

Photoionization Mass Spectrometry of the Fluoromethylsilanes $(\text{CH}_3)_n\text{F}_{4-n}\text{Si}$ ($n = 1-4$)

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Abstract: Photoionization efficiency curves for molecular ions P^+ and lowest energy fragments $(\text{P}-\text{CH}_3)^+$ for the series of methyl and fluoro substituted silanes $(\text{CH}_3)_n\text{F}_{4-n}\text{Si}$ ($n = 1-4$) are reported for photon energy ranges extending from 1 to 2 eV above the respective parent thresholds. Adiabatic ionization potentials of 9.80 ± 0.03 , 10.31 ± 0.04 , 11.03 ± 0.03 , and 12.48 ± 0.04 eV are determined for $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_3\text{SiF}$, $(\text{CH}_3)_2\text{SiF}_2$, and CH_3SiF_3 , respectively, with appearance thresholds of 10.03 ± 0.04 , 10.70 ± 0.04 , 11.70 ± 0.03 , and 13.33 ± 0.04 eV for siliconium ion fragments $(\text{CH}_3)_3\text{Si}^+$, $(\text{CH}_3)_2\text{FSi}^+$, $(\text{CH}_3)_2\text{F}_2\text{Si}^+$, and F_3Si^+ arising from CH_3 loss. These data are interpreted in terms of the thermochemistry of the various ionic and neutral silicon species. Derived heats of formation afford accurate calculation of fluoride affinities (heterolytic bond dissociation energies, $D[\text{R}_3\text{Si}^+-\text{F}^-]$) of 219.5, 237.3, 258.4, and 302.0 kcal/mol for the siliconium ions $(\text{CH}_3)_3\text{Si}^+$, $(\text{CH}_3)_2\text{FSi}^+$, $(\text{CH}_3)_2\text{F}_2\text{Si}^+$, and F_3Si^+ , respectively. These values are 30–50 kcal/mol higher than the analogous carbonium ions.

The involvement of tricoordinate siliconium ions, as intermediates in organosilicon chemical reactions, has been proposed by numerous investigators.^{2,3} However, many exhaustive experimental attempts to evidence *even the existence* of R_3Si^+ species in solution have been completely unsuccessful, even under conditions where analogous carbonium ions, R_3C^+ , are long-lived.^{4,5} By contrast, R_3Si^+ species are abundant in the mass spectra of a wide variety of organosilicon compounds.^{6,7} Thus, gas phase studies provide a unique opportunity for determinations of chemical properties of these elusive species.

Recent gas phase studies from this laboratory of the positive ion chemistry of fluoromethylsilanes, utilizing ion cyclotron resonance techniques, have provided information regarding the relative stabilities of substituted siliconium ions, $(\text{CH}_3)_n\text{F}_{3-n}\text{Si}^+$ ($n = 0-3$), in the absence of complicating solvation phenomena. It was shown that methyl- and fluoro-substituents effect variations in siliconium ion stabilities, $\text{F}_3\text{Si}^+ < (\text{CH}_3)_2\text{FSi}^+ < (\text{CH}_3)_2\text{F}_2\text{Si}^+ < (\text{CH}_3)_3\text{Si}^+$, for fluoride ion as reference base, paralleling trends previously observed in the analogous series of carbonium ions.⁸ Further, investigations of fluoride transfer reactions between substituted carbonium and siliconium ions⁹ have shown that siliconium ions are substantially less stable than their carbon analogues. The more complete ion stability order (with F^- as the reference base), $\text{F}_3\text{Si}^+ < (\text{CH}_3)_2\text{FSi}^+ < \text{CF}_3^+ < (\text{CH}_3)_2\text{F}_2\text{Si}^+ < \text{CH}_3\text{CF}_2^+ < (\text{CH}_3)_3\text{Si}^+ < (\text{CH}_3)_2\text{FC}^+ < (\text{CH}_3)_3\text{C}^+$, has been established.

Accurate carbonium ion heats of formation, obtained principally from high resolution electron and photon impact mass spectrometry,¹⁰⁻¹³ have been used to calculate quantitative fluoride affinities of carbonium ions. These values serve to bracket the siliconium ion stabilities within known bounds. A major factor hindering detailed interpretation of these results is the lack of thermochemical data describing ions and neutrals containing silicon. Experimental difficulties involved in calorimetric determinations for silicon containing compounds result in large uncertainties even in neutral heats of formation. Although some thermochemical data describing silicocations are available from electron impact mass spectral studies,^{14,15} associated experimental uncertainties again make comparison with carbonium ions somewhat unreliable. Photoionization mass spectrometry (PIMS) has been shown to afford accurate determinations of appearance potentials for fragmentation processes, much superior to conventional electron impact techniques.¹⁰⁻¹³ We have undertaken PIMS studies directed at providing more precise thermochemical information describing ions containing silicon.

In a preliminary report,¹⁶ we summarized results of photoionization studies of molecular ions and siliconium ion fragments derived from $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_3\text{SiF}$, $(\text{CH}_3)_2\text{SiF}_2$, and CH_3SiF_3 . Tetramethylsilane is the only organosilane previously studied by photoionization.^{15c} In the present report, we wish to provide details necessarily omitted from the preliminary account. Photoionization efficiency curves are presented for molecular ions and lowest energy siliconium ion fragments. Factors affecting the interpretation of observed ionization thresholds are discussed. Heats of formation and fluoride affinities of siliconium ions derived from these data allow a detailed evaluation of the effects of methyl- and fluoro-substitution α to carbon and silicon charge centers.⁹

Experimental Section

The photoionization mass spectrometer utilized in the present studies has been previously described in detail.¹⁷ For these studies the hydrogen molecular spectrum at 1.0–1.5 Å FWHM resolution was used as the photon source. Sample pressures were typically $\sim 1 \times 10^{-4}$ Torr as measured by an MKS Baratron Model 90H1-E capacitance manometer. Initially, repeller voltages of ~ 0.1 V were used, yielding ion residence times of approximately 50 μs . In order to minimize ion-molecule reactions in the ion source, measurements were also made at relatively high repeller voltages (~ 10.0 V) resulting in shorter ion residence times of ~ 5.0 μs . Although higher source repeller fields resulted in considerably poorer ion detection efficiency, both sets of conditions yielded essentially the same threshold energies for ion formation. No attempts were made to correct ion intensities for ^{13}C or $^{29,30}\text{Si}$ isotope contributions. All experiments were performed at ambient temperature (22 °C).

Samples of $(\text{CH}_3)_3\text{SiF}$, $(\text{CH}_3)_2\text{SiF}_2$, and CH_3SiF_3 (PCR, Inc.) were graciously provided by Professor J. G. Dillard. $(\text{CH}_3)_4\text{Si}$ was obtained from MCB Chemicals, Inc. All samples were subjected to multiple freeze-pump-thaw cycles to remove noncondensable impurities.

Quoted ionization and appearance potential values are obtained by extrapolation of the linearly rising portion of the appropriate efficiency curves to zero photoionization efficiency. Various considerations relevant to interpretation of observed thresholds are discussed in later sections of this report.

Results

$(\text{CH}_3)_4\text{Si}$. Photoionization efficiency curves for the molecular ion and lowest energy fragment $(\text{CH}_3)_3\text{Si}^+$ generated in $(\text{CH}_3)_4\text{Si}$ for photon energies between 9.4 and 10.8 eV are shown in Figure 1. These are the only ions observed in this energy range. The onset of molecular ion formation occurs at 1265 Å, giving a value of 9.80 ± 0.03 eV for the adiabatic ionization potential of the parent neutral. The ionization ef-

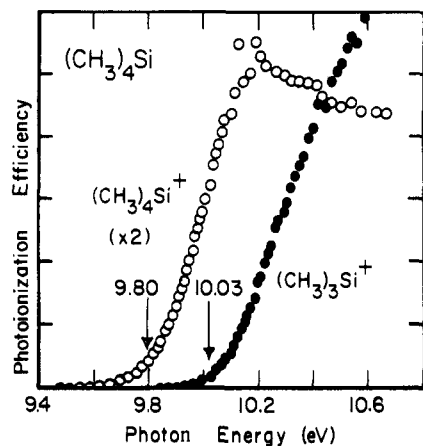


Figure 1. Photoionization efficiency curves for $(\text{CH}_3)_4\text{Si}^+$ and $(\text{CH}_3)_3\text{Si}^+$ generated from $(\text{CH}_3)_4\text{Si}$ in the photon energy range 9.4–10.6 eV.

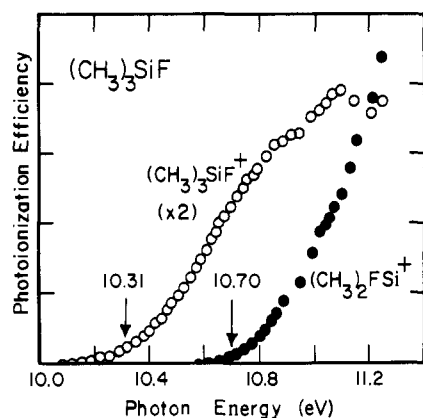
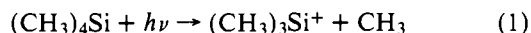


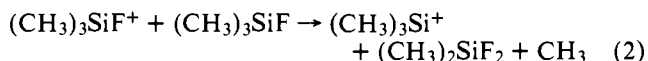
Figure 2. Photoionization efficiency curves for $(\text{CH}_3)_3\text{SiF}^+$ and $(\text{CH}_3)_2\text{SiF}^+$ generated from $(\text{CH}_3)_3\text{SiF}$ in the photon energy range 10.0–11.2 eV.

efficiency rises with photon energy as higher vibrational levels of the parent ion ground state are populated, peaks at an energy slightly above the onset of the first fragmentation, and declines slightly for higher photon energies. Fragmentation producing $(\text{CH}_3)_3\text{Si}^+$ by loss of methyl radical from the molecular ion, process 1, exhibits an onset at 1236 Å, corresponding to an appearance potential of 10.03 ± 0.04 eV.



Observed photoionization thresholds and various ion heats of formation derived therefrom are summarized in Table I. Also included in the table are the heats of formation of neutrals utilized in these calculations.

$(\text{CH}_3)_3\text{SiF}$. Photoionization efficiency curves for $(\text{CH}_3)_3\text{SiF}^+$ and $(\text{CH}_3)_2\text{SiF}^+$ generated in trimethylfluorosilane between 10.0 and 11.4 eV photon energies are shown in Figure 2. The onset of molecular ion formation occurs at 1202 ± 3 Å corresponding to an adiabatic ionization potential of 10.31 ± 0.04 eV. The efficiency curve for the molecular ion exhibits a gradual onset compared with those for all other molecular ions observed in this study. For long ion residence times a rapid ion–molecule reaction ($k = 6.5 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of $(\text{CH}_3)_3\text{SiF}^+$ with the parent neutral (reaction 2) yields small amounts of siliconium ion $(\text{CH}_3)_3\text{Si}^+$.



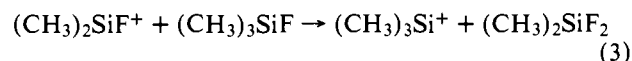
Reaction 2 is estimated to be ~ 43 kcal/mol exothermic and has been previously reported in the ion chemistry of

Table I. Photoionization Data for the Fluoromethylsilanes

Molecule	Ion	IP or AP (eV)	ΔH_f° (kcal/mol)
$(\text{CH}_3)_4\text{Si}$	$(\text{CH}_3)_4\text{Si}^+$	$9.80 \pm 0.03^{a,c,d}$	-42.4^f 183.5^j
	$(\text{CH}_3)_3\text{Si}^+$	$10.03 \pm 0.04^{a,c,d}$	154.8^k
$(\text{CH}_3)_3\text{SiF}$	$(\text{CH}_3)_3\text{SiF}^+$	$10.31 \pm 0.04^{a,e}$	-126.0^g 111.6^j
	$(\text{CH}_3)_2\text{SiF}^+$	$10.70 \pm 0.04^{a,e}$	86.6^k
	$(\text{CH}_3)_3\text{Si}^+$	$9.52,^l 12.99^m$	—
$(\text{CH}_3)_2\text{SiF}_2$	$(\text{CH}_3)_2\text{SiF}_2^+$	11.03 ± 0.03^a	-212.0^g 42.2^j
	$\text{CH}_3\text{SiF}_2^+$	11.70 ± 0.03^a	23.7^k
	$(\text{CH}_3)_2\text{SiF}^+$	$10.30,^l 13.77^m$	—
CH_3SiF_3	$\text{CH}_3\text{SiF}_3^+$	12.48 ± 0.04^a	$-296.0^{g,h}$ -6.3^j
	SiF_3^+	13.33 ± 0.04^a	-22.7^k
	$\text{CH}_3\text{SiF}_2^+$	$11.21,^l 14.68^m$	—
SiF_4	SiF_4^+	15.19^b	-386.0^i
	SiF_3^+	$13.10,^l 16.57^m$	-35.9^j —

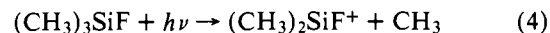
^a Ionization thresholds determined from this work by extrapolation of the linearly rising portion of the photoionization efficiency curve for the indicated neutral molecule. ^b Adiabatic IP[SiF_4] obtained from photoelectron spectroscopy, vertical IP[SiF_4] = 16.46 eV, ref 26. ^c Previous literature values: IP[$(\text{CH}_3)_4\text{Si}$] = 9.98 ± 0.03 eV and AP[$(\text{CH}_3)_3\text{Si}^+$] = 10.63 ± 0.13 eV, determined by RPD electron impact technique, ref 14a. ^d Previous values: IP[$(\text{CH}_3)_4\text{Si}$] = 9.86 ± 0.02 eV and AP[$(\text{CH}_3)_3\text{Si}^+$] = 10.09 ± 0.02 eV, determined by PIMS, ref 15c. ^e Previous values: IP[$(\text{CH}_3)_3\text{SiF}$] = 10.55 ± 0.06 eV and AP[$(\text{CH}_3)_2\text{SiF}^+$] = 11.11 ± 0.05 eV, determined by RPD electron impact technique, ref 14a. ^f Reference 14c. ^g ΔH_f° values determined as specified in the text. ^h Previous estimate $\Delta H_f^\circ[\text{CH}_3\text{SiF}_3] = -294.6$ kcal/mol, ref 22. ⁱ Reference 22. ^j Calculated from $\Delta H_f^\circ(\text{ion}) = \Delta H_f^\circ(\text{neutral}) + \text{IP}(\text{neutral})$. ^k Calculated from $\Delta H_f^\circ(\text{ion}) = \Delta H_f^\circ(\text{neutral}) - \text{AP}(\text{ion}) + \Delta H_f^\circ(\text{CH}_3)$, using $\Delta H_f^\circ(\text{CH}_3) = 34.0$ kcal/mol, ref 27. ^l Calculated for the pair processes $\text{R}_3\text{SiF} \rightarrow \text{R}_3\text{Si}^+ + \text{F}^-$ using fluoride affinities $D[\text{R}_3\text{Si}^+ - \text{F}^-]$ from Table II. ^m Calculated threshold for formation of R_3Si^+ by loss of F atom, from data in this table using eq 15, assuming no kinetic shift.

$(\text{CH}_3)_3\text{SiF}$.⁸ Not shown in Figure 2, the degree of $(\text{CH}_3)_3\text{Si}^+$ formation for low repeller voltages closely coincides with the shape of the molecular ion curve (though at only $\sim 20\%$ of the intensity) up to the appearance threshold of $(\text{CH}_3)_2\text{SiF}^+$, at which point $(\text{CH}_3)_3\text{Si}^+$ intensity increases in coincidence with the efficiency curve for $(\text{CH}_3)_2\text{SiF}^+$ due to the occurrence of fluoride transfer reaction 3 ($k = 3.4 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).⁸



$(\text{CH}_3)_3\text{Si}^+$ production is eliminated at high source repeller fields, where ion residence times are much reduced.

Fragmentation yielding $(\text{CH}_3)_2\text{SiF}^+$ by loss of methyl radical (reaction 4) exhibits a much sharper onset than is observed for molecular ion formation.



The threshold for process 4 occurs at 1158 ± 3 Å, yielding an appearance potential of 10.70 ± 0.04 eV. Table I summarizes observed ionization thresholds and derived ion heats of formation.

$(\text{CH}_3)_2\text{SiF}_2$. Photoionization efficiency curves for the molecular ion and lowest energy fragment $\text{CH}_3\text{SiF}_2^+$ generated from dimethyldifluorosilane in the photon energy range of 10.6–12.2 eV are shown in Figure 3. The molecular ion curve exhibits a well-behaved increase with photon energy, reaches a maximum near the onset of the lowest energy fragmentation,

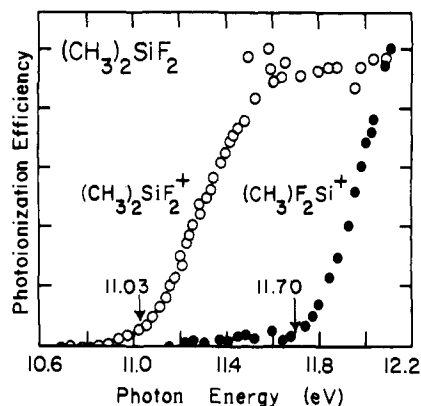
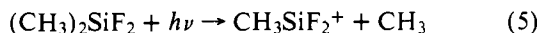
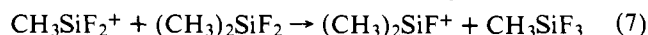
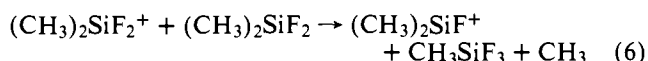


Figure 3. Photoionization efficiency curves for $(\text{CH}_3)_2\text{SiF}_2^+$ and $\text{CH}_3\text{SiF}_2^+$ generated from $(\text{CH}_3)_2\text{SiF}_2$ in the photon energy range 10.6–12.2 eV.

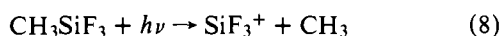
and remains roughly constant for higher photon energies. The onset of molecular ion formation occurs at $1124 \pm 3 \text{ \AA}$, corresponding to the adiabatic ionization potential of $11.03 \pm 0.03 \text{ eV}$. Process 5, production of $\text{CH}_3\text{SiF}_2^+$ by loss of CH_3 from the parent ion, exhibits a sharp onset at $1053 \pm 2 \text{ \AA}$, yielding an appearance potential of $11.70 \pm 0.03 \text{ eV}$.



As was found for the fragment $(\text{CH}_3)_3\text{Si}^+$ in $(\text{CH}_3)_3\text{SiF}$, at low repeller voltages the more stable siliconium fragment $(\text{CH}_3)_2\text{SiF}^+$ derived from dimethyldifluorosilane is observed in low abundance. Its production, not shown in Figure 3, closely matches the variations in efficiency curves for the molecular ion and the low energy fragment, $\text{CH}_3\text{SiF}_2^+$, in accord with previously reported⁸ reactions 6 and 7 ($k = 2.5$ and $3.1 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively). $(\text{CH}_3)_2\text{SiF}^+$ production is eliminated by high repeller voltages. Observed thresholds and derived ion heats of formation are shown in Table I.



CH_3SiF_3 . Between 12.0 and 14.0 eV photon energies, the only ions formed from direct photon impact on CH_3SiF_3 are the molecular ion and the trifluorosiliconium ion. Photoionization efficiency curves for these ions are shown in Figure 4. The threshold for formation of the molecular ion occurs at $993 \pm 3 \text{ \AA}$, corresponding to an adiabatic ionization potential of $12.48 \pm 0.04 \text{ eV}$. Fragmentation process 8, loss of CH_3 from the parent ion, exhibits an onset at $930 \pm 3 \text{ \AA}$, yielding $13.33 \pm 0.05 \text{ eV}$ for the appearance potential of SiF_3^+ from methyltrifluorosilane.



The siliconium ion $\text{CH}_3\text{SiF}_2^+$ is observed in low abundance. Its production under low repeller fields essentially parallels the efficiency curves of $\text{CH}_3\text{SiF}_3^+$ and SiF_3^+ and is eliminated with high repeller voltages, consistent with the occurrence of previously reported⁸ ion-neutral reactions 9 and 10 ($k = 0.67$ and $1.9 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively). Observed thresholds and derived ion heats of formation are summarized in Table I.



Discussion

Theoretical considerations suggest that, for molecules, the more favorable threshold law for photoionization results in

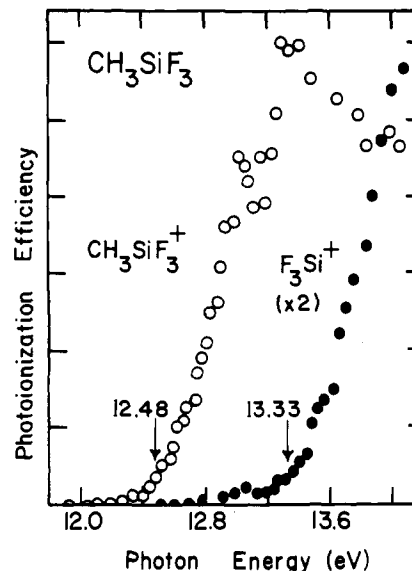


Figure 4. Photoionization efficiency curves for $\text{CH}_3\text{SiF}_3^+$ and SiF_3^+ generated from CH_3SiF_3 in the photon energy range 12.0–14.0 eV.

greater sensitivity at threshold than is observed for electron impact and provides for the precise determination of ionization thresholds. Even so, the interpretation of observed photoionization thresholds requires consideration of the contribution of thermal internal energy of the neutral to dissociation processes as well as the possibility of significant kinetic shifts. These phenomena have been discussed in detail elsewhere.^{18–21}

Since these photoionization measurements are conducted at ambient temperatures, the initial thermal energy of the parent neutral contributes to the total internal energy of the molecular ion and convolutes a Maxwellian energy distribution into the observed threshold curve. This results in a low energy tail on the fragment ionization efficiency curve, and causes a shift to lower energy of the apparent threshold by an amount equal to the mean thermal energy content of the parent neutral. Studies of fragmentation processes for the lower alkanes have demonstrated the importance of such effects.¹⁹

The kinetic shift is a displacement of an apparent fragmentation threshold to higher energy, an effect arising from instrumental limitations of the minimum detectable fragment ion signal. The magnitude of the kinetic shift is equal to the amount of energy, in excess of the true fragmentation threshold, required to raise the dissociation rate to a level sufficient for the production of detectable concentrations of fragment ions.^{18–21}

The effects of thermal energy and of kinetic shift are opposite in direction and can be comparable in magnitude. It is not expected in the present work that there will be significant kinetic shifts associated with the fragmentation processes of lowest energy, which correspond to the kinetically facile Si–C bond cleavage. The effects of thermal shifts are more difficult to evaluate since we do not have the ability to vary the source temperature in our apparatus. However, consistency of the present results with implications of fluoride transfer reactions of the siliconium ions^{9,16} suggests that the measured thresholds are reasonably accurate. Higher energy thresholds (those resulting from loss of F from the molecular ion), where kinetic shifts result from competition with lower energy fragmentation processes, are not utilized in the present study to derive thermochemical data. Also as noted above, the contribution of ion molecule reactions to these ionic species makes it difficult to determine precise thresholds.

Thermochemical Considerations. The observed ionization

Table II. Calculated Thermochemical Quantities

Ion [R ₃ Si ⁺]	D[R ₃ Si ⁺ -F] ^{a,b}	D[R ₃ Si ⁺ -CH ₃] ^{a,c}	D[R ₃ Si ⁺ -F] ^{a,d}	IP[R ₃ Si] ^e	ΔH _f [R ₃ Si] ^{a,h}
(CH ₃) ₃ Si ⁺	219.5	5.3	58.8	6.61 ^f	2.4
(CH ₃) ₂ FSi ⁺	237.3	9.0	63.2	7.23 ^g	-80.1
(CH ₃)F ₂ Si ⁺	258.4	15.4	50.7	8.23 ^g	-166.0
F ₃ Si ⁺	302.0	19.6	31.8	9.86 ^{g,i}	-250.0

^a In units of kcal/mol, calculated in each case as described in the text. ^b Calculated using eq 11 and ΔH_f[F⁻] = -61.3 ± 0.1 kcal/mol taken from ref 28. ^c Calculated using eq 14 and ΔH_f[CH₃] = 34.0 kcal/mol taken from ref 27. ^d Calculated using eq 16 and data in Table I, with ΔH_f[F] = 18.7 ± 1 kcal/mol taken from ref 28. ^e Radical ionization potentials are in eV. ^f Calculated using eq 12 with D[(CH₃)₃Si-CH₃] = 78.8 ± 3 kcal/mol taken from ref 25. ^g Calculated using eq 12 with estimated D[R₃Si-CH₃] = 80 kcal/mol. ^h Calculated using eq 13 and data in Tables I and II. ⁱ This value appears to be too high; see text for discussion.

Table III. Comparison of Thermochemical Properties of Silicon and Carbon Species

R ₃ M	ΔH _f [R ₃ C] ^a	ΔH _f [R ₃ Si] ^{a,c}	IP[R ₃ C] ^b	IP[R ₃ Si] ^{b,c}	ΔH _f [R ₃ -C ⁺] ^a	ΔH _f [R ₃ Si ⁺] ^{a,d}	D[R ₃ C ⁺ -F] ^a	D[R ₃ Si ⁺ -F] ^{a,c}
(CH ₃) ₃ M	6.8 ^e	2.4	6.93 ^e	6.61	167.0 ^e	154.8	182.0 ⁱ	219.5
(CH ₃) ₂ FM	-26.6 ^f	-80.1	7.14 ^f	7.23	138.0 ^f	86.6	206.5 ^f	237.3
(CH ₃)F ₂ M	-73.8 ^f	-166.0	7.92 ^f	8.23	108.8 ^f	23.7	225.7 ^f	258.4
F ₃ M	-112.2 ^h	-250.0	9.17 ^g	9.86 ⁱ	99.3 ^g	-22.7	253.0 ⁱ	302.0

^a Heats of formation and bond dissociation energies are in units of kcal/mol. ^b Radical ionization potentials are in units of eV. ^c Taken from data in Table II. ^d Taken from data in Table I. ^e Reference 10. ^f Reference 12. ^g Reference 20. ^h Reference 29. ⁱ Reference 30. ^j This value appears to be too high; see text for discussion.

thresholds (Table I) allow calculation of a variety of ion thermochemical properties, provided that accurate data describing the parent neutral molecules are available. Experimental difficulties associated with calorimetric determinations of heats of formation for compounds of silicon and of fluorine have led to considerable uncertainties in reported values.¹⁵ Indirect estimations of neutral heats of formation of organosilicon compounds, using the bond interaction term scheme of Allen in conjunction with electron impact appearance potential correlations,¹⁴ have met with reasonable success for the methylsilanes. In the present study we take ΔH_f^o values of the fluoromethylsilanes from an interpolation between those of (CH₃)₄Si^{14c} at -42.4 and SiF₄²² at -386 kcal/mol, along with the only available estimate for ΔH_f CH₃SiF₃²² of -294.6 kcal/mol. The values used (Table I) are fully consistent with limits on siliconium ion fluoride affinities established by direct ICR observations of thermal energy fluoride transfer reactions involving siliconium ions and carbonium ions.^{9,16} Reference thermochemical data on the carbonium ion species involved are known with considerable accuracy from previous investigations.¹⁰⁻¹³ The heats of formation of neutral silanes in Table I fit an approximately linear decrease of -85.9 kcal/mol for successive substitution of F for CH₃ throughout the series. Minor positive deviations from this decrease occur for values of ΔH_f of (CH₃)₃SiF, (CH₃)₂SiF₂, and CH₃SiF₃ (respectively, 1.7, 1.8, and 3.9 kcal). Similar thermochemical correlations are well known and form the basis of Benson's group additivity method²³ and the bond interaction term schemes of Allen.²⁴ Overall accuracy is conservatively estimated at ±5 kcal/mol in ΔH_f values, of which only ±1 kcal/mol is attributable to uncertainties in measured ionization thresholds.

Siliconium Ion Fluoride Affinities. Using the heat of formation data for the siliconium ions fragments R₃Si⁺ arising by loss of CH₃ radical from the series of neutrals (CH₃)_nF_{3-n}SiCH₃ (where n = 0-3), the relationship 11 is used to calculate the fluoride affinities for all four siliconium ions. The calculated values are summarized in Table II and exhibit a very marked increase with increasing fluorine substitution in place of methyl.

$$D[\text{R}_3\text{Si}^+-\text{F}^-] = \Delta H_f[\text{R}_3\text{Si}^+] + \Delta H_f[\text{F}^-] - \Delta H_f[\text{R}_3\text{SiF}] \quad (11)$$

Related Thermochemical Properties. Included in Table II are calculated values for ionization potentials and heats of formation of the various methyl and fluoro substituted silyl radicals and estimates of the excess energies required to fragment the various parent molecular ions, denoted as D[R₃Si⁺-X] (where X = CH₃, F).

Calculation of silyl radical IP's, using appearance potential data for siliconium fragments arising from CH₃ loss (Table I), with eq 12 requires knowledge of the Si-CH₃ bond dissociation energies in the neutral silanes.

$$\text{IP}[\text{R}_3\text{Si}\cdot] = \text{AP}[\text{R}_3\text{Si}^+] - D[\text{R}_3\text{Si}-\text{CH}_3] \quad (12)$$

The only direct measurement in the literature is that of D[(CH₃)₃Si-CH₃] = 78.8 ± 3 kcal/mol²⁵ obtained from the kinetics of thermal decomposition of (CH₃)₄Si. In light of the electron withdrawing effects of fluorine substituents and the relatively high polarizability of the methyl group, silicon-methyl homolytic bond dissociation energies might be expected to vary by an as yet unknown degree with increasing fluoro substitution on silicon. In Table II, IP's for (CH₃)₂FSi, (CH₃)F₂Si, and F₃Si are estimated using D[R₃Si-CH₃] = 80 kcal/mol in each case. This estimate may be questioned, at least for F₃SiCH₃. The calculated IP[F₃Si·] at 9.86 eV is approximately equal to the accurately known value of IP[CH₃·] = 9.84 eV.^{10b} From such similar ionization potentials, one might expect to observe appreciable abundance of CH₃⁺ in the mass spectra of CH₃SiF₃. In fact, for electron energies up to 70 eV, essentially no CH₃⁺ (≤0.1% of total ionization) is formed, while SiF₃⁺ is the base peak from CH₃SiF₃ from the onset of fragmentation to 70 eV.⁸ This suggests that IP[F₃Si·] is actually considerably less than 9.84 eV and, assuming the measured AP[F₃Si⁺] from CH₃SiF₃ to be correct, requires D[F₃Si-CH₃] to be somewhat greater than 80 kcal/mol. Similar uncertainties likely affect the IP values for (CH₃)₂FSi and (CH₃)F₂Si radicals. Even so, the calculated radical IP's show considerable increases with increasing fluorine substi-

tution. Radical heats of formation are calculated from eq 13 and are subject to the above considerations regarding estimates for Si-C bond dissociation energies.

$$\Delta H_f[\text{R}_3\text{Si}] = D[\text{R}_3\text{Si}-\text{CH}_3] - \Delta H_f[\text{CH}_3] + \Delta H_f[\text{R}_3\text{SiCH}_3] \quad (13)$$

Calculations of excess energies necessary to induce Si-CH₃ bond breaking in the silane molecular ions (Table II) using eq 14 require only a knowledge of relative ionization thresholds and do not depend on ΔH_f values of the neutral silanes. The calculated values are small but exhibit substantial increases with increasing fluorine substitution, ranging from 5.3 kcal/mol for (CH₃)₃Si⁺ to 19.6 kcal/mol for F₃Si⁺.

$$D[\text{R}_3\text{Si}^+-\text{CH}_3] = \text{AP}[\text{R}_3\text{Si}^+] - \text{IP}[\text{R}_3\text{SiCH}_3] \quad (14)$$

The analogous calculation of $D[\text{R}_3\text{Si}^+-\text{F}]$ values is inhibited by a lack of direct measurements of appearance thresholds for siliconium ion fragments arising from F loss. However, approximate AP's may be calculated using heat of formation data from Table I in eq 15.

$$\text{AP}[\text{R}_3\text{Si}^+] = \Delta H_f[\text{R}_3\text{Si}^+] - \Delta H_f[\text{R}_3\text{SiF}] + \Delta H_f[\text{F}\cdot] \quad (15)$$

These calculated AP's are included in Table I and allow calculation of Si-F bond energies in the parent molecular ions from eq 16.

$$D[\text{R}_3\text{Si}^+-\text{F}] = \text{AP}[\text{R}_3\text{Si}^+] - \text{IP}[\text{R}_3\text{SiF}] \quad (16)$$

It is interesting to note that these calculated values of $D[\text{R}_3\text{Si}^+-\text{F}]$ (Table II) are considerably larger than those for $D[\text{R}_3\text{Si}^+-\text{CH}_3]$ but exhibit an overall decrease with increasing fluorine substitution beyond (CH₃)₂FSi⁺, in contrast to the consistent increases observed throughout the $D[\text{R}_3\text{Si}^+-\text{CH}_3]$ series.

Comparisons of thermochemical data for trisubstituted silicon radicals and ions derived in the present study with literature data for the analogous carbon species are shown in Table III. These data represent the first quantitative comparisons available and facilitate interpretation of the effects of methyl and fluoro substitution on carbon and silicon centers. From the calculated fluoride affinities, an ion stability order SiF₃⁺ < (CH₃)₂F₂Si⁺ < CF₃⁺ < (CH₃)₂FSi⁺ < CH₃CF₂⁺ < (CH₃)₃Si⁺ < (CH₃)₂FC⁺ < (CH₃)₃Si⁺ is predicted. This is entirely consistent with the experimentally observed ordering as discussed in the introduction.

Particularly striking from the comparisons in Table III are large but consistent differences in heterolytic bond dissociation energies, $D[\text{R}_3\text{M}^+-\text{F}^-]$ (where M = C, Si). A given siliconium ion is found to bind F⁻ more strongly by 40 ± 9 kcal/mol than the carbonium ion analogue. Since the ionization potentials of similarly substituted carbon and silicon radicals are nearly identical, the differences in heterolytic bond dissociation energies reflect directly differences in C-F and Si-F homolytic bond dissociation energies. The present results bear significantly on repeated failures to detect siliconium ions in solution, under conditions where analogous carbonium ions are long-lived.^{4,5} While ion solvation can strongly influence ion stabilities in solution, the magnitude of the observed differences in siliconium and carbonium ion fluoride affinities in the gas phase suggests, in addition to effects due to C-Si electronegativity differences, a lack of π back-bonding from filled substituent orbitals into the Si 3p orbital as compared with the carbonium ions, due to poorer spatial overlap. Detailed dis-

ussion of these effects is the subject of a forthcoming report.⁹

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