≈ 3.2) is essentially the same as that in $W_2Me_8^{4-}$, we can enter a point for the latter on Sattelberger and Fackler's plot of the $\delta \rightarrow \delta^*$ transition energy vs. M-M distance.[25] As shown in Figure 3, the new point lies very close to the straight line previously established using the Cr, Mo, and Re compounds.

Acknowledgment. We are grateful to several co-workers for useful discussions or help in the early stages, especially Dr. L. W. Shive, who participated in some of the earliest preparative experiments, and Dr. D. M. Collins, who played a vital role in solving the crystal structure. This work was supported in part by the National Science Foundation.

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Methyl and Fluorine Substituent Effects on the Gas-Phase Lewis Acidities of Silanes by Ion Cyclotron Resonance Spectroscopy

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Received January 7, 1977

Abstract: Formation of gas-phase Lewis acid-base adducts $(CH_3)_nF_{4-n}SiF^-$ ($n = 0$-2) in reactions of SF_6^- and SF_5^- with neutral fluoromethylsilanes are examined using trapped-anion ion cyclotron resonance spectroscopy. Fluoride transfer reactions observed in binary mixtures of the silanes and of silanes with borane Lewis acids R_3B ($R = CH_3$, C_2H_5, i-C_3H_7, F), in the presence of trace amounts of SF_6 as the fluoride source, establish the Lewis acidity order $BF_3 > SiF_4 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > (CH_3)_2FB > CH_3SiF_3 > (CH_3)_3B > (CH_3)_2SiF_2 > SF_4 > (CH_3)_3SiF$ in the gas phase for F^- as reference base. Quantitative estimates of adduct bond dissociation energies $D[(CH_3)_nF_{4-n}Si\text{-}F^-]$ ($n = 0$-2) and heats of formation of adducts $(CH_3)_nF_{4-n}SiF^-$ are derived. Variations in adduct bond strengths are discussed in terms of the effects of methyl and fluorine substitution on silicon. Analogies are drawn to similar substituent effects observed in the isoelectronic neutral fluoromethylphosphoranes.

Electron-pair dative bond formation between acceptor species A, which possess low-lying vacant orbitals, and donors B, which have accessible lone pairs (phenomena most generally described by the Lewis theory of acid-base interactions[2]), encompass chemical behavior common to much of the periodic table. Among the more familiar Lewis acids are the group 3b acceptors (compounds of B, Al, Ga, etc.) and many metal cations (from groups 1a, 2a, and compounds of the transition metals).[3,4] Studies of dissociation equilibria (eq 1) and displacement reactions (eq 2),

$$AB \rightleftharpoons A + B \quad \Delta H \equiv D[A\text{-}B] \qquad (1)$$

$$A_1B + A_2 \rightleftharpoons A_1 + A_2B \qquad (2)$$

employing a common reference base B, have provided information on adduct bond dissociation energies and insight into relationships between molecular structure and chemical reactivity for a wide variety of polyatomic Lewis acids, both in solution and in the gas phase.[3,4]

By comparison, much less is known about Lewis acid properties of neutral group 4b acceptors R_4M (M = C, Sn, Ge, etc.), where formation of acid-base adducts requires coordinative expansion of nominally closed-shell (electron octet) systems. Under the influence of higher effective nuclear charge and with the availability of lower energy vacant d orbitals, the tendency for dative bonding is increased for the heavier members of the group (e.g., Ge, Sn, Pb).[5] For carbon systems, Dougherty has reported several anionic halide adducts {CH_3XY^- (where X, Y = Cl, Br, I),[6] $H_nCl_{4-n}CCl^-$ (n = 0-3),[7] and $R_3CBr_2^-$ (where R = H, alkyl)[8]} in the gas phase using high-pressure mass spectrometry. Only in the case of CCl_5^-, however, is the involvement of pentacoordinate carbon without controversy. Yamdagni and Kebarle[9] have attributed the stability of the chloride adduct with chloroform to strong hydrogen bonding of the type $[Cl_3C\cdots H\cdots Cl]^-$. From studies of the temperature dependence of equilibria such as eq 1 where $B = Cl^-$, bond dissociation energies $D[Cl_4C\text{-}Cl^-] = 14.2 \pm 0.7$ kcal/mol[7] and $D[Cl_3HC\text{-}Cl^-] = 15.2$ kcal/mol[9] have been determined.

A number of theoretical calculations[10-18] have examined adducts involving pentacoordinate carbon and silicon, with the primary interest being in the investigation of potential energy surfaces for bimolecular nucleophilic substitution (S_N2) reactions. Relevant to the present study are comparisons of the relative energies of separated reactants and transition states of the S_N2 surfaces (i.e., the reaction complexes corresponding to pentacoordinate adducts). Various calculations[10-14] show that for carbon and silicon systems, the most stable adduct geometries are of D_{3h} symmetry (trigonal bipyramidal). Recently, large basis set ab initio calculations by Baybutt[10] have compared the adducts $H\cdots CH_3\cdots H^-$, $F\cdots CH_3\cdots F^-$, $H\cdots SiH_3\cdots H^-$, and $F\cdots SiH_3\cdots F^-$. CH_5^- and $CH_3F_2^-$ were found to be less stable than the separated reactants by 61.2 and 2.1 kcal/mol, respectively, while SiH_5^- and $SiH_3F_2^-$ adducts were calculated to be more stable by 18.6 and 52.1 kcal/mol, respectively.[10] It was found that while d orbitals are not entirely responsible for the stability of the silicon adducts, their inclusion in the basis functions do increase the stabilities of SiH_5^- and $SiH_3F_2^-$ substantially (by ~10 kcal/mol).[10]

A number of pentacoordinate silicon adducts have been experimentally observed. Pentacoordinate amine adducts $(CH_3)_3NSiF_4$,[19] $(CH_3)_3NSiHF_3$,[20] and $(CH_3)_3NSi(CH_3)F_3$[21] have been observed in the gas phase. From measurements of dissociation equilibria of these complexes it is found that adduct stability decreases sharply with replacement of F by H on silicon and even more so with replacement of F by CH_3.[22] SiF_5^- was first reported as a salt $\{[(C_2H_5)_3P]_2PtCl(CO)\}^+SiF_5^-$, the unexpected product of heating C_2F_4 and $[(C_2H_5)_3P]_2PtHCl$ in a silica vessel.[23] NMR studies of SiF_5^-, $RSiF_4^-$, and $R'_2SiF_3^-$ species (R = alkyl, aryl; R′ = aryl) indicate trigonal-bipyramidal structures below −60 °C in solvents of low polarity.[24] Recent gas-phase studies using ion cyclotron resonance spectroscopy (ICR) and high-pressure mass spectrometry (HPMS) have examined the formation of anions containing pentacoordinate silicon. MacNeil and Thynne[25] report the formation of SiF_5^- by a rapid fluoride transfer reaction ($k = 2.2 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}) from SiF_3^-, generated by electron impact, in SiF_4. Dillard[26] has recently measured cross sections for anion transfer reactions

$$SF_6^- + (CH_3)_nF_{4-n}Si \rightarrow (CH_3)_nF_{4-n}SiF^- + SF_5 \quad (3)$$

(where $n = 1$–3) for reactant ion energies as low as 0.5 eV using HPMS. Reaction cross sections were observed to decrease rapidly with successive substitution of CH_3 for F on silicon; the fluoride adduct of $(CH_3)_3SiF$ was barely detectable. McDaniel[27] has reported an ICR study of fluoride transfer reactions (analogous to process 2) among a variety of inorganic Lewis acids. The observed relative Lewis acidity order $SF_4 < HCl < SiF_4 < BF_3$ served to establish the limits[27,28] $54 \leq D[F_4Si\text{-}F^-] < 71$ kcal/mol in the gas phase.

Recent ICR studies from this laboratory[29] of fluoride transfer reactions (analogous to processes 2 and 3) in mixtures of trialkylboranes and BF_3 indicate that the fluoride affinities $D[A\text{-}F^-]$ of acids R_3B and R_2FB ($R = CH_3$, C_2H_5, $i\text{-}C_3H_7$) all lie intermediate between SF_4 and BF_3. In the present report, we wish to describe results of trapped-anion ICR investigations of gas-phase fluoride transfer reactions occurring in the fluoromethylsilanes $(CH_3)_nF_{4-n}Si$ ($n = 0$–3), both alone and in binary mixtures, in the presence of SF_6 as the fluoride source. In addition, fluoride transfer reactions observed in mixtures of these silanes with the alkylboranes and BF_3 afford quantitative estimates of silane Lewis acidities, for F^- as reference base.

Experimental Section

All studies reported herein utilize a high-field ICR spectrometer (employing a 15-in. magnet system) constructed in the Caltech instrument shops. Details of the instrumentation and experimental techniques associated with ICR spectrometry are described elsewhere.[30] Gas mixtures utilized are prepared directly in the ICR cell by admission of appropriate sample components through separate variable leak valves in a parallel inlet manifold. Absolute gas pressures are determined using a Schulz–Phelps ionization gauge, adjacent to the ICR cell, calibrated separately for each component against an MKS Baratron capacitance manometer (Model 90H1-E).[30c] A linear calibration of Baratron pressure (absolute) vs. ionization gauge current affords pressure determinations over a range of 10^{-7}–10^{-4} Torr. Overall accuracy in pressure measurement for these studies is estimated to be ±20%, and represents the major source of error in reported reaction rate constants. All measurements are performed at ambient temperature (~22 °C). Bimolecular reaction rate constants are determined with knowledge of neutral gas pressures from the limiting slopes of semilog plots of trapped-ion abundance vs. time and by considering product distributions where applicable.

$(CH_3)_3B$ and $(C_2H_5)_3B$ were purchased from Alfa Inorganics and SF_6, SiF_4, BF_3, and SO_2 from Matheson. Samples of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3 were provided through the courtesy of Professor J. G. Dillard, and that of $(i\text{-}C_3H_7)_3B$ from Professor A. H. Cowley. Noncondensable impurities are removed from all samples by multiple freeze-pump-thaw cycles at liquid nitrogen temperatures; mass spectral analyses showed no detectable impurities in the samples utilized.

In all studies reported here, SF_6 is utilized as the source of fluoride ion. SF_6^- (~95%) and SF_5^- (~5%) are generated from neutral SF_6, typically present at ~10^{-8} Torr pressure, by rapid attachment of near thermal energy electrons produced in the ICR trapping well by inelastic collisions with neutrals present during the 10-ms electron beam pulse.[31-33] In mixtures containing $(CH_3)_3SiF$, SO_2F^- (generated by fluoride transfer from SF_6^- to SO_2[27,28a]) was also tried as a source of F^-. The electron beam energy utilized is nominally 70 eV for emission currents of ~10^{-7} A.

Data reported in tables and figures are normalized to monoisotopic abundances (^{12}C, 98.89%; ^{11}B, 80.22%; ^{28}Si, 92.21%; ^{32}S, 95.0%). Typically, ion concentrations comprising <1% of the total are not included in the reported data.

Results

Observed ion-molecule reactions between SF_6^- and each of the silanes $(CH_3)_nF_{4-n}Si$ ($n = 0$–3) are described below. Fluoride ion transfer reactions dominate the anion chemistry of these systems and ultimately yield stable pentacoordinate silane-fluoride adducts $(CH_3)_nF_{4-n}SiF^-$ ($n = 0$–2). Then reactions initiated by SF_6^- in binary mixtures of the silanes are examined to determine relative fluoride affinities (Lewis acidities) of the neutrals. Finally, in attempts to quantify the fluoride affinities of the silanes, studies of mixtures of the silanes with various borane Lewis acids R_3B (where $R = CH_3$, C_2H_5, $i\text{-}C_3H_7$, and F) are described. The gas-phase fluoride affinities of these boranes are available from recent studies[29] and provide reference points for quantitative comparisons. Experimentally determined reaction rate constants are summarized in Table I.

SF_6/SiF_4. In a sample of SiF_4 at 9.7×10^{-7} Torr pressure containing trace amounts of SF_6 (~10^{-8} Torr), production of SiF_5^- via the reaction

$$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5 \quad (4)$$

involving fluoride transfer from SF_6^- is in agreement with previous reports.[27,34] SF_5^- produced by dissociative electron capture in SF_6 also generates SiF_5^- via the fluoride transfer reaction

$$SF_5^- + SiF_4 \rightarrow SiF_5^- + SF_4 \quad (5)$$

Table I. Ion-Molecule Processes Observed

System	Reaction	No.[a]	Rate constant[b]	Thermochemical implications
SF_6/SiF_4	$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$	4	4.2	$D[SiF_4{-}F^-] > D[SF_5{-}F^-]$
	$SF_5^- + SiF_4 \rightarrow SiF_5^- + SF_4$	5	6.8	$D[SiF_4{-}F^-] > D[SF_4{-}F^-]$
SF_6/CH_3SiF_3	$SF_5^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_5$	6	1.5	$D[(CH_3)F_3Si{-}F^-] > D[SF_5{-}F^-]$
	$SF_5^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_4$	7	2.6	$D[(CH_3)F_3Si{-}F^-] > D[SF_4{-}F^-]$
$SF_6/(CH_3)_2SiF_2$	$SF_6^- + (CH_3)_2SiF_2 \xrightarrow{90\%} (CH_3)_2SiF_3^- + SF_5$	8	1.3[d]	$D[(CH_3)_2F_2Si{-}F^-] > D[SF_5{-}F]$
	$\xrightarrow{10\%} SF_5^- + \left\{\begin{matrix} HF + (CH_3)F_2CH_2 \\ \text{or} \\ CH_3F + (CH_3)F_2Si \end{matrix}\right.$	9	0.1[d]	$\Delta H_f[(CH_3)F_2SiCH_2] \leqslant -157.1$, $\Delta H = -3.5$[f]
	$SF_5^- + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF_3^- + SF_4$	10	0.3	$D[(CH_3)_2F_2Si] > D[SF_4{-}F^-]$
$SF_6/(CH_3)_3SiF$	$SF_6^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SF_5$	*c*	<0.01	$D[(CH_3)_3FSi{-}F^-] > D[SF_5{-}F^-]$
	$SF_5^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SF_5$	*c*	<0.01	$D[(CH_3)_3FSi{-}F^-] < D[SF_4{-}F^-]$
$SF_6/(CH_3)_3SiF/SO_2$	$SO_2F^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SO_2$	11[c]	<0.01	$D[(CH_3)_3FSi{-}F^-] < D[SO_2{-}F^-]$
	$SO_2F_2^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SO_2F$	12[c]	<0.01	$D[(CH_3)_3FSi{-}F^-] < D[SO_2F{-}F^-]$
$SF_6/(CH_3)_3SiF/(CH_3)_2SiF_2$	$(CH_3)_2SiF_3^- + (CH_3)_3SiF \rightarrow (CH_3)_3SiF_2^- + (CH_3)_2SiF_2$	13[c]	<0.01	$D[(CH_3)_3FSi{-}F^-] < D[(CH_3)_2F_2Si{-}F^-]$
$SF_6/(CH_3)_2SiF_2/CH_3SiF_3$	$(CH_3)_2SiF_3^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_2SiF_2$	14	2.2	$D[(CH_3)F_3Si{-}F^-] > D[(CH_3)_2F_2Si{-}F^-]$, $\Delta G < -2.6$[g]
$SF_6/CH_3SiF_3/SiF_4$	$CH_3SiF_4^- + SiF_4 \rightarrow SiF_5^- + CH_3SiF_3$	15	~3[e]	$D[F_4Si{-}F^-] > D[(CH_3)F_3Si{-}F^-]$
$SF_6/(CH_3)_3B/(CH_3)_2SiF_2$	$(CH_3)_2SiF_3^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2$	19	3.4	$D[(CH_3)_3B{-}F^-] > D[(CH_3)_2F_2Si{-}F^-]$, $\Delta G < -21.0$[g]
	$(CH_3)_2BF_2^- + (CH_3)_2SiF_2 \nrightarrow (CH_3)_2SiF_3^- + (CH_3)_2FB$	*c*	<0.01	$D[(CH_3)_2F_2Si{-}F^-] < D[(CH_3)_2FB{-}F^-]$
$SF_6/(CH_3)_3B/CH_3SiF_3$	$(CH_3)_3BF^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_3B$	20	9.5	$D[(CH_3)F_3Si{-}F^-] > D[(CH_3)_3B{-}F^-]$
	$(CH_3)_2BF_2^- + CH_3SiF_3 \nrightarrow CH_3SiF_4^- + (CH_3)_2FB$	*c*	<0.01	$D[(CH_3)F_3Si{-}F^-] < D[(CH_3)_2FB{-}F^-]$
$SF_6/(C_2H_5)_3B/CH_3SiF_3$	$CH_3SiF_4^- + (C_2H_5)_3B \rightleftharpoons (C_2H_5)_3BF^- + CH_3SiF_3$	24	$K_{eq} = 2.3$[h]	$D[(C_2H_5)_3B{-}F^-] > D[(CH_3)F_3Si{-}F^-]$, $\Delta G = 0.5 \pm 0.1$[g]
	$(C_2H_5)_2BF_2^- + CH_3SiF_3 \nrightarrow CH_3SiF_4^- + (C_2H_5)_2FB$	*c*	<0.01	$D[(CH_3)F_3Si{-}F^-] < D[(C_2H_5)_2FB{-}F^-]$
$SF_6/(C_2H_5)_3B/SiF_4$	$(C_2H_5)_3BF^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_3B$	25	2.8	$D[F_4Si{-}F^-] > D[(C_2H_5)_3B{-}F^-]$
	$(C_2H_5)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_2FB$	26	2.0	$D[F_4Si{-}F^-] > D[(C_2H_5)_2FB{-}F^-]$
$SF_6/(i\text{-}C_3H_7)_3B/SiF_4$	$(i\text{-}C_3H_7)_3BF^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_3B$	30	2.2	$D[F_4Si{-}F^-] > D[(i\text{-}C_3H_7)_3B{-}F^-]$, $\Delta G < -1.7$[g]
	$(i\text{-}C_3H_7)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_3B$	31	1.5	$D[F_4Si{-}F^-] > D[(i\text{-}C_3H_7)_2FB{-}F^-]$
$SF_6/BF_3/CH_3SiF_3$	$CH_3SiF_4^- + BF_3 \rightarrow BF_4^- + CH_3SiF_3$	34	2.1	$D[F_3B{-}F^-] > D[(CH_3)F_3Si{-}F^-]$
$SF_6/BF_3/SiF_4$	$SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4$	35	~3[e]	$D[F_3B{-}F^-] > D[F_4Si{-}F^-]$

[a] Reaction numbers refer to reactions specified in the text. [b] Rate constants are in units of × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, determined from the limiting slopes of reactant ion disappearance, considering product distributions where applicable. [c] Reactions not observed by double resonance, see text for discussions. [d] Total disappearance rate constant for reaction of SF_6^- with $(CH_3)_2SiF_2$; product distributions determined in cyclotron ejection experiments. [e] Rate constants estimated though quantitative data were not obtained, see text for discussion. [f] Calculated using data in Table II. [g] Free energy changes in units of kcal/mol, determined as specified in the text. [h] Equilibrium constant for reaction 24, determined as specified in the text.

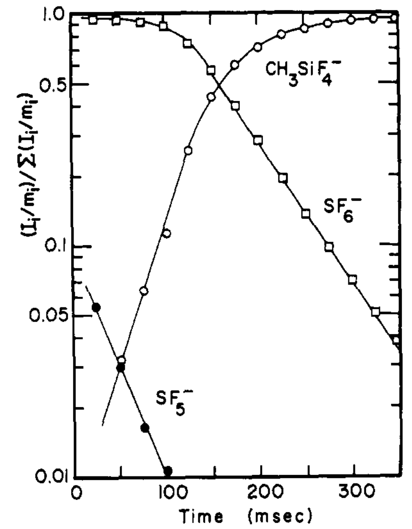


Figure 1. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in 2.8×10^{-6} Torr CH_3SiF_3 in the presence of trace amounts of SF_6.

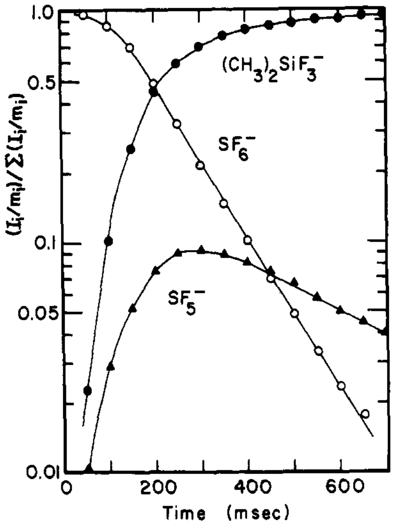


Figure 2. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in 1.6×10^{-6} Torr $(CH_3)_2SiF_2$ in the presence of trace amounts of SF_6.

SiF_5^- appears stable to further reaction under these conditions.

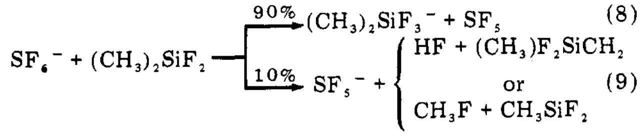
SF_6/CH_3SiF_3. The temporal variation of ion abundances initiated by the electron beam pulse in 2.8×10^{-6} Torr CH_3SiF_3 in the presence of trace amounts of SF_6 is displayed in Figure 1. Fluoride transfer reactions

$$SF_6^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_5 \qquad (6)$$

$$SF_5^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_4 \qquad (7)$$

yielding $CH_3SiF_4^-$, are detected by double resonance. In contrast to processes described below in the $SF_6/(CH_3)_2SiF_2$ system, SF_5^- is not produced by reaction of SF_6^- with CH_3SiF_3. $CH_3SiF_4^-$ produced by reactions 6 and 7 does not react further under the present conditions.

$SF_6/(CH_3)_2SiF_2$. Electron impact in a sample of $(CH_3)_2SiF_2$ at 1.6×10^{-6} Torr containing trace amounts of SF_6 results in the temporal variation of trapped anion abundances shown in Figure 2. The pentacoordinate $(CH_3)_2SiF_3^-$ anion is formed by fluoride transfer reactions 8 and 10, analogous to processes



$$SF_6^- + (CH_3)_2SiF_2 \begin{cases} \xrightarrow{90\%} (CH_3)_2SiF_3^- + SF_5 & (8) \\ \xrightarrow{10\%} SF_5^- + \left\{ \begin{array}{c} HF + (CH_3)F_2SiCH_2 \\ \text{or} \\ CH_3F + CH_3SiF_2 \end{array} \right. & (9) \end{cases}$$

$$SF_5^- + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF_3^- + SF_4 \qquad (10)$$

observed in SiF_4 and CH_3SiF_3. In addition, double resonance indicates reaction 9 to be responsible for the initial increase in SF_5^- shown in Figure 2. Generation of SF_5^- has previously been reported in reactions of SF_6^- with a variety of molecules (e.g., HX, where X = Cl, Br, I;[28a] R_3B, where R = CH_3, C_2H_5, i-C_3H_7;[29,35] HCO_2H, CH_3CO_2H, H_2S[33b]). The neutral products in reaction 9 remain uncertain. Formation of CH_3F and CH_3SiF_2 radical is calculated to be ~3.5 kcal/mol exothermic.[36] $(CH_3)_2SiF_3^-$ appears stable to further reaction under these conditions.

$SF_6/(CH_3)_3SiF$ and $SF_6/SO_2/(CH_3)_3SiF$. Under a variety of experimental conditions, no silicon-containing anions are produced in either $SF_6/(CH_3)_3SiF$ or $SF_6/SO_2/(CH_3)_3SiF$ mixtures. Specifically, no pentacoordinate $(CH_3)_3SiF_2^-$ is observed. These gas mixtures were examined by variation of pressure (up to $\sim 10^{-4}$ Torr) and of ion trapping time at constant pressure ($\sim 10^{-6}$ Torr $(CH_3)_3SiF$). In the $SF_6/(CH_3)_3SiF$ mixture, SF_6^- (~95%) and SF_5^- (~5%), generated by electron capture processes in SF_6, remain completely unreactive as a function of pressure and trapping time. Generation of SF_5^- by processes analogous to eq 9 are not observed. In the presence of SO_2, SF_6^- and SF_5^- react to generate SO_2F^- and $SO_2F_2^-$.[28a] The latter anion reacts further with SO_2 by fluoride transfer to yield SO_2F^- as the final stable product ion. SO_2F^- and $SO_2F_2^-$ do not react with $(CH_3)_3SiF$. In particular, fluoride transfer reactions 11 and 12 are not observed.

$$SO_2F^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SO_2 \qquad (11)$$

$$SO_2F_2^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + SO_2F \qquad (12)$$

$SF_6/(CH_3)_3SiF/(CH_3)_2SiF_2$. In further attempts to generate $(CH_3)_3SiF_2^-$ from $(CH_3)_3SiF$, anion reactions in mixtures of SF_6, $(CH_3)_3SiF$, and $(CH_3)_2SiF_2$ are examined as a function of pressure and trapping time. The only silicon-containing anion detected is $(CH_3)_2SiF_3^-$ produced by reactions 8–10 as described above. Notably, fluoride transfer from $(CH_3)_2SiF_3^-$ to $(CH_3)_3SiF$ (reaction 13) is not observed.

$$(CH_3)_2SiF_3^- + (CH_3)_3SiF \nrightarrow (CH_3)_3SiF_2^- + (CH_3)_2SiF_2 \qquad (13)$$

$SF_6/(CH_3)_2SiF_2/CH_3SiF_3$. The variations in trapped-anion abundances initiated by the electron beam pulse in a 4.7:1 mixture of $(CH_3)_2SiF_2$ and CH_3SiF_3 (in the presence of traces of SF_6) at 3.4×10^{-6} Torr total pressure are displayed in Figure 3. In addition to reactions 6–10 described above, the fluoride transfer reaction

$$(CH_3)_2SiF_3^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_2SiF_2 \qquad (14)$$

accounts for the disappearance of $(CH_3)_2SiF_3^-$ at long times in Figure 3. $CH_3SiF_4^-$ is unreactive in this mixture.

$SF_6/CH_3SiF_3/SiF_4$. In an ~1:1 mixture of CH_3SiF_4 and SiF_4 at $\sim 2 \times 10^{-6}$ Torr, $CH_3SiF_3^-$ and SiF_5^- are produced initially by reactions 4–7 described above. Difficulties in maintaining constant pressure in the mixture[37] precluded detailed examination of the kinetics, but is apparent that the fluoride transfer reaction 15

$$CH_3SiF_4^- + SiF_4 \rightarrow SiF_5^- + CH_3SiF_3 \qquad (15)$$

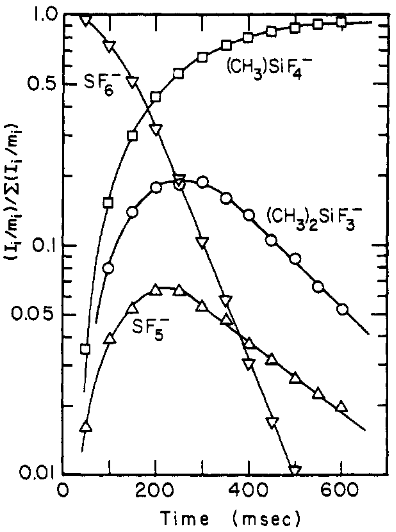


Figure 3. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in a 4.7:1 mixture of $(CH_3)_2SiF_2$ and CH_3SiF_3 at 3.4×10^{-6} Torr in the presence of trace amounts of SF_6.

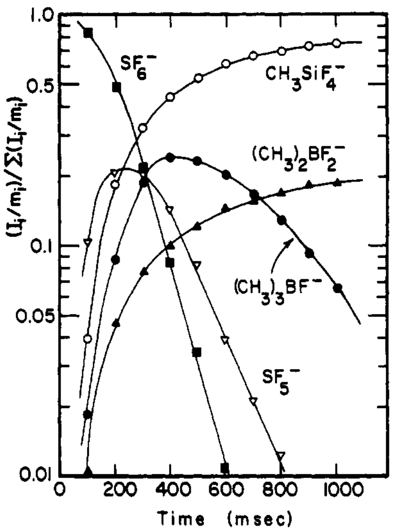


Figure 5. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in a 4.4:1 mixture of $(CH_3)_3B$ and CH_3SiF_3 at 5.4×10^{-7} Torr in the presence of trace amounts of SF_6.

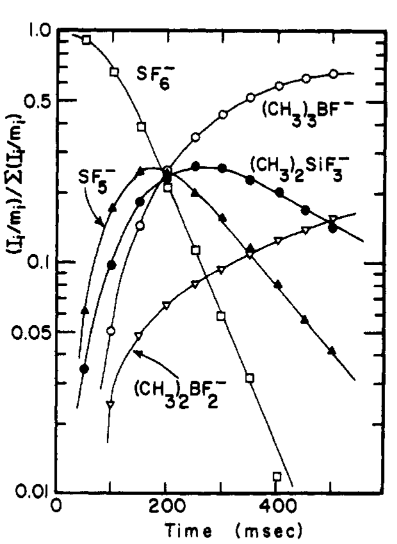


Figure 4. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in a 7.5:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_3B$ at 2.2×10^{-6} Torr in the presence of trace amounts of SF_6.

(confirmed by double resonance) proceeds rapidly to completion.

$SF_6/(CH_3)_3B/(CH_3)_2SiF_2$. The temporal variation in anion abundances initiated by the electron beam pulse in a 7.5:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_3B$ at a constant pressure of 2.2×10^{-6} Torr in the presence of traces of SF_6 is shown in Figure 4. Reactions 16–18

$$SF_6^- + (CH_3)_3B \longrightarrow \begin{cases} SF_5^- + HF + (CH_3)_2BCH_2 & (16) \\ (CH_3)_2BF_2^- + SF_4 + CH_3 & (17) \end{cases}$$

$$SF_5^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + SF_4 \quad (18)$$

have been previously reported in $SF_6/(CH_3)_3B$ mixtures.[29,35] In addition to reactions 8–10 described above, fluoride transfer from $(CH_3)_2SiF_3^-$ to $(CH_3)_3B$

$$(CH_3)_2SiF_3^- + B(CH_3)_3 \rightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2 \quad (19)$$

is detected by double resonance, accounting for the decay of $(CH_3)_2SiF_3^-$ at long times in Figure 4. Both $(CH_3)_3BF^-$ and $(CH_3)_2BF_2^-$ are stable to further reaction in this mixture.

$SF_6/(CH_3)_3B/CH_3SiF_3$. Figure 5 shows the time evolution of anion concentrations following the electron beam pulse in a 4.4:1 mixture of $(CH_3)_3B$ and CH_3SiF_3 at a total pressure of 5.4×10^{-7} Torr in the presence of trace amounts of SF_6. In addition to reactions 6 and 7 described above and reactions 16–18 previously reported in the $SF_6/B(CH_3)_3$ system,[29,35] the fluoride transfer reaction

$$(CH_3)_3BF^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + B(CH_3)_3 \quad (20)$$

is observed in the $SF_6/(CH_3)_3B/CH_3SiF_3$ mixture. $(CH_3)_2BF_2^-$ does not react with CH_3SiF_3. $CH_3SiF_4^-$ is also stable to further reaction in the mixture.

$SF_6/B(C_2H_5)_3/CH_3SiF_3$. In a 1:1 mixture of $(C_2H_5)_3B$ and CH_3SiF_3 at a constant pressure of 7.9×10^{-7} Torr containing traces of SF_6, the temporal variation of anion abundances depicted in Figure 6 is initiated by the electron beam pulse. Boron-containing anions, $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$, are initially produced via reactions 21–23, previously reported from

$$SF_6^- + (C_2H_5)_3B \longrightarrow \begin{cases} SF_5^- + HF + (C_2H_5)_2BC_2H_4 & (21) \\ (C_2H_5)_2BF_2^- + SF_4 + C_2H_5 & (22) \end{cases}$$

$$SF_5^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + SF_4 \quad (23)$$

studies of $SF_6/(C_2H_5)_3B$ mixtures.[29] $CH_3SiF_4^-$ is produced, at short reaction times in Figure 6, by processes 6 and 7 described above. For trapping times beyond ~500 ms in Figure 6, the relative concentrations of $(C_2H_5)_3BF^-$ and $CH_3SiF_4^-$ approach a constant ratio of 2.30 ± 0.05. Double resonance indicates that the reaction

$$CH_3SiF_4^- + (C_2H_5)_3B \rightleftharpoons (C_2H_5)_3BF^- + CH_3SiF_3 \quad (24)$$

proceeds in both forward and reverse directions. These results suggest that a fluoride transfer equilibrium is established between $(C_2H_5)_3B$ and CH_3SiF_3 with the balance lying preferentially to the right in reaction 24. The equilibrium constant $K_{eq} = 2.3$ is determined,[38] corresponding to a free energy change $\Delta G = -0.5 \pm 0.1$ kcal/mol. With the conditions used, $(C_2H_5)_2BF_2^-$ is not observed to react further with CH_3SiF_3.

$SF_6/(C_2H_5)_3B/SiF_4$. In trapped-ion experiments on a 5.4:1 mixture of $(C_2H_5)_3B$ and SiF_4 at 1.2×10^{-6} Torr in the presence of trace amounts of SF_6, ions SiF_5^-, $(C_2H_5)_3BF^-$, and $(C_2H_5)_2BF_2^-$ are formed initially via processes 4, 5, and 21–23 described above for the individual components. At long reaction times SiF_5^- abundance continues to increase at the

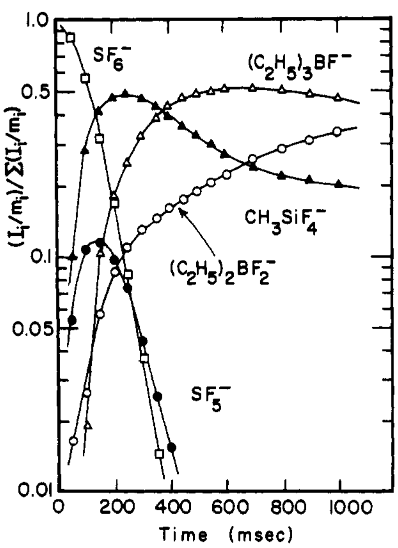


Figure 6. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in a 1:1 mixture of $(C_2H_5)_3B$ and CH_3SiF_3 at 7.9 × 10^{-7} Torr in the presence of trace amounts of SF_6.

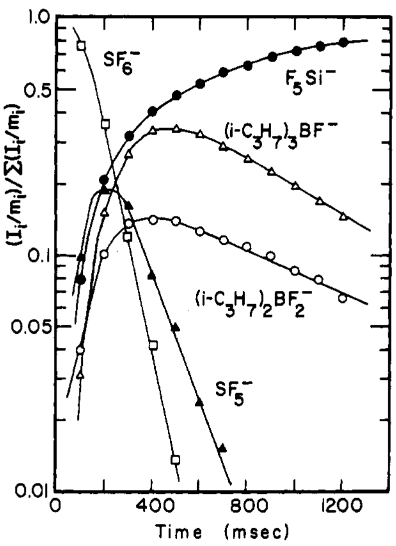


Figure 7. Temporal variation of trapped-anion abundances following a 10-ms 70-eV electron beam pulse in a 3.5:1 mixture of $(i\text{-}C_3H_7)_3B$ and SiF_4 at 9.4 × 10^{-7} Torr in the presence of trace amounts of SF_6.

expense of $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$. Double resonance indicates the occurrence of the rapid fluoride transfer reactions

$$(C_2H_5)_3BF^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_3B \qquad (25)$$

$$(C_2H_5)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_2FB \qquad (26)$$

SiF_5^- eventually comprises ~100% of the ion abundance and is not observed to react further under the present conditions.

$SF_6/B(i\text{-}C_3H_7)_3/SiF_4$. The temporal variation of ion concentrations following the electron beam pulse in a 3.5:1 mixture of $B(i\text{-}C_3H_7)_3$ and SiF_4 at 9.4 × 10^{-7} Torr total pressure (in the presence of trace SF_6) is displayed in Figure 7. Boron-containing anions are formed initially by reactions 27–29, previously observed in $SF_6/(i\text{-}C_3H_7)_3B$ mixtures.[29]

$$SF_6^- + B(i\text{-}C_3H_7)_3 \begin{cases} \rightarrow SF_5^- + HF + (i\text{-}C_3H_7)_2BC_3H_6 & (27) \\ \rightarrow (i\text{-}C_3H_7)_2BF_2^- + SF_4 + i\text{-}C_3H_7 & (28) \end{cases}$$

$$SF_5^- + B(i\text{-}C_3H_7)_3 \rightarrow (i\text{-}C_3H_7)_3BF^- + SF_4 \qquad (29)$$

In addition to processes 4 and 5 described above, SiF_5^- is generated by the fluoride transfer reactions

$$(i\text{-}C_3H_7)_3BF^- + SiF_4 \rightarrow SiF_5^- + B(i\text{-}C_3H_7)_3 \qquad (30)$$

$$(i\text{-}C_3H_7)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_2FB \qquad (31)$$

and is not observed to react further under the present conditions.

$SF_6/BF_3/CH_3SiF_3$. In trapped-ion experiments on a 1.1:1 mixture of CH_3SiF_3 and BF_3 at 1.2 × 10^{-6} Torr pressure containing trace amounts of SF_6, $CH_3SiF_4^-$ is produced initially via reactions 6 and 7 described above and BF_4^- is generated by previously reported processes 32 and 33.[27,29,33a] BF_4^- is produced by fluoride transfer from $CH_3SiF_4^-$ (reaction 34). No evidence is obtained for the reverse of reaction 34, and BF_4^- appears stable to further reaction under the conditions utilized.

$$SF_6^- + BF_3 \rightarrow BF_4^- + SF_5 \qquad (32)$$

$$SF_5^- + BF_3 \rightarrow BF_4^- + SF_4 \qquad (33)$$

$$CH_3SiF_4^- + BF_3 \rightarrow BF_4^- + CH_3SiF_3 \qquad (34)$$

$SF_6/BF_3/SiF_4$. In an ~1:1 mixture of SiF_4 and BF_3 at ~1 × 10^{-6} Torr pressure in the presence of trace amounts of SF_6, fluoride transfer reactions 4, 5, 32, and 33 described above lead to the formation of SiF_5^- and BF_4^-. Although experimental difficulties in maintaining stable gas pressures in this mixture[37] inhibit detailed examination of the reaction kinetics, it is clear that fluoride transfer from SiF_5^- to BF_3

$$SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4 \qquad (35)$$

proceeds rapidly to completion. No evidence is obtained for the back reaction and BF_4^- does not appear to react further under the present conditions.

Discussion

SF_6^-,$SF_5^-/(CH_3)_nF_{4-n}Si$ (n = 0–3). Observations of pentacoordinate anions SiF_5^-, $CH_3SiF_4^-$, and $(CH_3)_2SiF_3^-$ formed by fluoride transfer reactions, between the respective neutral silanes and SF_6^- and SF_5^- (Table I), are in agreement with previous studies.[26] However, under no conditions was fluoride transfer to $(CH_3)_3SiF$ observed in the present work. The discrepancy between this result and the observations of Dillard[26] are not fully understood, although differences in the energy of reactants SF_6^- and SF_5^- between the two studies may be responsible. In trapped-ion ICR, inelastic collisions with neutral molecules during the long trapping times effectively thermalize the ions. Thus, reactions observed are assumed to be exothermic or thermoneutral for thermal energy reactants.

Reactions 5, 7, and 10 require that the fluoride affinities of $(CH_3)_2SiF_2$, CH_3SiF_3, and SiF_4 exceed ~54 kcal/mol, the value previously reported[28a] for $D[SF_4\text{-}F^-]$. Failure to detect $(CH_3)_3SiF_2^-$ by reaction with SF_6^- implies that $D[(CH_3)_3FSi\text{-}F^-] < D[SF_5\text{-}F^-] = 11 \pm 8$ kcal/mol,[28a] a drastic decrease in Lewis acidity of $(CH_3)_3SiF$ as compared with the more highly fluorinated silanes. It is possible that fluoride transfer from SF_6^- to $(CH_3)_3SiF$ is not observed due to kinetic rather than thermodynamic effects.[28a] The fluoride affinity of SO_2, though not known precisely, is very near that of SF_4.[27,28a] Failure to observe $(CH_3)_3SiF_2^-$ by reaction of SO_2F^- or SF_5^- requires that $D[(CH_3)_3FSi\text{-}F^-]$ be <54 kcal/mol.

SF_6/Silane Mixtures. Reactions 13–15 imply the order of Lewis acidities $(CH_3)_3SiF < (CH_3)_2SiF_2 < CH_3SiF_3 < SiF_4$. As previously observed in studies of anion transfer processes in borane Lewis acids,[29,35] alkyl substitution in place of fluorine α to the acceptor center results in decreased acidity.

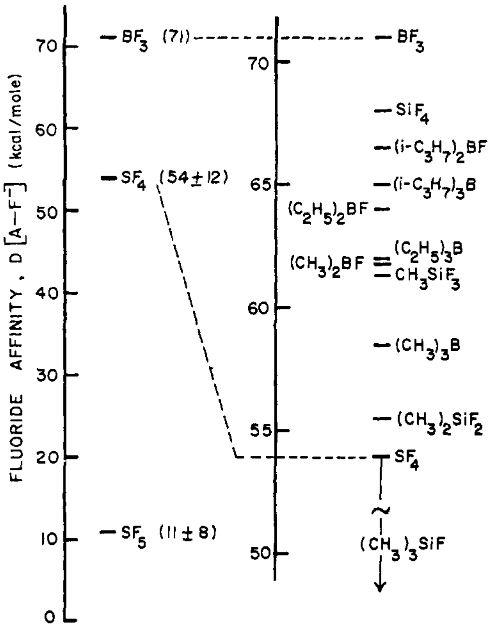


Figure 8. Schematic representation of Lewis acidities of neutral acceptors A using F^- ion as reference base (expressed as fluoride affinities $D[A-F^-]$).

SF_6/Silane–Borane Mixtures. The fluoride affinity of SiF_4 is known from previous studies to be below that of BF_3 (71 kcal/mol).[27] Quantification of the fluoride affinities of $(CH_3)_2SiF_2$, CH_3SiF_3, and SiF_4, within the 17-kcal range bracketed by SF_4 and BF_3, is obtained from the preferred directions of fluoride transfer reactions with borane Lewis acids previously shown to span this same fluoride affinity range.[29] Taken collectively with previous results,[29] these reactions (Table I) establish the fluoride affinity order $(CH_3)_3SiF < SF_4 < (CH_3)_2SiF_2 < (CH_3)_3B < CH_3SiF_3 < (CH_3)_2FB < (C_2H_5)_3B < (C_2H_5)_2FB < (i\text{-}C_3H_7)_3B < (i\text{-}C_3H_7)_2FB < SiF_4 < BF_3$ in the gas phase. Only in the case of reaction 24 in the $SF_6/(C_2H_5)_3B/CH_3SiF_3$ system is evidence of an equilibrium obtained.

Thermochemical Considerations. The observed $K_{eq} = 2.3$ favoring fluoride bound to $(C_2H_5)_3B$ requires that a free energy change of ~0.5 kcal/mol accompany reaction 24. Trapped-ion ICR techniques are generally able to provide accurate determinations of similar anion transfer equilibria and associated free energy changes up to values of ~3 kcal/mol. Larger free energy changes yield equilibrium constants (and forward and reverse rate constants) exceeding the dynamic range of the technique.

Considering the relative order of fluoride affinities stated above, it is noteworthy that reactions 14, 19, and 30 proceed only in the forward direction. This conclusion is apparent from data in Figures 3, 4, and 7 and the failure to detect the reverse reactions by double resonance. The ratios of reactant and product ions at long times and ratios of neutral acid pressures place lower limits on K_{eq} of >83.2, >34.9, and >18.9 for reactions 14, 19, and 30, respectively, corresponding to free energy changes of <−2.6, <−2.1, and <−1.7 kcal/mol. Similar limits apply to reactions 15 and 30.

A quantity more relevant to discussion of adduct bond energies $D[A-F^-]$ is the enthalpy change ΔH, which is related to the free energy change $\Delta G = \Delta H - T\Delta S = -RT \ln K_{eq}$. The present ICR instrumentation is limited to measurements at ambient temperatures, precluding experimental determination of ΔH from variations of K_{eq} and thus ΔG with temperature. Within reasonable assumptions, the statistical mechanical formalism of Searles and Kebarle[39] may be used to estimate that ΔS for reaction 24 is negligible. Thus $\Delta H \cong -0.5$ kcal/mol for fluoride transfer from $CH_3SiF_4^-$ to $(C_2H_5)_3B$.

Table II. Thermochemical Quantities[a] Utilized in the Calculations

A	$\Delta H_f(A)$	$D[A-F^-]$
SF_4	-183 ± 6^b	54 ± 12^b
SF_5	-232 ± 4^b	11 ± 8^b
SF_5^-	-298 ± 6	
SF_6^-	-304.4 ± 3.5^b	
CH_3F	-55.9^c	
HF	-64.9 ± 0.3^b	
CH_3SiF_2	-166.0^d	
$(CH_3)_3SiF$	-126.0^d	
$(CH_3)_2SiF_2$	-212.0^d	
CH_3SiF_3	-296.0^d	
SiF_4	-386.0^d	$<71^f$
$(CH_3)_3B$	-29.3^e	58.5^e
$(CH_3)_2FB$	$\leq -61.9^e$	61.8^e
$(C_2H_5)_3B$	-36.0^e	62.0^e
$(C_2H_5)_2FB$	$\leq -58.1^e$	64.0^e
$(i\text{-}C_3H_7)_3B$	-56.3^e	65.0^e
$(i\text{-}C_3H_7)_2FB$	$\leq -67.5^e$	66.5^e
BF_3	-271.7^e	71^f
BF_4^-	-404.0^e	
F^-	-61.3 ± 0.3^b	

[a] All data are in units of kcal/mol at 298 K. [b] Reference 28a. [c] M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 2085 (1977). [d] J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 427 (1971). [e] Reference 29. [f] Reference 27.

Table III. Thermochemical Quantities[a] Describing Ions and Neutrals of Silicon

Acid, A	$D[A-F^-]^b$	$\Delta H_f[A]^c$	$\Delta H_f[AF^-]^d$
SiF_4	68.0	−386.0	-515.3^e
CH_3SiF_3	61.5	−296.0	-418.5^f
$(CH_3)_2SiF_2$	55.5	−212.0	-328.5^g
$(CH_3)_3SiF$	<54	−126.0	$>-241.0^h$

[a] All data are in units of kcal/mol at 298 K. [b] Bond dissociation energies determined as specified in the text. [c] Heats of formation of the silanes from Table II. [d] Calculated using data in Table II and this table. [e] Calculated from $\Delta H_f[SiF_5^-] = \Delta H_f[SiF_4] + \Delta H_f[BF_4^-] - \Delta H_f[BF_3] - \Delta H_r$, where $\Delta H_r = -3$ kcal/mol for reaction 35. [f] Calculated from $\Delta H_f[CH_3SiF_4^-] = \Delta H_f[CH_3SiF_3] + \Delta H_f[(C_2H_5)_3BF^-] - \Delta H_f[(C_2H_5)_3B] - \Delta H_r$, where $\Delta H_r = -0.5$ kcal/mol for reaction 24. [g] Calculated from $\Delta H_f[(CH_3)_2SiF_3^-] = \Delta H_f[(CH_3)_3BF^-] + \Delta H_f[(CH_3)_2SiF_2] - \Delta H_f[(CH_3)_3B] - \Delta H_r$, where $\Delta H_r = -3$ kcal/mol for reaction 19. [h] Estimated from $\Delta H_f[(CH_3)_3SiF_2^-] > \Delta H_f[SF_5^-] + \Delta H_f[(CH_3)_3SiF] - \Delta H_f[SF_4]$ from failure to observe F^- transfer from SF_5^- to $(CH_3)_3SiF$.

Evaluation of the present results along with the results of the previous study of the boranes,[29] assuming a minimum separation of ~3 kcal/mol in cases where no reverse reactions were evidenced, affords a quantitative scale of fluoride affinities, which is fully consistent with all available data, as displayed schematically in Figure 8. Using available thermochemical data (Table II) and estimates of 68, 61.5, and 55.5 kcal/mol for the fluoride affinities of SiF_4, CH_3SiF_3, and $(CH_3)_2SiF_2$, heats of formation for the silane-fluoride Lewis adduct anions can be derived (Table III). Taking −3, −0.5, and −3 kcal/mol for the enthalpy changes for reactions 19, 24, and 35, respectively, yields estimates of $\Delta H_f((CH_3)_2SiF_3^-) = -328.5$, $\Delta H_f(CH_3SiF_4^-) = -418.5$, and $\Delta H_f(SiF_5^-) = -515.3$ kcal/mol. Failure to observe $(CH_3)_3SiF_2^-$ by reaction of $(CH_3)_3SiF$ with SF_5^- or SO_2F^- requires that $\Delta H_f((CH_3)_3SiF_2^-)$ exceed −241.0 kcal/mol. Thermochemical data describing the neutral silane Lewis acids and fluoride adducts are summarized in Table III.

Substituent Effects on Silane Lewis Acidity. From the data in Figure 8 and Table III, which quantitatively describe the gas-phase Lewis acidities of the fluoromethylsilanes with fluoride ion as the reference base, it is apparent that the intrinsic acceptor strengths (measured as fluoride affinities, $D[A-F^-]$) of borane and silane Lewis acids are quite comparable in absolute magnitude. The effects of fluorine and alkyl substituents on boron and silicon follow similar trends, namely that alkyl groups lower the acidity relative to fluorine substituents. Alkyl groups appear to more strongly destabilize the silane-fluoride relative to the borane-fluoride adducts (Figure 8). In contrast to the present results, adduct strengths of these same silanes toward $(CH_3)_3N$ as reference base have been previously shown to be much lower than those for borane Lewis acids.[22b] Measurements of gas-phase dissociation equilibria for processes such as eq 1 where $B = (CH_3)_3N$ indicate a Lewis acidity order $(CH_3)_3B \gg SiF_4 \gg CH_3SiF_3$.[19-21,22b,40] The steric requirements of the bulky amine base clearly have a marked effect on the stability of adducts with the silanes. Attenuation of steric effects are expected for adducts involving the smaller monatomic fluoride ion as reference base.

Upon replacement of F by CH_3, the fluoride affinity of CH_3SiF_3 is decreased by ~6.5 kcal/mol relative to that of SiF_4. Similarly, $(CH_3)_2SiF_2$ binds F^- ~6 kcal/mol less strongly than does CH_3SiF_3. While the actual value of the fluoride affinity of $(CH_3)_3SiF$ is yet to be determined, the failure to observe F^- transfer from SF_6^- $\{D[SF_5-F^-] = 11 \pm 8$ kcal/mol[28a]$\}$ implies a dramatic decrease in acceptor strength of ~40 kcal/mol resulting from substitution of a third CH_3 for F on silicon.

Methyl substituent effects on the stability of pentacoordinate fluoromethylsilyl anions observed in the present work have interesting analogies in the isoelectronic neutral methylfluorophosphorane series PF_5, CH_3PF_4, $(CH_3)_2PF_3$, and $(CH_3)_3PF_2$.[41,42] The species $(CH_3)_4PF$ is unknown and it has been proposed that this least stable member of the phosphorane series would better be described as an ionic phosphorium salt $[(CH_3)_4P]^+F^-$.[42] By a variety of spectroscopic techniques, it has been conclusively demonstrated that the phosphoranes have trigonal-bipyramidal geometry with the less electronegative organic groups preferentially occupying equatorial sights.[41] Apical metal-substituent bond lengths are substantially longer than bonds at equatorial positions. Low-temperature ^1H and ^{19}F NMR spectra of SiF_5^-, $CH_3SiF_4^-$, and $(C_6H_5)SiF_4^-$ in low polarity solvents[24] indicate that these fluorosilicate anions also have trigonal-bipyramidal structures with the organic groups occupying equatorial sights. This positional preference, governed primarily by differences in substituent electronegativity, has previously been termed "the polarity rule" and is known to be general to a variety of trigonal-bipyramidal complexes.[5,41]

Analogous to the present observations of decreasing silane-fluoride bond strengths accompanying successive substitution of CH_3 for F, axial P-F bonds are known to lengthen and weaken in going from PF_5 to CH_3PF_4, $(CH_3)_2PF_3$, and $(CH_3)_3PF_2$.[41,42] Under the influence of the electrostatic field imposed by a trigonal-bipyramidal array of electronegative fluorine substituents, the $3d_{z^2}$ orbital contracts sufficiently to make its inclusion in the bonding energetically favorable.[42,43] Successive replacement of F by the more electropositive CH_3 would result then in a concomitant decrease in the net positive character of the central atom and lead to a gradual withdrawal of the d orbitals from the bonding scheme. Ultimately the five-coordinate trigonal-bipyramidal structure would cease to be energetically attractive.[42] In the pentacoordinate silicon anions, the $3d_{z^2}$ orbital is probably much more diffuse than in the neutral phosphorus compounds. Thus, abrupt decrease in stability of the adducts occurs upon substitution of just three CH_3 groups on the central atom.

Acknowledgment. This work was supported in part by the Energy Research and Development Administration under Grant No. E(04-3)767-8. The spectrometer used for these experiments was funded in part by the National Science Foundation under Grant No. NSF-GP-18383.

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(38) For an equilibrium such as reaction 2, $K_{eq} = [A_2B][A_1]/[A_1B][A_2]$; for reaction 24 $[A_1B]$ and $[A_2B]$ are the ion abundances of $CH_3SiF_4^-$ and $(C_2H_5)_3BF^-$, respectively, from data at long time in Figure 6, and A_1 and A_2 are the pressures of neutrals CH_3SiF_3 and $(C_2H_5)_3B$, respectively.

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