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α-Silyl-Substituent Stabilization of Carbanions and Silyl Anions

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Abstract: The electron affinities for a series of α-silyl-substituted silyl and carbon radicals have been measured. These electron affinities (kcal/mol) include the following: EA($(Me_3Si)_2CH$) = 36.0 ± 0.2, EA($Me_2HSiSiMe_2$) = 32.3 ± 0.8, *EA*($(Me_3Si)_2SiH$) = 44.7 ± 1.9, and *EA*($(Me_3Si)_3Si$) = 46.8 ± 2.0. The electron affinity of the dimethylsilyl radical was also determined to be 24.7 ± 0.5 kcal/mol. From these electron affinities and the bond dissociation energies, we derive the gas-phase acidities for these compounds. These quantities allow us to compare the stabilization in carbon and silyl anions by α-silyl groups. *Ab initio* calculations aid in understanding the stabilization mechanism.

Introduction

In this work we have measured the electron affinities for a series of α-silyl-substituted carbon and silyl radicals to probe the effect of α-silyl substituents on the stabilities of carbanions and silyl anions.

Carbanions are among the most important synthetic intermediates, and they are used extensively to form carbon–carbon bonds.[1,2] Silyl groups stabilize carbanions in solution,[3] and much synthetic work takes advantage of their stability;[4–7] silyl anions are used extensively to synthesize silicon–carbon bonds.[8] In solution these anions are solvated and they are complexed with alkali metal cations.

Gas-phase experiments, in the absence of solvent, allow the determination of the thermodynamic properties of anions through the measurement of acidities and electron affinities, so that the relative stabilities of the anions can be compared. In the gas phase, most simple carbanions are very weakly bound[9] or unbound[10–13] with respect to electron loss. In contrast, silyl anions are much more stable, with correspondingly higher electron affinities (EA(SiH_3) = 32.4 kcal/mol[14,15] vs EA(CH_3) = 1.8 kcal/mol[9]).

Third period elements are known, from measurements of gas-phase acidities[16–22] and electron affinities,[20,23,24] to stabilize carbanions. α-Silyl groups have been shown from previous gas-phase measurements of acidity[19] and electron affinity[24] to stabilize a carbanion by about 20 kcal/mol. The effect of multiple α-silyl substituents on the gas-phase acidities of carbon acids, however, has not been determined. Much less is known about the effect of substituents on the stability of silyl anions.[15,19] Extensive theoretical work has probed the effects of third period α-substituents in carbanions,[25–34] while very little theoretical work has examined the effect of these substituents in silyl anions.[26,35–39]

In this paper we report the electron affinities for a series of α-silyl-substituted carbon and silyl radicals. From the electron affinities and bond dissociation energies, we derive gas-phase acidities for the corresponding carbon and silyl acids. The relative anion stabilities are compared for these two classes of anions. *Ab initio* calculations are used to aid in understanding the stabilization mechanisms for these two classes of anions.

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In addition, the electron affinity of the dimethylsilyl radical was determined. This electron affinity serves as a model for the effect of dimethyl substitution on the electron affinity of a silyl radical, and it is used to derive the acidity for dimethylsilane. This acidity is of interest because of discrepancies in the previously measured acidities of methylsilane and trimethylsilane.[15,19] Our derived acidity is compared with the previously determined value.

Experimental Section

Materials. 1,1,2,2-Tetramethyldisilane was prepared in the laboratory of Professor Edwin Hengge. We purified this compound using gas chromatography (Hewlett-Packard 5790A, column SE-30, 8 ft., 0.25 in.) to remove other silane impurities. Tris(trimethylsilyl)methane and tetrakis(trimethylsilyl)silane were purchased from Aldrich and used as received. Tris(trimethylsilyl)silane was purchased from Fluka and used as received. Nitrogen trifluoride was purchased from Ozark Mahoning. Before introduction into the high vacuum chamber, all neutrals were degassed by several freeze–pump–thaw cycles on the foreline.

Ion generation. Fluoride ion was generated by the dissociative electron capture of nitrogen trifluoride, NF_3.

$$NF_3 + e^- \rightarrow F^- + NF_2 \qquad (1)$$

Anions were then generated by proton abstraction from the corresponding neutral or by nucleophilic displacement reactions. Proton abstraction was used to generate the (dimethylsilyl)dimethylsilyl anion. Nucleophilic displacement, modeled on the methods used by DePuy and co-workers to generate carbanions in the gas phase,[40,41] was used to generate the other anions, eq 2.

$$F^- + (Me_3Si)_3SiH \rightarrow Me_3SiF + (Me_3Si)_2SiH^- \qquad (2)$$

This method is used to generate the silyl anions unambiguously.

Instruments. Experiments were performed in an ion cyclotron resonance (ICR) spectrometer operating in the CW mode,[42] which allows continuous ion generation and detection. The signal-to-noise ratio obtained with CW ICR is ideal for measuring small changes in the ion population (<1%). Single-frequency phase-sensitive detection was accomplished using home-built capacitance bridge detection (CBD) circuitry,[43] together with a commercial lock-in amplifier (Princeton Applied Research Corp., Model 124A). The voltage output from the CBD is proportional to the number of ions in the ICR cell.[44] A frequency-lock system[43] was employed to correct for frequency shifts (typically ± 0.1 kHz in 150 kHz) induced during photochemical experiments.

Light Sources. The ions were irradiated with light from an arc lamp or a dye laser. Low-resolution spectra were obtained using a 1000-W xenon arc lamp (Canrad-Hanovia) in conjunction with a 0.25-m high intensity grating monochromator (Kratos Analytical). Spectral bandwidths were 20–50 nm, fwhm. The grating was calibrated using the expanded output from a helium–neon laser. Lamp power was measured using a thermopile (Eppley Laboratory, Inc.). Because of the configuration of our experimental setup, arc lamp power measurements could not be performed simultaneously with the detachment data and were obtained separately.

A dye laser (Coherent 590) pumped by a Coherent argon ion laser (Innova 200/15) was used to irradiate the ions. Wavelengths were selected with a three-plate birefringent filter; the spectral bandwidth was typically 1 cm^{-1}. Laser dyes (Exciton) used and wavelength ranges include the following: Rhodamine 590 (570–650 nm), DCM (605–705 nm), LDS 698 (670–750 nm), and LDS 751 (700–820 nm). The dye laser was calibrated by using the optogalvanic effect.[45,46] The output from the dye laser is introduced into a Ca/Ne hollow cathode lamp and the current of the lamp is monitored as the laser is tuned. The current changes if the laser is tuned to an electronic transition of the species in the lamp. The dye laser was calibrated using the known transitions for these elements.[47] Dye laser power was measured simultaneously with data collection by splitting off a small portion of the beam and directing it into a thermopile (Eppley Laboratory, Inc.).

Data Acquisition and Processing. Electron photodetachment experiments were performed by monitoring the anion population (A^-) as a function of the wavelength (energy) of irradiated light.

$$A^- + h\nu \rightarrow A + e^- \qquad (3)$$

Data collection typically involved measuring the ion intensity without light at the beginning and the end of a scan and collecting signal measurements at 10–100 consecutive steps; the signal was measured and averaged for 3 to 5 s at each step and step sizes were 5 nm for the arc lamp data and less than 1.5 nm for the laser data. The relative cross section, $\sigma(\lambda)$, was calculated from the fractional ion signal change, $F(\lambda)$, the wavelength, λ, and the energy of the light at that wavelength, $E(\lambda)$, using the steady state model.[48]

$$\sigma(\lambda) = \frac{F(\lambda)}{\lambda E(\lambda)[1 - F(\lambda)]} \qquad (4)$$

A minimum of three scans were averaged together for each wavelength region. Each photodetachment spectrum was comprised of several small, overlapping wavelength regions, spliced together.

Calculations. *Ab initio* molecular orbital calculations were performed using Gaussian 92.[49] Structures were defined using symmetry and were not verified as global minima, because only relative geometry and energetic information were desired. Determination of global minima is expected to give only minor changes in the structure and energetics of these systems.

Results

Photodetachment Spectra. The photodetachment spectra obtained are shown in Figures 1–5. All spectra show cross sections that are smoothly increasing functions above threshold. The cross section at any particular wavelength is the sum of all available transitions from the ground state anion to the various rotational, vibrational, and electronic states of the neutral and of the excited electronic states of the anion. Transitions to these excited states will be superimposed on the background detachment and will appear as slope changes in the spectrum.

The threshold for photodetachment is the energy at which the cross section first rises from zero. This threshold is generally assigned as the adiabatic electron affinity for the radical, presuming that the Franck–Condon factor for the $v' = 0$ $(J',K' = 0) \leftarrow v'' = 0$ $(J'',K'' = 0)$ transition is strong enough to be observed and that hot band transitions are unimportant.

The photodetachment thresholds for all ions display slowly rising cross sections. Predictions regarding the slope of the photodetachment spectrum at threshold can be made based on the type of orbital from which the electron is removed.[50] *Ab initio* studies predict that carbon and silyl anions are quite pyramidal (H–M–H angle = 109° and 95–97°, respectively).[51] The silyl anion is observed experimentally to have a H–Si–H angle of 95°,[14] leading us to predict that in the silyl anions the "extra" electron resides in an orbital with substantial s character. The detached electron is therefore expected to be a p wave, which should show a cross section whose slope at threshold is proportional

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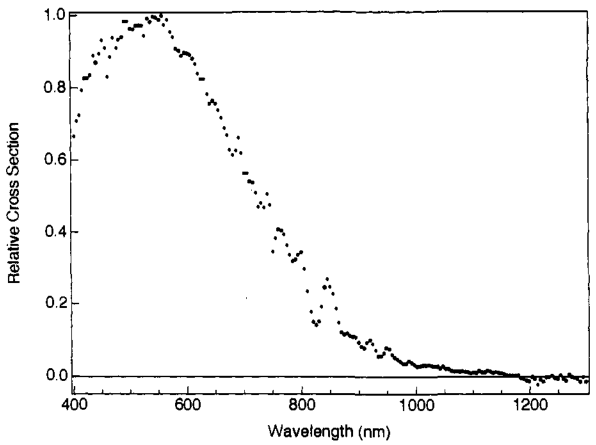

Figure 1. Low-resolution electron photodetachment spectrum for Me_2HSi^-; bandwidth = 20 nm fwhm.

to $E^{3/2}$, where E is the energy of the ejected electron. Thus, the cross section should rise slowly, and we believe the first onset we observe corresponds to the adiabatic electron affinity.

Onsets were assigned using two methods. The first involved a linear extrapolation of the data to zero cross section. The second method involved taking the derivative of a smoothed cubic spline function determined from a least-squares fit of the data.[52] Onsets from the arc lamp data are corrected for the bandwidth by subtracting the full width at half maximum; the uncertainties in the onsets are assigned as the spectral bandwidth (20–25 nm). For two of the anions, higher resolution data were also obtained using a dye laser; spectral features were assigned from these data with an uncertainty of ± 5 nm. The onset assignments and uncertainties are discussed in more detail below for the individual ions.

Experimental Results. (a) Me_2SiH. The low-resolution photodetachment spectrum for the dimethylsilyl anion is shown in Figure 1. The onset, based on the value from the differentiated spline, appears at 1178 ± 20 nm. The monochromator bandwidth was subtracted from the spline-derived value, yielding a bandwidth-corrected onset of 1158 ± 20 nm, corresponding to an adiabatic electron affinity of 24.7 ± 0.5 kcal/mol. This spectrum displays a broad resonance centered at approximately 530 ± 20 nm. This resonance peak is indicative of a transition to an electronically excited state of the anion. The energy of this state is approximately 2.3 eV above the ground state of the anion. This is nearly identical with the transition energy observed[15] for an excited electronic state in Me_3Si^-. The apparent structure in the spectrum between 600 and 1000 nm is probably a consequence of power fluctuations in the arc lamp output, and we do not believe it to have any physical significance.

(b) $Me_2SiHSiMe_2$. The photodetachment spectrum of the (dimethylsilyl)dimethylsilyl anion is shown in Figure 2. The spectrum displays a smoothly rising cross section above approximately 900 nm, with no observed resonances. The onset was assigned as 904 ± 20 nm, based on the results of the differentiated spline method. This yields a bandwidth-corrected onset of 884 ± 20 nm, corresponding to an adiabatic electron affinity of 32.3 ± 0.8 kcal/mol.

(c) $(Me_3Si)_2SiH$. The low-resolution arc lamp photodetachment spectrum for this anion is displayed in Figure 3. This anion displays a smoothly rising cross section above 664 nm. Correction for the bandwidth (25 nm) yields an electron affinity of 639 ± 25 nm (44.7 ± 1.9 kcal/mol). No evidence of excited electronic states is seen for energies less than 3.5 eV (350 nm).

(d) $(Me_3Si)_3Si$. The low-resolution arc lamp spectrum for this anion is shown in Figure 4. This anion displays an onset at

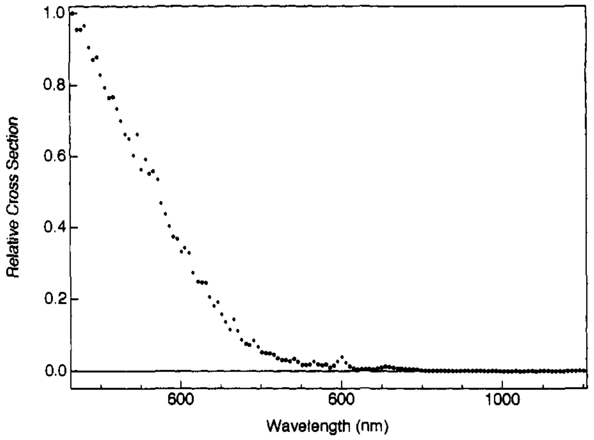

Figure 2. Low-resolution electron photodetachment spectrum for $Me_2HSiSiMe_2^-$; bandwidth = 20 nm fwhm.

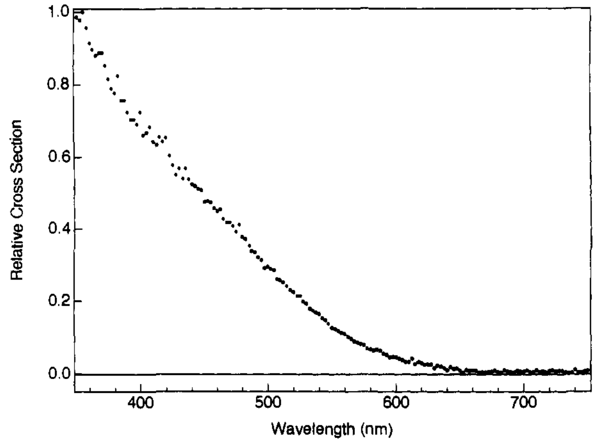

Figure 3. Low-resolution electron photodetachment spectrum for $(Me_3Si)_2SiH^-$; bandwidth = 25 nm fwhm.

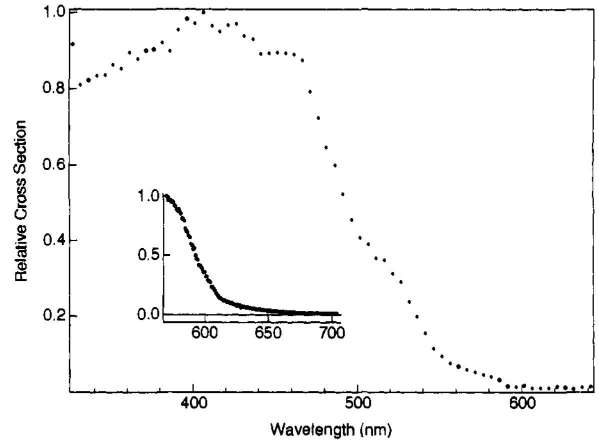

Figure 4. Electron photodetachment spectrum for $(Me_3Si)_3Si^-$. The bandwidth is 25 nm fwhm. The high-resolution laser spectrum is shown as an inset.

604 nm. Correction for the bandwidth yields an onset of 579 ± 25 nm (49.4 ± 1.8 kcal/mol). The high-resolution electron photodetachment spectrum is shown as an inset. A slowly rising cross section is seen, with a slope change at 611 nm. The long tail between 611 and 700 nm may be partly due to a hot band. A hot band of this magnitude (6 kcal), however, is unexpected. Assignment of the onset at 700 nm would give an electron affinity that is not consistent with those for the other silanes. Therefore, because of the uncertainty in the onset assignment, we estimate large error bars and assign the onset as 611 ± 25 nm (46.8 ± 2 kcal/mol).

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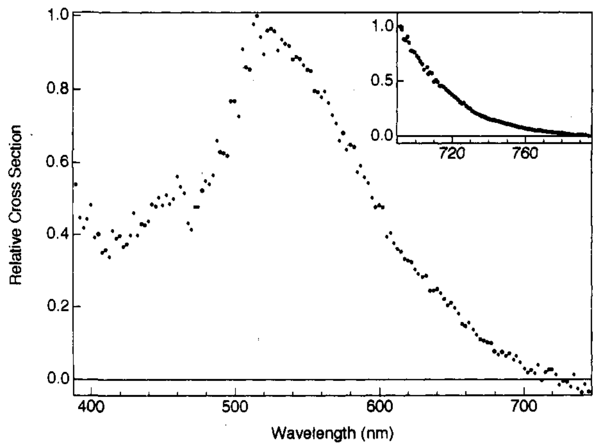

Figure 5. Electron photodetachment spectrum for $(Me_3Si)_2CH^-$. The bandwidth is 25 nm fwhm. The high-resolution laser spectrum is shown as an inset.

(e) $(Me_3Si)_2CH$. The low-resolution electron photodetachment spectrum for this anion is shown in Figure 5. A slowly rising cross section is seen, with an onset of 734 nm. A resonance appears at approximately 530 nm (2.3 eV), suggesting the presence of an excited state of the anion. This is nearly identical in energy to the resonance seen[24] in the electron photodetachment spectrum of $(Me_3Si)CH_2^-$. The high-resolution spectrum shown as an inset shows a slow, smoothly rising cross section, with an onset of 795 ± 5 nm. Therefore, we assign the electron affinity as 36.0 ± 0.2 kcal/mol.

Discussion

We have determined here the electron affinities for several silyl-substituted carbon and silyl radicals, and we now examine these electron affinities to learn about the magnitude of α-silyl stabilization. The electron affinity measures the stability of an anion relative to its neutral.

$$A^- \rightarrow A + e^- \quad EA(A) \tag{5}$$

A comparison of electron affinities reveals the stabilization of the anions relative to their corresponding radicals. To learn about relative anion stabilities we compare acidities (eq 6), and to learn about relative radical stabilities we compare bond dissociation energies (eq 7).

$$AH \rightarrow A^- + H^+ \quad \Delta H^\circ_{acid}(AH) \tag{6}$$

$$AH \rightarrow A + H \quad D^\circ(AH) \tag{7}$$

In this paper we compare the observed electron affinity trends for α-silyl-substituted silanes and methanes with those for other α-substituted compounds. We then discuss observed and estimated bond dissociation energies for the neutral compounds, as an estimate of the radical stabilities. From the electron affinities and the bond dissociation energies we compute acidities for these compounds, allowing us to compare the stabilization of these anions. *Ab initio* calculations are used to help understand the mechanism of the anion stabilization.

Electron Affinities. (a) Carbon Radicals. We have measured the electron affinity of $(Me_3Si)_2CH$ as 36.0 ± 0.2 kcal/mol. The electron affinity of Me_3SiCH_2 was previously determined[24] to be 21.9 ± 0.3 kcal/mol, and the electron affinity of CH_3 is 1.8 ± 0.7 kcal/mol.[9] Replacement of a hydrogen by a trimethylsilyl group thus increases the electron affinity by about 20 kcal/mol for the first silyl substituent and 14 kcal/mol for the second. This is a dramatic effect: the stabilization obtained from one trimethylsilyl group is on the order of the resonance stabilization energy measured for one phenyl group (the electron affinity of the benzyl radical is[53] 21.0 ± 0.14 kcal/mol) and there is relatively little "saturation" effect when a second group is added.

We can compare this with the effect observed by substitution of other α-substituents. The replacement of a hydrogen by an alkyl group generally decreases the electron affinity, because the radical is stabilized relative to the anion. Indeed, most simple alkyl anions are not bound with respect to electron loss.[10-13] As substituents, some other second period elements (O, N) also appear to decrease the electron affinity; electron affinities for CH_2OH and CH_2NH_2 are calculated to be negative and these anions have not been observed.[54] In contrast, *ab initio* calculations using isogyric reactions predict that fluorine substitution should increase the electron affinity[33] and CH_2F^- has been observed experimentally.[13,55]

Third period substituents are stabilizing. For example, the electron affinity of $MeSCH_2$ was measured to be 20.0 ± 1.2 kcal/mol using photoelectron spectroscopy,[23] similar to the effect of silyl substitution. *Ab initio* calculations using isogyric reactions suggest that substitution of multiple chlorine atoms increases the electron affinity approximately 13–16 kcal/mol per substituted chlorine atom.[33] The adiabatic electron affinity of CCl_3 has been calculated using approximate density functional theory (DFT) to be 54.4 kcal/mol[34] and derived from acidity measurements as 51.9 ± 2.3 kcal/mol.[22] Thus, these calculations suggest that chlorine atoms show a similar effect to that seen for silyl groups.

(b) Silyl radicals. As we have done with carbon radicals, we can explore substituent effects on electron affinities of silyl radicals. The silyl anion is quite stable;[14,15,51,56] its radical has a much higher electron affinity than that of the methyl radical[9] (32.4 vs 1.8 kcal/mol). In this work, we have determined the electron affinity of Me_2SiH to be 24.7 kcal/mol, showing that substitution of two methyl groups decreases the electron affinity of the silyl radical by ~8 kcal/mol. The electron affinities of the other methyl silyl radicals have previously been determined,[15] and the electron affinity of the dimethylsilyl radical is consistent with these measurements: $EA(MeSiH_2) = 27.5 \pm 0.8$ kcal/mol; $EA(Me_2SiH) = 24.7 \pm 0.5$ kcal/mol; $EA(SiMe_3) = 22.4 \pm 0.6$ kcal/mol. Thus, substitution of a methyl group for a hydrogen decreases the electron affinity ~2–5 kcal/mol per methyl group. This electron affinity value for Me_2SiH allows us to derive the acidity of Me_2SiH_2 and helps to resolve some differences in the literature regarding this acidity, as discussed below. Substitution of a phenyl for hydrogen is known to have essentially no effect on the electron affinity ($EA(SiH_3) = 32.4 \pm 0.6$ kcal/mol vs $EA(PhSiH_2) = 33.1 \pm 0.1$ kcal/mol).[15]

In this work, we have also found that substitution of two and three (Me_3Si)– groups gives an electron affinity of 44.7 and 46.8 kcal/mol, respectively. Although the electron affinity of the singly substituted compound (Me_3SiSiH_2) was not determined, we can estimate the electron affinity change for substitution of one silyl group by comparing the electron affinities for Me_2SiH and $Me_2SiHSiMe_2$.

$$Me_2SiHSiMe_2 + Me_2SiH^- \rightarrow Me_2SiHSiMe_2^- + Me_2SiH \tag{8}$$

The ΔH°_{rxn} is −7.6 kcal/mol. If we assume that (Me_3Si)– or (Me_2SiH)– show essentially the same effect, substitution of a (Me_3Si)– group for H increases the electron affinity of silyl radicals ~2–8 kcal/mol per silyl group. Obviously then, the effect of α-silyl substitution on silyl radical electron affinity is considerably smaller than the effect of α-silyl substitution on carbon radical electron affinity (2–8 vs 14–20 kcal/mol). It is

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likely that most of this attenuation is a consequence of the substantially greater stability (electron affinity) of the silyl radical itself. From considerations of perturbation theory, we expect that as a system becomes more stable, stabilization interactions of this type will be diminished.

Bond Dissociation Energies. (a) C–H Bonds. The relative stabilities of the radicals can be examined in a similar manner by comparing the bond dissociation energies of the neutral molecules. The only silyl substituted methane bond dissociation energy measured is for tetramethylsilane, CH_3SiCH_2–H, determined[57] to be 99.2 ± 1.2 kcal/mol, nearly identical with that obtained for the analogous carbon compound, neopentane[57] (99.7 kcal/mol). A separate determination[58] suggested that an α-silyl substituent stabilizes a primary alkyl radical by 2.6 ± 1 kcal/mol. This, together with the typical primary C–H bond energy, recently revised to 101.1 ± 0.4 kcal/mol,[59,60] yields a C–H bond energy of 98.5 ± 1 kcal/mol in tetramethylsilane. Both of these determinations are consistent with silyl groups providing a small amount of stabilization to a carbon radical, slightly more than that seen by an addition of an alkyl group. *Ab initio* calculations by Coolidge and Borden[61] indicate that $D°$(C–H) for SiH_3CH_3 is 1.1 kcal/mol less than $D°$(C–H) for ethane, while calculations by Allendorf and Melius predict that $D°$(C–H) for CH_3SiH_3 is 100.9 kcal/mol,[62] also consistent with substitution of a silyl group for a methyl group providing a small amount of stabilization. We expect the addition of a second silyl group will further stabilize the radical by approximately the same amount and we estimate the C–H bond dissociation energy of $(Me_3Si)_2CH$–*H* as 96 kcal/mol.

(b) Si–H bonds. Si–H bond dissociation energies have been measured for a variety of silicon compounds. From these measurements, it appears that $D°$ (Si–H) is essentially independent of the number of methyl groups present (ca. 90 kcal/mol).[57,63] The bond dissociation energies of silane, methylsilane, and trimethylsilane were also derived[15] via a thermochemical cycle from the electron affinities of the corresponding radicals and the acidities of the neutrals: $D°(SiH_4)$ = 91.6 ± 2 kcal/mol; $D°(MeSiH_3)$ = 92.2 ± 2 kcal/mol; $D°(Me_3SiH) \geq 91.0$ kcal/mol. *Ab initio* calculations[62,64] for a series of methyl-substituted silanes suggest there may be a small increase in $D°$(Si–H) for successive substitution of methyl groups (<0.9 kcal/mol per methyl group). This difference is within the experimental error limits and would be difficult to observe experimentally. Because of the difficulties in measuring $D°$(Si–H) directly, we have chosen to estimate $D°(Me_2SiH_2)$ using the above derived $D°$(Si–H); therefore we assign $D°(Me_2SiH_2)$ = 92 ± 2 kcal/mol.

$D°$(Si–H) shows a slight decrease with silyl substitution: $D°$(Si–H) for SiH_3SiH_2–H[57], $Me_3Si(Me_2)Si$–H,[65] and $(Me_3Si)_3Si$–H[65] are 86.3, 85.3, and 79.0 kcal/mol, respectively. *Ab initio* calculations have also been used by Coolidge and Borden to study the effect of silyl substitution on $D°$(Si–H).[61] They compute a 2.9 kcal/mol decrease in $D°$(Si–H) from silane to disilane and a difference of 8.2 kcal/mol between silane and $(SiH_3)_3Si$–H. They attribute the lowering of $D°$(Si–H) to silicon being less electronegative than hydrogen. Sax and Kalcher have used *ab initio* methods to calculate $D°$(Si-H) for SiH_4, H_3SiSiH_3, and $(H_3Si)_2Si$–H_2 as 91.6, 89.5, and 86.3 kcal/mol, respectively,[66] suggesting that silyl substitution decreases $D°$ (Si-H) by 2-3 kcal/mol per silyl group.

Table 1. Carbon Thermochemistry[a]

A•	EA(A•)	$D°$(H–A)	$\Delta H°_{acid}$(HA)
CH_3	1.8 ± 0.7[b]	104.9[c]	417
$(CH_3)_3CCH_2$	4.8[d]	101.1[c]	409 ± 1[d]
		99.7[g]	411 ± 10[e]
Me_3SiCH_2	21.9 ± 0.3[f]	99.2[g]	387 ± 3[h]
$(Me_3Si)_2CH$	36.0 ± 0.2	96 ± 4[i]	374 ± 4

[a] All values in kcal/mol. Acidities calculated using eq 9. [b] Reference 9. [c] The 1°, 2°, and 3° $D°$(C–H) have recently been revised.[59,60] The new value for a primary alkyl radical is used for neopentane. [d] Reference 11. [e] Reference 55. [f] Reference 24. [g] Reference 57. [h] Reference 19. [i] Estimated from the $D°$(C–H) for $(CH_3)_3SiCH_2$–H,[57] assuming each trimethylsilyl group decreases the $D°$(H–A) by approximately 3 kcal/mol.

Acidities. The gas-phase proton affinity is defined as the enthalpy change for the heterolytic H–A bond dissociation (eq 6). The smaller the $\Delta H°_{acid}$(HA) value, the more acidic the compound. If we assume that the relative stabilities of the neutral species are not affected by substitution, the relative anion stabilities can be obtained by comparing the acidities. Acidities can be derived from the electron affinities using the bond dissociation energy of H–A, $D°$(H–A), and the ionization potential of hydrogen, IP(H).

$$\Delta H°_{acid}(HA) = D°(H{-}A) - EA(A) + IP(H) \qquad (9)$$

EA(A) and IP(H) are 0 K values, while $\Delta H°_{acid}$(HA) and $D°$(H-A) are 298 K values. Correction of $\Delta H°_{acid}$(HA) for the integrated heat capacities is expected to make only a minor contribution to this value, less than the error limits. Therefore we have not included these contributions.

Acidities can also be measured by equilibrium or bracketing techniques. Attempts to bracket the acidity using alkoxides were complicated by the formation of the trimethylsiloxide ion. This chemistry has previously been observed by DePuy and coworkers.[11,67]

$$RO^- + (Me_3Si)_2CH_2 \rightarrow Me_3SiO^- + (Me_3Si)CH_2R \qquad (10)$$

The structure of the neutral molecule is postulated, based on their work. Trimethylsiloxide ion can deprotonate the silyl neutral, depending on the acidity of the neutral ($\Delta G°_{acid}(Me_3SiOH)$ = 352 ± 4[68] and 356.0 ± 4.0 kcal/mol[69]). Because of these complications, experimental acidity determinations were not successful.

The derived acidities for carbon and silyl are summarized in Table 1 and Table 2, respectively.

Carbon Acids. A summary of the electron affinities, bond dissociation energies, and calculated acidities is shown in Table 1. The acidity, relative to neopentane, increases by 22 and 13 kcal/mol for the addition of one and two trimethylsilyl groups, respectively. The stabilization causes $(Me_3Si)_2CH_2$ to be more acidic than methanol and comparable in acidity to *tert*-butyl alcohol.[70] This remarkable stabilization can be compared with the stabilization seen from other α-substituents.

The substitution of a methyl group for a hydrogen in the anion is destabilizing, resulting in $\Delta H°_{acid}$ increasing approximately 6 kcal/mol.[11] Not surprisingly electron delocalization into an aromatic ring decreases $\Delta H°_{acid}$; however the decrease is only

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Table 2. Silane Thermochemistry[a]

$A^\bullet$	$EA(A^\bullet)$	$D^\circ(H{-}A)$	$\Delta H^\circ_{acid}(HA)$
SiH_3	32.4 ± 0.6[b]	90.3 ± 1[d]	373 ± 2[b]
	32.4 ± 0.3[c]	91.8 ± 0.5[e]	371 ± 2[f]
Me_2SiH	24.7 ± 0.5	92 ± 2[g]	380 ± 2
			383 ± 3[f]
$Me_2HSiSiMe_2$	32.3 ± 0.8	86 ± 2[h]	366 ± 3
$(Me_3Si)_2SiH$	44.7 ± 1.9	82 ± 4[i]	352 ± 6
$(Me_3Si)_3Si$	46.8 ± 2.0	79 ± 1[j]	346 ± 3

[a] All values in kcal/mol. [b] Reference 15. [c] Reference 14. [d] Reference 57. [e] References 75 and 60. [f] Reference 19. [g] Estimated as described in text. [h] Derived from D°(Si–H) for $Me_3SiMe_2Si{-}H$ (85.3 ± 1 kcal/mol)[65] and $H_3SiH_2Si{-}H$ (86.3 ± 1 kcal/mol).[57] [i] Estimated to lie between $Me_3SiMe_2Si{-}H$ (85.3 ± 1 kcal/mol[65]) and $(Me_3Si)_3Si{-}H$ (79 ± 1 kcal/mol[65]). [j] Reference 65.

Table 3. Calculated Substituent Stabilization Energies of Methyl and Silyl Anions[a]

n	6-31G(d)	6-311+G(d,p)
$(SiH_3)_nCH_{4-n} + CH_3^- \rightarrow (SiH_3)_nCH_{3-n}^- + CH_4$ ΔH°_{rxn}		
1	−37	−25
2	−64[b]	−47[b]
3	−85	−66
$(SiH_3)_nSiH_{4-n} + SiH_3^- \rightarrow (SiH_3)_nSiH_{3-n}^- + SiH_4$ ΔH°_{rxn}		
1	−12	−11
2	−21	−19
3	−28	−27

[a] All values in kcal/mol; symmetries used for the calculations for the molecules and anions are defined in Table 4. [b] Because of the symmetry chosen for $(SiH_3)_2CH_2$, there are two eclipsing interactions present in this molecule which are not present in Si_3CH_3 and $(SiH_3)_3CH$; from our other calculations these interactions are expected to contribute approximately 4 kcal/mol to the decrease in the ΔH°_{rxn}.

slightly greater than that measured here:[70] $\Delta H^\circ_{acid}(C_6H_5CH_3) = 380.8 \pm 2.4$; $\Delta H^\circ_{acid}((C_6H_5)_2CH_2) = 363.6 \pm 2.3$; and $\Delta H^\circ_{acid}((C_6H_5)_3CH) = 358.7 \pm 2.9$ kcal/mol. The replacement of hydrogen by other third period elements shows similar stabilization effects to that seen for silyl groups, as observed from the measured ΔH°_{acid}: Me_2PCH_3 (391.1 ± 2[17] and 383.9 ± 3.1 kcal/mol[18]), $MeSCH_3$ (393.2 ± 2 kcal/mol[17]), CH_3SH (394 ± 2.9 kcal/mol[20]), and $ClCH_3$ (399.6 ± 2.5 kcal/mol[21]). Multiple substituent effects on acidity have been studied for a few other third period compounds. The acidities of CH_2Cl_2 and $CHCl_3$ are 374.6 ± 3.9[70] and 357.6 ± 2.0 kcal/mol,[22] respectively. *Ab initio* calculations suggest a 17–21 kcal/mol acidity increase per Cl substituted.[33] The acidity of 5,5-dimethyl-1,3-dithiane has been measured[16] to be 372.9 ± 2.1 kcal/mol. We expect the acidity of this compound should be quite similar to that of $(MeS)_2CH_2$. From these results it appears that multiple silyl, sulfur, or chlorine substituents have similar effects on the acidity of methane, but silyl substituents may be the most stabilizing

The anion stabilization for these compounds can also be calculated using *ab initio* methods. We have performed calculations using two different basis sets. To minimize the calculation time, we calculated geometries and energies for the ($-SiH_3$) substituted compounds, rather than the ($-SiMe_3$) substituted compounds, and we used symmetry to define the geometries. Global minima were not calculated; we expect only minor differences in the stabilization energies as a result of this. Isodesmic reactions are used to estimate the stabilization energies. While we do not expect the absolute value of these numbers to be correct because we have not included electron correlation and zero point energies, we expect that the trends should be correct. From these calculations, the stabilization at the 6-31G(d) level ranges from −37 (1 silyl group) to −28 kcal/mol per silyl group (3 silyl groups), while that at the 6-311+G(d,p) level ranges from −25 (1 silyl group) to −22 kcal/mol for each silyl group (3 silyl groups); both sets of calculations are consistent with a roughly additive increase in the acidity with substitution of multiple substituents. Basis sets without diffuse orbitals are believed to overestimate stabilization energies[28,71] and electron correlation appears to be necessary to calculate acidities accurately.[38] Bernardi and co-workers[32] determined the stabilization of a single silyl group to be −23.2 kcal/mol (MP2/6-31G(d)//3-21+G(d)), using the identical isodesmic reaction. Numerous calculations using various basis sets have shown that silyl groups stabilize carbanions[25–28,32] and that third period elements stabilize carbanions.[25–34,54]

Table 4. 6-311+G(d,p) Geometries

	bond distances (Å)		
methanes	C–Si	C–H	angle (deg)
CH_4 (T_d)		1.084	HCH 109.5
H_3SiCH_3 (C_{3v})	1.882	1.086	SiCH 110.9; HCH 108.0
$(H_3Si)_2CH_2$ (C_{2v})	1.884	1.090	SiCSi 116.9; SiCH 108.3
$(H_3Si)_3CH$ (C_{3v})	1.890	1.074	SiCSi 113.2; SiCH 105.4

	bond distances (Å)		
methyl anions	C–Si	C–H	angle (deg)
CH_3^- (C_{3v})		1.098	HCH 109.0
$(H_3Si)CH_2^-$ (C_v)	1.780	1.085	SiCH 120.2; HCH 113.4
$(H_3Si)_2CH^-$ (C_s)	1.787	1.085	SiCSi 128.4; SiCH 115.7
$(H_3Si)_3C^-$ (C_{3v})	1.801		SiCSi 120.0

	bond distances (Å)		
silanes	Si–Si	Si–H	angle (deg)
SiH_4 (T_d)		1.477	HSiH 109.5
H_3SiSiH_3 (D_{3h})	2.364	1.480	SiSiH 110.3; HSiH 108.6
$(H_3Si)_2SiH_2$ (C_{2v})	2.366	1.483	SiSiSi 112.5; SiSiH 109.1; HSiH 107.8
$(H_3Si)_3SiH$ (C_{3v})	2.368	1.486	SiSiSi 110.8; SiSiH 108.1

	bond distances (Å)		
silyl anions	Si–Si	Si–H	angle (deg)
SiH_3^- (C_{3v})		1.535	HSiH 96.9
$(H_3Si)SiH_2^-$ (C_s)	2.398	1.529	SiSiH 95.8; HSiH 97.0
$(H_3Si)_2SiH^-$ (C_s)	2.388	1.526	SiSiSi 98.2; SiSiH 96.2
$(H_3Si)_3Si^-$ (C_{3v})	2.379		SiSiSi 98.6

We can examine the neutral and anion geometries, to learn more about the mechanism of the stabilization (Table 4). An examination of the C–Si bond lengths shows that, in general, bond lengths are found to decrease by approximately 0.1 Å upon deprotonation. This is consistent with an earlier prediction that hyperconjugation plays an important role in the stabilization of the carbanion.[24,28,72] In addition, the central bond angle at the carbon increases upon deprotonation. The Mulliken population analysis indicates that in the neutral molecule, the central carbon has close to a full negative charge. Upon deprotonation, most of the charge is picked up throughout the rest of the molecule.

Schleyer, Houk, and co-workers[28] performed *ab initio* calculations to study the stabilization of carbanions. They concluded that third period elements are more stabilizing than second period elements, as a result of their more electropositive character, more effective negative hyperconjugation, and the greater polarizability of these elements. They concluded that the stabilization energies are not greatly affected by the inclusion of d-orbitals and therefore d-orbitals are not important for describing the stabilization of carbanions. They are important, however, for describing the geometries properly.

Silyl Acids. The derived acidities of the silanes allow us to compare the effects of methyl and silyl substituents on the acidities of silyl compounds.

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We were especially interested in the effect of methyl substitution on the acidity of silane, because of the discrepancies observed in two previous independent measurements of the acidities of the methyl silanes. Damrauer and co-workers[19] used bracketing techniques to measure the acidity of silane as 371 ± 2 kcal/mol and the acidities of methylsilane, dimethylsilane, and trimethylsilane each as 383 ± 3 kcal/mol, concluding that the alkylsilanes were less acidic than silane, but that alkylsilane acidities did not vary with the number of substituted methyl groups. Wetzel *et al.*[15] previously used equilibrium measurements to determine the acidities of silane, methylsilane, and trimethylsilane; these were determined to be 372.8 ± 2, 378.3 ± 2, and $\geq$ 382.8 ± 2 kcal/mol, respectively, consistent with an acidity decrease of ~3–6 kcal/mol per substituted methyl group. From the experiments reported here, we derive the acidity of dimethylsilane as 380 ± 2 kcal/mol, consistent with an acidity decrease of 2–6 kcal/mol per substituted methyl group. The electron affinities of the methyl-substituted radicals show incremental decreases with methyl substitution (2–5 kcal/mol per substituted methyl),[15] while the Si–H bond energies are expected to be essentially unchanged[57] or show slight increases upon methyl substitution,[62,64] as discussed earlier. Therefore we expect the acidities should decrease approximately 2–5 kcal/mol with successive methyl substitution. The small changes we see for successive methyl substitution may be obscured in the previous bracketing determination of the Si–H acidities of the methylsilanes by Damrauer and co-workers.[19] These bracketing experiments are also complicated by the presence of a relatively acidic C–H site in these molecules (ΔH°_{acid}(C–H) = 388–391 kcal/mol[19] vs ΔH°_{acid}(Si–H) = 378–383 kcal/mol). Therefore, our derived acidity of dimethylsilane is consistent with a small decrease in the acidities of the methylsilanes upon successive methyl substitution.

The effect of silyl group substitution on the acidity of silanes was also derived. A comparison of dimethylsilane and $Me_2SiHSiMe_2H$ shows that substitution of a silyl group increases the acidity by approximately 14 kcal/mol, a consequence of an 8 kcal/mol increase in EA and a decrease of ~6 kcal/mol in bond energy. Examination of the other substituted silanes shows that the overall trend is a stabilization of 6–14 kcal/mol per silyl group. This a remarkable amount of stabilization, considering that the silyl anion itself is so stable. Interestingly, the substitution of a phenyl group has been shown to have essentially no effect on the acidity of silanes,[15] suggesting that π delocalization does not play a role in the stabilization of silyl anions. This is supported both by studies of the NMR chemical shifts in various phenyl silyl anions[73] and by the absorption spectra of phenyl silyl lithium salts in THF.[74]

The anion stabilization for these compounds was also calculated using *ab initio* methods, as for the carbanions, summarized in Table 3. From this it can be seen that the calculated stabilization energies are one-third (6-31G(d)) to one-half (6-311+G(d,p)) those seen for the analogous carbon compounds. The stabilization calculated using the 6-311+G(d,p) basis set agrees quite well with our experimental estimates (8–11 vs 6–14 kcal/mol for each silyl group). The disilane acidity was previously calculated[38] to be 362 kcal/mol (MP2/6-311++G(3df,2pd)), consistent with a silane stabilization of approximately 11 kcal/mol, suggesting that electron correlation does not have a large effect on the stabilization energies of silyl anions. Interestingly, substitution of other third period elements is predicted to yield a stabilization quite similar to that exhibited by silyl.

Previous calculations have examined the effect of second period substituents on the stability of silyl anions and have concluded that methyl groups destabilize silyl anions,[26,35,36] consistent with experimental observations.

Examination of the geometries of the neutral molecules and deprotonated anions shows a few interesting trends. Upon deprotonation, the Si–Si bond lengths actually increase slightly. This suggests that hyperconjugation is not an important factor for silyl anions, in contrast to the carbanions. This is not surprising, given the long length of these bonds and the poor π-overlap expected. Other studies of the effect of second period[38,72] and third period elements[38] on the stability of silyl anions have shown that the Si–X (X = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl) and Si–H bond lengths increase upon deprotonation. In addition, the central Si bond angle decreases substantially upon deprotonation, from approximately 110–111° to 95–98°. The small central angles in the anions suggests that there is substantial p-character in the bonds, and that the extra electron is located in an orbital with substantial s-character. An orbital with substantial s-character would be expected to bind an electron more tightly than one with more p-character, as seen in the carbanion system. In addition, the Mulliken populations suggest that a substantial amount of the charge in the anion remains on the central silicon, consistent with the electron being tightly bound in the s-orbital.

Conclusions

Silyl groups stabilize both carbanions and silyl anions, as seen from electron affinity measurements and derived acidities. *Ab initio* calculations also suggest that the stabilization increase is approximately additive for the number of silyl groups. The stabilization for carbanions is approximately 14–20 kcal/mol per silyl group and the stabilization for silyl anions is approximately 6–14 kcal/mol per silyl group. *Ab initio* calculations suggest that the stabilization results from hyperconjugation in the carbanion, consistent with previous work, but does not result from hyperconjugation in the silyl anion.

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