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Nuclear Magnetic Resonance Studies on Pentacoordinate Silicon Fluorides

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The F^{19} and H^1 nmr spectra of fluorosilicate anions SiF_5^-, $RSiF_4^-$ (R = alkyl, aryl), and $(C_6H_5)_2SiF_3^-$ have been examined as a function of temperature and solvent polarity. The spectra are consistent with the thesis that these anions exist as pentacoordinate entities *in solvents of low polarity*. The low-temperature spectra of SiF_5^- and $RSiF_4^-$ show spectroscopic equivalence of all fluorine atoms in these species, probably the result of rapid intramolecular rearrangements. The spectrum of $(C_6H_5)_2SiF_3^-$ establishes two different fluorine atom environments at low temperature which are ascribed to axial and equatorial positions in a trigonal-bipyramidal (C_{2v}) configuration for the anion. Above −40°, these two environments are averaged out into a single resonance. Spin coupling between silicon and fluorine nuclei (Si^{29}–F^{19}), as well as between fluorine and hydrogen nuclei (F^{19}–Si–C–H^1), vanishes upon addition of excess fluoride ion or in protonic solvents such as water and alcohol. This in conjunction with the dramatic broadening of the F^{19} resonances observed under these conditions is rationalized in terms of rapid intermolecular exchange, $RSiF_4^- + F^{*-} \rightleftharpoons RSiF_3F^{*-} + F^-$.

Pentacoordination in main group elements other than group V elements is a subject of relatively recent interest and recognition.[1] This is particularly evident for group IV elements. A number of pentacoordinate structures with tin as the central atom are well authenticated for the crystalline state,[1] but definitive data for other physical states are singularly lacking. Structural data on five-coordinate germanium compounds are much more scant, the trigonal-bipyramidal geometry of GeF_2 in the solid state[2] being a notable exception. For discrete silicon species there is to our knowledge no rigorously established example of pentacoordination in the crystalline state.[2a] Coordination of a silicon atom to five donor atoms has been suggested or implicated in a number of instances,[3] usually in organosilanes coordinated to ligands which can function as chelating agents. Five-coordinate transition states have been invoked in the rationalization of kinetic data for the racemization of organosilanes.[4] Perhaps the best evidence to date for a pentacoordinate complex of silicon stems from the discovery of a stable liquid complex of composition $CHF_2CF_2SiH_3 \cdot N(CH_3)_3$.[5] Nuclear magnetic resonance data of this compound strongly imply but do not rigorously establish a trigonal-bipyramidal structure with the three hydrogen atoms in equatorial positions. Silicon tetrafluoride is of special interest because its relatively high acceptor activity should facilitate the tendency of silicon to expand its coordination shell. Adducts of the type $(CH_3)_3N \cdot SiF_4$ are known,[6] but they are probably not unimolecular in the solid state and they dissociate readily in the gas phase. A methyltetrafluorosilicate has been briefly described by Müller and Dathe.[7] However, this compound has not been characterized beyond a partial compositional analysis.

We wish to report in this article the preparation of tetraalkylammonium salts of the anions SiF_5^-, $RSiF_4^-$, and $(C_6H_5)_2SiF_3^-$ and to present nuclear magnetic resonance data which we feel provide fairly conclusive structural evidence for these anions *in solution.*

Synthesis and Properties

Alkyl- and aryltrifluorosilane and diphenyldifluorosilane react exothermally with tetraalkylammonium fluorides in methanol solution to give tetraalkylammonium salts of the anions $RSiF_4^-$ and $(C_6H_5)_2SiF_3^-$, respectively. The composition of the salts that precipitate from these concentrated solutions displays little dependency on the molar ratio of the reactants used. Even when a large excess of fluoride ions is present, a second fluoride ion is not added to give hexacoordinate anions of the types $RSiF_5^{2-}$ and $R_2SiF_4^{2-}$, respectively.[8] Trialkyl- and triarylfluorosilanes do not react with fluoride ion under these conditions, and we have found no evidence for $R_3SiF_2^-$ ions in solution. The $(CH_3)_2SiF_3^-$ may have a transient existence in solution but is too unstable to be isolable as a solid salt.

Silicon tetrafluoride reacts with aqueous ammonium fluoride precipitating a double salt of composition $(NH_4)_2SiF_6 \cdot NH_4F$, which, in the absence of knowledge about the structure of this solid, could alternatively be formulated as $NH_4SiF_5 \cdot 2NH_4F$. A crystalline salt containing the anion SiF_5^- is easily obtained, however, by

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[1] For a comprehensive review on pentacoordination, see E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[2] J. Trotter, M. Akhtar, and N. Bartlett, *J. Chem. Soc., Sect. A*, 30 (1966).

[2a] NOTE ADDED IN PROOF.—After submittal of this article, X-ray structure results on two compounds containing pentacoordinate silicon have been reported: See R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Am. Chem. Soc.*, **89**, 5157 (1967); J. Turley, F. Boer, and C. Frye, *Chem. Eng. News*, **45**, No. 42, 46 (1967).

[3] (a) C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961); (b) C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *ibid.*, **88**, 2727 (1966); (c) J. C. Corey and R. West, *ibid.*, **85**, 4034 (1963); (d) R. Müller and L. Heinrich, *Ber.*, **94**, 1943 (1961); (e) C. L. Frye, Canadian Patent 751,461 (1967).

[4] For a discussion of this point, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[5] D. I. Cook, R. Fields, R. N. Haszeldine, B. R. Files, A. Jones, and M. F. Newlands, *J. Chem. Soc., Sect. A*, 887 (1966).

[6] J. E. Ferguson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *ibid.*, 99 (1959).

[7] R. Müller and C. Dathe, *Z. Anorg. Allgem. Chem.*, **343**, 150 (1966).

[8] The formation of tetramethylammonium salts of $CH_3SiF_5^{2-}$, $(CH_3)_2SiF_4^{2-}$, and even $(CH_3)_3SiF_3^{2-}$ has been reported to occur by the direct interaction of the appropriate fluorosilane with $(CH_3)_4NF$ under 5 atm pressure: J. J. Moscony and A. G. MacDiarmid, *Chem. Commun.*, 307 (1966).

passing gaseous silicon tetrafluoride into a methanolic solution of tetrapropylammonium fluoride.[9]

Although the precipitated salts usually give correct analyses for the formula $[R_4N][SiF_{5-x}R_x]$ $(0 < x < 2)$, analytical composition alone does not suffice to establish the nature of these compounds because the anions might actually exist as fluorine-bridged dimers, at least in some physical states. Moreover, the crude products invariably contain small but highly detrimental amounts of impurities, detrimental in the sense that these impurities (usually hydrolysis products) grossly perturb the F^{19} nmr resonances. Painstaking purification from nonprotonic solvents is usually necessary to obtain products of sufficient purity for a meaningful nmr investigation. The F^{19} nmr spectra are highly sensitive probes for purity of salts of the anions $[SiF_{5-x}R_x]^-$. Infrared spectra, on the other hand, seem to be rather insensitive for an assessment of purity. We have enountered several examples in which both band positions and relative intensities of infrared absorptions of fluorosilicate salts were strikingly invariant to the presence of relatively large amounts (10% or more) of added tetraalkylammonium fluoride and similar extraneous material. Melting points, however, are frequently very markedly affected by impurities, large differences of 20° or more among different preparations not being uncommon.

Müller and his co-workers,[10] as well as Tansjö,[11] have described miscellaneous compounds of empirical composition $M_2[RSiF_5]$, where M represents an alkali metal or a primary ammonium cation, and R is an organic substituent such as alkyl, aryl, vinyl, etc. We have repeated some of these preparations and obtained the same products. While most of these salts are quite water soluble, none of the compounds possesses sufficient solubility in organic solvents to make an nmr investigation feasible, especially at low temperatures. We have extended the reaction between primary amines and phenyltrifluorosilane described by Tansjö to secondary amines because the intractability of the compounds $[RNH_3]_2[SiF_5C_6H_5]$ generated in the former case thwarted all attempts at a structural investigation. Secondary amines react smoothly with $C_6H_5SiF_3$ to give salts of the phenyltetrafluorosilicate anion, $[R_2NH_2][SiF_4C_6H_5]$, which are distinguished by a much higher solubility in nonpolar solvents. Notwithstanding this fact, the F^{19} nmr spectra were unrevealing in being dominated by dynamic exchange phenomena and not displaying fine structure (*vide infra*). The hydrolytic stability of the solid dialkylammonium salts is notably smaller than that of the corresponding tetraalkylammonium salts. Furthermore, there may be extensive hydrogen bonding among anion and cation aggregates in solutions of the former which may provide for additional pathways to fluorine exchange and thus enhance the kinetic lability of the system. Molecular weight data on di-*n*-propylammonium phenyltetrafluorosilicate are consistent with this speculation. The apparent molecular weight is about 5 times the formula weight in chloroform and rises to 13 times the formula weight in benzene.

Nmr Data

In Table I, the F^{19} and H^1 nmr data for some organofluorosilanes are summarized. Literature data were available only for $(CH_3)_3SiF$, and in this case our parameters are in excellent agreement with those reported.[12] In Table II, all of the relevant nmr data are presented for tetraalkylammonium salts of fluorosilicate anions.

TABLE I

F^{19} AND H^1 SPECTRA OF $R_{4-x}SiF_x$ COMPOUNDS $(x = 1, 2, 3)$

	F^{19} spectrum			H^1 spectrum		
	ϕ, ppm	J_{Si-F}, cps	J_{H-F}, cps	τ,[a] ppm	J_{H-F}, cps	J_{Si-H}, cps
CH_3SiF_3	139.2	260[c]	4.0	10.14	4.0	4.9
$(CH_3)_2SiF_2$	133.3	289	6.0	10.17	6.1	7.6
$(CH_3)_3SiF$	159.3	266	7.0	10.23	7.0	6.8
$C_6H_5SiF_3$	143.0	266				
$(C_6H_5)_2SiF_2$	144.1	290				
$(C_6H_5)_3SiF$[b]	147.0	292				
n-$C_4H_9SiF_3$	140.4	282	2.8[d]			

[a] CH_3 resonance. [b] In CH_2Cl_2 solution; all other compounds as neat liquids. [c] $J_{Si-F} \pm 2$ cps; J_{H-F} and $J_{Si-H} \pm 0.1$ cps. [d] Slightly broadened triplet due to coupling with α-CH_2 group.

The low-temperature spectra of $(C_6H_5)_2SiF_3^-$, $C_6H_5SiF_4^-$, and SiF_5^- in nonpolar media are strikingly analogous to those of the isoelectronic fluorophosphoranes. Thus, the disubstituted ion, $(C_6H_5)_2SiF_3^-$, displays at low temperature an F^{19} spectrum consisting of two lines of relative intensities 2 and 1 as was found earlier for the dialkylfluorophosphoranes.[13] These data are consistent with a five-coordinate species of trigonal-bipyramidal geometry with the two phenyl substituents at equatorial positions. Although these data alone do not rigorously establish the stereochemical orientation of the phenyl substituents, the conclusion that they are in fact in equatorial positions is strongly supported by analogy with the corresponding phosphorus–fluorine system.[13,14]

The nmr spectral data for $CH_3SiF_4^-$ define this anion as a five-coordinate structure in chlorohydrocarbon solvents. The F^{19} nmr spectrum consists of a quartet due to coupling of three spectroscopically equivalent protons with four spectroscopically equivalent fluorine atoms (Figure 1). Consistently, the Si–CH_3 resonance in the H^1 nmr spectrum measured under the same conditions is split into an AB_4 quintet (Figure 3) due to HF coupling. Satellites due to Si^{29}–F^{19} coupling were also observed establishing that no rapid Si–F bond-breaking process occurs at −58.° As can be seen from Figure 1, however, exchange

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(9) (a) The SiF_5^- anion has just recently been described in the literature: H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 3360 (1967); (b) H. C. Clark and K. R. Dixon, *Chem. Commun.*, 717 (1967).

(10) R. Müller, *Z. Chem.*, **5**, 220 (1965); *Organometal. Chem. Rev.*, **1**, 359 (1966).

(11) L. Tansjö, *Acta Chem. Scand.*, **18**, 465 (1964).

(12) (a) G. R. Holzman, P. C. Lauterbur, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, **25**, 172 (1956); (b) S. S. Danyluk, *J. Am. Chem. Soc.*, **86**, 4504 (1964).

(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(14) E. L. Muetteries, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

TABLE II

F^{11} NMR SPECTRA OF FLUOROSILICATE ANIONS

Compound	Solvent	ϕ,[a] ppm	J_{Si-F}, cps	J_{H-F}, cps	Comments
$[(CH_3H_7)_4N][SiF_4CH_3]$	CH_2Cl_2	110.9	218 ± 1	4.8 ± 0.2	−60°; AB_3 pattern
$[(C_4H_9)_4N][SiF_4CH_3]$	CH_2Cl_2	110.5	218	4.8	−60°
$[(C_3H_7)_4N][SiF_4C_6H_5]$	$CHCl_3$	119.2	206 ± 2		35°
$[(CH_3)_4][SiF_4C_6H_5]$	$(CH_3)_2SO$	116.8	205		25°
$[(C_3H_7)_4N][SiF_4C_4H_9]$	CH_2Cl_2	116.6	223 ± 2	3.5	−62°
$[(C_2H_5)_4N][SiF_3(C_6H_5)_2]$	CH_2Cl_2	98.0	254 ± 4		F_{axial}
		134.0	212 ± 2		$F_{equatorial}$ (see text)
$[(C_3H_7)_4N][SiF_5]$	CH_2Cl_2	136.0	148 ± 2		−66°
$(NH_4)_3SiF_6 \cdot NH_4F$	H_2O	128.2	110 ± 2		SiF_6^{2-}
		115.3			F^-; intensity ratio 6:1
SiF_4	Neat	160.3	178		From ref 10

[a] Reference: $CFCl_3$.

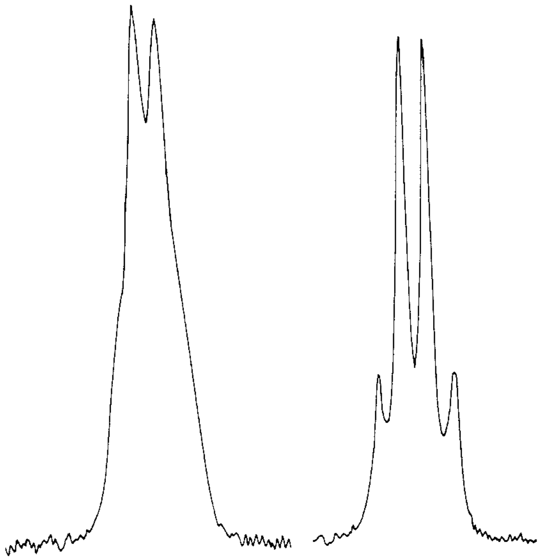

Figure 1.—F^{19} nmr spectrum of $[(C_3H_7)_4N][SiF_4CH_3]$ in methylene chloride: left, at 25°; right, at −58°.

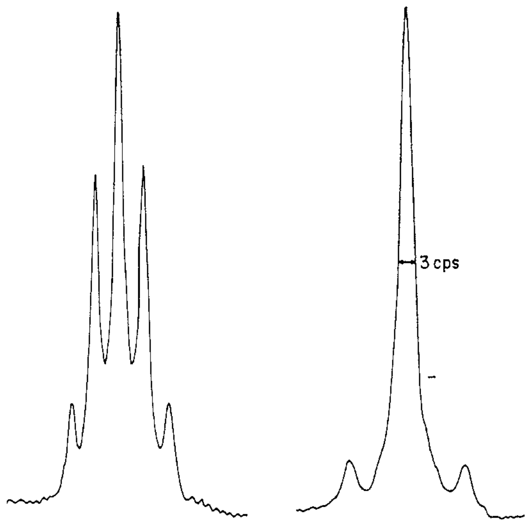

Figure 3.—Si–CH$_3$ resonance (H^1 nmr spectrum) of $[C_3H_7)_4]$-$[SiF_4CH_3]$: left, in methylene chloride at −58°; right, in methanol at −58°. The symmetrical pair of small peaks on the right are spinning side bands.

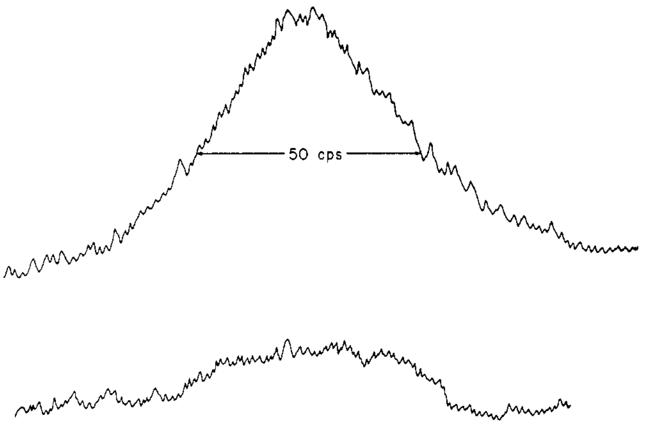

Figure 2.—F^{19} nmr spectrum of $[(C_3H_7)_4N][SiF_4CH_3]$: top, at 25° in methanol; bottom, in 10% methanolic $(C_3H_7)_4NF$ solution.

phenomena begin to become operative at room temperature causing incipient but distinct broadening of the resonance. Similarly, $C_6H_5SiF_4^-$ shows spectroscopic equivalence of fluorine atoms as well as Si^{29}–F^{19} fine structure. Because of the spectroscopic equivalence of the fluorine atoms, it is not possible to assign unequivocally a stereochemistry for these monosubstituted fluorosilicate anions. However, this type of spectral behavior for an RMF_4^{x-} species is to be expected when considered in the context of the detailed nmr studies of the monoalkylfluorophosphoranes.[1,13,14] For example, the structure of CH_3PF_4, which also shows spectroscopic equivalence of fluorine atoms,[13] has been proved by electron diffraction[15] to be a trigonal bipyramid with the methyl group at an equatorial position, as had been earlier inferred from an analysis of the nmr data.[13] Hence, we propose that $CH_3SiF_4^-$ and C_6H_5-SiF_4^- have nearly trigonal-bipyramidal geometry with the organic group in the equatorial position.

All monomolecular MF_5 molecules and ions display spectroscopic equivalence of fluorine atoms,[1] and, of the species investigated to date, all have been shown to have trigonal-bipyramidal geometry. Equivalence of fluorine atoms as well as spin–spin coupling between the fluorine and silicon nuclei is also found in the SiF_5^- anion below −60°. The data themselves permit no structural conclusions. In view of the structural principles previously established within this class of compounds,[1,13] we believe, however, that this pentafluorosilicate anion has trigonal-bipyramidal geometry. Parenthetically, it may be noted that the observed

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[15] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).

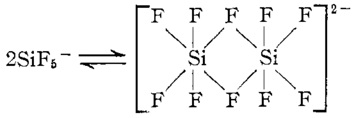
$\mathrm{Si^{29}}$–$\mathrm{F^{19}}$ coupling constant for the $\mathrm{SiF_5^-}$ ion is almost precisely the arithmetic mean of the values for $\mathrm{SiF_4}$ and $\mathrm{SiF_6^{2-}}$ which is in accord with the *apparent* regular decrease of s character in the Si–F bonds from $\mathrm{SiF_4}$ to $\mathrm{SiF_6^{2-}}$.

Exchange Phenomena

Since spin–spin coupling of the silicon and fluorine nuclei in $\mathrm{SiF_5^-}$ is maintained below −60° in chloroform solution, the dominant exchange process for the equilibration of fluorine atom environments in $\mathrm{SiF_5^-}$ probably is an intramolecular rearrangement involving bending motions, as first outlined by Berry[16] for the analogous $\mathrm{PF_5}$ molecule. At temperatures above −60°, the pentafluorosilicate anion spectrum gradually begins to broaden and the $\mathrm{Si^{29}}$–$\mathrm{F^{19}}$ coupling is apparently lost. Thus, another dynamic process is taking place in this system, which process must involve scission of the silicon–fluorine bonds. Such behavior is not observed in phosphorus pentafluoride where the P–F coupling is maintained over a very wide temperature range. Thus, any P–F bond-breaking process in this molecule must be very slow relative to the nmr time scale. The observed fast Si–F bond-breaking process at temperatures above −60° may be due to trace impurities in our samples. This possibility cannot be rigorously excluded. However, if our samples were representative of pure pentafluorosilicate salts, the fast Si–F bond-breaking process could be due to either a dissociative-type process

$$\mathrm{SiF_5^-} \rightleftharpoons \mathrm{SiF_4} + \mathrm{F^-}$$

or to an associate process in cwhih a dimeric (or polymeric) species is generated through fluorine bridge bonds, *e.g.*



We are not particularly attracted to the dissociative alternative because the pentafluorosilicate anion should, in fact, possess significant acceptor properties. The hexafluorosilicate dianion is well established and is quite resistant to exchange processes, particularly dissociative processes, except under conditions where the hydrogen ion concentration is relatively high.[17] We would expect a dissociative exchange process in the pentafluorosilicate anion to have a much higher barrier than found in the hexafluorosilicate dianion. Associative exchange through fluorine bridge bonds would be consistent with the postulate that the pentafluorosilicate dianion has residual acceptor function.

Of the two monosubstituted fluorosilicate anions investigated, the methyl derivative appears to be the more susceptible to intermolecular fluorine exchange in chloroform solution. The expected $\mathrm{AB_3}$ pattern in the $\mathrm{F^{19}}$ spectrum of $\mathrm{CH_3SiF_4^-}$ is well-resolved only at lower temperatures. In contrast, the phenyl derivative has a quite narrow central main peak with $\mathrm{Si^{29}}$–$\mathrm{F^{19}}$ satellites at room temperature, and there is no discernible perturbation of the $\mathrm{F^{19}}$ spectrum over the temperature range from −125° to +25° in chloroform or methylene chloride solution, and even in dimethyl sulfoxide at 25°. It is to be expected that substitution of fluorine atoms in the pentafluorosilicate anion by alkyl substituents lowers the Si–F bond energies and that this occurs to a lesser degree in the phenyl substituent. This is equivalent to saying that the order of acceptor properties is: $\mathrm{SiF_5^-} > \mathrm{C_6H_5SiF_4^-} > \mathrm{CH_3SiF_4^-}$. Thus, in contrast to our postulate that intermolecular fluorine exchange is the dominant process in the $\mathrm{SiF_5^-}$ ion above −60°, we would favor a dissociative exchange process for the $\mathrm{CH_3SiF_4^-}$ ion.

Addition of fluoride ion or a protonic substance such as methanol (or water) to nonpolar solutions of alkyl- or aryltetrafluorosilicate anions leads to significant upfield shifts of the resonance (about 10 ppm), considerable broadening (up to 100 cps), and loss of silicon–fluorine hyperfine structure. These effects are illustrated in Figures 2 and 4. The exchange in the case of fluoride ion addition is most likely due to a bimolecular process such as

$$\mathrm{RSiF_4^-} + \mathrm{F^{*-}} \rightleftharpoons \mathrm{RSiF_3F^{*-}} + \mathrm{F^-}$$

The $\mathrm{F^{19}}$ spectrum of $(\mathrm{C_6H_5})_2\mathrm{SiF_3^-}$ is a single broad peak at 110 ppm ($\Delta v_{1/2} = 70$ cps) at room temperature. As the temperature is lowered, a transient range from −20 to −50° is traversed wherein the line width is so large as to render the fluorine resonance essentially undetectable. Below −60°, the two peaks characteristic of the environmentally nonequivalent fluorine atoms appear initially quite broad, but as the temperature approaches −100° there is considerable sharpening of the two peaks, and the silicon satellites appear. The observed phenomena are completely reversible when the solution is warmed again. It was not feasible to lower the temperature significantly below −100° owing to solubility problems in the nonpolar media employed. Thus, nonobservation of F–F coupling in this system may have been a reflection of the intrinsic broad resonance at −100°. In any case, it does not appear that the F–F coupling in this system is particularly large, presumably <5 cps. It is apparent from these temperature data that, of the species investigated, the diphenyltrifluorosilicate anion is the least stable toward intermolecular fluorine exchange. This is not particularly surprising in view of the fact that $(\mathrm{C_6H_5})_2\mathrm{SiF_2}$ is the weakest acceptor molecule of the reference acids employed, *e.g.*, $\mathrm{SiF_4}$ and $\mathrm{RSiF_3}$. Thus, a dissociative-type process involving silicon–fluorine bond breaking would be expected to be most dominant in this particular system

$$(\mathrm{C_6H_5})_2\mathrm{SiF_3^-} \rightleftharpoons (\mathrm{C_6H_5})_2\mathrm{SiF_2} + \mathrm{F^-}$$

Extrapolating from the data obtained for the diphenyl derivative, we would predict that in solution the ion $(\mathrm{CH_3})_2\mathrm{SiF_3^-}$ should be largely dissociated, at least at room temperature, and that the ion, if capable

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[16] S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

[17] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

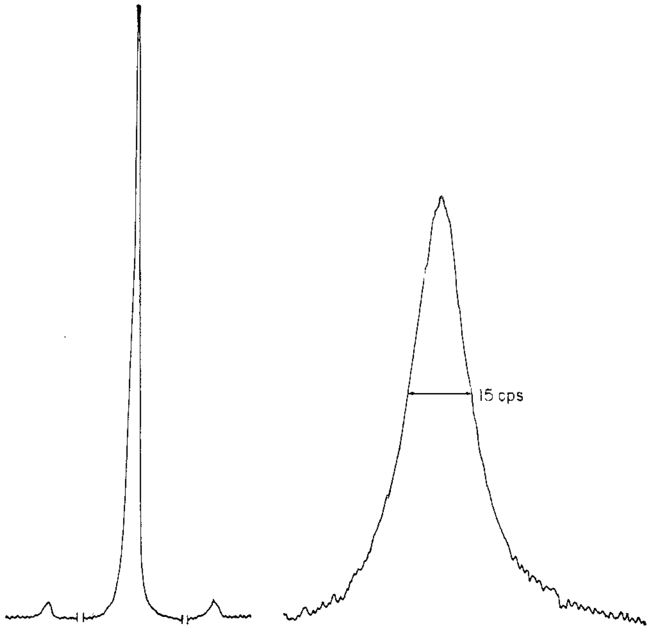

Figure 4.—F^{19} nmr spectrum of $[(C_3H_7)_4N][C_6H_5SiF_4]$: left, at 25° in methylene chloride (Si^{29} satellites shown); right, at −58° in solution of 10% $(C_3H_7)_4NF$ in methylene chloride.

of existence in solution, will undergo very rapid intermolecular fluorine exchange even at very low temperatures. Least stable of the alkyl-substituted ions would, of course, be $(CH_3)_3SiF_2^-$. It should perhaps be reemphasized that all of the comments relating to structure and to dynamic processes involving these five-coordinate silicon anions pertain only to the *solution state* in nonprotonic solvents. In the solid state or in basic solvents, it *may* be possible to obtain even six-coordinate alkyl-substituted fluorosilicates.

We have examined the F^{19} nmr spectra of the compounds formulated by Müller[10] as salts of the $RSiF_5^{2-}$ anion. The spectra for aqueous solution consist of a broad structureless resonance at 110–115 ppm. In some cases, a second much weaker resonance is discernible at about 128 ppm. For example, "$Cs_2SiF_5CH_3$" shows only one broad ($\Delta\nu_{1/2}$ = 30 cps) peak at 115 ppm in its F^{19} nmr spectrum. The methyl resonance appears as a sharp singlet at τ 10.00 in the H^1 spectrum, disproving any F^{19}–Si–C–H^1 coupling. (Si^{29}–C–H^1 coupling is observed, however, where J = 9.1 cps.) The compounds formulated as $(NH_4)_2SiF_5CH_3$ and $(NH_4)_2SiF_5CH_3 \cdot NH_4F$ show a similar behavior in aqueous solution. Both compounds display a broad signal at 111 ppm and a much weaker absorption at 128 ppm. Interestingly the relative intensity of this second peak is about twice as high in the $(NH_4)_2SiF_5CH_3 \cdot NH_4F$ salt as in solutions of $(NH_4)_2SiF_5CH_3$. Thus, we tentatively attribute the absorption at 128 ppm to the F$^-$ ion,[18] and the broadened low-field signal may then be ascribed to a $[SiF_4CH_3]^-$ or a $[SiF_4CH_3(H_2O)]^-$ ion which is involved in rapid fluorine exchange. Clearly the actual coordination number of the silicon atom in these solutions is a moot point.

Experimental Section

General Material.—F^{19} nmr spectra were measured on Varian HR 56 and AR 56 spectrometers with variable-temperature probes. Trimethylfluorosilane, dimethyldifluorosilane, and methylfluorosilane were commercial products obtained from Pierce Chemical Co., Rockford, Ill. The purity criterion was gas density and nmr measurements (neat liquids in sealed tubes). Phenylfluorosilanes $(C_6H_5)_{4-x}SiF_x$ (x = 1, 2, 3) were prepared by minor modifications of established procedures[19] from the corresponding phenylchlorosilanes and anhydrous zinc fluoride. Their physical properties agreed with those in the literature.[19] Tetraalkylammonium fluorides were prepared by neutralization of aqueous solutions of tetraalkylammonium hydroxides with stoichiometric amounts of hydrofluoric acid. The water was then removed under reduced pressure on the rotating evaporator as far as possible, and the resulting syrupy oils were redissolved in methanol and again evaporated to dryness. The redissolution in methanol and evaporation step was usually repeated another time. The final products were dried at about 100° (0.001 mm). This preparation of tetraalkylammonium fluorides (as methanol solvates) is by far the simplest and the best procedure we are aware of.[20] Our analytical data are summarized in Table III. The calculated and found values for the last three compounds in the table do not agree quite as well with each other as for the others, because the lack of adequate solubility in nonaqueous systems complicated attempts to purify the ammonium and cesium salts by recrystallization or made this impossible. Details of the preparation of a few representative compounds follow.

Preparation of $[(n\text{-}C_3H_7)_4][SiF_4CH_3]$.—Gaseous methyltrifluorosilane (2.0 g, 0.020 mole) was passed into 50 ml of methanol solution containing 5 g (0.025 mole) of tetra-*n*-propylammonium fluoride. The solution was concentrated on the rotating evaporator under reduced pressure to a volume of 2–3 ml when a crystalline solid (0.7 g) precipitated. This was filtered off, washed with ether, and recrystallized from 40 ml of anhydrous 1,2-dimethoxyethane to give 0.4 g of glittering, micalike plates of tetra-*n*-propylammonium methyltetrafluorosilicate. The H^1 spectrum in $CDCl_3$ solution shows peaks at τ 6.74 (α-CH_2), 8.20 (β-CH_2), 8.40 (triplet, CH_3), and 9.90 (quintet, Si–CH_3) in the expected ratio 8:8:12:3.

A tetra-*n*-butylammonium methyltetrafluorosilicate was prepared similarly. The crude salt (mp 78–80°) was recrystallized initially from methylcyclohexane–benzene (5:1), but better results were obtained by chilling a 1,2-dimethoxyethane solution to −78°. The resulting crystals (mp 93–94°) were still rather small and nontransparent.

Preparation of $[(n\text{-}C_3H_7)_4N][SiF_4C_6H_5]$.—Freshly distilled phenyltrifluorosilane (4.8 g, 0.030 mole) was added to a solution of 6 g (0.030 mole) of tetra-*n*-propylammonium fluoride in 60 ml of methanol. An exothermic reaction occurred. Reduction of the volume in the solution to 25 ml and chilling precipitated a total of 4.6 g of relatively coarse crystals which were purified by recrystallization from 40 ml of warm 1,2-dimethoxyethane. Slow cooling of this solution to 0° led to a recovery of 4.4 g of large, spearlike crystals of tetra-*n*-propylammonium phenyltetrafluorosilicate. The H^1 nmr spectrum in $CDCl_3$ was confirmatory showing absorption at τ 2.01 (*o*-H), 2.68 (*m*- and *p*-H), 7.06 (α-CH_2), 8.50 (β-CH_2), and 9.10 (CH_3) in the proper intensity ratio.

The tetramethylammonium phenyltetrafluorosilicate was made analogously. It is insoluble in chloroform and methylene chloride and soluble in acetonitrile and acetone. It was purified by

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(18) This assignment has to be viewed with caution because the chemical shift of the F$^-$ ion in solution varies enormously with solvent and also with concentration. This is illustrated by the following examples: 45% NH_4F in H_2O, 102 ppm; 20% NH_4F in H_2O–CH_3OH (3:1), 115 ppm; saturated KF in H_2O, 120 ppm; $(CH_3)_4NF$ in CH_3OH–CH_2Cl_2 (1:1), 139 ppm; $(C_3H_7)_4NF$ in CH_3OH, 150 ppm; $(C_3H_7)_4NF$ in H_2O, 155 ppm.

(19) See C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960.

(20) We have been unable to obtain tetramethylammonium fluoride free of chloride ion by procedures described by R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963), and in German Patent 1,191,813 (1965). The resulting products invariably contained at least 1–2% chloride ion. A commercial sample of tetramethylammonium fluoride contained 6.6% chlorine.

TABLE III

ANALYTICAL RESULTS AND MELTING POINTS

Compound	Mp, °C	Calculated, %					Found, %				
		C	H	N	F	Si	C	H	N	F	Si
$[(C_3H_7)_4N][SiF_4CH_3]$	161–164	51.1	10.2	4.6	24.9	9.2	51.2	10.2	4.6	24.7	9.6
$[(C_4H_9)_4N][SiF_4CH_3]$	93–94	56.5	10.9	3.9	21.0	7.8	56.5	11.0	3.8	20.6	7.9
$[(C_3H_7)_4N][SiF_4C_6H_5]$	102–103	58.8	9.1	3.8	20.7	7.6	58.8	9.0	3.9	20.7	7.8
$[(CH_3)_4N][SiF_4C_6H_5]$	129–130	47.0	6.7	5.5	29.8	11.0	47.1	6.7	5.6	29.8	11.3
$[(CH_3)_4N][SiF_3(C_6H_5)_2]$	229–232	61.3	7.1	4.5	18.2	9.0	61.2	7.2	4.8	18.1	9.2
$[(C_2H_5)_4N][SiF_3(C_6H_5)_2]$	62–63	65.0	8.2	3.8	15.4	7.6	64.6	8.2	3.9	15.9	7.9
$[(C_3H_7)_4N][SiF_3(C_6H_5)_2]$	65–67	67.7	9.0	3.3	13.4	6.6	67.3	9.4	3.5	13.1	7.0
$[(CH_3)_4N][SiF_4C_4H_9]$	139–141	40.8	9.0	6.0	32.3	11.9	41.0	9.2	6.0	32.2	11.7
$[(C_3H_7)_4N][SiF_4C_4H_9]$	72–75	55.3	10.7	4.0	21.9	8.1	55.5	10.7	4.0	21.6	8.2
$[(C_3H_7)_2NH_2][SiF_4C_6H_5]$	109–111	50.9	7.5	4.9	26.8	9.9	50.9	7.7	5.0	26.4	10.0
$[(C_3H_7)_4N][SiF_5]$	205–207	46.6	9.1	4.5	30.7	9.1	46.7	9.1	4.5	30.3	9.1
$[NH_4]_2[SiF_5CH_3]$	162 dec	6.9	6.4	16.1	54.5	16.1	6.3	6.5	16.2	54.4	15.4
$Cs_2[SiF_5CH_3]$	>400	3.0	0.8	...	23.5	7.0	3.4	0.9	...	23.6	...
$(NH_4)_2SiF_6 \cdot NH_4F$	Dec	...	5.6	19.5	61.8	13.1	...	5.7	19.5	60.1	...

rapidly chilling a solution of the crude salt in methanol to −78°. The pure product crystallizes as colorless needles.

Preparation of $[(CH_3)_4N][SiF_3(C_6H_5)_2]$.—Freshly prepared diphenyldifluorosilane (5.7 g, 0.026 mole) was added to a solution of 5.0 g (0.054 mole) of tetramethylammonium fluoride in 100 ml of methanol with immediate formation of a white precipitate (7.5 g). This was collected, washed with methanol and ether, and then recrystallized from 75 ml of anhydrous acetonitrile. The recovery was 6.0 g of colorless prisms of tetramethylammonium diphenyltrifluorosilicate. The H^1 nmr spectrum in CD_3CN shows absorption at τ 2.40 (*o*-H), 3.05 (*m*- and *p*-H), and 7.28 (N–CH_3; 1:1:1 triplet; $J_{N^{14}-C-H^1}$ = 0.5 cps) in the ratio 33:49:98 = 4:6:12. The corresponding tetraethylammonium and tetra-*n*-propylammonium salts of the diphenyltrifluorosilicate anions were prepared similarly. As the size of the cation increased, purification became more difficult. The $(C_2H_5)_4N^+$ salt was best recrystallized from 1,2-dimethoxyethane–methanol (10:1), and the $(C_3H_7)_4N^+$ salt, from tetrahydrofuran.

Preparation of $[(CH_3)_4N][n\text{-}C_4H_9SiF_4]$.—Freshly distilled *n*-butyltrifluorosilane (9.5 g, 0.067 mole) was added to a solution of 9 g (0.010 mole) of tetramethylammonium fluoride in 100 ml of methanol. White fluffy crystals (7.8 g) precipitated when the solution volume was slowly reduced on the rotating evaporator. The crude product was recrystallized from 175 ml of hot 1,2-dimethoxyethane to give 5.5 g of colorless, interwoven needles. Tetra-*n*-propylammonium *n*-butyltetrafluorosilicate was prepared and purified analogously.

Preparation of $[(n\text{-}C_3H_7)_2NH_2][SiF_4C_6H_5]$.—A solution of 11.2 g (0.068 mole) of phenyltrifluorosilane in 50 ml of anhydrous ether was treated with 14.5 g (0.145 mole) of di-*n*-propylamine in 50 ml of ether. The resulting white precipitate (3.5 g) was filtered off under nitrogen, washed with 50 ml of ether, and dried at 60° *in vacuo*. A portion of this was recrystallized from benzene to give white, fluffy crystals. The molecular weight of di-*n*-propylammonium phenyltetrafluorosilicate indicated increasing association with diminishing polarity of the solvent. For $[(C_3H_7)_2NH_2][SiF_4C_6H_5]$, formula weight: 283; molecular weight: cryoscopic in dimethyl sulfoxide, 76; ebullioscopic in chloroform, 1312, 1323; ebullioscopic in benzene, 3640.

Reactions of phenyltrifluorosilane with di-*n*-hexylamine, dicyclohexylamine, and di-*n*-heptylamine proceeded analogously but gave less pure products.

Preparation of $[(n\text{-}C_3H_7)_4N][SiF_5]$.—Gaseous silicon tetrafluoride was passed into a solution containing 5 g of tetrapropylammonium fluoride in 50 ml of methanol. A vigorously exothermic reaction ensued heating the solvent to reflux. The mixture was then slowly concentrated on the rotating evaporator. When the solution was reduced to about half its original volume, a white crystalline solid (4.0 g) started to precipitate, which was collected by filtration and washed with ether. It slowly etched glass. The solid was recrystallized from 20 ml of a methylene chloride–1,2-dimethoxyethane (1:1) mixture. The final product (3.2 g) was dried at 60° (0.001 mm).

When silicon tetrafluoride was passed into a 45% aqueous solution of NH_4F in a polyethylene flask, the precipitate, after a vigorously exothermic reaction, consisted of the double salt $(NH_4)_2SiF_6 \cdot NH_4F$ (see Table III). This was filtered off, washed with methanol and ether, and air dried. No further purification was attempted.

Preparation of $(NH_4)_2[SiF_5CH_3]$.—A solid of empirical composition $(NH_4)_2(SiF_5CH_3) \cdot NH_4F$ was made by fluorination of methyltrichlorosilane with aqueous ammonium fluoride as described by Müller and Dathe.[21] Surprisingly, we obtained precisely the same product by fluorination of methyldichlorosilane, CH_3SiHCl_2, under the same conditions. The H^1 nmr spectrum of the salt showed a sharp singlet (in D_2O) at τ 10.27 with $J_{Si^{29}-C-H^1}$ = 9.2 cps. We have made numerous unsuccessful attempts to prepare a CH_2Cl_2-soluble "$SiF_5CH_3^{2-}$" salt by metathetical ion-exchange experiments with large cations. Invariably, $(NH_4)[SiF_4CH_3] \cdot NH_4F$ (alias $(NH_4)_2[SiF_5CH_3]$) precipitated as the least soluble component. This salt was made in larger quantity by dissolving the crude salt from above in hot water and adding sufficient methanol to the filtered aqueous solution to effect precipitation of white, nontransparent needles. It is perhaps noteworthy that $(NH_4)_2[SiF_5CH_3]$ reacts very violently with hydronium ions liberating copious amounts of gas.

Infrared Spectra.—To distinguish silicon–fluorine vibrations unambiguously in infrared spectra having an abundance of bands due to cations and the organic part of the anion in the critical regions of absorption is a highly problematical endeavor. Nevertheless, a few bands can be assigned to Si–F stretching vibrations with a high degree of probability. These occur at 875 and 790 cm^{-1} in the SiF_5^- anion, and at 855, 807, and 690 cm^{-1} in the $SiF_4CH_3^-$ anion. We are much less certain about the positions of Si–F absorptions in the phenyl-substituted couterparts because *both* Si–F *and* phenyl absorptions appear to vary from one compound to another. Tentative assignments for positions of Si–F bands are at 855 and 720 cm^{-1} for $[SiF_4C_6H_5]^-$, and at 710 and 675 cm^{-1} for the $[SiF_3(C_6H_5)_2]^-$ ion. This latter anion definitely does not absorb in the 900–800-cm^{-1} region of the spectrum. A common characteristic of Si–F vibrations in all of the compounds (examined as Nujol mulls and KBr wafers) is an appreciable half-width of the bands. This effect is even more pronounced in salts of the type $K_2SiF_5CH_3$ and $Cs_2SiF_5CH_3$, respectively, which show two huge broad bands centered at 830 and 720 cm^{-1}. As a minor point, we observed that the spectrum of the double salt $(NH_4)_2SiF_6 \cdot NH_4F$ is precisely the same as that published for $(NH_4)_2SiF_6$ by Müller.[10] This implies that the infrared spectra of the two compounds are either identical within the limits of detectability, or that the presence of NH_4F in the published spectrum has not been noticed. In any event, the spectrum is practically featureless except for a broad band with a shallow maximum at 720 cm^{-1}.

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(21) R. Müller and C. Dathe, *Chem. Ber.*, **98**, 235 (1965).