 65·6, 227 °C; 65·4, 261 °C; and 65·6, 290 °C (Calc. for fully dissociated $SiF_4,2NHMe_2$: *M*, 64·7).

System SiF_4–NMe_3.—The 1 : 2 adduct was prepared by mixing the appropriate amounts of tetrafluorosilane and amine in the tensimeter; the vapour pressure of the product was <0·1 mmHg at −23 °C. At room temperature, the adduct could be handled only in an atmosphere of trimethylamine; under these conditions in a sealed tube, it sublimed readily to give well-formed crystals. Its i.r. spectrum (mull) showed the following bands (cm^{-1}): 3200vw, 1240m, 1100w, 990s, 930w, 880m, 825vs, and 725w.

Saturated vapour pressures in the range 256—313 K determined the equation: $\log p/\text{mmHg} = 11{\cdot}58 - 2952/T$ (lit.,[16] $\log p = 11{\cdot}89 - 3029/T$). Unsaturated vapour of concentration $2{\cdot}00 \times 10^{-3}$ mol l^{-1} had the following apparent molecular weights: 75·7, 63 °C; 75·6, 69 °C; 75·1, 82 °C; 74·8, 94 °C; 74·9, 107 °C; 74·1, 120 °C; 75·0, 128 °C; 74·7, 136 °C; 74·1, 154 °C; 74·5, 160 °C; 74·1, 170 °C; and 74·0, 181 °C, 189 °C, and 196 °C (Calc. for fully dissociated $SiF_4,2NMe_3$: *M*, 74·0).

System SiF_4–$NHEt_2$.—Gas-titration established the reactivity ratio as 1 : 2·0. Values of the saturated vapour

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[13] T. S. Piper and E. G. Rochow, *J. Amer. Chem. Soc.*, 1954, **76**, 4318.

[14] R. C. Aggarwal and M. Onyszchuk, *Canad. J. Chem.*, 1963, **41**, 876.

[15] D. B. Miller and H. H. Sisler, *J. Amer. Chem. Soc.*, 1955, **77**, 4998; 1956, **78**, 6421.

[16] C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 1953, 927.

pressure of the adduct defined the parameters of the equation: $\log p/\text{mmHg} = 13{\cdot}65 - 3877/T$ (312—339 K) and $4{\cdot}47—777/T$ (339—380 K). The adduct melted fairly sharply at 66 °C; above *ca.* 110 °C, time-dependent irreversible increases in pressure were evident.

System SiF$_4$–NEt$_3$.—Aliquot portions of tetrafluorosilane were added to triethylamine held at -64 °C. The pressure, initially zero, rose steadily after more than 0·5 mol SiF$_4$ per mol NEt$_3$ had been added. Removal of excess of tetrafluorosilane left a 1 : 2 adduct, and there was no evidence for 1 : 1 product. Values of saturated vapour pressures in the range 217—245 K determined the equation: $\log p/\text{mmHg} = 13{\cdot}52 - 2730/T$. The vapour (i.r.) was almost entirely tetrafluorosilane, with a trace of triethylamine above -35 °C.

System SiF$_4$–NMeEt$_2$.—This behaved very similarly to the SiF$_4$–NEt$_3$ system to give a 1 : 2 adduct involatile at -64 °C. The vapour-pressure equation (221—264 K) was $\log p/\text{mmHg} = 8{\cdot}97 - 1879/T$. Vapour was mainly tetrafluorosilane (i.r.).

System SiF$_4$–NBu$^n_3$.—No adduct formation at pressures of tetrafluorosilane up to 1 atm and at temperatures down to -96 °C was observed. Tri-n-butylamine was sealed in a tube with tetrafluorosilane (7 atm/25 °C), and a white solid slowly formed at -64 °C. (The m.p. of pure tri-n-butylamine is below -90 °C). When the tube was warmed to room temperature, the solid first disappeared, then the liquid foamed, and finally became clear. This cycle could be repeated indefinitely.

TABLE 1

Hydrolysis of SiF$_4$,2B adducts

B	NH$_3$	NH$_2$Me	NHMe$_2$	NMe$_3$	NH$_2$Et	NHEt$_2$	NEt$_3$	NMeEt$_2$	NMe$_2$Et	NH$_2$Bu^s
Moist air	+ [a]	+	++	+++	+ [c]	++	+++	+++	+++	++ [d]
Water	+ [b]	+ [b]	+++	+++	+	+++	+++	+++	+++	++

[a] Ref. 15. [b] See text. [c] Slight after 3 days. [d] Slight after 5 h.

+ slow; ++ moderate; +++ rapid.

System SiF$_4$–NC$_5$H$_5$.—All experiments in which tetrafluorosilane and pyridine were allowed to warm together slowly from -196 °C to room temperature gave a combining ratio of 1 : 2·0. Also when vapour of one component was injected (in a stream of nitrogen, if necessary) into an excess of the other's vapour, the 1 : 2 adduct was the sole product. When, however, pyridine (0·1708 g, 1·72 mmol) and tetrafluorosilane (0·2165 g, 2·08 mmol) were successively frozen at -196 °C on the inside surface of a narrow tube and then warmed rapidly to room temperature with a hot-air blower, 0·0555 g (0·53 mmol) of tetrafluorosilane could be removed after 30 min, giving a combining ratio of 1 : 1·11. Other similar experiments gave ratios between 1 : 1·07 and 1 : 1·69; when the order of addition of reactants was reversed, a higher ratio (1 : 1·88) was observed. Further, all these adducts slowly lost tetrafluorosilane on pumping (even at -96 °C) to re-form the 1 : 2 adduct.

A sample of SiF$_4$,2NC$_5$H$_5$ (0·58 mmol) was equilibrated with tetrafluorosilane at 30 cmHg pressure at -64 °C, whereupon 0·66 mmol of the latter was sorbed, corresponding to a solid composition of SiF$_4$,0·94NC$_5$H$_5$. At 25 °C under corresponding conditions, none was sorbed.

The vapour-pressure equation of SiF$_4$,2NC$_5$H$_5$ in the range 345—410 K was $\log p/\text{mmHg} = 11{\cdot}72 - 3724/T$. In a sealed tube, the adduct melted at 189 °C (lit.,[4] 170—180 °C) at a calculated pressure of 12·5 atm, and blackened at 195 °C. Unsaturated vapour of concentration $2{\cdot}9 \times 10^{-3}$ mol l^{-1} had the following apparent molecular weights: 89·9, 139 °C; 89·7, 150 °C; 89·4, 158 °C; 88·9, 169 °C; 88·9, 180 °C; 88·3, 197 °C; 87·9, 203 °C; 87·9, 209 °C; 87·8, 216 °C; and 87·7, 221 °C (Calc. for fully dissociated SiF$_4$,2NC$_5$H$_5$: *M*, 87·3).

Base Competition Experiments.—*System* SiF$_4$–NH$_3$–NH$_2$Me. (*a*) When SiF$_4$,2NH$_2$Me (0·825 mmol) and ammonia (1·65 mmol) reacted at room temperature for 1 week in a sealed tube, the volatile products were ammonia (1·25 mmol, 77%) and methylamine (0·37 mmol, 23%). (*b*) Tetrafluorosilane, ammonia, and methylamine were sealed in a tube in the mol ratio 1 : 2 : 2, heated at 250 °C for 1 h, then slowly cooled. The volatile products were ammonia (45%) and methylamine (55%).

System SiF$_4$–NH$_2$Me–NHMe$_2$. When SiF$_4$,2NHMe$_2$ and methylamine reacted in the mole ratio 1 : 2·1 at 20 °C for 1 week, the volatile products were methylamine (13%) and dimethylamine (87%).

System SiF$_4$–NHMe$_2$–NMe$_3$. After 12 h at 20 °C, SiF$_4$,2NMe$_3$ and dimethylamine in the mol ratio 1 : 2·05 gave dimethylamine (11%) and trimethylamine (89%) as volatile products.

Other systems. SiF$_4$,2NH$_2$Me heated with aniline or triethylamine to 200 °C then cooled to room temperature yielded only starting materials. When SiF$_4$,2NHMe$_2$ was sealed with aniline in the mol ratio 1 : 2 for 24 h at room temperature, dimethylamine was quantitatively displaced.

Hydrolysis of Adducts.—(a) SiF$_4$,2NH$_3$. A known quantity of the adduct was added to a large excess of water and the mixture stirred. Successive titrations of aliquot portions gave the following results (time in min; % total fluorine consumed): 12, 44%; 16, 65%; 20, 71%; 28, 95%; and 30, 97%.

(b) SiF$_4$,2NH$_2$Me. Successive titrations as above showed that after 5, 6, 10, and 20 min respectively 44, 50, 68, and 99% of the adduct had reacted. A sample exposed to air for 30 days changed little in weight, but removal of volatile materials and sublimation *in vacuo* showed (i.r.) that methylamine, water, (MeNH$_3$)$_2$SiF$_6$, and silica were present.

(c) *Other cases.* Qualitative assessment of ease of hydrolysis in air was made by exposing powdered samples and noting the growth of i.r. bands due to Si–O and protonated base. Table 1 shows the results, together with ease of attack by water. All the adducts reacted readily with 2N-hydrochloric acid or alkali; concentrated sulphuric acid liberated tetrafluorosilane quantitatively, but smaller amounts were given by concentrated nitric or hydrochloric acids.

RESULTS

Stoicheiometry.—There was no evidence for formation of other than 1 : 2 adducts when tetrafluorosilane reacted with NH_xMe_{3-x} (x = 1—3), NH_xEt_{3-x} (x = 0 or 1), and $NMeEt_2$. Reaction conditions (detailed in the Experimental section) included gas–gas titrations, gas–liquid, liquid–liquid, and liquid–solid systems, with a range of reacting ratios.

In less thorough studies of other systems, the amine and a known excess of tetrafluorosilane were mixed at room temperature, then cooled to −64 or −96 °C after which tetrafluorosilane was pumped away and measured. Observed combining ratios were: (1 : 2) with NH_2R (R = Et, Pr^n, Bu^n, Bu^s, Bu^t, or Ph), NHR_2 (R = Pr^n or Bu^n; R_2 = C_4H_8 or C_5H_{10}), NMe_2Et; and (1 : 1) with the bidentate amines $NHR{\cdot}[CH_2]_n{\cdot}NHR$ (n = 2, R = Me or Et; n = 3, R = Me). Tri-n-butylamine gave a solid adduct of undetermined stoicheiometry only under *ca.* 5 atm pressure of tetrafluorosilane at −64 °C; the report of a 2 : 3 adduct,[17] solid at room temperature, is therefore in error.

Only with the system SiF_4–NC_5H_5 was there evidence for variation in adduct composition. Gas–gas or gas–liquid reactions with either component in excess gave exclusively a 1 : 2 adduct. However when conditions in low-temperature experiments were chosen so that pyridine melted before tetrafluorosilane had appreciably sublimed, the ensuing solid–liquid reaction gave an adduct approaching a 1 : 1 composition. On pumping, the normal 1 : 2 adduct was slowly produced.

Solid $SiF_4,2NC_5H_5$ was shown to sorb tetrafluorosilane at −64 °C (but not at 25 °C) to yield an approximately 1 : 1 species. This lost tetrafluorosilane to re-form the 1 : 2 adduct far more readily than the *ca.* 1 : 1 adduct described in the previous paragraph, and is considered to be a distinct species.

Dissociation Equilibria.—Vapour-density measurements showed that the vapours of adducts from the following bases were almost completely dissociated in the temperature ranges shown: NH_3 (213—333 °C); NH_2Me (198—297 °C); $NHMe_2$ (191—290 °C); NMe_3 (69—196 °C); NC_5H_5 (169—221 °C). Any slight deviations can probably be attributed to non-ideal behaviour of the amine vapour. The i.r. spectrum of the vapour in equilibrium with solid $SiF_4,2NMe_3$ also indicated complete dissociation.

In early experiments,[18] saturated vapour pressure measurements (at lower temperatures than those above) led to an S-shaped plot of pressure against temperature and a corresponding non-linear graph of log (pressure) against $(\text{temperature})^{-1}$. This was initially attributed to the presence of undissociated adduct in the gas phase and the equilibria (1). It became clear later that these effects

$$SiF_4,2B(c) \rightleftharpoons SiF_4,2B(g) \rightleftharpoons SiF_4(g) + 2B(g) \qquad (1)$$

were spurious, being caused by cooling of the spoon-gauge when air was admitted to the tensimeter jacket, and could be eliminated by additional heating of the jacket. Normal plots were then obtained, interpretable in terms of equilibrium (2). Thermodynamic functions are related to the

$$SiF_4,2B(c) \rightleftharpoons SiF_4(g) + 2B(g) \qquad (2)$$

observed pressure p by the expressions: $\ln p = -\Delta H_d^\circ/3RT$ + constant, and: $\Delta G_d^\circ = -3RT\ln p - RT\ln(4/27) = \Delta H_d^\circ - T\Delta S_d^\circ$. Values derived in this way are given in Table 2.

TABLE 2

Derived thermodynamic data for dissociation of adducts of tetrafluorosilane[a]

Adduct	Equilibrium[b]	ΔH° kcal mol^{-1}	ΔG°_{298} kcal mol^{-1}	ΔS°_{298} cal mol^{-1} K^{-1}	Ref.
$SiF_4,2NH_3(c)$	(2)	52·7 ± 1·9	19·7 ± 2·3	111 ± 13	*c*
	(2)	54·6	20·2	—	*d*
$SiF_4,2NH_2Me(c)$	(2)	58·1 ± 1·9	20·5 ± 2·5	126 ± 13	*c*
$SiF_4,2NHMe_2(c)$	(2)	55·2 ± 0·7	15·8 ± 0·9	132 ± 5	*c*
	(2)	54·8 ± 1·0	—	—	*e*
$SiF_4,2NHEt_2(c)$	(2)	53·2 ± 1·7	10·3 ± 2·2	144 ± 11	*c*
(l)	(3)	10·7 ± 0·8	5·3 ± 1·3	18 ± 6	*c*
$SiF_4,2NC_5H_5(c)$	(2)	51·1 ± 0·7	16·1 ± 0·9	117 ± 5	*c*
	(2)	53·1 ± 0·3	—	—	*f*
	(2)	37·1 ± 0·3	—	—	*g*
$SiF_4,2NMe_3(c)$	(2)	40·5 ± 0·4	6·1 ± 0·6	116 ± 3	*c*
	(2)	41·5	—	—	*h*
$SiF_4,2NMeEt_2(c)$	(4)	8·6 ± 0·3	0·3 ± 0·5	28 ± 2	*c*
	(2)	23·0 ± 0·5	−2·0 ± 1·0	84 ± 5	*c, i*
$SiF_4,2NEt_3(c)$	(4)	12·5 ± 0·2	−2·0 ± 0·4	49 ± 2	*c*
	(2)	27·5 ± 0·5	−1·6 ± 1·0	105 ± 5	*c, j*

[a] Errors quoted in this work refer to standard deviations, calculated from least-squares linear regression analysis. [b] Refers to equation in text. [c] This work. [d] Ref. 15. [e] Ref. 6. [f] Ref. 5. [g] Calculated from data in ref. 8. [h] Calculated from data of ref. 16; also for SiF_4,NMe_3, ΔH° = 27·4 kcal mol^{-1}. [i] Calculated from properties of $NMeEt_2$ given by J. L. Copp, *Trans. Faraday Soc.*, 1955, **51**, 1056. [j] Calculated from properties of NEt_3 given by J. L. Copp and D. H. Everett, *Discuss. Faraday Soc.*, 1953, **15**, 174.

In the case of $SiF_4,2NHEt_2$, the plot of log p against $1/T$ showed two linear portions which intersected at a point corresponding to the observed m.p. (66 °C). Despite slow irreversible changes above this temperature,[2c] values of functions corresponding to equilibrium (3) could be derived.*

$$SiF_4,2NHEt_2(l) \rightleftharpoons SiF_4(g) + 2NHEt_2(g) \qquad (3)$$

Adducts with tertiary aliphatic amines have relatively high dissociation pressures at room temperature. When

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* Solubility effects will tend to make p smaller, especially at lower temperatures. Thus the derived value of ΔH_d represents a maximum value.

[17] J. A. Gierut, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 786.

[18] I. A. Ellis, Ph.D. Thesis, University of Aberdeen, 1962.

such amines have high b.p.s, equilibrium (4) is appropriate, the observed vapour pressure is due solely to tetrafluorosilane, and $\ln p = \Delta H_d{}^\circ/RT +$ constant. The composition of the vapour phase showed this to be reasonably appropriate for triethylamine, and rather less so for

$$SiF_4,2B(c) \rightleftharpoons SiF_4(g) + 2B(l) \qquad (4)$$

N-methyldiethylamine, but trimethylamine was best described by equilibrium (2).

Competition Experiments.—At room temperature, there was slow and nearly complete displacement of dimethylamine by methylamine or aniline, and of trimethylamine by dimethylamine. Ammonia and $SiF_4,2NH_2Me$ gave an indecisive result because of very slow reaction, but after the components had been heated together and then cooled to room temperature, the solid comprised $SiF_4,2NH_3$ (55%) and $SiF_4,2NH_2Me$ (45%). Neither aniline nor triethylamine displaced methylamine under these conditions. The orders of base strength are therefore: $NH_3 \geqslant NH_2Me > NH_2Ph > NHMe_2 > NMe_3$; $NH_2Me > NEt_3$.

Hydrolysis.—Quantitative experiments with $SiF_4,2NH_3$ and $SiF_4,2NH_2Me$ showed that first-order kinetics were reasonably well obeyed up to about 75% reaction; the respective rate constants were $1{\cdot}0 \times 10^{-3}$ and $1{\cdot}9 \times 10^{-3}$ s^{-1} at 25 °C. Qualitatively the order was extended to: $NH_3 < NH_2Me \sim NH_2Et < NH_2Bu^s < NHMe_2 \sim NHEt_2 < NMe_3 \sim NMe_2Et \sim NMeEt_2 \sim NEt_3$ and $NC_5H_5 < NMe_3$. In all cases, equation (5) appeared to be obeyed.

$$3SiF_4,2B + 2H_2O \longrightarrow 2(BH)_2SiF_6 + SiO_2 + 2B \qquad (5)$$

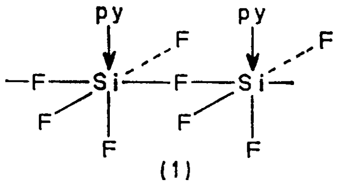
It was shown for $SiF_4,2NH_2Me$ in air that the expected weight gain was almost exactly offset by loss of methylamine; this effect may well have led earlier workers to underestimate the extent of hydrolysis.

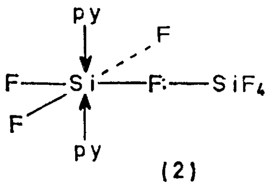
I.r. Spectra.—Detailed studies of $SiF_4,2NH_2Me$ revealed considerable differences between mull and disc spectra, particularly in the region 3000—3500 cm^{-1}. Our findings are in general agreement with those of Bürger *et al.*,[9] apart from medium bands at 745 and 1504 cm^{-1} that we did observe, and a strong band at 1310 cm^{-1} we find in mull spectra. Wider discrepancies are shown, however, from the KBr disc spectra reported in ref. 12*b*.

DISCUSSION

The normal combining ratio for adducts of tetrafluorosilane with unidentate amines is 1 : 2. Early reports of other ratios must often be discounted because precautions against hydrolysis were inadequate.[19] The present work confirms this ratio in the case of ammonia,[1,9,15,20] methylamine,[6,7,9,12b,21] dimethylamine,[1c,6,12b,21] trimethylamine,[16,22] pyrrolidine,[4] piperidine,[4] pyridine [4,10,23,24] and aniline [1c,11,12a] and reports it in the new examples of NH_xR_{3-x} ($x = 2$, R = Et, Pr^n, Bu^n, Bu^s, or Bu^t; $x = 1$, R = Et, Pr^n, or Bu^n) and NMe_xEt_{3-x} ($x = 0$—2). *X*-Ray evidence shows $SiF_4,2NC_5H_5$ to be a *trans*-octahedral molecular complex,[25] and it seems likely that all the above complexes are similarly octahedral; on the basis of vibrational spectra, it has been persuasively argued that those of ammonia [9] and methylamine [9] are *cis* and that of trimethylamine [26] is *trans*, although similar predictions in other cases have not always been fulfilled.[27]

The 1 : 1 adduct SiF_4,NMe_3 is well-authenticated,[16,22,28] but reports [23] of a similar pyridine adduct have not been confirmed.[4,10] A recent claim [12a] to have prepared SiF_4,NH_2Ph is less than convincing, but repeated vacuum sublimation of $SiF_4,2ND_3$ produced a solid [9] of approximate composition $SiF_4,1{\cdot}5ND_3$. Under the special conditions wherein liquid pyridine reacts with solid tetrafluorosilane, we now believe an adduct of limiting 1 : 1 composition can be made, which changes into the 1 : 2 adduct below room temperature. When the incipient fluorine-bridging in solid tetrafluorosilane is borne in mind,[30] where each Si–F bond is directed towards another silicon atom, it seems possible that (1)


(1)


(2)

represents the adduct's structure.* Electron donation by pyridine would strengthen fluorine's bonding ability; nevertheless, fluorine linked to silicon will not be so basic as F^-, which can displace pyridine from tetrafluorosilane, and any free pyridine subsequently produced by dissociation will therefore break the bridges and form discrete 1 : 2 units.

The approximately 1 : 1 adduct formed at low temperatures between tetrafluorosilane and $SiF_4,2NC_5H_5$ is thought to be similar to the adducts formed between boron trifluoride and BF_3,NC_5H_5 (ref. 31) or BF_4^- (ref. 32). Again, the added electron density of the system as a whole enhances the electron-donor power of fluorine (2). It seems reasonable that this should occur in a case where the steric requirements of the base and the dipolar and/or hydrogen-bonded interactions between complex molecules are thought to be relatively small (see below).

The 1 : 1 adducts prepared in this work with the

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* Fluorine-bridging has been suggested for other 1 : 1 adducts of Group IV tetrafluorides.[19,28]

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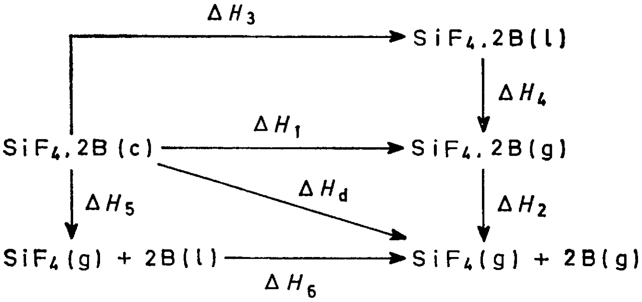
potentially chelating ligands $NHR\cdot[CH_2]_n\cdot NHR$ ($R =$ Me, $n = 2$ or 3; $R =$ Et, $n = 2$) seem similar in type to those reported for $Me_2N\cdot[CH_2]_n\cdot NMe_2$ with $n = 2$ (ref. 10) and $n = 1$—4 or 6 (ref. 6).

When the 1 : 2 adducts are heated, enthalpy changes may be described by the annexed Scheme,* and the observed enthalpy of dissociation ΔH_d for equilibrium (2) is the sum of the lattice energy of the complex ΔH_1 and the gaseous enthalpy of dissociation ΔH_2. Contributions to ΔH_1 include dipole–dipole forces (particularly between *cis*-adduct molecules) and intermolecular hydrogen-bonding, while ΔH_2 is determined chiefly by the strengths of N→Si bonds and, if appropriate, intramolecular hydrogen bonds. The essentially complete dissociation of all the adducts in Table 2 in the vapour phase, long known for ammonia[20] and trimethylamine[16] systems, suggests that $\Delta H_2 \ll \Delta H_1$. Earlier determinations of ΔH_d by the same method for $SiF_4,2NH_3$ (ref. 15) and $SiF_4,2NMe_3$ (ref. 16) agree reasonably well with those given here, while the correspondence with the calorimetrically-determined values for $SiF_4,2NHMe_2$ (refs. 6 and 21) and $SiF_4,2NC_5H_5$ (refs. 3 and 5) (but not with that in ref. 8 for the latter compound) is very close. The values of ΔH_d and hence ΔS_d for $SiF_4,2NMeEt_2$ may be somewhat low, reflecting the non-validity of equilibrium (4).



SCHEME

Table 2 shows that the dissociation enthalpy ΔH_d varies little for solid adducts of ammonia, primary and secondary amines, and pyridine, but falls significantly for those of tertiary aliphatic amines.† Also the apparent enthalpy (ΔH_3) and entropy of fusion of $SiF_4,2NHEt_2$ are about 42 kcal mol^{-1} and 126 cal mol^{-1} K^{-1} respectively. The equivalent values[33] for a weight of water corresponding to a mole of $SiF_4,2NHEt_2$ are 20 kcal and 73 cal K^{-1}; in both cases the effects of diminished intermolecular forces and reduced order are apparent. These facts reinforce the conclusion that $\Delta H_2 \ll \Delta H_1$ and suggest that hydrogen-bonding may be a major factor contributing to lattice energies.‡ It has been concluded on the basis of vibrational spectra[9] that hydrogen-bonding, although present in $SiF_4,2N_2H_4$, was not significant in $SiF_4,2NH_3$, because bands assigned to ν(N–H) in the latter compound were not unduly broad and occurred above 3200 cm^{-1}. However, it appears that these conditions may sometimes be met in cases where $N–H\cdots X$ interactions are generally accepted.§ Absorptions of $SiF_4,2NH_2Me$ below 3200 cm^{-1} reported here and by Bürger *et al.*[9] provide rather stronger evidence for hydrogen-bonding.

The large value of ΔH_d for pyridine deserves comment. Special pleading in terms of $C–H\cdots F$ interactions or silicon-ring π-bonding is possible but not particularly convincing, and it seems more likely that, as in the case of adducts with hindered boranes,[34] the particularly favourable steric requirements of pyridine are responsible.

Free-energy changes shown in Table 2 lead to an order of adduct stability: $NH_3 \sim NH_2Me > NHMe_2 \sim NC_5H_5 > NHEt_2 > NMe_3 > NMeEt_2 > NEt_3$, consistent with the orders derived here from competition experiments. It has also been noted in other studies that aziridine[35] is displaced by ammonia, and pyridine[4] or hydrazine[14] by ethylenediamine. The general pattern is that ammonia and primary amines are more effective than secondary amines, which are in turn more effective than tertiary amines; this is appropriate for control by hydrogen-bonding and/or steric effects, although pyridine's position favours the latter.

The order of relative ease of hydrolysis is almost the exact opposite of the order of ΔG above, and there is clear evidence that more sterically demanding bases give adducts that hydrolyse more readily. Thus it appears that adduct dissociation is a necessary (and rate-determining) step.

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* Only in the case of $SiF_4,2NHEt_2$ do further slow irreversible changes occur under the conditions used here.

† Given by $\Delta H_5 + \Delta H_6$ in the case of adducts of NEt_3 and $NMeEt_2$.

‡ The low value of the dissociation enthalpy for $SiF_4,2NHEt_2(l)$ ($\Delta H_2 + \Delta H_4$ is only 11 kcal mol^{-1}) implies that the Si←N bond energy is very small, probably not exceeding 5 kcal mol^{-1}.

§ Solid ammonia at −190 °C absorbs at 3378 and 3223 cm^{-1}.

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