= 14.9 Hz, ^3J(H–P) $\simeq$ 0 Hz, 1 H, CH_2), 5.19 (A*B*X, $^2J(H_A–H_B)$ = 14.9 Hz, ^3J(H–P) = 10.3 Hz, 1 H, CH_2), 6.8–7.8 (m, 15 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 81.92 (d, ^2J(C–P) = 8.5 Hz, OCH_2), 196.78 (d, ^2J(C–P) = 8.5 Hz, cis CO); IR (decalin) ν(CO) 2075 (m), 1960 (vs), 1950 (sh) cm^{-1}; mass spectrum (^{184}W) *m*/*e* (relative intensity) 640 (M, 40), 612 (M – CO, 23), 556 (M – 3CO, 91), 500 (M – 5CO, 100). Anal. Calcd for $C_{26}H_{17}O_6PW$: C, 48.78; H, 2.68; P, 4.84; W, 28.72. Found: C, 48.98; H, 2.58; P, 4,82; W, 28,92.

Reduction of 8 with $NaBH_4$. Complex 8 (1.2 g, 2.2 mmol) was added to $NaBH_4$ (0.1 g, 2.6 mmol) in *i*-PrOH at room temperature. After being stirred for 30 min the reaction mixture was hydrolyzed. The solvent was removed and the residue extracted with methylene chloride and chromatographed with toluene to yield 0.54 g (45%) of colorless oil. **19**: ^{31}P NMR (CH_2Cl_2) δ –31.06 ($^1J(^{183}W–^{31}P)$ = 225 Hz); ^{1}H NMR (C_6D_6) δ 0.72 (t, ^3J(H–H) = 7.3 Hz, 3 H, Me), 0.88 (t, ^3J(H–H) = 7.4 Hz, 3 H, Me), 1.9–2.2 (m, 4 H, CH_2), 3.82 (*AB*, $^2J_{AB}$ = 12.6 Hz, 1 H, CH_2), 3.94 (A*B*, J_{AB} = 12.6 Hz, 1 H, CH_2), 6.16 (d, ^1J(H–P) = 349 Hz, 1 H, PH), 6.8–7.8 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) 13.22 (s, Me), 13.86 (s, Me), 24.06 (d, ^3J(C–P) = 8.6 Hz, CH_2); 25.60 (d, ^2J(C–P) = 13.1 Hz, CH_2), 62.71 (d, ^3J(C–P) = 12.6 Hz, CH_2OH), 197.07 (d, ^2J(C–P) = 6.5 Hz, cis CO), 199.30 (d, ^2J(C–P) = 20.6 Hz, trans CO); IR (decalin) ν(CO) 2070 (m), 1940 (vs) cm^{-1}; IR (KBr) ν(OH) 3400 cm^{-1}; mass spectrum (^{184}W) *m*/*e* (relative intensity) 544 (M – 2H, 10), 528 (M – H_2O, 11), 544 (M – CO, 8), 460 (M – 2H – 3CO, 20), 404 (M – 2H – 5CO, 26), 388 (M – H_2O – 5CO, 31), 236 ($C_{13}H_{17}PO$, 100).

Registry No. **3**, 74363-95-4; **7**, 97704-77-3; **8**, 97704-78-4; **9**, 111958-68-0; **10**, 111958-69-1; **11**, 111958-70-4; **12a**, 111958-71-5; **12b**, 112065-79-9; **13a**, 111958-72-6; **13b**, 112019-13-3; **15**, 111958-73-7; **16**, 111958-74-8; **19**, 111958-75-9; dimethyl acetylenedicarboxylate, 762-42-5; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; morpholine, 110-91-8.

Gas-Phase Acidities of Methylsilanes: C–H versus Si–H

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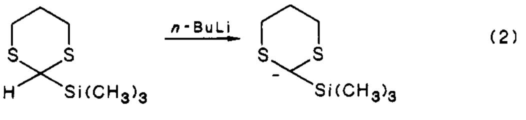
The gas-phase acidities of silane, methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane, and phenylsilane have been measured in the flowing afterglow by using standard techniques. In those methylsilanes having both C–H and Si–H bonds, abstraction occurs from both positions and, correspondingly, both C–H and Si–H acidities are reported. Quite unusually, the thermodynamically more stable products resulting from Si–H abstraction by base are not the first formed products. Thus, C–H abstraction occurs readily by a kinetically more accessible path. The measured gas-phase acidities are used to calculate electron affinities for the corresponding anions. The electron binding energies and basicity of the methyl-substituted silyl anions do not vary with methyl substitution. Furthermore, phenyl-substituted silyl anion has the same electron binding energy and basicity as the silyl anion itself.

α-Silyl carbanions ($R_3SiCH_2^-$) and silyl anions (R_3Si^-) play important roles in synthetic chemistry, the α-silyl species in the Peterson olefination and a wide variety of condensation reactions and the silyl anion in its 1,4-addition to α,β-unsaturated ketones.[1] These anions are prepared in solution as organometallic species in a number of ways using metalation, halogen–metal exchange, addition, and exchange reactions. However, they have been less often prepared by proton abstraction despite the direct nature of such an approach. Thus, demonstrations that KH reacts with trisubstituted silanes to give the corresponding silyl anion (eq 1) and that silyl-substituted

$$R_3SiH + KH \xrightarrow[\text{HMPA}]{\text{DME or}} R_3SiK \qquad (1)$$

$$R = CH_3CH_2,\ C_6H_5$$

thioketals react with BuLi to form α-silyl carbanions (eq 2) are among the relatively few direct deprotonations re-



(2)

ported in solution.[1] In the gas phase the trimethylsilyl anion results from reaction of hexamethyldisilane and fluoride ion (eq 3) and proton abstraction from tetramethylsilane with amide ion forms the α-silyl carbanion, $(CH_3)_3SiCH_2^-$ (eq 4).[2] Bowie and co-workers reported, and

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{F^-} (CH_3)_3Si^- + (CH_3)_3SiF \qquad (3)$$

$$(CH_3)_4Si \xrightarrow{NH_2^-} (CH_3)_3SiCH_2^- \qquad (4)$$

we confirmed, that when strong bases react with trimethylsilane to give its M – 1 ion (eq 5), the α-silyl carbanion is formed.[3] Bowie's group used a deuterium label to demonstrate that proton abstraction occurs from a methyl group rather than from silicon, while we were led to the same conclusion through the development of a reaction scheme using N_2O in which α-silyl carbanions and silyl anions can be distinguished (eq 6 and 7).[4] We now

$$(CH_3)_3SiH \xrightarrow{NH_2^-} (CH_3)_2SiHCH_2^- \qquad (5)$$

$$\underset{m/z\ 73}{(CH_3)_2Si\ HCH_2^-} \xrightarrow{N_2O} \underset{m/z\ 75}{(CH_3)_2SiHO^-} \qquad (6)$$

$$\underset{m/z\ 73}{(CH_3)_3Si^-} \xrightarrow{N_2O} \underset{m/z\ 89}{(CH_3)_3SiO^-} \qquad (7)$$

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report that under certain conditions the silyl anion can also be produced by proton abstraction (eq 8). This finding,

$$(CH_3)_3SiH \xrightarrow{NH_2^-} (CH_3)_2SiHCH_2^- + (CH_3)_3Si^- \quad (8)$$

as well as the recognition that so little was known about the relative stability of the anions resulting from proton abstraction, led us to undertake a detailed flowing afterglow study of the four methylsilanes and of phenylsilane. Such an approach has allowed us to probe the intrinsic stabilities of the various anions while eliminating any solvation or counterion (organometallic) effects.

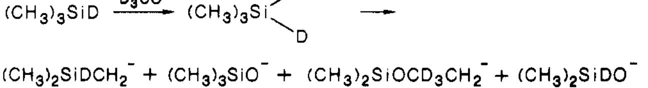
Experimental Section

These experiments were performed in a flowing afterglow (FA) system at 298 K as previously described.[5] Amide and fluoride ions were made by electron impact on ammonia and NF_3, respectively; hydroxide ions were generated by dissociative electron attachment to N_2O to form O^- followed by hydrogen atom abstraction from methane; other anions like CH_3O^-, H_2P^-, and the M − 1 of furan and fluorobenzene were prepared by reaction of their conjugate acid with amide ion. Typical helium pressures and flow rates were 0.4 Torr and approximately 160 STP cm^3/s, respectively. Neutral reactants, including the silanes, were obtained from commercial suppliers and used without purification.

The identity of products was determined not only from mass-to-charge (*m/z*) ratios but also by reaction with neutral molecules like N_2O (see Results and Discussion and ref 4 for additional details). Since neutral products cannot be determined in the FA, their identity was inferred from knowledge of the reactants and the identification of the anionic products.

Results

The C–H and Si–H acidities in methylsilanes have not been determined previously despite the important synthetic roles played by α-silyl carbanions and silyl anions. In fact, very little is known about either the proton abstraction reactions of methylsilanes or the acidity of silanes either in solution or in the gas phase. With the exception of gas-phase determinations of the acidity of SiH_4, where a value of $\Delta H°_{acid}$ of 371.5 ± 2 kcal/mol is generally accepted,[6,7] no systematic study of gas-phase C–H or Si–H acidity in silanes has been published. Quantitative studies of the gas-phase reactivity of silanes have, however, been reported. ICR experiments by Bowie and co-workers showed that trimethylsilane and methoxide ion give a small amount of an M − 1 ion arising exclusively from C–H abstraction.[3] The major reaction course, however, involved Si–H cleavage after pentacoordination at silicon (eq 9).



$$(CH_3)_3SiD \xrightarrow{D_3CO^-} (CH_3)_3\overset{-}{Si}(OCD_3)(D) \longrightarrow (CH_3)_2SiDCH_2^- + (CH_3)_3SiO^- + (CH_3)_2SiOCD_3CH_2^- + (CH_3)_2SiDO^-$$

(9)

We subsequently reported that trimethylsilane and amide ion react in the FA to give only the anion resulting from C–H proton abstraction (eq 5).[4] Our demonstration that α-silyl carbanions and silyl anions gave dramatically different reaction with N_2O (eq 6 and 7) provided us with the tool necessary for a more comprehensive study of methylsilane acidities. To our knowledge these demonstrations that the less acidic hydrogen is more rapidly extracted are unique in the gas phase. They serve as a caution to gas-phase chemists that chemical characterization of ions be an essential aspect of gas-phase studies.[4]

Table I. Gas-Phase Acidities of Compounds Used in This Study[7,8] (in kcal/mol)

compd	acidity	compd	acidity
NH_3	404	CH_3OH	381
$(CH_3)_2NH$	396	CH_3CH_2OH	377
H_2O (D_2O)	391 (393)	HF	371
C_6H_5F (fluorobenzene)	387	PH_3	370
C_4H_4O (furan)	386	C_3H_6O (acetone)	368
C_3H_4 (propyne)	380–2		

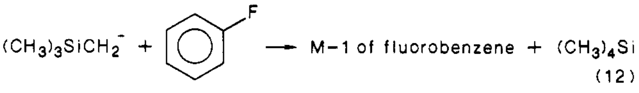
We began by studying the acidity of SiH_4, both to check its accepted value and to evaluate the bracketing method for the silanes. This method has been used to determine relative gas-phase acidities; its utility depends not only on the availability of acids whose acidities closely match those of the acid under determination, but on acids whose absolute acidities have been determined independently. The bracketing technique assumes that exothermic proton transfer is rapid, which is almost always true. On a more practical level, the availability of comparison acids in a variety of acidity ranges can sometimes be problematic. Table I shows the acids we have used in this study as well as their acidities.[7]

SiH_4 is deprotonated in the flowing afterglow by $CH_3C{\equiv}C^-/HC{\equiv}CCH_2^-$ (380–382 kcal/mol) and F^- (371 kcal/mol), suggesting that it is more acidic than HF (thus, the $\Delta H°_{acid}$ of SiH_4 is less than 371 kcal/mol). Furthermore, H_3Si^- readily abstracts a proton from PH_3 (370 kcal/mol) while PH_2^- deprotonates SiH_4 with difficulty. This indicates that SiH_4 is less acidic than PH_3 ($\Delta H°_{acid}$ of SiH_4 is greater than 370 kcal/mol), but quite close to it. The literature value of 371.5 ± 2 kcal/mol and our measurements are, thus, in good agreement.

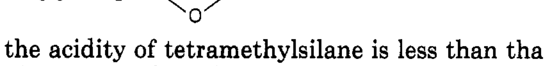
We next measured the acidity of tetramethylsilane, $(CH_3)_4Si$. Amide (404 kcal/mol) and the dimethylamide (396 kcal/mol) ion both abstract a proton giving $(CH_3)_3SiCH_2^-$ (eq 4). Hydroxide (391 kcal/mol) and methoxide (381 kcal/mol) ions both react by alternate paths as expected (eq 10 and 11). The M − 1 anion of fluorobenzene (387 kcal/mol)[7,8] reacts sluggishly with $(CH_3)_4Si$ giving $(CH_3)_3SiCH_2^-$. This α-silyl carbanion did abstract a proton from both fluorobenzene (387 kcal/mol) (eq 12) and furan (386 kcal/mol) (eq 13).[7] These experiments demonstrate that the acidity of tetramethylsilane is less than that of furan ($\Delta H°_{acid}$ of $(CH_3)_4Si$ greater than 386 kcal/mol) and very close to that of fluorobenzene at 387 kcal/mol.

$$(CH_3)_4Si \xrightarrow{OH^-} (CH_3)_3SiO^- + CH_4 \quad (10)$$

$$(CH_3)_4Si \xrightarrow{^-OCH_3} (CH_3)_4\overset{-}{Si}OCH_3 \quad (11)$$



(12)



(13)

The three methylsilanes that have both C–H and Si–H bonds are methylsilane, dimethylsilane, and trimethyl-

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[6] Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522.

[7] (a) Bartmess, J. E.; McIver, R. T., Jr., In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2. All acidity values quoted come from this source or an updated, but unpublished, version recently obtained from J. E. Bartmess. (b) DePuy, C. H.; Kass, S. R., Submitted for publication in *J. Am. Chem. Soc.* This paper reports the gas-phase acidities of a variety of heterocyclic compounds.

[8] Briscese, S. M. J.; Riveros, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 230. Bartmess has cited this paper in giving a 387 ± 6 kcal/mol ΔH_{acid} value for fluorobenzene. We have bracketed fluorobenzene between water (391 kcal/mol) and furan (386 kcal/mol) with experiments indicating its acidity is very close to that of furan. We have, thus, assigned it an acidity of 387 ± 3 kcal/mol.

silane. Their acid–base reactions have been probed by using N_2O to obtain information on their dual reactivity sites. In our earliest experiments, we thought that trimethylsilane provided a simple, though puzzling, story. Thus, when we obtained its M − 1 anion with amide ion (404 kcal/mol), we were able to show it resulted from exclusive proton abstraction from the carbon.[4] This was, of course, not the expected result given the respective acidities of 371 and 387 kcal/mol obtained for silane and tetramethylsilane. More recent studies have revealed that under certain conditions both the C–H and the Si–H abstraction products are present when trimethylsilane is deprotonated by base (eq 8). We have found that the product distribution is a sensitive function of the flow of trimethylsilane and that only under conditions with high trimethylsilane flows can $(CH_3)_3Si^-$ be detected, presumably by slow reaction of $(CH_3)_2HSiCH_2^-$ (which forms first and rapidly) and $(CH_3)_3SiH$. We have observed similar behavior for each of the methylsilanes. To measure both the C–H and Si–H acidities, we studied mixtures of the M − 1 anions of varying composition ranging from those very rich in the C–H abstraction product to ones which were approximately 50/50 in C–H and Si–H abstraction products. We determined the ratios by reaction with N_2O.

An M − 1 mixture rich in $(CH_3)_2HSiCH_2^-$ (4–5:1 over the silyl anion) abstracts a deuteron (proton) from CH_3OD (381 kcal/mol), furan (386 kcal/mol), and fluorobenzene (387 kcal/mol) giving, respectively, CH_3O^- and the M − 1 anions of furan and fluorobenzene. Both amide (404 kcal/mol) and dimethylamide (396 kcal/mol) ions react with trimethylsilane giving mixtures of C–H and Si–H abstraction products whose composition depends on the exact conditions used. It was impossible, however, to probe the reaction between the M − 1 anion of fluorobenzene (387 kcal/mol) and trimethylsilane because of the low reactivity of the trimethylsilane. Thus, when the required large flow of trimethylsilane is added, its small chloride ion impurity becomes magnified and the HCl_2^- so produced under these conditions dominates the m/z region around 73, which is also where the M − 1 ion of trimethylsilane is located. Thus, we can only crudely assign a C–H acidity of 391 ± 4 kcal/mol to trimethylsilane.

We have studied the Si–H acidity of trimethylsilane by preparing $(CH_3)_3Si^-$ from the reaction of hexamethyldisilane and F^- (eq 3).[2] This anion gives no reaction with D_2O (393 kcal/mol) or furan (386 kcal/mol); however, the corresponding alkoxide ions are obtained from ethanol (377 kcal/mol) and methanol (381 kcal/mol). The Si–H acidity of trimethylsilane then lies between 381 and 386 kcal/mol. We assign to it a value of 383 ± 3 kcal/mol. Interestingly, we can show that when a trimethylsilane M − 1 mixture contains both the C–H and Si–H abstraction products, it exhibits selective reactivity with furan (386 kcal/mol). Such a mixture does not totally react with furan, and the M − 1 left unreacted can be shown to be the Si–H abstraction product by downstream reaction with N_2O. Thus, the C–H abstraction product with a higher basicity (391 kcal/mol) reacts with furan while the less basic Si–H product (383 kcal/mol) is unreactive.

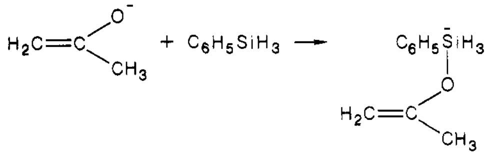
The situation is similar for both methylsilane and dimethylsilane. Each reacts with amide ion to give a mixture of C–H and Si–H abstraction products whose composition depends on the silane flow (eq 14 and 15). The α-silyl

$$CH_3SiH_3 \xrightarrow{NH_2^-} CH_3\overset{-}{Si}H_2 + H_3SiCH_2^- \qquad (14)$$

$$(CH_3)_2SiH_2 \xrightarrow{NH_2^-} (CH_3)_2\overset{-}{Si}H + CH_3SiH_2CH_2^- \qquad (15)$$

carbanion (C–H abstraction product) forms in a primary reaction and decreases with increasing silane flow while the silyl anion (Si–H abstraction) forms by complex secondary reactions with increasing silane flow. We have measured the C–H and Si–H acidities of methylsilane and dimethylsilane in the following way. Both of these silanes form an M − 1 anion mixture with amide (404 kcal/mol) and dimethylamide (396 kcal/mol) ion. Methylsilane sluggishly reacts with the M − 1 of fluorobenzene (387 kcal/mol) giving the M − 1 of methylsilane. Dimethylsilane also reacts sluggishly with the M − 1 of fluorobenzene; however, no corresponding M − 1 of dimethylsilane could be detected. When an M − 1 mixture of either methylsilane or dimethylsilane is rich in the C–H abstraction product and reacts with fluorobenzene, the M − 1 of fluorobenzene is obtained. This indicates that the ΔH°_{acid} of each of these methylsilanes is less than 396 kcal/mol. The C–H acidity of methylsilane is apparently quite close to that of fluorobenzene (387 kcal/mol) and is assigned a value of 388 ± 3 kcal/mol. That of dimethylsilane, because its M − 1 is not observed on reaction with the fluorobenzene anion, is assigned a value of 391 ± 3 kcal/mol. The Si–H acidity for both methylsilane and dimethylsilane has been determined by reactions with furan (386 kcal/mol) and CH_3OH (381 kcal/mol). M − 1 mixtures of either methylsilane or dimethylsilane react completely with CH_3OH, but only partially with furan. Downstream analysis with N_2O indicates that only the C–H abstraction product reacts with furan. Thus, the Si–H acidity of these two silanes is between 381 and 386 kcal/mol and is assigned a value 383 ± 3 kcal/mol.

We have also determined the Si–H acidity of phenylsilane, $C_6H_5SiH_3$, to be 370 ± 3 kcal/mol. Fluoride ion (371 kcal/mol) reacts with phenylsilane to give $C_6H_5SiH_2^-$. This anion has been characterized by reaction with N_2O, although it reacts quite sluggishly. Reaction of $C_6H_5SiH_2^-$ and acetone (368 kcal/mol) gave the M − 1 of acetone. Interestingly, the reverse reaction, that between the M − 1 of acetone and phenylsilane, cleanly gave the pentacoordinate siliconate (eq 16).



(16)

Discussion

The gas-phase acidities determined in this study (Table II) indicate (1) that there is little effect of methyl substitution on C–H acidity, (2) that, although there is a substantial difference in the Si–H acidities of silane and the methylsilanes, there is no methyl substitution effect on Si–H acidity for the methylsilanes, and (3) that phenyl substitution has no effect on Si–H acidity. We have observed contrasting behavior in carbon chemistry.[9] Indeed, kinetic acidity measurements of a series of weakly acidic hydrocarbons, $(CH_3)_nCH_{4-n}$, gave C–H acidities of 416.6, 421, 419, and 414 kcal/mol with n varying from 0 to 3, respectively. Although these values show no obvious monotonic trends, several comments are warranted. The values for methane, ethane, and the secondary C–H position of propane closely match high-level theoretical predictions. They indicate not only that the first methyl substitution affects (decreases) C–H acidity as it does for Si–H acidity in the silicon series but also that, in contrast to the silicon compounds, additional methyl substitution alters C–H acidity. We have noted that the tertiary C–H acidity of isobutane does not mirror the theoretical pre-

Table II. C–H and Si–H Acidities (in kcal/mol)

compd	C–H	Si–H
SiH_4		371 ± 2
CH_3SiH_3	388 ± 3	383 ± 3
$(CH_3)_2SiH_2$	391 ± 3	383 ± 3
$(CH_3)_3SiH$	391 ± 4	383 ± 3
$(CH_3)_4Si$	387 ± 3	
$C_6H_5SiH_3$		370 ± 3

Table III. Bond Dissociation Energies Used in This Study[10] (in kcal/mol)

compd	C–H	Si–H
SiH_4		90.3
CH_3SiH_3	*a*	89.6
$(CH_3)_2SiH_2$	*a*	89.4
$(CH_3)_3SiH$	*a*	90.3
$(CH_3)_4Si$	99.2	
$C_6H_5SiH_3$		88.2

[a] No known value.

Table IV. Calculated Electron Affinities (in kcal/mol)

anion	electron affinity
H_3Si^-	33 ± 3
$CH_3SiH_2^-$	20 ± 3
$(CH_3)_2SiH^-$	20 ± 3
$(CH_3)_3Si^-$	21 ± 3
$(CH_3)_3SiCH_2^-$	26 ± 3
$C_6H_5SiH_2^-$	32 ± 3

dictions, perhaps because of relief of strain in the cleavage reactions used to study these kinetic acidities. Kinetic acidity measurements of these weakly acidic hydrocarbons are the only way to "measure" such acidities since the corresponding carbanions are generally not bound or weakly bound states with respect to their corresponding carbon radicals. We also note that phenyl substitution has a large effect on acidity in carbon chemistry where toluene has a ΔH°_{acid} of 378.2 compared to that of methane (416.6 kcal/mol).[7]

In Table III the bond dissociation energies (BDE) for the silanes studied are given.[10] Though the C–H BDE's for methylsilane, dimethylsilane, and trimethylsilane are unknown, that for tetramethylsilane is 99 kcal/mol. The corresponding Si–H BDE's hardly vary at all, having values between 88 and 90 kcal/mol indicating that the corresponding silyl radicals have nearly the same stability. ΔH°_{acid}, BDE, the ionization potential of the hydrogen atom, and the electron affinity of A are related in a thermodynamic cycle[11] for the reaction $AH \rightarrow A^- + H^+$. Since we know the first three of these quantities for the Si–H bond of silane, phenylsilane, and the methylsilanes, we can estimate the electron affinities for the corresponding radicals (Table IV). The large difference between the Si–H acidities for silane or phenylsilane, and the methylsilanes is a reflection of the large difference between their electron affinities and, thus, gives us a measure of anion stability. With the addition of one or more methyl groups to silicon the electron affinity is lowered some 12 kcal/mol. Thus, the methyl-substituted silyl anions are less stable that H_3Si^-. Such a methyl lowering effect is apparently general[11] as both HO^- and HS^- have higher electron affinities than CH_3O^- and CH_3S^-. Similarly, CH_3^- has a higher electron affinity than that of the unbound ethyl anion.[9] Substitution of a phenyl group, however, has little effect on the stability of $C_6H_5SiH_2^-$. It has a binding energy quite close to that of H_3Si^- suggesting that delocalization of electron density by phenyl has no stabilizing role for $C_6H_5SiH_2^-$.

The C–H and Si–H acidities and C–H and Si–H reactivities, which clearly demonstrate that the less acidic C–H bond reacts with base faster than the Si–H bond, offer a stark and unusual contrast for gas-phase chemists. We have considered more than one possible explanation. For example, it is possible, though considered unlikely, that the more hindered Si–H bond in the methylsilanes is less reactive. It is also conceivable that these abstraction reactions occur exclusively through pentacoordinate adducts (siliconates) where, because of the mode of attack and the intermediate geometry, C–H reactivity is favored. To assess these as well as other possibilities, collaborative computational investigations have been undertaken using both MNDO and ab initio techniques.[12] These studies, largely directed toward explaining the differences between our acidity and reactivity measurements, are in progress and will be reported in due course. One result, however, calculated by Professor M. S. Gordon at the MP4-(SDQ)/6-31++G(d) level, indicates that $CH_3SiH_2^-$ is more stable than $H_3SiCH_2^-$ by 19.7 kcal/mol.[13] Other calculations have been reported and mirror our observed trends. Hopkinson and Lien, using a double-ζ basis set with polarization functions, find that $CH_3SiH_2^-$ is more stable than $H_3SiCH_2^-$ by between 13.5 and 28.7 kcal/mol, respectively, depending on the polarization function used.[14] Calculations of the Si–H acidity of SiH_4 and CH_3SiH_3, and the C–H acidity of CH_3SiH_3 vary in the same way as our experimental results;[14] however, the magnitude of their acidities do not match our results very well. Finally, we have considered a simple electrostatic explanation based on electron populations. This method developed by Bader[15] has more recently been applied by Wiberg[16] to methylsilane. In methylsilane, the Si–H hydrogen has an electron population of –0.752 while the C–H hydrogen is much more positive with a population of –0.048. Given such a large difference, it is not surprising that the C–H abstraction occurs more readily than Si–H abstraction. The computational studies in progress should provide additional insight on the stark differences between the thermodynamic and kinetic acidities discussed here.

Finally, we bring attention to what appears to be a general phenomenon which we are unable to explain. In contrast to a wide variety of anions that undergo H–D exchange with an appropriate source of deuterium, we have had no success in repeated attempts to carry out H–D exchange on either silyl anions or α-silyl carbanions. Furthermore, this appears common for second-row elements since sulfur and phosphorus anions of various types also undergo H–D exchange sluggishly or not at all.

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Registry No. SiH_4, 7803-62-5; CH_3SiH_3, 992-94-9; $(CH_3)_2SiH_2$, 1111-74-6; $(CH_3)_3SiH$, 993-07-7; $(CH_3)_4Si$, 75-76-3; $C_6H_5SiH_3$, 694-53-1; H_3Si^-, 15807-96-2; $CH_3SiH_2^-$, 75919-37-8; $(CH_3)_2SiH^-$, 111959-30-9; $(CH_3)_3Si^-$, 54711-92-1; $(CH_3)_3SiCH_2^-$, 88036-00-4; $C_6H_5SiH_2$, 31386-75-1.

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