Synthesis of Methylfluorosilicates and Trifluorosilyl Ethers and Amines

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RECENT investigations[1-3] have shown that compounds which may be formulated as containing a pentafluorosilicate anion, $(RSiF_5)^{2-}$, (R=Me, Et, Ph, CH_2=CH) may be prepared by several different but related methods. These compounds have been synthesized either by the reaction of $RSiF_3$ with solid potassium fluoride or by the reaction of $RSiF_3$ with potassium, ammonium, or alkylammonium fluorides in the presence of an appropriate solvent. In certain instances the $RSiF_3$ and/or the alkylammonium fluorides were prepared *in situ*. Attempts to prepare more highly organo-substituted anions such as $(Me_2SiF_4)^{2-}$ and $(Me_3SiF_3)^{2-}$ were unsuccessful.

In the present investigation the SiF_6^{2-}, $(MeSF_5)^{2-}$, $(Me_2SiF_4)^{2-}$, and $(Me_3SiF_3)^{2-}$ anions have been synthesized in the form of tetramethylammonium salts by the direct interaction of the appropriate fluorosilane at approximately 5 atm. pressure with solid tetramethylammonium fluoride at room or slightly elevated temperatures. In each case exactly 0·5 mole of fluorosilane was absorbed per mole of tetramethylammonium fluoride. *X*-Ray examination indicated that very little, if any, unchanged tetramethylammonium fluoride was present in the solid products. No reaction took place between tetramethylsilane and tetramethylammonium fluoride. At higher pressures (20—50 atm.) there was a tendency for solid compounds containing equimolar quantities of tetramethylammonium fluoride and fluorosilane to be formed.

The existence of the ions is not dependent simply on lattice stabilization of the solid, since proton n.m.r. spectra of solutions of the species in dimethyl sulphoxide showed that no experimentally detectable dissociation to methylfluorosilane (and tetramethylammonium fluoride) took place at room temperature. The formulation of the species as anions is consistent with the observation that the proton resonance frequencies of the anions fall 0·33—0·75 p.p.m. to higher field of those of their respective parent fluorosilanes. The proton n.m.r. spectra (saturated solutions in dimethyl sulphoxide) all consist of unresolved multiplets. Values (upfield from dimethyl sulphoxide): $(MeSiF_5)^{2-}$, 2·74 p.p.m.; $(Me_2SiF_4)^{2-}$, 2·76 p.p.m.; $(Me_3SiF_3)^{2-}$, 2·71 p.p.m. The resonance frequencies of the $(Me_4N)^+$ group vary only slightly and are all within 0·09 p.p.m. of that observed for tetramethylammonium fluoride.

The infrared spectra of the compounds also suggest the presence of organo-substituted fluorosilicate anions. The Si–F stretching vibration falls at a considerably lower frequency in the SiF_6^{2-} ion[4] than in the parent tetrafluorosilane species. Analogously, the Si–F stretching and the methyl deformation and rocking vibrations fall at appreciably lower frequencies in the methylfluorosilicate anions than in the parent fluorosilanes.

As might be expected, the $(Me_3SiF)^{2-}$ ion was the least stable thermally. It dissociated reversibly on heating. [$p(Me_3SiF)$ = 760 mm. at 85·9° (extrap.); $\Delta H_{diss.}$ = 17·6 kcal./mole.] Analogous

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[2] L. Tansjo, *Acta Chem. Scand.*, 1964, **18**, 456; 1964, **18**, 465.
[3] N. M. Alpatova, A. I. Gorbanev, Yu. M. Kessler, and L. G. Lozhkina, *Dolkady Akad. Nauk SSSR*, 1962, **142**, 1073.
[4] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762.

thermodynamic data could not be obtained for the other fluorosilicates, since the $(Me_4N)^+$ cation began to decompose before measurable vapour pressures due to reversible dissociation of the complexes could be obtained. Preliminary results indicate that other fluorosilanes combine with tetramethylammonium fluoride in an analogous manner to the methylfluorosilanes to form what appear to be substituted fluorosilicate anions.

During this investigation a convenient general method for converting a trialkylsilyl compound into the corresponding trifluorosilyl compound was discovered. The trialkylsilyl compounp was heated with an approximately threefold excess of tetrafluorosilane (20—30 atm. pressure) at approximately 150° for 30 minutes or less, *viz.*

$$(Me_3Si)_2O + SiF_4 \rightarrow Me_3Si{\cdot}O{\cdot}SiF_3 + Me_3SiF$$
$$Me_3Si{\cdot}O{\cdot}SiF_3 + SiF_4 \rightarrow (SiF_3)_2O + Me_3SiF$$
$$Me_2N{\cdot}SiR_3 + SiF_4 \rightarrow Me_2N{\cdot}SiF_3 + R_3SiF \ (R = Me, Et)$$
$$Me_3Si{\cdot}N{=}C{=}N{\cdot}SiMe_3 + SiF_4 \rightarrow Me_3Si{\cdot}N{=}C{=}N{\cdot}SiF_3 + Me_3SiF$$

The new compound $Me_3Si{\cdot}O{\cdot}SiF_3$ [m.p. −77·8°; b.p. (extrap.), 42·9°] was obtained in 30—40% yield. It decomposed slowly at room temperature with elimination of silicon tetrafluoride. When $Me_3Si{\cdot}O{\cdot}SiF_3$ was heated further with silicon tetrafluoride, small quantities of $(SiF_3)_2O$ were formed. Ninety-five percent yields of the new species $Me_2N{\cdot}SiF_3$ [m.p. −111·7°; b.p. (extrap.), 21·7°] were readily obtained from Me_2NSiEt_3 by using the reaction conditions described above, but smaller quantities were also formed even when a 200 mm. pressure of silicon tetrafluoride was employed.

The new compound $Me_3Si{\cdot}N{=}C{=}N{\cdot}SiF_3$ [m.p. −127·5°; b.p. (extrap.) 117·2°], which is believed to have the carbodi-imide structure, was prepared in 30—40% yield. It decomposed at a measurable rate at room temperature to form SiF_4, Me_3SiF, and a polymeric material.

Proton n.m.r. data were obtained by using 15% (by volume) solutions in a mixture of hexane (5%) and fluorochloroform (95%). Fluorine-19 data were obtained using a 20% (by volume) solution in fluorochloroform. Proton chemical shifts are given in p.p.m. upfield (+) or downfield (−) from hexane and fluorine-19 shifts are given in p.p.m. upfield from fluorochloroform.

$Me_3Si{\cdot}O{\cdot}SiF_3$: δ(H) + 1·22; δ(F) 158·5; $J_{^{29}Si\text{-}F}$ 184·2 c./sec.

$Me_2N{\cdot}SiF_3$: δ (H) −1·15; δ(F) 156·5; $J_{^{29}Si\text{-}F}$ 201·4 c./sec.

$Me_3Si{\cdot}N{=}C{=}N{\cdot}SiF_3$: δ(H) + 1·19; δ(F) 150·3; $J_{^{29}Si\text{-}F}$ 187·6 c./sec

The Si–N bond in $Me_2N{\cdot}SiF_3$ is cleaved readily at low temperatures by HX (X = Br, I), *viz.*,

$$Me_2N{\cdot}SiF_3 + 2HX \rightarrow SiF_3X + (Me_2NH_2)X$$

Excess of HCl cleaved the Si–N bonds in $Me_3Si{\cdot}N{=}C{=}N{\cdot}SiF_3$ in an analogous manner to give quantitative yields of Me_3SiCl, SiF_3Cl, and $NH_2CN,2HCl$. These reactions offer a convenient method for synthesizing trifluorosilyl halides.

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