Chemistry and Thermochemistry of Silicon-Containing Anions in the Gas Phase

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I. Introduction

Gas-phase studies of silicon-containing anions offer the potential for exploring the chemistry and fundamental properties of highly reactive neutral silicon species. In addition such studies serve as direct probes of the reactivity of silicon-containing anions that cannot be readily studied in the condensed phase. These studies are possible because a wide variety of such anionic species can be formed and are stable in the lower pressure regimes of gas-phase instruments. Thus, it has been possible to prepare anions whose corresponding properties are determined free from possible interfering solvent effects. Unusual bonding arrangements can be probed without the constraints of sterically bulky substitutents that are typically required for stabilization in condensed phase.

The reactivity of silicon-containing anions can be probed with an assortment of neutral reagents and this topic forms the basis of a large part of what we discuss in this review. Silicon anions provide the means to determine various thermochemical properties, in both direct and indirect ways. Gas-phase acidities, electron affinities, bond dissociation energies, heats of formation, and anion affinities are all accessible from various anion studies.

Reviews of both gas-phase positive and negative ion silicon chemistry have been published.[1-4] In considering only negative ion silicon chemistry in the present review, one of our major goals is to emphasize the application of negative ion gas-phase chemistry as a tool that reveals otherwise difficult to obtain information about silicon-containing species. Since our reviews of gas-phase negative ion silicon work in 1987, 1990, and 1993,[3-5] additional silicon studies have been undertaken. Many newer aspects of negative ion silicon chemistry will be considered in this chapter. Although gas-phase studies have been carried out using a variety of instrumental techniques, instrumental methods in and of themselves will not be emphasized here. Rather, we consider them only when required to understand the nature of a particular study. Computational chemistry has become an important adjunct to many silicon studies. The general subject of computational silicon chemistry will not be detailed here. However, some computational studies will be considered in this review not only because they provide a better understanding of the observed chemistry, but because they can provide chemical knowledge not easily obtained experimentally.

In section II, we will present a general discussion of how negative ion gas-phase studies are used to obtain various thermochemical properties. Section III will consider various specific examples of thermochemical properties of silicon-containing species obtained from negative ion gas-phase studies, comparing silicon and carbon analogs when possible. Finally, in section IV we will consider some of the various general aspects of the reactivity of silicon-containing anions. This will enable us to explore reactivity relationships, reaction mechanisms, and properties of silicon anions.

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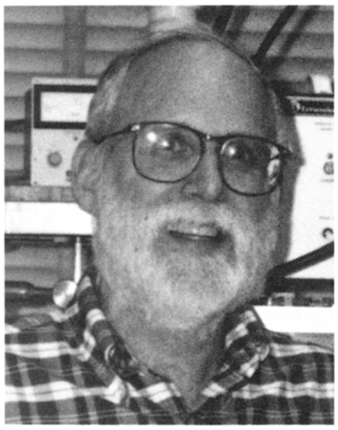
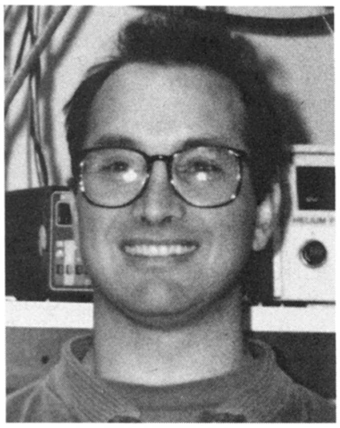


Robert Damrauer came to the University of Colorado at Denver in 1968 and built the first experimental laboratory on campus. Undergraduate, Master of Science, and postdoctoral students have carried out condensed-phase organosilicon research since that time. In 1980, Damrauer's research expanded to a more effluvial* phase when collaborative work with Charles H. DePuy and Veronica M. Bierbaum began at the University of Colorado in Boulder. The latter work has focused on the ion chemistry of the main group elements. Damrauer received his B.S. degree at the University of Michigan in 1963 and his Ph.D. working with Dietmar Seyferth at the Massachusetts Institute of Technology in 1967. He spent the following year at Harvard University working with Paul D. Bartlett.

*Effluvium (from *The American Heritage Dictionary of the English Language*): (1) an outflow or rising vapor of invisible or barely visible gas or particles; (2) foul-smelling vapor or fumes emanating from decaying matter; (3) an imaginary outflow of imponderable radiation or invisible vapor.



Joseph Hankin is an graduate student in organic chemistry at the University of Colorado at Boulder working with Robert Damrauer (in collaboration with Charles H. DePuy and Veronica M. Bierbaum). He was born in Chicago in 1955. He attended McGill University from 1973 to 1975, and completed a B.A. degree in Special Education in 1982 at the Northeastern Illinois University. After working with multiply handicapped children for several years, Joe completed a second B.A. in Biology (1989) and an M.S. in Chemistry (1992) at the University of Colorado at Denver. He is currently involved in several projects in gas-phase ion chemistry.

II. Negative Ion Gas-Phase Studies and Thermochemistry

Certain thermochemical properties of neutral molecules can be obtained from negative ion gas-phase studies.[6] Often, such properties can be more easily obtained from gas-phase ion studies than by other techniques. In this section, we outline in general terms some of the thermochemical cycles that have been used in negative ion gas-phase silicon chemistry. In section III, specific examples of their application will be given.

The thermochemical cycle shown in eq 1 links the gas-phase acidity of an acid, HA (ΔH_{acid}), with the bond dissociation energy of H–A (BDE), the electron affinity (EA) of the radical A, and the ionization potential of a hydrogen atom (IP):[6,7]

$$\begin{array}{llllr}
\text{H}-\text{A} & \longrightarrow & \text{H} + \text{A} & \text{BDE} & (1a) \\
\text{A} + e^- & \longrightarrow & \text{A}^- & -\text{EA} & (1b) \\
\text{H} & \longrightarrow & \text{H}^+ + e^- & \text{IP} & (1c) \\
\hline
\text{HA} & \longrightarrow & \text{H}^+ + \text{A}^- & \Delta H_{\text{acid}} = \text{BDE} - \text{EA} + \text{IP} & (1)
\end{array}$$

Equation 1 can be used to obtain different thermochemical parameters depending on what thermochemical information is already known about a system under study. For example, since the ionization potential of hydrogen atom is accurately known, gas-phase acidity measurements can be combined to obtain either electron affinities if bond dissociation energies are known or BDEs if EAs are known.[7,8] Similarly, if BDEs and EAs are known, gas-phase acidities may be obtained. While considerable effort has been placed on direct measures of BDEs and EAs, they are generally more difficult to measure than acidities. (It should be noted that eq 1 compares quantities generally measured at different temperatures. As a referee has pointed out, this leads to the implied assumption that the heat capacities of A and A^- do not vary between 0 and 298 K. Indeed, such temperature effects are generally small.) Thus, the relative ease of obtaining gas-phase acidities has made their measurement a central feature of many gas-phase ion studies and one of the subjects emphasized in this review.

Gas-phase acidities are generally measured by equilibrium, bracketing, or from collision-induced dissociation studies with proton-bound dimers.[6,8-10] Equilibrium studies are usually quite accurate and either are carried out by measuring the rate coefficients for the forward and reverse reactions between HA and a suitable base (B^-)[6,8] or by directly measuring the concentrations of A^- and B^- (eq 2). Two

$$\text{HA} + \text{B}^- \rightleftharpoons \text{A}^- + \text{HB} \qquad (2)$$

kinetic methods have been used to obtain gas-phase acidities. Bracketing determinations are carried out by allowing an anion (A^-) to react with a series of reference acids (HB's in eq 2).[6,8] Some of these acids transfer a proton to A^- to give HA; others do not. Assuming rapid proton transfer whenever a reaction is thermodynamically favorable, those HB acids reacting with A^- are more acidic than HA and those not reacting are less acidic than HA. By choosing HB acids carefully, a narrow acidity bracket (the range of acidity values between the closest reacting and nonreacting HB reference acids) can be obtained. Another method of accurately measuring acidities is the collision-induced dissociation method developed by Cooks and co-workers[9,10] in which proton-bound anion dimers are collisionally dissociated and the relative yields of the anions are related to their relative basicity. This method offers distinct advantages for accurate acidity determinations.[9-11] Equilibrium acidity measurements are often carried out, but are impossible for many unstable or otherwise difficult to obtain acids or in situtations when the acidities are too far apart. The bracketing method is often more flexible, particularly in terms of the problems that can beset equilibrium determination involving silicon species. As a result, acid–base bracketing measurements are commonly used in studying silicon-containing compounds.

Gas-phase acidities often have played a central role in the estimation of other thermochemical parameters; however, they can serve as links to these quantities only when information is available to complete the appropriate thermochemical cycles. For example, the heat of formation of acid H_2X can be determined from its acidity (eq 3), the heat of formation of H^+ (a well-known value),[6] and the heat of formation of HX^- (eq 4). The heats of formation

$$H_2X \longrightarrow H^+ + HX^- \qquad (3)$$

$$\Delta H_f(H_2X) = \Delta H_f(HX^-) + \Delta H_f(H^+) - \Delta H_{acid}(H_2X) \qquad (4)$$

of anions like HX^-, however, may not be as available as the heats of formation of neutral species.[6] If no such value is known, an independent determination must be made, which requires that relevant chemical behavior of HX^- can be probed. Thus, when HX^- reacts as a H^- donor, the hydride affinity ($\underline{HA}$) of X, as defined in eq 5, often can be determined by

$$HX^- \longrightarrow X + H^- \qquad (5)$$

bracketing experiments.[12] The hydride affinities for various neutral molecules have been compiled.[13] The heat of formation of HX^- can then be obtained from eq 6, since the heat of formation of many simple X

$$\Delta H_f(HX^-) = \Delta H_f(X) + \Delta H_f(H^-) - \underline{HA}(X) \qquad (6)$$

species are known,[6] the heat of formation of H^- is accurately known, and, under the circumstances just described, $\underline{HA}$ (X) can be determined.

Gas-phase acidities also can be used to determine the affinity of neutral X for Y^- , provided certain chemical behavior of the ion XY^-. Under favorable circumstances, affinity determinations can be made when the gas-phase species, XY^-, reacts with a series of reference acids, HB, according to eq 7 and a narrow bracket of the reference acids is obtained. Application of the themochemical cycle shown in eq 8 is possible when the acidities of both HB and HY are

$$XY^- + HB \longrightarrow X + HY + B^- \qquad (7)$$

$$\begin{array}{lll}
XY^- \rightarrow X + Y^- & \underline{YA}(X) \text{ Affinity of X for } Y^- & (8a) \\
HB \rightarrow H^+ + B^- & \Delta G_{acid}\ (HB) & (8b) \\
H^+ + Y^- \rightarrow HY & -\Delta G_{acid}\ (HY) & (8c) \\
\hline
XY^- + HB \rightarrow X + HY + B^- & \Delta G_{rxn} = \underline{YA}(X) + \Delta G_{acid}\ (HB) & \\
 & \quad - \Delta G_{acid}\ (HY) & (8)
\end{array}$$

known and when suitable estimates of the entropy of reaction 8a can be made.[14] Implicit in this analysis is a specific requirement that any intermediate species like $[YHB]^-$ fragment to the products shown without kinetic barriers. Although anion affinity measurements often can be made directly by gas-phase equilibrium measurements,[12,15,16] the method just described offers certain advantages, particularly when X cannot be easily obtained but XY^- can, or when X undergoes side reactions.

III. Thermochemical Properties from Negative Ion Gas-Phase Studies

A. Electron Affinities (EA)

The electron affinities (EA) of a number of silicon-centered and related carbon-centered radicals have been determined, primarily by electron detachment experiments of anions by Brauman, Lineberger, Ellison, Neumark, Leopold, and their respective co-workers.[17-28] Since the electron affinity is a measure of anion stability relative to the corresponding radical (eq 1b), the EA values listed in Table 1 illustrate the differences in stability between silicon- and carbon-centered anions as well as the effect of substitutuents on these differences. The simple silicon anions, Si^-, SiH^-, and SiH_2^- are quite stable with respect to electron detachment as Lineberger and co-workers have shown in measuring the laser photoelectron spectra of these anions.[19] They also thoroughly investigated the accessible excited states of these species. In a recent study, Reid showed that Si^+ and SiH^+ gave mixtures of their corresponding excited state anions in double collision charge inversion experiments.[29] The EA of Si_2 was recently determined by Neumark and co-workers[24] to be 50.8 kcal/mol, which is in close agreement with earlier work by Nimlos, Harding, and Ellison.[23] The EA of C_2 is approximately 76 kcal/mol.[24] In related work, the EAs of Si_3 and Si_4 were determined to be 53.0 and 50.0 kcal/mol (the EAs of C_3 and C_4 are 46.0 and 89.5 kcal/mol).[24] The electronic structures of these species are very complex and have yet to be fully understood. As Neumark noted, however, the similarities in their electronic structures are more striking than their differences. A number of *ab initio* studies have been carried out to help interpret the complex photoelectron spectroscopy of these species.[24,30-36] This computational work is an important adjunct to direct EA measurements for silicon-centered radicals, often serving as a test of the applicability of various computational approaches for the prediction of unknown EAs.

While the EAs of Si, C, SiH, and CH are all about 30 kcal/mol, the EAs of SiH_2 and SiH_3 are considerably larger than those of their carbon analogs (Table 1). These differences are similar to those found for many substituted silicon-centered radicals. Fully saturated silicon and carbon anions illustrate this in greater detail. Typically the silicon anions are quite stable with respect to electron detachment while their carbon analogs have a weakly bound electron (small EA) or are unstable (negative EA). Increased alkyl substitution at silicon-centered radicals attenuates EA values, but usually not in such a dramatic fashion as for SiH versus CH_3Si. Decreases in the EA upon alkyl substitution are not strictly a silicon phenomenon. Computational studies comparing CH and CH_3C indicate a similar trend and suggest that CH_3C^- is unstable with respect to the loss of an

Table 1. Electron Affinities (EA) of Representative Silicon- and Carbon-Centered Radicals

silicon-centered radical	EA (kcal/mol)	carbon-centered analog	EA (kcal/mol)
Si	31.9[17]	C	29.1[17]
SiH	29.4[17]	CH	28.5[17]
CH_3Si	19.6[18]	CH_3C	
SiH_2	25.9[17]	CH_2	15.0[17]
SiH_3	32.4[17]	CH_3	1.84[17]
SiD_3	32.0[17]	CD_3	
CH_3SiH_2	27.5[17]	CH_3CH_2	−6.4[27]
$(CH_3)_2SiH$	24.7[17]	$(CH_3)_2CH$	−9.5[27]
$(CH_3)_3Si$	22.4[17]	$(CH_3)_3C$	−5.9[27]
$C_6H_5SiH_2$	33.1[17]	$C_6H_5CH_2$	19.9[17]
$C_6H_5(CH_3)SiH$	30.7[17]	$C_6H_5(CH_3)CH$	
$(CH_3)_3CSiH_2$		$(CH_3)_3CCH_2$	4.8[25,26,27]
$(CH_3)_3SiSiH_2$		$(CH_3)_3SiCH_2$	21.9[28]
$(CH_3)_2(H)SiSi(CH_3)_2$	32.3[22]	$(CH_3)_2SiHC(CH_3)_2$	
$[(CH_3)_3Si]_2SiH$	44.7[22]	$[(CH_3)_3Si]_2CH$	36.0[22]
$[(CH_3)_3Si]_3Si$	46.8[22]	$[(CH_3)_3Si]_3C$	
SiF_3	<68.0[17]	CF_3	
Si_2	50.8[24]	C_2	75.5[24]
Si_3	53.0[24]	C_3	46.0[24]
Si_4	50.0[24]	C_4	89.5[24]
$CH_2{=}SiH$	46.4[18]	$CH_2{=}CH$	15.4[17]

electron.[31] Thus, the EA of CH is listed as 28.5 kcal/mol in Table 1, but a value for CH_3C would presumably be negative. (The result of the CH_3C computational study has been questioned and CH_3C^- may well be bound[37]). The silabenzyl anion and H_3Si^- have nearly identical relative stabilities, indicating that phenyl conjugative stabilizing effects are not important at silicon centers.[20,38] Methyl substitution effects are small, but the replacement of a hydrogen by a methyl group at a silicon center consistently decreases the relative stability of the corresponding silicon anion (CH_3SiH_2, $(CH_3)_2SiH$, and $(CH_3)_3Si$ have EAs of 27.5, 24.7, and 22.4, repectively).[20,22] A similar trend has been observed for $C_6H_5SiH_2$ and $C_6H_5Si(CH_3)H$.[20]

The negative EAs listed in Table 1 for three alkyl radicals have been indirectly determined in a kinetic study that serves to illustrate the role negative ion silicon chemistry can play in providing information in other areas of chemistry (see section IV.A.1 on reactivity for greater detail). Although a discussion of carbanion stability is beyond the scope of this review, we emphasize that "negative EAs" for various alkyl anions have been considered both computationally[39] and experimentally.[25–27,40]

Recent studies by Brinkman, Berger, and Brauman have considered the effects of silicon substitution on silicon- and carbon-centered species.[22] Silicon substitutions of these anions dramatically increase their stability. The substitution of one silicon group gives an EA of 32.3 kcal/mol for $(CH_3)_2(H)SiSi(CH_3)_2$, which is about a 10 kcal/mol increase in stability over $(CH_3)_3Si$. Additional silicon substitutions in $[(CH_3)_3Si]_2SiH$ and $[(CH_3)_3Si]_3Si$ give EAs of 44.7 and 46.8 kcal/mol, respectively. The effect of silyl substitution at a carbon-centered radical is even more dramatic. Earlier studies by Brauman and co-workers found the EA of $(CH_3)_3SiCH_2$ to be 21.9 kcal/mol and estimated that of $(CH_3)_3CCH_2$ to be 4.8 kcal/mol, showing that a trimethylsilyl substitution on carbon has about the same stabilizing effect as a phenyl group.[28] A second silicon substitution in $[(CH_3)_3Si]_2CH$ increases the EA about another 14 kcal/mol. These studies will be considered in more detail in the section on gas-phase acidities.

Bengali and Leopold recently reported the EA of $CH_2{=}SiH$, an interesting low-coordinate silicon-centered radical.[18] Their findings once again demonstrate the greater stability of a silicon- over a carbon-centered anion. Indeed, the difference in the EA between $CH_2{=}SiH$ and $CH_2{=}CH$ is among the largest given in Table 1.

B. Bond Dissociation Energies (BDE)

When appropriate acidity data are available (eq 1), EA measurements like those just discussed can be used to estimate Si−H and C−H bond dissociation energies (BDE).[20,41] Although BDEs calculated this way are generally in good agreement with bond energy determinations by other methods, they sometimes do not resolve small differences in substitutent effects.[42,43] Table 2 presents a limited number of BDEs related to the silicon-containing radicals and anions discussed in the previous section. These data are a mix of values calculated from EAs and gas-phase acidities (eq 1),[20,21] values obtained from other experimental techniques,[22] and predicted values derived from computational studies.[44] Various other sources, both experimental and computational, should be consulted for a more comprehensive discussion of silicon BDEs.[42,43]

Experimental estimates of the effect of methyl substitution at silicon-centered radicals are not refined enough to show any trends. They consistently give a Si−H BDE very close to 90 kcal/mol.[42,43] Computational studies, on the other hand, indicate a very small increase in the Si−H BDE with increasing methyl substitution.[44] As a result, various authors have come to depend more and more on computational studies for BDEs, particularly using these and EAs to estimate gas-phase acidities.[22] An opposite trend in Si−H BDEs is observed both experimentally[22] and computationally[45] for silicon substitution at a silicon center. Thus, the substitution of SiH_3 for hydrogen decreases the Si−H BDE more than 4 kcal/mol ($H_3Si{-}H$ versus $SiH_3SiH_2{-}H$). Additional silicon substitution in $[(CH_3)_3Si]_3Si{-}H$ decreases the Si−H bond strength an additional 6 kcal/mol. A similar decreasing trend in C−H BDEs is suggested for silicon substitution on carbon centers

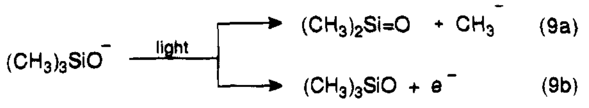
Table 2. Si−H and C−H Bond Dissociation Energies (BDE)

	BDE (kcal/mol)		
compound	from eq 1	estimated or from other experiments	from computational sources
$H_3Si{-}H$	90.3[21] 91.6[20]	90.3[42,43]	91.7[44]
$CH_3SiH_2{-}H$	92.2[20]	~89.6[42,43]	92.4[44]
$(CH_3)_2SiH{-}H$		92[22] ~89.4[42,43]	93.5[44]
$(CH_3)_3Si{-}H$	≥91.0[20]	~90.3[42,43]	94.6[44]
$C_6H_5SiH_2{-}H$	90.2[20]	~88.2[42,43]	
$C_6H_5(CH_3)SiH{-}H$	91.3[20]		
$SiH_3SiH_2{-}H$		86.3[22]	89.5[22]
$(SiH_3)_2SiH{-}H$			86.3[22]
$(CH_3)_3SiSi(CH_3)_2{-}H$		85.3[22]	
$[(CH_3)_3Si]_3Si{-}H$		79.0[22]	
$(CH_3)_3SiCH_2{-}H$		99.2[42,43] 98.5[22]	
$[(CH_3)_3Si]_2CH{-}H$		96[22]	
$CH_2{=}SiH{-}H$			97[44]
$CH_3Si{-}H$			78[44]

with the C−H BDE in $[(CH_3)_3Si]_2CH{-}H$ being about 3 kcal/mol weaker than that in $(CH_3)_4Si$.[22] Finally, Si−H BDEs computed by Allendorf and Melius were used as part of the photoelectron spectroscopy study of Bengali and Leopold and are given in Table 2.[18,44] Although the $CH_3Si{-}H$ BDE of 78 kcal/mol is consistent with a crude value reported for HSi−H of 77 kcal/mol,[42] the computational results for $CH_3SiH_2{-}H$, $CH_3SiH{-}H$, and $CH_3Si{-}H$ (92, 68, and 78 kcal/mol, respectively) seem to defy simple explanation.[44] The 97 kcal/mol BDE value for $CH_2{=}SiH{-}H$ is interesting to compare with that for $CH_2{=}CH{-}H$ (110 kcal/mol).[18]

Negative ion gas-phase chemistry has also provided information on the question of π-bond strengths of the silicon-to-carbon and silicon-to-oxygen double bonds. In a recent study Allison and McMahon report the π-bond strengths of several substituted silenes.[46] Proton affinity (positive ion chemistry) and fluoride affinity (negative ion chemistry) measurements (see section III.E) have been used in two different thermochemical cycles, thus giving independent measures of the π-bond strengths of $(CH_3)_2Si{=}CH_2$ (39 kcal/mol), $(CH_3)FSi{=}CH_2$ (45 kcal/mol), and $F_2Si{=}CH_2$ (50 kcal/mol). These values as well as those from related *ab initio* calculations indicate that increasing fluorine substitution enhances the Si=C π-bond strength. Estimates of the π-bond strengths of the analogous alkenes using Benson additivity calculations are 57, 60, and 66 kcal/mol. Allison and McMahon have also estimated that the Si−F BDE in these compounds is 137−148 kcal/mol and that the Si−F BDE in $(CH_3)_3SiF$ is about 130 kcal/mol. This latter value appears to be too small based on other ion-molecule studies. Since F^- reacts with allyltrimethylsilane to give allyl anion, then combining the EAs of both F (78 kcal/mol)[6] and allyl (8 kcal/mol)[6] and the BDE of allyltrimethylsilane (70 kcal/mol)[42] would give a minimum value for the Si−F BDE in $(CH_3)_3SiF$ of 140 kcal/mol, assuming that the heat of reaction is 0 kcal/mol. Since the reaction is likely exothermic, the Si−F BDE would be larger still.

Brauman and co-workers estimated a 62 kcal/mol upper limit on the π-bond strength in $(CH_3)_2Si{=}O$ in a study of laser-induced fragmentation of $(CH_3)_3SiO^-$ (eq 9).[47] Analysis of the energetics of these reaction



channels, as well as those of the related fragmentation of $(CH_3)_2(H)SiO^-$, allows their π-bond strengths to be estimated. Comparison of this experimental estimate with computated values obtained for simple silanones suggests that an upper limit of 62 kcal/mol is reasonable.

C. Acidities (ΔH_{acid})

1. Tetracoordinate Species

A large number of gas-phase acidities are known from negative ion gas-phase experiments.[6] The gas-phase acid strengths of several tetracoordinate silicon-containing compounds are given in Table 3.[6,20,22,38,46,48−51] These are arranged by silicon substitution pattern and compared with analogous carbon species. Since gas-phase acidity reactions are always endothermic, larger values of ΔH_{acid} correspond to weaker acids. The acidities have been arranged to emphasize two different substitution effects on silicon. The α-effect shows how substituents on silicon affect the Si−H acidity. The β-effect probes how changing substitution patterns on silicon affect the acidity of an adjacent C−H, O−H, or N−H group.

Cursory examination of both the α- and β-effect acidities indicates that silicon-containing compounds tend to be more acidic than their carbon analogs. The difference can be large as in the case of SiH_4 and CH_4 (~40 kcal/mol) or quite small as recorded for $C_6H_5(CH_3)SiH_2$ and $C_6H_5(CH_3)CH_2$ (~6 kcal/mol). The α-effect shows a pronounced narrowing of the acidity difference between silicon and carbon species as substituents that classically have large conjugative effects at carbon are incorporated on silicon and carbon. Such "conjugative" substituents have a much greater acid strengthening effect on C−H than on Si−H centers. Thus, both SiH_4 and $C_6H_5SiH_3$ have the same acidity while CH_4 and $C_6H_5CH_3$ differ by some 40 kcal/mol. Alkyl substitution effects, on the other hand, are somewhat larger at silicon, since $(CH_3)_3SiH$ is a weaker acid than SiH_4 by about 10 kcal/mol and $(CH_3)_3CH$ is reported to be only a slightly stronger acid than CH_4. Thus, the gap narrows in one case because conjugation is important on carbon but not on silicon, and in the other case because α-alkyl substitution effects decrease the acidity of silanes, but have a smaller effect on carbon compounds. Because α-alkyl substitution effects likely incorporate both acid strengthening dispersion (polarization) and acid weakening inductive effects,[5,27,40] they are by no means simply estimated.

The thermochemical cycle given in eq 1 often is useful for evaluating the dominant effects in a particular acidity comparison. For example, both the BDEs and EAs (see Tables 1 and 2) contribute to the increased acidity of SiH_4 compared to CH_4: the BDE of CH_4 is stronger by 15 kcal/mol than that of SiH_4 and the EAs show H_3Si^- to be more stable to electron detachment than H_3C^- by more than 30 kcal/mol. The effects of methyl α-substitution are complex in alkanes, with the first alkyl substitution (methane to ethane) decreasing C−H acid strength and each additional one increasing it.[27,40] This results from the competing effects indicated above. Thus, the first methyl substitution inductively destabilizes the carbanion, but additional methyl substitutions stabilize carbanions as polarization effects overcome inductive ones. This is not the case in the silicon series where Brauman and co-workers have recently shown that the first methyl substitution (silane to methylsilane) gives a fairly large decrease in Si−H acid strength.[20,22] Additional α-methyl groups lead to small decreases in Si−H acidity with each substitution. The acid weakening effects of α-methyl substitution in silanes is dominated by the EAs. This is made clear by reference to Table 1, which shows that the corresponding silicon-centered radicals have decreasing EAs with α-methyl substitution (about 2−4 kcal/mol per methyl), and to Table 2, which shows that the

Table 3. Gas Phase Acidities of Tetracoordinate Silicon and Carbon Compounds[a]

silicon compound	ΔH_{acid}[a] (kcal/mol)	carbon analog	ΔH_{acid}[a] (kcal/mol)
α-Effect			
$H_3Si-\underline{H}$	373 (E)[20] 371 (B)[38]	$CH_3-\underline{H}$	417[27]
$CH_3SiH_2-\underline{H}$	378 (E)[20]	$CH_3CH_2-\underline{H}$	420[27]
$(CH_3)_2SiH-\underline{H}$	383 (B)[38] 380 (D)[22]	$(CH_3)_2CH-\underline{H}$	419[27]
$(CH_3)_3Si-\underline{H}$	383 (B)[38] ≥382.8 (E)[20]	$(CH_3)_3C-\underline{H}$	413[27]
$C_6H_5SiH_2-\underline{H}$	370 (B)[38] 371 (E)[20]	$C_6H_5CH_2-\underline{H}$	381[6]
$C_6H_5(CH_3)SiH-\underline{H}$	374 (E)[20]	$C_6H_5(CH_3)CH-\underline{H}$	380[6]
$(CH_3)_2(H)SiSi(CH_3)_2-\underline{H}$	366 (D)[22]	$(CH_3)_2(H)SiC(CH_3)_2-\underline{H}$	
$[(CH_3)_3Si]_2SiH-\underline{H}$	352 (D)[22]	$[(CH_3)_3Si]_2CH-\underline{H}$	374 (D)[22]
$[(CH_3)_3Si]_3Si-\underline{H}$	346 (D)[22]	$[(CH_3)_3Si]_3C-\underline{H}$	
$[(CH_3)_3Si]_2N-\underline{H}$	356 (E)[48]	$[(CH_3)_3C]_2N-\underline{H}$	
β-effect			
$H_3SiCH_2-\underline{H}$	388 (B)[38]	$H_3CCH_2-\underline{H}$	420[27]
$CH_3SiH_2CH_2-\underline{H}$	391 (B)[38]	$CH_3CH_2CH_2-\underline{H}$	416[27]
$(CH_3)_2SiHCH_2-\underline{H}$	391 (B)[38]	$(CH_3)_2CHCH_2-\underline{H}$	413[27]
$(CH_3)_3SiCH_2-\underline{H}$	391 (D)[28]	$(CH_3)_3CCH_2-\underline{H}$	409[27]
$F(CH_3)_2SiCH_2-\underline{H}$	387 (B)[46]	$F(CH_3)_2CCH2-\underline{H}$	
$F_2(CH_3)SiCH_2-\underline{H}$	379 (B)[46]	$F_2(CH_3)CCH_2-\underline{H}$	
$F_3SiCH_2-\underline{H}$	367 (B)[46]	$F_3CCH_2-\underline{H}$	
$H_3SiNH-\underline{H}$	375 (B)[50]	$H_3CNH-\underline{H}$	403[6]
$(CH_3)_3SiNH-\underline{H}$	378 (B)[48]	$(CH_3)_3CNH-\underline{H}$	397[49]
$FSiH_2NH-\underline{H}$	373 (B)[50]	$FCH_2NH-\underline{H}$	
$C_6H_5SiH_2NH-\underline{H}$	373 (B)[50]	$C_6H_5CH_2NH-\underline{H}$	
$CH_3OSiH_2NH-\underline{H}$	375 (B)[50]	$CH_3OCH_2NH-\underline{H}$	
$CH_3SiF_2NH-\underline{H}$	370 (B)[50]	$CH_3CF_2NH-\underline{H}$	
$H_3SiO-\underline{H}$	359 (B)[51]	$H_3CO-\underline{H}$	380[6]
$CH_3SiH_2O-\underline{H}$	360 (B)[51]	$CH_3CH_2O-\underline{H}$	377[6]
$(CH_3)_2SiHO-\underline{H}$	360 (B)[51]	$(CH_3)_2CHO-\underline{H}$	376[6]
$(CH_3)_3SiO-\underline{H}$	360 (B)[51] 362 (B)[48]	$(CH_3)_3CO-\underline{H}$	375[6]
$CH_3CH_2(CH_3)_2SiO-\underline{H}$	360 (B)[51]	$CH_3CH_2(CH_3)_2CO-\underline{H}$	
$(CH_3CH_2)_2(CH_3)SiO-\underline{H}$	360 (B)[51]	$(CH_3CH_2)_2(CH_3)CO-\underline{H}$	372[6]
$(CH_3CH_2)_3SiO-\underline{H}$	360 (B)[51] 358 (E)[48]	$(CH_3CH_2)_3CO-\underline{H}$	
$C_6H_5SiH_2O-\underline{H}$	355 (B)[51]	$C_6H_5CH_2O-\underline{H}$	370[6]
$C_6H_5(CH_3)_2SiO-\underline{H}$	360 (B)[51]	$C_6H_5(CH_3)_2CO-\underline{H}$	
$C_6H_5(CH_3)SiHO-\underline{H}$	357 (B)[51]	$C_6H_5(CH_3)CHO-\underline{H}$	
$CH_3O(CH_3)_2SiO-\underline{H}$	360 (B)[51]	$CH_3O(CH_3)_2CO-\underline{H}$	
$(CH_3O)_2(CH_3)SiO-\underline{H}$	355 (B)[51]	$(CH_3O)_2(CH_3)CO-\underline{H}$	
$(CH_3O)_3SiO-\underline{H}$	355 (B)[51]	$(CH_3O)_3CO-\underline{H}$	
$(CH_3O)_2SiHO-\underline{H}$	355 (B)[51]	$(CH_3O)_2CHO-\underline{H}$	
$F(CH_3)_2SiO-\underline{H}$	355 (B)[51]	$F(CH_3)_2CO-\underline{H}$	
$F_2(CH_3)SiO-\underline{H}$	347 (B)[51]	$F_2(CH_3)CO-\underline{H}$	
$F_3SiO-\underline{H}$	340 (B)[51]	$F_3CO-\underline{H}$	
$Cl_3SiO-\underline{H}$	325 (B)[51]	$Cl_3CO-\underline{H}$	

[a] B = bracketing acidity measurement. E = equilibrium acidity measurement. D = acidity measurement derived from BDEs and EAs.

relevent BDEs change very little.[22] Nearly identical BDEs and EAs for the relevent silicon species help explain the similar acid strengths of $C_6H_5SiH_3$, $C_6H_5(CH_3)SiH_2$, and SiH_4. In contrast, the large acid strength differences between CH_4 and $C_6H_5CH_3$ is a consequence of quite different BDEs and EAs for the relevant carbon analogs. CH_4 has a stronger C−H bond than $C_6H_5CH_3$ and CH_3^- is a far less stable anion than $C_6H_5CH_2^-$.

Brinkman, Berger, and Brauman recently reported large effects on acidities when silanes are α-substituted by silicon groups.[22] A single α-silicon substitution gives an acid strengthening of about 14 kcal/mol (compare $(CH_3)_2SiH_2$ and $(CH_3)_2(H)SiSi(CH_3)_2H$). A second silicon substitution increases the acidity by about 14 kcal/mol more; a third, by 6 kcal/mol (to $[(CH_3)_3Si]_2SiH_2$ and $[(CH_3)_3Si]_3SiH$, respectively). These effects are consequences of increasing EA and decreasing BDE values with α-silyl substitution. Brinkman, Berger, and Brauman comment that these are huge effects considering the inherent stability of silyl anions. α-Silicon substitution at both carbon and nitrogen in $[(CH_3)_3Si]_2CH_2$ and $[(CH_3)_3Si]_2NH$ also increases acid strength (by approximately 17 and 22 kcal/mol over $(CH_3)_3SiCH_3$ and $(CH_3)_3SiNH_2$, respectively).[22,48]

The effect of β-methyl substitution on C−H acidity is more regular for the alkanes with each β-methyl addition leading to an increase in acid strength.[5,27,40] Neopentane is some 11 kcal/mol more acidic than ethane with the dominating effect being attributable to polarization effects. Polarization effects of this type are common in gas-phase behavior and were first carefully considered in pioneering studies by Brauman and Blair on the gas-phase acidity of alcohols and amines.[52,53] Brauman and Blair discovered that incremental β-methyl substitution leads to monotonic increases in acid strength with *tert*-butyl alcohol being more acidic than ethyl alcohol in the gas-phase. In protic solvents, the acid strength of alcohols decreases with incremental β-methyl substitution.

β-Methyl substitution on silicon shows no such effect (Table 3).[27,40] We see that C−H acidity in the series $(CH_3)_nSi(H)_{3-n}CH_2\text{-}\underline{H}$ varies only slightly and certainly does not show a monotonic acid strengthening with β-methyl substitution. Such results are consistent with an interpretation that the two major competing substituent effects, inductive and polarization, have about the same magnitude here. The polarization effect, which has an r^{-4} distance dependence,[54] is attenuated relative to the inductive effect (r^{-2} distance dependence)[54] in the silicon versus alkane series because the critical distances are greater in the silicon series.[55]

When β-substitutions other than methyl are made at silicon, there are greater effects on C−H acidity. Allison and McMahon have shown that substitution of a methyl by fluorine to give $(CH_3)_3SiF$ increases C−H acid strength by about a 4 kcal/mol over $(CH_3)_4Si$.[46] Two more fluorine-for-methyl substitutions giving $(CH_3)_2SiF_2$ and CH_3SiF_3 increase acid strength by an additional 8 and 12 kcal/mol. Although these substituent effects are in line with what we expect from the strongly electron withdrawing fluorine, we will see that such simple expectations based on our understanding of carbon substituent effects will not always work with silicon compounds.

Silaamines are more acidic than the corresponding silaalkanes by the same amount that NH_3 (404 kcal/mol) is more acidic than CH_4 (417 kcal/mol), indicating that there is no special silicon substitution effect in amines (compare H_3SiNH_2 and H_3SiCH_3).[20,50] That is, silyl substitution has similar effects on N−H and C−H acidities. Silyl substitution also increases N−H acid strength relative to carbon substitution. Thus, the N−H acid strength of SiH_3NH_2 and $(CH_3)_3SiNH_2$[6] are about 20 kcal/mol greater than those of CH_3NH_2 and $(CH_3)_3NH_2$. The effect on N−H acidity of other β-substitutions at silicon is similar to analogous β-substitutions in methylsilanes, although the magnitude of the effects for fluorine substitution are smaller. Thus, three β-methyl substitutions (SiH_3NH_2 to $(CH_3)_3SiNH_2$) decrease acid strength by 3 kcal/mol, β-C_6H_5 and β-CH_3O substitutions have very small effects, and two β-fluorine substitutions increase N−H acid strength by about 5 kcal/mol.[50]

Silanols have been studied in more detail than either of the less acidic silaalkanes or silaamines.[51] The O−H acidity of SiH_3OH is 29 kcal/mol greater than the C−H acidity of CH_3SiH_3, which is much the same as the difference between water and CH_4 (26 kcal/mol). In parallel with N−H acidity in amines, silicon substitution has little effect on differences between O−H and C−H acidity. β-Methyl and ethyl substituent effects at silicon are very small. Thus, the O−H acidity of alkyl silanols are virtually indistinguishable using bracketing methods. It is particularly important to point out here that substituent effect studies of silanol acidities cannot be carried out in a direct way since few silanols are easily synthesized. A bracketing study was made possible by the preparation of a wide variety of siloxide anions by reaction of hydroxide with various silanes (see eq 23 in section IV.A.1). It was determined that methyl-, dimethyl-, and trimethylsilanol as well as three ethyl-substituted silanols are more acidic than silanol itself, but only by a very small amount. Grimm and Bartmess have reported slightly different acidity values for β-alkyl-substituted silanols.[48] They report that $(CH_3CH_2)_3SiOH$ is about 4 kcal/mol more acidic than $(CH_3)_3SiOH$, attributing this difference to "known substituent effects". In contrast, we have suggested that the nearly identical acidity of these silanols results from a balance between polarization and inductive effects. Since this is not an easy matter to resolve experimentally, we undertook computational studies in collaboration with M. S. Gordon to try to assess the effect of β-methyl and ethyl substitution on silanol acidity.[56] These *ab initio* computations at various levels demonstrated very small substitution effects (MP4/6-31++G(d,p) for $CH_3CH_2SiH_2OH$ and MP4/6-311++G-(2d,2p) for H_3SiOH and CH_3SiH_2OH with all structures optimized at the HF/6-31G(d) level). The acidities of SiH_3OH, CH_3SiH_2OH, and $CH_3CH_2SiH_2OH$ were within 1 kcal/mol of each other at MP4/6-31++G(d,p). At MP4/6-311++G(2d,2p), CH_3SiH_2OH was 1.5 kcal/mol less acidic than SiH_3OH. Such computations do not unequivocally resolve this issue, particularly in terms of multiple ethyl substitutions. They are, however, consistent with the very small effects previously observed and do not suggest an acid-strengthening effect of single β-ethyl substitution. Other experimental evidence bearing on this point shows that β-methyl substitutions of $C_6H_5SiH_2OH$ (i.e. $C_6H_5(CH_3)(H)SiOH$ and $C_6H_5(CH_3)_2SiOH$) decrease O−H acidity.[51]

Other aspects of silanol acidities are interesting as well. $C_6H_5CH_2OH$ and $C_6H_5SiH_2OH$ have acid strengths of 370 and 355 kcal/mol compared to 380 kcal/mol for CH_3OH and 359 kcal/mol for SiH_3OH.[51] Since the phenyl substituent cannot interact conjugatively in either benzyl alcohol or $C_6H_5SiH_2OH$, polarization and inductive effects must account for the acidity increases.[54,57] The acid strengthening effect of β-phenyl substitution is larger for the alcohols than the silanols because the distance is shorter. The silanol is somewhat more acidic with phenyl substitution although the difference relative to the alcohols is attenuated.

Silanol acid strengths vary from small to quite large when all three hydrogens of SiH_3OH are replaced.[51] Thus, $(CH_3O)_3SiOH$, F_3SiOH, and Cl_3SiOH have acidity values of 355, 340, and 325 kcal/mol compared with that of 359 kcal/mol for H_3SiOH. The extremely high acid strength of Cl_3SiOH places it among the very strong gas-phase acids, comparable in acidity to HNO_3 and HBr (both 324 kcal/mol).[6] The greater acidity of Cl_3SiOH over F_3SiOH may at first be surprising, but such effects have also been reported for $HCCl_3$ and HCF_3 (358 and 375 kcal/mol).[6,58]

The difficulty of obtaining experimental acidities for a number of tetra-coordinate silicon species has led to a systematic computational study of the Si−H and element−H (that is, C−H, N−H, and O−H) acidities of $XSiH_2CH_3$, $XSiH_2NH_2$, $XSiH_2OH$, X_2SiHCH_3, X_2SiHNH_2, and X_2SiHOH.[59] These acidity values obtained using G2 methodology[60] were compared with acidity values from other computational

Table 4. Si−H and Element−H Acidities of Tetracoordinate Silicon Compounds Obtained by G2[60] *ab Initio* Computations[59]

compound	Si−H acidity[a]	element−H[a] (element = C, N, or O)
SiH_3CH_3	379	390
$FSiH_2CH_3$	377	378
F_2SiHCH_3	370	376
SiH_3NH_2	380	375
$FSiH_2NH_2$	378	368
F_2SiHNH_2	370	361
SiH_3OH	378	356
$FSiH_2OH$	375	348
F_2SiHOH	360	341

[a] These G2 values correspond to ΔH_{acid} at 0 K.

studies.[61,62] In evaluating the effect of silicon substitution on the Si−H and element−H acidities for X = H and F, some surprising new findings have been obtained (Table 4). A striking feature of these and others' results is the insensitivity of Si−H acidities to substitution on silicon, even when silicon is substituted by several electronegative substituents. Thus, the six silanes ($XSiH_2CH_3$, $XSiH_2NH_2$, and $XSiH_2OH$) have Si−H acidities between 375 and 380 kcal/mol with five of the six compounds having values between 377 and 380 kcal/mol. Gordon and Volk have computed the Si−H acidity of SiH_3X for X = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl at the MP4/MC-311++G(3df,2pd)//6-31G(d) level.[61] Their results, those of previous workers, and the G2 results are qualitatively the same. They show that electronegative substituents tend to increase acid strength when substituted on silicon, but that the effects are small. These studies also show that a NH_2 substitution weakens acidity relative to CH_3 substitution. Rodriquez and Hopkinson have recently studied the acidities of polyhalogenated silanes (SiH_nX_{4-n} for X = F and Cl and n = 1−4) to explore the so-called negative hyperconjugation effect.[63] They found that a first Cl substitution increases acidity by about 13 kcal/mol, but that the effect with F is much smaller (4 kcal/mol). Additional substitutions enhanced acidities linearly for Cl. With F, on the other hand, negative hyperconjugation is suggested to explain the effect of a small acidity strengthening on first substitution (4 kcal/mol at MP4SDTQ/6-31++G(d,p)//6-31++G(d,p)) followed by larger acidity increases with more fluorine substitution (8 and 16 kcal/mol for the second and third substitution). Our results in Table 4, although generally similar, show smaller first F substitution effects. Interestingly, the effect of the first fluorine substitution on SiH_3NH_2 and SiH_3OH is no different than that on SiH_3CH_3 even though $FSiH_2NH_2$ and $FSiH_2OH$ have two electronegative groups that might strongly interact by negative hyperconjugation.

The G2 results can be compared with an earlier study by Hopkinson and Lien in which the energy differences between the structures obtained by Si−H and element−H loss for SiH_3CH_3, SiH_3NH_2, and SiH_3OH were computed.[62] They observed that $^-SiH_2CH_3$ was more stable than $SiH_3CH_2^-$ by about 14 kcal/mol, that $^-SiH_2NH_2$ was more stable than SiH_3NH^- by about 2 kcal/mol, but that element−H loss from SiH_3OH gave the more stable structure (by about 22 kcal/mol). The G2 results contrast in that SiH_3NH^- is more stable than $^-SiH_2NH_2$ by about 5 kcal/mol.

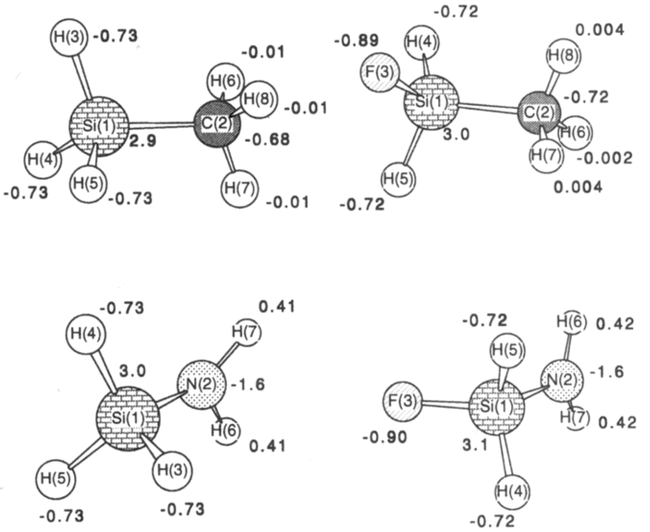


Figure 1. Charge densities using Bader's atoms in molecules method.[64]

In this study charge density analysis using Bader's atoms-in-molecules methodology[64] was applied to try to explain the differences between the effect of substituents on Si−H and element−H acid strength (obtained from wave functions computed at the MP2/6-31+G(d,p) level). The four representative structures shown in Figure 1 indicate that charge on silicon is basically unaffected by its substitution pattern. The structures all show an approximate charge of 3 on silicon whether it is substituted by just carbon and hydrogen on one extreme or by both electronegative fluorine and nitrogen at the other extreme. Similarly, the charges on silicon's hydrogen substituents are basically invariant. These data might help explain why the Si−H acidity is unaffected by substitution on silicon. However, it is also true that the charges on carbon, nitrogen, and their respective hydrogens are hardly affected by fluorine substitution at silicon, even though fluorine substitution affects the C−H and N−H acidities in the G2 computations. We are currently unable to explain the G2 acidity results at Si−H and element−H in simple terms. Studies along these lines continue.

2. Low-Coordinate Species

Table 5 presents the acidities of highly reactive silicon species and their carbon analogs. These data were obtained indirectly from studies of the corresponding conjugate base anions.[18,65−73] Although such studies are sometimes the only means of studying such acidities, they can be ambiguous in terms

Table 5. Gas-Phase Acidities of Low-Coordinate Silicon and Carbon Compounds

silicon compound	ΔH_{acid} (kcal/mol)	carbon analog	ΔH_{acid} (kcal/mol)
$HSi(O){-}H$	362[66]	$HC(O){-}H$	393[6]
$CH_3OSi(\overline{O}){-}\underline{H}$	362[72]	$CH_3OC(\overline{O}){-}\underline{H}$	
$HSi(S){-}H$	340[65]	$HC(S){-}H$	
$CH_3Si{-}\overline{H}$	372[18]	$CH_3C{-}\overline{H}$	
$CH_2{=}Si\overline{H}{-}H$	364[18]	$CH_2{=}C\overline{H}{-}H$	408[73]
$CH_3Si(O)C\overline{H_2}{-}\underline{H}$	363[72]	$CH_3C(O)C\overline{H2}{-}\underline{H}$	369[6]
$Si{=}CH{-}H$	360[67]	$HC{\equiv}C{-}H$	376[73]
$CH_2{=}Si(\overline{C}H_3)CH_2{-}\underline{H}$	~374[68]	$CH_2{=}C(\overline{C}H_3)CH_2{-}\underline{H}$	390[6]
$CH_3SiCH_2{-}\underline{H}$	~379[69]	$CH_3CCH_2{-}\underline{H}$	
$HSiNH{-}H$	359[65]	$HCNH{-}H$	
$HSi(O)N\overline{H}{-}\underline{H}$	357−362[70]	$HC(O)N\overline{H}{-}\underline{H}$	360[6]

of where a particular anion protonates. We have adopted the convention in recent studies that the most stable isomeric species will form when an anion can be protonated at more than one site (usually determined from computational studies).[65] We have done so primarily for the sake of simplicity and have not meant to imply that protonation necessarily occurs to make the most stable isomer. Barriers to proton transfer may be important and computational studies are under way to examine this question.[74] Indeed, a recent *ab initio* study by Gronert carefully investigated the potential energy surfaces for a variety of proton transfer reactions and found a large barrier (12 kcal/mol) in the $SiH_4 \cdots {}^-SiH_3$ system.[75,76]

Both H_2SiO and $CH_2{=}SiH_2$ have Si−H acid strengths which are considerably greater than their carbon analogs.[18,77] (Interestingly, H_2SiO is only very slightly more stable than HSiOH computationally.)[78] Other Si−H acidities have been reported as well. That of $(CH_3O)(H)SiO$ is the same as H_2SiO, indicating a structural similarity of the anions that were protonated.[72] The acid strength of H_2SiS is more than 20 kcal/mol greater than that of H_2SiO.[65] Computational studies by Kudo and Nagase indicate that H_2SiS is about 9 kcal/mol more stable than HSiSH.[79] The weakest Si−H acid of these low-coordinate species is CH_3SiH.[18] It is a weaker acid than $CH_2{=}SiH_2$ by 8 kcal/mol, which is a reflection of the very large difference between the EAs of CH_3-Si and $CH_2{=}SiH$.

The C−H acidities of only a few low-coordinate silicon-containing compounds have been reported. Silaacetone is a slightly stronger acid than acetone (about 6 kcal/mol).[72] Given the earlier discussion of the effects of silicon substitution on C−H acidity, it is surprising that the Si=O group does not more effectively stabilize an adjacent carbanion. The acidity of the neutral $SiCH_2$ derives from bracketing studies of $HCSi^-$.[67] Extensive computations by several groups have established that $SiCH_2$ is far more stable than the silaacetylene.[67] The acidities of $(CH_3)_2Si{=}CH_2$ and $(CH_3)_2Si$, two organosilicon compounds of considerable interest to silicon chemists have also been measured.[68,69] Acidities were measured by introducing these reactive neutrals (eqs 46−47), prepared by pyrolysis of the appropriate precursors, directly into the flow tube and studying their acid−base chemistry. Such experiments proved to be very difficult; as a result, the acidities measured for dimethylsilene and dimethylsilylene were only approximate. Nevertheless, the C−H acid strength of dimethylsilene is about 15 kcal/mol greater than that of isobutene and it is a stronger acid than tetramethylsilane by about the same amount that isobutene is more acidic than neopentane. In view of the small conjugative effects seen earlier in silicon systems, it is likely these comparisons reflect polarization and inductive effect differences between silicon and carbon. The acid strength of dimethylsilylene is approximately 379 kcal/mol, making it the weakest C−H acid among the few low-coordinate silicon-containing acids that have been studied.

It is important to note elegant experiments that have been carried out by Schwarz and co-workers to determine minimum lifetimes of some of the low-coordinate parent acids discussed above.[80−83] Thus, HSiOH, H_2SiO, CH_2Si, and other related species have been shown to have lifetimes on the order of a microsecond (1 μs). In one of several variations of such an experiment, a beam of mass-selected positive ions, whose connectivity can be independently established, is neutralized by collision with xenon. The fast moving neutral beam is subsequently reionized in a second experiment with oxygen, and a mass spectrum of the ionic fragments arising from the recovered positive ion is compared to that from the initial positive ion. The flight time of the neutralized ion beam prior to reionization gives the lifetime of the neutral species.

The acidity of two low-coordinate N−H compounds has been reported, one from $HSiNH^-$,[65] the other from $HSi(O)NH^-$.[70] No comparison with its carbon analog can be made for $HSiNH_2$, but $HSi(O)NH_2$ has roughly the same acid strength as formamide.

D. Heats of Formation (ΔH_f°)

Only a few heats of formation of neutral compounds and negative ions have been obtained from gas-phase negative ion experiments because of a general lack of the required auxilllary data needed for thermochemical cycles. As pointed out in section II, links from one thermochemical cycle to another require the appropriate thermochemical parameters and these, like so many thermochemical parameters for silicon, are often not available. This situation is ameliorated somewhat by computational studies that provide theoretical heats of formation of a variety of silicon-containing compounds. The studies of Allendorf, Melius, Pople, Curtiss, Raghavachari, Schlegel, Schaefer, Grev, Sax, Kalcher, and others are particularly important.[44,45,84−90]

Larson and McMahon[91] estimated the heats of formation of $F_2Si{=}O$ and F_3SiO^- from negative ion gas-phase experiments on F_3SiO^-. This anion, prepared as shown in eq 10, transfers F^- to various

$$(CH_3)_3CO^- + SiF_4 \longrightarrow F_3SiO^- + [C_4,H_9,F] \qquad (10)$$

neutral reference compounds allowing a determination of the fluoride affinity (see section III.E. and eqs 5 and 8a) of $F_2Si{=}O$ (102 kcal/mol). Estimates of the heat of formation of $F_2Si{=}O$ (−231 kcal/mol) were made and give a heat of formation for F_3SiO^- of −393 kcal/mol (eq 11). The heat of formation of F_3SiOH

$$\Delta H_f^\circ(F_3SiO^-) = \Delta H_f^\circ(F_2SiO) + \Delta H_f^\circ(F^-) - \text{Fluoride Affinity}(F_2SiO) \qquad (11)$$

can be estimated to be −370 kcal/mol by combining the heat of formation of F_3SiO^- with ΔH_{acid} for F_3-SiOH (eq 4).[51]

Since $HSiO^-$, produced by the collision-induced dissociation (CID) of H_3SiO^- (see section IV.C.1 and eq 49), transfers H^- to a number of reference compounds, the hydride affinity ($\underline{HA}$) of SiO could be bracketed at 49 kcal/mol (see eqs 4 and 5 and section III.E).[77] This indicates that SiO binds hydride far more strongly than CO, its carbon analog, which has a HA of only 6 kcal/mol. A heat of formation for $HSiO^-$ of −38 kcal/mol has been determined using HA(SiO) in equation 6. This combines with ΔH_{acid} for $H_2Si{=}O$ (eq 4) to give a heat of formation of −36 kcal/mol for $H_2Si{=}O$. In a recent review, Walsh states that the best value for this heat of formation is −21.5 kcal/mol.[42] A similar analysis in studies of $HSiS^-$ estimated heats of formation of $HSiS^-$ and H_2SiS of −5 and 22 kcal/mol.[65]

Since so few heats for formation of Si=O containing compounds and ions are known, it is difficult to evaluate the few thermochemical results that have been obtained from negative ion gas-phase chemistry, although, as indicated earlier, a variety of heats of formation have been obtained computationally. The value of −369 kcal/mol for the heat of formation of F_3SiOH and that of −120 kcal/mol for $(CH_3)_3SiOH$ (reported by Walsh)[42] are the only heats of formation for silanols found in the chemical literature. Similarly, the heats of formation of the $H_2Si{=}O$ (−36 kcal/mol) and $F_2Si{=}O$ (−231 kcal/mol) represent the only values reported for Si=O containing molecules determined by negative ion gas-phase methods.

E. Anion Affinities

Bartmess considered several anion affinity studies of silicon-containing molecules in a recent review.[12] Other more qualitative affinity studies have been reported as well.[92−96] Because of the interest in pentacoordinate silicon anions (siliconates) as intermediates in silicon substitution reactions,[97−99] a great deal of experimental[98,100] and computational work[98,101] has concentrated on these species. As a result, a number of anion affinities (eq 12) of tetracoordinate

$$R_4SiY^- \longrightarrow R_4Si + Y^- \qquad (12)$$

silanes have been measured (Table 6) and the conditions under which siliconates are prepared in the gas-phase have been explored (see section IV.A).[102,103]

Hajdasz, Ho, and Squires recently reported a detailed study of SiH_5^- and various $RSiH_4^-$ species.[14] Although facile hydride transfer reactions by these anions suggest that they have low hydride binding energies, the limited number of reference compounds made direct hydride affinity bracketing measurements impractical. An indirect approach involving the reaction between a series of reference acids and the siliconates under study (eq 13) allowed determination

$$R_4SiH^- + HB \longrightarrow R_4Si + B^- + H_2 \qquad (13)$$

of the HAs using the thermochemical scheme illustrated in eq 8 for the general eq 7. This method requires not only the determination of a narrow bracket for the reference acids, but also that no barriers retard hydride transfer. Since the determinations of the HAs of the $RSiH_4^-$ species (including R = H) are consistent with a number of computational studies on siliconates, these requirements seem to have been met. (A related experimental and computational study attempting to determine several anion affinities of trimethylaluminates, however, was unsuccessful, probably because high barriers negated the validity of the thermochemical analysis.)[104] The HAs reported as 19−20 kcal/mol for SiH_4 and the $RSiH_3$ species are among the smallest measured for neutral molecules.[14] Attempts were also made to measure equilibrium HAs by reactions between various $RSiH_4^-$ and $R'SiH_3$ compounds both in the flow tube of a flowing afterglow instrument and in the second quadrupole of a triple quadrupole detector. The observation of reversible hydride transfer among these species established that the HA values of alkylsilanes are quite similar. In contrast, attempts to transfer hydride from SiH_5^- to alkylsilanes failed, both in the flow tube and in the second quadrupole. Although this might suggest that the HA of SiH_4 is much greater than that of the alkylsilanes, the authors argue that it is the result of a competing reaction. This will be discussed in more detail in the section on reactivity of siliconates (section IV.A.2). Equilibrium HA measurements were successful for hydride transfer between $(CH_3CH_2)_3SiH$ and n-pentylSiH_3. Combining the quantitative and qualitative results, the authors give an HA ordering of HA(SiH_4) ≥ HA(n-pentylSiH_3) ≥ HA($(CH_3CH_2)_2SiH_2$) ≥ HA($(CH_3CH_2)_3SiH$). Thus, increasing alkyl substitution results in slightly decreasing HAs. Although no experimental comparisons can be made with these results, earlier semiempirical and *ab initio* computations confirm the magnitudes of the HAs estimated in this study.[103] AM1(MOPAC) computations carried out in this study by Hajdasz, Ho, and Squires confirm both the orderings and the small differences in hydride affinity among the alkylsilanes.

Table 6. Anion Affinities of Normal- and Low-Coordinate Silicon Compounds

compound	anion	anion affinity (kcal/mol)
$(CH_3)_4Si$	F	29.9[15]
$(CH_3)_3SiF$	F	38.2[15]
$(CH_3)_2SiF_2$	CN	16.8[16]
CH_3SiF_3	F	50.5[15]
CH_3SiF_3	Cl	16.1[15]
CH_3SiF_3	CN	22.6[16]
SiF_4	F	62[15]
SiF_4	Cl	23.4[15]
SiF_4	CN	27.2[16]
$SiCl_4$	Cl	24.2[15]
SiH_4	H	19−20[14]
n-$C_5H_{11}SiH_3$	H	19−20[14]
$(CH_3CH_2)_3SiH$	H	19−20[14]
other simple alkyl silanes	H	19−20[14]
SiO	H	49[66]
SiS	H	65[65]

McMahon and co-workers carried out direct equilibrium measures of fluoride,[15] chloride,[15] and cyanide anion[16] affinities of several silanes as part of a comprehensive study of periodic trends of anion affinities. Their results indicate that fluoride is always bound to tetracoordinate silicon more strongly than chloride, and that cyanide is more strongly bound than chloride. The fluoride effect results from fluorine's small size, its greater covalent bond energies, and its greater basicity. Cyanide and chloride, which were found to make equally strong hydrogen bonds to Brønsted acids in earlier studies by McMahon and co-workers,[16] have different covalent interactions with Lewis acids like the silanes. Thus, the greater cyanide anion affinities are said to be a reflection of greater covalent bonding contributions over those with chloride. Such trends are also observed for other main group elements.[16] In addition, these authors show that chloride and fluoride affinities become larger as the silanes become more highly substituted by fluorine.

We have carried out a related study on siliconates in which flowing afterglow experimental work and computational studies were combined.[103] Various affinities of silanes possessing a variety of substituents (eq 14) were predicted by both semiempirical and

$$H_3SiXY^- \longrightarrow H_3SiY + X^- \qquad (14)$$

ab initio methods. The flowing afterglow experiments were designed to test the validity of the computations. As a result, a series of new siliconates were prepared, which had been predicted to be stable by the calculations. Although 91 combinations of X and Y were studied, only five of these (X = SiH_3 and Y = CH_3, NH_2, OCH_3, F, or H) were predicted to yield unstable siliconates (i.e., negative anion affinities). All other combinations of X = Y = OH, OCH_3, CH_3, NH_2, H, PH_2, SH, SCH_3, F, Cl, Br, I, and SiH_3 had positive anion affinities by computation. Interestingly, the anion affinities of Larson and McMahon[15] and Hajdasz, Ho, and Squires[14] are readily accommodated by these computations. For example, for Y = OH, the fluoride affinity is 39.5 and the chloride affinity is 9.1 kcal/mol (*ab initio*). Similarly, when Y = F, the fluoride affinity is 49.4 and the chloride affinity is 15.6 kcal/mol. The hydride affinities for Y = OH, CH_3, F, H, SH, and Cl are 31.6, 18.2, 42.2, 16.7, 46.6, and 58.2 kcal/mol. The results for Y = CH_3 and H are reasonably consistent with experiment. The extemely large hydride affinities for Y = SH and Cl are remarkable and reminiscent of other effects for third row elements.[105]

Hydride affinities of low-coordinate silicon species have been obtained in negative ion studies as well. The hydride affinities of SiO (49 kcal/mol)[77](see section IV.C) and SiS (65 kcal/mol)[65] have been determined by bracketing experiments. The latter value is identical to a recently computated value obtained at the MP4 level (65 kcal/mol).[106]

IV. The Preparation and Reactivity of Silicon-Containing Negative Ions in the Gas Phase

In the following sections we consider representative studies related to the reactivity of silicon anions. The sections are arranged according to silicon coordination number. We will see that the reactivity of some silicon anions is not coordination number dependent.

Most of the results that are discussed come from mass spectroscopic studies of ion-molecule reactions. It is important to emphasize that gas-phase ion−molecule reactions are often quite similar to reactions in solution.[77,107] When simple energy differences between reactions occurring in the two phases are taken into account, the similarities between reactions in solution and the gas-phase greatly outnumber their differences.

It is equally important to realize that the mass spectrocsopic techniques used to study ion−molecule reactions in the gas-phase typically provide only mass-to-charge ratios (*m/z*) as output. Neutral products are generally not determined directly, but are inferred on the basis of mechanistic considerations.

A. Pentacoordinate Silicon Anions (Siliconates)

1. Unstable Siliconates

Although hypercoordinate silicon species with coordination numbers higher than five are being studied actively[100] and are important as synthetic reagents,[100] gas-phase studies of hypercoordinate silicon species are limited to pentacoordinate silicon anions (called siliconates here for simplicity). Siliconates have long been considered as intermediates in nucleophilic substitution reactions at silicon.[97−99] Such species, once considered elusive, are now prepared readily in condensed phase and have been studied thoroughly.[100]

Since early work on siliconates was initiated in the 1970s,[94−96] gas-phase studies have been actively pursued by a number of workers.[14,108] Some of this work has necessarily been discussed in earlier sections. The importance of computational studies in understanding the preparation and reactivity of siliconates in the gas-phase cannot be emphasized too strongly. As briefly discussed in section III.E, computational studies have established that siliconates are nearly always stable species.[103] More detailed reference to computational work will accompany specific discussions of siliconates.

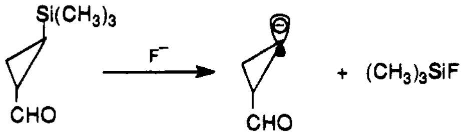
While studies of stable gas-phase siliconates are the main subject of section IV.A, siliconates that are not stable products are also of special importance in reactions of silanes. In particular, they have been proposed as "unstable" intermediates in studies that serve in different ways to illustrate their importance in gas-phase studies. These will be considered before examining stable siliconates.

DePuy and co-workers reported in 1980 that the reaction between F^- and appropriately substituted silanes efficiently gives carbanions useful for study in the gas-phase.[109,110] The significance of this report is illustrated in eqs 15 and 16, where isomeric carbanions are prepared regiospecifically. This

$$(CH_3)_3SiC{\equiv}CCH_3 + F^- \longrightarrow CH_3C{\equiv}C^- + (CH_3)_3SiF \qquad (15)$$

$$(CH_3)_3SiCH_2C{\equiv}CH + F^- \longrightarrow HC{\equiv}CCH_2^- + (CH_3)_3SiF \qquad (16)$$

method has found wide application in preparing carbanions. A report by Kass and co-workers (eq 17)

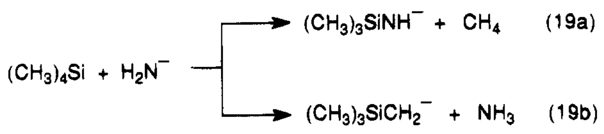


(17)

provides a very recent example of regioselective and diastereoselective anion formation.[111] The efficacy of this technique is a result of the delicate balance between siliconate formation and decomposition. Siliconates generally form by addition of a nucleophile to the silicon of a tetracoordinate silane. Unless the excess energy from their formation is dissipated (usually by collisional deactivation), the siliconates react further. In the cases illustrated above, the siliconates react to yield stable carbanions.

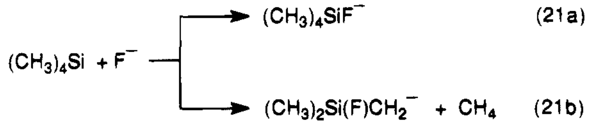
When silanes have carbon substituents not likely to yield stable carbanions upon siliconate decomposition, their reactions with nucleophiles generally take a different course (eqs 18–21).[3,4,27,40,109]

$$(CH_3)_4Si + HO^- \longrightarrow (CH_3)_3SiO^- + CH_4 \quad (18)$$



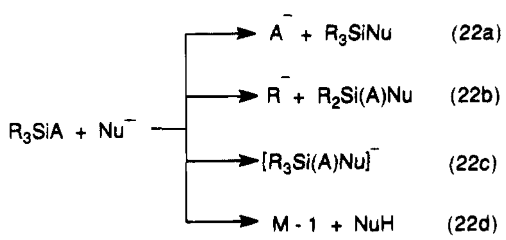
$$(CH_3)_4Si + H_2N^- \longrightarrow (CH_3)_3SiNH^- + CH_4 \quad (19a)$$
$$(CH_3)_4Si + H_2N^- \longrightarrow (CH_3)_3SiCH_2^- + NH_3 \quad (19b)$$

$$(CH_3)_4Si + (CH_3)_2N^- \longrightarrow (CH_3)_3SiCH_2^- + (CH_3)_2NH \quad (20)$$



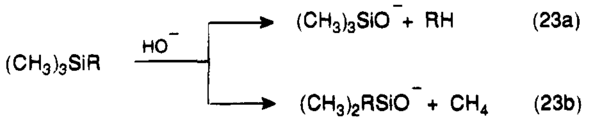
$$(CH_3)_4Si + F^- \longrightarrow (CH_3)_4SiF^- \quad (21a)$$
$$(CH_3)_4Si + F^- \longrightarrow (CH_3)_2Si(F)CH_2^- + CH_4 \quad (21b)$$

The general picture of silane reactivity with nucleophiles/bases is given in eq 22. The balance between cleavage reactions (eqs 22a,b), siliconate formation (eq 22c), and proton abstraction (eq 22d) depends on the nature of the nucleophile/base and/or the structure of the silane. Both the cleavage and siliconate products are likely formed from siliconate intermediates. In contrast, the proton abstraction reaction is presumably a direct one involving no siliconate intermediate. The examples shown in eqs 19–21 exemplify the complexity of such reactions. A base stronger than HO$^-$, namely H$_2$N$^-$, gives cleavage and proton abstraction while the less basic analog, (CH$_3$)$_2$N$^-$, reacts only by proton abstraction.[109] In contrast, fluoride, which is the weakest base among these nucleophiles, gives both siliconate formation and a small amount of cleavage.



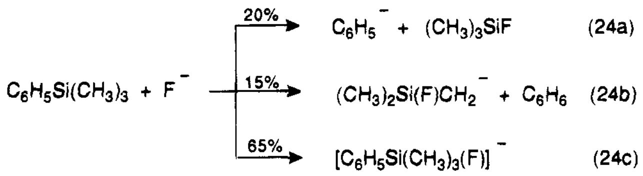
$$R_3SiA + Nu^- \longrightarrow A^- + R_3SiNu \quad (22a)$$
$$R_3SiA + Nu^- \longrightarrow R^- + R_2Si(A)Nu \quad (22b)$$
$$R_3SiA + Nu^- \longrightarrow [R_3Si(A)Nu]^- \quad (22c)$$
$$R_3SiA + Nu^- \longrightarrow M-1 + NuH \quad (22d)$$

When more than one possible HO$^-$ cleavage can occur, the less basic carbanion is cleaved more readily from silicon than a more basic one (eq 23).[5,27,40] The measured ratio of such cleavage reactions can be used to determine the acidity of weakly acidic hydrocarbons (section III.A). Indeed, some of these acidities cannot be determined by other methods, since many of the corresponding carbanions do not have a bound electron (see negative EAs in Table 1). Detailed computational studies by Sheldon and Gordon and their respective co-workers provide a consistent picture of the mechanism of the HO$^-$ cleavage reaction, supporting that this reaction occurs through an intermediate siliconate.[112,113]

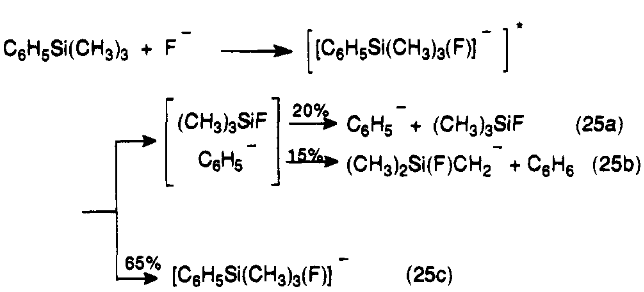


$$(CH_3)_3SiR \xrightarrow{HO^-} (CH_3)_3SiO^- + RH \quad (23a)$$
$$(CH_3)_3SiR \xrightarrow{HO^-} (CH_3)_2RSiO^- + CH_4 \quad (23b)$$

The reactions of structurally more complex silanes and nucleophiles are often explicable in terms of initial siliconate formation. This is well illustrated for the reaction of C$_6$H$_5$Si(CH$_3$)$_3$ and F$^-$ (eq 24) using the general mechanistic scheme given in eq 25.[109]



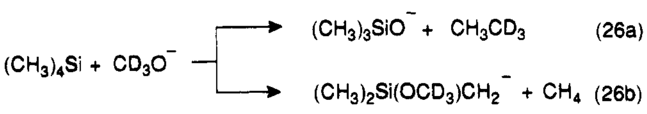
$$C_6H_5Si(CH_3)_3 + F^- \xrightarrow{20\%} C_6H_5^- + (CH_3)_3SiF \quad (24a)$$
$$C_6H_5Si(CH_3)_3 + F^- \xrightarrow{15\%} (CH_3)_2Si(F)CH_2^- + C_6H_6 \quad (24b)$$
$$C_6H_5Si(CH_3)_3 + F^- \xrightarrow{65\%} [C_6H_5Si(CH_3)_3(F)]^- \quad (24c)$$



$$C_6H_5Si(CH_3)_3 + F^- \longrightarrow \left[[C_6H_5Si(CH_3)_3(F)]^-\right]^*$$
$$\longrightarrow \begin{bmatrix}(CH_3)_3SiF \\ C_6H_5^-\end{bmatrix} \xrightarrow{20\%} C_6H_5^- + (CH_3)_3SiF \quad (25a)$$
$$\xrightarrow{15\%} (CH_3)_2Si(F)CH_2^- + C_6H_6 \quad (25b)$$
$$\xrightarrow{65\%} [C_6H_5Si(CH_3)_3(F)]^- \quad (25c)$$

Since the formation of the siliconate is highly exothermic, its excess energy must somehow be dissipated. This can occur by collisions with buffer gas, leading to the observed siliconate product (eq 25c). The energetic siliconate can also lose C$_6$H$_5^-$ to yield the product complex shown. This complex can decompose to (1) C$_6$H$_5^-$ and (CH$_3$)$_3$SiF (eq 25a) or (2) (CH$_3$)$_2$Si(F)CH$_2^-$ and C$_6$H$_6$ (eq 25b). The latter products form by proton abstraction and are consistent with the ΔH_{acid} values for (CH$_3$)$_3$SiF (387 kcal/mol)[46] and C$_6$H$_6$ (402 kcal/mol).[114]

Other studies have been carried out that involve unstable siliconates. Bowie and co-workers examined nucleophilic substitution at silicon in a variety of studies, principally with alkoxides and alkoxide/alcohol clusters as nucleophiles.[115–120] Virtually all this work has been accompanied by *ab initio* studies carried out by Sheldon. The early studies established not only that a variety of cleavage reactions occur depending on the structure of the reactant silane, but that stable siliconates are formed as well. Among the many interesting results of these studies involving alkoxide nucleophiles, two will be emphasized. The reaction between (CH$_3$)$_4$Si and CD$_3$O$^-$ in eq 26 involves a reaction pathway not yet discussed.[115,117] The proposed intermediate [(CH$_3$)$_4$SiOCD$_3$]$^-$ can decompose giving CH$_3^-$, which not only abstracts a proton in eq 26b , but cleaves the CD$_3$–O bond as well (eq 26a). Computational results for this system are consistent with this mechanistic interpretation.



$$(CH_3)_4Si + CD_3O^- \longrightarrow (CH_3)_3SiO^- + CH_3CD_3 \quad (26a)$$
$$(CH_3)_4Si + CD_3O^- \longrightarrow (CH_3)_2Si(OCD_3)CH_2^- + CH_4 \quad (26b)$$

Bowie, Nibbering, and co-workers discovered that alkoxides that are monosolvated with alcohols react very specifically with silanes in nucleophilic substitutions.[119] For example, when [R$_L$O$^-$···H$^+$···$^-$OR$_S$] (R$_L$ is larger than R$_S$) reacted with (CH$_3$)$_3$SiOR′, the major substitution product was always the one where the smaller alkoxide had been substituted, namely (CH$_3$)$_3$SiOR$_S$. Computational studies suggested that the relative amount of [R$_L$OH ···$^-$OR$_S$] versus [R$_L$O$^-$···HOR$_S$] determined the specificity of the substitution reactions.

A recent study by Brauman and co-workers determined the relative amounts of proton abstraction versus siliconate formation in the reaction of HO^- and $(CH_3)_3SiCH_2C(CH_3)_2OH$.[121] This reaction, which gives only the ionic product $(CH_3)_3SiO^-$, could occur either (1) by proton abstraction at OH followed by O^- attack at silicon and subsequent β-elimination of $(CH_3)_2C{=}CH_2$ or (2) by direct siliconate formation and its subsequent decomposition to $(CH_3)_3SiO^-$ and $(CH_3)_3COH$. When HO^- enriched in ^{18}O was used, it was determined that the rate of deprotonation was roughly 50% of the rate of direct siliconate formation. In an earlier study, McMahon and co-workers observed Wittig-like reactions for $F_3SiCH_2^-$ and various carbonyl compounds.[130]

2. Stable Siliconates

Siliconates as major products in ion–molecule reactions were reported as early as 1970;[94–96] however, work commencing around 1980 established that siliconates were frequently encountered in the negative ion gas-phase chemistry of silicon.[3,92,93] This section on stable siliconates will highlight important aspects of the preparation and properties of these species.

Hajdasz, Ho, and Squires recently reported a detailed study[14] of the formation and properties of SiH_5^- and several simple alkyl substituted siliconates that is based on preliminary work published in 1986.[122] They demonstrated that direct H^- addition (formed by electron ionization of NH_3 or CH_4) to several simple silanes, including n-$C_5H_{11}SiH_3$, n-C_4H_9-SiH_4^- , and $(CH_3CH_2)_3SiH$ is quite efficient (eq 27).

$$RSiH_4 + H^- \longrightarrow RSiH_4^- \qquad (27)$$

The authors emphasize the remarkable specificity of this addition, which occurs despite the availability of exothermic proton abstraction chan- nels. They also note that conventional H^- transfer agents like cyclohexadienyl anion, HNO^-, and methoxide do not yield siliconates while a number of other nucleophiles react directly with these simple silanes to form siliconates (eg. CF_3^-).

Hajdasz, Ho, and Squires prepared SiH_5^- (eq 28)

$$RSiH_4^- + SiH_4 \longrightarrow SiH_5^- + RSiH_3 \qquad (28)$$

by means of hydride transfer from a siliconate to SiH_4. "Soft" anion transfers, such as the one shown in eq 28, are easily understood in energetic terms. Thus, while direct reaction of an anion to form a siliconate is highly exothermic,[103] "soft" transfer of an anion to form a siliconate is often successful because the resulting siliconate is formed in a less exothermic reaction and the neutral product can take up some of the excess energy. Hajdasz, Ho, and Squires observed, however, that such transfers (eq 29b) can occur along with other reactions (eq 29a).

$$(CH_3CH_2)_3SiH_2^- + SiH_4 \xrightarrow{68\%} SiH_3^- + (CH_3CH_2)_3SiH + H_2 \qquad (29a)$$

$$\xrightarrow{32\%} SiH_5^- + (CH_3CH_2)_3SiH \qquad (29b)$$

They observed that the best yields of SiH_5^- were obtained by reactions of n-$BuSiH_4^-$ or n-$C_5H_{11}SiH_4^-$ and SiH_4.

The parent SiH_5^- has been the subject of other experimental and computational studies.[14] Attempts to prepare SiH_5^- directly by H^- addition to SiH_4 were unsuccessful, as originally shown by Bohme and co-workers in 1976.[123] Only SiH_3^- was detected in this reaction, although reaction with D^- gave some SiH_2D^-, suggesting the possibility of an intermediate siliconate that could not be stabilized. Indeed, computational studies indicate that SiH_5^- is unstable with respect to decompositon to SiH_3^- and H_2.[14] However, a substantial barrier exists for this decomposition, which suggested that it should be possible to prepare this ion under mild conditions. Dihydrogen loss from other siliconates has been studied computationally and has been found to be exothermic when Y = H, CH_3, NH_2, and OH in SiH_4Y^-.[103] When Y = F, PH_2, SH, and Cl, however, these siliconates are predicted to be stable with respect to H_2 loss.[103]

Hajdasz, Ho, and Squires demonstrated that hydridosiliconates transfer H^- to various other species as well. Reactions with CO_2, COS, and CO_2 all give the corresponding H^- adducts. $Cr(CO)_6$ and $(CH_3CH_2)_3B$ react with hydridosiliconates to yield $(CO)_5CrCHO^-$ and $(CH_3CH_2)_3BH^-$. Aliphatic aldehydes and ketones undergo carbonyl reduction with accompanying siliconate formation as illustrated for acetone (eq 30). The identity of this product was

$$nBuSiH_4^- + (CH_3)_2CO \longrightarrow BuSiH_3OCH(CH_3)_2^- \qquad (30)$$

determined by collision-induced dissociation (CID) studies, where $(CH_3)_2CHO^-$ fragments were identified.[14]

These workers also discovered some very specific secondary alkyl transfer reactions that occur between hydridosiliconates and alkylsilanes (eq 31).[14] Alkyl

$$(CH_3CH_2)_2SiH_3^- + (CH_3CH_2)_2SiH_2 \longrightarrow (CH_3CH_2)_3Si^- + CH_3CH_2SiH_3 + H_2 \qquad (31a)$$

$$\longrightarrow (CH_3CH_2)_2Si(H)CHCH_3^- + CH_3CH_2SiH_3 + H_2 \qquad (31b)$$

anion transfers are extremely rare in the gas-phase.[124] Those observed in this study have been clearly shown to involve alkyl transfer from the siliconate to the neutral silane. Both silyl anions and the α-silyl carbanions have been characterized using N_2O as described in section IV.B.2. Mechanistic details of reactions like 31 are under study.[37]

One of the most elegant applications of negative ion gas-phase chemistry relates to this work. Ho and Squires developed a protocol to study diastereoselectivity in gas-phase H^- reductions of cyclohexanones.[125,126] The two diastereomerically pure 2-methylcyclohexyl alkoxide ions ($C_7H_{13}O^-$) were allowed to react with n-hexylSiH$_3$ to give $[C_7H_{13}OSiH_3(n\text{-hexyl})]^-$. Each of these in turn reacted with 3-pentanone to give $[C_7H_{13}OSiH_2(n\text{-hexyl})(OC_5H_{11})]^-$. The ratios of CID fragments produced ($C_7H_{13}O^-$ and $C_5H_{11}O^-$) from the two pure diastereomeric alkoxides were then compared to the ratio obtained from the siliconate produced by reduction of 2-methylcyclohexanone by $[C_5H_{11}OSiH_3(n\text{-hexyl})]^-$. The gas-phase reduction carried out in this way gave 68% trans and

32% cis products. A similar application to 4-*tert*-butylcyclohexanone gave 99% trans product.

Hajdasz, Ho, and Squires also studied the protonolysis of these simple siliconates in detail.[14] One ramification of this reactivity has already been discussed in section III.E in the context of indirect hydride affinity measurements. The reaction with CH_3CH_2OH (eq 32) illustrates some of the complexities of protonolysis. Three anionic products were detected in significant yields (13%, 15%, and 72%, respectively). Furthermore, none of these siliconates undergoes alkyl cleavage. A wide variety of acids including ketones, nitriles, thiols, and carboxylic acids are effective protonolysis reagents. The relative yield of the three possible reactions appears to be controlled, at least in part, by the gas-phase acidity of the acid and the corresponding silanes. Thus, relatively acidic formic acid gives only the reaction analogous to eq 32a while weaker acids like CH_3CH_2OH give the three reaction types shown in eq 32. One of the most interesting aspects of protonolysis is that neutral silanes may also act as the acid in these reactions.

$$n\text{-BuSiH}_4^- + CH_3CH_2OH \longrightarrow n\text{-BuSiH}_3 + H_2 + CH_3CH_2O^- \quad (32a)$$

$$\longrightarrow n\text{-BuSi(H)}_3(OCH_2CH_3)^- + H_2 \quad (32b)$$

$$\longrightarrow n\text{-BuSiH}_2^- + H_2 + CH_3CH_2OH \quad (32c)$$

Isotope labeling studies also reveal some interesting features of siliconates in this study.[14] The reaction of n-$BuSiH_4^-$ with SiD_4 produces all possible deuterium labeled siliconates, $[n\text{-BuSiD}_nH_{4-n}]^-$, where $n = 1-4$. Thus, in addition to protonolysis, the siliconate undergoes isotope exchange (eq 33). The authors suggest that their data are consistent with a "sequence of slow, single exchanges per collision" rather than multiple exchanges in a "single ion/molecule encounter". A series of hydride transfer reactions between various labeled hydridosiliconates and CO_2 give HCO_2^- and DCO_2^-. The ratio of normal-to-deuterated formate was used as a measure of the structural equivalence of hydrogen and deuterium. Carefully measured, statistically corrected ratios have demonstrated that the hydrogens and deuteria become equivalent in the course of these reactions, presumably by rapid Berry pseudorotation.

$$RSiH_4^- + SiD_4 \rightleftharpoons [RSiH_4^- \cdots SiD_4] \quad (33a)$$

$$[RSiH_4^- \cdots SiD_4] \rightleftharpoons [RSiH_3 \cdots SiD_4H^-] \quad (33b)$$

$$[RSiH_3 \cdots SiD_4H^-] \rightleftharpoons [RSiH_4D^- \cdots SiHD_3] \quad (33c)$$

$$[RSiH_4D^- \cdots SiHD_3] \rightleftharpoons RSiH_4D^- + SiHD_3 \quad (33d)$$

Other direct siliconate syntheses from a nucleophile and a silane (eq 34) have been considered in detail in the experimental and computational study referred to earlier in section III.E on anion affinities.

$$(CH_3)_3SiX + Y^- \longrightarrow [(CH_3)_3SiXY]^- \quad (34)$$

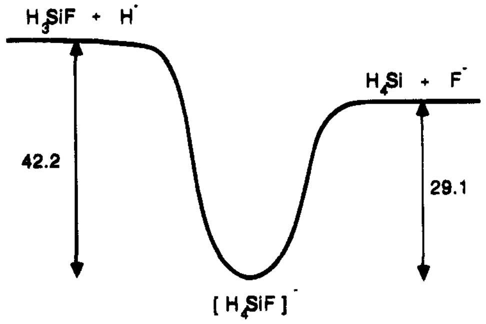


Figure 2.

A large number of siliconate anion affinities were computed in that study,[103] and some general principles were outlined for preparing siliconates. Thus, siliconates tend to form in direct reactions when the silane lacks a good leaving group, and when the nucleophile lacks an easily abstracted hydrogen and is not too strong a base. Several examples of siliconate formation under such conditions have already been given (eqs 21a, 24c, and 25c). Another example from early work by Bowie and co-workers is given here (eq 35).[115] It is often possible to prepare siliconates when the general conditions just mentioned are not met. To do so requires a recognition of the energetics of siliconate formation from a different perspective. Recent computational studies suggest that siliconates may be formed in a number of experimental situations.[103] The computed reaction coordinate (Figure 2) for the H_3SiF/SiH_4 system (used for computational simplicity) shows that the two approaches to the siliconate are quite different. The reaction between H_3SiF and H^- will give substitution products by an exothermic reaction. The reverse substitution reaction, however, is endothermic, and would be expected to give H_4SiF^-, which could be stabilized by collision with a third body.[103] The related experimental result, carried out using flowing afterglow techniques, showed that $[(CH_3)_3Si(F)(H)]^-$ could indeed be prepared from $(CH_3)_3SiH$ and F^- as shown (eq 36).[103] Other examples demonstrate the validity of this approach.

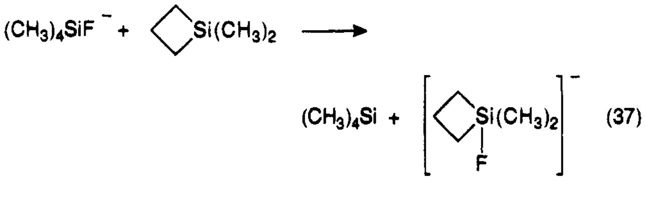
$$(CH_3)_3SiOCH_3 + CH_3O^- \longrightarrow [(CH_3)_3Si(OCH_3)_2]^- \quad (35)$$

$$(CH_3)_3SiH + F^- \longrightarrow [(CH_3)_3Si(H)(F)]^- \quad (36)$$

A recent study by O'Hair and Bowie addressed the question of whether every reaction between a silane and a nucleophile must form a siliconate intermediate.[120] In reacting CH_3O^- with $(CH_3)_3SiOCD_3$ and CD_3O^- with $(CH_3)_3SiOCH_3$ and trapping the adducts, the authors could test whether only siliconates were formed by subsequent collision-induced dissociation (CID) experiments. If a rapidly equilibrating siliconate is formed, then the subsequent CID results should be identical. Should these two reactions produce other adducts in addition (there is no doubt that the major pathway in these reactions is siliconate formation), then the CID spectra would likely differ. On the basis of *ab initio* studies, the authors proposed the formation of small amounts of

$[CH_3O^- \cdots HCH_2Si(CH_3)_2OCD_3]$ and $[CD_3O^- \cdots HCH_2Si(CH_3)_2OCH_3]$ as possible adducts in these two reactions. CID spectra were different for these adducts and are consistent with the formation of small amounts of such complexes. O'Hair and Bowie conclude that siliconates are not the sole intermediates in the reactions of nucleophiles with silanes. They, like previous authors, emphasize the importance of ion–dipole complexes involving C–H dipoles in a wide variety of gas-phase reactions.

Some additional siliconates have been prepared which illustrate the wide range of structural types that are possible. Siliconates derived from strained silanes have been prepared efficiently only by soft transfer reactions (eq 37).[93] In view of the angle strain of 1,1-dimethylsilacyclobutane (DMSCB), it might be expected that ring opening processes would dominate its reactions with nucleophiles. Indeed, direct reaction of DMSCB and F^- yields the siliconate in only 40% yield, along with 60% of a ring cleavage product. Fluoride affinities estimated by bracketing techniques suggest that dialkylsilacyclobutanes have fluoride affinities that are 15–20 kcal/mol greater than those of dimethylsilacyclohexane or other tetraalkylsilanes. This difference is attributed to geometrical factors which give unusual stability to the siliconates of the silacyclobutanes. Other studies of the parent silacyclobutane by Squires are in progress.[37] DMSCB also has served as the starting point for the preparation of a siliconate bearing five carbon substitutents.[93] Until allyl anion was successfully added to DMSCB in 1981, no siliconate had been prepared that did not have at least one electronegative substituent.[93,100] The knowledge gained concerning siliconate preparation in the subsequent years suggests that the siliconate with five carbon substituents is probably not as great a curiosity as originally thought. The final example of siliconate preparation comes from a recent study in which Moylan, Green, and Brauman reported the formation of a small amount of $SiCl_5^-$ by electron impact of $SiCl_4$.[127] In previous electron impact studies under a variety of conditions, this ion was not observed, although it had been prepared by Larson and McMahon in their determination of the chloride affinity of $SiCl_4$.[15]



B. Standard-Coordinate Silicon Anions

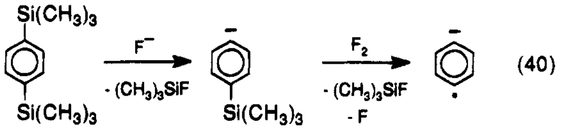
1. Preparations of Standard-Coordinate Anions

Several reactions have been given (section IV.A.2) in which standard-coordinate silicon-containing anions are formed (standard-coordinate anions are ones where silicon is either trivalent, but saturated or tetravalent and saturated—typical examples are given below). Thus, (1) reaction of HO^- with neutral silanes gives siloxide ions (eqs 18 and 23), (2) reaction of H_2N^- with silanes can lead to silamides (eq 19), (3) H_2N^- and $(CH_3)_2N^-$ reacted by proton abstraction yielding α-silyl carbanions (eqs 19 and 20), and (4) reaction of F^- with silanes can lead to α-silyl carbanions by alkyl or aryl cleavage (eqs 21b and 24b). Other reactions lead to tricoordinate silicon-containing anions as well. Of particular importance is the reaction of F^- with polysilanes which results in cleavage of Si–Si bonds (eqs 38 and 39).[22,128]

$$(CH_3)_3SiSi(CH_3)_3 + F^- \longrightarrow (CH_3)_3SiF + (CH_3)_3Si^- \quad (38)$$

$$((CH_3)_3Si)_3SiH + F^- \longrightarrow ((CH_3)_3Si)_2SiH^- + (CH_3)_3SiF \quad (39)$$

Wenthold, Hu, and Squires have recently reported a regioselective synthesis of biradical anions that involves some interesting silicon chemistry.[129] When F^- is reacted with an appropriately substituted bis(trimethylsilyl) compound, the normal F^- displacement occurs to give a carbanion. Subsequent reaction with F_2 leads to the removal of a second trimethylsilyl group, and formation of a radical anion, as illustrated with *p*-benzyne anion (eq 40). This method has been used to prepare the corresponding *m*-benzyne and trimethylenemethane anions as well.



2. Chemical Characterization of Standard-Coordinate Anions

A practical question yet to be addressed in this review is how do we know the structure of various anionic products, especially since all of the techniques used in these studies are mass spectroscopic ones that measure only a mass-to-charge (*m/z*) ratio? While ion structural assignments are often based on assumptions about the mechanisms of the reactions studied, definitive structural assignments require an experimental basis. CID studies often lead to structural assignments of ions. Gas-phase chemists also have sought to find specific chemical reactions for different anion types, ones that can be used for qualitative structure determination.[128,130]

The proton abstraction reaction involving trimethylsilane (eq 41) illustrates one chemical characterization method. In this reaction, product anion with *m/z* 73 is observed.[128] It could be either the silyl anion (eq 41a), the α-silyl carbanion (eq 41b), or a mixture of both. Independent experiments showed that the trimethylsilyl anion reacts with N_2O to give the product with *m/z* 89 anion as shown (eq 42) and that the α-silyl carbanion isomer reacts with N_2O to give a product with *m/z* 75 (eq 43). When trimethylsilane

$$(CH_3)_3SiH + H_2N^- \longrightarrow \begin{cases} (CH_3)_3Si^- + NH_3 & (41a) \\ (CH_3)_2Si(H)CH_2^- + NH_3 & (41b) \end{cases}$$

$$\underset{m/z\ 73}{(CH_3)_3Si^-} + N_2O \longrightarrow \underset{m/z\ 89}{(CH_3)_3SiO^-} \quad N_2 \quad (42)$$

$$\underset{m/z\ 73}{(CH_3)_2Si(H)CH_2^-} + N_2O \longrightarrow \underset{m/z\ 75}{(CH_3)_2Si(H)O^-} \quad CH_2N_2 \quad (43)$$

Table 7. Summary of the Reactions Used To Characterize Simple Silicon-Containing Anions

silicon-containing anion	characterizing reagent	anionic product
$(CH_3)_3Si^-$	N_2O[128]	$(CH_3)_3SiO^-$
$(CH_3)_3SiCH_2^-$	N_2O[128]	$(CH_3)_3SiO^-$
$(CH_3)_3SiO^-$	N_2O[59]	NR
$(CH_3)_3Si^-$	CO_2[132]	$(CH_3)_3SiO^-$
$(CH_3)_3SiCH_2^-$	CO_2[59]	$(CH_3)_3SiO^-$
$(CH_3)_3SiO^-$	CO_2[59]	$(CH_3)_3SiOCO_2^-$
$(CH_3)_3Si^-$	CS_2[132]	$(CH_3)_3SiS^-$
$(CH_3)_3SiCH_2^-$	CS_2[59]	$(CH_3)_3SiS^-$
$(CH_3)_3SiO^-$	CS_2[133]	$(CH_3)_3SiS^-$
$(CH_3)_3Si^-$	COS[132]	$(CH_3)_3SiS^-$
$(CH_3)_3SiCH_2^-$	COS[59]	$(CH_3)_3SiS^-$
$(CH_3)_3SiO^-$	COS[133]	$(CH_3)_3SiS-$

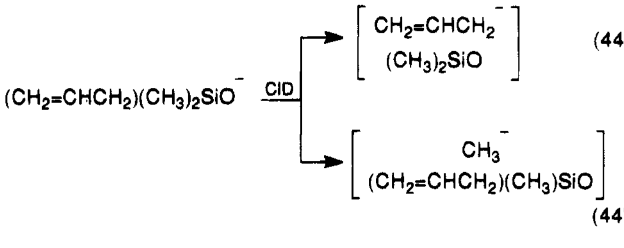
is deprotonated by H_2N^- and N_2O is added downstream, signals appear at both *m/z* 75 and *m/z* 89, demonstrating that both isomeric anions are produced. The earlier discussion of G2 computations of Si−H versus element−H acidities (section III.C.1) indicates that this reaction is kinetically rather than thermodynamically controlled, since a large amount of the less acidic α-silyl carbanion is observed (eq 41b). A number of reports recognize kinetic control in gas-phase proton transfer reactions.[131]

Other reagents like CO_2, CS_2, and COS have also been used to characterize silicon-containing negative ions.[132,133] The observed products of N_2O, CO_2, CS_2, and COS each reacting with $(CH_3)_3Si^-$, $(CH_3)_3SiCH_2^-$, and $(CH_3)_3SiO^-$ are given in Table 7.[38,128,132,133] Other reagents like SO_2, CH_3NCO, and CH_3NCS have been used to characterize silicon anion structures, but to a lesser extent.[132,133] Although the reactions given in Table 7 apply for $(CH_3)_3Si^-$, $(CH_3)_3SiCH_2^-$, and $(CH_3)_3SiO^-$, caution is necessary in generalizing reactivity patterns. For example, $(CH_3)_3SiS^-$ is formed from the reaction of $(CH_3)_3SiCH_2^-$ and COS. However, McMahon and co-workers showed that the analogous product may not form when silicon is fluorine substituted.[130] Thus, $(CH_3)_{3-n}F_nSiCH_2^-$ gives both F_3SiO^- and F_3SiS^- for $n = 3$ and exclusively $(CH_3)_{3-n}F_nSiO^-$ for $n = 1$ and 2. These fluorinated α-silyl carbanions had attenuated reactivity with N_2O.

Model studies of the mechanism of reactions of various standard-coordinate silicon-containing anions have been carried out using computational methods.[132,133] Rate coefficients and efficiencies of the reactions of H_3Si^- and $(CH_3)_3Si^-$ with CO_2, COS, CS_2, SO_2, N_2O, CH_3NCO, and CH_3NCS were reported along with computational studies that were carried out at the 6-31G level for reactions of H_3Si^- with CO_2, CS_2, SO_2, and N_2O. These computations gave a general picture of the reaction mechanism and were consistent with the observed rates. The reaction of H_3SiO^- and CO_2 involves silicon attack at carbon while the reaction of H_3SiO^- and CS_2 appears to occur by attack at sulfur. A related study of the mechanism and computational aspects of the sulfur substitution reactions of H_3SiO^- and $(CH_3)_3SiO^-$ with CS_2, COS, and CH_3NCS has been reported.[133] The computational studies carried out at the HF/6-31G and HF/6-31++G levels for H_3SiO^- plus CS_2 suggest that attack at carbon leading to $H_3SiOCS_2^-$ is highly exothermic. This adduct then passes over a barrier which is characterized as a cyclic siliconate and is formed by sulfur attachment at silicon. This four-membered ring species leads to H_3SiS^- and COS.

3. Reactions of Standard-Coordinate Anions

Standard-coordinate anions have served as starting points for several studies of the thermochemical properties of silicon-containing compounds as earlier illustrated (section III.A, III.C, and III.D). They also have been very important as precursors in low-coordinate silicon anion syntheses as we will see in section IV.C. To gain some appreciation of these low-coordinate anion syntheses, we briefly consider the collision-induced dissociation of two different standard-coordinate silicon anions here. In early gas-phase work on silicon-containing anions, it was of considerable importance to discover reactions that cleanly produced the anions of interest; however, recent advances in gas-phase techniques have made mass selection routine enough that silicon-containing negative ions often can be readily studied even if they are not produced cleanly. The first systematic CID studies of silicon-containing anions were carried out by Bowie and co-workers on alkyl and aryl siloxides and on silyl anions.[134−136] These anions typically dissociate in a variety of ways depending on the structure of the silicon-containing anion. As a representative example, CID of $(CH_2{=}CHCH_2)(CH_3)_2SiO^-$ gives a mixture of silicon-containing anions derived from predominant hydrogen atom loss as well as smaller amounts of anions resulting from the loss of H_2, CH_4, CH_3CH_3, $CH_3CH{=}CH_2$, and C_4H_8. A small amount of $CH_2{=}CHCH_2^-$ was detected as well. The authors suggested that these high-energy processes typically occur by the loss of an anion that can either react further or dissociate. In eq 44, the formation of two intermediate complexes is illustrated:

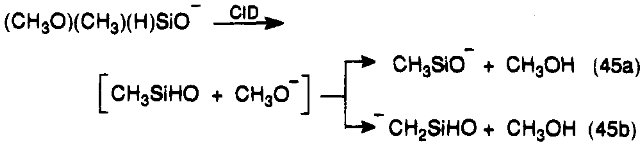


(44a)

(44b)

One (eq 44a) would lead to the formation of both CH_3-$CH{=}CH_2$ and $CH_3Si(O)CH_2^-$ by proton transfer and to $CH_2{=}CHCH_2^-$ and $(CH_3)_2SiO$ by dissociation. The second complex (eq 44b) likely would decompose in a similar fashion, but only the proton abstraction giving CH_4 would be observable, since CH_3^- loss could likely not be detected because of facile electron detachment under these conditions (see Table 1). When the siloxide undergoing CID has H substitution on silicon, large amounts of H_2 loss are observed. This, of course, is readily accommodated by dissociation to give H^-, which subsequently abstracts a proton.

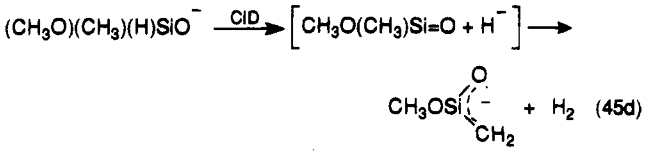
In a later study, CID of siloxides was used to produce low-coordinate anions for further study.[72] Despite the complex nature of many of these processes, CID conditions could be adjusted so that mass selection of particular anions for further study could be carried out. This is illustrated in eqs 45a–d for



$$(CH_3O)(CH_3)(H)SiO^- \xrightarrow{CID} [CH_3SiHO + CH_3O^-] \rightarrow CH_3SiO^- + CH_3OH \quad (45a)$$

$$\rightarrow {}^-CH_2SiHO + CH_3OH \quad (45b)$$

$$(CH_3O)(CH_3)(H)SiO^- \xrightarrow{CID} [CH_3OSiHO + CH_3^-] \rightarrow \underset{m/z\ 75}{CH_3OSiO^-} + CH_4 \quad (45c)$$



(45d)

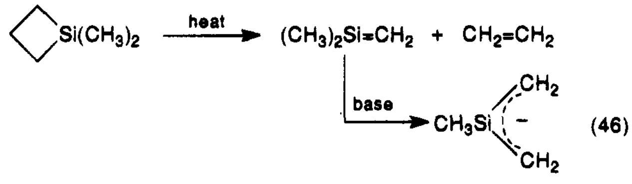
the CID of $(CH_3O)(CH_3)(H)SiO^-$. Mass selection of the anion with *m/z* 75 and study of its reaction with various reference acids allowed a determination of the acidity of $CH_3OSi(O)H$ (Table 5).

Early studies by Bowie and co-workers established that although these collision-induced dissociations are high-energy processes, they occur by mechanisms similar to those proposed for the cleavage reactions discussed earlier. Because the energies involved in CID are greater than those associated with bimolecular reactions under thermal conditions, there is less specificity of product formation. In the following section, we will see that under favorable circumstances CID can be accomplished in a reaction chamber prior to mass selection. In these cases, large signals of cleanly selected anions can be studied.

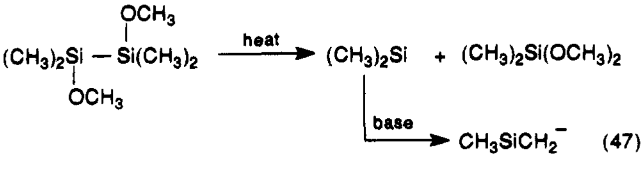
C. Low-Coordinate Silicon Anions

1. Preparation

Low-coordinate silicon-containing negative ions typically have been prepared either by proton abstraction of low-coordinate neutral compounds produced by pyrolysis (eqs 46 and 47)[68,69] or by activated

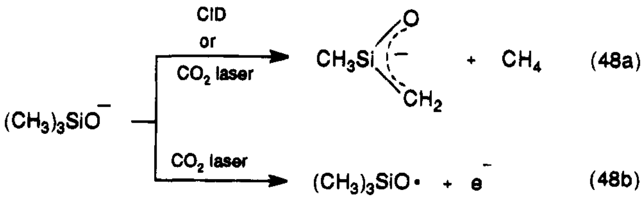


(46)



(47)

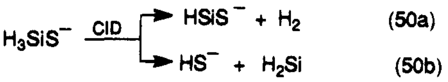
decomposition reactions such as CID or photodissociation (eqs 48–52).[47,65,70,71,77]



(48a)

(48b)

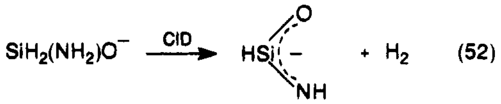
$$H_3SiO^- \xrightarrow{CID} HSiO^- + H_2 \quad (49)$$



$$H_3SiS^- \xrightarrow{CID} HSiS^- + H_2 \quad (50a)$$

$$\rightarrow HS^- + H_2Si \quad (50b)$$

$$H_3SiNH^- \xrightarrow{CID} [HSiNH]^- + H_2 \quad (51)$$



(52)

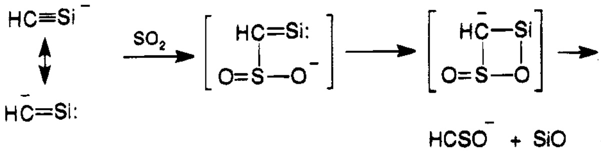
2. Reactivity Studies of Silaacetone Enolates

Froelicher, Freiser, and Squires were the first to carry out reaction 48a, reporting the preparation of silaacetone enolate by CID in 1984.[71] They reported interesting reactions with various alcohols, CO_2, and SO_2. Reactions with Brønsted acids were also examined from which the acidity of silacetone could be determined (see section III.C.2). Silaacetone enolate does not undergo H/D exchange with CH_3OD, CH_3CH_2OD, or $(CH_3)_2CHOD$, in contrast to expectations based on the fact that acetone enolate undergoes five fast exchanges with each of these alcohols. Examination of the ionic products of the alcohol reactions revealed that two major processes were occurring. It was proposed that silaacetone enolate and alcohol form an initial complex $[ROH\cdots{}^-CH_2Si(O)CH_3]$ from which proton transfer occurs. In the resulting $[RO^-\cdots CH_3Si(O)CH_3]$ complex, the alkoxide adds to Si=O giving a siloxide ion, $(CH_3)_2(RO)SiO^-$. This siloxide intermediate either gives $(CH_3)_2(HO)SiO^-$ and alkene by a six-centered elimination mechanism, or a silaester enolate $ROSi(=O)CH_2^-$ and CH_4 if R cannot be eliminated. Contrasting the lack of reaction of acetone enolate with both CO_2 and SO_2, silaacetone enolate gives $CH_3SiO_2^-$ with both. It was also shown that $CH_3SiO_2^-$ undergoes CID to yield SiO_2^-.

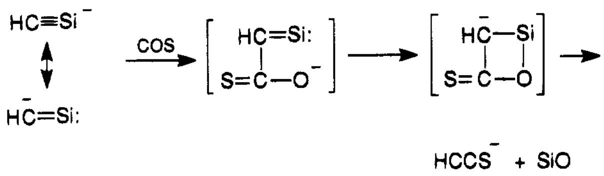
Tumas, Saloman, and Brauman also prepared silaacetone enolate as part of a general study of the activation of oxide ions by infrared multiphoton photochemistry.[47] Both $(CH_3)_3SiO^-$ (eq 48a) and $(CH_3)_2SiHO^-$ undergo photodissociation to silaacetone enolate by a mechanism similar to that proposed for the decomposition of *tert*-butoxide.[137] The authors suggested that the activation causes initial formation of silaacetone and CH_3^- or H^-, followed by proton transfer giving CH_4 or H_2 and silaacetone enolate. These activated siloxides display a feature that the alkoxides do not, namely a reaction channel for electron loss (eqs 48b and 9b). This pathway was verified by efficient electron capture with CCl_4. Double resonance experiments in the ion cyclotron resonance spectrometer indicated that both silaacetone enolate and electrons were photoproducts of trimethyl siloxide. On the other hand, in low-power continuous laser irradiation only electron loss was reported. Both pulsed and continuous laser irradiation of dimethyl siloxide gave silaacetone enolate and electron loss with no evidence of a CH_4 decomposition pathway. A detailed thermochemical analysis involving the thresholds for anion and electron loss was used to estimate the SiO π-bond strength as mentioned in section III.B.

3. Reactivity Studies of HCSi$^-$

The first application of selected ion flow tube (SIFT) technology in silicon chemistry was reported in a study looking for evidence of the long sought silicon–carbon triple bond.[67] Electron impact ionization of methylsilane in a tandem flowing afterglow-SIFT source led to a very complex array of some 20 silicon-containing anions from which the anion with *m/z* 41 was mass selected. This negative ion corresponds to a [Si,C,H] composition. Since anions are formed in the high-energy plasma of the source before they are stabilized by collision, their connectivity cannot be inferred from the starting material. Chemical reactivity studies using various neutral reagents (eqs 53 and 54) and computational studies by Schmidt and Gordon[138] strongly suggested that the anion with *m/z* 41 is $HCSi^-$. Reaction with both SO_2 and COS are readily understood if the carbon in $HCSi^-$ reacts as a nucleophile at sulfur and carbon, respectively. Whether nucleophilic attack and ring formation is sequential (as shown) or concerted is impossible to determine in these experiments; however, the $CSiH^-$ structure for the anion with *m/z* 41 is inconsistent with the products formed in these reactions. Carbon dioxide reacts with $HCSi^-$ in an manner analogous to that shown in reaction 54, but this result can only be discerned with isotopically-labeled CO_2, since the unlabeled product, $HCCO^-$, has the same *m/z* as reactant $HCSi^-$.



(53)



(54)

In their detailed computational study, Schmidt and Gordon clearly addressed these results and provided two important insights that had not been deduced from the experimental work.[138] They suggested that $HCSi^-$ should react with COS to yield $HCCO^-$ and SiS, a possibility could not be examined experimentally because its mass is the same as $HCSi^-$. The question of the mechanism of reactions of low-coordinate silicon anions with COS is interesting because two possible intermediate species can be envisaged. In this case, Schmidt and Gordon suggested that the reaction would lead to $Si{=}CHC(S)(O)^-$ (shown in eq 54), which could form two different four-membered ring intermediates and their related products.

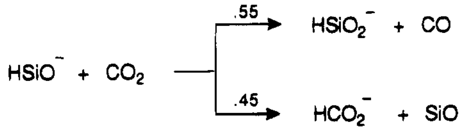
The Schmidt and Gordon study[138] also explains the observation that CS_2 does not react with $HCSi^-$. While this reaction is quite exothermic (55 kcal/mol), the initial interaction between $HCSi^-$ and CS_2 must overcome a 20 kcal/mol barrier (MP2/6-31++G(d,p). Since no such barrier is present in the reactions of CO_2, COS, and SO_2, it is not surprising that they react and CS_2 does not.

The location of hydrogen on carbon in $HCSi^-$ raised the question of the nature of bonding between carbon and silicon. The structures shown in eqs 53 and 54) suggest the possibility of triple-bond character, but the apparent nucleophilicity of carbon suggests that it bear considerable negative charge.[67] Schmidt and Gordon indicate that the anion is best thought of as a silicon–carbon triple-bonded species, basing their argument on SiC bond lengths and stretching frequencies for $HCSi^-$.[138]

4. Reactivity Studies of HSiO$^-$

The SIFT techniques enable the use of CID to prepare low-coordinate silicon-containing species. This was first demonstrated in the synthesis of $HSiO^-$ (eq 49).[77] Analogous studies of the chemistry of CH_3SiO^- and CH_3OSiO^- have also been reported.[72] These studies as well as others to be discussed have considered the relationship of such anions to their neutral, Si=O-containing, parent compounds (section III.C.2). The thermochemical aspects of $HSiO^-$ have already been considered (section III.D).

The reaction chemistry and properties of $HSiO^-$ have been extensively studied both experimentally[77] and computationally.[139] Extensive use of labeling was required to fully understand several reactions. For example, the reaction of $HSiO^-$ with CO_2, produces two products in roughly equal yields (eq 55).



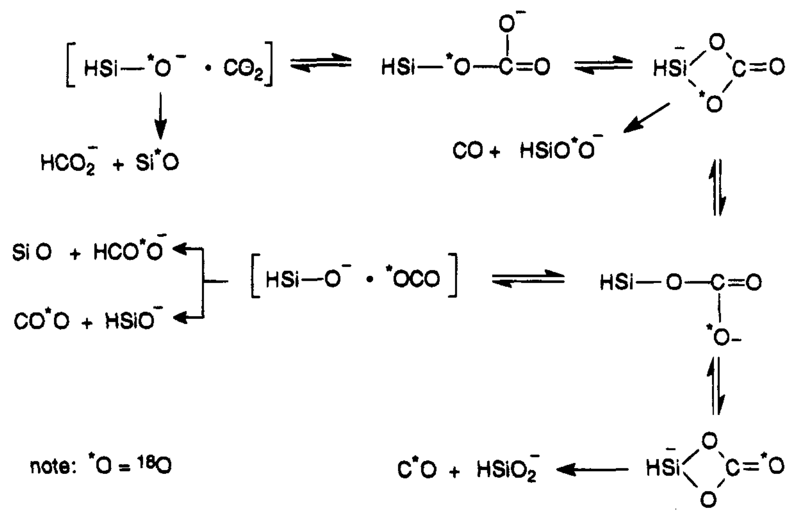
$$HSiO^- + CO_2 \xrightarrow{.55} HSiO_2^- + CO \qquad (55a)$$

$$HSiO^- + CO_2 \xrightarrow{.45} HCO_2^- + SiO \qquad (55b)$$

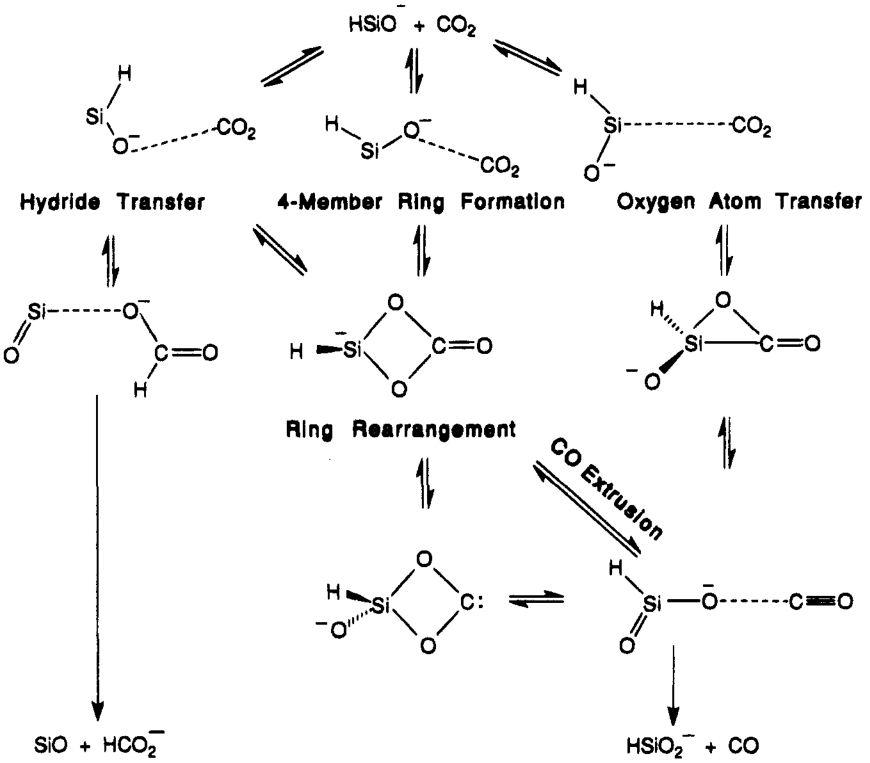
Identification of HCO_2^- as a product required the use of labeled $HSiO^-$, since its nominal mass is the same as $HSiO^-$. While hydride transfer to CO_2 is a common gas-phase reaction (eq 55b), oxygen atom transfer by CO_2 is quite unusual (eq 55a). Labeling studies helped elucidate many details of this reaction and led to the proposal of the reaction scheme shown in Scheme 1.

A recent comprehensive computational study (MP4/6-311++G(d,p)//MP2(Full)6-31++G(d,p) exploring the potential energy surface for this reaction supports much of the proposed detailed mechanism while suggesting some mechanistic features that could not be examined experimentally.[139] The most important findings suggest that oxygen atom transfer by CO_2 may occur through a three-membered intermediate (Scheme 2) and that oxygen exchange may occur through a four-membered ring intermediate.

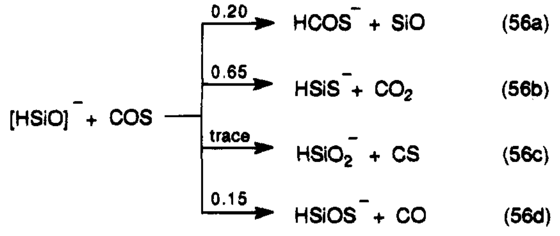
Scheme 1



Scheme 2



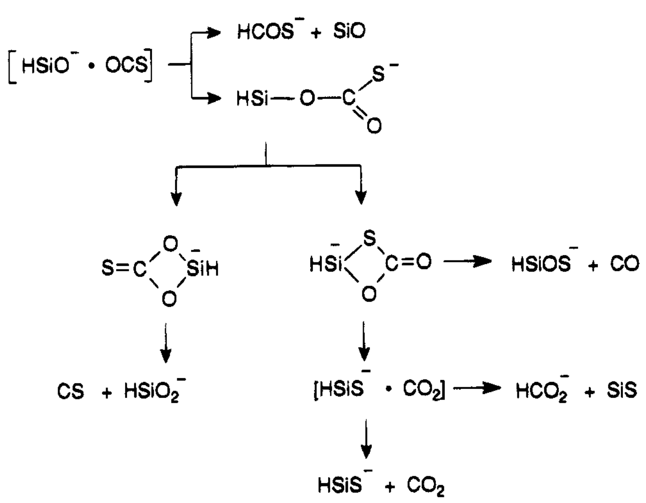
The experimental studies of $HSiO^-$ have uncovered other important and unusual reaction chemistry. One aspect of the COS reaction worthy of note (eq 56) is



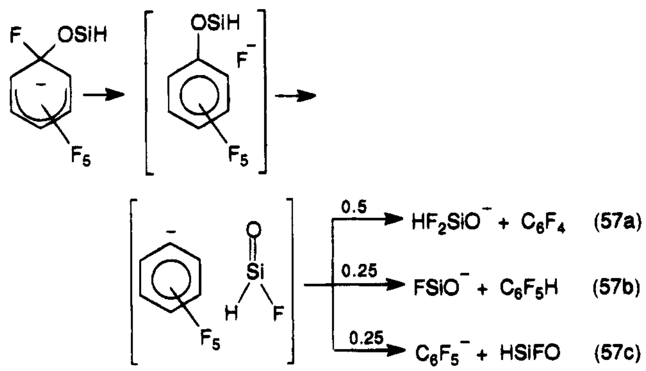
$$[HSiO]^- + COS \xrightarrow{0.20} HCOS^- + SiO \quad (56a)$$
$$\xrightarrow{0.65} HSiS^- + CO_2 \quad (56b)$$
$$\xrightarrow{\text{trace}} HSiO_2^- + CS \quad (56c)$$
$$\xrightarrow{0.15} HSiOS^- + CO \quad (56d)$$

that only a trace of products apparently derive from the four-membered ring intermediate having two oxygens in the ring while some 80% of the products arise from a four-membered intermediate ring with both oxygen and sulfur in the ring (see Scheme 3).[77] Examples like this suggest that intermediates in COS reactions with sulfur in the ring are strongly favored and control product formation. Surprisingly, a computational study of this reaction by O'Hair at the MP2(Full)/6-31++G(d,p)//MP2(Full)/6-31++G-(d,p) level of theory suggests that the proposed four-membered ring intermediate with sulfur in the ring is only about 4 kcal/mol more stable than its isomer with the sulfur exocyclic.[140] However, the pathway leading to the observed products is lower in energy for the endocyclic sulfur.[140] It is also important that although a three-membered ring intermediate with sulfur in the ring is the most stable species found in this computational study, its intermediacy cannot explain the formation of $HSiS^-$ and CO_2, which are major products (65%).

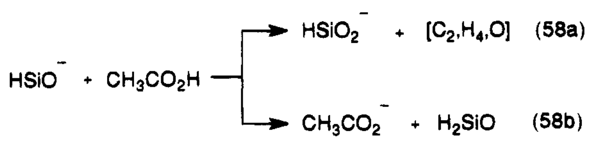
Scheme 3



Equation 57 illustrates several interesting products of the reaction of $HSiO^-$ and hexafluorobenzene that serve to show its unusual reactivity.[77] Ipso attack of $HSiO^-$ on carbon has been proposed to give the Meisenheimer intermediate shown, which decomposes to the two complexes that lead to products.



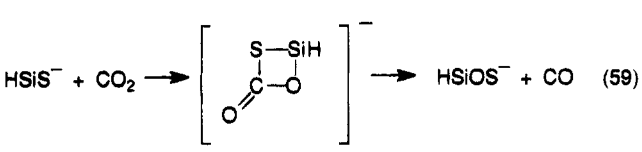
The reaction between $HSiO^-$ and acetic acid is mechanistically complex.[77] Acid–base reaction products were obtained in 50% yield (eq 58b). The other products were $HSiO_2^-$ and $[C_2,H_4,O]$ (eq 58a) with the latter neutral product assumed to be acetaldehyde. Labeling studies using CH_3CO_2D give equal amounts of $HSiO_2^-$ and $DSiO_2^-$, suggesting the intermediacy of a mixed anhydride, $CH_3CO_2Si(H)(D)O^-$. However, its formation and decomposition to products are speculative.



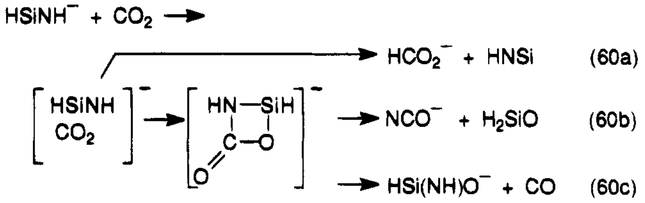
5. Reactivity Studies of HSiS⁻ and HSiNH⁻

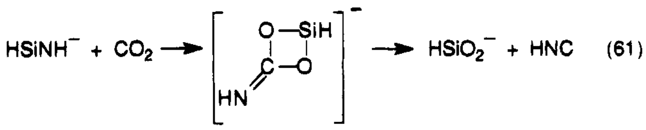
The chemistry of closely related $HSiS^-$ and $HSiNH^-$ recently have been examined.[65] Details concerning the acidity of their conjugate acids have been considered earlier (section III.C2). MP2/6-31++G(d,p)//HF/6-31++G(d,p) level computations[65] suggest that $HSiS^-$ is some 45 kcal/mol more stable than $SiSH^-$, a result in accord with the large stability difference between $HSiO^-$ and $SiOH^-$ (about 42 kcal/mol at MP2/6-31++G(d,p)//6-31G(d,p)).[77] Although the charge distribution in this anion was not investigated, the electronegativity difference between silicon and sulfur suggests that considerable charge may be on sulfur. This is consistent with the reaction chemistry exhibited by this anion. Computations also suggest that trans $HSiNH^-$ is slightly more stable than its cis isomer (1 kcal/mol), but considerably more so than either H_2SiN^- (24 kcal/mol) or $SiNH_2^-$ (24 kcal/mol). Electronegativity differences suggest that charge is likely concentrated on nitrogen.

These silicon-containing anions undergo reaction in a manner similar to that of $HSiO^-$ with a few interesting differences. Consideration of their reactions with CO_2 illustrates some key features of these species. In contrast to $HSiO^-$, which reacts with CO_2 by H^- transfer, oxygen transfer, and oxygen exchange (eq 55a and Scheme 1),[77] $HSiS^-$ gives only the oxygen transfer reaction shown in eq 59.[65] The absence of H^- transfer was an important result for determining the H^- affinity of SiS (section III.E).



The reaction of $HSiNH^-$ and CO_2, on the other hand, produced four products believed to form as shown in eqs 60 and 61.[65] The four-membered ring intermediate shown in eq 60 is analogous to the one formed with $HSiO^-$ and the products derived from it are readily understood in an analogous fashion. The small amount of $HSiO_2^-$ which forms presumably does so when the four-membered intermediate in eq 60 opens and then recloses to a different four-membered ring intermediate from which HNC can be extruded (eq 61).

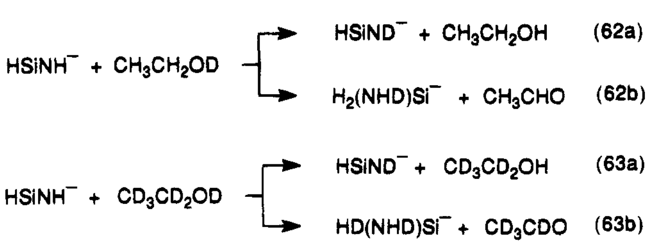




Although the reactions of $HSiS^-$ and $HSiNH^-$ with COS, CS_2, and several other neutral reagents have been studied in detail and provide confirmation of the general reactivity patterns proposed for such species, they generally give little additional information on the reactivity of low-coordinate anions. Their reactions with alcohols and acetic acid reveal reactivity that follows different pathways.[65]

The reactions of $HSiNH^-$ with deuterated alcohols proceed by H/D exchange and by H_2 abstraction (eqs

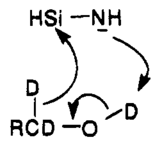
62–65) ($HSiS^-$ is unreactive with alcohols).[65] The



$$HSiNH^- + CH_3CD_2OH \longrightarrow HD(NH_2)Si^- + CH_3CDO \quad (64)$$

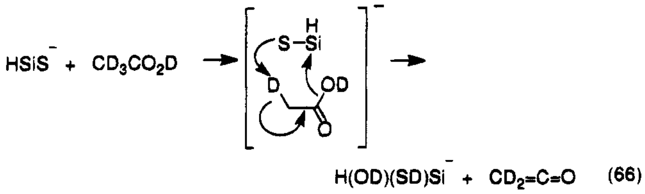
$$HSiNH^- + CD_3CH_2OH \longrightarrow H_2(NH_2)Si^- + CD_3CHO \quad (65)$$

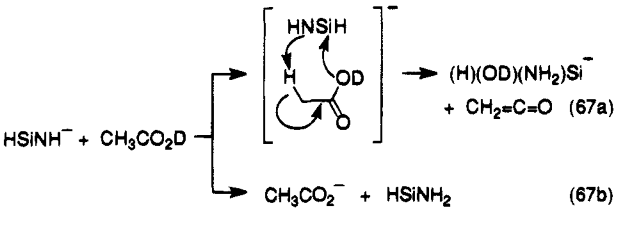
H_2 abstraction reaction involves one of the β-hydrogens in the alcohol and may occur through a cyclic, six-membered ring transition state as



Alcohols such as *tert*-butyl alcohol having no β-hydrogens are unreactive with $HSiNH^-$.

The reactions of both $HSiS^-$ and $HSiNH^-$ with acetic acid and its various deuterated derivatives take a very different course from that of $HSiO^-$. $HSiS^-$ gives the reaction shown in eq 66 with no proton abstraction. $HSiNH^-$ gives reaction 67a as well as proton abstraction (eq 67b). Since labeling studies established that α-hydrogens or deuteria and O–H or O-D are transferred in these reactions, cyclic mechanisms like those illustrated (eqs 66 and 67) were proposed although specific stepwise processes could occur as well.[65]



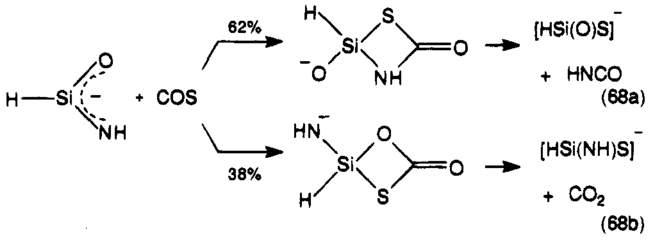


6. Reactivity Studies of Silaformamide Anion

The anion $HSi(O)NH^-$ has recently been formed and studied in the gas-phase.[70] Existence of the isomer $^-Si(O)NH_2$ was not evident despite *ab initio* computations suggesting that it is is 5.5 kcal/mol more stable than $HSi(O)NH^-$ (at the MP4(SDTQ)/6-311++G(d,p)//MP2/6-31+G(d,p) level). At more highly correlated levels this gap widens slightly suggesting that this result is unlikely to change, even at better theoretical levels. However, computational studies, while indicative of the greater stability of $^-Si(O)NH_2$, tell nothing about the structure of this observed anion. Both labeling and reactivity studies have established its connectivity as $HSi(O)NH^-$.

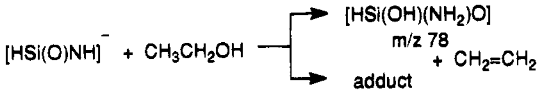
The relative stabilities of related ions derived from deprotonation of $HS(O)OH$, $HSi(O)CH_3$, $HSi(NH)OH$, $HSi(NH)NH_2$, $HSi(NH)CH_3$, $HSi(CH_2)OH$, $HSi(CH_2)NH_2$, and $HSi(CH_2)CH_3$ have been calculated at the MP4(SDTQ)/6-311++G(d,p)//MP2/6-31+G(d,p) level.[70] The silylene anions obtained by deprotonation of the Si–H site of $HSi(O)CH_3$, $HSi(NH)NH_2$, $HSi(NH)CH_3$, $HSi(CH_2)NH_2$, and $HSi(CH_2)CH_3$ are predicted to be more stable than those from deprotonation at NH_2 or CH_3. In contrast, the most stable anion derived from $HSi(O)OH$, $HSi(NH)OH$, and $HSi(CH_2)OH$ is calculated to be the one obtained by deprotonation at O-H. This suggests that electronegativity effects are controlling where deprotonation occurs, and that all three $HSi(X)O^-$ anions are favored over their silylene isomers because the negative charge is best accommodated by the more electronegative oxygen.

Previous studies of the mechanisms of reactions involving low-coordinate silicon-containing anions provide a means of understanding the reactivity of the negative ion $HSi(O)NH^-$. The reaction of $HSi(O)NH^-$ with COS has clearly established ambident reactivity. Equation 68a illustrates reactivity at the nitrogen center while oxygen-centered reactivity in evident in eq 68b. In yet another example of the preference of sulfur to bond in the ring, the presumed first-formed intermediate reacts further to form the four-membered rings shown (no $HSiO_2^-$ is observed). Reactions 68a and 68b are the first examples of ambident behavior in a low-coordinate silicon anion, although other non-silicon-containing species have been shown to exhibit ambident behavior in the gas-phase.[141–145] In particular, formamide and other imidate anions have been studied by Nibbering and co-workers.[143,144]



The reactions of alcohols and $HSi(O)NH^-$ contribute to an expanded view of the reactivity of low-coordinate silicon-containing anions.[70] Particularly interesting and complex are reactions with 2-fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol. The product distribution in these reactions depends strongly on the energetics of formation of the proton abstraction complexes $[HSi(O)NH_2 \cdot\cdot {}^-OCH_2CFXY]$ (where X and Y = H or F). Studies with CF_3CD_2OD are also consistent with the mechanistic interpetation.

The reactions of $HSi(O)NH^-$ and aliphatic alcohols have also been studied. They involve alcohols that are less acidic than the fluoro alcohols and consequently behave differently. The most interesting feature of their reactivity is illustrated for ethanol in eq 69a. Aliphatic alcohols having β-hydrogens undergo this elimination reaction which has not been observed with fluorinated alcohols. The β-elimination has been established by labeling studies. In addition to the elimination pathway, the alcohols typically give adducts as well as secondary products that are complex alcohol–adduct clusters.

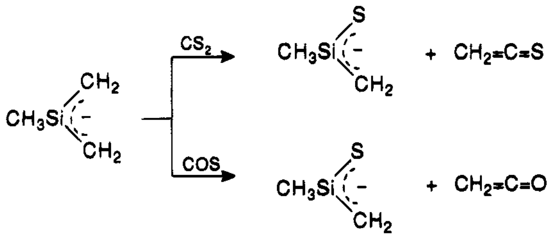


(69a)

(69b)

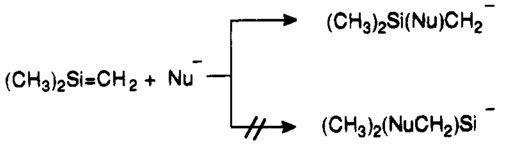
7. Reactivity Studies of Anions Derived from Dimethylsilene and Dimethylsilylene

The final low-coordinate anions to be discussed are two that have been prepared by proton abstraction from the low-coordinate species dimethylsilene[68] and dimethylsilylene[69] (eqs 46 and 47). These studies were among the first involving low-coordinate silicon-containing anions. The dimethylsilene anion undergoes sulfur replacement with both CS_2 and COS (eqs 70 and 71).[68] We have now seen such reactions for a variety of silicon-containing anions having wide structural variations. It was also shown that addition of allyl anion and cyanide to dimethylsilene occurred by addition at the silicon center (eq 72a) as opposed to 72b.



(70)

(71)



(72a)

(72b)

The $CH_3SiCH_2^-$ anion (eq 47) is quite unreactive compared to other low-coordinate silicon anions. Although it reacts with CS_2 to give CH_3SiS^-, it is unreactive with COS or CO_2. Computational studies of this anion by Gordon indicate that a significant amount of the negative charge is on silicon, suggesting that its attenuated reactivity with these reagents may have resulted from the absence of the requisite α-silyl carbanion character.[69] Gordon's result is interesting in light of a number of recent charge density determinations using Bader's atoms-in-molecules approach, where it has been shown that silicon-containing negative ions tend to have relatively low negative charge density at silicon. Thus, the series of anions $HSi(X)CH_2^-$, $HSi(X)NH^-$, and $HSi(X)O^-$ all have charges on silicon very close to +3, but the corresponding silylene anions, $^-Si(X)CH_3$, $^-Si(X)NH_2$, and $^-Si(X)OH$, have silicon charges near +1.5 (for X = CH_2, NH, and O).[70]

Despite the attenuated reactivity of $CH_3SiCH_2^-$, the silylene-silene isomerization (eq 73) could be

$$(CH_3)_2Si: \rightleftharpoons CH_3(H)Si{=}CH_2 \qquad (73)$$

explored under flowing afterglow conditions. Reaction of fluoride ion with the silene and silylene pyrosylates obtained at various pyrolysis temperatures gave the products shown in eqs 74 and 75.

$$(CH_3)_2Si: + F^- \longrightarrow (CH_3)_2(F)Si^- \xrightarrow[CO_2]{N_2O\ \text{or}} \underset{m/z\ =93}{(CH_3)_2(F)SiO^-} \qquad (74)$$

$$CH_3(H)Si{=}CH_2 + F^- \longrightarrow CH_3(H)(F)SiCH_2^- \xrightarrow[CO_2]{N_2O\ \text{or}} \underset{m/z\ =79}{(CH_3)(H)(F)SiO^-} \qquad (75)$$

Subsequent addition of N_2O or CO_2 allowed product characterization. At low temperatures, the products indicate the presence of the silylene; as the temperature increases, the fluoride addition product derived from the silene increases. Although it has been shown by Davidson, Barton, and co-workers[146,147] that a number of other products are present at the temperatures studied, the rates at which these react with fluoride must be slow relative to eqs 74 and 75.

V. Summary

Silicon anions studied in the gas-phase can be used to obtain a variety of basic thermochemical properties. The stability and reactivity of unusual silicon-containing species can often be examined by studying the corresponding anions of such species. *Ab initio* calculations provide a useful adjunct to gas-phase studies by elucidating structures and mechanistic pathways that are only indirectly inferred in experiments. They help to provide a fuller, enriched picture of gas-phase reactions.

VI. Acknowledgments

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on its improvement. We thank him for his special effort in improving the review.

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