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# How Strong Is the Si=C Bond in Fluoro- and Methyl-Substituted Silaethylenes? An Experimental Determination of π Bond Strengths

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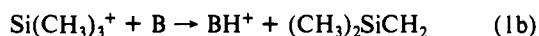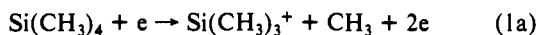
**Abstract:** Measurements have been made of the proton affinities and fluoride affinities of three methyl- and fluoro-substituted silaethylenes. These quantities have been used to calculate the strength of the Si=C π bond in these compounds via two independent thermochemical cycles. Values obtained indicate that the Si=C π bond is of considerable strength and that fluorine substitution strengthens the π bond, with respect to the analogous methyl-substituted species. An estimate of the Si–F bond strength in these compounds of 137–147 mol$^{-1}$ has been deduced from thermochemical considerations.

Considerable effort has been made to isolate, determine the physical properties of, and characterize the bonding in silenes, such as I, the silicon analogues of olefins.[1] Due to the varying stabilities and high reactivities of silenes (varying from stable in an argon matrix at low temperature to stable for years in controlled environments at room temperature[2]), measurements of the physical properties of these compounds has been difficult.

$$CH_3\diagdown \atop CH_3\diagup Si{=}CH_2$$

I
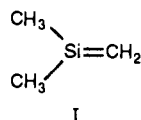
It was initially believed that if silenes could be synthesized they would be unstable and the π bond would be weaker than that in the corresponding olefins due to the poor overlap between the orbitals of the silicon and carbon. In the mid 1960's, indirect evidence for the existence of Si=C π bonding was obtained by Gusel'nikov and Flowers[3] who observed cleavage of dimethyl-silacyclobutane followed by (2 + 2) ring formation to produce tetramethyldisilacyclobutane. Many stable substituted silenes have now been isolated, and structural characteristics of these species have been determined. However, little is yet known of the smaller olefin analogue silenes due to the difficulty in measuring properties of these species, which as yet have been trapped only at low temperature in argon matrices.[4] Information about these silenes, such as the silicon-to-carbon bond length and the strength of the π bond, has come from indirect experiments[5] or from theoretical calculations.[6-12]

In the gas phase it is relatively straightforward to generate silenes as the products of ion–molecule reactions such as deprotonation of methylsilyl cations by a base with a greater proton affinity than the silene, eq 1.

$$Si(CH_3)_4 + e \rightarrow Si(CH_3)_3{}^+ + CH_3 + 2e \qquad (1a)$$

$$Si(CH_3)_3{}^+ + B \rightarrow BH^+ + (CH_3)_2SiCH_2 \qquad (1b)$$

Although isolating the neutral silene from this reaction is not practical, Hehre has demonstrated that measurement of some intrinsic thermochemical properties is possible under the conditions present in an ion cyclotron resonance spectrometer.[5] These properties can then be used to calculate π bond strengths and other thermochemical quantities of interest.

Some contention exists concerning the strength of the π bond in silenes; indeed no single method for theoretically defining π bond strengths holds. This question of π bond strength has been addressed by using both theoretical and experimental approaches. Experimentally, Pietro and Hehre[5] estimate the π bond strength

in dimethylsilaethylene (I) to be 38 kcal mol$^{-1}$, based on ion cyclotron resonance bracketing experiments where proton transfer from trimethylsilyl cation should generate the silene. A thermochemical cycle was used in conjunction with the measured proton affinity and assumed heats of formation of the neutral species to estimate the strength of the incipient π bond. Unfortunately, the heats of formation required in this type of calculation are not known reliably.

Theoretical determination of silene π bond strengths have also been carried out. Hanamura et al.[6] have calculated the barrier to rotation about the π bond and used this as a measure of the π bond strength in I, finding it to be 47 kcal mol$^{-1}$. The same value was also obtained by these workers for the strength of the π bond in silaethylene ($H_2SiCH_2$). Schmidt et al.[7] have similarly calculated the π bond strength in silaethylene to be 36 kcal mol$^{-1}$ from differences in the energies of the planar silaethylene (π bonded) and a perpendicular biradical structure. Dobbs and Hehre[8] also use this criterion to assign the value of the π bond in silaethylene as 35 kcal mol$^{-1}$. In the former calculation,[7] the structure of the biradical about the silicon atom was assumed to be nonplanar, however, which leads to an artificially high bond strength. Dobbs and Hehre have also used a method suggested by Benson[13] for defining π bond strength, i.e., the difference between the bond dissociation energy for hydrogen atoms on either side of the π bond. The π bond strength obtained in this manner was calculated to be equal to that obtained by the theoretically calculated energy difference between the planar and perpendicular geometries (35 kcal mol$^{-1}$). More recently in several ab initio studies of π bond strengths involving second- and third-row atoms[9-11] a π bond energy in $CH_2{=}SiH_2$ of 36 ± 1 kcal mol$^{-1}$ has been arrived at on a consistent basis.

Although there now appears to be some general agreement as to the π bond strength in silaethylene, the estimates for the larger

(1) Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 24 and references contained therein.

(2) For a review of the chemistry of silenes, see: Brook, A. G.; Baines, K. M. In *Advances in Organometallic Chemistry*; Academic Press: Vol. 25.

(3) (a) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864. (b) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419.

(4) Maier, G.; Mihm, G.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2351.

(5) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329.

(6) Hanamura, M.; Nagase, S.; Morokuma, L. *Tetrahedron Lett.* **1981**, *22*, 1813.

(7) Schmidt, M. W.; Gordon, M. S.; Dupuis, M. *J. Am. Chem. Soc.* **1985**, *107*, 2585.

(8) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *104*, 4352.

(9) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352.

(10) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5717.

(11) Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275.
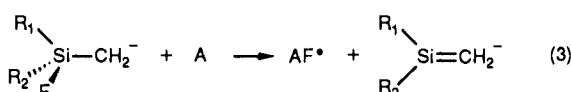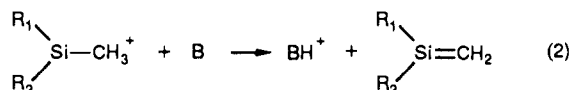
(12) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(13) Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; Wiley: New York, 1976.

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silene, I, are not as consistent. The experimental determination relies on the thermochemical data of unknown reliability (heats of formation), and the theoretical determinations do not consider the effect of structural changes around the silicon atom or the conceivable change in $\sigma$ bond strength in going from the planar to perpendicular structures.[7]

The present study uses Fourier transform ion cyclotron resonance[14] to measure the proton affinities and the fluoride affinities of a series of fluorine- and methyl-substituted silaethylenes as well as the gas-phase acidities of the parent silanes. These quantities are then used in conjunction with thermochemical cycles, which do not require individual heats of formation be known, to estimate the strength of the $\pi$ bond in the silenes. This extra uncertainty introduced into the previous type of calculation is therefore removed. The present method involves bracketing measurements of the energy required to remove a proton from the silyl cations, eq 2 (silene proton affinity[15]), and of the energy required to remove a fluoride ion from the methyl- and fluorosilylcarbanions, eq 3 (the fluoride affinity[15]).

$$\underset{R_2}{\overset{R_1}{\diagdown}}Si-CH_3^+ + B \longrightarrow BH^+ + \underset{R_2}{\overset{R_1}{\diagdown}}Si=CH_2 \qquad (2)$$

$$\underset{R_2}{\overset{R_1}{\diagdown}}\underset{F}{Si}-CH_2^- + A \longrightarrow AF^\bullet + \underset{R_2}{\overset{R_1}{\diagdown}}Si=CH_2^- \qquad (3)$$
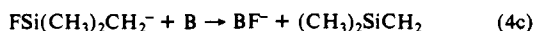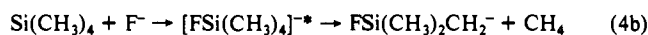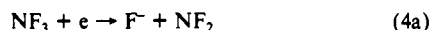
The proton affinities and fluoride affinities thus obtained are used in thermochemical cycles to calculate the $\pi$ bond strengths in three silaethylenes: $(CH_3)_2Si=CH_2$ (I), $F(CH_3)Si=CH_2$ (II), and $F_2Si=CH_2$ (III). The differences between values obtained from the proton and fluoride affinity cycles have been used to infer new values of Si–C and Si–F bond strengths in the parent silanes.

$$\underset{CH_3}{\overset{F}{\diagdown}}Si=CH_2 \qquad \underset{F}{\overset{F}{\diagdown}}Si=CH_2$$

II                           III
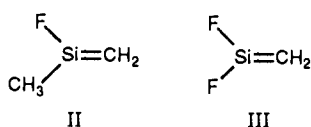
## Experimental Section

All experiments were carried out on a Spectrospin CMS-47 Fourier transform ion cyclotron resonance spectrometer equipped with a 4.7-T, 150-mm horizontal bore superconducting magnet, a 60 mm × 60 mm cylindrical ICR cell, a vacuum system pumped by a Balzers TPU330 300 L s⁻¹ turbomolecular pump, and an Aspect 3000 minicomputer with 256 kB memory, an array processor, and a 160 MB Winchester hard disk. The base pressure of the vacuum system was typically in the low $10^{-10}$ Torr region as measured by a Balzers IMR132 ionization gauge.[16]

For the proton affinity measurements, the parent silane and a base of known proton affinity were introduced independently to the vacuum system through molecular leak valves (Balzers BDV035) to a typical total pressure of 4 × 10⁻⁸ Torr in a 1:1 ratio. The appropriate silyl cation was readily generated by electron impact. Fluoride affinity measurements were performed similarly but with a premixed (1:1) sample of $NF_3$ and the silane precursor and a fluoride acceptor of known fluoride affinity to a similar total pressure. Fluoride attachment to the parent silane resulted in methane elimination to yield a fluoride adduct of the silaethylene of interest, e.g., eq 4b.

$$NF_3 + e \rightarrow F^- + NF_2 \qquad (4a)$$

$$Si(CH_3)_4 + F^- \rightarrow [FSi(CH_3)_4]^{-\bullet} \rightarrow FSi(CH_3)_2CH_2^- + CH_4 \qquad (4b)$$

$$FSi(CH_3)_2CH_2^- + B \rightarrow BF^- + (CH_3)_2SiCH_2 \qquad (4c)$$

Both experiments can be described by using the pulse sequence shown in Figure 1. A quench pulse applied to the ICR cell ensured all ions had
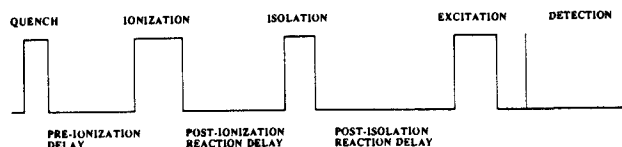


**Figure 1.** Typical pulse sequence used for the experiments. Pulses and delays are not to scale.

left the cell. After a short delay, an ionization pulse of 70 eV electrons formed the reactant ions desired. These initially formed ions were then allowed to react (post ionization delay) to form the reagent ions of interest. After the ion of interest was formed, e.g., $Si(CH_3)_3^+$ or $F(C-H_3)_2SiCH_2^-$, an isolation pulse eliminated all ions, except the ion of interest, from the cell. A variable reaction delay was then used to monitor the reaction of this single ion with the neutral species present. If proton transfer (fluoride transfer) occurred, the intensity of the trapped ion would decrease, and the intensity of the product ion (the new $H^+$ or $F^-$ adduct) would increase. The pulse sequence could be repeated to increase the signal-to-noise ratio. The exact composition of each ion of interest was obtained under high-resolution conditions.

**Calculations.** Ab initio calculations were performed by using the GAUSSIAN 86 package.[17] Geometries were optimized with the 3-21G* basis set with single-point energies then being calculated at the MP3/6-31G* level (third-order Moller–Plesset perturbation theory[18] using the 6-31G* basis set). These calculations are designated MP3/6-31G*//3-21G*.

## Results

**Proton Affinity Measurements.** Previous experiments by Pietro and Hehre[5] have bracketed the proton affinity of $(CH_3)_2SiCH_2$ between that of piperidine (226.9 kcal mol⁻¹—no proton transfer observed) and that of isopropylethylamine (228.4 kcal mol⁻¹—proton transfer observed),[19] leading to a value of 228 ± 2 kcal mol⁻¹ for the proton affinity of $(CH_3)_2SiCH_2$. Our experiments have confirmed this value by bracketing the proton affinity of $(CH_3)_2SiCH_2$ between those of piperidine (226.9 kcal mol⁻¹), where very slow endothermic proton transfer was observed, and diisopropylamine (230.2 kcal mol⁻¹), where exothermic proton transfer was observed. We thus also assign the proton affinity of $(CH_3)_2SiCH_2$ as 228 ± 2 kcal mol⁻¹.

The spectra presented in Figures 2 and 3 illustrate the experiments in which the proton affinity of $(CH_3)_2SiCH_2$ was measured by using tetramethylsilane (TMS) as a source of trimethylsilyl cations which were then reacted with either piperidine or diisopropylamine. Both slow endothermic proton transfer (piperidine, Figure 2) and exothermic proton transfer (diisopropylamine, Figure 3) can be seen. For both figures, spectra (a) show that initially both trimethylsilylcation and the protonated amine of interest are present. Spectra (b) show clean isolation of the trimethylsilyl cation in both cases. Spectra (c) were recorded after a reaction delay of 20 s (trimethylsilyl cations trapped in the cell) and show that there is proton transfer to both protonated piperidine and protonated diisopropylamine after 20 s. However, also apparent in the spectra were cluster ions for the trimethylsilyl cation adduct of the amine and $[M - H]^+$ ions for the amines. For piperidine, continuous ejection of the $m/z$ 84 ion during the post-ionization delay reduces the intensity of both the $m/z$ 84 and 86 ions; these are the amine $[M - H]^+$ and $[M + H]^+$ ions, respectively. This indicates that most of the protonated piperidine arises from proton transfer from the $m/z$ 84 ion. After a 20-s reaction delay with continuous ejection of $m/z$ 84, the intensity of the $m/z$ 86 increases slightly, showing that proton transfer directly from the silyl cation is very slow and probably somewhat endothermic.

In similar fashion $FSi(CH_3)_2^+$ was found to undergo exothermic proton transfer to acetonitrile but not to acetaldehyde, and $F_2SiCH_3^+$ was found to undergo exothermic proton transfer to

(14) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282. (b) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

(15) Proton affinity is defined as the negative enthalpy change for the reaction: $XH^+ \rightarrow X + H^+$. Fluoride affinity is similarly described as the negative enthalpy change for the reaction: $XF^- \rightarrow X + F^-$.

(16) (a) Alleman, M.; Kellerhalls, Hp.; Wanczek, K.-P. *Int. J. Mass Spectrom. Ion Proc.* **1983**, *46*, 139. (b) Kofel, P.; McMahon, T. B. *J. Phys. Chem.* **1988**, *92*, 6174.

(17) GAUSSIAN 86: Frisch, Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.
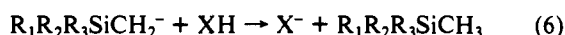
(18) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quant. Chem.* **1977**, *11*, 149.
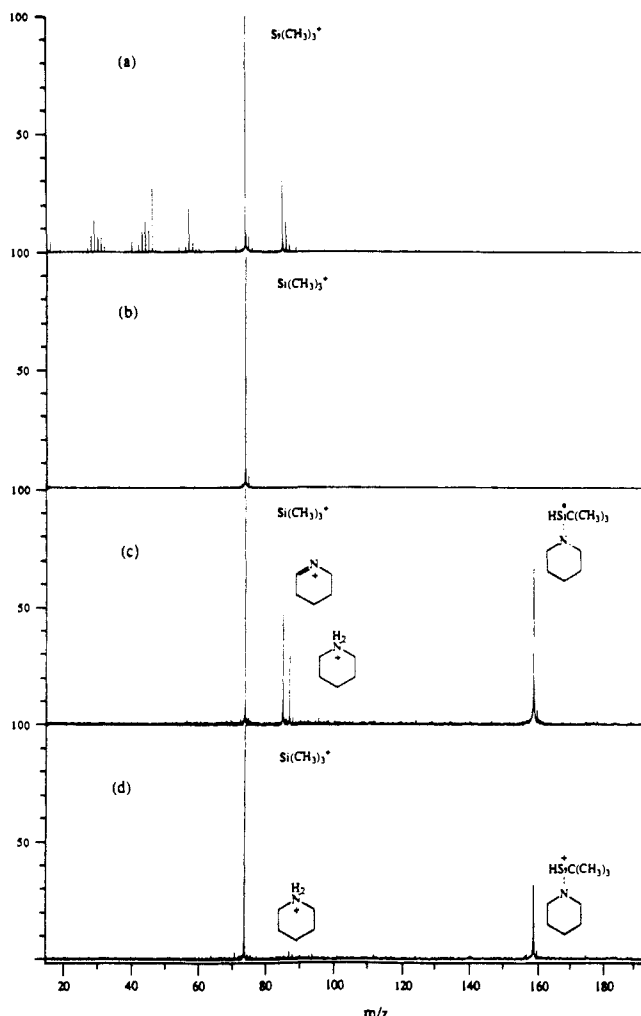
Figure 2. Sequential spectra for bracketing the proton affinity of (C-H$_3$)$_2$SiCH$_2$ using TMS and piperidine: (a) TMS and piperidine, (b) isolation of the trimethylsilyl cation ($m/z$ 73), (c) after a 20-s reaction delay, and (d) reaction delay of 20 s with continuous ejection of $m/z$ 84 (amine [M − H]$^+$). Almost all protonated amine, $m/z$ 86, is removed, although a small amount remains due to slightly exothermic proton transfer.

nitromethane but not to difluoroethylene. These data thus bracket the proton affinities of F(CH$_3$)Si=CH$_2$ and F$_2$Si=CH$_2$ as 187 ± 2 and 178 ± 2 kcal mol$^{-1}$, respectively.

**Gas-Phase Acidity Measurements.** In order to evaluate $\pi$ bond strengths from negative ion experiments it was necessary to also obtain the gas-phase acidities of each of parent silanes. This was done in two groups of experiments in which, first, a series of anions, whose conjugate acids have known gas-phase acidity, were generated and proton abstraction from the appropriate silane was looked for, eq 5, and, second the silyl carbanion was generated and proton abstraction from a series of compounds of known gas-phase acidity was attempted, eq 6.

$$X^- + R_1R_2R_3SiCH_3 \rightarrow R_1R_2R_3SiCH_2^- + HX \quad (5)$$

$$R_1R_2R_3SiCH_2^- + XH \rightarrow X^- + R_1R_2R_3SiCH_3 \quad (6)$$

In this way the gas-phase acidity of FSi(CH$_3$)$_3$ was determined to be between those of hydroxylradical and water (387 ± 5 kcal mol$^{-1}$), that of F$_2$Si(CH$_3$)$_2$ was determined to be between those of fluoroform and toluene (379 ± 3 kcal mol$^{-1}$), and that of F$_3$SiCH$_3$ was found to be between those of acetone and acetaldehyde (368 ± 2 kcal mol$^{-1}$).

**Fluoride Affinity Measurements.** As described above the fluoride affinities of the silenes were also required for the $\pi$ bond energy calculations. The fluorosilyl carbanions generated by either proton abstraction or fluoride addition followed by loss of CH$_4$ from the appropriate silane (eq 4b) were allowed to react with

| Proton Affinities[a] (kcal mol$^{-1}$) | | Gas-Phase Acidities[c] | |
|---|---|---|---|
| diisopropylamine | 230.2 | (CH$_3$)$_4$Si | 391 |
| piperidine | 226.9 | H$_2$O | 391 |
| (CH$_3$)$_2$Si=CH$_2$ | 228 ± 2[f] | FSi(CH$_3$) | 387 ± 5[f] |
| isopropylethylamine | 228.4 | OH | 382 |
| acetonitrile | 188.4 | toluene | 381 |
| F(CH$_3$)Si=CH$_2$ | 187 ± 2[f] | F$_2$Si(CH$_3$)$_2$ | 379 ± 2[f] |
| acetaldehyde | 186.6 | CF$_3$H | 377 |
| nitromethane | 179.2 | (CH$_3$)$_2$CO | 369 |
| F$_2$Si=CH$_2$ | 178 ± 2[f] | F$_3$SiCH$_3$ | 367 ± 2[f] |
| CF$_2$=CH$_2$ | 176 | CH$_3$CHO | 366 |

| Fluoride Affinities[b] | | Bond Dissociation Energies[d] | |
|---|---|---|---|
| AsF$_3$ | 48.2 | (CH$_3$)$_3$SiCH$_2$–M | 99.2 |
| F$_2$Si=CH$_2$ | 46 ± 2[f] | (CH$_3$)$_3$Si–CH$_3$ | 85 |
| F$_2$Si(CH$_2$)$_2$ | 44 | F$_3$Si–CH$_3$ | 85[g] |
| F$_2$CO | 42.6 | | |
| F(CH$_3$)Si=CH$_2$ | 40 ± 2[f] | Appearance Energies[e] (eV) | |
| FSi(CH$_3$)$_3$ | 38.2 | ((CH$_3$)$_3$Si$^+$)$_{(CH_3)_4Si}$ | 10.03 |
| (CH$_3$)$_2$Si=CH$_2$ | 37 ± 2[f] | ((CH$_3$)$_2$SiF$^+$)$_{(CH_3)_3SiF}$ | 10.70 |
| SO$_2$F$_2$ | 35.8 | ((CH$_3$)SiF$_2$$^+$)$_{(CH_3)_2SiF_2}$ | 11.70 |

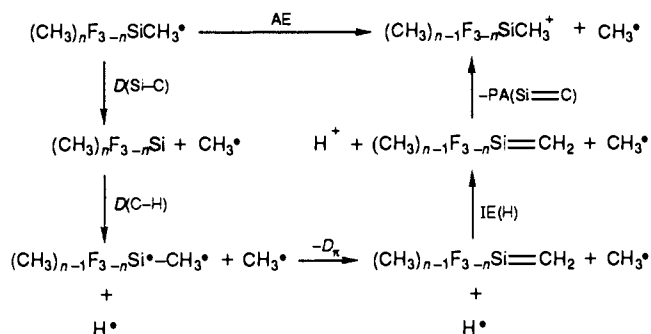[a] Proton affinities of reference compounds taken from ref 19. [b] Fluoride affinities of reference compounds taken from: Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* 1985, *107*, 766. [c] Gas-phase acidities of reference compounds taken from ref 27. [d] Reference 21. [e] Reference 20. [f] This work. [g] See text.

**Scheme I**



a number of Lewis acids of known fluoride affinity (eq 4c). In this way F(CH$_3$)$_2$Si-CH$_2^-$ was found to fluoride transfer to FSi(CH$_3$)$_3$ but not to SO$_2$F$_2$ establishing the fluoride affinity of (CH$_3$)$_2$Si=CH$_2$ as 37 ± 2 kcal mol$^{-1}$. Similarly F$_2$(CH$_3$)Si–CH$_2^-$ was found to fluoride transfer to F$_2$CO but not to FSi(CH$_3$)$_3$ giving a fluoride affinity of F(CH$_3$)Si=CH$_2$ of 40 ± 2 kcal mol$^{-1}$. Finally, F$_3$SiCH$_2^-$ was found to fluoride transfer to AsF$_3$ but not to F$_2$Si(CH$_3$)$_2$ establishing a fluoride affinity of F$_2$Si=CH$_2$ of 46 ± 2 kcal mol$^{-1}$. Fluoride transfer experiments are illustrated in Figures 4 and 5 for the AsF$_3$ and F$_2$Si(CH$_3$)$_2$ experiments, respectively.

**Thermochemical Data.** All proton affinities, fluoride affinities, and gas-phase acidities for the silanes and silenes obtained in this work as well as those of the appropriate reference compounds are summarized in Table I and can be found in detail in ref 18 and 19. In addition, appearance energy measurements of the silyl cations derived from the parent silanes[20] and experimentally determined bond dissociation energies,[21] used as described below, are also included.

## Discussion

**Thermochemical Cycles.** Two independent thermochemical cycles, Schemes I and II, can be constructed from the positive ion and negative ion data, respectively. This ionic data coupled with appropriate homolytic bond dissociation energies for neutral

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(20) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1977, *99*, 2085.
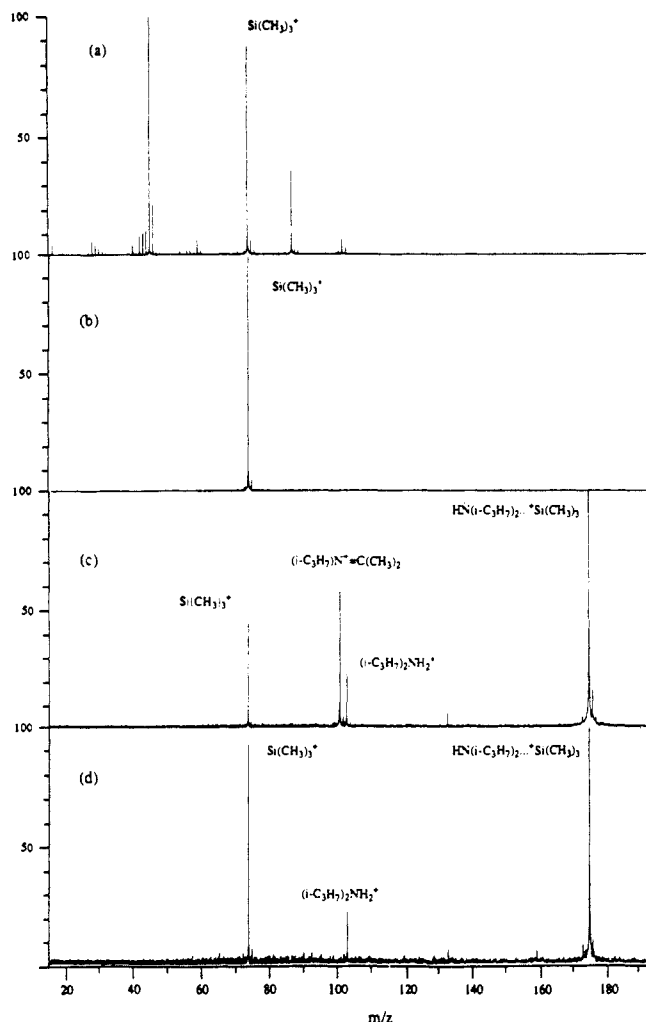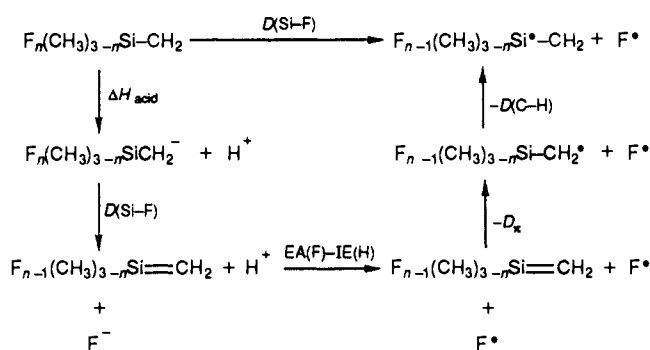(21) Walsh, R. *Acc. Chem. Res.* 1981, *14*, 246, and references contained therein.

*Experimental Determination of π Bond Strengths*

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**Figure 4.** Sequential spectra for bracketing the fluoride affinity of $F_2$-$SiCH_2$ using $NF_3$ and $F_2Si(CH_3)_2$: (a) $F_2Si(CH_3)_2$ and $NF_3$, (b) isolation of $F_3SiCH_2^-$, and (c) after a 5-s reaction delay. No fluoride transfer is observed.



**Figure 3.** Sequential spectra for bracketing the proton affinity of $(C-H_3)_2SiCH_2$ using TMS and diisopropylamine: (a) TMS and diisopropylamine, (b) isolation of the trimethylsilyl cation ($m/z$ 73), (c) after a 20-s reaction delay, and (d) reaction delay of 20 s with continuous ejection of $m/z$ 100 (amine $[M - H]^+$). The protonated amine, $m/z$ 102, is unaffected.

**Scheme II**



compounds can be used to calculate π bond energies as defined by Benson.[13] The π bond energies obtained from eq 7 and 8 should

$$D\pi = D(\text{Si-C}) + D(\text{C-H}) + \text{IE(H)} - \text{AE} - \text{PA(Si}=\text{C)} \quad (7)$$

$$D\pi = D(\text{Si-F}) + D(\text{C-H}) + \text{IE(H)} - \\ D(\text{Si-F}^-) - \text{EA(F)} - \Delta H^\circ_{acid} \quad (8)$$

then be the same for the same silene if the attendant thermochemical data are reliable. A discussion of the accuracy of each of the thermochemical quantities is therefore in order.

The appearance energy measurements for each of the fluoromethyl silyl cations of relevance for this work are all available
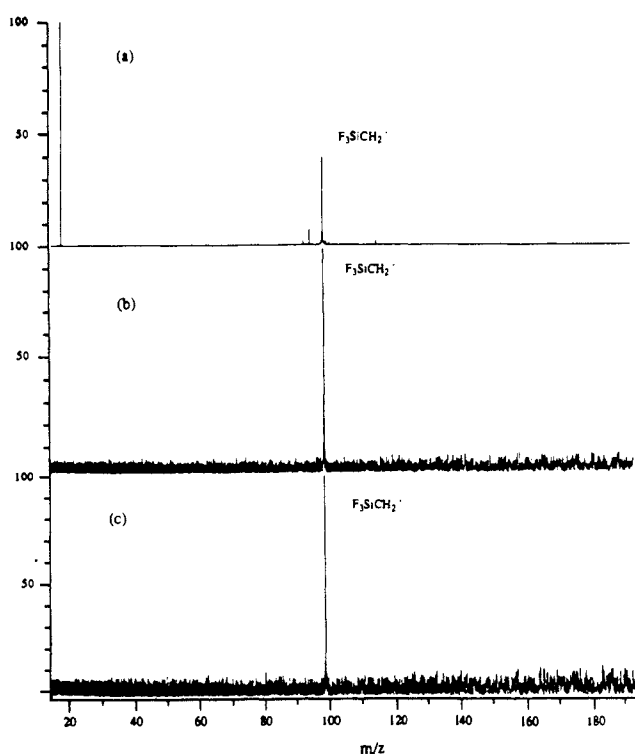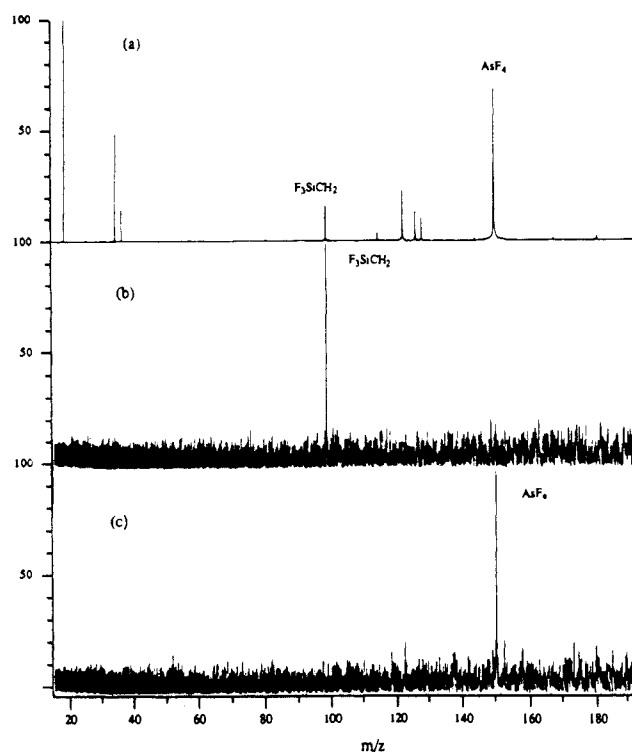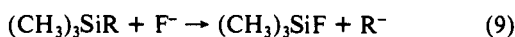
**Figure 5.** Sequential spectra for measuring the fluoride affinity of $F_2$-$SiCH_2$ using $NF_3$, $F_2Si(CH_3)_2$, and $AsF_3$: (a) $F_2Si(CH_3)_2$, $NF_3$, and $AsF_3$, (b) isolation of $F_3SiCH_2^-$, and (c) after a 5-s reaction delay. All fluoride anion is transferred to the $AsF_3$.

from a photoionization study by Murphy and Beauchamp.[20] Such experiments are generally acknowledged to provide an upper limit to appearance energies which implies that these data will lead to a lower limit to the π bond energy. However, since in each case the fragmentation observed is the lowest energy dissociation, each threshold observed is expected to be accurate to within ±1 kcal mol⁻¹.

The C–H bond dissociation energy in tetramethylsilane has been accurately determined by Walsh and co-workers to be 99.2 kcal mol$^{-1}$.[22] It should be emphasized that this is a kinetic determination of the bond-dissociation energy itself that does not depend upon a knowledge of individual heats of formation of parent silane or silyl radical. Walsh further concludes that $\alpha$ silicon substitution should have virtually identical effects with $\alpha$ carbon substitution giving rise to the conclusion for this work that all C–H bonds in the methyl- and fluorosilanes will be 99 ± 1 kcal mol$^{-1}$.
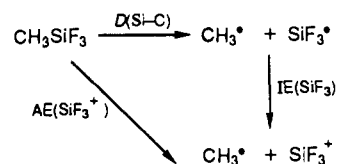
The only reliable Si–C bond dissociation energy directly measured with any accuracy is that in Si(CH$_3$)$_4$, also. The value of 85 kcal mol$^{-1}$ has been obtained by Potzinger et al.[23] and by Baldwin et al.[24] The remaining components of eq 7 are the ionization energy of a hydrogen atom which is well-defined and the proton affinity of dimethylsilene which has been determined here. These data can therefore be combined to give a value of the $\pi$ bond energy of I as 38 ± 6 kcal mol$^{-1}$. This is in good agreement with the work of Hehre et al. where the $\pi$ bond energy was calculated based on derived heats of formation. The agreement with high level theoretical calculations is also excellent.

If this value is then accepted as an accurate estimate of the $\pi$ bond energy in 1, it should then be reproduced by eq 8 where (CH$_3$)$_3$SiF is the silane considered. All of the quantities in eq 8 are available from the literature ($D$(C–H) see above; IE(H), EA(F)) or have been determined here ($D$(Si–F$^-$), $\Delta H°_{acid}$) with the exception of the Si–F bond energy in (CH$_3$)$_3$Si–F. The only Si–F bond energy for which any data are available is that in SiF$_4$ where the values range from 147 to 160 kcal mol$^{-1}$. However, given the fact that increasing fluorine substitution at carbon gives rise to increasing C–F bond dissociation energy, it would appear risky to accept even values in this range as appropriate estimates for $D$(Si–F) in (CH$_3$)$_3$Si–F. Instead, it is of interest to use the $\pi$ bond energy from the positive ion calculation to estimate $D$-(Si–F). Doing this leads to a value of 128 ± 15 kcal mol$^{-1}$. A similar conclusion may be drawn from an examination of reactions of the form of eq 9 where for R = Si(CH$_3$)$_3$, C$_3$H$_5$, CH$_2$COCH$_3$, and CH$_3$CO the reaction proceeds readily, whereas in R = OH, NH$_2$, C$_2$H$_3$, CH$_3$, and NHCH$_3$ no reaction is observed. The available thermochemical data for species involved in these reactions again suggest that $D$((CH$_3$)$_3$Si–F) is 135 ± 10 kcal mol$^{-1}$.[25] Thus an Si–F bond energy in the vicinity of 130 kcal mol$^{-1}$ for (CH$_3$)$_3$SiF is strongly suggested.

$$(CH_3)_3SiR + F^- \rightarrow (CH_3)_3SiF + R^- \qquad (9)$$

Applying eq 7 to F(CH$_3$)Si=CH$_2$ while continuing to use 85 ± 1 kcal mol$^{-1}$ as the Si–C bond energy yields a $\pi$ bond energy of 64 ± 5 kcal mol$^{-1}$. A similar calculation for F$_2$Si=CH$_2$ gives rise to a $\pi$ bond energy of 50 ± 5 kcal mol$^{-1}$. Ab initio calculations of Si–C bond lengths have shown that the Si–C bond is considerably shorter in F$_2$SiCH$_2$ than in H$_2$SiCH$_2$,[9] and hence an increase in $\pi$ bond energy with increased fluorine substitution is quite reasonable. However, the anomalously high value of $\pi$ bond energy in F(CH$_3$)Si=CH$_2$ does not fit any rational explanation based on cumulative substituent effects. The reason for this anomaly is discussed below. If the value of 50 ± 5 kcal mol$^{-1}$ is accepted as the $\pi$ bond energy in F$_2$Si=CH$_2$, however, eq 8 can again be applied to calculate the Si–F bond energy in CH$_3$SiF$_3$ leading to a value of 130 ± 10 kcal mol$^{-1}$. Therefore, the conclusion can be drawn that if the Si–C bond dissociation energies are the same in (CH$_3$)$_4$Si and (CH$_3$)$_2$SiF$_2$, then the Si–F bond energies in (CH$_3$)$_3$SiF and CH$_3$SiF$_3$ are the same to within the experimental uncertainty of the present experiment (±10 kcal mol$^{-1}$). However, the only logical direction to change either the Si–C or Si–F bond dissociation energies with increasing fluorine
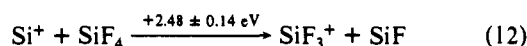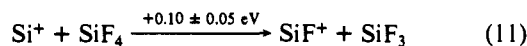
**Scheme III**



substitution is upwards. If these values are then revised upwards, the result is a further increase in the $\pi$ bond energy.

To consider the extent to which the Si–C and Si–F bond energies might change with increasing fluorine substitution it is useful to examine the thermochemical cycle shown in Scheme III and eq 10.

$$D(\text{Si–C}) = AE(SiF_3^+)_{CH_3SiF_3} - IE(SiF_3) \qquad (10)$$

Armentrout[26] has recently provided new thermochemical data for SiF$_3$ and SiF$_3^+$ based on observations of thresholds for the endothermic processes in eq 11 and 12. These data give a dif-

$$Si^+ + SiF_4 \xrightarrow{+0.10 \pm 0.05 \text{ eV}} SiF^+ + SiF_3 \qquad (11)$$

$$Si^+ + SiF_4 \xrightarrow{+2.48 \pm 0.14 \text{ eV}} SiF_3^+ + SiF \qquad (12)$$

ference in ionization energies of SiF and SiF$_3$ of 2.38 eV. If the spectroscopic value of IE(SiF) of 7.26 eV[27] is accepted, then IE(SiF$_3$) of 9.64 ± 0.19 eV is obtained. Armentrout argues against the use of 7.26 eV for IE(SiF) instead recommending 7.54 eV which results in IE(SiF$_3$) of 9.92 eV. However, both electron impact and photoionization studies of CH$_3$SiF$_3$[20] show that at all ionizing energies no appreciable CH$_3^+$ is generated which strongly implies that IE(SiF$_3$) must be less than the IE(CH$_3$) which is well established as 9.84 eV. Recently, Freund et al.[28] have obtained direct measurements of IE(SiF$_3$) of 9.6 ± 0.6 eV and IE(SiF) of 7.4 ± 0.1 eV. On the basis of these and the failure to observe CH$_3^+$ from CH$_3$SiF$_3$ we place greater confidence in an IE(SiF$_3$) of 9.64 eV. If this value is combined with the appearance energy of SiF$_3^+$ from CH$_3$SiF$_3$ of 13.33 eV from the photoionization appearance energy measurements of Murphy and Beauchamp[20] in eq 10, then the Si–C bond strength is found to be 85 ± 5 kcal mol$^{-1}$, identical with that in (CH$_3$)$_4$Si. As noted above, using this value in eq 7 results in a $\pi$ bond energy in F$_2$SiCH$_2$ of 50 kcal mol$^{-1}$. Taking this as the $\pi$ bond energy in eq 8 to obtain $D$(Si–F) in CH$_3$SiF$_3$ yields 130 kcal mol$^{-1}$. A larger value of $D$(Si–F) on the order of 145–150 kcal mol$^{-1}$ would require $D$(Si–C) in CH$_3$SiF$_3$ of 100–105 kcal mol$^{-1}$ and from eq 10 would demand either a substantially greater AE(SiF$_3^+$)$_{CH_3SiF_3}$ or substantially smaller IE(SiF$_3$). The former possibility is extremely improbable since appearance energy measurements in general already yield upper limits.

Alternatively, it might be considered that the measurements described here are somehow in error and that substantially smaller proton affinities (in the positive ion experiments) and substantially smaller fluoride affinities or gas-phase acidities (in the negative ion experiments) must be required. The probability that all of these measurements are somehow in error by the same amount is, however, very small. Taking values of $D$(Si–C) of 85 kcal mol$^{-1}$ and $D$(Si–F) of 130 kcal mol$^{-1}$ the positive ion experiments give values of $\pi$ bond energy of 38, 64, and 50 kcal mol$^{-1}$ for I, II, and III, respectively. Similarly, the negative ion experiments yield $\pi$ bond energies of 40, 45, and 50 kcal mol$^{-1}$ for I, II, and III. The combined uncertainties of the individual quantities used to arrive at the $D_\pi$ values is ±10 kcal mol$^{-1}$ in both the positive and negative ion experiments. However, the uncertainty in the differences in $\pi$ bond energies is much less due to the fact that the

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(25) Campanaro, A.; Marvin, C. H.; Morehouse, S. P.; McMahon, T. B. *Org. Mass Spectrom.* **1988**, *23*, 663.

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(28) (a) Hayes, T. R.; Wetzel, R. C.; Baiocchi, F. A.; Freund, R. S. *J. Chem. Phys.* **1988**, *88* 823. (b) Hayes, T. R.; Shul, R. J.; Baiocchi, F. A.; Wetzel, R. C.; Freund, R. S. *J. Chem. Phys.* **1988**, *89*, 4035.

**Table II.** Geometric Parameters for the Silene Isomers Described by Figure 6[a]

| species | $R_1$ | $R_2$ | $d$ | r1 | r2 | r3 | r4 | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | $CH_3$ | $CH_3$ | 1.690 | 1.877 | 1.877 | 1.077 | 1.077 | 123.4 | 123.4 | 122.7 | 122.7 |
| II | F | $CH_3$ | 1.674 | 1.590 | 1.862 | 1.075 | 1.067 | 121.3 | 128.9 | 123.1 | 121.6 |
| III | F | F | 1.659 | 1.571 | 1.571 | 1.074 | 1.074 | 127.2 | 127.2 | 121.9 | 121.9 |

[a] Bond lengths in Å, bond angles in deg.

**Table III.** Geometric Parameters for the Silylene Isomers Described by Figure 7[a]

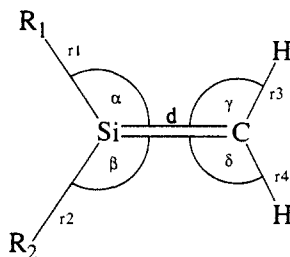| species | $R_1$ | $R_2$ | $d$ | r1 | r2 | r3 | r4 | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IA | $CH_3$ | $CH_3$ | 1.911 | 1.919 | 1.550 | 1.093 | 1.093 | 99.2 | 115.4 | 108.2 | 123.3 |
| IIA | F | $CH_3$ | 1.898 | 1.602 | 1.552 | 1.092 | 1.092 | 99.5 | 113.2 | 109.1 | 122.7 |
| IIB | $CH_3$ | F | 1.909 | 1.918 | 1.421 | 1.089 | 1.089 | 96.2 | 110.8 | 111.3 | 120.6 |
| IIIA | F | F | 1.911 | 1.600 | 1.424 | 1.087 | 1.087 | 96.6 | 107.1 | 112.6 | 119.4 |

[a] Bond lengths in Å, bond angles in deg.



**Figure 6.** Schematic for the optimized geometries (3-21G*) of the silenes.
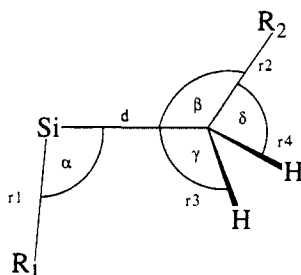


**Figure 7.** Schematic for the optimized geometries (3-21G*) of the silylenes.

same quantities are used. The regular increase of 5 kcal mol⁻¹ for each fluorine for methyl substitution in the negative ion experiments suggests that the measured proton affinity of $F(C-H_3)Si=CH_2$ is somehow anomalous. One obvious possibility is that the measured proton affinity is too low because an ion of less stable structure than $FSi(CH_3)_2^+$ has been formed by electron impact on $F_2Si(CH_3)_2$. Alternatively, it may be that a neutral of more stable structure than II is formed in the deprotonation of $FSi(CH_3)_2^+$. The recent attention focussed on the relative stability of silenes vs silylenes caused us to investigate this possibility further by using ab initio calculations. Calculations using the GAUSSIAN 86 package were performed to obtain the relative energies of the seven species describes by Figures 6 and 7 and by Tables II and III. Total energies, in hartrees, and the resultant relative energies, in kcal mol⁻¹, are given in Table IV. For $(CH_3)_2SiCH_2$ and $F_2SiCH_2$ the silenes are clearly the more stable isomers, by 9.3 and 37.3 kcal mol⁻¹, respectively, at the level of theory used, in agreement with the findings of Hanamura et al.[6] and Gordon.[9] The $FCH_3SiCH_2$ system indicates that the silene (II) is 55 kcal mol⁻¹ more stable than the fluoromethylmethylsilylene (IIB), but 5 kcal mol⁻¹ *less* stable than the ethylfluorosilylene (IIA). We therefore surmise the most stable of these isomers (IIA) to be the species formed by proton abstraction from the silyl cation, eq 13.

$$F(CH_3)SiCH_3^+ + B \rightarrow FSiC_2H_5 + BH^+ \qquad (13)$$

With this in mind, the proton affinity measured by using the proton-transfer reactions is likely that for IIA and not the silene II. By using the π bond strength calculated for the silene from the negative ion experiments, the thermochemical cycle can be

**Table IV.** Total Energies (hartrees) and Calculated Relative Energies (kcal mol⁻¹) for the Seven Species Described by Figures 6 and 7 and Tables VI and VII

| species | total energy[a] | rel energy[b] |
|---|---|---|
| I | −407.649 030 1 | 0 |
| IA | −407.634 258 3 | +9.3 |
| II | −467.542 675 2 | 0 |
| IIA | −467.550 217 8 | −4.7 |
| IIB | −467.460 775 4 | +51.4 |
| III | −527.433 760 9 | 0 |
| IIIA | −527.374 250 7 | +37.3 |

[a] One hartree ≈ 627.5 kcal mol⁻¹. [b] Relative energies for the silylenes are expressed with respect to the energy of the silene species I, II, and III.

**Table V.** Thermochemical Data for Silenes

| silene | proton affinity[a] | fluoride affinity[a] | π bond energy[a] |
|---|---|---|---|
| $(CH_3)_2Si=CH_2$ | 228 ± 2 | 37 ± 2 | 39 ± 6 |
| $F(CH_3)Si=CH_2$ | 187 ± 2 | 40 ± 2 | 45 ± 5 |
| $F_2Si=CH_2$ | 178 ± 2 | 46 ± 2 | 50 ± 5 |

[a] All values in kcal mol⁻¹.

reversed to allow the proton affinity of $FCH_3SiCH_2$ to be calculated as 206 kcal mol⁻¹. The final π bond strengths, proton affinities, and fluoride affinities of the three silenes are given in Table V.

In considering the Si=C π bonds comparisons might be made with the π bonds in the analogous olefins. Surprisingly, these are not well-characterized. By using Benson type calculations[13] we estimate from heats of formation the analogous C=C π bonds to be 57, 60, and 66 kcal mol⁻¹ for $(CH_3)_2CCH_2$, $FCH_3CCH_2$, and $F_2CCH_2$, respectively, which shows that the strength of the π bond increases with F substitution, as in the silenes. Support for this observation comes from Gordon's calculations[9] which show that with increasing F substitution at both Si and at C centers, the Si–C bond length decreased corresponding to a stronger bond. The Si=C π bonds are all about 10 kcal mol⁻¹ weaker than the corresponding C=C π bonds.

**Conclusions**

Positive and negative ion–molecule reactions of ions derived from methyl- and fluorosilanes have been used to determine proton affinities and fluoride affinities of silenes as well as gas-phase acidities of the corresponding parent silanes. These data used in conjunction with existing thermochemical data in the literature give rise to the following general conclusions: (1) The π bond energy in silenes increases with increasing fluorine substitution from 39 ± 6 kcal mol⁻¹ in dimethylsilene (I) to 50 ± 5 kcal mol⁻¹ in difluorosilene (III). (2) The Si–C bond energy is constant with increasing replacement of methyl by fluorine in silanes at 85 ± 5 kcal mol⁻¹. (3) The Si–F bond strength is constant with increasing replacement of methyl by fluorine from $(CH_3)_3SiF$ to $CH_3SiF_3$ at 130 ± 10 kcal mol⁻¹. Available thermochemical data for $SiF_4$ are not sufficiently reliable to determine whether a similar Si–F bond energy holds in the perfluorosilane.