in the gas phase, both the neutral and cation radicals can be generated and characterized as distinct species.

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Quantitative Measure of α-Silyl Carbanion Stabilization. The Electron Affinity of (Trimethylsilyl)methyl Radical

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Abstract: We have generated (trimethylsilyl)methyl anion, $(CH_3)_3SiCH_2^-$, in the gas phase and measured cross sections for electron photodetachment using ion cyclotron resonance spectrometry. From the electron photodetachment spectrum we obtain the electron affinity of (trimethylsilyl)methyl radical, EA = 21.9 ± 0.3 kcal/mol, and derive the proton affinity of the anion, PA = 390.9 ± 1.5 kcal/mol. These thermochemical parameters provide a quantitative measure of α-silyl carbanion stabilization of about 20 kcal/mol.

The phenomenon of carbanion stabilization by α-silyl groups has received considerable attention from theoretical and experimental chemists over the past few years. Synthetic chemists, taking advantage of the enhanced α-CH acidity in organosilicon compounds, have developed a powerful class of reagents, α-silyl organometallics.[1] These reagents have been used in the conversion of carbonyl compounds to alkenes,[2] as Grignard reagents,[3] and in nucleophilic displacement reactions.[3] Dramatic kinetic effects upon substitution of an α-silyl moiety have been observed (rates increased by factors of[4] 5 to orders of magnitude[5]) in reactions proceeding through carbanionic intermediates or transition states. Results of dynamic NMR studies (measuring rotational barriers in π-conjugated carbanions)[6] have suggested significant delocalization of electron density into *p*-silyl-substituted phenyl rings. Prompted by experimental evidence, theoreticians have worked to both quantify and explain the stabilization which appears to dictate observed organosilane chemistry.[7-9]

Although the α-CH reactivity in organosilicon compounds indicates enhanced stability, it does not provide direct evidence that α-silyl carbanions exist as isolated, stable species. Such direct evidence is provided, however, by the results of recently reported gas-phase experiments. α-Silyl carbanions were observed in the reaction of amide ion with alkylsilanes[10,11] and in the reactions of trimethylsilane with methoxide ion.[12]

Gas-phase experiments have proven to be useful in obtaining quantitative measures of intrinsic molecular properties[13] and are thus appropriate for obtaining a measure of α-silyl carbanion stabilization. One attractive approach for evaluating the relative stability of anionic species is through comparisons of experimental gas-phase proton affinities (acidities of the conjugate acids). The usual method for obtaining proton affinities (proton-transfer equilibria studies) is difficult in the case of α-silyl carbanions, since organosilanes are very weak acids. Reference acids (whose $\Delta H^\circ_{\text{acid}}$'s have been precisely measured) are scarce in this regime. Water, which does have an acidity in the correct range, cannot be used as a reference acid in proton-transfer reactions involving organosilanes due to competing nucleophilic displacement reactions.[14]

Experiments bracketing organosilane acidities have been reported. The acidities of isobutylene ($Me_2C{=}CH_2$) and α-silicon analogue, dimethylsilene ($Me_2Si{=}CH_2$), have been estimated.[15] Proton-transfer reactions indicated that dimethylsilene, whose acidity falls between that of *tert*-butyl alcohol[16] and water,[16] is

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[13] (a) *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapters 11-13. (b) *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: Orlando, FL, 1984; Vol. 3, Chapters 21 and 22. (c) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513.

[14] We observed the reaction $Me_3SiCH_2 + H_2O \rightarrow Me_3SiO^- + CH_4$. Damrauer et al. have also observed this reaction.[11]

[15] Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2050. The acidity of $MeSi({=}O)CH_3$ has also been measured: Froehlicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863. Tumas, W.; Salomon, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541.

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more acidic than isobutylene.[16] The acidity of tetramethylsilane lies between that of fluorobenzene and dimethylamine,[16] also showing enhanced acidity (relative to methane[16]) upon α-silyl substitution.

An alternative approach to proton-transfer equilibria acidity measurements is measurement of the adiabatic electron affinity of an α-silyl-substituted carbon radical. This can also be used to determine the magnitude of α-silyl stabilization energy, from the relative stability of the corresponding anion. In conjunction with a known bond dissociation energy, it can be used to derive the proton affinity.

We have generated the (trimethylsilyl)methyl anion (**1**) and determined the electron affinity of the corresponding radical from the onset in the measured electron photodetachment spectrum. Comparison of this electron affinity to that of a methyl radical provides a quantitative measurement of α-silyl stabilization. We have also derived the proton affinity of **1** and compare the result to previous experiments and to theoretical predictions.

Experimental Section

Electron photodetachment spectroscopy was used to monitor the process shown in eq 1. In the experiment, the (trimethylsilyl)methyl anion (**1**) was generated in the gas phase by ion-molecule chemistry (described below), trapped, and irradiated. The abundance of anions

$$\underset{\mathbf{1}}{Me_3SiCH_2^-} \xrightarrow{h\nu} Me_3SiCH_2^\bullet + e^- \qquad (1)$$

is measured before and after irradiation, giving relative cross sections for electron photodetachment as a function of wavelength. The onset for transition from the ground state of the anion to the ground state of the neutral (adiabatic electron affinity) was assigned from the photodetachment spectrum.

Ion Generation. (Trimethylsilyl)methyl anion was prepared by a nucleophilic substitution reaction of bis(trimethylsilyl)methane and fluoride ion, as shown in eq 2. We chose this symmetric bis(silyl)methane neutral

$$Me_3SiCH_2SiMe_3 + F^- \rightarrow \underset{\mathbf{1}}{Me_3SiCH_2^-} + Me_3SiF \qquad (2)$$

precursor in order to generate the carbanion unambiguously, modeling the ion-molecule reaction on previous studies by DePuy and co-workers.[10]

(Trimethylsilyl)methyl anion has previously been generated by reaction of amide or dimethylamide ion and tetramethylsilane.[10,11] In the ICR, this method produces low yields of the α-silyl carbanion; deprotonation is the minor product, the major product being Me_3SiNH^-. The advantage of using the nucleophilic displacement reaction (eq 2) is that only one ionic product is formed.[17]

Fluoride ion was generated by the dissociative electron capture of NF_3 (typical electron energies used were 1 eV). Both neutral precursors, NF_3 (Ozark Mahoning) and bis(trimethylsilyl)methane (Petrarch Systems), were used as purchased, after degassing via several freeze-pump-thaw cycles on the foreline. Typical operating pressures were in the 10^{-7}-Torr range, as measured with an uncalibrated ionization gauge (Varian, UHV-24). Best signals were obtained with a ratio of 3:1 bis(silyl)-methane/nitrogen trifluoride.

Instrumental Procedures. Anions were trapped and detected with an ion cyclotron resonance (ICR) spectrometer.[18] The photodetachment experiments were performed by operating the ICR in continuous mode, in which ions were continuously formed and detected.

Single-frequency phase-sensitive detection was used in the ICR system, incorporating a commercial lock-in amplifier (PAR 124A) in conjunction with home-built capacitance-bridge[19] circuitry. Detection frequencies were typically 150 kHz, 800-μV (rms) amplitude. Amplified voltage (0–10 V) from the capacitance-bridge detector corresponded to the number of ions in the trap.[20]

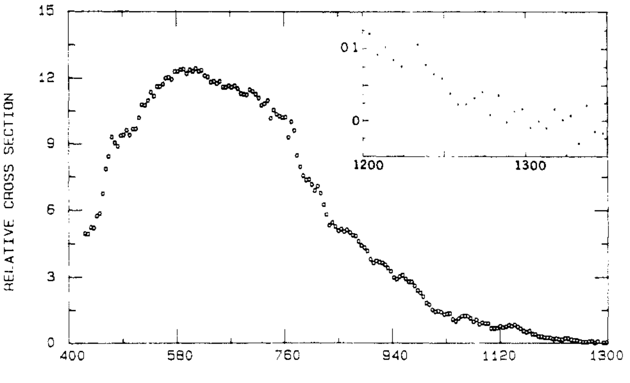

Figure 1. Photodetachment spectrum of $Me_3SiCH_2^-$. The cross section in the threshold region, ×10, appears in the inset.

The cyclotron frequency depends on the number of ions in the trap. When the ion concentration decreases, due to irradiation and subsequent electron detachment, the cyclotron resonance frequency shifts slightly. Because of the narrow line widths, the small (ca. ±0.1 kHz from 150 kHz) frequency shifts which occur with photodecreases, present difficulties. In order to ensure that the detection frequency always corresponded to the cyclotron frequency of the ions being monitored in the detachment experiment, a detection frequency lock was used. The lock circuitry provides a continuous correction signal to the detection frequency generator by means of field modulation, controlled and monitored by a second lock-in amplifier (PAR HR-8). A detailed description of the components and operation of the frequency lock system appears elsewhere.[21]

Light Sources. Trapped ions were irradiated by light in the 300–1400-nm range obtained from a 1000-W xenon arc lamp (Canrad Hanovia), used in conjunction with a 0.25-m high intensity grating monochromator (Kratos Analytical). Spectral bandwidth, determined by selection of matched entrance and exit slits in the monochromator, was chosen as small as possible for reproducibly measurable photodecreases. In the threshold region bandwidths were typically 20 nm (fwhm).

Lamp power measurements were obtained from the amplified response of a thermopile (Eppley Laboratory, Inc.). Because of the configuration of the experimental apparatus, power measurements could not be obtained simultaneously with photodecrease measurements and were therefore obtained separately.

The output of the xenon arc lamp in the 800–1000-nm region consists of several strong emission lines superimposed on the continuum radiation. Large photodecreases occurred at the positions of these emission lines and it was necessary to include long pauses (up to 5 s) between setting the wavelength and measuring the amount of signal decrease. This allowed time for the steady-state ion population to be established and the detection frequency controller circuitry to adjust for resonance shifts. Although the cross sections are corrected for photon intensity, the large signal changes and resonance shifts in this region make the data noisy. The observed dips and bumps do not indicate fine structure in the detachment spectrum.

Data Acquisition. In the experiment, anion concentrations were measured before and after irradiation. Fractional changes at each wavelength, corresponding to the number of ions detaching an electron, were converted to relative cross sections after normalization of photon flux.[22]

Detachment data were obtained by automated scans. An IBM-XT was used to acquire and process ion signals and to select the wavelength by means of a stepper-motor-driven grating mount. Ion signals were obtained with no irradiation (base line) before and after a scan and at each wavelength in the spectral region. Each signal measurement corresponded to 20 000 readings obtained over a period of typically 2–6 s.

Because base-line signals remained constant (within 0.1%) for periods of 5–10 min, scans over small wavelength regions, usually ≤200 nm, were

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(16) Bartmess, J. E. *J. Phys. Chem. Ref. Data*, in press. $\Delta H^\circ_{acid}(t\text{-BuOH}) = 374.6$ kcal/mol, $\Delta H^\circ_{acid}(H_2O) = 390.7$ kcal/mol, $\Delta H^\circ_{acid}(Me_2C{=}CH_2) > 390$ kcal/mol, $\Delta H^\circ_{acid}(C_6H_5F) = 387.2$ kcal/mol, $\Delta H^\circ_{acid}(Me_2NH_3) = 396.2$ kcal/mol, $\Delta H^\circ_{acid}(CH_4) = 416.6$ kcal/mol.

(17) We assign the structure of **1** because it gives an ion of *m/z* 89 on reaction[14] with H_2O. If either $(CH_3)_2HSiCHCH_3^-$ or $(CH_3)_2(CH_3CH_2)Si^-$ were present, reaction with water would result in the formation of a siloxide of *m/z* 103, $(CH_3)_2(CH_3CH_2)SiO^-$.

(18) For a general description of ICR as used in these laboratories in experiments involving electron detachment, see: Wetzel, D. M.; Brauman, J. I. *Chem. Rev.* **1987**, *87*, 607.

(19) Circuitry development reported in: McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65.

(20) Performance analysis of the capacitance-bridge detector showing linear response with ion concentration reported in: McIver, R. T., Jr.; Ledford, E. B., Jr.; Hunter, R. L. *J. Chem. Phys.* **1980**, *72*, 2535.

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Table I. Electron Affinities of Substituted Methyl Radicals, $XCH_2^{\bullet}$ (kcal/mol)

$XCH_2^{\bullet}$	EA($XCH_2^{\bullet}$)	$XCH_2^{\bullet}$	EA($XCH_2^{\bullet}$)
$HCH_2^{\bullet}$	1.8[a]	$Me_3SiCH_2^{\bullet}$	21.9[c]
$Me_3CCH_2^{\bullet}$	1–2[b]	$C_6H_5CH_2^{\bullet}$	19.9[d]

[a] Reference 29. [b] Reference 30. [c] This work. [d] Reference 31.

conducted. An entire photodetachment spectrum consists of overlapping points from several scanned regions, each region the average of 5–10 runs.

Results

The photodetachment spectrum of the (trimethylsilyl)methyl anion is displayed in Figure 1. Because photodetachment involves bound to continuum transitions, the spectrum is integral in nature. Onsets appear as slope changes in the cross-section curve. From the spectrum two features are apparent: (1) the onset of electron detachment occurs in the near-IR region and (2) above threshold cross sections increase to a maximum and then decrease.

The photodetachment cross section has a maximum at about 600 nm. Since the decreasing cross section below 600 nm was not due to a lack of light intensity, the observed cross-section behavior suggests that transitions in addition to simple continuum photodetachment were occurring during the optical experiment. The broad feature centered at about 600 nm can be attributed to transitions to an excited electronic state of the anion embedded in the continuum.[23] Such features have been observed previously, for instance, in the photodetachment spectra of organosilyl anions[24] and substituted acetophenone enolate ions.[25] The observed λ_{max} of 610 ± 20 nm places the excited state approximately 2.0 ± 0.1 eV above the ground state of the anion.

The wavelength at which detachment onset was observed, obtained from linear extrapolation of the data, is 1316 nm. Correction for the monochromator bandwidth, half the fwhm, results in a threshold of 1306 ± 20 nm. Error bars reflect the uncertainty of assigning the first nonzero cross section ($\Delta\lambda$ between the data points is 5 nm in the near-IR region) and the spectral bandwidth (20-nm fwhm). Absolute calibration of the light source (±2 nm) was not the limiting error. Since this was the only onset observed in the photodetachment spectrum, it was assigned as the $0 \leftarrow 0$ transition. The electron affinity for the (trimethylsilyl)methyl radical is thus 21.9 ± 0.3 kcal/mol (0.95 ± 0.01 eV).

When we use our measured electron affinity of (trimethylsilyl)methyl radical, the C–H bond dissociation energy in tetramethylsilane,[26] $D°(Me_3SiCH_2\text{–}H) = 99.2 \pm 1.2$ kcal/mol, and the thermochemical cycle relating neutral and ionic thermochemistry,[27] the C–H enthalpy of heterolytic dissociation (acidity) of tetramethylsilane can be derived. From the values stated above, the derived acidity is $\Delta H°_{acid}(Me_3SiCH_2\text{–}H) = 390.9 \pm 1.5$ kcal/mol. Damrauer, Kass, and DePuy[11] have recently reported an acidity for tetramethylsilane of $\Delta H°_{acid} = 387 \pm 3$ kcal/mol. This was based on deprotonation reactions, which indicated the acidity of tetramethylsilane to be very close to that of fluorobenzene. The acidity of fluorobenzene is itself only known from bracketing, however (falling between that of water and furan). Our measured acidity is consistent with the deprotonation reactions, which Damrauer et al. observed, in that fluorobenzene, tetramethylsilane, and water are all of comparable acidity.

Bowie and co-workers have previously studied the reaction between methoxide ion and trimethylsilane[12] and detected small amounts of deprotonation, exclusively at carbon. If MeO^- were responsible for this deprotonation, then the CH acidity of trimethylsilane would be comparable to the acidity of MeOH, $\Delta H°_{acid} \simeq 380$ kcal/mol, and the electron affinity of the $Me_2HSiCH_2^{\bullet}$ radical would necessarily be[28] ca. 31 kcal/mol. Both the CH acidity and the electron affinity are difficult to rationalize when compared to the tetramethylsilane system (since the data suggest that the replacement of one β-methyl group by hydrogen enhances the stability of the carbanion by 10 kcal/mol) and are inconsistent with the results of Damrauer.[11] Thus, we suspect that deprotonation is accomplished by a base other than methoxide ion.[24] Alternately, the ions may be translationally hot and thus capable of driving an endothermic proton-transfer reaction.

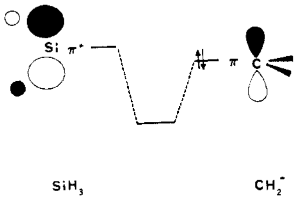

Figure 2. Orbital interaction between CH_2^- and the α-silyl fragment.

Table II. Comparison of Experimental and Calculated Relative Proton Affinities of α-Substituted Methyl Anions, XCH_2^- (kcal/mol)

XCH_2^-	PA(XCH_2^-)	XCH_2^-	PA(XCH_2^-)
$Me_3SiCH_2^-$	25.7 (exptl)[b]	$MeSCH_2^-$	23.2 (exptl)[d]
$H_3SiCH_2^-$	24.9 (calc),[a] 29.3 (calc)[c]	$HSCH_2^-$	20.9 (calc)[a]
$Me_2PCH_2^-$	25.4 (exptl)[d]	$ClCH_2^-$	20.6 (exptl)[d]
$H_2PCH_2^-$	23.0 (calc)[a]	$ClCH_2^-$	13.8 (calc)[a]

[a] Reference 9. [b] This work. [c] Reference 8a. [d] Reference 34.

Discussion

The electron affinities of substituted methyl radicals, $XCH_2^{\bullet}$, are listed in Table I. Comparison between the electron affinity of methyl radical[29] (X = H), neopentyl radical[30] (X = Me_3C), and (trimethylsilyl)methyl radical (X = Me_3Si) indicates the magnitude of α-silyl stabilization. Replacement of H by a Me_3C substituent in $CH_3^{\bullet}$ results in an anion of comparable stability. However, substitution by Me_3Si results in an increase of close to 20 kcal/mol in the absolute stability with respect to the neutral radical. This is a dramatic effect, the same order of magnitude as stabilization energy gained from resonance delocalization in benzyl anion (reflected by the electron affinity of benzyl radical,[31] X = C_6H_5, also shown in Table I).

Ab initio studies assessing the α-silyl stabilization from calculated proton affinities have been reported.[8,9] The quantitative calculation, which can be compared directly to our experimental measurement, is the proton affinity, relative to methane, evaluated by the isodesmic proton-transfer reaction shown in eq 3. The

$$CH_4 + H_3SiCH_2^- \rightarrow CH_3^- + H_3SiCH_3 \qquad (3)$$

relative proton affinity of $H_3SiCH_2^-$ obtained from the calculated ΔE for the reaction shown in eq 3 is[9] 24.9 and[8a] 29.3 kcal/mol. The relative proton affinity of $Me_3SiCH_2^-$, determined from our experimental acidity, is 25.7 kcal/mol, relative to methane.

We did not study $SiH_3CH_2^-$, the anion for which calculations were carried out, but we expect β-substituent effects (CH_3 vs H) to contribute only a modest perturbation to the energetics, so that

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(23) For a discussion on assignment of such features to excited electronic state transitions, see: Zimmerman, A. H.; Gygax, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766.

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(26) Doncaster, A. M.; Walsh, R. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908.

(27) The thermochemical cycle used to derive enthalpy of heterolytic bond dissociation is $\Delta H°_{acid}(R\text{–}H) = D°(R\text{–}H) - EA(R^{\bullet}) + IP(H^{\bullet})$; see: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11.

(28) Assuming that $D°(Me_2HSiCH_2\text{–}H)$ is comparable to that in tetramethylsilane, 99 kcal/mol.[26]

(29) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(30) The electron affinity of neopentyl radical appearing in Table I was estimated on the basis of the results from collision-induced decarboxylation (CID) experiments. In these experiments, alkyl carbanions were generated from CID reaction of organic carboxylate anions ($RCO_2^- \rightarrow R^- + CO_2$). Because both methyl and neopentyl anions were generated under similar conditions, their stabilities were assumed to be comparable. See: Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607.

(31) Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285.

comparison between the experimental and calculated relative proton affinity is reasonable.

In both of these computational studies it was found that inclusion of d orbitals did not significantly change the relative proton affinity values. It was thus concluded that stabilization is not a result of delocalization into empty Si d orbitals. Evidence such as increased Si–H bond lengths in the silylmethyl anion (compared to those in the neutral molecule, CH_3SiH_3) suggested hyperconjugation between negatively charged carbon and the adjacent silyl group could be responsible for the stabilization.

Hyperconjugative interactions in α-silyl-substituted carbanions are possible because of the electropositive nature of Si. The Si–H bonds in CH_3SiH_3 are polarized, with electron density predominantly on the H atoms.[32] The coefficients are large on H in the bonding orbitals and therefore large on Si in the antibonding orbitals. Electron donation from the p-type highest occupied molecular orbital (HOMO) of the carbanion into the Si–H antibonding orbital, represented pictorially in Figure 2, is possible because of the large amount of overlap and the similarity in energetics and symmetry between the orbitals involved.

Mixing of lone-pair anionic electrons with nearby antibonding orbitals is especially favorable because of the unusually high energy of the anion. Such mixing has been shown to be responsible for the stabilization of alkoxide anions by large alkyl groups.[33]

Experiments[34] and calculations[35a] indicate that second-row substituents are more effective at stabilizing carbanions than those of the first row. The electron affinity and acidity measurements in this study complete the series of data available for second-row α-heteroatom methyl anions (XCH_2^-). Table II lists the relative proton affinities (again, relative to methyl anion) of α-substituted methyl anions obtained from experiments. Listed beneath each experimental value is a calculated relative proton affinity, for comparison. The systems being compared are not identical; nevertheless, agreement in magnitude and the second-row trend is shown.

The relative proton affinities indicate that silicon is most effective at stabilizing a carbanion. All of the second-row substituents, however, considerably stabilize methyl anion. Hyperconjugation and polarization arguments have been similarly invoked to rationalize carbanion stabilization by α-P and -S substituents.[35]

Interestingly, an α-silyl substituent does not appreciably stabilize a carbon radical. This had been noted previously, based on the results of bond dissociation energy measurements[36] and gas kinetic studies of organosilane pyrolysis,[37] indicating an α-silyl stabilization of only 1 kcal/mol. This is probably a consequence of the relative energetics of the radical center and the adjacent bonding and antibonding orbitals. Again in analogy to alkoxyl radicals,[33] the energy of the radical center is such that mixing with both the bonding (destabilizing interaction) and antibonding (stabilizing interaction) orbitals occurs, resulting in no net stabilization. The HOMO in the carbanion is closer in energy to the Si–H antibonding orbitals, such that mixing with these orbitals predominates.

Conclusions

We have measured the electron photodetachment spectrum of the (trimethylsilyl)methyl anion, from which we have determined the electron affinity of the corresponding neutral radical and the acidity of the conjugate acid. Comparison of these thermochemical data to those known for methyl radical (methane) gives a direct, quantitative measure of α-silyl stabilization. The stabilization energy is large in magnitude and in good agreement with previous quantum calculations.

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Registry No. 1, 88036-00-4; $Me_3SiCH_2^{\bullet}$, 19469-02-4.

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Hydrogen Atom Tunneling in the Thermal Tautomerism of Porphine Imbedded in a *n*-Hexane Matrix

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Abstract: Rate constants and the kinetic isotope effect for the tautomerization of porphine imbedded in a *n*-hexane Shpol'skii matrix near 110 K have been measured with laser-induced fluorescence spectroscopy. A one-dimensional tunneling model calculation has been used to compare the feasibility of the synchronous and asynchronous hydrogen migration mechanisms. Only the asynchronous tunneling model is consistent with the rate constants and kinetic isotope effects measured near 110 K and near room temperature.

It has been established by both NMR[1] and X-ray crystallographic structure studies[2] that the inner hydrogens of free-base porphyrins are located on opposite pyrole rings (Figure 1). NMR studies on ring-substituted porphyrins have shown that the exchange of the inner hydrogens from one pair of nitrogens to the

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