

Positive Ion Chemistry of Fluoromethylsilanes, $(\text{CH}_3)_n\text{SiF}_{4-n}$ ($n = 1-3$), by Ion Cyclotron Resonance Spectroscopy. Fluorine and Methyl Substituent Effects on the Relative Stabilities of Siliconium Ions, R^+ , and Disilylfluoronium Ions, $\text{RR}'\text{F}^+$, in the Gas Phase

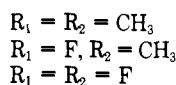
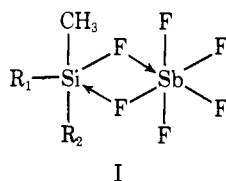
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Abstract: The gas phase ion chemistry of the fluoromethylsilanes $(\text{CH}_3)_n\text{SiF}_{4-n}$ ($n = 1-3$) has been investigated using the techniques of ion cyclotron resonance spectroscopy. Reaction pathways and rate constants have been determined for parent and major fragment ions by examination of ion abundances as a function of neutral pressure and of ion trapping time. Fluoride transfer reactions are a dominant feature of the observed ion chemistry and provide information relating to siliconium ion stabilities. Fluoride affinities of siliconium ions [$D(\text{R}^+-\text{F}^-)$, heterolytic bond dissociation energies] indicate the order of decreasing relative stability of the fluoromethylsiliconium ions to be $(\text{CH}_3)_3\text{Si}^+ > (\text{CH}_3)_2\text{SiF}^+ > \text{CH}_3\text{SiF}_2^+ > \text{SiF}_3^+$. A second important feature of the observed ion chemistry concerns the formation and reactions of the fluorine and methyl substituted disilylfluoronium ions, $\text{RR}'\text{F}^+$. Clustering reactions forming these species from R^+ and $\text{R}'\text{F}$ are shown to occur bimolecularly at low pressure, while collisional stabilization enhances the cluster formation rate at higher pressures. Subsequent displacement reactions indicate that the binding energies of the fluoromethylsiliconium ions to the fluoromethylsilanes decrease with increasing fluorine substitution in the neutral and in the siliconium ion moiety.

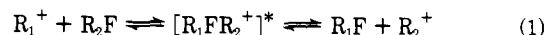
The study of ion-molecule reactions in the gas phase, utilizing the techniques of ion cyclotron resonance spectroscopy (ICR), affords the opportunity to investigate the properties and reactions of ions and neutrals in the absence of solvation effects. This is especially important to the study of ionic reactions of organosilicon compounds, with particular emphasis on siliconium cations, R^+ . Siliconium ions with a trigonal planar structure, analogous to known stable carbonium ions, have been proposed as reaction intermediates in many organosilicon chemical reactions. While these species comprise major fractions of the ions obtained in the mass spectra of a wide variety of organosilicon compounds,² attempts to demonstrate their *existence* in solution have proven entirely futile.³ For example, in extremely low nucleophilicity magic acid media ($\text{SbF}_5\text{-SO}_2\text{ClF}$ solution) Olah and co-workers have utilized NMR techniques to study a wide variety of long-lived carbonium ions.⁴ Under similar conditions, siliconium ion formation was not observed. Instead, the rapidly exchanging donor-acceptor complexes, I, envisaged to be pentacoordinate



about silicon were detected.⁵ In view of these results, it appears that in solution the availability of low lying silicon 3d orbitals makes coordinative expansion from tetrahedral sp^3 to trigonal-bipyramidal sp^3d more favorable than contraction to trigonal-planar sp^2 as occurs in carbocation analogues.

The study of substituent effects on the stabilities of ions both in solution and in the gas phase have proven useful in elucidating relationships between chemical structure, properties,

and reactivity.⁵⁻¹² Recent gas phase studies along these lines from this laboratory include the determination of relative carbonium ion stabilities, using heterolytic bond dissociation energies, $D[\text{R}^+-\text{X}^-]$ (where $\text{X}^- = \text{H}^-, \text{F}^-, \text{Br}^-$, etc.), as a measure of ion stability.⁹⁻¹¹ Fluoride ion transfer reactions, generalized in eq 1, are observed to be relatively fast and have proven particularly useful in ordering ion stabilities.



In favorable cases, relative fluoride affinities accurate to ± 0.1 kcal/mol have been determined using trapped ion ICR techniques.¹⁰ The determination of ion stabilities using this experimental methodology has advantages over appearance potential measurements, where adiabatic thresholds for ion formation are often difficult to extract from experimental data.

A logical extension of the above studies is the examination of systems where the charged center is another group 4 atom, silicon. To accomplish this objective in part, this report describes ICR studies of the positive ion-molecule reactions in the fluoromethylsilanes, $(\text{CH}_3)_n\text{SiF}_{4-n}$ ($n = 1-3$), both alone and in mixtures.

Previous gas phase studies of the ion chemistry of organosilanes are few in comparison with analogous carbon compounds.¹³ Of particular relevance to studies reported herein is the work of Lampe and co-workers who used high pressure and tandem mass spectrometry to study monosilane, SiH_4 ,¹⁴ disilane, Si_2H_6 ,¹⁵ the methylsilanes, $(\text{CH}_3)_n\text{SiH}_{4-n}$ ($n = 1-4$),¹⁶ and mixtures of SiH_4 with H_2O ,¹⁷ CH_4 ,¹⁸ C_2H_4 ,¹⁹ and C_2H_2 .²⁰ In addition, Henis and co-workers have reported ICR studies of positive ion reactions in SiH_4 , SiD_4 , and in mixtures of these with CH_4 and CD_4 .^{21,22} Observations indicate the major reaction occurring in systems containing hydrogen bound to silicon is that of H^- transfer from the neutral RH to the attacking siliconium ion R^+ . Not surprisingly, the preferred direction of hydride transfer indicates that methyl groups stabilize siliconium ions relative to hydrogen.^{16b,d-h,18,21a,22a,b} In addition, hydride transfer was found to be relatively fast (k

Table I. ICR Mass Spectra^a of (CH₃)_nSiF_{4-n} (*n* = 1-3)

<i>m/e</i>	Composition	Ion intensity ^{b,c}		
		FSi(CH ₃) ₃	F ₂ Si(CH ₃) ₂	F ₃ SiCH ₃
33	CH ₂ F ⁺			0.090
43	SiCH ₃ ⁺	0.021		
47	SiF ⁺	0.183	0.227	0.203
49	SiH ₂ F ⁺	0.149 (0.041)	0.018	
62	SiFCH ₃ ⁺	0.019		
63	SiFCH ₄ ⁺	0.046	0.033	
66	SiF ₂ ⁺		0.028	0.040
73	Si(CH ₃) ₃ ⁺	0.102 (0.061)		
76	SiFC ₂ H ₅ ⁺	0.016		
77	SiF(CH ₃) ₂ ⁺	1.000 (1.000)	0.168 (0.131)	
80	SiF ₂ CH ₂ ⁺		0.040	0.169 (0.198)
81	SiF ₂ CH ₃ ⁺		1.000 (1.000)	0.463 (0.234)
85	SiF ₃ ⁺			1.000 (1.000)
92	SiF(CH ₃) ₃ ⁺	0.084 (0.110)		
96	SiF ₂ (CH ₃) ₂ ⁺		0.208 (0.248)	
99	SiF ₃ CH ₂ ⁺			0.033
100	SiF ₃ CH ₃ ⁺			0.211 (0.387)

^a Taken at 70 eV electron energy and 1×10^{-6} Torr neutral gas pressure. ^b Single resonance ICR mass spectral peak heights are divided by ion mass and normalized to the base peak at 1.000 ion intensity. ^c Numbers in parentheses are the ion abundances at 18 eV for (CH₃)₃SiF and CH₃SiF₃, and at 20 eV for (CH₃)₂SiF₂, corresponding to conditions under which the ion-molecule reactions are examined in this report.

$\sim 10^{-10}$ to 10^{-9} cm³ molecule⁻¹ s⁻¹).^{16b,d-h,21a}

Literature describing the thermochemistry of the fluoromethylsilane neutrals and ions generated therefrom is very limited, and due to experimental difficulties, available values of heats of formation are subject to considerable uncertainties.^{2,16a,c,g,23} Electron impact mass spectrometry studies have been reported for (CH₃)₄Si,^{2,16a,c} (CH₃)₃SiF,^{2,16a} and SiF₄.² Distefano has reported a photoionization mass spectral study of (CH₃)₄Si and found the parent ionization potential, IP[(CH₃)₄Si] = 9.86 ± 0.02 eV, to be considerably lower than previously reported electron impact results.^{23c} A number of reports have appeared on the photoelectron spectra of (CH₃)₄Si and SiF₄.²⁴⁻²⁹

Experimental Section

ICR instrumentation and experimental techniques have been previously detailed elsewhere.^{30,31} Gas mixtures utilized are prepared directly in the ICR cell by admission of the 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 from each component using an MKS Baratron Model 90H1-E capacitance manometer.¹⁰ A linear calibration of Baratron pressure vs. ionization gauge current affords pressure determinations over a range of 10^{-7} to 10^{-4} Torr. The overall accuracy in pressure measurement of a single component for the fluoromethylsilanes in studies reported here is estimated to be $\pm 20\%$ and represents the major source of error in reported reaction rate constants. All experiments were performed at ambient temperatures.

Data reported in tables and figures are for total silicon content, normalized to the ²⁸Si isotope (²⁸Si, 92.2%; ²⁹Si, 4.7%; ³⁰Si, 3.1%). Typically, ion concentrations comprising less than 1% of the total are not included in the reported data. The presence of two silicon atoms in observed high mass products was confirmed by the characteristic silicon isotope pattern.³²

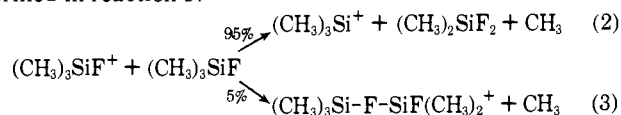
Samples of (CH₃)₃SiF, (CH₃)₂SiF₂, and CH₃SiF₃ (PCR, Inc.) were kindly provided by Professor J. G. Dillard. Noncondensable impurities were removed by multiple freeze-pump-thaw cycles. ICR single resonance mass spectra at low pressure showed low level impurities, at *m/e* 155 (0.2% of the total ionization at 20 eV) in (CH₃)₂SiF₂ and *m/e* 163 (2% at 18 eV) in CH₃SiF₃, containing two silicon atoms. Throughout this report these ions are considered to contain only silicon, fluorine, carbon, and hydrogen. In view of previous difficulties encountered in mass spectral studies of organo-

halosilanes, it is possible, however, that these ions may arise from disilyl ether impurities, resulting from reaction with traces of water on inlet manifold surfaces. This problem is most severe in CH₃SiF₃, where ionization of a probable ether impurity, [(CH₃)₂Si]₂O, would yield *m/e* 163 by CH₃ loss.

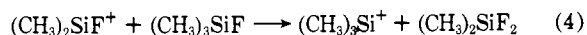
Results

The positive ion chemistry of the fluoromethylsilanes has not been previously reported. Ions observed in the single resonance mass spectra of the fluoromethylsilanes at 70 eV and low pressure (Table I) agree well with conventional mass spectrometry.^{2,33} In addition to the parent molecular ions, the major fragments at 70 eV are those corresponding to loss of F and CH₃. To facilitate study of these siliconium ion fragments, studies reported herein are conducted at ionizing energies a few electron volts above the first ionization potential where the siliconium ion species comprise $\geq 80\%$ of the total ionization in all of the fluoromethylsilanes (Table I).

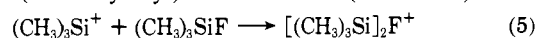
(CH₃)₃SiF. The variation of ion abundances with (CH₃)₃SiF pressure at 18 eV electron energy is shown in Figure 1. The parent molecular ion at *m/e* 92 reacts predominantly to yield the trimethylsiliconium ion at *m/e* 73 (reaction 2) and to a much lesser extent via reaction 3 to yield *m/e* 169. As is the usual case for ion-molecule reactions, the neutral products in process 2 are assumed. Other possibilities include (CH₃)₃SiF + F and (CH₃)₂SiF + CH₃F. Although these choices cannot be experimentally distinguished, available data suggest that the displayed products are thermodynamically favored. They may in fact result from the dissociation of the fluoronium ion formed in reaction 3.



The major fragment ion (CH₃)₂SiF⁺, at *m/e* 77 undergoes fluoride transfer, reaction 4, to yield *m/e* 73.



(CH₃)₃Si⁺ reacts only to form a symmetrical cluster at *m/e* 165, the bis(trimethylsilyl)fluoronium ion (reaction 5).



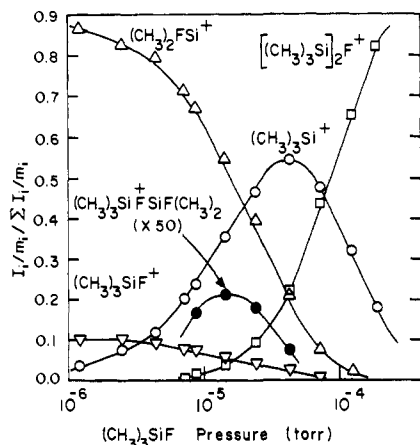
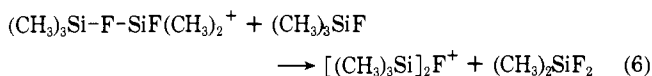


Figure 1. Variation of ion abundances as a function of $(\text{CH}_3)_3\text{SiF}$ pressure at 18 eV electron energy.

The unsymmetrical fluoronium ion product of reaction 3 undergoes displacement, reaction 6, to yield m/e 165, accounting for the predominance of the symmetrical fluoronium ion cluster at higher pressures.



The temporal variation of ion abundances in 1.2×10^{-6} Torr $(\text{CH}_3)_3\text{SiF}$ following a 10-ms 18 eV electron beam pulse is shown in Figure 2 and exhibits behavior in accord with reactions 2–6 above. The low abundance of m/e 169 did not permit its observation in the trapped ion experiment. Reaction rate constants determined from the limiting slopes for reactant ion disappearance in Figure 2 are summarized in Table II.

While the production of the terminal cluster ion,

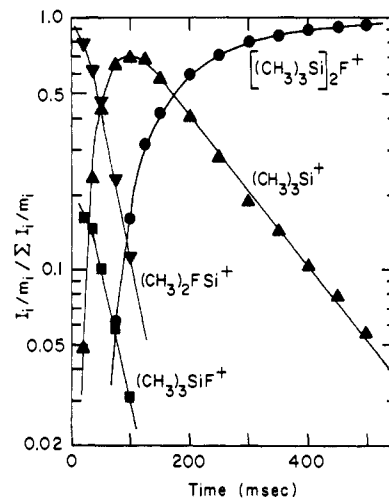


Figure 2. Temporal variation of trapped-cation abundances following a 10-ms electron beam pulse at 18 eV in $(\text{CH}_3)_3\text{SiF}$ at a constant pressure of 1.2×10^{-6} Torr.

$[(\text{CH}_3)_3\text{Si}]_2\text{F}^+$, observed in the pressure data (Figure 1) could perhaps be accounted for by collisional stabilization of an excited intermediate complex (reaction 7), the rapid buildup and eventual predominance of $[(\text{CH}_3)_3\text{Si}]_2\text{F}^+$ in the trapped ion study (Figure 2) at low pressure is somewhat surprising.

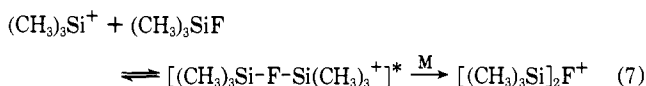


Table III shows the variation, as a function of $(\text{CH}_3)_3\text{SiF}$ pressure, of the ratio of apparent disappearance rate constants for $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)_2\text{SiF}^+$ over a range of $(\text{CH}_3)_3\text{SiF}$ pressure varying by a factor of approximately 5.4. The bi-

Table II. Ion-Molecule Reaction Rate Constants and Product Distributions Observed in the Fluoromethylsilanes Alone

Reaction ^a	Reaction ^b	Product distribution ^c	Rate constant ^d
2	$(\text{CH}_3)_3\text{SiF} + (\text{CH}_3)_3\text{SiF}^+ \rightarrow (\text{CH}_3)_3\text{Si}^+ + (\text{CH}_3)_2\text{SiF}_2 + \text{CH}_3$	0.95	6.2
3	$\rightarrow (\text{CH}_3)_3\text{Si-F-SiF}(\text{CH}_3)_2^+ + \text{CH}_3$	0.05	0.33
4	$+ (\text{CH}_3)_2\text{SiF}^+ \rightarrow (\text{CH}_3)_3\text{Si}^+ + (\text{CH}_3)_2\text{SiF}_2$	1.00	7.4
5	$+ (\text{CH}_3)_3\text{Si}^+ \rightarrow [(\text{CH}_3)_3\text{Si}]_2\text{F}^+$	1.00	1.8
6	$+ (\text{CH}_3)_3\text{Si-F-SiF}(\text{CH}_3)_2^+ \rightarrow [(\text{CH}_3)_3\text{Si}]_2\text{F}^+ + (\text{CH}_3)_2\text{SiF}_2$	1.00	<i>f</i>
8	$(\text{CH}_3)_2\text{SiF}_2 + (\text{CH}_3)_2\text{SiF}_2^+ \rightarrow (\text{CH}_3)_2\text{SiF}^+ + \text{CH}_3\text{SiF}_3 + \text{CH}_3$	0.97	1.9
9	$\rightarrow (\text{CH}_3)_2\text{FSi-F-SiF}_2(\text{CH}_3)^+ + \text{CH}_3$	0.03	0.06
10	$+ \text{CH}_3\text{SiF}_2^+ \rightarrow (\text{CH}_3)_2\text{SiF}^+ + \text{CH}_3\text{SiF}_3$	0.98	3.1
11 ^e	$\rightarrow \text{Si}_2\text{C}_3\text{H}_6\text{F}_3^+ + \text{HF} + \text{H}_2$	0.02	0.06
12	$+ (\text{CH}_3)_2\text{SiF}^+ \rightarrow [(\text{CH}_3)_2\text{FSi}]_2\text{F}^+$	0.98	0.45
13 ^e	$\rightarrow \text{Si}_2\text{C}_4\text{H}_9\text{F}_2^+ + \text{HF} + \text{H}_2$	0.02	0.01
14	$+ (\text{CH}_3)_2\text{FSi-F-SiF}_2(\text{CH}_3)^+ \rightarrow [(\text{CH}_3)_2\text{FSi}]_2\text{F}^+ + \text{CH}_3\text{SiF}_3$	1.00	<i>f</i>
15	$\text{CH}_3\text{SiF}_3 + \text{CH}_3\text{SiF}_3^+ \rightarrow \text{CH}_3\text{SiF}_2^+ + \text{SiF}_4 + \text{CH}_3$	0.64	0.43
16	$\rightarrow (\text{CH}_3)_2\text{Si-F-SiF}_3^+ + \text{CH}_3$	0.01	0.01
17	$\rightarrow (\text{CH}_3)_2\text{SiF}_2\text{SiF}_3^+ + \text{HF}$	0.03	0.02
18	$\rightarrow [(\text{CH}_3)_2\text{Si}]_2\text{F}^+ + \text{F}$	0.32	0.21
19	$+ \text{CH}_2\text{SiF}_2^+ \rightarrow (\text{CH}_3)_2\text{SiF}_2\text{SiF}_3^+$	0.06	0.04
20 ^e	$\rightarrow \text{Si}_2\text{C}_2\text{H}_3\text{F}_4^+ + \text{HF} + \text{H}$	0.86	0.52
21	$\rightarrow \text{F}_2\text{SiCH}_2\text{SiF}_3^+ + \text{CH}_3$	0.08	0.05
22	$+ \text{SiF}_3^+ \rightarrow \text{CH}_3\text{SiF}_2^+ + \text{SiF}_4$	1.00	1.9
23	$+ \text{CH}_3\text{SiF}_2^+ \rightarrow [(\text{CH}_3)_2\text{Si}]_2\text{F}^+$	0.63	0.08
24 ^e	$\rightarrow \text{Si}_2\text{C}_2\text{H}_3\text{F}_4^+ + \text{HF} + \text{H}_2$	0.37	0.05
25	$+ (\text{CH}_3)_2\text{FSi-F-SiF}_3^+ \rightarrow [(\text{CH}_3)_2\text{FSi}]_2\text{F}^+ + \text{SiF}_4$	1.00	<i>f</i>

^a Reaction numbers refer to reactions specified in the text. ^b Neutral products assumed. ^c Product distributions determined by ICR double resonance ejection techniques. ^d Rate constants in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, determined from the limiting slopes of reactant ion disappearance and partitioned in accord with relative product distributions. ^e Product ion compositions indicated assume only silicon, carbon, hydrogen, and fluorine content. It is possible that product ions in these reactions are due to minor disilyl ether impurities and correspond to compositions $\text{Si}_2\text{O}(\text{CH}_3)_n\text{F}_{5-n}^+$ ($n = 0-3$). ^f Not determined due to low reactant ion abundance.

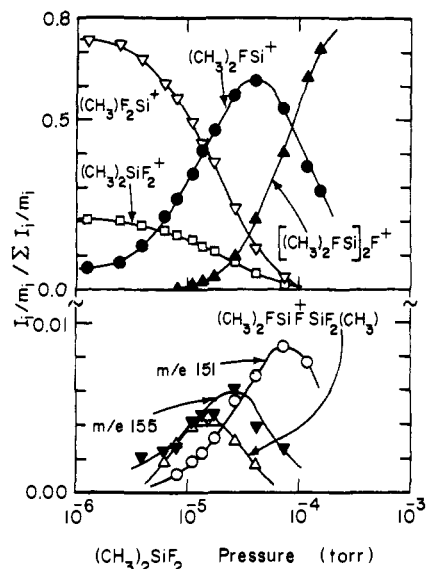


Figure 3. Variation of ion abundances as a function of $(\text{CH}_3)_2\text{SiF}_2$ pressure at 20 eV electron energy.

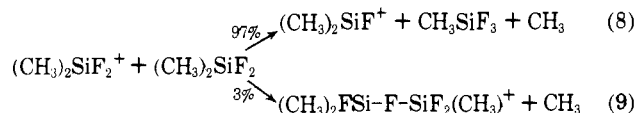
Table III. Ratio of Apparent Disappearance Rate Constants^a for $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)_2\text{SiF}^+$ vs. $(\text{CH}_3)_3\text{SiF}$ Pressure

Pressure ^b	Rate ratio ^c	Pressure ^b	Rate ratio ^c
0.76	0.177	2.43	0.250
1.37	0.174	4.08	0.326

^a Determined for the limiting decay slopes of trapped ion abundance as a function of time at 18 eV. ^b Pressure in units of 10^{-6} Torr. ^c Ratio of the apparent disappearance rate constants for $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)_2\text{SiF}^+$, respectively. See reactions 4, 5, and 7 and the text for an explanation of the significance of the rate ratio.

molecular reaction 4 is the only decay channel for $(\text{CH}_3)_2\text{SiF}^+$ and the rate constant for this process should therefore remain constant as a function of pressure. On the other hand a termolecular stabilization step would enhance cluster formation (reaction 7) at higher pressures. Data in Table III indicate just such an increase in the rate ratio with increasing pressure, but at lower pressures the observed constancy of the rate ratio provides evidence for the participation of a bimolecular clustering process occurring without the expulsion of a neutral fragment to disperse excess internal energy in the formation of $[(\text{CH}_3)_3\text{Si}]_2\text{F}^+$.

$(\text{CH}_3)_2\text{SiF}_2$. The ion molecule reactions observed in $(\text{CH}_3)_2\text{SiF}_2$ are qualitatively analogous to those occurring in $(\text{CH}_3)_3\text{SiF}$, with minor exception. The variation of ion abundances with increasing $(\text{CH}_3)_2\text{SiF}_2$ pressure at 20 eV is shown in Figure 3. The parent ion at m/e 96 undergoes reactions 8 and 9 (analogous to reactions 2 and 3 in $(\text{CH}_3)_3\text{SiF}$)



to generate m/e 77 and 177, respectively. The major fragment at m/e 81 reacts predominantly via fluoride transfer, reaction 10, to yield $(\text{CH}_3)_2\text{SiF}^+$ (analogous to reaction 4 in $(\text{CH}_3)_3\text{SiF}$). In addition, to a much lesser extent, $\text{CH}_3\text{SiF}_2^+$ participates in reaction 11 to yield m/e 155.

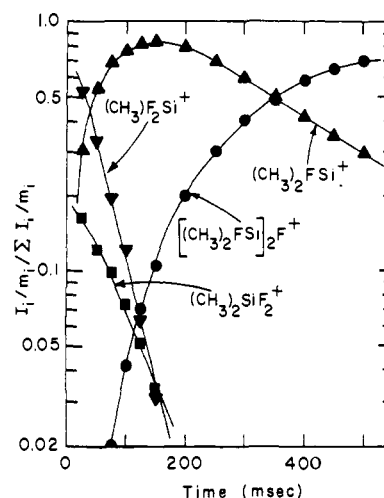
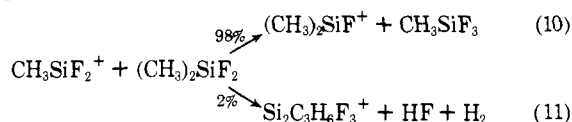
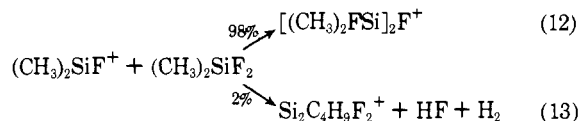
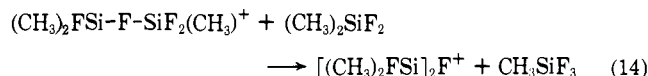


Figure 4. Temporal variation of trapped-cation abundances following a 10-ms electron beam pulse at 20 eV in $(\text{CH}_3)_2\text{SiF}_2$ at a constant pressure of 2.3×10^{-6} Torr.

$(\text{CH}_3)_2\text{SiF}^+$ undergoes clustering, reaction 12, to yield the symmetrical bis(fluorodimethylsilyl)fluoronium ion at m/e 173 and, in a process resembling reaction 11, yields m/e 151 as a minor product via reaction 13. The unsymmetrical fluoronium



ion, m/e 177, generated in reaction 9, undergoes displacement, reaction 14,

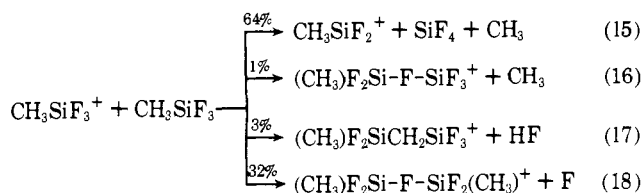


to yield the symmetrical cluster m/e 173. Products of reactions 11 and 13 at m/e 155 and 151, respectively, appear to react slowly at higher pressures. Due to their low abundances the reactions of these ions were not further characterized.

The temporal variation of ion abundances following a 10-ms 20 eV electron beam pulse in 2.3×10^{-6} Torr $(\text{CH}_3)_2\text{SiF}_2$ (Figure 4) exhibits behavior in accord with reactions 8–14 indicated above. The low abundance of m/e 177, 155, and 151 did not permit their observation in the trapped ion experiment. Reaction rate constants determined from the limiting slopes of reactant ion decays (Figure 4) and by consideration of the indicated product distributions for reactions 8–14 are summarized in Table II.

CH_3SiF_3 . The major features of observed reactions in CH_3SiF_3 follow trends observed in the mono- and difluoro compounds, with additional complexity due to the reactions of the radical ion $\text{CH}_2\text{SiF}_2^+$ (m/e 80) produced by primary ionization.

The variation of ion abundances as a function of CH_3SiF_3 pressure at 18 eV electron energy is shown in Figure 5. The parent ion (m/e 100) undergoes reactions 15 and 16 to generate m/e 81 and 185, respectively, analogous to processes observed in $(\text{CH}_3)_3\text{SiF}$ and $(\text{CH}_3)_2\text{SiF}_2$. In addition, $\text{CH}_3\text{SiF}_3^+$ reacts to produce m/e 180 and 181, via reactions 17 and 18, respec-



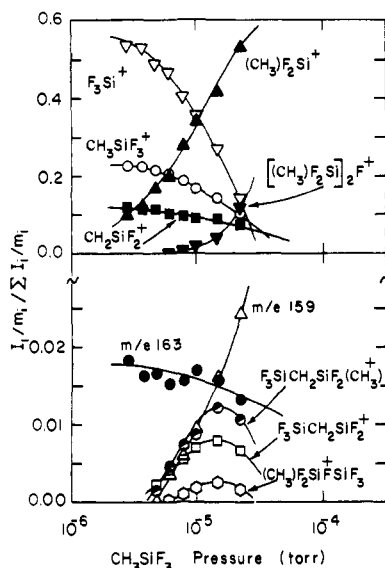
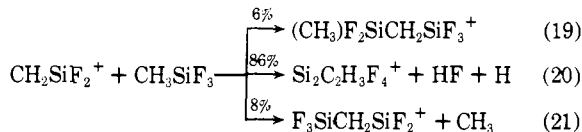


Figure 5. Variation of ion abundances as a function of CH_3SiF_3 pressure at 18 eV electron energy.

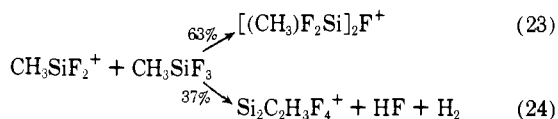
tively. Double resonance indicates that approximately 50% of the observed m/e 180 results from reaction 17 of the parent ion, while the remainder arises from a direct process involving $\text{CH}_2\text{SiF}_2^+$ (reaction 19). $\text{CH}_2\text{SiF}_2^+$ also generates m/e 159



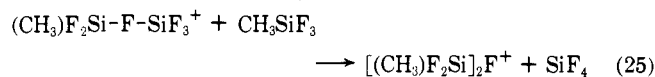
and 165 via reactions 20 and 21, respectively. The major fragment ion SiF_3^+ (m/e 85) undergoes fluoride transfer, reaction 22,



to yield $\text{CH}_3\text{SiF}_2^+$ (m/e 81), which subsequently clusters with the neutral (reaction 23), to yield the symmetrical bis(difluoromethylsilyl)fluoronium ion at m/e 181. $\text{CH}_3\text{SiF}_2^+$ also participates in reaction 24 to yield m/e 159 in analogy with



reaction 13 in $(\text{CH}_3)_2\text{SiF}_2$. The unsymmetrical cluster ion (m/e 185) undergoes displacement reaction 25 to yield the symmetrical fluoronium ion (m/e 181).



Reactions leading to the disappearance of m/e 165 and 180 at higher pressures were not further characterized.

The temporal variation of ion abundances following a 10-ms 20 eV electron beam pulse in 2.9×10^{-6} Torr CH_3SiF_3 is shown in Figure 6. The low abundances of m/e 165 and 180 did not permit their observation in the trapped ion experiment. Reaction rate constants determined from the limiting slopes for reactant ion disappearance and by consideration of the indicated product distributions for reactions 15–25 are summarized in Table II.

Mixtures of the Fluoromethylsilanes. In addition to ion molecule reactions observed in the pure components, several cross-reactions, unique to the mixed systems, were examined. As in the pure compounds, the ion chemistry at low pressure is dominated by processes involving the siliconium ion species and the disilylfluoronium ion clusters.

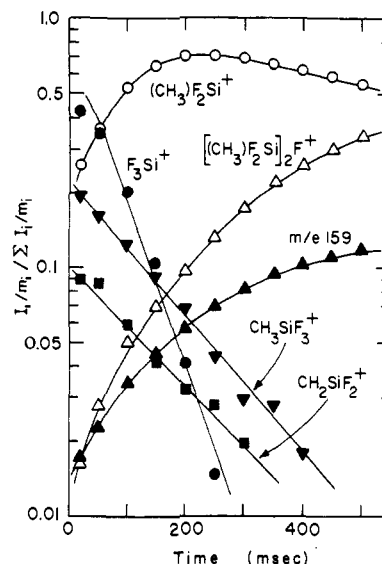
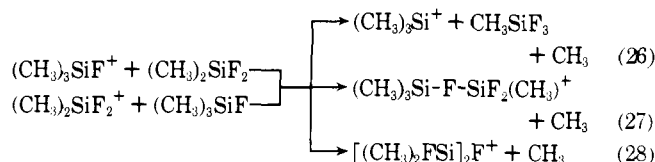
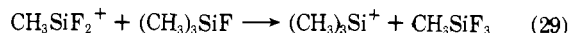


Figure 6. Temporal variation of trapped-cation abundances following a 10-ms electron beam pulse at 18 eV in CH_3SiF_3 at a constant pressure of 2.9×10^{-6} Torr.

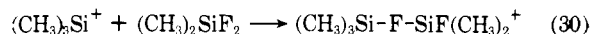
$(\text{CH}_3)_3\text{SiF}$ and $(\text{CH}_3)_2\text{SiF}_2$. A 10-ms 18 eV electron beam pulse in a 1.8:1 mixture of $(\text{CH}_3)_3\text{SiF}$ and $(\text{CH}_3)_2\text{SiF}_2$ at a constant total pressure of 2.7×10^{-6} Torr initiates the temporal variation of ion abundances shown in Figure 7. The parent ions of $(\text{CH}_3)_3\text{SiF}$ and $(\text{CH}_3)_2\text{SiF}_2$ participate in cross-reactions 26–28 to yield common products at m/e 73 and 173. No experimental distinction can be made between the unsymmetrical and symmetrical product clusters at m/e 173 in reactions 27 and 28, respectively.



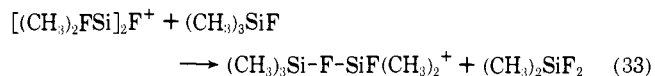
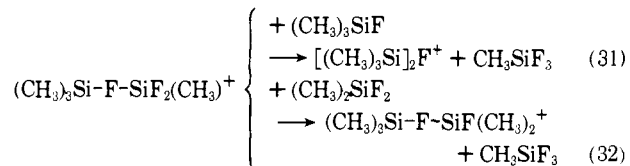
$\text{CH}_3\text{SiF}_2^+$ (m/e 81), the major primary ionization fragment from $(\text{CH}_3)_2\text{SiF}_2$, undergoes cross-reaction 29,



involving fluoride transfer to yield $(\text{CH}_3)_3\text{Si}^+$ (m/e 73). The product of reaction 29 subsequently clusters with $(\text{CH}_3)_2\text{SiF}_2$ to generate the unsymmetrical fluoronium ion at m/e 169 (reaction 30).



In addition to the displacement reactions 6 and 14 observed in the pure components, the cluster ion products of reactions 27 and 28 (which are likely to both be present in an undetermined ratio) react further. These species would likely react as indicated in processes 31–33 in the mixture to generate the



symmetrical and unsymmetrical fluoronium ions at m/e 165 and 169, respectively. $[(\text{CH}_3)_3\text{Si}]_2\text{F}^+$ does not react further in the mixed system.

$(\text{CH}_3)_2\text{SiF}_2$ and CH_3SiF_3 . The temporal variation of ion

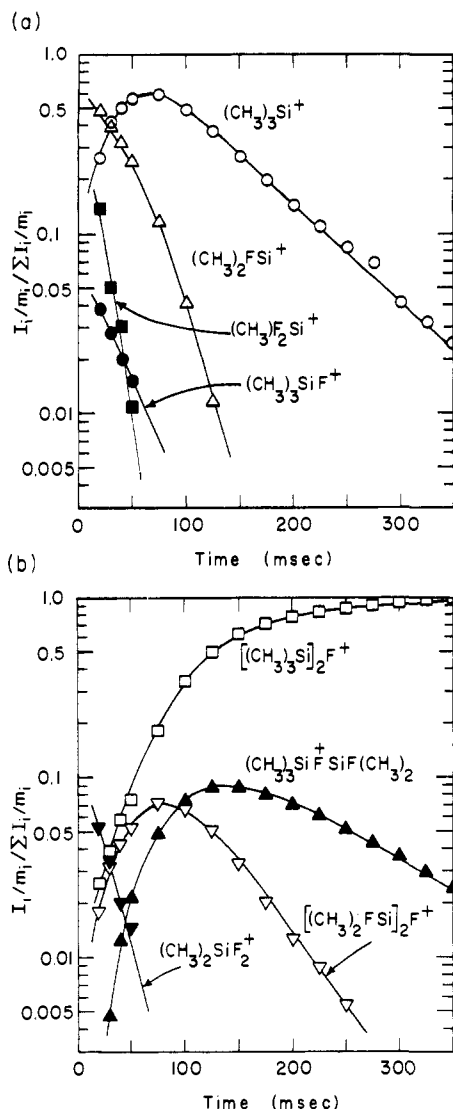
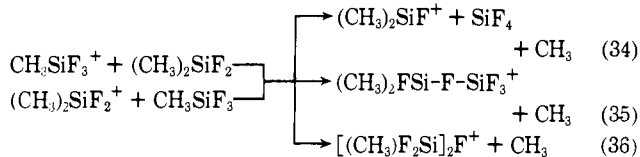
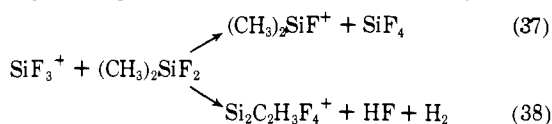


Figure 7. Temporal variation of trapped-cation abundances following a 10-ms electron beam pulse at 18 eV in a 1.8:1 mixture of $(\text{CH}_3)_3\text{SiF}$ and $(\text{CH}_3)_2\text{SiF}_2$ at a constant total pressure of 2.7×10^{-6} Torr. The ion indicated as $[(\text{CH}_3)_2\text{FSi}]_2\text{F}^+$ may in part be the unsymmetrical species $(\text{CH}_3)_3\text{SiFSiF}_2\text{CH}_3^+$.

abundances following a 10-ms electron beam pulse at 18 eV in a 2.7:1 mixture of CH_3SiF_3 and $(\text{CH}_3)_2\text{SiF}_2$ at a constant total pressure of 2.6×10^{-6} Torr is displayed in Figure 8. The parent ions of CH_3SiF_3 and $(\text{CH}_3)_2\text{SiF}_2$ undergo cross-reactions 34–36 to yield common products at m/e 77 and 181.



SiF_3^+ (m/e 85), the major fragment arising from ionization of CH_3SiF_3 , undergoes cross reactions 37 and 38 to yield the



fluoride transfer product $(\text{CH}_3)_2\text{SiF}^+$ (m/e 77) and m/e 159, respectively. The product of reaction 37, $(\text{CH}_3)_2\text{SiF}^+$, clusters with CH_3SiF_3 to yield the unsymmetrical cluster at m/e 177 (reaction 39) and also produces m/e 155 via reaction 40.

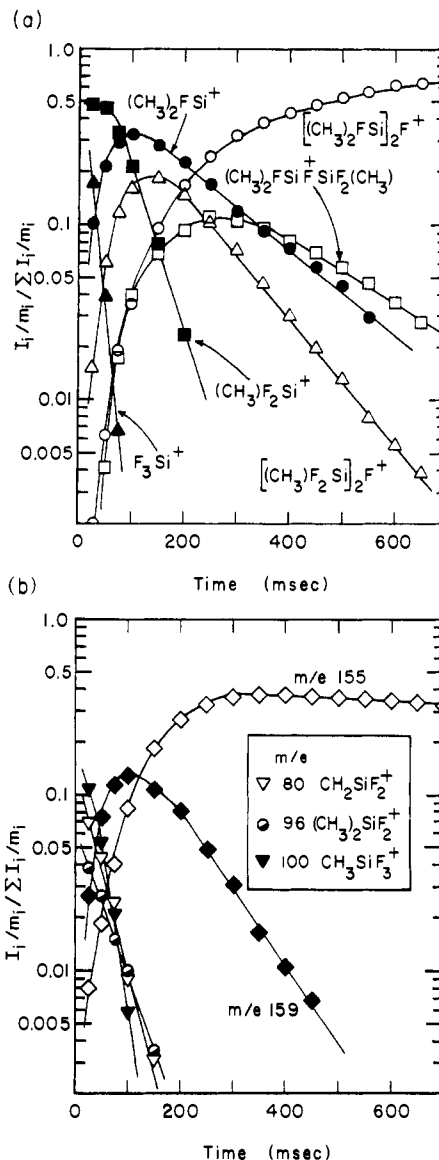
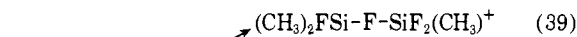
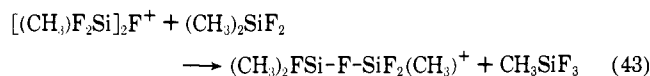
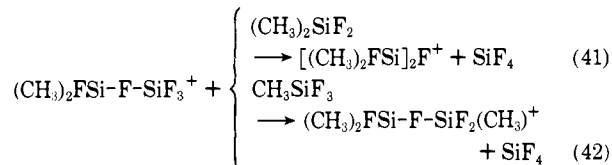


Figure 8. Temporal variation of trapped-cation abundances following a 10-ms electron beam pulse at 18 eV in a 2.7:1 mixture of CH_3SiF_3 and $(\text{CH}_3)_2\text{SiF}_2$ at a constant total pressure of 2.6×10^{-6} Torr. The ion indicated as $[(\text{CH}_3)_2\text{FSi}]_2\text{F}^+$ may in part be the unsymmetrical species $(\text{CH}_3)_2\text{FSiFSiF}_3^+$.



In addition to displacement reactions 14 and 25 observed in the pure components, reactions 41–43 are unique to the



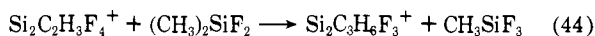
mixture, generating the m/e 173 and 177 fluoronium ion clusters from unsymmetrical and symmetrical m/e 181 species. $[(\text{CH}_3)_2\text{FSi}]_2\text{F}^+$ (m/e 173) does not react further in the mixed system.

Table IV. Relative Heterolytic Bond Strengths^a of Siliconium Ions to F⁻ and Neutral Fluoromethylsilanes

Base	Acid			
	(CH ₃) ₃ Si ⁺	(CH ₃) ₂ FSi ⁺	(CH ₃) ₂ Si ⁺	F ₃ Si ⁺
(CH ₃) ₃ SiF	(CH ₃) ₃ SiF-Si(CH ₃) ₃ ⁺			
(CH ₃) ₂ SiF ₂	(CH ₃) ₂ FSiF-Si(CH ₃) ₃ ⁺	>	(CH ₃) ₂ FSiF-SiF(CH ₃) ₂ ⁺	
CH ₃ SiF ₃	(CH ₃) ₂ SiF-Si(CH ₃) ₃ ⁺	(> ^b)	(CH ₃) ₂ SiF-SiF(CH ₃) ₂ ⁺	>
SiF ₄			F ₃ SiF-SiF(CH ₃) ₂ ⁺	(> ^b)
F ⁻	F ⁻ -Si(CH ₃) ₃ ⁺	<	F ⁻ -SiF(CH ₃) ₂ ⁺	<
				<
			F ⁻ -SiF ₂ (CH ₃) ⁺	<
				F ⁻ -SiF ₃ ⁺

^a Arrows indicate the observed order of heterolytic bond strengths (> = greater than). ^b Arrows in parentheses, (>), indicate inferred relative bond strength ordering, based on trends observed in the other cases.

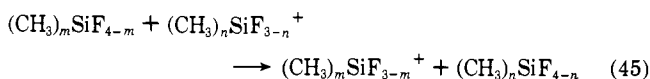
The species at *m/e* 159 undergoes reaction 44 to yield the *m/e* 155 ion, which then appears to react very slowly (Figure 8). This further reaction of *m/e* 155 was not characterized.



Discussion and Conclusions

The positive ion chemistry of the fluoromethylsilanes, (CH₃)_nSiF_{4-n} (*n* = 1-3), both alone and in binary mixtures, is largely dominated by reaction sequences initiated by the fluoromethylsilanium ions, (CH₃)_nSiF_{3-n}⁺ (*n* = 0-3). These tricoordinate silicon cations are envisaged to have a trigonal planar structure in analogy with known carbonium ions^{3,34-37} and are observed to participate in two major reactions with the fluoromethylsilane neutrals: fluoride transfer and clustering.

Fluoride transfer from the more highly methylated neutral silane to the more highly fluorinated siliconium ion is generalized in reaction 45 which proceeds to the right whenever *m* > *n*.

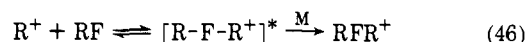


Consideration of reactions 4, 10, and 22 in the pure compounds and reactions 29 and 37 in the mixed systems serves to establish an ordering of the fluoride affinities (i.e., heterolytic bond dissociation energies, *D*[R⁺-F⁻]) of the various fluoro- and methyl-substituted siliconium ions such that SiF₃⁺ > CH₃SiF₂⁺ > (CH₃)₂SiF⁺ > (CH₃)₃Si⁺. Using fluoride ion as the reference base provides a measure of the relative stabilities of the siliconium ions as a function of substituent *α* to the positively charged silicon center and yields an ion stability order precisely the reverse of the fluoride affinity order shown above. Thus a methyl substituent stabilizes the positive charge relative to fluorine. These trends are shown schematically in Table IV and are qualitatively the same as has been previously found for analogous carbonium ion species, where reported fluoride affinities span a range of about 70 kcal/mol (CF₃⁺, 253; CH₃CF₂⁺, 226; (CH₃)₂CF⁺, 206; (CH₃)₃C⁺, 182 kcal/mol).^{12,36,37}

In the carbon systems, the quantitative differences in fluoride affinities are the result of competition between stabilizing (H₃C → C⁺ and F → C⁺ π hyperconjugative donation, and H₃C → C⁺ σ polarization) and destabilizing (C⁺ → F σ polarization, resulting from the high fluorine electronegativity) effects of α-methyl and fluorine substituents on the carbonium ion center.^{9,10,34-36} A quantitative comparison of the fluoride affinities of the carbonium and siliconium ion analogues may help to explain why siliconium ions have remained undetected in solution, under conditions where analogous carbonium ions are known to be long lived.³⁻⁵ It is expected that hyperconjugative π donation from CH₃ and F would be less effective in stabilizing siliconium ions than it is in stable carbonium ions, since π bonding between atoms of the first and second rows of

the periodic table is generally assumed to be less important than between atoms of the same row.

The second major reaction in which the siliconium ions participate is clustering with the neutral fluoromethylsilanes to yield disilylfluoronium ions as generalized in reaction 46.



The data in Table III for (CH₃)₃SiF suggest that this clustering can occur bimolecularly at low pressure, with collisional relaxation of the excited intermediate complex enhancing the rate of formation of the stable fluoronium ion at higher pressures. While investigation of the variation of clustering rates as a function of pressure was undertaken only for (CH₃)₃SiF, it is apparent from the relative magnitudes of reaction rate constants shown in Table II (reactions 5, 12, and 23) that the collisional stabilization of the excited intermediate is more important in the (CH₃)₂SiF₂ and CH₃SiF₃ systems, where the intermediate clusters possess successively fewer degrees of freedom into which the excess internal energy may be partitioned. The apparent clustering reaction rate constants decrease from 1.8 to 0.45 to 0.08 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ in going from (CH₃)₃SiF to (CH₃)₂SiF₂ to CH₃SiF₃ (reactions 5, 12, and 23, respectively) despite the fact that the pressure of the neutral fluoromethylsilane is successively higher in each case (1.2, 2.3, and 2.9 × 10⁻⁶ Torr, respectively).

As is particularly apparent in the mixed systems, the fluoronium ion clusters undergo displacement reactions which convert clusters containing more highly fluorinated silyl substituents to those which contain more highly methylated silyl groups. Reactions 6, 14, and 25 in the pure compounds and reactions 31-33 and 41-43 in the mixed systems serve to establish an ordering of binding energies of the various fluoromethylsilanium ions to the neutral fluoromethylsilanes. These orderings are shown schematically in Table IV. For example, consideration of reactions 6 and 32 indicates that the relative binding energies of (CH₃)₃Si⁺ to the neutral fluoromethylsilanes decrease in the order (CH₃)₃SiF > (CH₃)₂SiF₂ > CH₃SiF₃. In addition, reaction 33 demonstrates that (CH₃)₃Si⁺ binds more strongly to (CH₃)₂SiF₂ than does (CH₃)₂SiF⁺.

The siliconium ions, (CH₃)_nSiF_{3-n}⁺ (*n* = 0-3), may be considered as acids (A) in the Lewis sense, accepting an electron lone pair from a Lewis base (B) to form a covalent adduct as depicted in reaction 47 (where A = siliconium ion, B = F⁻ or FSi(CH₃)_nF_{3-n} for *n* = 0-3).



Comparison of the bond strength orders in Table IV shows a reversal in Lewis acid strengths (adduct bond dissociation energies) of the siliconium ions with a change in the character of the reference Lewis base. With F⁻ the Lewis acidities of the siliconium ions increase with increasing fluorine substitution in place of methyl α to the charge center. On the other hand, for a given fluoromethylsilane neutral as reference base, for

example, CH_3SiF_3 , the adduct bond strength or the Lewis acidity of the siliconium ion decreases with increasing fluorine substitution in place of methyl α to the siliconium ion center. The observed reversal in the order of bond strengths of the fluoromethylsiliconium ions to fluoride ion and to the neutral fluoromethylsilanes is due primarily to the absence and presence, respectively, of a positive charge in the adduct. In the case of the disilylfluoronium ion clusters, $\text{R}-\text{F}-\text{R}^+$, the presence of a positive charge causes destabilization of the ion as the number of fluorine substituents on silicon increases. This effect is due to unfavorable interaction of the $\text{Si} \rightarrow \text{F}$ bond dipoles with the positive charge at silicon. In the case of the neutral molecules, $\text{R}-\text{F}$, formed by F^- transfer to the siliconium ions R^+ , such charge-bond dipole interactions are absent. Here, increased fluorine substitution on silicon results in a higher degree of positive charge at the siliconium ion center, thus increasing the fluoride affinity. This reversal in the Lewis acidities of the siliconium ions with a change in character of the reference base bears analogy to previous reports on the relative bond strengths of fluoromethyl cations to the neutral fluoromethanes $\text{CH}_n\text{F}_{4-n}$ ($n = 1-4$).^{10,36}

Considering the ordering of adduct bond strengths (Table IV) for a given siliconium ion as the reference Lewis acid, the increasing substitution of fluorine in place of methyl α to the silicon in the neutral fluoromethylsilane decreases the Lewis basicity of the neutral. For example, the adduct bond strengths to $(\text{CH}_3)_3\text{Si}^+$ decrease in the order $(\text{CH}_3)_3\text{SiF} > (\text{CH}_3)_2\text{SiF}_2 > \text{CH}_3\text{SiF}_3$. These trends in the basicity of the fluoromethylsilanes again parallel behavior observed in analogous carbon systems.^{10,34,35}

Ions at m/e 151, 155, 159, and 163 have been formulated herein as $\text{Si}_2\text{C}(\text{CH}_3)_n\text{F}_{5-n}^+$ ($n = 0-3$). However, in view of the tendency for silanes in general to hydrolyze easily in the presence of traces of water, it is possible that these ions may result from reactions of minor disilyl ether impurities.^{2,38,39} These ions may thus be formulated as $\text{Si}_2\text{O}(\text{CH}_3)_n\text{F}_{5-n}^+$ ($n = 0-3$) species.

In summary, the results of this investigation indicate that tricoordinate siliconium ions may be generated in abundance and the effects of α substituents on their relative stabilities determined in the absence of the effects of solvation. Fluoride transfer reactions leading to the more stable siliconium ions are rapid relative to clustering processes which generate disilylfluoronium ions. Although qualitative, the present observations indicate the ion stability orders to parallel behavior found for carbonium ion analogues. A quantitative comparison of the two series would be expected to show the effects of greatly diminished hyperconjugative stabilization in the case of silicon. Further efforts to quantify the stabilities of the fluoromethylsiliconium ions for comparison with known carbonium ion analogues are currently in progress in this laboratory utilizing photoionization mass spectrometry for accurate determination of ionic heats of formation and by examination of fluoride transfer reactions in mixtures of fluoromethylsilanes and analogous carbon compounds for direct determination of siliconium and carbonium ion fluoride affinities. These efforts will be the subject of forthcoming reports.

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